SYNTHESIS AND REACTIVITY OF METAL CLUSTERS CONTAINING A Ru_3 OR Os_3 TRIANGLE

by

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B.Sc.(Hons.) Dip.Ed.

A THESIS PRESENTED FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

The Department of Physical and Inorganic Chemistry
The University of Adelaide

June 1983

And you will seek Me and find Me, when you search for Me with all your heart, and I will be found by you, declares the Lord.

Jeremiah 29:13,14

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SUMMARY

The rapid development of metal cluster chemistry has proven to be a source of new and interesting reactions. Many new bonding modes of organic ligands have been observed in trinuclear compounds. In particular, the ligand often donates more electrons to the metal core in these complexes than is observed in mononuclear species. Thus, an isocyanide ligand in $Ru_5(CO)_{14}(CNBu^t)_2$ contributes six electrons, whilst in mononuclear complexes two electron addition is the observed bonding mode. This obviously implies a potentially different chemistry for the trinuclear complexes from that established for mononuclear systems, and emphasises the necessity for an extensive comparative study of the chemistry of trinuclear systems. The natural extension of such investigations to heteronuclear complexes offers a further variation in chemical reactivity, particularly if this involves the use of metals such as platinum and gold, which often form stable derivatives with 14e or 16e configurations.

Chapter One outlines a study of the substitution chemistry (with respect to Group VB ligands) of $Ru_3(CO)_{12}$. The following three objectives formed the impetus for this work:

i) to synthesize specifically substituted derivatives, $Ru_3(CO)_{12-n}L_n$ (n = 1-4) in high yield, with a view to forming mixed ligand derivatives of the form $Ru_3(CO)_9L^1L^2L^3$.

ii) to investigate the reactivity of some of these substituted derivatives toward unsaturated organic ligands. For example, the reactivity of $Ru_3(CO)_9(PMe_3)_3$ with cyclopentadiene and azulene was investigated.

iii) to investigate the structural and spectroscopic relationships between various mono-, di-, tri-, or tetra-substituted derivatives of $Ru_3(CO)_{12}$.

In describing this work, reference is made to current bonding theories of metal clusters, kinetic investigations of substitution processes, and relevant electrochemical studies.

Chapter Two focuses on a fourth objective:

iv) the synthesis of heterometallic clusters incorporating both ruthenium and platinum.

The reactivity of $Ru_3(CO)_{11}(CNBu^t)$ towards suitable zerovalent platinum reagents was investigated, leading to the synthesis of a highly unstable intermediate. On the basis of subsequent reactivity with two-electron donor ligands, this intermediate was postulated to be $RuPt_2(CO)_4(PPh_3)_3$, containing a Pt=Pt bond.

The early work of Nyholm and Lewis showed that stable gold-osmium clusters could be obtained by oxidative-addition of $AuX(PR_3)$ (X = halide) to osmium carbonyl clusters. An interesting extension of this work is the use of Group IB acetylides (as their tertiary phosphine complexes), whereby mixed metal-osmium clusters containing potentially reactive acetylide functions would be obtained. It was first necessary to develop efficient high yield syntheses of $Au(C_2R)PR'_3$ compounds. Chapter Three outlines these synthetic studies, and extends them to copper and silver complexes.

Chapter Four then outlines the reactivity of Group IB phosphine acetylide complexes with $H_2Os_3(CO)_{10}$. For example, $Au(C_2C_6F_5)(PPh_3)$ reacts with $H_2Os_3(CO)_{10}$ to give $AuOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)(PPh_3)$ in quantitative yield. The subsequent reactivity of such clusters was investigated. For instance, initial pyrolysis of $AuOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)(PPh_3)$ gave $HAuOs_3(CO)_8(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)(PPh_3)$ in good yield. The reactivity of Group IB phosphine acetylide complexes

toward $Ru_3(CO)_{12}$ was also investigated. For instance, when $Cu(C_2Ph)(PPh_3)$ reacts with $Ru_3(CO)_{12}$ a host of products are produced, from which $HCuRu_3(CO)_{10}(PPh_3)$, $CuRu_3(CO)_9(C_2Ph)(PPh_3)$ and $Cu_2Ru_3(CO)_7(C_2Ph)_2(PPh_3)_2$ can be isolated.

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text of this thesis.

Janis G. Matisons

ACKNOWLEDGEMENTS

I am most grateful to the Lord Jesus Christ, my Maker, Redeemer and Friend, on whose advice I undertook this project, and with whose help I finished it. I am also very grateful to my wife, Ina, whose support and encouragement never lapsed throughout the course of this work.

I am deeply indebted to my supervisor, Professor M.I. Bruce, for his guidance and encouragement during the course of this research project. The structural studies within this work were undertaken with considerable skill by Professor A.H. White, Dr. B.K. Skelton, Dr. J.M. Patrick, Dr. M. Snow, Dr. J.R. Rodgers and Mr. E. Horn. Thanks are due to my colleagues and the staff of the Chemistry Department for their help; in particular to Dr. B.K. Nicholson, Dr. J. Walsh and Dr. R.C. Wallis, for their collaboration on some aspects of this work, to Dr. A.G. Swincer, who proofed the entire manuscript, and to Mr. R. Morris, whose skill in technical drawing is evident throughout the script.

I wish to acknowledge the prompt replies and/or prepublished material sent by Professor Sir J. Lewis, Professor F.G.A. Stone, Professor R. Bau, Dr. J. Simpson, Dr. P. Braunstein, Dr. J. Takats and Dr. L. Garlaschelli. Finally, I am thankful for the speed and precision of Miss E. Clark, who typed and corrected the entire manuscript in two weeks.

A Commonwealth Postgraduate Award and University Research Grant are both gratefully acknowledged.

ABBREVIATIONS

Å	angstroms
atm	atmospheres
bpy	2,2'-bipyridine
Bu^s	*sec*-butyl
Bu^t	*tert*-butyl
CDT	1,5,9-cyclododecatriene (mixture 2:1 - *trans:cis*)
COT	cycloocta-1,3,5,7-tetraene
Cp	cyclopentadienyl
Cy	cyclohexyl
dec.	decomposed
diars	*o*-phenylene bis(dimethyl arsine)
DMA	dimethylacetylenedicarboxylate
dpae	1,2-bis (diphenyl arsino) ethane
dpam	bis (diphenyl arsino) methane
dppe	1,2 bis (diphenyl phosphino) ethane
dppm	bis (diphenyl phosphino) methane
e.g.	for example
Et	ethyl
ff	and following pages
ffars	tetrafluorocyclobutene bis (dimethyl arsine) $(CH_3)_2AsC{=}C[As(CH_3)_2]CF_2CF_2$
ffos	tetrafluorocyclobutene bis (diphenyl phosphine) $Ph_2PC{=}C(PPh_2)CF_2CF_2$
$f_6$fos	hexafluorocyclohexene bis (diphenyl phosphine) $Ph_2PC{=}C(PPh_2)CF_2CF_2CF_2$
h	hours
Hz	Hertz
i.e.	that is
i.r.	infra-red
Me	methyl

mg	milligrams
min	minutes
ml	millilitres
mmol	millimoles
m.p.	melting point
n.m.r.	nuclear magnetic resonance
p.p.m.	parts per million
Ph	phenyl
Pr^n	*n*-propyl
thf	tetrahydrofuran
tms	tetramethyl silane
tosmic	4-toluenesulphonylmethylisocyanide

For Infra-red Spectroscopy

br	broad
cm^{-1}	wave numbers (reciprocal centimetres)
m	medium
s	strong
sh	shoulder
vs	very strong
vw	very weak
w	weak

For n.m.r. Spectroscopy

d	doublet
m	multiplet
q	quartet
qu	quintet
s	singlet
t	triplet

CHAPTER ONE

SYNTHESIS AND REACTIVITY OF SUBSTITUTED DODECACARBONYLTRIRUTHENIUM CLUSTERS

INTRODUCTION

Outline

This chapter contains a survey of substituted $Ru_3(CO)_{12-n}L_n$ complexes (where L = Group $\underline{VB}$ donor ligand). The results are discussed in terms of:

i) synthesis and facile reactivity of $Ru_3(CO)_{11}L$ (where L = isocyanide ligand).

ii) radical ion-initiated syntheses of ruthenium cluster carbonyls containing tertiary phosphines, phosphites, arsines, $SbPh_3$ or isocyanides.

iii) structural studies of substituted ruthenium carbonyl clusters.

iv) miscellaneous reactions of $Ru_3(CO)_{12}$ and its substituted derivatives.

The final experimental section describes the reactions in the sequence they appear in the text.

General Chemistry of $Ru_3(CO)_{12}$

During the last two decades, there has been growing interest in the field of the preparation and characterisation of molecular complexes of transition metals with metal-metal bonds.[1-8] The best known cluster carbonyl complex of ruthenium is dodecacarbonyltriruthenium - $Ru_3(CO)_{12}$. Since its discovery in 1961,[9] the chemistry of this polynuclear ruthenium complex has expanded rapidly.

Two molecular orbitals, which play an essential role in a wide range of chemical reactions, are referred to under the general term "frontier orbitals," and are abbreviated frequently by HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). Electron delocalization between the HOMO and LUMO is generally

the principal factor determining the ease of a chemical reaction, irrespective of whether an intra- or intermolecular process occurs.[10]

Reactions of polynuclear metal carbonyls can be classifed according to the type of electron transfer in the initial reaction step; that is, electrons may either be added, subtracted, or transferred from the frontier cluster orbitals. Nucleophilic attack and/or reduction involves addition of electrons to LUMO, whereas electrophilic attack and/or oxidation involves removal of electrons from HOMO. Pyrolysis and photolysis reactions, however, are considered to involve an intramolecular transfer of electrons from HOMO to LUMO.[11]

The presence of carbon monoxide as a ligand allows considerable changes in the electron density of a cluster by adjusting back-donation between CO groups and metal atoms. Electrophilic attack (removal of electron density from cluster HOMO toward reagent LUMO) is compensated by decreased OC $\xrightarrow{\pi}$M back-donation. Nucleophilic attack (addition of electron density at the cluster HOMO) is also compensated by increased OC $\xrightarrow{\pi}$M back donation.[12-19] Therefore, the presence of CO can offset changes in electron density, thus favouring reactivity of cluster carbonyls with both electrophilic and nucleophilic reagents.[20-22]

Separation between frontier orbitals increases on passing down a subgroup, causing the corresponding polynuclear metal carbonyls to become progressively more thermostable and chemically inert. The decreasing reactivity is also accentuated by increasing metal-metal bond strength in going down a subgroup. Thus, the reactivity of metal clusters, differing only in the metal atom of a particular subgroup, will show this trend. Hence, $Fe_3(CO)_{12}$ shows a reactivity pattern consistent with cluster degradation (breaking of metal-metal bonds) under reaction

conditions,[23-39] while $Os_3(CO)_{12}$ retains the triangular Os_3 network under a variety of conditions.[40-48] Not suprisingly, $Ru_3(CO)_{12}$ displays reactivity intermediate between $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$.[49]

Initial reactions of $Ru_3(CO)_{12}$ showed that the complex reacted with a wide range of ligands.[49-51] As the chemistry of $Ru_3(CO)_{12}$ emerged, it was essential to have crystallographic structure determinations of not only the final products, but also of intermediates which indicated the course of the reactions.

Many photoreactions of $Ru_3(CO)_{12}$ (by irradiation near the $\sigma \longrightarrow \sigma^*$ transition [391 nm[52]] of the Ru_3 triangle) result in declusterification (*via* transfer of electrons from HOMO to antibonding LUMO).[53-55] The reaction quantum yields are little affected by CCl_4, a radical trap, but are significantly affected by the presence of weak Lewis bases (such as thf).[56] This suggests that the key intermediate(s) in the photofragmentation is not a diradical, as thought previously,[57], but is coordinatively unsaturated.[56]

Alkali metal or electrochemical reduction of $Ru_3(CO)_{12}$ generated the $Ru_3(CO)_{12}^{\bullet-}$ radical anion.[58,59] This radical anion is unstable above 233 K, but below 193 K satellite signals due to Ru hyperfine coupling (9G) were seen.[58,59] The reduction of $Ru_3(CO)_{12}$ is more difficult than that of $Fe_3(CO)_{12}$,[60] but a chemically and electrochemically irreversible reduction step appears even at 195 K ($E_{\frac{1}{2}}$ -0.82V vs. Ag/AgCl). The second step at -2.0 V involves cluster degradation.[58,59]

Reactivity of $Ru_3(CO)_{12}$ with Group VB Donor Ligands

(a) Monodentate tertiary ligands

The chemistry of $Ru_3(CO)_{12}$ has been explored far more widely than that of any of its simple substituted derivatives [e.g. $Ru_3(CO)_{12-n}(L)_n$ with L = Group VB donor ligands].[49] This contrasts with the situation existing for mononuclear complexes where tertiary phosphine and arsine complexes abound, and their reactions are well known.[49,61-75] The main reason for these differences lies in the reactivity of $Ru_3(CO)_{12}$.

High temperatures are required for $Ru_3(CO)_{12}$ to react with various phosphines. The usual product from such reactions is $Ru_3(CO)_9(PR_3)_3$.[76,77] (See Table I). Mono- and di-substituted complexes (see Table I[49,76-91]) are obtainable under special conditions (e.g. under CO,[92,93] or by using sterically demanding ligands,[94] or alternatively as by-products from reactions designed to afford other products[95]). Trifluorophosphine is the only ligand known to displace more than four carbonyl ligands.[96]

Substitution reactions of $Fe_3(CO)_{12}$ with phosphines, except under the mildest of conditions, give mononuclear complexes.[23-39] When compared with $Fe_3(CO)_{12}$, the ruthenium analogue is more robust as it retains the metal triangle in most reactions (see Table I). Cluster degradation (metal-metal bond rupture) is uncommon, and occurs only where sufficient energy is supplied, either thermally or photochemically, to rupture the Ru-Ru bonds.[79,97-101]

Kinetic studies[85,102-105] indicate that the formation of $Ru_3(CO)_{11}(PR_3)$ is the rate-determining step in substitution reactions. Subsequent substitution steps forming $Ru_3(CO)_{10}(PR_3)_2$ and $Ru_3(CO)_9(PR_3)_3$ are fast.[85,102,104] Hence, it is to be expected that $Ru_3(CO)_9(PR_3)_3$ would be the major product formed, if not the sole product.

Interestingly, a kinetic study[105] of the thermal reaction of $Ru_3(CO)_9(PPh_3)_3$, in the presence of PBu^t_3 or CO, resulted in the construction of a mechanistic scheme having the V-shaped diradical, $(Ph_3P)(CO)_3\dot{R}u - Ru(CO)_3(PPh_3) - \dot{R}u(CO)_3(PPh_3)$, as the initial intermediate. This reversible, homolytic fission of metal-metal bonds by thermal or photochemical means is common.[106-124]

Poë and Twigg[102] report that substitution reactions of $Ru_3(CO)_{12}$ with Group VB ligands most reasonably occur through a simple dissociative mechanism, involving CO loss and formation of the coordinatively unsaturated intermediate $Ru_3(CO)_{11}$. Such unsaturated intermediates are electronically not very discriminating.[125,126] Steric effects are then of major importance, although the nucleophile is definitely present in the transition state.[102] These substitution reactions all proceed by reaction paths that are kinetically of mixed zero and first order in [nucleophile].[103] In effect either unimolecular CO dissociation (k_1) or bimolecular substitution (k_2), respectively, is the rate-determining step:-

$$Ru_3(CO)_{12} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru_3(CO)_{11} \xrightarrow[L]{k_2} Ru_3(CO)_{11}L$$

$$k_{obsd} = k_1 + k_2[L]$$

The basicity of the ligand L becomes more significant as k_2 increases. Thus, ligand basicity, steric and kinetic factors all determine the degree of substitution finally observed.[88] Hence, in several instances, the mono- and di-substituted complexes have been chromatographically isolated.[88] Reactions between $Ru_3(CO)_{12}$ and $Pt(PR_3)_4$ or $Pt(PR_3)_2(C_2H_4)$ also result in the formation of these mono- and di-substituted complexes.[77,127] Unfortunately, low yields were obtained in both instances.

TABLE 1 Some Properties of Complexes $[Ru_3(CO)_{12-n}L_n]$ (L = ER_3, CNR)

L	n[a]	Colour	ν(CO) (cm^{-1})	Reference
$PMe_2(CH_2Ph)$	3	reddish-purple	2043w, 2017w, 1973s, 1937m	76
PMe_2Ph	1	orange-red	2092m, 2039s, 2026s, 2010s, 1998(sh), 1991(sh), 1980m, 1973(sh), 1956(sh)	88
	2	red	2069w, 2013s, 1989s(br), 1969(sh)	88
	3	red	2040w, 1972(sh), 1966s, 1938m	88
$PMePh_2$	2	red	2070m, 2016s, 1993s(br), 1969(sh)	88
	3	red	2042w, 1966s, 1939(sh)	88
PBu_3	3	dark red	2035vw, 1960s, 1927(sh)	83
$P(C_2Bu^t)Ph_2$	3	dark red	1991vs, 1977vs, 1950m	84
PPh_3	1	yellow	2097m, 2046s, 2030(sh), 2023(sh), 2014s, 1996(sh), 1986m, 1972(sh), 1960(sh)	87,90
	3	dark violet	2044w, 1978(sh), 1967s(br)	77,82,83,86,88
$P(C_6H_4Me\text{-}m)_3$	3	red	2044w, 1979(sh), 1967s(br)	88
$P(C_6H_4Me\text{-}p)_3$	3	red	2039vw, 2017w, 1977(sh), 1965s(br)	88
$P(OMe)_3$	3	red	2054w, 2001(sh), 1988s, 1963(sh)	88
$PPh(OMe)_2$	2	red	2080m, 2029s, 2005s, 1984(sh), 1972(sh)	88
	4	red	2031w, 1983s, 1965s, 1913(sh)	88
$P(OPh)_3$	2	red	2089w, 2038s, 2018(sh), 2010s, 1993(sh)	87
	3	red	2070w, 2012s, 1999s, 1977(sh)	83,87
$P(OC_6H_4Me\text{-}p)_3$	3	red	2065w, 2009s, 1995s, 1977(sh)	87
$P(NMe_2)_3$	3	red	1987(sh), 1975s, 1937w	88
dppm	(2)	red-orange	2080m, 2040w, 2010s, 1988(sh), 1960m	78
dppe	(2)	red	2082m, 2021(sh), 2016s, 2001s, 1983(sh), 1965w, 1935w(br)	88,89
ffos	(2)	red	2087m, 2027(sh), 2019s, 2007s, 1989(sh), 1974w, 1960w, 1950(sh)	79
	(4)	dark red	2048m, 1996(sh), 1978(sh), 1972s, 1944(sh), 1898w	79
(-)-diop	(3)[b]	deep violet	1995s, 1977s, 1965s, 1950(sh)	80
$MeSi(PBu_2)_3$	(3)	yellow		81
$AsMe_2(CH_2Ph)$	3	purple	2043w, 2016vw, 1982s, 1971s, 1935m, 1921m	76
$AsMe_2Ph$	3	red	2050w, 1988(sh), 1976s, 1943s	88
$AsPh_3$	2	red-purple	2099w, 2075w, 2047w, 2026s, 2015s, 1995s, 1979(sh), 1959(sh)	88,91
ffars	(2)	dark red	2087m, 2024(sh), 2014s, 2007(sh), 1980(sh), 1967w, 1950(sh), 1938w	79
	(4)	dark red	2045m, 1991(sh), 1978s, 1971s, 1948(sh), 1844w	79

[a] For polydentate ligands, number in parentheses is number of CO groups displaced.

[b] $[Ru_3(CO)_9]_2[(-)\text{-diop}]_3$.

Ligands present on metal clusters show an ability to accelerate CO dissociation (see Table 2),[128-136] making k_1 the dominant term in the rate law. The rates of CO dissociation from several octahedral-metal carbonyl complexes can be explained in terms of *cis*-labilization, a term used to describe the increased readiness of a carbonyl group to dissociate when *cis* to a ligand.[135-146]

TABLE 2[135] Some Relative Rates of CO Dissociation from Transition-Metal Carbonyl Clusters

n	$Ru_3(CO)_{12-n}(PPh_3)_n$	$Co_4(CO)_{12-n}[P(OMe)_3]_n$	$Ir_4(CO)_{12-n}(PPh_3)_n$
0	1	1	1
1	55	0.9	220
2	40	1.3	3500

The hypothesis that *cis*-labilization is operative can be used to explain the observed substitution behaviour of $Ru_3(CO)_{12}$.[85,102-104] It was observed that substitution by PPh_3 leads only to the trisubstituted species $Ru_3(CO)_9(PPh_3)_3$.[85,102] The rate law being first order in carbonyl and zero order in ligand requires that the successive first-order rate constants increase with increasing degree of substitution.

The necessity for further investigation in this area has been highlighted by recent notes by Atwood[147] and Poe.[148a,b]

An alternative approach was proposed by Darensbourg,[129-131,133,134] based on steric induction arguments. Rate accelerations, ascribed to sterically induced ligand dissociation, only require that the co-ordination site of the leaving CO ligand be in close proximity to the phosphorus ligand *and not necessarily at the same metal site*

(*cis*-labilization effect). The origin of the steric accelerations may be a ground state property (as reflected in the structure of $Ir_4(CO)_8(PMe_3)_4$[149]), though in the transition state the relief of interligand steric repulsions upon ligand dissociation can allow the remaining metal-ligand bonds to attain values closer to their electronic equilibrium positions.[133,134] Steric factors alone, however, cannot explain why $Ru_3(CO)_{12}$ reacts with $AsPh_3$ to form the disubstituted derivative, $Ru_3(CO)_{10}(AsPh_3)_2$, whilst PPh_3 (with a larger cone angle[150]) forms the trisubstituted derivative $Ru_3(CO)_9(PPh_3)_3$.[88,91] Here, electronic considerations also must influence the substitution processes.

The following *cis*-labilization order has been established using tetrahedral Ir_4 clusters:[135,136]

$$CO < P(OPh)_3 < AsPh_3 < PPh_3 < PBu^t_3$$

The *cis*-labilization studies of Atwood and Brown[137-142] are directly related to the kinetic studies by Poë,[92,93,102-111] considering that the relative *cis*-labilization order represents a measure of the combined steric capacity as well as ligand basicity associated with each donor ligand.

The order of *cis*-labilizing abilities is just the reverse of the *trans*-effect order for these same ligands.[151-153] However, ligands which are relatively small, but reasonably nucleophilic (such as OH^-, Cl^-, Br^-, I^-, CN^-, SCN^-, $CNBu^t$) show an associative pathway for substitution of metal clusters.[141,142,154-156]

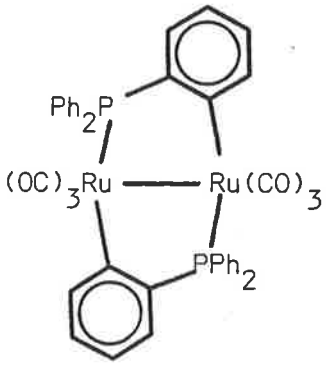
Carbonyl i.r. spectra indicate that solutions of substituted ruthenium clusters contain only terminal CO ligands.[79-91] The kinetic data accumulated by Poë indicate, however, that the struc-

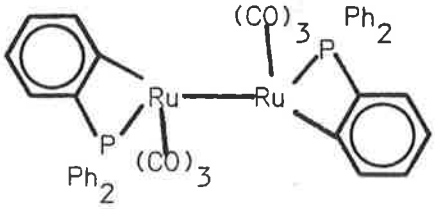
ture of $Ru_3(CO)_9L_3$ intermediates should vary considerably with the nature of L; as the greater the steric bulk of the substituting ligands, the higher the tendency of the Ru_3 cluster to accommodate bridging CO ligands.[92]

The chemistry of phosphine substituted derivatives of $Ru_3(CO)_{12}$ has not been explored to a large degree. This is because thermal reactions of $Ru_3(CO)_{12}$ with phosphines tend to generate the trisubstituted derivative $Ru_3(CO)_9(PR_3)_3$, which in turn is unreactive except under very forcing conditions. Substituted $Ru_3(CO)_{12-n}L_n$ complexes undergo pyrolytic reactions forming *ortho*-metallated derivatives.[87,88] For example, when $Ru_3(CO)_9[P(p\text{-tolyl})_3]_3$,[88] $Ru_3(CO)_9[P(OPh)_3]_3$[87] or $Ru_3(CO)_9[P(OC_6H_4Me\text{-}p)_3]$[87] were refluxed in decalin, $Ru_3(CO)_7[P(p\text{-tolyl})_2]_2MeC_6H_3$,[88] $Ru(CO)_2[P(OC_6H_4)(OC_6H_5)_2]_2$[87] and $Ru(CO)_2[P(OC_6H_3Me\text{-}p)(OC_6H_4Me)_2]_2$[87] respectively were formed as major products. These and other products are shown in Figure 1. The characteristic feature of these pyrolytic reactions is the elimination of one of the aryl groups to form the cyclometallated derivative.

The pyrolytic reaction between $Os_3(CO)_{12}$ and PPh_3 resulted in the formation of nine complexes, all retaining the Os_3 framework.[157-160] Six of the compounds characterised were $HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$, $Os_3(CO)_7(PPh_2)_2(C_6H_4)$, $HOs_3(CO)_7(PPh_2)(PPh_3)(C_6H_4)$, $HOs_3(CO)_7(PPh_2)(PPh_2C_6H_4C_6H_3)$, $Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$ and $HOs_3(CO)_8(PPh_3)(PPh_2C_6H_4)$ (see Figure 2). The retention of the Os_3 framework is not surprising, as the Os - Os bond strength is greater than the Ru - Ru or Fe - Fe bond strengths.[161-168] The Os_3 cluster reactions do, however, parallel the Ru_3 case, and so give an indication of the nature of the reactive Ru_3 intermediates, which could not be isolated.

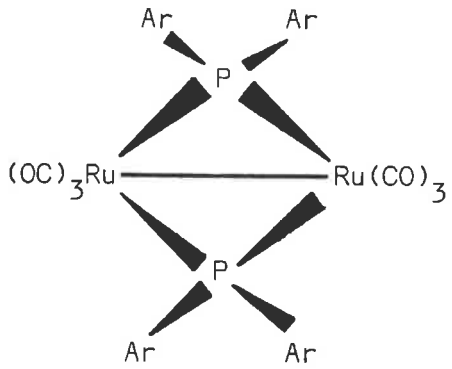
FIGURE I



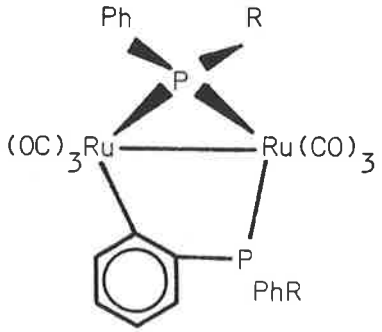


$Ru_2(CO)_6[PPh_2(C_6H_4)]_2$

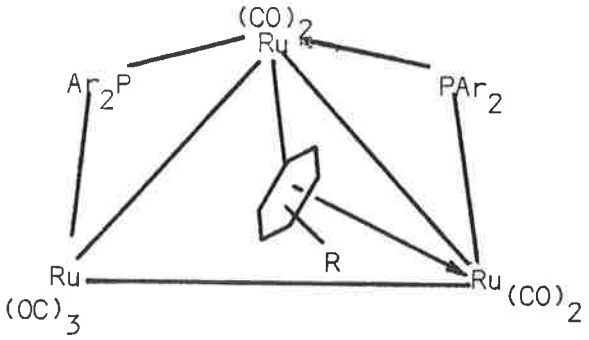
two possibilities



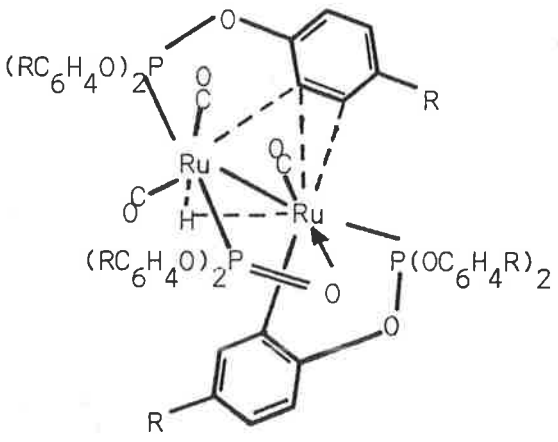
$Ru_2(CO)_6(PAr_2)_2$



$Ru_2(CO)_6[PPhR(C_6H_4)](PPhR)$



$Ru_3(CO)_7(PAr_2)_2(C_6H_5R)$

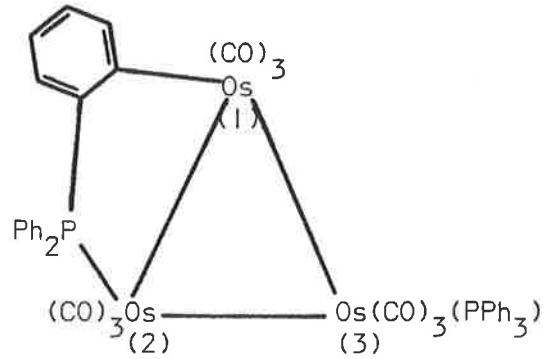


$HRu_2(CO)_3[P(OC_6H_3R)(OC_6H_4R)_2]_2[OP(OC_6H_4R)_2]$

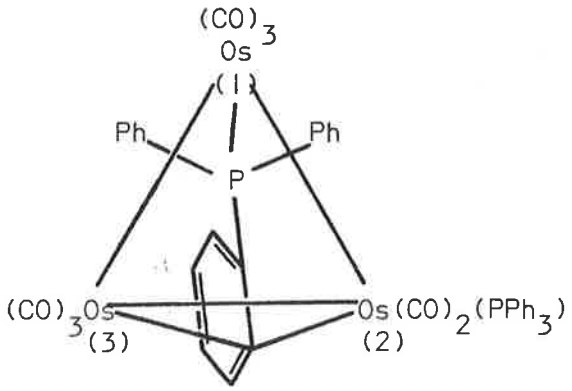
Ar = Ph, *m*-MeC_6H_4, *p*-MeC_6H_4

R = H or Me

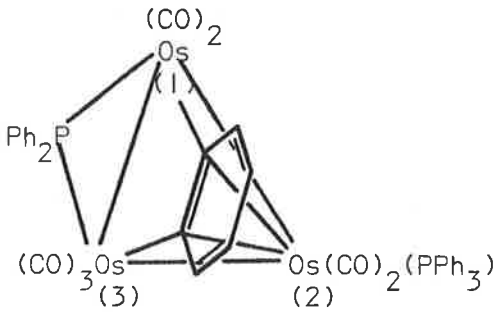
FIGURE 2



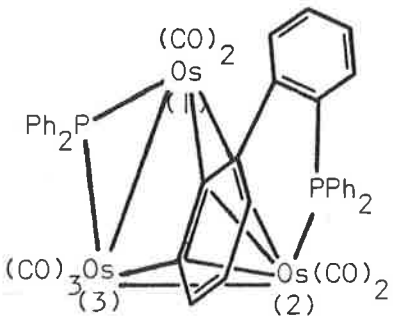
$HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$



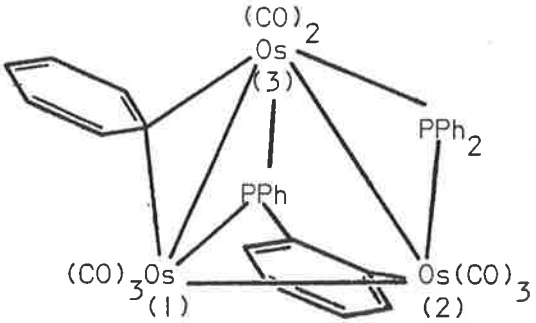
$HOs_3(CO)_8(PPh_3)(PPh_2C_6H_4)$



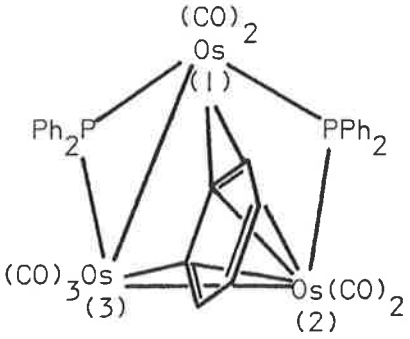
$HO_3(CO)_7(PPh_2)(PPh_3)(C_6H_4)$



$HOs_3(CO)_7(PPh_2)(PPh_2C_6H_4C_6H_3)$



$Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$



$Os_3(CO)_7(PPh_2)_2(C_6H_4)$

For aryl phosphites, the following processes are occurring:

i) migration of phosphite ligands from one metal atom to another

ii) cleavage of an *ortho*-C-H bond, which may occur *via* oxidative addition to the Ru-Ru bond, or

iii) elimination of arene from an ArO group with concomitant formation of the bridging aryl phosphonate group.

Processes i) - iii) can combine to form a dimetallated arene (or benzyne) ligand by the addition of a P-bond of a cyclometallated $PR_2(C_6H_4)$ group to the Ru-Ru bond. This can then be followed by further interaction of the aromatic π system with the third Ru atom (see Figures 1 and 2).

The substituted derivative $Ru_3(CO)_9(PPh_3)_3$ reacts with X_2 (where X = Cl, Br, I) to yield $RuX_2(CO)_3(PPh_3)$, which on heating loses CO to give $[RuX_2(CO)_2(PPh_3)]_2$.[86,169] The latter reacts with excess PPh_3 to yield $RuX_2(CO)_2(PPh_3)_2$.[86,169] Similar chemistry (when X = Cl) is observed with $Ru_3(CO)_9(PPh_3)_3$ and $Ru_3(CO)_{10}(AsPh_3)_2$ in chloroform or carbon tetrachloride.[86,91] $Ru_3(CO)_9(PPh_3)_3$ also reacts with RCO_2H (where R = H, Me or Et)[170] or *p*-toluenesulphonyl azide[171] to give $Ru_2(CO)_4(RCO_2)_2(PPh_3)_2$ and $Ru\{N[(SO_2R)CON(SO_2R)]\}(CO)_2(PPh_3)_2$ (R = C_6H_4Me-*p*), respectively. Pyrolysis of $Ru_3(CO)_9(PPh_3)_3$ in the presence of oxygen results in the formation of an uncharacterised yellow precipitate.[172]

(b) Bidentate and tridentate ligands

Reactions of $Ru_3(CO)_{12}$ with bidentate or tridentate phosphine or arsine ligands produce substituted clusters (see Table 1), which are able to withstand forcing reaction conditions without cluster degradation.[81] These ligands are also efficient in the template synthesis of clusters.[81,173-176] The reaction of the tripod ligand $[HC(PPh_2)_3]$ with $Ru_3(CO)_{12}$ gives low yields of the products, as the ligand necessitates axial substitution of three carbonyls, which is sterically unfavourable.[177]

Bidentate phosphines, particularly *bis*-(diphenylphosphino) methane (dppm), generally, give better yields of substituted $Ru_3(CO)_{12}$ derivatives.[78,79,88,175-181] The bidentate dppm ligand in $Ru_3(CO)_{10}$(dppm) bridges two Ru atoms in the equatorial plane.[78] The low temperature ^{13}C n.m.r. spectrum is consistent with the structure below (Figure 3), if the Ru-Ru-P-C-P ring is puckered and flips rapidly to make the pairs of axial CO groups equivalent. A high energy process for exchange of CO on the two types of Ru atoms assumes that the dppm ligand does not move, and involves the concerted formation of three CO bridges on the Ru_3 face.[78] It is thought that this type of CO exchange serves as a model for CO migration on a metal surface.[178-185]

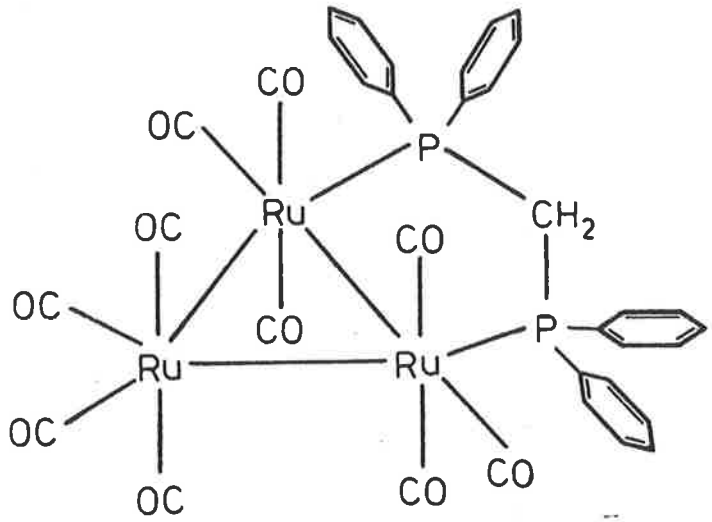
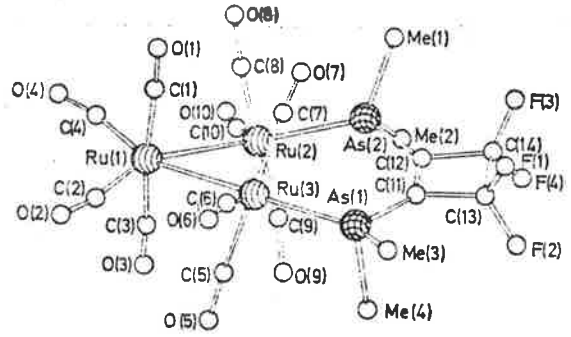


FIGURE 3 $Ru_3(CO)_{10}$(dppm)

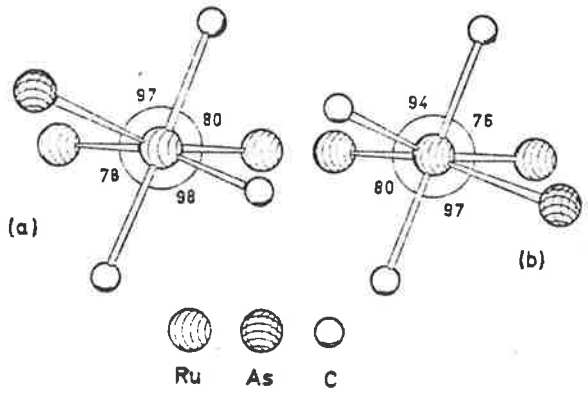
An early report suggested the formation of $Ru_3(CO)_6(dppe)_3$,[85] but this has not been confirmed. Only complexes of the types $Ru_3(CO)_{10}L$ (where L = dppm,[78] dppe,[191] ffars,[79] ffos[79] and $f_6$fos[79]) and $Ru_3(CO)_8L_2$ (where L = dppm,[188] dpam,[190] ffars,[79] ffos[79] and $f_6$fos[79]) have been fully characterised. The structures of $Ru_3(CO)_{10}$(dppe),[191] $Ru_3(CO)_{10}$(ffars),[189] $Ru_3(CO)_8(dppm)_2$[187] and $Ru_3(CO)_8$(ffars)[186] have been determined (see Figure 4). The bidentate ligands bridge two metal atoms in an equatorial plane in each of these structures.

FIGURE 4

A.

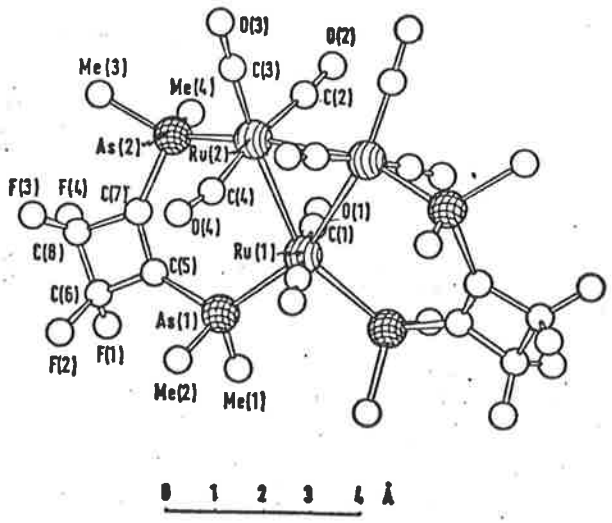


$Ru_3(CO)_{10}(ffars)$



The orientation of axial CO groups

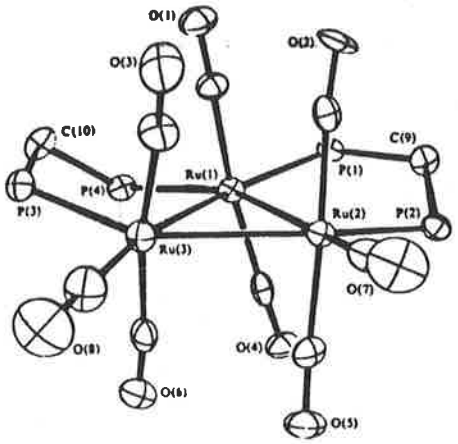
B.



$Ru_3(CO)_8(ffars)_2$

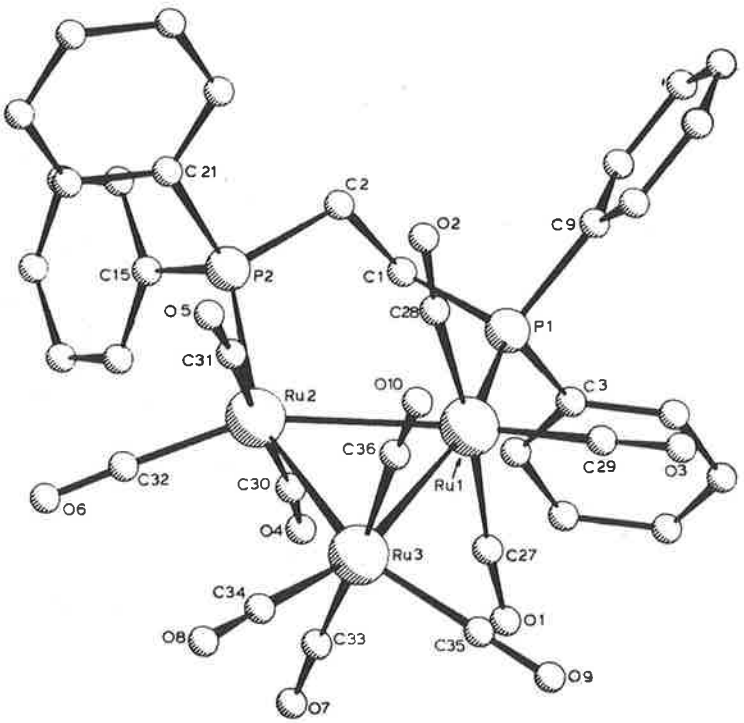
FIGURE 4 (cont.)

C.



$Ru_3(CO)_8(dppm)$
(phenyl rings omitted)

D.



$Ru_3(CO)_{10}(dppe)$

In the case of a bidentate ligand the bite angle has an influence on the metal-metal separation.[150] Unlike ligands having a rigid frame,[192] dppm is known to accommodate a wide range of metal-metal distances in binuclear species.[193-195] This accommodation is related to possible internal rotational conformations,[196] allowing the ligand to fit the appropriate metal-metal bond length. Hence, little variation between Ru-Ru bond distances in these substituted clusters is to be expected.

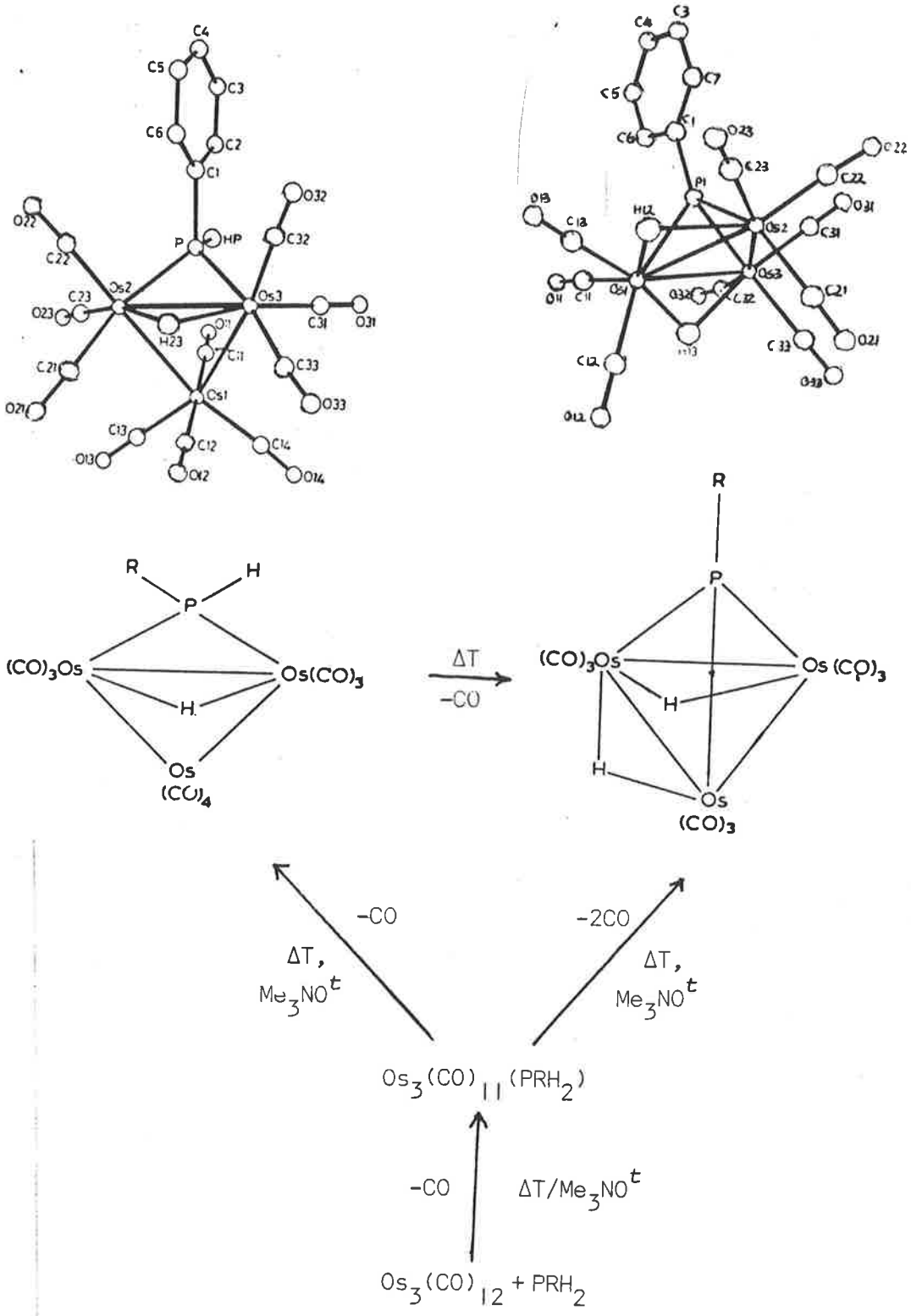
All structural information to this point indicates that these bidentate ligands are reluctant to chelate, preferentially bridging metal-metal bonds.[186-195,197] In fact, only two examples (to the best of my knowledge) are known where a bidentate ligand chelates preferentially to bridging a metal-metal bond. These are $Fe_2(bpy)(CO)_7$[198] and $Fe_3(CO)_{10}(diars)$,[199] [where bpy = 2, 2'-bipyridine and diars = *o*-phenylenebis(dimethylarsine)].

The tridentate phosphine, $MeSi(PBu_2)_3$, reacts with $Ru_3(CO)_{12}$ to yield yellow $Ru_3(CO)_9[MeSi(PBu_2)_3]$,[81] which is the only phosphine-substituted ruthenium cluster known to possess bridging CO ligands. This observation is in agreement with the hypothesis discussed earlier that with increasing substitution on the metal cluster there will be a tendency toward bridging CO ligands. Little of the chemistry of bridging ligands has yet been explored.

(c) Primary and secondary phosphine and arsine ligands

Primary phosphines react with trinuclear carbonyl complexes $M_3(CO)_{12}$ (M = Fe, Ru, Os) under rather mild conditions to give μ_3-PR-capped dihydrido clusters $(\mu_2\text{-H})M_3(CO)_9(\mu_3\text{-PR})$ in fair to low yields.[200-219] These resulting substituted clusters do not undergo cluster degradation as do the $Ru_3(CO)_{12-n}L_n$ derivatives [Section (a)], but cluster expansion occurs.[202,203,213]

FIGURE 5



Synthesis of Phosphido-Bridged Os_3 Clusters

As the carbonyl groups of $Os_3(CO)_{12}$ are far less labile to substitution than those of ruthenium,[220] the intermediates involved in the formation of $H_2M_3(CO)_9(PR)$ can be isolated. Hence, in the presence of Me_3NO,[221,222] $Os_3(CO)_{12}$ reacts with PRH_2 to give $Os_3(CO)_{11}(PRH_2)$ and $HOs_3(CO)_{10}(PRH)$,[219] which in refluxing nonane subsequently give $H_2Os_3(CO)_9(PR)$.[219] At higher temperatures, $Os_3(CO)_{11}(PRH_2)$ is transformed into clusters with doubly or triply bridging P ligands (see Figure 5).[219] This occurs by the stepwise loss of up to two CO ligands and concomitant hydrogen migrations accompanied by formation of additional Os-P bonds. It is possible that the reactions of $Ru_3(CO)_{12}$ with PRH_2 proceed by similar mechanisms, since the Ru-Ru bond is weaker than the Os-Os bond.[161-168]

The reactive hydrogens in the complexes $HM_3(CO)_9(PR)$ undergo a variety of base induced reactions, and offer a good synthetic route to phosphine stabilised heterometallic clusters.[208,214,217,220] Hence, synthesis of heterometallic clusters is possible either by (i) removing a proton from the H_nRu_3P core, with subsequent attack by an electrophile containing a transition metal[208] or (ii) by reacting $Ru_3(CO)_{12}$ with $Me_2As\text{-}M(CO)_nCp$ (formed by deprotonation of Me_2AsH in the presence of $M(CO)_nCp$.[214,217,220]

RESULTS AND DISCUSSION

Foreword

In undertaking a study of the ligand chemistry of $Ru_3(CO)_{12}$ (particularly with respect to two electron donor ligands) the following objectives were formulated:

i) The preparation of mono-, di-, or tri-substituted complexes in good yields.

ii) The preparation of complexes containing different ligands on adjacent Ru centres.

iii) The investigation of the reactivity of unsaturated organic ligands with $Ru_3(CO)_{12}$ and its substituted derivatives.

iv) The investigation of the reactivity of $Ru_3(CO)_{11}$ $(CNBu^t)$.

v) The investigation and general reactivity of mono-, di-, and tri-susbstituted Ru_3 complexes.

In the course of the work, thermal and radical initiation were extensively used to activate $Ru_3(CO)_{12}$ toward substitution and further reactivity. Radical initiation, though the more successful approach, was only recently discovered.[223] Prior to the discovery of the radical initiated method (giving specific CO substitution by two electron donor ligands), the only means of accomplishing most of the above objectives was *via* the uniquely facile reactions of $Ru_3(CO)_{11}(CNBu^t)$.

(a) The Chemistry and Reactivity of $Ru_3(CO)_{11}(CNBu^t)$[224,225]

Substitution chemistry with carbon-donor ligands on $Ru_3(CO)_{12}$ is limited to a brief description of the carbene complex $Ru_3(CO)_{11}$-$[\overline{CNEt(CH_2)_2NEt}]$[226] and the complex $HRu_3(CO)_{10}(CNMe_2)$.[227,228]

The former complex was formed when the electron rich olefin $EtN(CH_2)_2EtNC = \overline{CNEt(CH_2)_2NEt}$ reacts with $Ru_3(CO)_{12}$,[262]

while the latter complex was formed by reacting $Me_2NCH_2SnMe_3$ with $Ru_3(CO)_{12}$.[263]

Isocyanides form complexes with metals in low and normal oxidation states. Within the low-valent category, the similarity to CO in terms of both structure and reactivity has been noted.[229] Isocyanides exhibit a variety of bonding modes (terminal, edge-bridging, face-bridging, two, four and six electron donor).[229-231] They also participate in the fluxional site-exchange processes observed in metal clusters.[232-239]

In a remarkably facile reaction, *t*-Butyl isocyanide reacts with an equimolar amount of the cluster carbonyl $Ru_3(CO)_{12}$ in light petroleum at 50° for 1-2 h to give a high yield of red $Ru_3(CO)_{11}(CNBu^t)$ (1). This complex was readily identified by elemental microanalysis and its spectroscopic properties. In the infra-red spectrum, a band at 2170 cm^{-1} is readily assigned to ν(CN), and the six-band ν(CO) spectrum is similar to those of other $Ru_3(CO)_{11}L$ molecules. In the ^1H n.m.r. spectrum, the protons of the CMe_3 group resonate as a sharp singlet at δ 1.53, while in the ^{13}C n.m.r. spectrum, all CO groups give rise to a singlet at δ 201.1; the CMe_3 carbons are found at δ 30.1 and 59.0, but the isocyanide carbon was not detected. This simple spectrum indicates that (1) is fluxional at room temperature, and indeed the CO resonance does not change at -100°. In this, the complex resembles the parent $Ru_3(CO)_{12}$, which is also fluxional at low temperatures. The solid state structure of (1) is discussed below.

Reactions with increasing amounts of Bu^tNC have given the deep red complexes $Ru_3(CO)_{12-n}(CNBu^t)_n$ (n = 1-3). The disubstituted complex (2) shows ν(CN) at 2155 cm^{-1}, and also has a six-band ν(CO) spectrum. The ^1H n.m.r. and ^{13}C n.m.r. spectra are similar to those of (1), although the isocyanide carbons were also observed as a singlet at δ 144.1; again, the spectra indicate that (2) is highly fluxional.

Table 3 Spectroscopic properties of $M_3(CO)_{12-n}(CNR)_n$ complexes[a]

M	Ru	Os	Ru	Ru	Ru	Os	Os	Ru	Os
R	Bu^t	Bu^t	4-$MeOC_6H_4$	4-$MeOC_6H_4$	Cy	Bu^t	Bu^t	4-$MeOC_6H_4$	4-$MeOC_6H_4$
n	1	1	1	1	1	2	2	2	2
ν(CN) (cm^{-1})	2170w	2177w	2155w	2164m	2155w	2155w	2164m	2154m	2147m
ν(CO) (cm^{-1})	2093w	2100m	2092w	2097s	2092w	2065w	2069m	2093m	2069m
	2047s	2054s	2071vw	2055s	2071vw	2020s	2026(sh)	2066m	2056m
	2040s	2039s	2062w	2040s	2062w	2007m	2024s	2048s	2036(sh)
	2016m	2021s	2049s	2022s	2049s	1996s	2003(sh)	2040s	2029s
	1998m	2005s	2041vs	2015(sh)	2041vs	1990m	1996(sh)	2030vs	2007(sh)
				2006s					2001(sh)
	1995m	2000(sh)	2019m	2002(sh)	2019m	1986m	1987s	2022s	1992s
		1988s	1999m	1990s	1999m		1973s	1997s	1979s
		1986(sh)	1992m	1986(sh)	1992m		1966s	1990s	1974s
^1H CMe_3 (δ)	1.53	1.5				1.54	1.5		
^{13}C CMe_3 (δ)	30.1	29.9				30.2	29.8		
CO (δ)	201.1	180.7		178.3		204.0	183.9		180.3

[a]Data for Os complexes from Reference 232.

The trisubstituted complex (3) is much more sensitive to oxidation than the other two derivatives, and I have not been able to obtain satisfactory microanalytical results. The spectral properties are consistent with substitution at all three metal atoms, with a three-band ν(CO) spectrum, and a singlet for the CO groups in the ^{13}C n.m.r. spectrum.

The mass spectra of these complexes are detailed in the Experimental section. They are characterised by parent ions which fragment by competitive loss of CO and $CNBu^t$ ligands; the near-equivalence of 3CO (84 daltons) and $CNBu^t$ (83 daltons) results in a series of 14 ion clusters spaced at approximately 28 units, although overlap of the ion clusters corresponding to $[P-4CO]^+$ and $[P-CO-CNBu^t]^+$ centred on *m/e* 584, and subsequent fragment ions, is apparent from the different intensity pattern compared with those of $[P-nCO]^+$ (n = 0-3). This suggests that loss of CO and $CNBu^t$ ligands become competitive after initial cleavage of one Ru-CO bond on each metal atom.

Similar complexes have been obtained with other isocyanides. Cyclohexyl isocyanide affords $Ru_3(CO)_{11}(CNCy)$ (4), whose infrared spectrum closely resembles that of (1), although the frequency of the ν(CN) band is some 15 cm^{-1} lower. The mono- (5) and di-substituted (6) *p*-methoxyphenyl isocyanide derivatives are yellow and red, respectively, and contain characteristic methoxy resonances in their ^1H n.m.r. spectra. Again, the ν(CO) spectra are similar to those found previously for $Ru_3(CO)_{12-n}(L)_n$ (n = 1 or 2) complexes. The reaction between $Ru_3(CO)_{12}$ and *p*-toluenesulphonylmethyl isocyanide contrasts with the above, in that the only product obtained under a variety of conditions was the purple-brown $Ru_3(CO)_9(CNCH_2SO_2C_6H_4Me\text{-}p)_3$ (7), which readily crystallises from the reaction mixture. Complex (7) is also

unusual in that the i.r. spectrum contains only one broad but strong ν(CO) band, at 1980 cm^{-1}, in addition to the ν(CN) absorption at 2168 cm^{-1}.

The infrared and n.m.r. spectra of some of these complexes are given in Table 3 and compared with those of similar osmium complexes described recently.[232] From this, it is evident that the various ν(CN) and ν(CO) frequencies are similar in position, but differ markedly in relative intensities when the two series are compared. Similarly, it is found that the ^{1}H and ^{13}C resonances are not very closely related. The osmium complex exists in two isomeric forms, with axial and equatorial isocyanide subsituents. The fluxional process is slowed sufficiently at -60° for individual ^{13}C resonances to be assigned, but the weighted mean for the axial isomer is some 20 ppm to lower field than found for (I). The ν(CO) spectra of the two complexes have similar patterns, most bands being shifted to higher frequencies by *ca.* 5-7 cm^{-1}. Similar comparisons between $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ show that these shifts form part of a general pattern, and indeed are consistent with the replacement of Ru by the heavier Os.

The nature of the substitution product obtained from $Ru_3(CO)_{12}$ and simple 2e donor ligands will depend on a number of factors, of which two practically important ones are the relative magnitudes of the rate constants for the successive reactions

$$Ru_3(CO)_{12} + L \underset{}{\overset{k_1}{\rightleftharpoons}} Ru_3(CO)_{11}(L) + CO \qquad (i)$$

$$Ru_3(CO)_{11}(L) + L \overset{k_2}{\rightleftharpoons} Ru_3(CO)_{10}(L)_2 + CO \qquad (ii)$$

$$Ru_3(CO)_{10}(L)_2 + L \overset{k_3}{\rightleftharpoons} Ru_3(CO)_9(L)_3 + CO \quad \ldots \text{ etc} \qquad (iii)$$

and the solubility of the various substituted products. In the case

of L = tertiary phosphine, k_2 and k_3 appear to be larger than k_1, i.e. reaction (i) is the rate-determining step, and even with a deficiency of tertiary phosphine, $Ru_3(CO)_9(L)_3$ is the usual product. However, if the reaction is carried out in a closed system, the partial pressure of CO may become sufficient to enable the intermediate products to be isolated.[240] I have shown also that the solubility of the products is an important factor, and that for L = PPh_3, for example, the complex $Ru_3(CO)_{10}(PPh_3)_2$ may be readily prepared by using hexane as solvent.

Reactions between $Ru_3(CO)_{12}$ and some isocyanides evidently have rate constants for reactions (i)-(iii) which allow successive formation (and isolation) of the three substitution products $Ru_3(CO)_{12-n}(L)_n$ (n = 1-3). Indeed, in most cases, reaction (iii) is so slow that forcing conditions are required. In one of the limited range of reactions studied, a trisubstituted product (7) was the only product isolated; in this instance the limited solubility of the complex is probably a factor aiding its formation under the reaction conditions I employed.

I have studied the reactions of $Ru_3(CO)_{11}(CNBu^t)$ (1) with several 2e donor ligands, including CO and phosphorus-, arsenic- and antimony-containing molecules. In most of these reactions, competing pathways involving loss of CO or $CNBu^t$ lead to the observed products.

Thus, with CO, the products are $Ru_3(CO)_{12}$ and $Ru_3(CO)_{10}(CNBu^t)_2$ (2), although most of the initial complex (1) was recovered. Optimum conditions were not established for any of these reactions. The former is formed by displacement of isocyanide by CO, in a reaction which reverses the formation of (1):

$$Ru_3(CO)_{11}(CNBu^t) + CO \rightleftharpoons Ru_3(CO)_{12} + CNBu^t$$

The displaced isocyanide is not volatile; hence it is not removed under these reaction conditions, and reacts with (1) to give the disubstituted complex (2).

A similar result was obtained with tertiary phosphines. With triphenylphosphine, the known complex $Ru_3(CO)_{11}(PPh_3)$ was obtained in low yield, being formed by displacement of $CNBu^t$ from (1). The major product, however, was the new, mixed ligand cluster $Ru_3(CO)_{10}(CNBu^t)(PPh_3)$ (8), readily identified by analysis and from its spectroscopic properties. In particular, the ν(CN) absorption at 2161 cm^{-1} indicated the presence of the isocyanide ligand, while the ν(CO) spectrum resembled that of other $Ru_3(CO)_{10}(L)_2$ complexes previously reported. The 1:1 ratio of isocyanide and tertiary phosphine ligands was confirmed by the presence of resonances of the appropriate chemical shifts and intensitites in the ^1H n.m.r. spectrum. Complex (8) may be formed by displacement of CO from (1) by the tertiary phosphine, or by reaction between free $CNBu^t$ and the monophosphine complex. The latter is suggested by the result obtained with tri-*p*-tolylphosphine, which after a short time (30 min) gave $Ru_3(CO)_{11}[P(C_6H_4Me\text{-}p)_3]$, whereas after 2 h, only the mixed ligand complex $Ru_3(CO)_{10}(CNBu^t)[P(C_6H_4Me\text{-}p)_3]$ (9) was obtained.

In both cases, reactions between (1) and excess tertiary phosphine gave the known $Ru_3(CO)_9(PR_3)_3$ (R = Ph or *p*-MeC_6H_4), the product normally isolated from thermal reactions with $Ru_3(CO)_{12}$ with these ligands.

The reaction between tricyclohexylphosphine and (1) gave several complexes in minor amount, which were not satisfactorily characterised. The major product, however, was $Ru_3(CO)_{10}(CNBu^t)(PCy_3)$ (10), also obtained from the isocyanide and $Ru_3(CO)_{11}(PCy_3)$. Satisfactory analyses were not obtained for the complex from either source, although their

identity was established from i.r. and ^1H n.m.r. spectroscopy; the latter contained resonances arising from the cyclohexyl and CMe_3 protons with correct relative intensitites. The product formed by displacement of isocyanide by tertiary phosphine, namely $Ru_3(CO)_{11}(PCy_3)$, was also isolated from the former reaction.

The thermal reaction between $Ru_3(CO)_{12}$ and $AsPh_3$ has long been known to give a disubstituted complex, $Ru_3(CO)_{10}(AsPh_3)_2$.[5] Accordingly, it was no surprise to find this complex among the products from the reaction of (1) with triphenylarsine; however, we did not find any evidence for the formation of $Ru_3(CO)_{11}(AsPh_3)$. In this case, the mixed isocyanide-tertiary arsine complex $Ru_3(CO)_{10}(CNBu^t)(AsPh_3)$ (11) was a minor purple product, which has similar spectroscopic properties to those of complex (8).

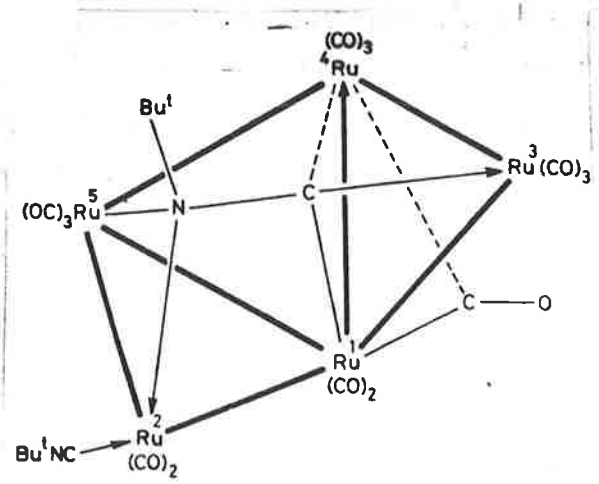
Perhaps of most interest was the reaction using triphenylstibine. Attempts to obtain derivatives of $Ru_3(CO)_{12}$ containing this ligand afforded only the mononuclear complex $Ru(CO)_4(SbPh_3)$.[241] However, the reaction of (1) and $SbPh_3$ afforded two complexes, yellow-orange $Ru_3(CO)_{10}(CNBu^t)(SbPh_3)$ (12) and brown $Ru_3(CO)_9(CNBu^t)(SbPh_3)_2$ (13). The former was fully characterised by analysis and from its spectral properties, which again resemble those of the analogous phosphorus and arsenic derivatives. Complex (13) could only be tentatively identified on the basis of its i.r. spectrum, containing a $\nu(CN)$ band at 2156 cm^{-1}, and a $\nu(CO)$ pattern similar to those of other $Ru_3(CO)_9L_3$ complexes, and its ^1H n.m.r. spectrum, which indicated the presence of one CMe_3 and six Ph groups. These are the first stibine-containing ruthenium cluster carbonyls to have been described, apart from a cursory mention of an uncharacterised complex $Ru_3(CO)_9(SbPh_3)_3$ said to be formed from $Ru_3(CO)_{12}$ and $SbPh_3$ during a kinetic study.[85]

The complex $Ru_3(CO)_{11}(CNBu^t)$ (1) exhibits a significantly different reactivity from that found for the parent carbonyl, $Ru_3(CO)_{12}$. Apparently competing reactions with 2e donor ligands result in displacement of either $CNBu^t$ or CO from (1) to give $Ru_3(CO)_{11}(L)$ or the new mixed-ligand complexes $Ru_3(CO)_{10}(CNBu^t)(L)$, respectively; subsequent reactions of initially-formed products with the displaced isocyanide ligand also afford the mixed-ligand complexes (Scheme 2). These reactions provide a new route to monosubstituted derivatives of $Ru_3(CO)_{12}$, and in somewhat higher yield, disubstituted complexes with predetermined combinations of ligands. The ease of displacement of either CO or isocyanide suggests that the isocyanide complex will be a useful precursor for a variety of new and unusual ligand combinations on the Ru_3 cluster; the potential utility is demonstrated here by the synthesis of the mixed isocyanide-tertiary stibine complex (12). Were the mono- or di-substituted Group VB donor ligand complexes generally available, one would predict that these would be even more useful, since we should not expect an isocyanide to displace the Group VB ligand easily. Work on this objective is described in following sections.

Pyrolysis of $Ru_3(CO)_{11}(CNBu^t)$ (1)

On heating powdered $Ru_3(CO)_{11}(CNBu^t)$ (1) at 120°, under a 0.5 atmosphere of nitrogen (16 h), a dark brown solid is obtained. Preparative t.l.c. gives a dark purple pentaruthenium cluster in low yield, characterised as $Ru_5(CO)_{14}(CNBu^t)_2$ (14) by X-ray crystallography (see Figure 6; Table 4).[265] Among the four other products isolated are residual (1), some (2) as well as a purple product, tentatively identified as $Ru_6(CO)_{15}(CNBu^t)_2$ (15) on the basis of mass spectrometric data. Pyrolysis of $Ru_3(CO)_{10}(CNBu^t)_2$ (2) also gave $Ru_5(CO)_{14}(CNBu^t)_2$ (14) and two other uncharacterised purple fractions.

FIGURE 6



$Ru_5(CO)_{14}(CNBu^t)_2$

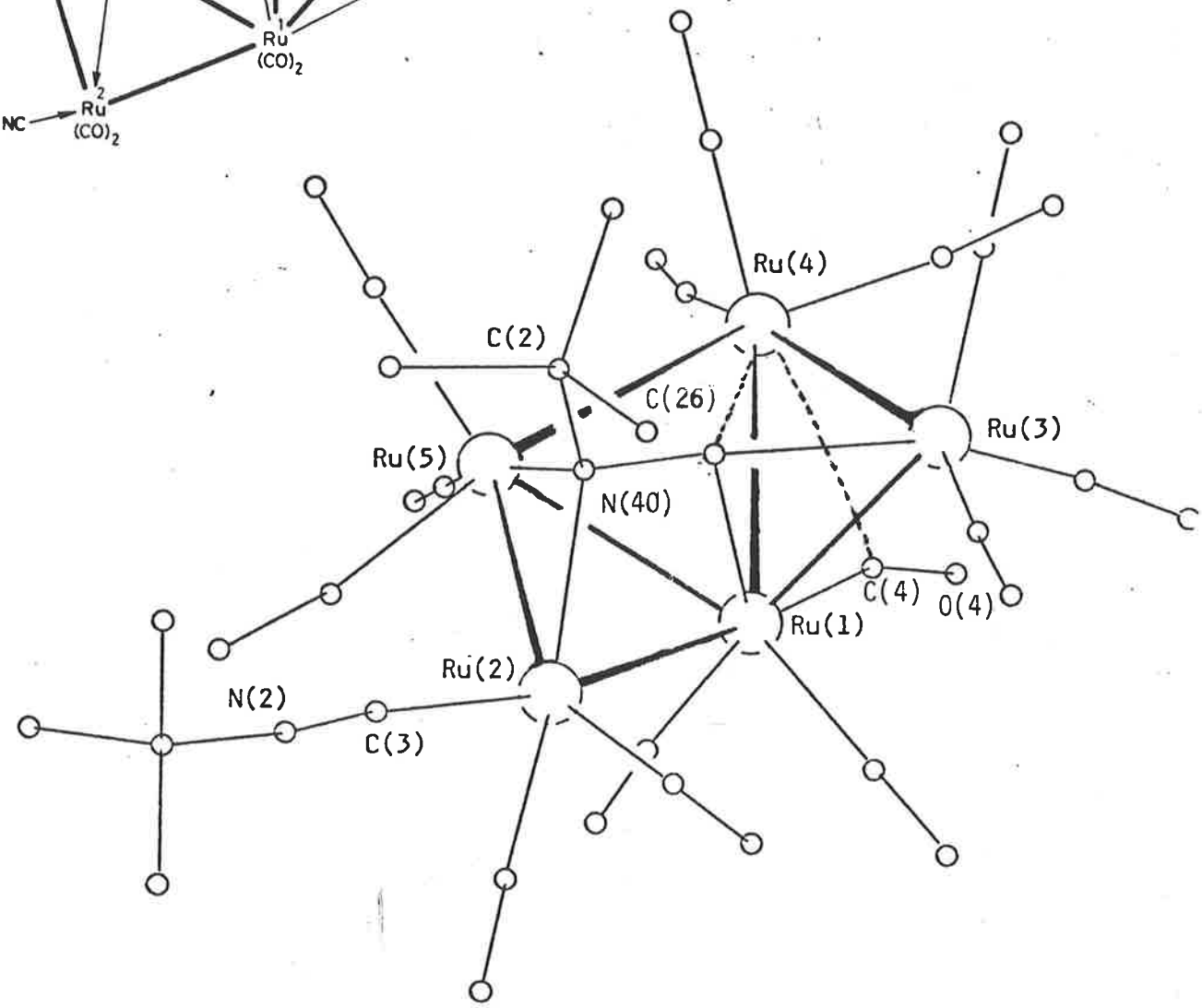


TABLE 4 Interatomic distances (Å)

Ru(1)-Ru(2)	2.784(1)	Ru(3)-C(26)	1.923(7)
Ru(1)-Ru(3)	2.833(1)	C(26)-N(40)	1.375(8)
Ru(1)-Ru(4)	2.776(1)	N(40)-Ru(2)	2.128(4)
Ru(1)-Ru(5)	2.778(1)	N(40)-Ru(5)	2.151(1)
Ru(2)-Ru(5)	2.745(1)	N(40)-C(2)	1.544(7)
Ru(3)-Ru(4)	2.767(1)	Ru(2)-C(3)	2.083(1)
Ru(4)-Ru(5)	2.864(1)	C(3)-N(2)	1.122(7)
Ru(1)-C(26)	2.156(5)	Ru(1)-C(4)	1.898(7)
Ru(4)-C(26)	2.388(5)	Ru(4)-C(4)	2.653(1)

The crystal structure shows that the five metal atoms form an open array of three edge-joined triangles, bent at these edges to form a swallow-shaped cluster, with Ru-Ru distances in the range 2.74-2.86 Å. Each metal atom is attached to three terminal 2e donor ligands (14 CO groups and one $CNBu^t$ ligand).

The attachment of the second isocyanide ligand is also noteworthy. The cluster electron count requires that this ligand should act as a 6e donor if the cluster is electron-precise, and this novel situation is achieved, formally at least, by N(40) acting as a 3e bridging atom to Ru(2)-Ru(5), while C(26) interacts with Ru(1) and Ru(3), also as a 3e donor. The C(26)-N(40) bond length [1.375(8) Å] and the Bu^t-N-C angle [122.2(5)°] are consistent with a reduction of the CN bond order.

This formal electron book-keeping results in Ru(4) being electron-deficient and Ru(1) electron-rich. However, if the interaction between these two metals takes the form of a donor bond from Ru(1) to Ru(4), this anomaly is removed. This interpretation is also supported by the geometry of the Ru(1)-C(4)-Ru(4) and Ru(1)-C(26)-Ru(4) interactions. Although the Ru(4)-C(4) and Ru(4)-C(26) distances are too long to be considered single bonds, the angles subtended by the two metal atoms at these carbon atoms [75.1(2) and 72.9(2)°, respectively] show that they can be considered to be new examples of ***semibridging*** interactions. Their function is to allow a redistribution of electron density over this part of the cluster.[198,266]

The formation of formidoyl ligands from isocyanide is common to the series $M_3(CO)_{12}$ (where M = Fe,[233,242-247] Ru[248,249] and Os[250-255]). Subsequent formation of higher nuclearity clusters by pyrolysis is, however, evident only for M = Ru and Os;[256] in accord with their greater metal-metal bond strength.[161-168]

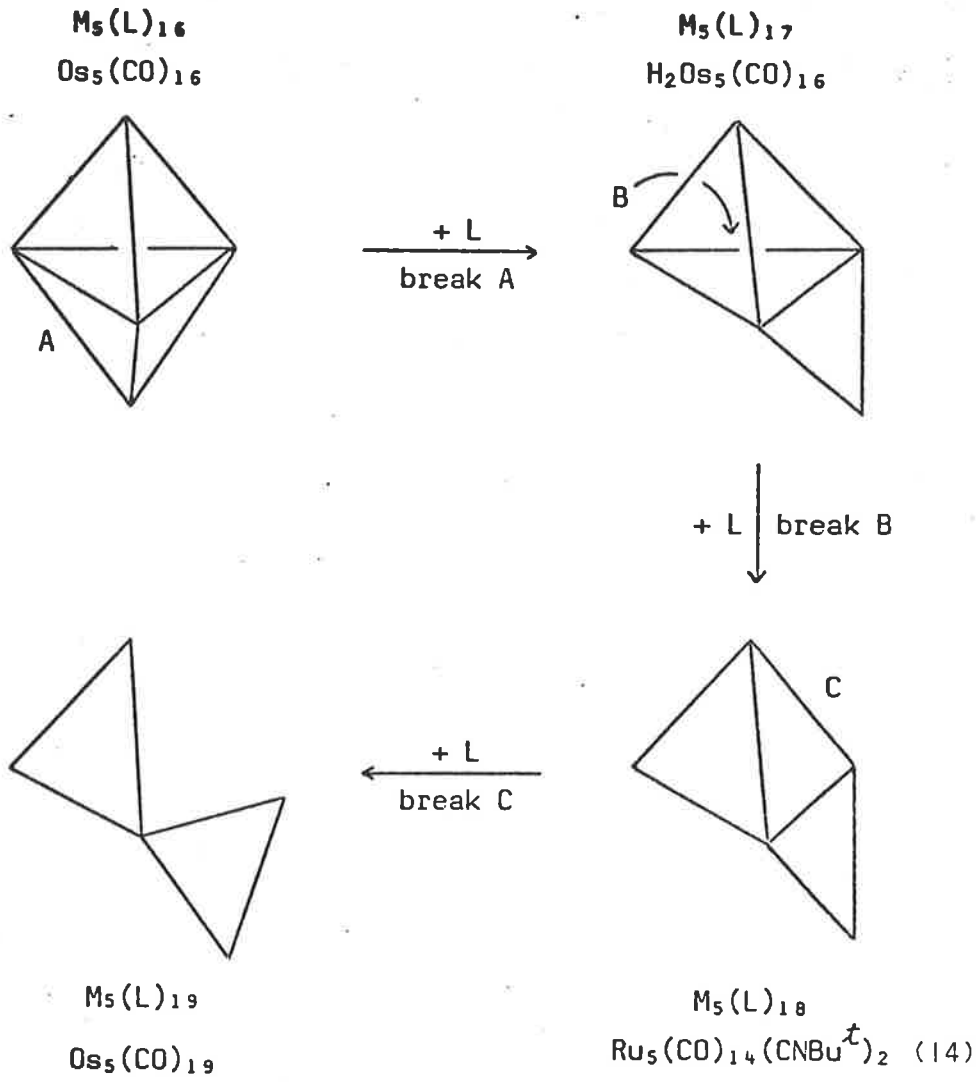
As part of a wider study[257,258] of substitution reactions of metal clusters initiated by Ph_2CO^- under mild conditions B. K. Nicholson synthesized $Fe_3(CO)_{11}(CNBu^t)$ in excellent yield.[259,260] Pyrolysis of this mono-substituted cluster at 90°-100° produces $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)$ also in good yield.[259] The isocyanide ligand lies across the face of the Fe_3 triangle, bonding in a $\sigma + 2\pi$ fashion to all three iron atoms.

This type of bonding is unprecedented for an isocyanide ligand, though it is known in isoelectronic nitrile[246] or acetylide ligands.[261-264] Pyrolysis of $Fe_3(CO)_{11}(CNCMe_3)$ up to 140° gave not only $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CNBu^t)$ but also a small amount of $Fe_3(CO)_8(\eta^1\text{-}CNBu^t)(\mu_3\text{-}\eta^2\text{-}CNBu^t)$, which contains a terminal mono-hapto $CNBu^t$ as well as the $\mu_3\text{-}\eta^2\text{-}CNBu^t$ ligand.[260] Subsequent pyrolysis above 140° resulted in cluster degradation. No clusters of higher nuclearity were detected at any stage.

Complex (14) is related to the *closo*-polyhedron[267-271] found in $[Os_5(CO)_{16}]$[272] and $[H_2Os_5(CO)_{15}]$;[273] the latter is known to react with $P(OMe)_3$ to give an adduct with an edge-bridged tetrahedron (B)[274] while the former affords $[Os_5(CO)_{19}]$ with the open cluster (D) by direct reaction with CO.[275] Complex (1) occupies an intermediate position, and completes a series of M_5 clusters (A)-(D) formally related by successive addition of 2e donor ligands and concomitant cleavage of one 2e metal-metal bond (Scheme 1).

The Ru-Ru bond distances are distributed into two groups of five between 2.745 and 2.784 Å, and two considerably longer bonds of 2.833 and 2.864 Å. The former are in the range found for Ru-Ru bonds in $Ru_3(CO)_{12}$ or $Ru_3(CO)_{11}(CNBu^t)$,[276] the shortest of these being the result of the presence of the $\mu\text{-}NBu^t$ group. The lengthening

SCHEME I



of the Ru(1)-Ru(3) and Ru(4)-Ru(5) bonds recalls the situation in $Os_5(CO)_{16}$, where bonds to the unique $Os(CO)_4$ group are longer than the other Os-Os bonds; however, in the present case, there is no such obvious explanation.

Interestingly, pyrolysis of $Os_3(CO)_{11}(CNBu^t)$ affords $Os_6(CO)_{16}(CNBu^t)_2$, which has the same metal skeleton as $Os_6(CO)_{18}$; in contrast, addition of isocyanide to the latter affords the adduct $Os_6(CO)_{18}(CNR)_2$, in which the μ_2-CNR ligand acts as a 4e donor, with a rearranged metal skeleton.[277]

The highly reactive $Ru_5(CO)_{14}(CNBu^t)_2$ complex readily adds two-electron ligands in a breakdown of the Ru_5 cluster to yield Ru_3 clusters.[278] Thus, bubbling CO through the purple hexane solutions of $Ru_5(CO)_{14}(CNBu^t)_2$ or the tentatively identified complex $Ru_6(CO)_{15}(CNBu^t)_2$, at 40-45° produces bright yellow solutions. On chromatography, these solutions yield $Ru_3(CO)_{12}$, $Ru_3(CO)_{11}(CNBu^t)$ (1) and $Ru_3(CO)_{10}(CNBu^t)_2$ (2), among other minor products. Infra-red spectroscopy indicates that the initial yellow solution has changed significantly after chromatography, to produce disproportionation products. The nature of this change, however, could not be elucidated.

(b) Thermal and Radical Ion-Initiated Synthesis of Specifically Substituted Ruthenium Cluster Carbonyls

In the experimental section, an improved synthesis of $Ru_3(CO)_{12}$ is described. Previously,[278,279] carbonylation of methanol solutions of hydrated ruthenium trichloride under moderate conditions of pressure and temperature, in the presence of zinc as a reducing agent and halogen acceptor, gave $Ru_3(CO)_{12}$ in approximately 70% yield. Exploration of the effects of temperature and pressure on the reaction has shown that the conversion of ruthenium trichloride to $Ru_3(CO)_{12}$ proceeds efficiently if the reaction is carried out at 125°, under a CO pressure of 50 atmospheres, *in the absence of zinc*. Under these conditions essentially quantitative conversion occurs. The carbon monoxide acts both as a reducing and carbonylating agent; by-products of the reaction are presumably hydrogen chloride and methyl formate. Recycling the mother liquor enables further 55-60 gms of ruthenium trichloride to be converted into $Ru_3(CO)_{12}$. Further recycling results in formation of more $Ru_3(CO)_{12}$ together with significant quantities of $H_4Ru_4(CO)_{12}$ (10-23%). Initially the mother liquor is orange-yellow, but recycling this solution (10-25 gms of $RuCl_3$) gives a green colour, which after further turnovers produces an intermediate red-brown colour

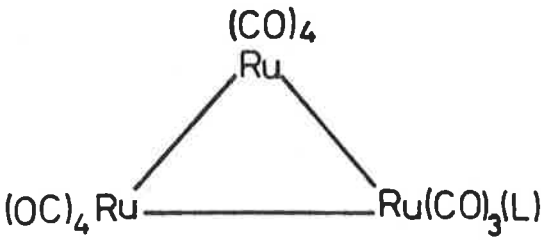
leading finally to a dark brown solution. The poor solubility of $Ru_3(CO)_{12}$ in methanol enables its isolation from each solution by filtration. Under milder conditions (less than 10 atmospheres CO/70°C) the major product is $[RuCl_2(CO)_3]_2$, but this may be accompanied by up to 18% $Ru_3(CO)_{12}$.[278]

As mentioned in the introduction to this chapter, the reaction between $Ru_3(CO)_{12}$ and substituted phosphines usually proceeds without the isolation of mono- or di-substituted derivatives. Substitution of carbonyl ligands in metal clusters is generally effected under thermal or photochemical conditions, and often leads to incomplete reactions and/or to a mixture of mono- and poly-substituted compounds.

Recently it was shown that specific carbonyl substitution can be electrochemically induced.[223] The application of this reaction to the sequential incorporation of various ligands allows designed syntheses of a wide range of cluster complexes containing two or more ligands to be achieved.[257,258,280] These reactions proceed at or just above room temperature with reaction times of between a few minutes and half an hour. The progress of the reaction can be monitored conveniently by inspection of the ν(CO) region of the i.r. spectrum of the reaction mixture. Isolation of the product is a simple routine of solvent removal and crystallisation, thus avoiding tedious chromatography, which in some cases may result in alteration or loss of product.

The large number of complexes that are obtained is best discussed on a ligand-by-ligand basis, and Figure 7 illustrates the general formulae of the cluster derivatives, and lists the ligands used. A study of substitutions promoted by heat was initially undertaken and these results are summarised together with the radical ion promoted substitutions. The majority of complexes obtained *via* the latter route (ad-

FIGURE 7



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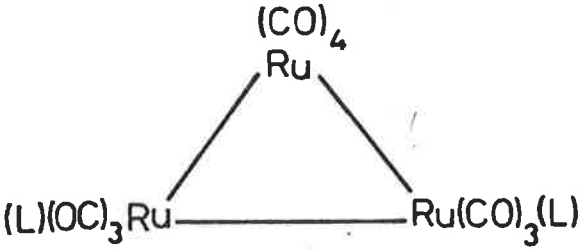

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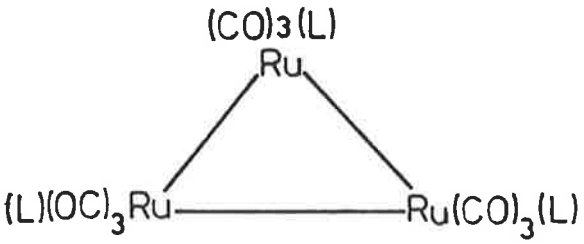

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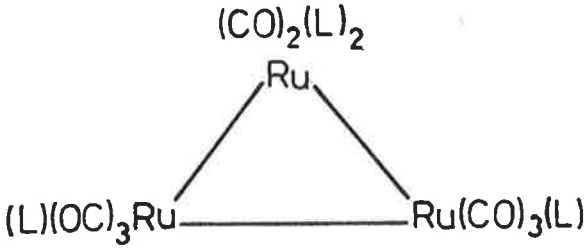

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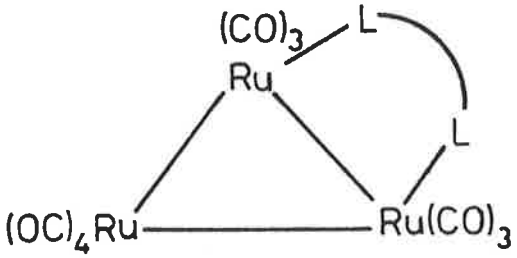

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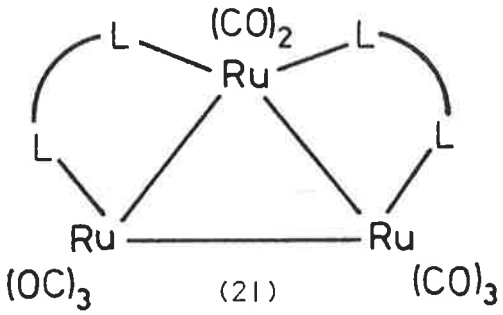

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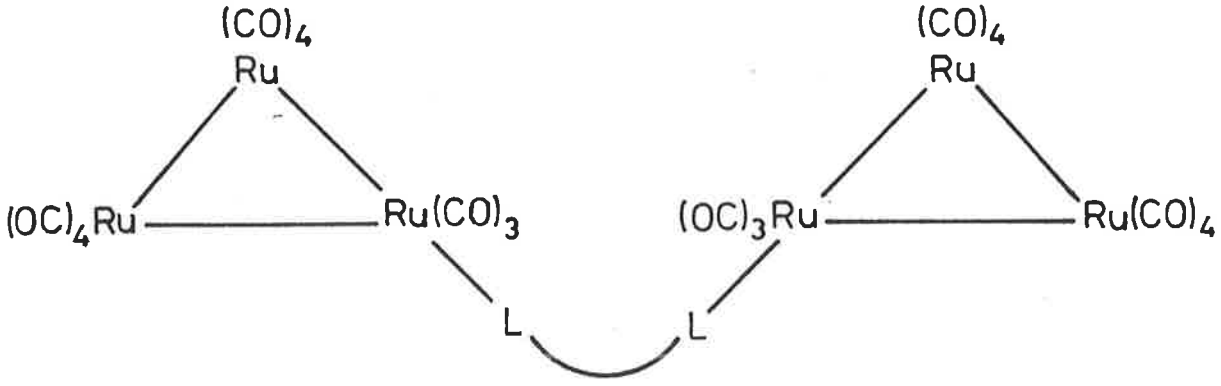

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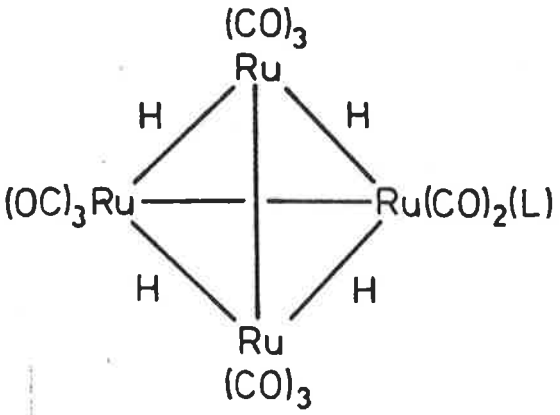
FIGURE 7 (cont.)



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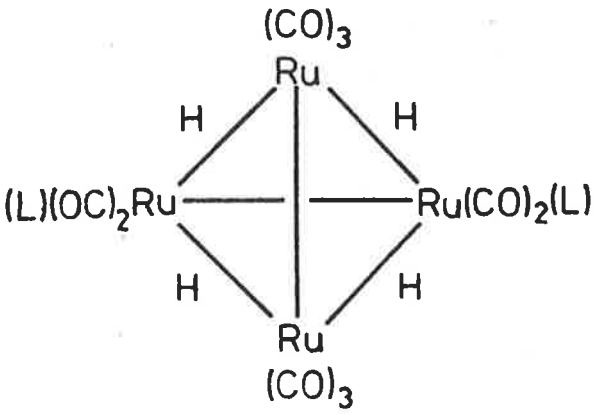

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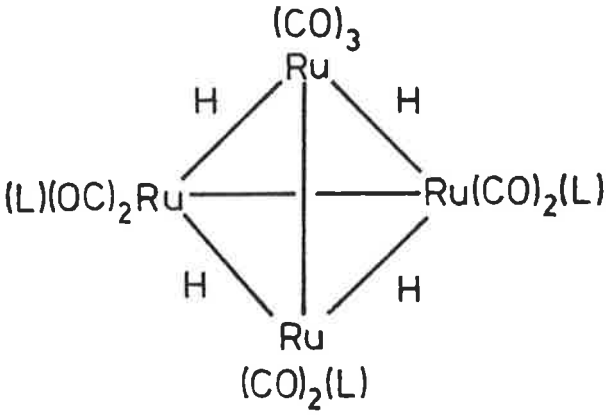

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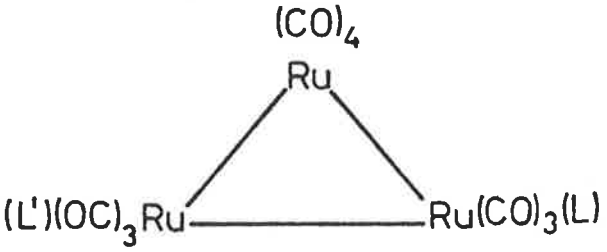

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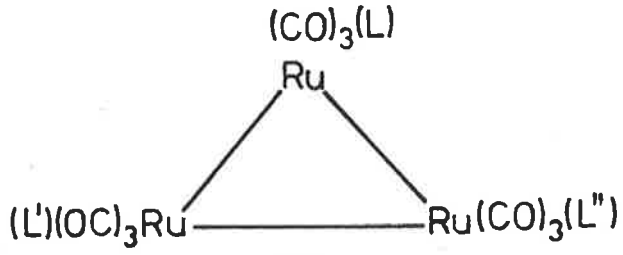

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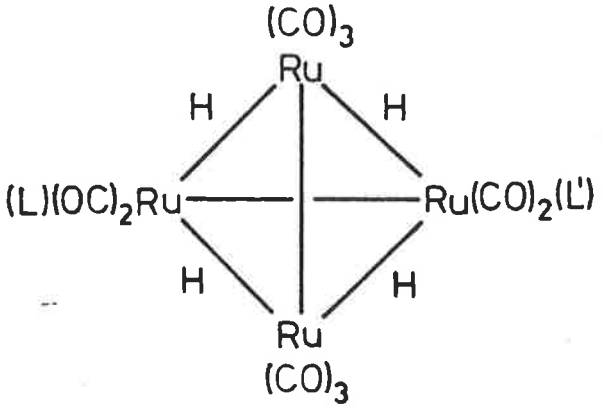

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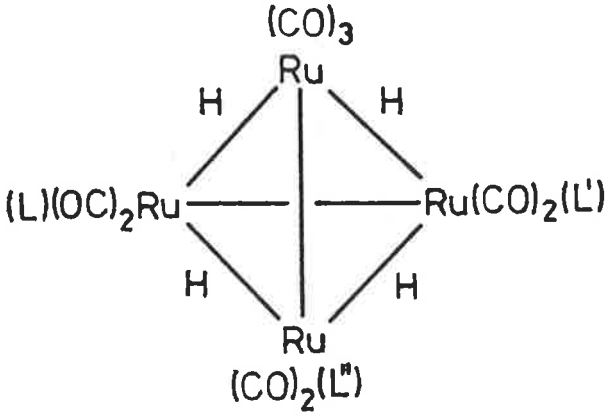

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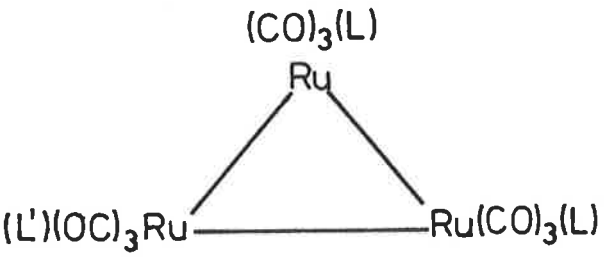


(30)

dition of sodium diphenylketyl to a stoichiometric mixture of $Ru_3(CO)_{12}$ and the ligand in tetrahydrofuran) are described in the Experimental section. The substitution chemistry of $H_4Ru_4(CO)_{12}$, as completed by Dr. B. K. Nicholson, is discussed briefly, but not incorporated in the Experimental section.

(a) Trimethylphosphine. To my knowledge, no complexes of types 16-19 containing PMe_3 have been described hitherto. First studied was the thermally induced reaction which at Australian summer room temperature proceeded readily to give (16a) and (17a), and on moderate heating, complexes (18a) and (19a), the relative proportions depending on the relative amounts of reactants present. This behaviour contrasts with the usual reactions between $Ru_3(CO)_{12}$ and PR_3, which afford the tri-substituted derivative; the Experimental section records the best of a limited number of experiments designed to optimise the yields of each complex. A minor product from a relatively large scale reaction employing *ca.* four mole equivalents of the phosphine was (19a), obtained as a dark-red solid.

As with all complexes described herein, the PMe_3 derivatives were readily characterised by analysis and spectroscopy: the i.r. spectra are discussed below. The ^1H n.m.r. spectra of (16a), (17a) and (18a) contained characteristic doublets for the P*Me* groups; that of (19a) contained two equal intensity doublets, suggesting a structure in which two Ru atoms each bear one equatorial PMe_3 substituent, while the third has two PMe_3 substituents, either both axial or both equatorial. Since (18a) is known to have the three PMe_3 ligands attached one to each Ru in an equatorial position,[281] the latter is preferred. Presumably steric interaction of the fourth PMe_3 ligand with the other PMe_3 and CO groups on the cluster renders the formation of (19a) difficult, leading to its isolation in only very low yield. The mass

spectrum of (19a) contains a parent ion cluster centred on *m/e* 833, which fragments by stepwise loss of the eight CO groups.

(b) Dimethylphenylphosphine. Complexes (16b), (17b) and (18b) have been described previously,[88] being obtained from thermal reactions between $Ru_3(CO)_{12}$ and the phosphine [(16b), 3%; (17b), 17%; (18b), 19%]. The present method offers a significant improvement in yield.

(c) Triphenylphosphine. Complex (18c) is perhaps the best-known of the Group V ligand derivatives of $Ru_3(CO)_{12}$, having been studied on numerous occasions.[77,83-88,90,282] The mono- and di-substituted complexes (16c) and (17c) have also been described by several workers, being obtained from (18c) and CO[240] or from $Ru_3(CO)_{12}$ and $Pt(\eta^2\text{-stilbene})(PPh_3)_2$.[88] The radical ion-initiated reactions afford these complexes specifically and in high yield. It is also of interest that we have found that these materials can also be obtained from short thermally induced reactions between $Ru_3(CO)_{12}$ and PPh_3, albeit with the necessity for chromatographic purification if (16c) or (17c) are required.

(d) Tris(p-tolyl)phosphine. Previous reports have described (18d),[88] and I obtained this complex, free from either (16d) or (17d), from a reaction between $Ru_3(CO)_{12}$ and $P(C_6H_4Me\text{-}p)_3$ in refluxing hexane. The previously unreported (17d) was obtained in 79% yield from the radical-ion initiated reaction in thf.

(e) Tris(o-tolyl)phosphine. This sterically demanding ligand does not give simple substitution products in thermal reactions with $Ru_3(CO)_{12}$. Only low yields of (16e) were obtained from the radical-ion initiated reaction.

(f) Tricyclohexylphosphine. A maximum of two CO groups can be displaced by the bulky PCy_3 ligand in either thermally or radical ion-induced reactions. Complex (17f) is unusual in being eluted before the mono-substituted complex (16f), perhaps as a result of the hydrocarbon-like envelope of cyclohexyl groups in the former complex which reduces its affinity for the chromatographic adsorbent. With a large excess of PCy_3 breakdown of the cluster occurs to give a low yield of a complex of composition $Ru(CO)_2(PCy_3)_3$; the two ν(CO) bands indicate a *cis*-$Ru(CO)_2$ arrangement. The high ν(CO) frequencies, oxidative stability and high melting point suggest that it is not a simple ruthenium(0) derivative, however.

(g) Tris(2-cyanoethyl)phosphine. The addition of sodium diphenylketyl to the stoichiometric mixture of $Ru_3(CO)_{12}$ and $P(CH_2CH_2CN)_3$ produced a deep red solution (after 1-2 min.) with considerable effervesence (CO evolution). These reactions were unusual as continued stirring (5-10 min.) gives a yellow-orange (17g) or orange (18g) precipitate. Filtration afforded the new complexes (17g) and (18g). Infra-red and other data (see Experimental section) are consistent with these complexes being the di- and tri-substituted derivatives. Infra-red spectra of the initial deep red solution, however, were not compatible with the final complexes isolated. The mono-substituted complex (16g) could not be obtained. The data suggests that the CN functional group interacts with the Ru_3 triangle during the course of the reaction, and possibly in the final products. The extent and nature of this interaction can only be determined by X-ray structural studies.

The low solubility of complexes (17g) and (18g) suggests a possible multi-centre interaction linking Ru_3 triangles by alternate $P\rightarrow$ and $C\equiv N\rightarrow$ coordination to Ru centres on the different Ru_3 triangles. The analytical data, however, does not affirm this. The thermal re-

activity of $P(CH_2CH_2CN)_3$ was not studied. It is noteworthy that the unusual nature of $P(CH_2CH_2CN)_3$ has been observed both with respect to its stability toward oxidation,[283] its low basicity[284] and its unique reactivity with $Ni(CO)_4$ to yield a tetrahedral nickel cluster.[285]

(h) Trimethylphosphite. The advantages of the new route to these substituted complexes are again illustrated in the reactions of $P(OMe)_3$, from which high yields of specifically mono-, di- or tri-substituted products were obtained. These contrast with the low yields of mixtures of products obtained on heating the two reactants, and this reaction is one example where the tri-substituted complex is not formed as a preferred product.

(i) Dimethylphenylphosphinite. Complexes (17i) and (19i) containing $PPh(OMe)_2$ have been obtained previously in low yield from thermal reactions between $Ru_3(CO)_{12}$ and the ligand.[88] Moderate to high yields of the pure complexes (16i) and (18i) were obtained by the reactions described here.

(j) Tri-p-tolyl phosphite. Each of the complexes (16j), (17j) and (18j) was obtained pure from stoichiometric proportions of reactants; the solubility of (17j) proved to be higher than usual, resulting in only 26% isolated yield of this complex.

(k) 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane. The constrained phosphite $P(OCH_2)_3CEt$ reacted similarly to give the first triruthenium carbonyl complexes containing this ligand.

(l) Triphenylarsine. Only the disubstituted complex (17l) was obtained from heating $Ru_3(CO)_{12}$ and $AsPh_3$ in refluxing hexane.[88,91] The radical ion-initiated reaction of appropriate proportions of reactants afforded

(171) and (181), the latter identified by comparison with a known sample, but no tri-substituted complex could be obtained.

(m) Triphenylstibine. The only product isolated from the reaction between $Ru_3(CO)_{12}$ and $SbPh_3$, on irradiation in hexane solution, was the mononuclear $Ru(CO)_4(SbPh_3)$, formed by breakup of the Ru_3 cluster.[241] In contrast, our reaction conditions enabled isolation of orange (16m) as the first organostibine derivative of $Ru_3(CO)_{12}$ to be described.

(n) t-Butyl isocyanide. The present results show that these complexes may also be obtained in high yield by the radical ion-initiated reaction. The $CNBu^t$ derivatives (1) and (2) were obtained.

(o) Cyclohexyl isocyanide. As found for most of these reactions, the yield of (4) was considerably greater than that obtained by thermal reaction.[281]

(p) R-(+)-α-methylbenzyl isocyanide. Complex (16p), containing an optically active isocyanide ligand, was so soluble in hexane that only a poor isolated yield was obtained.

(q) Bis(diphenylphosphino)methane. The reaction between $Ru_3(CO)_{12}$ and dppm has been described recently.[188] In xylene at 80-85°, complex (20q) was obtained in 73% yield, while at 130°, oxidative addition of the ligand to the Ru_3 cluster occurred to give $Ru_3(\mu_3\text{-}PPh)(\mu\text{-}CHPPh_2)(CO)_7(dppm)$. A similar reaction in refluxing cyclohexane afforded both (20q) and (21q), together with some of the phosphinidene complex. Complexes (20q) and 21q) were obtained as the sole products in stoichiometric reactions carried out according to our general procedure; no alteration product was produced in these reactions which went to completion in a few minutes at room temperature. As found with the related bidentate ligand

dppe,[191] reaction of $Ru_3(CO)_{12}$ with 0.5 mole equivalent of dppm afforded a complex containing two $Ru_3(CO)_{11}$ units bridged by a dppm ligand (22q).

(r) Bis(diphenylarsino)methane. A mixture of (20r) and (21r) can be obtained from reactions carried out in refluxing toluene, although some evidence for further reaction on longer heating was obtained. The radical ion-initiated syntheses proceeded well for (20r), but unusually only a very low yield of (21r) was isolated from the 1:2 reaction.

(s) 1,2-Bis(diphenylarsino)ethane. With this ligand, the complex (20s) has been isolated as the only product of the reaction initiated by $Na[Ph_2CO]$. The thermal reaction of $Ru_3(CO)_{12}$ and ligand requires chromatographic purification.

Reactions of $H_4Ru_4(CO)_{12}$. Thermally-induced reactions of $H_4Ru_4(CO)_{12}$ with a number of tertiary phosphines and phosphites have been described, and are characterised by the formation of most, if not all, of the substitution products $H_4Ru_4(CO)_{12-n}L_n$. Similar reactions carried out in the presence of $Na[Ph_2CO]$ radical initiator gave smooth reactions affording high yields of a single pure complex, the composition of which reflected the molar ratio of the reactants. Thus, whereas the reaction between $H_4Ru_4(CO)_{12}$ and $P(OMe)_3$ gave a complex mixture of $H_4Ru_4(CO)_{12-n}[P(OMe)_3]_n$ (n = 0-4) complexes which required extensive chromatography to obtain pure complexes,[286] two of these compounds can be obtained pure in room temperature reactions between $H_4Ru_4(CO)_{12}$ and one or three molar equivalents of $P(OMe)_3$. Interestingly, increasing amounts of initiator are required as the degree of substitution increases. Similar results were obtained with PPh_3, $P(OC_6H_4Me\text{-}p)_3$ and

$CNBu^t$, the products being characterised by comparison with reported spectroscopic data.[249,287]

Preparation of mixed ligand derivatives of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$

As far as I am aware, the only references to derivatives of $Ru_3(CO)_{12}$ containing ~~more than one~~ two or more different tertiary phosphines are to the ligand exchange reactions between $Ru_3(CO)_9(PPh_3)_3$ and PEt_3, in which all possible complexes $Ru_3(CO)_9(PEt_3)_n(PPh_3)_{3-n}$ (n = 1-3) were detected spectroscopically, but not otherwise characterised.[282] A reaction between $Ru_3(CO)_9(PPh_3)_3$ and PBu_3 is reported to give $Ru_3(CO)_9(PBu_3)_3$, but no intermediate complexes were described.[104]

The ready availability of specifically substituted derivatives of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$, such as those described above, suggested that successive reactions with different ligands might afford designed synthesis of new complexes containing two or more different ligands, other than CO. The appropriate experiments showed this to be the case, and complexes can be made containing several different combinations of ligands.[280] The new complexes were characterised by the usual combination of analytical and spectroscopic methods, the significant data being summarised in Tables 8-11 (see Experimental section). As with poly-substitution with one ligand, reactions leading to tri-substituted complexes require somewhat more radical ion initiator than those giving mono- or di-substituted derivatives; these reactions are also best carried out by warming the reaction mixture (to *ca.* 40-50°) for 15-30 minutes.

In one instance, a ligand other than CO is replaced. The radical-initiated reaction between $Ru_3(CO)_{11}(AsPh_3)$ (16l) and $P(OCH_2)_3CEt$ gives the two complexes $Ru_3(CO)_{12-n}[P(OCH_2)_3CEt]_n$ [(n = 1 and 2) (16k) and

(17k)] in addition to the expected $Ru_3(CO)_{10}[P(OCH_2)_3CEt](AsPh_3)$ (26kl). The total conversion amounts to 92% (based on separated isolated products). The formation of the phosphite-substitution products can be explained by competitive loss of CO and $AsPh_3$ from the intermediate radical anion (*vide infra*). Indeed, free $AsPh_3$ was detected on the thin-layer chromatogram of the reaction products. Not surprisingly, when $CNBu^t$ was added to the above reaction mixture (in the initial expectation that the mixed phosphite-arsine complex was the only product), six complexes were isolated. The major product was $Ru_3(CO)_9(CNBu^t)[P(OCH_2)_3CEt]_2$ (30kn) and the expected $Ru_3(CO)_9(AsPh_3)(CNBu^t)[P(OCH_2)_3CEt]$ (27kln) was obtained only in trace amounts. These results indicate that although the radical-anion initiated route to mixed-ligand clusters can be used successfully in many cases, caution must be exercised in the synthesis of complexes containing ligands of widely differing basicity. In these cases, it is likely that high yields of the desired products will be obtained by only one of the several permutations of the individual synthetic routes, which will be determined by the relative basicities of the ligands employed.

Reactions of $Os_3(CO)_{12}$ and $H_4Os_4(CO)_{12}$. Thermally induced reactions of $Os_3(CO)_{12}$ or $H_4Os_4(CO)_{12}$ with tertiary phosphines and arsines have been described, and are characterised by the formation of most, if not all, of the substitution products.[159,288-294] Similar reactions carried out in the presence of $Na[Ph_2CO]$ resulted in an analogous product distribution. Thus, no improvement over the thermal reactions has occurred. The lower temperature required for these reactions, however, gives improved yields of primary substitution products, with little or no decomposition (see Experimental section).

Reactions of $HRu_3(CO)_9(C \equiv C\text{-}Bu^t)$. The hydride complex, $HRu_3(CO)_9(C_2Bu^t)$, reacted with t-butylisocyanide or triphenylphosphine, in the presence of sodium diphenylketyl, to give a host of products, among which could be identified $HRu_3(CO)_8(CNBu^t)(C_2Bu^t)$ (53) or $HRu_3(CO)_8(PPh_3)(C_2Bu^t)$ (52), respectively. Both reactions were followed by i.r. and t.l.c., and there appeared to be several competing reactions taking place; the mono-substituted derivatives being isolated in low yield. Better yields can be obtained by reacting the appropriate phosphine-substituted $Ru_3(CO)_{12}$ derivative with the acetylene in refluxing hydrocarbon solvents (*vide infra*).

Preparation of $Ru_6(CO)_{18}^{2-}$. Introduction of two equivalents of $Na[Ph_2CO]$ to $Ru_3(CO)_{12}$ in a thf solution results in considerable effervescence. Subsequent addition of a large cation to the resultant deep red solution gives $Ru_6(CO)_{18}^{2-}$ (54) in 94% yield. This product was characterised by comparison with previous data.[295-298] The yield obtained [$(Et_4N^+)_2$ counterion] is the best thus far reported. The synthesis is also quick (15 min.), and the subsequent work-up of the reaction only involves solvent removal and recrystalisation (CH_2Cl_2/n-hexane); thus representing an improvement over previous reports.[295-298]

Discussion of Mechanism

There is ample precedent in the extant literature that odd-electron species are more labile toward substitution than their diamagnetic organometallic precursors.[299] Pletcher and Pickett[300,301] found the cation radical $Cr(CO)_6^+$ to be substantially more persistent in trifluoroacetic acid than in the more nucleophilic acetonitrile. Furthermore, the substitution of CO ligands by phosphines and phosphites is accelerated in several cobalt and iron carbonyl complexes upon one-electron reduction.[223,302] The cyclic voltammetric data

presented by Rieger *et al.*[223,302] indicated rapid substitution of the anion radical. The radical produced by the reversible homolytic scission of the Mn-Mn bond is responsible for ligand exchange in $[Mn(CO)_4(PPh_3)]_2$.[303-306] In a series of elegant studies, Brown and co-workers[112,117,118,307] have demonstrated the chain substitution of $HM(CO)_5$ (where M = Re, Mn) to form $HM(CO)_4L$ *via* the $M(CO)_5^{\bullet}$ radical. Similarly substitution of $HM(CO)_3Cp$ (where M = Mo, W) involves the analogous $M(CO)_3Cp^{\bullet}$ radicals.[119] Furthermore, the radical $Co(CO)_4^{\bullet}$ is the substitution-labile species in the chain reactions of $Cl_3SnCo(CO)_4$ and $Co_2(CO)_8$ (L = PR_3, AsR_3) to form $[Co(CO)_3L_2]^+SnCl_3^-$ and $[Co(CO)_3L]$ respectively.[120-124,308,309]

The results to hand are similar to an electron transfer catalysis process (ETC),[310-312] which proceeds *via* a $S_{RN}1$ mechanism [equations (1)-(3)],[310-316] common in organic chemical reactions.

$$[RX]^{\bullet -} \longrightarrow R^{\bullet} + X^- \quad \ldots (1)$$

$$R^{\bullet} + Y^- \longrightarrow [RY]^{\bullet -} \quad \ldots (2)$$

$$[RY]^{\bullet -} + RX \longrightarrow RY + [RX]^{\bullet -} \quad \ldots (3)$$

When $[RY]^{\bullet -}$ is a reasonably long-lived radical anion (correspondingly RY is then an easily reduced species), and equation (3) occurs rapidly, then an electron-transfer chain catalysed process is established. The proposed mechanism for the electron transfer process with $Ru_3(CO)_{12}$ is outlined in equations (4)-(6).

$$Ru_3(CO)_{12} + [Ph_2CO]^{\bullet -} \longrightarrow [Ru_3(CO)_{12}]^{\bullet -} + Ph_2CO \quad \ldots (4)$$

$$[Ru_3(CO)_{12}]^{\bullet -} + L \longrightarrow [Ru_3(CO)_{11}L]^{\bullet -} + CO \quad \ldots (5)$$

$$[Ru_3(CO)_{11}L]^{\bullet -} + Ru_3(CO)_{12} \longrightarrow Ru_3(CO)_{11}L + [Ru_3(CO)_{12}]^{\bullet -} \quad \ldots (6)$$

The process relies on the increased susceptibility of the radical anion

of $Ru_3(CO)_{12}$ toward nucleophilic attack, as compared with the neutral parent cluster. This probably results from the extra electron entering a Ru-Ru antibonding orbital, thus facilitating Ru-Ru bond cleavage to generate a labile 17 electron metal centre. An alternative mechanism is proposed for a reaction involving CO loss from an intact Fe_3 cluster;[317] the evidence presented is more applicable to an ETC chain process.[318,319] On the basis of a brief electrochemical study of $Ru_3(CO)_{12}$,[58,59] where it was shown that the $[Ru_3(CO)_{12}]^{\bullet-}$ radical anion has a very short lifetime (in acetone), Robinson *et al.*,[319] have suggested that substitution at $Ru_3(CO)_{12}$ initiated by $[Ph_2CO]^{\bullet-}$ does not involve an ETC process, but occurs by an alternative, unspecified route. Any mechanism incorporating cluster degradation, however, must account for the ready formation of $Ru_6(CO)_{18}^{2-}$ (54) and the specific generation of Ru_3 derivatives containing mixed ligands in high yield. For organic systems the ETC process is known to be highly selective and generally gives a major product in high yield.[310]

The following general points can be made about the substitution reactions studied:-

(1) For $Ru_3(CO)_{12}$, mono-, di- and tri-substitution can be brought about by catalytic amounts of $Ph_2CO^{\bullet-}$, although efficiencies decrease with higher substitution. For example, formation of $Ru_3(CO)_{12-n}[P(OCH_2)_3CEt]_n$ required 2 mol % (n = 1), 3 mol % (n = 2) and 30 mol % (n = 3) of initiator. This is not unexpected; reduction of a cluster to the corresponding anion is rendered more difficult as CO is replaced by poorer π-acceptor ligands PR_3, presumably slowing the electron transfer step (equation 6). At the same time, steric and statistical factors will tend to discourage higher substitution.

(2) For most examples, the infra-red spectra of the crude reaction mixtures indicate that quantitative conversion to one product had occurred; yields quoted are isolated yields of recrystallised products, some of which have quite high solubilities in hydrocarbons.

(3) Reactions with PR_3, $P(OR)_3$ and CNR were all efficiently initiated but those with AsR_3, SbR_3 and BiR_3 were decreasingly so, to the extent that no $Ru_3(CO)_{11}(BiPh_3)$ complex is isolated. This trend presumably reflects the decreasing nucleophilicity of MR_3 as the atomic weight of M increases.

(4) For neither of the ruthenium clusters studied were products arising from cluster breakdown observed as co-products.

(5) Reactions with $H_4Ru_4(CO)_{12}$ were noticeably less efficient than with $Ru_3(CO)_{12}$. Possible chain-termination processes of $H_4Ru_4(CO)_{12}^{\cdot}$ (the postulated intermediate) by loss of hydride ligands may be responsible for this. It was noted in stepwise reactions with $H_4Ru_4(CO)_{12}$ that the second substitution was apparently more facile than the first. However, this may be an artefact arising from the poor solubility of $H_4Ru_4(CO)_{12}$ (compared with most $H_4Ru_4(CO)_{11}L$ complexes) which meant that reactions had to be carried out with dilute and/or warmed solutions which are likely to have an adverse effect on the reaction because of decreased electron transfer rates or increased radical-anion decay.

(6) The maximum degree of substitution obtainable with $H_4Ru_4(CO)_{12}$ depends on the incoming nucleophile. Thus, with excess $P(OMe)_3$ the trisubstituted $H_4Ru_4(CO)_9[P(OMe)_3]_3$ was the final product, whereas with excess PPh_3 only $H_4Ru_4(CO)_{10}(PPh_3)_2$ could be obtained despite the addition of up to 30 mmol% initiator.

Spectroscopic studies

The isolation of a number of specifically substituted derivatives of $Ru_3(CO)_{12}$ has enabled us to record definitive ν(CO) spectra and to establish some features of these spectra in relation to the degree of substitution. Figure 8 shows some typical spectra of the complexes $Ru_3(CO)_{12-n}L_n$, and Table 10 (see Experimental section) lists the frequencies of the main absorptions for each of the complexes studied.

For n = 1, there are three, sometimes four, strong bands between 1985 and 2055 cm^{-1}, together with a weak to medium absorption between 2090-2100 cm^{-1}. As expected, the frequencies of all bands decrease as the basicity of the ligand increases. The spectra of the disubstituted complexes show two main bands, the profiles of which indicate that the envelope contains three or more absorptions, between 1966 and 2050 cm^{-1}, with a high-energy absorption between 2070 and 2090 cm^{-1}. There is a general decrease in frequency with the introduction of the second ligand. The trends in the tri-substituted complexes are less obvious, with the ν(CO) spectra being much less well resolved; the major absorptions again lie between 1965 and 2050 cm^{-1}, as broad envelopes which may be resolved into individual maxima, with the highest energy band being found between 2050 and 2085 cm^{-1}. For n = 4, where a wide range of complexes is not available for comparison, the overall absorption pattern is shifted to lower energies by some 20 cm^{-1} from the tri-substituted complexes, reflecting the distribution of electron density from the phosphorus ligands into the CO antibonding orbitals. There is no pronounced band at higher frequencies.

These spectra have proved useful in monitoring most of the reactions reported above, and the most diagnostically useful features are the high frequency bands mentioned above. These tend to be separated from the major absorption, and are sufficiently different in fre-

FIGURE 8(i)

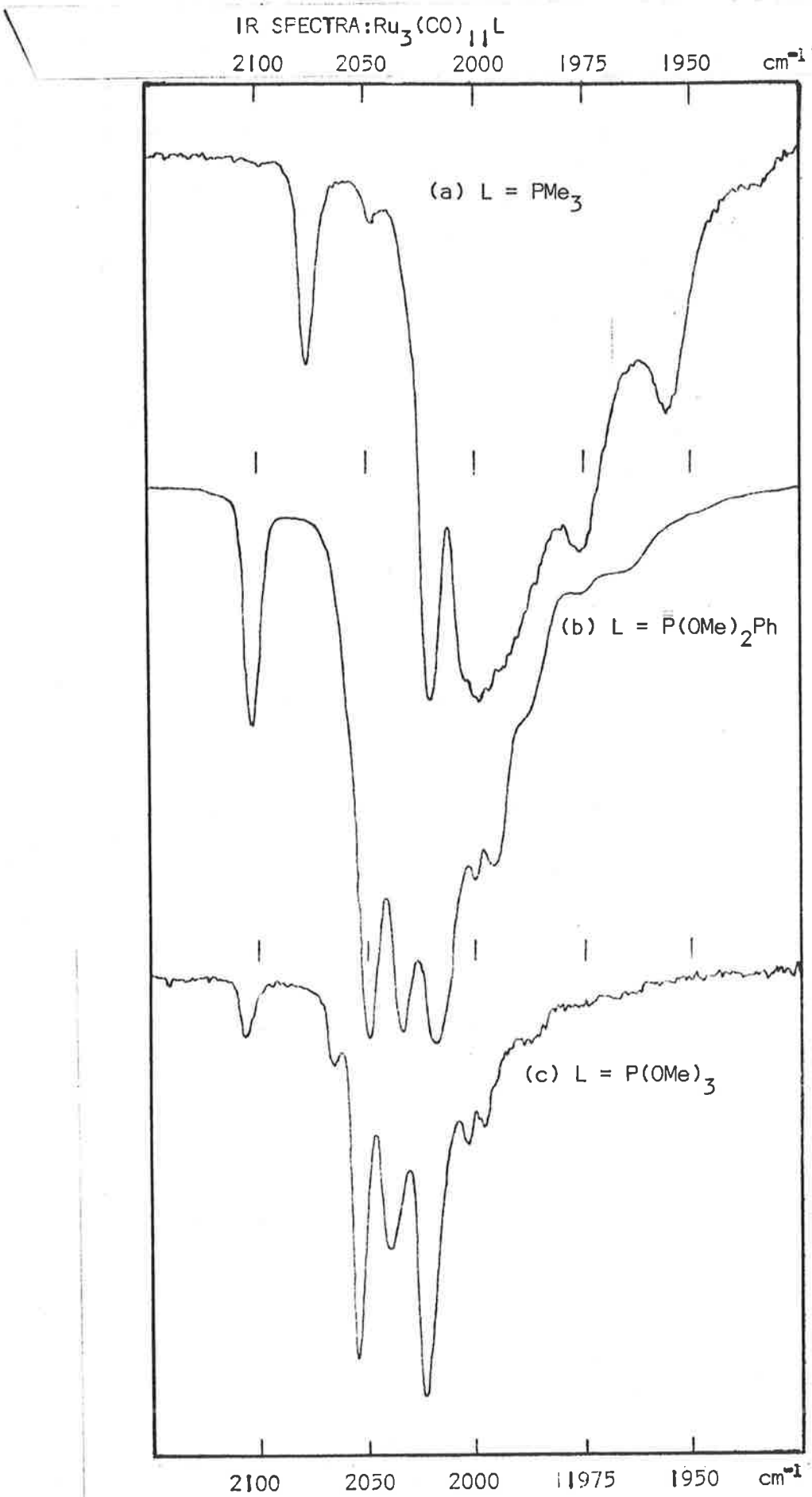

IR SPECTRA: $Ru_3(CO)_{11}L$
2100
2050
2000
1975
1950
cm^{-1}
(a) L = PMe_3
(b) L = $P(OMe)_2Ph$
(c) L = $P(OMe)_3$

FIGURE 8(ii)

IR SPECTRA: $Ru_3(CO)_{10}L_2$

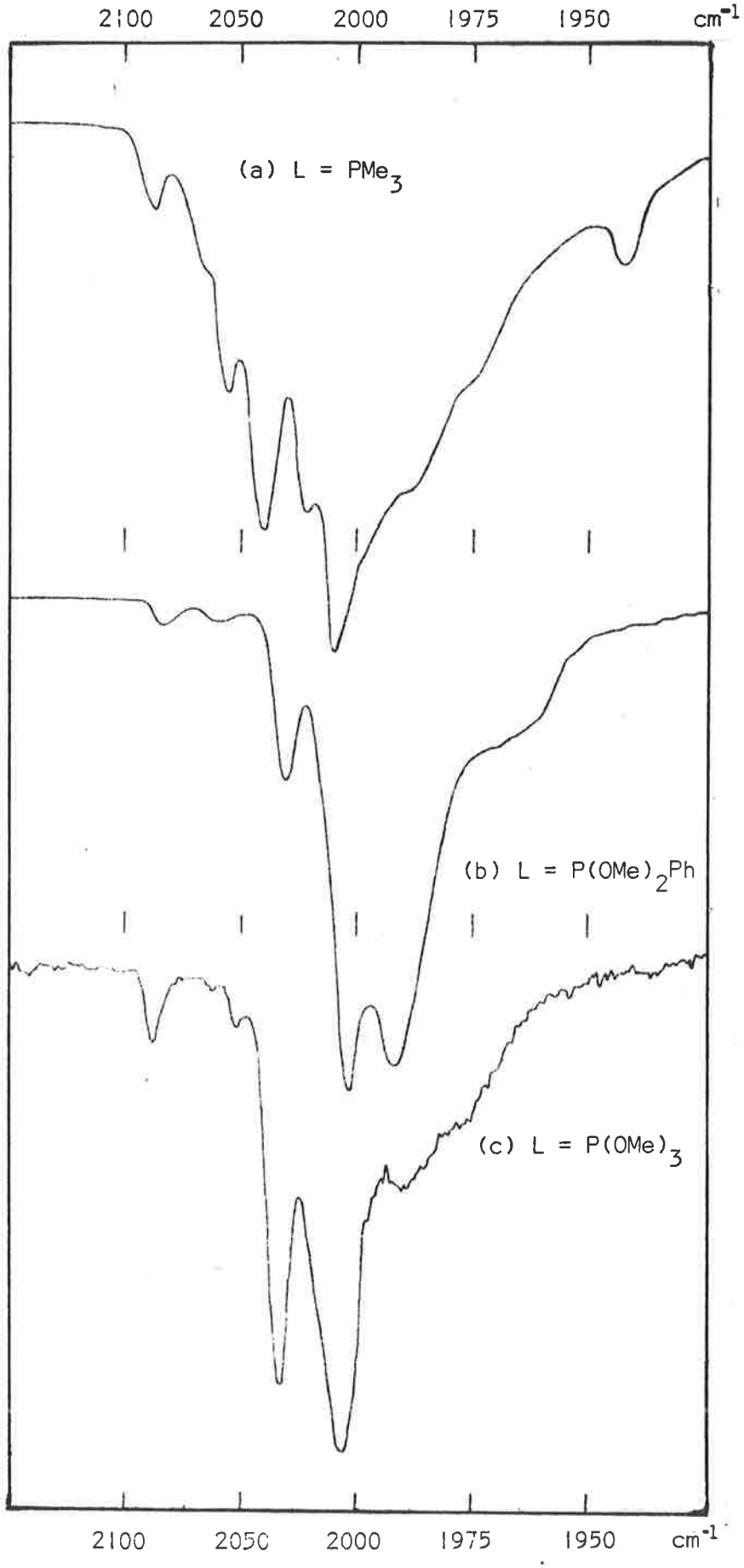
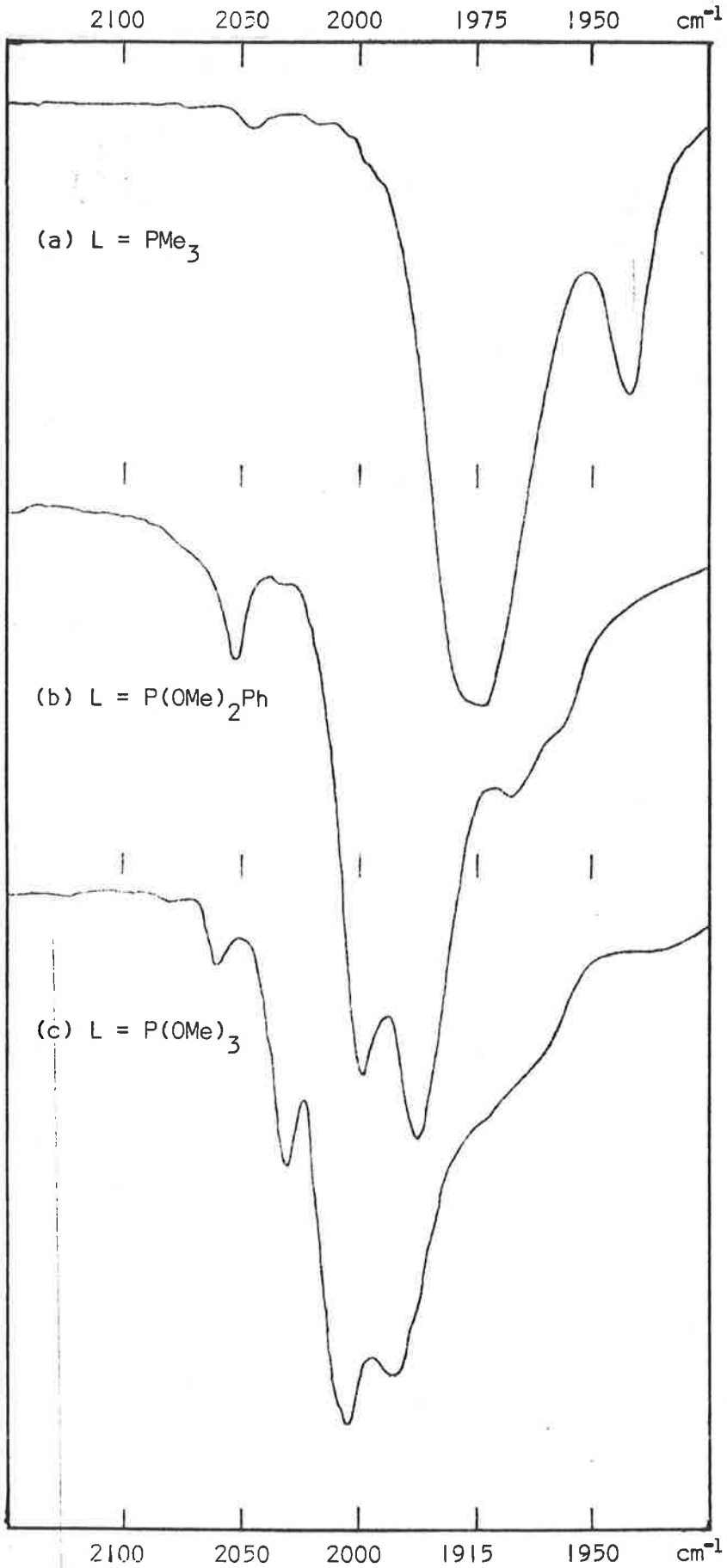


FIGURE 8(iii)

IR SPECTRA: $Ru_3(CO)_9L_3$



quency that the growth or decay of a particular complex can be conveniently followed for the mono- or di-substituted complexes.

Concluding remarks

Electrochemical procedures have been previously used to synthesize metal carbonyl complexes. For example, the cathodic reduction of various transition metal salts under CO pressure affords metal carbonyls.[320-327] This electrochemical method has been applied to the preparation of a variety of phosphine-substituted derivatives of Group 6B metal and iron carbonyls.[324,326] Cathodic reduction of $M(CO)_6$ and $(R_3P)_nM(CO)_{6-n}$ (where M = Cr, Mo, W) in the presence of amines and phosphines produces substitution products at the anode.[328,329] Whether any of these processes proceed by related chain mechanism (ETC processes) is unknown.

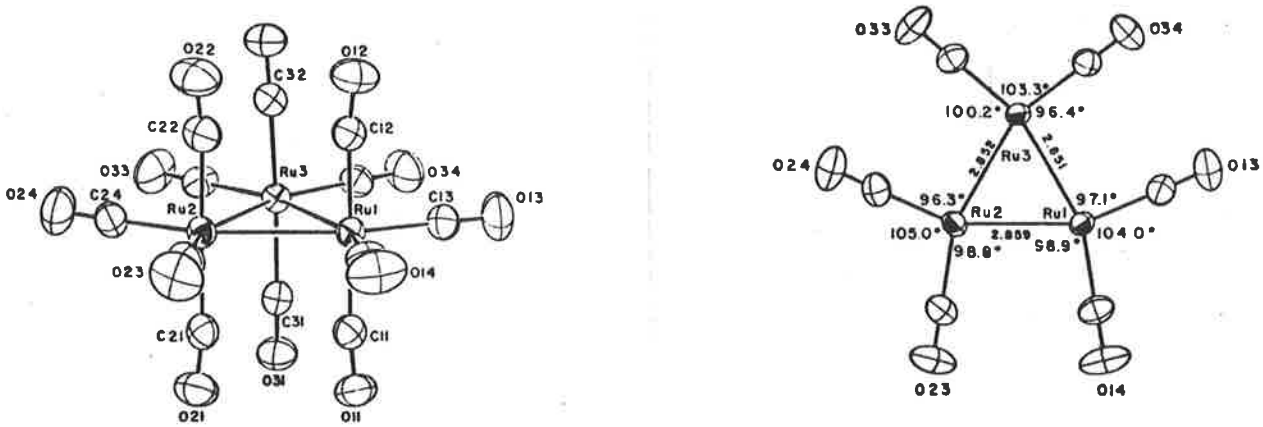
The radical-ion initiated syntheses described above generate many new complexes, which cannot be obtained by thermal or photochemical reactions. The short reaction times, mild conditions and easy product isolation all facilitate further study of these initial reactions, thus enabling the specific effect of ligand substitution to be assessed.

(c) Structural Studies of Substituted Ruthenium Carbonyl Clusters

The molecular structure of $Ru_3(CO)_{12}$ (Figure 9) consists of a triangular cluster of ruthenium atoms, each of which has four terminal carbonyl groups.[330,331] The Ru-Ru bond lengths differ slightly, one being 2.859 $\overset{0}{A}$ and the remaining two being 2.851 $\overset{0}{A}$.[331] This slight difference in bond length is attributed to crystal forces.[331] The axial C-O bonds (1.942 $\overset{0}{A}$) are longer than the equatorial C-O bonds (1.921 $\overset{0}{A}$) as a result of the competition for d_π electron density between the (mutually *trans*) axial CO ligands. The van der Waal's

repulsions of the carbonyl oxygens cause the axial Ru-C-O groupings to be bent by 7° from linearity.[331]

FIGURE 9



$Ru_3(CO)_{12}$

The structural differences between $Fe_3(CO)_{12}$,[332-334] $Ru_3(CO)_{12}$[330,331] and $Os_3(CO)_{12}$[335,336] are attributed to the size of the cavity in the polyhedron formed by the twelve CO groups.[337-340] Only the Fe_3 triangle can be accommodated in an icosahedron (formed by joining the oxygen atoms of CO ligands), while the larger Ru_3 or Os_3 triangles require an anticuboctahedron.[337,340]

Fluxionality is the result of a reorientation of the metal cluster within the ligand polyhedron. A relatively minor reorientation of the ligands about the central M_n cluster can often bring about an apparently major change in the overall structure. This is the case with $Fe_3(CO)_{12}$. Fluxional behaviour recently detected in crystalline $Fe_3(CO)_{12}$,[341] is consistent with the time averaging of the two disordered molecules observed crystallographically.[333,334] Gross structural changes are generally considered in terms of simple terminal-to-bridging transformations, or if present, of differing degrees of symmetry of the μ-CO groups.[342,343,381]

Nuclear magnetic resonance spectroscopy is the only technique which gives precise information on the location and mobility of ligands bonded to the metal framework. $Ru_3(CO)_{12}$ exhibits a single ^{13}CO n.m.r. signal at -100°C,[344] while $Os_3(CO)_{12}$ has 2 peaks below 60°C.[345] The interchange mechanism of axial and equatorial carbonyls in $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ is not clear. The introduction of other ligands reduces the overall symmetry of these clusters, and ^{13}C n.m.r. studies indicate that successive phosphine substitution lowers the activation energy for CO scrambling.[78,346] These studies also show that polytopal rearrangement (a rearrangement which exchanges axial and equatorial CO's of each individual $M(CO)_4$ unit) occurs in a variety of substituted clusters.[347,348] No internuclear scrambling of CO groups is detected.

Early structural investigations of cluster carbonyl derivatives include references to disorder, where the M_3 or M_4 metal core takes up one of two orientations (related by a 60° rotation about a vector normal to the M_3 plane).[333,334,349-353] Most of these examples have one of the partial occupancy factors considerably less than 0.5.[354] Presumably, if ligand occupancy was similar, the resulting atom peaks for the minor component in the final electron density map would be at the limits of resolution. The disorder requires only a small rearrangement of the M-L vectors for the ligand polyhedron to remain unchanged.[349,350]

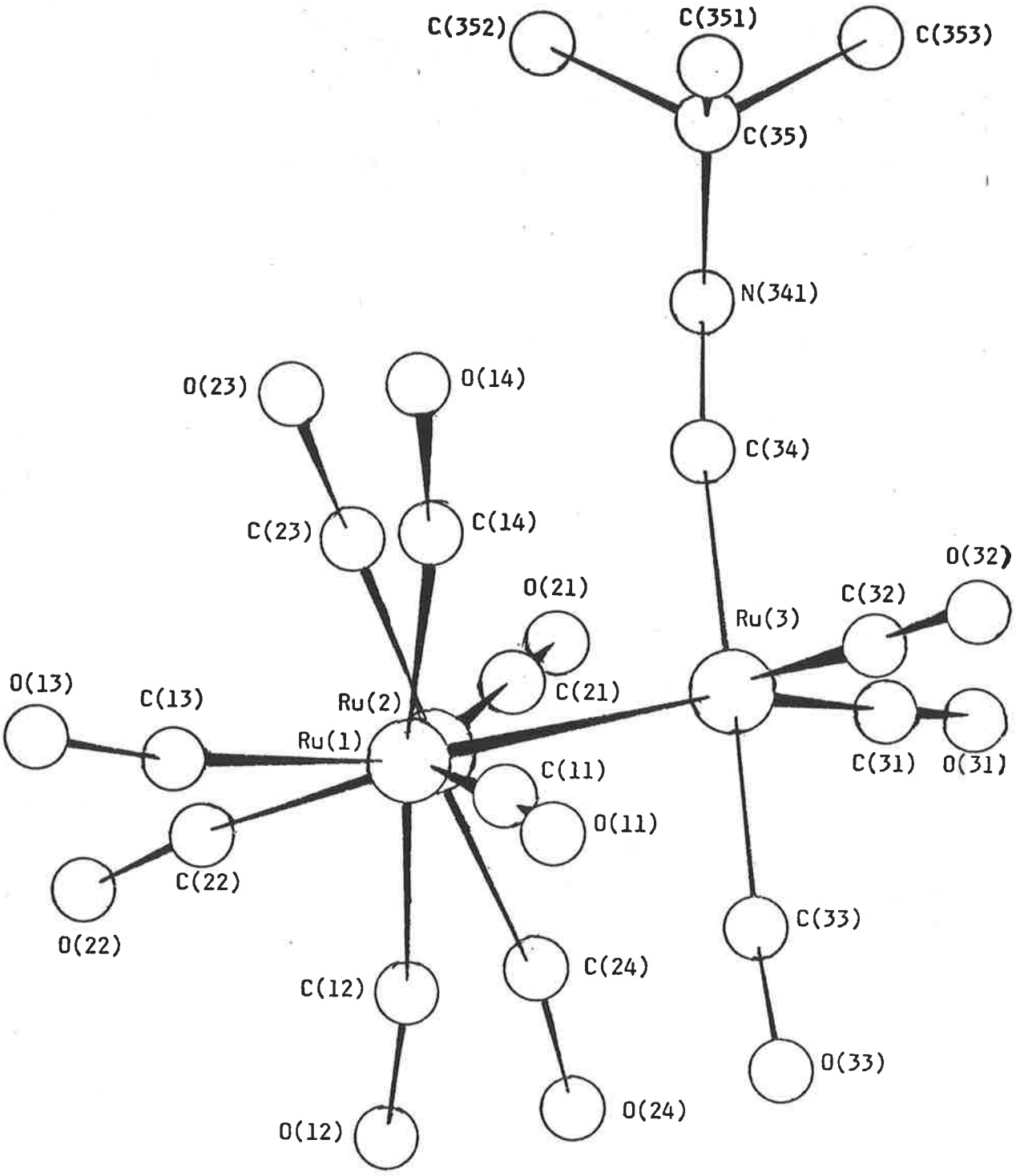
Previous structural studies on complexes with isocyanide ligands reveal a wide variety of coordination geometries, ranging from linear with short C-N bond lengths, to strongly bent conformations (CNR ~ 120°), with much longer C-N bond lengths.[355-369] These longer C-N distances are usually associated with edge-bridging or face-bridging isocyanides,[361,364,366,369] or alternatively, with isocyanides in electron-rich complexes.[229-231]

Disorder is observed in the structure determinations of $Ru_3(CO)_{11}(CNBu^t)$ (I) and $Ru_3(CO)_{10}(CNBu^t)_2$ (2).[370,371] The molecular structures of (I) and (2) are shown in Figures 10 and 11 (Table 6a). Both complexes contain a Ru_3 triangle [isosceles for (2)], in which isocyanide ligands occupy axial sites and all CO ligands are terminal. The observed disorder is with respect to the ruthenium atoms only, and is refined as previously indicated.[354]

In $Ru_3(CO)_{11}CNBu^t$ (I), two shorter metal-metal bonds [2.8477(8), 2.8575(8) Å] are to Ru(1), to which is bonded the isocyanide; the longer of these is the same as found for $Ru_3(CO)_{12}$ [2.854(1) Å].[331] The remaining bond, within the $Ru_2(CO)_8$ fragment, is significantly longer, at 2.8668(11) Å; this lengthening may be associated with the twisting of the two $Ru(CO)_4$ groups about this bond (*vide infra*). The average Ru-Ru length [2.856(1) Å] is the same as that found in the parent carbonyl.[331] In (2), the longest bond is that between the two isocyanide-bearing metal atoms, Ru(1)-Ru(2), 2.849(2) Å, whereas those to Ru(3) are considerably shorter, at 2.837(3) Å. Compared with $Ru_3(CO)_{12}$, there is a considerable contraction of the metal triangle in $Ru_3(CO)_{10}(CNBu^t)_2$(2) [average Ru-Ru, 2.841 (1) Å].

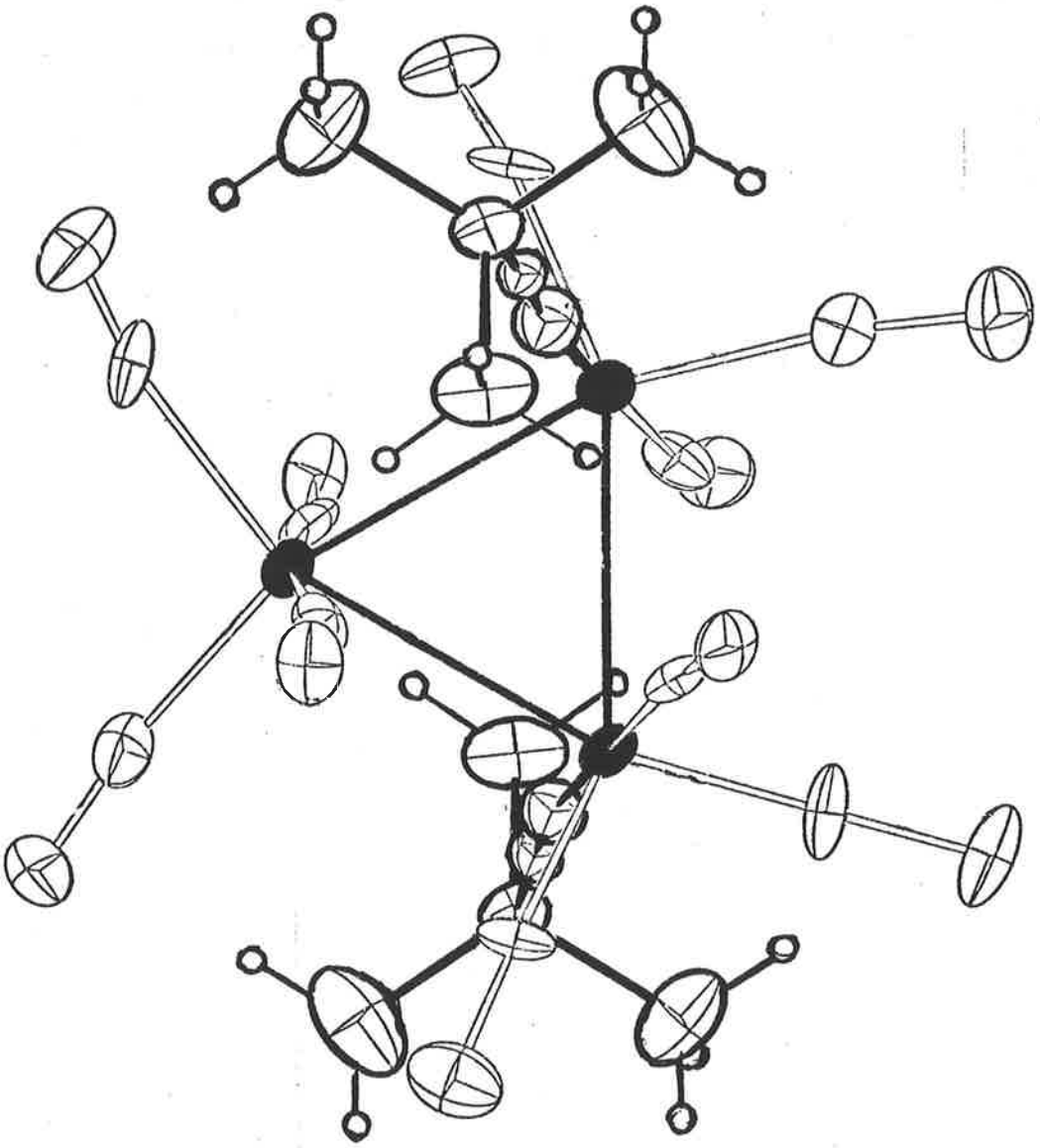
The Ru-CO distances in the $Ru(CO)_4$ groups in (I) range from 1.923-1.961(6) Å, but there are no significant differences observed between the axial and equatorial bond lengths. In the parent carbonyl, such differences are *ca.* 0.02 Å. In both molecules, the shortest Ru-CO distances are those *cis* to the isocyanide ligand on Ru(1). The isocyanide ligands in both complexes are approximately linear. The Ru-C distances [2.041(5) Å in (I), 2.042, 2.040(7) Å in (2)] are longer than those involving carbonyl groups, reflecting the weaker π-acceptor properties of the isocyanide.

FIGURE 10



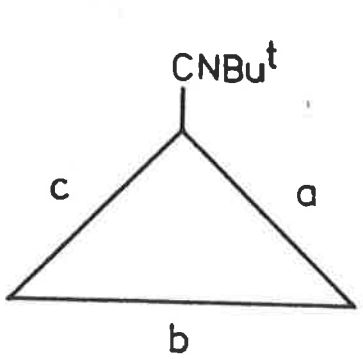
$Ru_3(CO)_{11}(CNBu^t)$ (1)

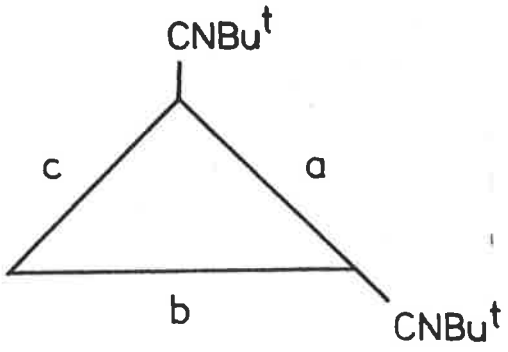
FIGURE II



$Ru_3(CO)_{10}(CNBu^t)_2$ (2)

TABLE 6a





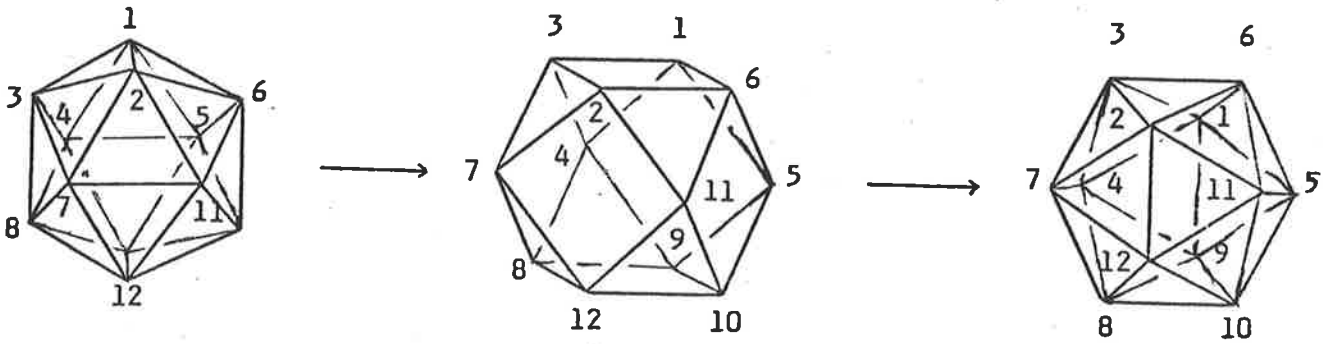
a	2.8575(8)	2.849(2)
b	2.8668(1)	2.837(4)
c	2.8477(8)	2.837(3)
Average	2.8574	2.841
Ru-CO(average)		
axial	1.946	1.94
equatorial	1.928	1.91
Ru-CNBu^t	2.041(5)	2.042(7)
		2.040(7)
Average	2.041(5)	2.041(7)

The structures of the isocyanide-substituted complexes are unusual in that they show that axial substitution has occurred, in contrast to the situation found for tertiary phosphines, for example. The only other axially substituted M_3 clusters containing simple 2e donor ligands are the pair of acetonitrile complexes $Os_3(CO)_{12-n}(NCMe)_n$ (n = 1 and 2).[372]

Substitution of carbon monoxide by a weaker π-acceptor base, such as *t*-BuNC, is expected (on electronic considerations) to favour an axial site ***trans*** to CO rather than one ***trans*** to an Ru-Ru bond. In this way, the π-bonding to the remaining CO ligands is maximised. Steric factors, however, predict that bulky ligands would prefer the less crowded equatorial sites. Therefore, the observed pattern can be rationalised in terms of a lower steric requirement for $CNBu^t$, allowing occupation of the axial site, whereas the bulky phosphine and arsine ligands would preferentially occupy the least hindered sites.

There is much current interest in the fluxional properties of metal cluster carbonyls and their derivatives, and an approach to the interpretation of these properties in terms of structure has been made.[346-348] As noted above, complex (I) is highly fluxional, and a considerable topological perturbation of the parent $Ru_3(CO)_{12}$ ligand anticuboctahedron is evident. This can be described as a twist of the environment of each ruthenium about the pseudo-two-fold axis which passes through it. Examination of the polyhedron formed by the eleven CO groups and the CN part of the isocyanide ligand (Figure 12), and comparison with that found for $Ru_3(CO)_{12}$, shows that the polyhedron more closely approximates the icosahedron found for $Fe_3(CO)_{12}$ and several $M_4(CO)_{12}$ species. Recalling that the equivalence of the CO groups in these cluster carbonyls has been explained in terms of rearrangement of the icosahedron by lengthening of edges and concomitant flattening of pairs of two edge-joined triangular faces to form the square faces of the anti-cuboctahedron. Further distortion (by movement of the diagonal apices towards each other) regenerates an icosahedron with apices interchanged.

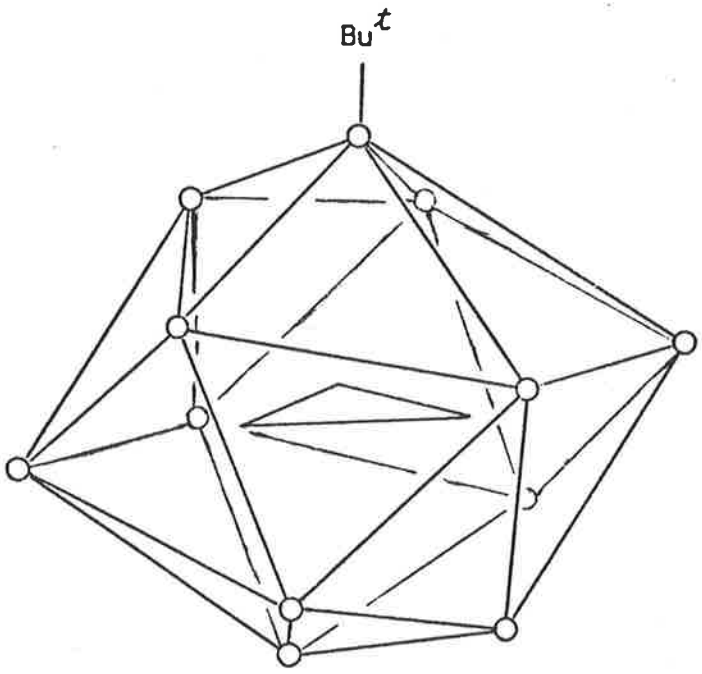
FIGURE 12



Initial icosahedron

cuboctahedron

Final icosahedron



$Ru_3(CO)_{11}(CNBu^t)$

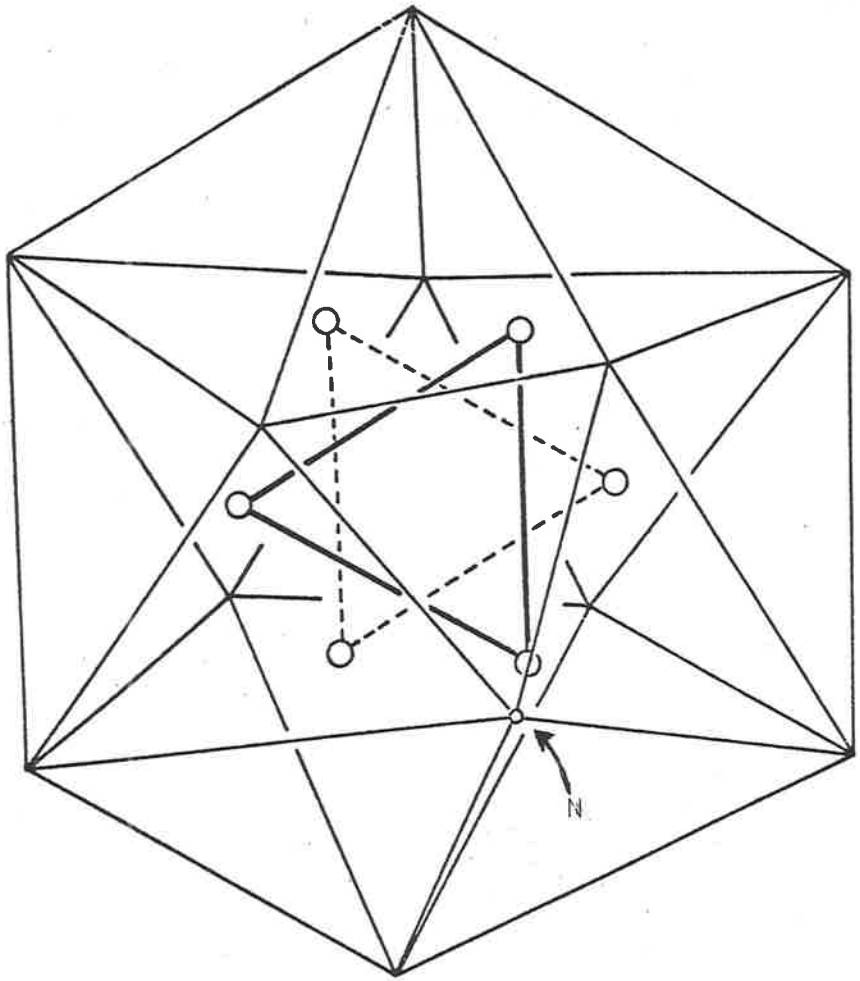
In (2) similarly, we find that the environments of the ruthenium atoms are perturbed from the $Ru_3(CO)_{12}$ anticuboctahedral ideal by a set of concerted twists about the two-fold axes of the triangles (Figure 13). While the distortion of the ligand polyhedron results in disorder of the ten CO groups, the atoms of the two isocyanide ligands in each molecule are located in positions close to (or encompassed by the thermal ellipsoids) of the similar ligands on the centrosymmetric alternative. The structure was thus found to be refinable in terms of a model in which the asymmetric unit was a full molecule with a population 0.5, with only one *t*-butyl substituent at its periphery but that with a population of 1.

The twisting of the $Ru(CO)_4$ groups about the Ru(2)-Ru(3) bond in (1) is then seen to be a method of accommodating the different requirements of the packing of eleven CO groups and one isocyanide ligand about the Ru_3 cluster, compared with the regular anticuboctahedral arrangement adopted by the twelve CO groups in $Ru_3(CO)_{12}$.

I believe that the disorder observed in these structures provides further evidence supporting the idea that the fluxional behaviour of metal cluster carbonyls can be rationalised, at least in part, by the movement of the metal atom cluster within the ligand polyhedron, with some small deformation of the latter, as proposed by Johnson.[348] In the present case, it is the peripheral atoms which define the polyhedron. Conversion of one tautomer to another can occur by bending of the M-C-R (R = O or NBu^t) bond.

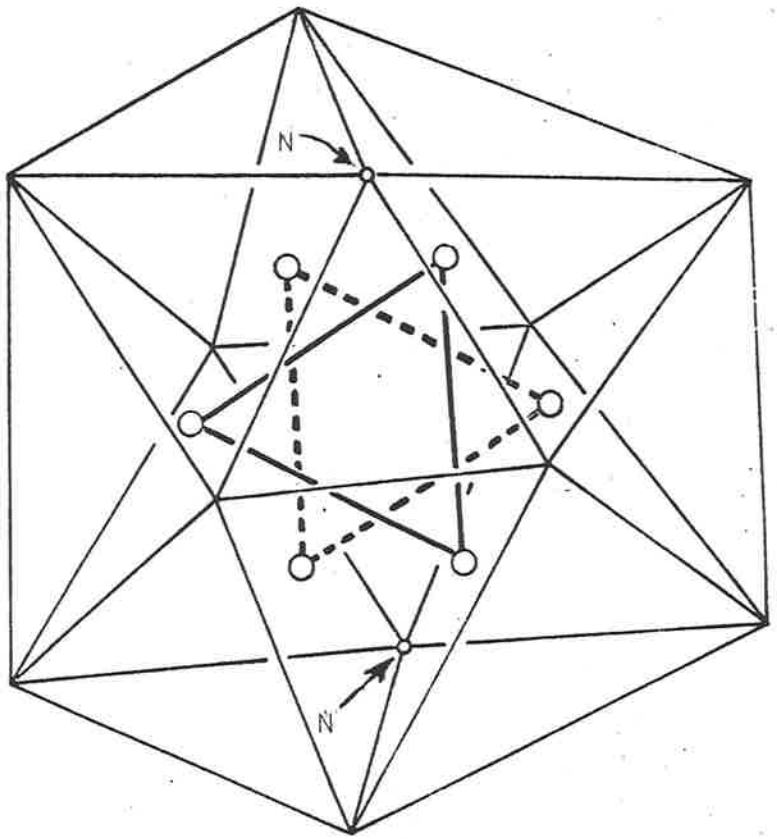
The axial substitution of the *t*-BuNC ligand also affects the reactivity of (1), making it far more reactive than $Ru_3(CO)_{12}$.[260] This can be attributed to the ability of the axial isocyanide ligand to dissociate from the cluster.

FIGURE 13



$Ru_3(CO)_{11}(CNBu^t)$ (1)

0.14/0.86



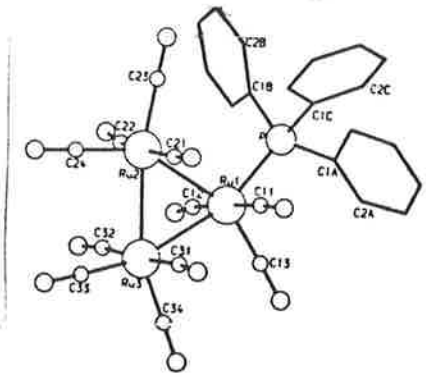
$Ru_3(CO)_{10}(CNBu^t)_2$ (2)

0.5/0.5

Ligand polyhedra indicating population levels of alternative Ru_3 cores

The only structurally characterised trinuclear ruthenium cluster containing an unbridged monodentate phosphine ligand is $Ru_3(CO)_{11}(PPh_3)$ (see Figure 14).[90] This complex was formed on irradiation of $Ru_3(CO)_{12}$ in the presence of PPh_3, and chromatographically isolated from $Ru(CO)_4(PPh_3)$ and $Ru(CO)_3(PPh_3)_2$.[90,373] The phosphorus ligand co-ordinates in an equatorial position, which is consistent with the observations reported for $Fe_3(CO)_{11}(PPh_3)$[374] and $Os_3(CO)_{11}[P(OCH_3)_3]$.[375]

FIGURE 14



$Ru_3(CO)_{11}(PPh_3)$

Steric factors, as indicated previously, prevail in determining the degree of substitution in clusters.[126,127,129-134] Structurally, this is reflected in increasing metal-metal bond lengths as the cone angle[150] of the phosphine increases.[129-134] Thus, the average Ru-Ru distances in $Ru_3(CO)_{11}(PPh_3)$[90] are predictably greater than those of $Ru_3(CO)_{12}$.[330,331] A similar elongation of metal-metal bonds is also observed in $Fe_3(CO)_{11}(PPh_3)$[374] as compared with $Fe_3(CO)_{12}$,[332-334] or with $Os_3(CO)_{11}[P(OMe)_3]$[375] as compared with $Os_3(CO)_{12}$.[335,336] Ligands of lower π-acceptor strength than that of CO (such as PPh_3) are less efficient than a CO group at removing π antibonding electron density from the metal cluster. Hence, the higher electron density in the metal cluster is relieved by metal-metal bond expansion. Thus, electronic factors must also be responsible, in part, for the metal-

metal bond elongation observed in $Ru_3(CO)_{11}(PPh_3)$,[90] as compared with $Ru_3(CO)_{12}$.[330,331]

No significant ligand polyhedral distortion (with vertices defined by the CO ligand oxygen atoms) from that of a 'twinned cuboctahedron,'[340] is observed either for $Ru_3(CO)_{11}(PPh_3)$ or for $Os_3(CO)_{11}[P(OCH_3)_3]$. Such a distortion was observed, however, when a bulky ligand was introduced into the $Fe_3(CO)_{12}$ ligand polyhedron.[332]

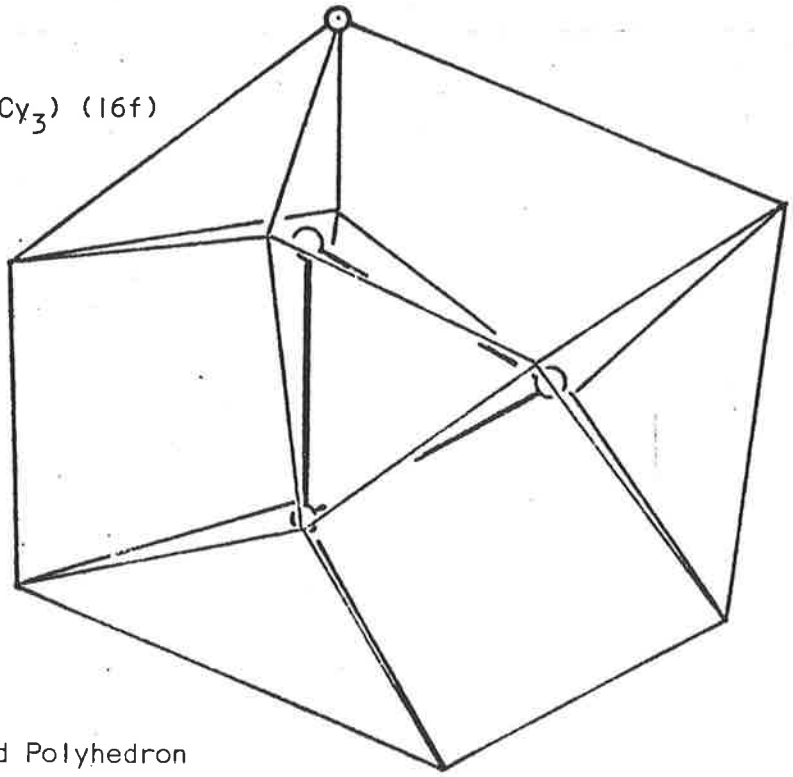
A large number of mono-, di- and tri-substituted derivatives of $Ru_3(CO)_{12}$ containing Group VB donor ligands have been synthesized by radical-ion initiated reactions, and the structural parameters of several complexes determined. In the course of this investigation it became apparent that the solid-state structures of many of these complexes are disordered. The disorder could be refined in terms of a model involving two symmetry-related positions of the Ru_3 core within a ligand polyhedron, of which the peripheral atoms (that is, the O of CO and the P of PR_3) occupy only twelve distinct sites.

Molecular Structure of $Ru_3(CO)_{11}(PCy_3)$ (16f)[376]

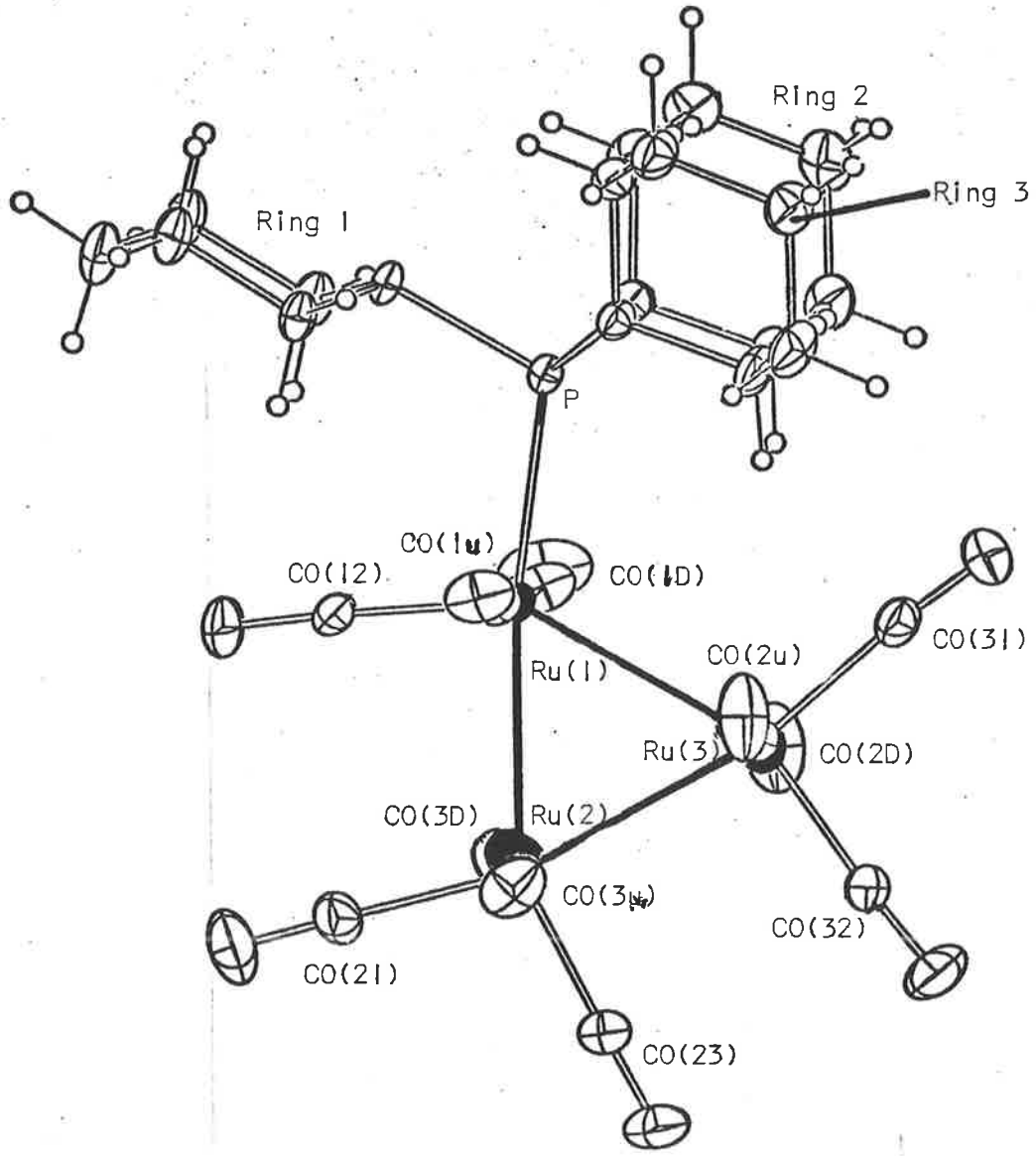
The complex $Ru_3(CO)_{11}(PCy_3)$ (see Figure 15, Table 6b) is formed by replacing an equatorial CO ligand with the PCy_3 ligand. Unlike $Ru_3(CO)_{11}(CNBu^t)$(*vide supra*), there is no disorder in the Ru_3 triangle of $Ru_3(CO)_{11}(PCy_3)$ (16f). This is reflected by the manner in which the axial carbonyl substituents lie approximately normal to the Ru_3 plane. Equatorial substitution by PCy_3 of CO reflects the greater effective bulk of the PCy_3 ligand. It also indicates that electronically PCy_3 is a better σ donor and weaker π-acceptor than tertiary butyl isocyanide. The ligand polyhedron

FIGURE 15

$Ru_3(CO)_{11}(PCy_3)$ (16f)



Ligand Polyhedron



envelope (Figure 15) is severely distorted by the presence of the PCy_3 ligand.

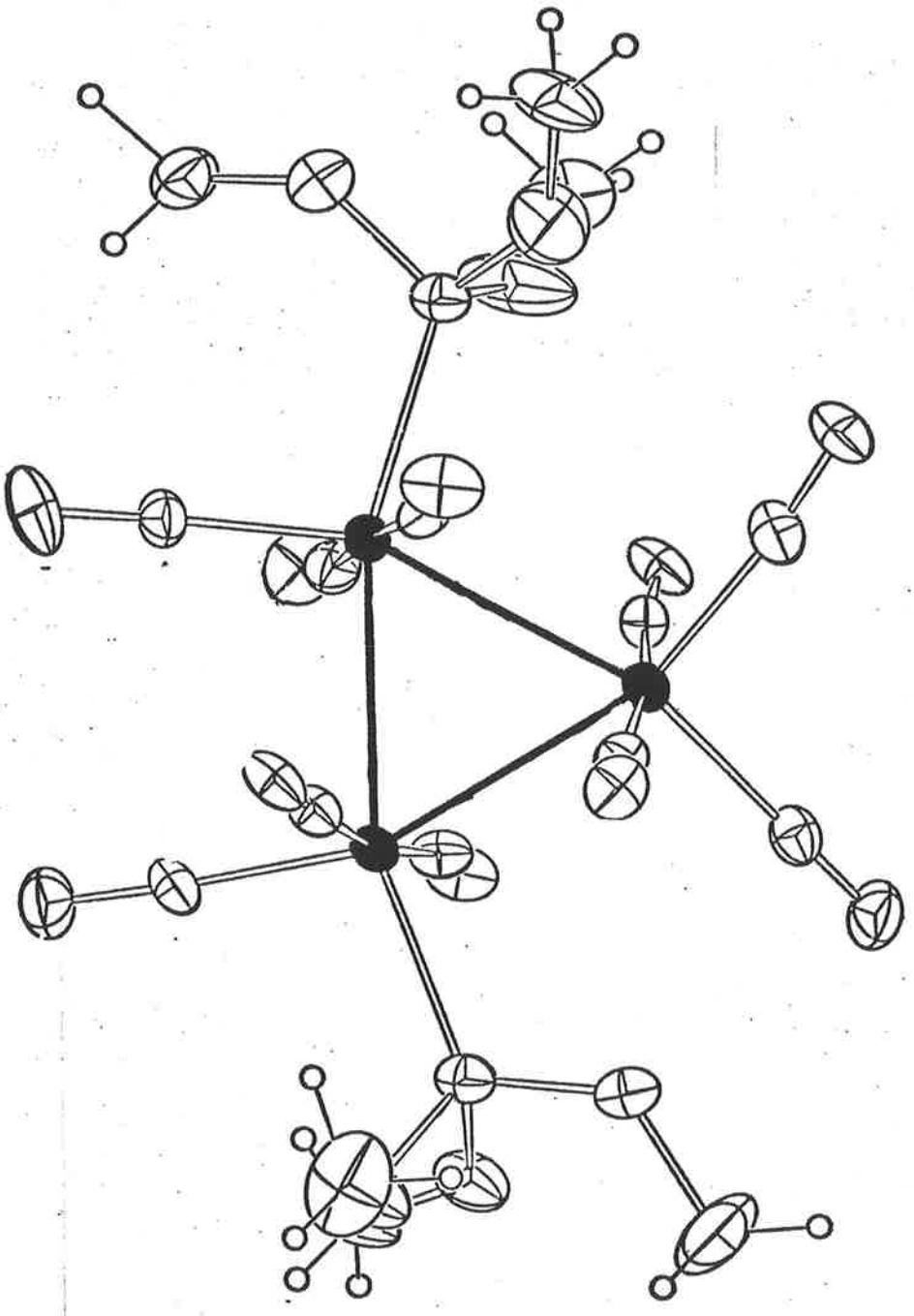
Molecular Structure of $Ru_3(CO)_{10}[P(OMe)_3]_2$ (17h)[376]

The structures of $Ru_3(CO)_{10}[P(OMe)_3]_2$ (see Figure 16, Table 6b) and $Ru_3(CO)_{10}(CNBu^t)_2$, are similar in that they have a centrosymmetrically related pair of disordered molecules, each with population 0.5. Unlike the case of the *t*-butyl isocyanide derivative, in which the two substituents are axially disposed and attached on opposite sides of the Ru_3 plane to two different Ru atoms, Figure 16 shows that the two phosphine ligands are equatorially disposed about two different Ru atoms. The probable cause of preferential equatorial substitution is the greater effective bulk of $P(OMe)_3$ as compared to *t*-BuNC, though phosphines are weaker π-acceptors and stronger σ-donors than isocyanides. As in (2) all atoms were resolved into half-populated components, but the phosphorus atom occupies a fully populated site. This requires half-populated substituents in two different orientations as dictated by the direction of coordination to the respective Ru_3 cores [see Figure 16(ii) and 18(ii)]. There are considerable concerted twist distortions of the ruthenium environments about the two-fold axes of the triangle, correlating again with the proportion of disorder. Figure 16(ii) illustrates the oscillation of the equatorial ligand-to-metal bonds about the O or P atoms required to accommodate the two orientations of the Ru_3 core.

Molecular Structure of $Ru_3(CO)_{10}(PPh_3)_2$ (17c)

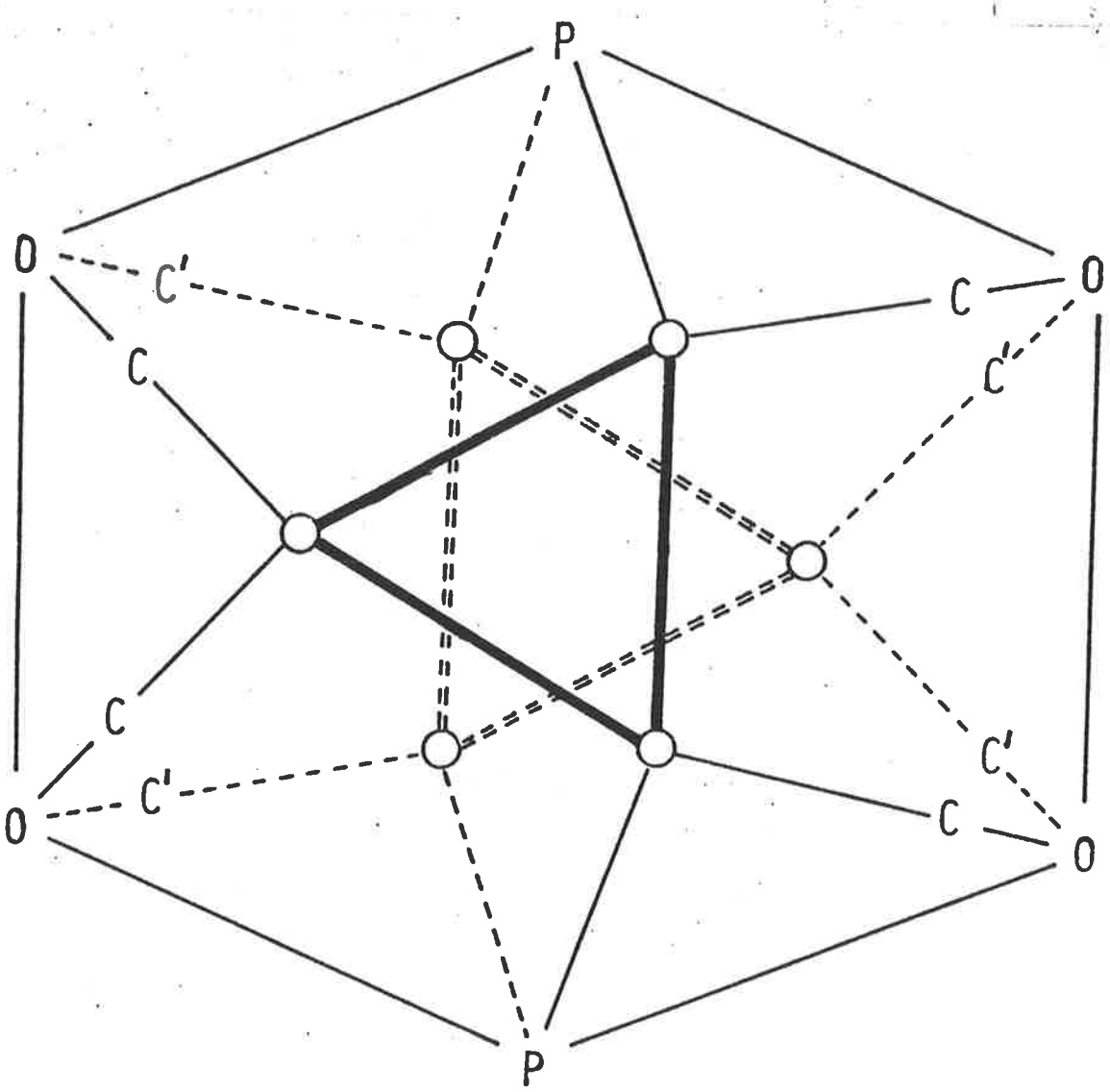
The structure thus far refined (see Figure 17, Table 6b) agrees well with the observations made for $Ru_3(CO)_{10}[P(OMe)_3]_2$ (17h) and to a lesser extent $Ru_3(CO)_{10}(CNBu^t)_2$ (2). Both phosphine substituents occupy equatorial sites on different Ru atoms of the disordered pair (population 0.5). The effective steric bulk associated with the PPh_3

FIGURE 16(i)



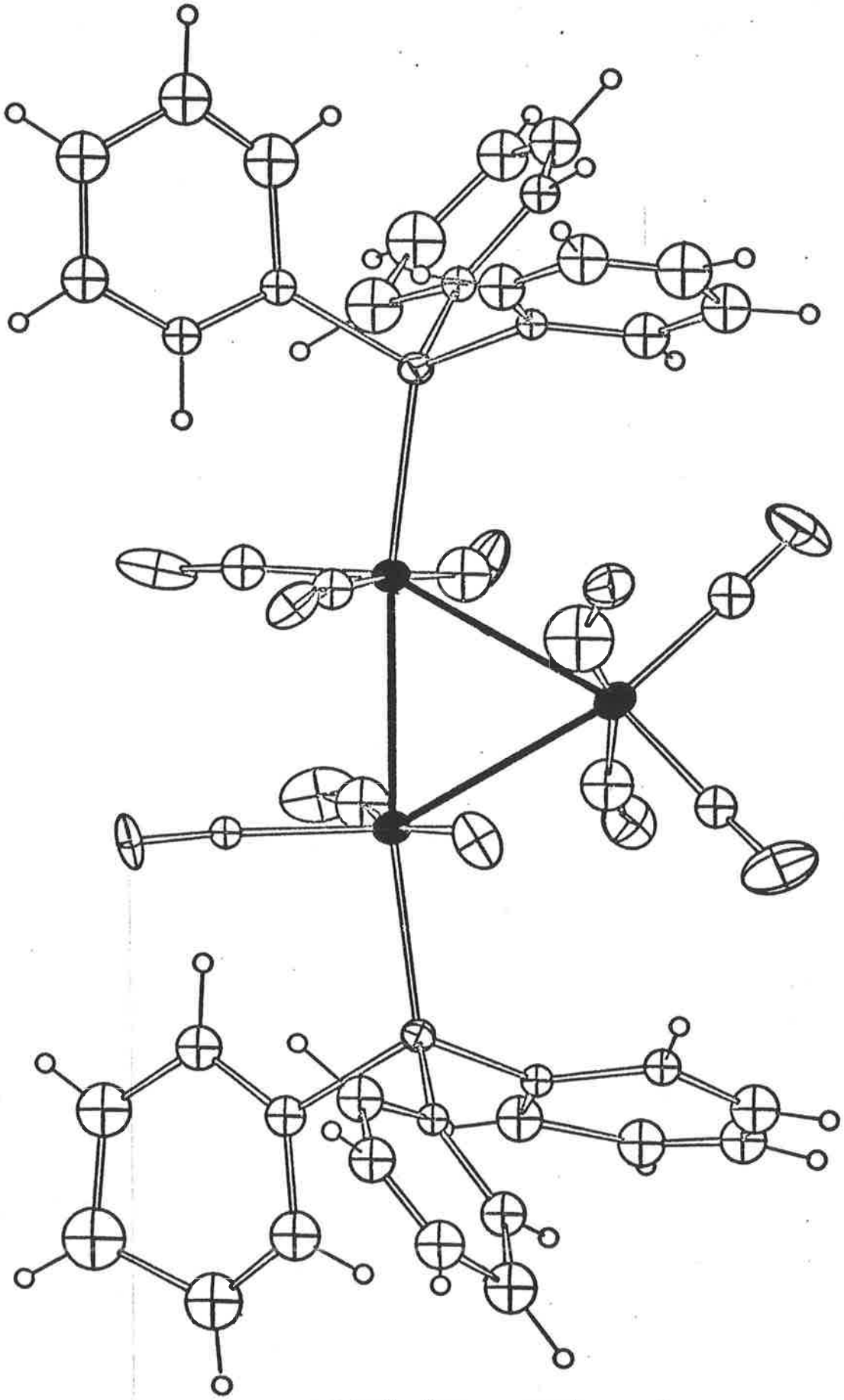
$Ru_3(CO)_{10}[P(OMe)_3]_2$ (17h)

FIGURE 16(ii)



Ligand polyhedron of $Ru_3(CO)_{10}[P(OMe)_3]_2$
showing both orientations of the Ru_3 core

FIGURE 17



$Ru_3(CO)_{10}(PPh_3)_2$ (17c)

ligands not only results in them being equatorially located, but also causes considerable distortion of the CO ligands from linearity (see Figure 17). The inherent disorder in the molecule has hampered refinement of the phenyl rings.

Molecular Structure of $Ru_3(CO)_9(PMe_3)_3$ (18a)[376]

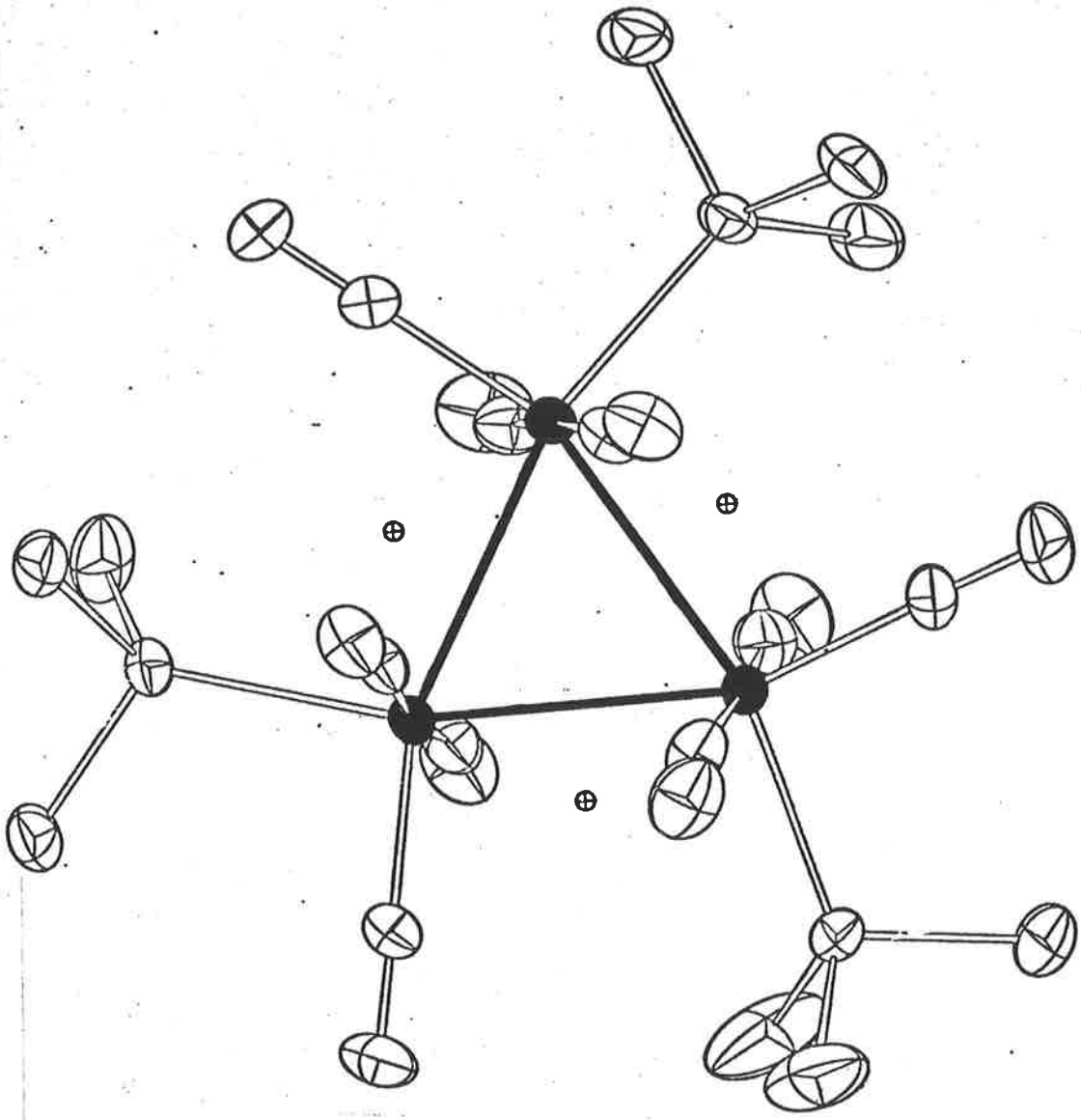
The molecular structure of $Ru_3(CO)_9(PMe_3)_3$ is basically that of $Ru_3(CO)_{12}$ with three equatorial CO groups replaced by PMe_3 ligands [Figure 18(i), Table 6b]. Each metal has one PMe_3 ligand attached, giving the molecule a 3m symmetry. As with $Ru_3(CO)_{11}(CNBu^t)$, disorder is observed in the Ru_3 core; refinement of the populations showed these to be 0.932 and 0.068. This disorder is accompanied by similar twist distortions in the Ru environments about the two-fold axes of the Ru_3 triangle [see Figure 18(ii)].

Molecular Structure of $Ru_3(CO)_8[P(OMe)_2Ph]_4$ (19i)[377]

While $Fe_3(CO)_{12}$ and several of its substituted derivatives [$Fe_3(CO)_{12-n}L_n$ (n = 1-3) L = monodentate ligand] are known to have the bridged structure (see Figure 19, Table 6b),[332-334,374,382,383] $Ru_3(CO)_{12}$ and its substituted derivatives have the nonbridged structures (see Figure 9).[90,330,331,376] Only three $Ru_3(CO)_8L_4$ complexes are known; with L = PH_3,[82] PMe_3[258] and $PPh(OMe)_2$.[88,258]

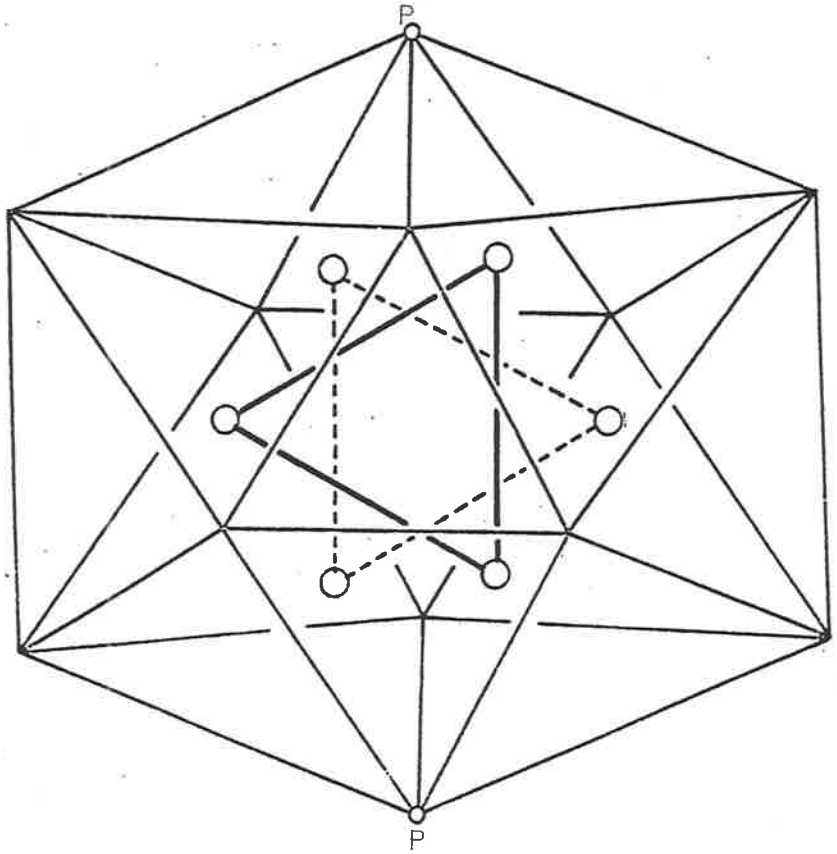
The molecular structure of $Ru_3(CO)_8[PPh(OMe)_2]_4$ is shown in Figure 20(i), from which it is immediately apparent that it is of the CO-bridged $Fe_3(CO)_{12}$ type (see Figure 19). One Ru-Ru bond of the isosceles triangular Ru_3 core is asymmetrically-bridged by two CO groups (see Table 6b), and the Ru-Ru separation is 0.06 Å shorter than that found in $Ru_3(CO)_{12}$.[330,331] In contrast, the other two Ru-Ru bonds are significantly longer [2.879(1) Å; see Table 6b], as expected when CO is replaced by a better σ donor. All phosphonite ligands oc-

FIGURE 18(i)

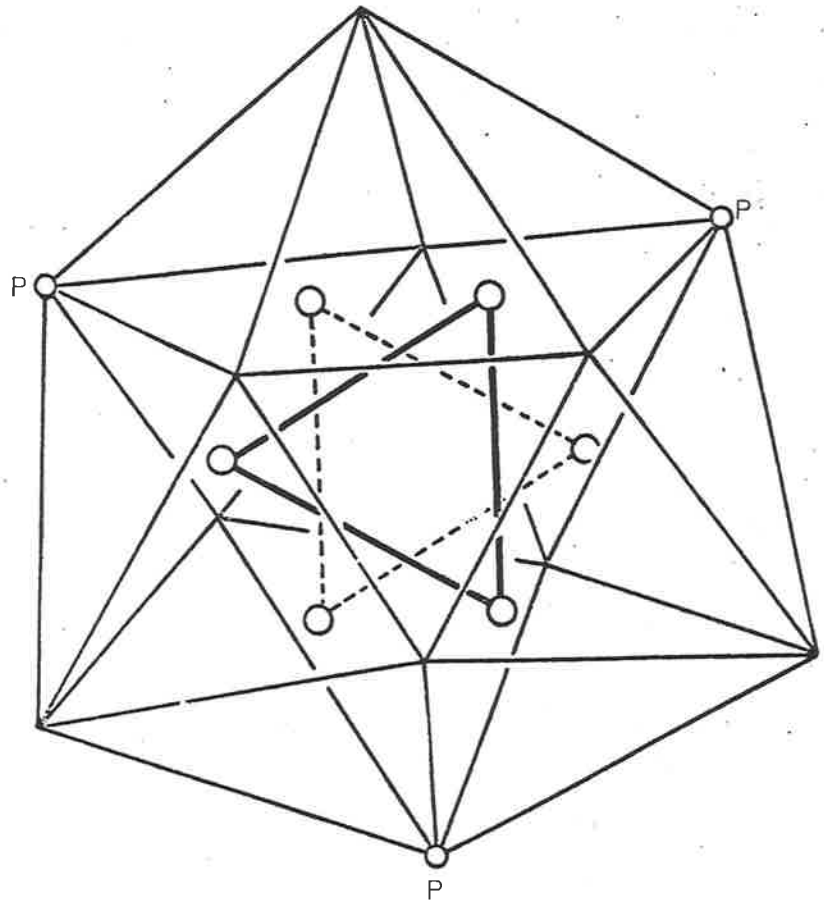


$Ru_3(CO)_9(PMe_3)_3$ (19i)

FIGURE 18(ii)



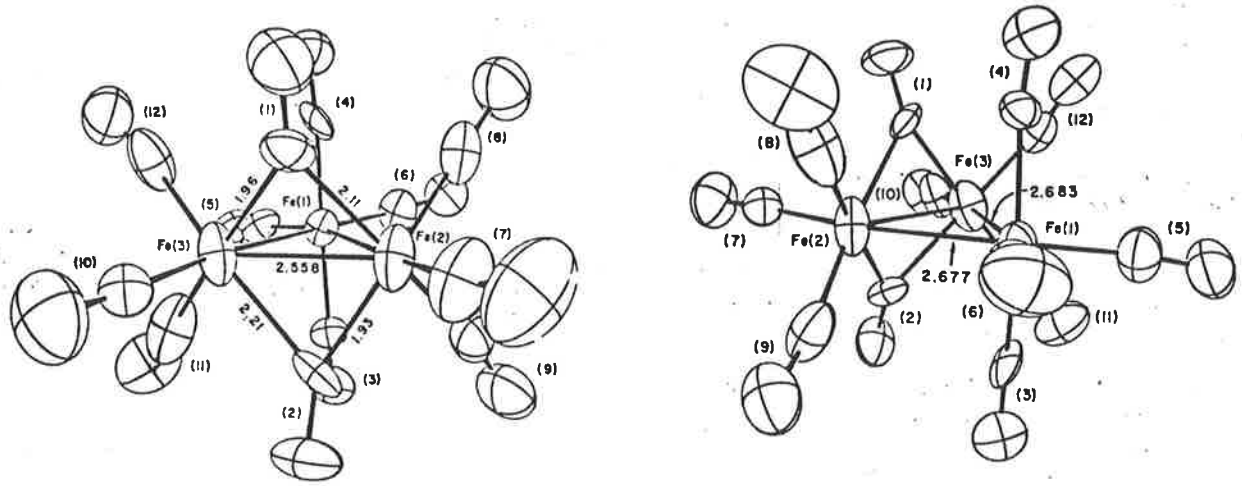
$Ru_3(CO)_{10}[P(OMe)_3]_2$
0.5/0.5



$Ru_3(CO)_9(PMe_3)_3$
0.06/0.94

Ligand polyhedra showing populations and orientations of the Ru_3 triangle

FIGURE 19



$Fe_3(CO)_{12}$: two perspectives

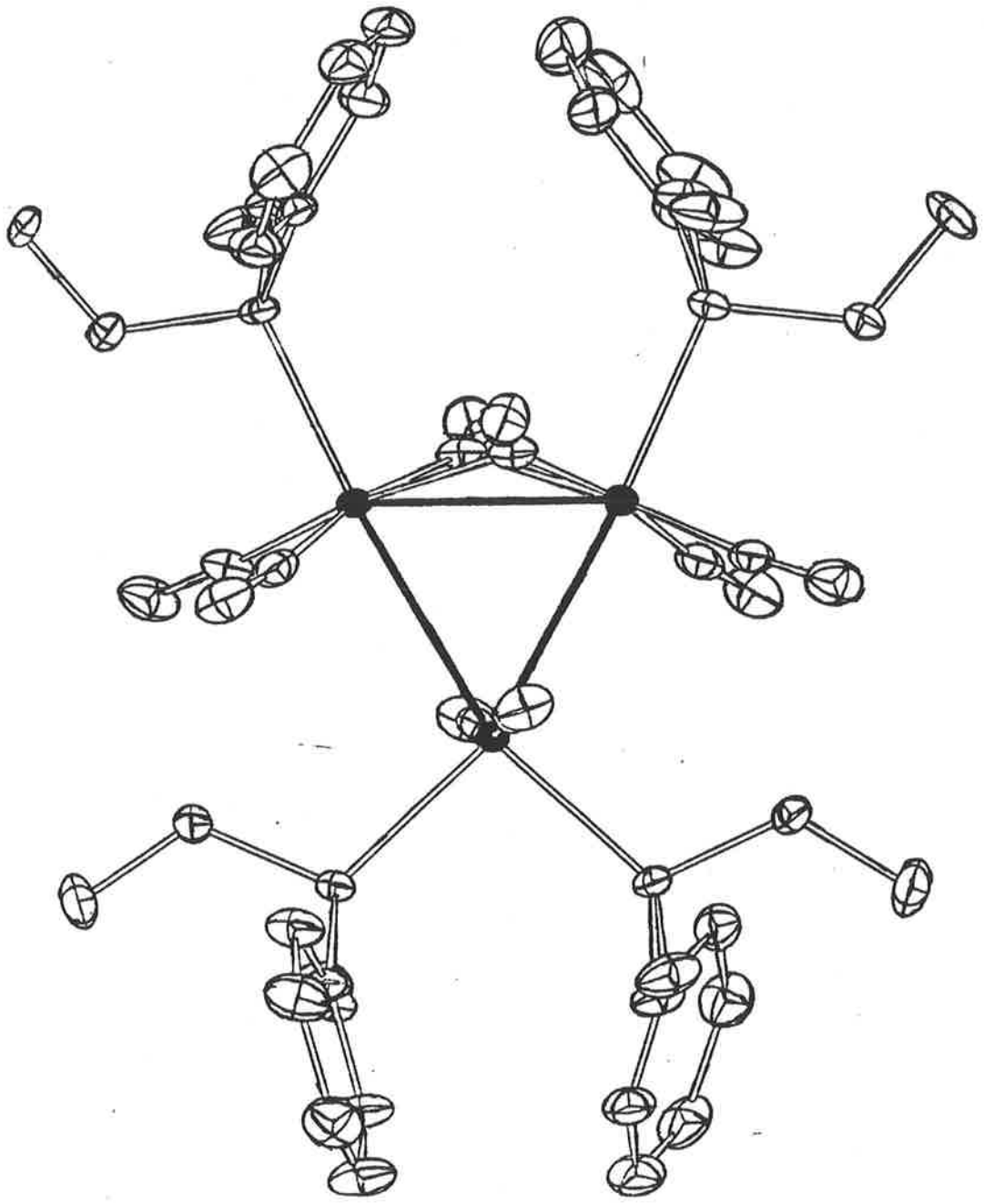
cupy equatorial positions; one on each of the CO-bridged Ru atoms (*trans* to the nonbridged Ru-Ru vectors), and two on the third Ru atom. Both pairs of phosphonite ligands are disposed so that one Ph group of each pair is above the Ru_3 plane, and the second pair below this plane.

The peripheral atom polyhedron is still a distorted icosahedron, the Ru_3 plane being rotated about its two-fold axis [see Figure 20(ii)]. The observed CO-bridged structure results from a minimisation of the combined effective steric bulk. The bridging CO ligands are difficult to observe in the i.r. spectrum but are assigned to weak bands at 1810, 1760 cm^{-1} (CH_2Cl_2) or 1820, 1772, 1718 cm^{-1} (Nujol).

General Structural Considerations (Refer also to Tables 6b and 7)

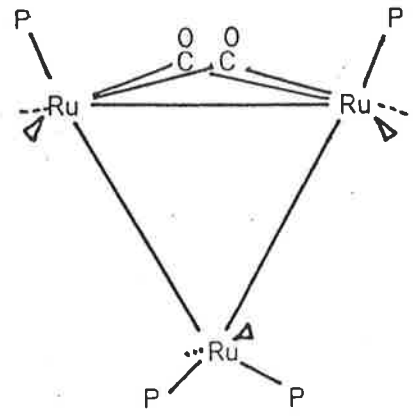
The size of the Ru_3 core increases on increasing phosphine substitution, when compared with $Ru_3(CO)_{12}$.[331] The increasing Ru_3 core size reflects the increase in electron density occurring on replacement

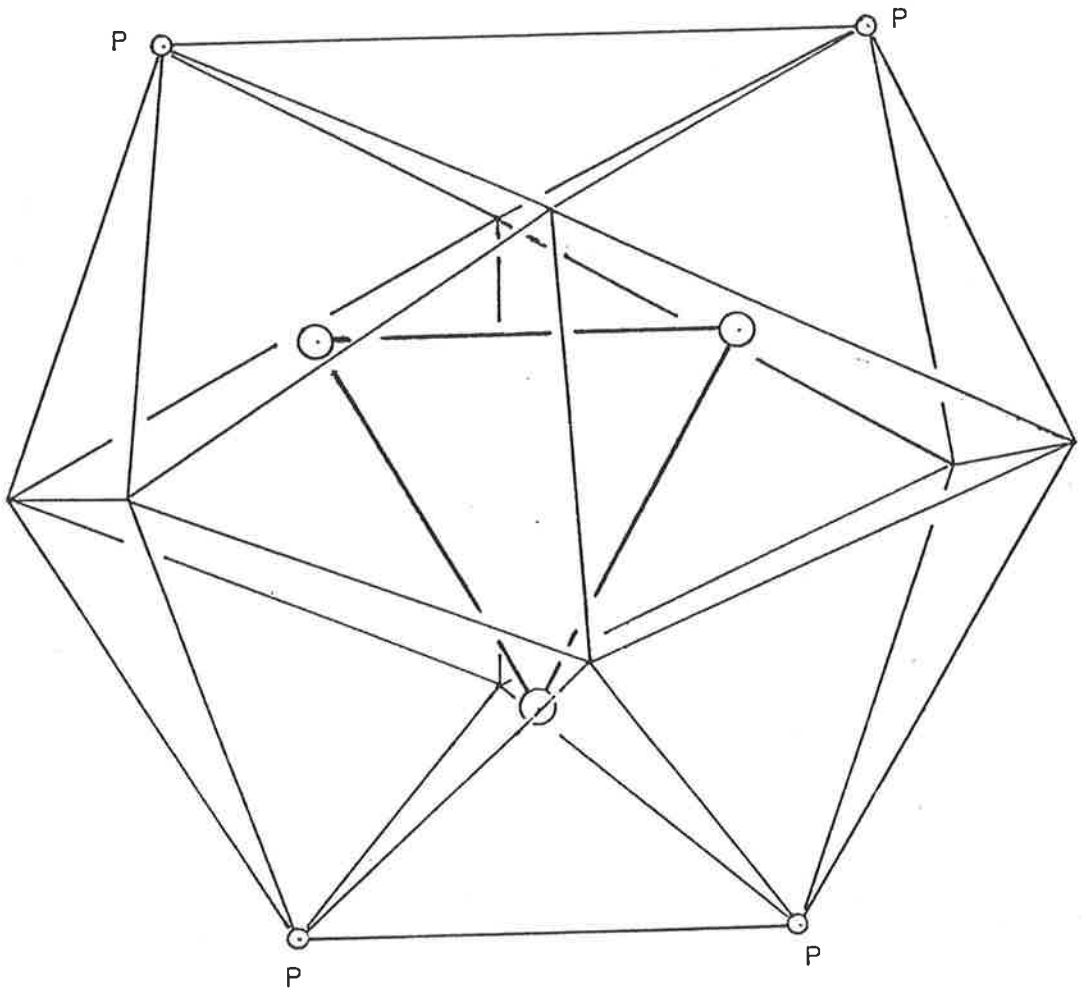
FIGURE 20(i)



$Ru_3(CO)_8[P(OMe)_2Ph]_4$ (19i)

FIGURE 20(ii)

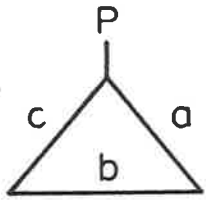


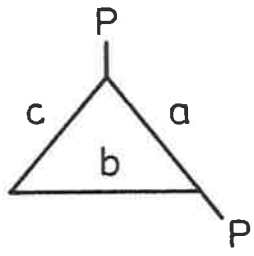


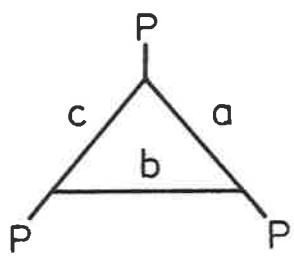
Ligand Polyhedron

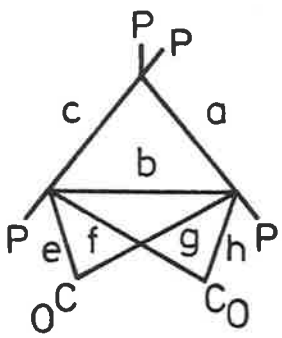
$Ru_3(\mu\text{-}CO)_2(CO)_6[PPh(OMe)_2]_4$ (19i)

TABLE 6b









	PPh_3	PCy_3	$P(OMe)_3$	PMe_3	$P(OMe)_2Ph$
a	2.907(3)	2.878(2); 2.875(2)	2.860(1)	2.860(1)	2.879(1)
b	2.875(3)	2.859(2); 2.874(2)	2.862(2)	2.862(2)	2.797(1)
c	2.876(3)	2.902(2); 2.920(2)	2.854(1)	2.854(1)	2.879(1)
Average	2.886	2.885	2.859	2.859	2.852
Ru-CO					e 1.885(1); g 2.057(8)
(average)					f 2.068(8); h 2.399(8)
axial	1.94	1.936; 1.940	1.935	1.920	1.918
equatorial	1.89	1.918; 1.899	1.900	1.869	1.888
Ru-P	2.380(6)	2.425(3); 2.420(3)	2.330(1) 2.265(2)	2.336(2) 2.328(2) 2.327(2)	2.277(2) 2.281(2) 2.265(2) 2.270(2)
Average	2.380	2.422	2.298	2.330	2.273

TABLE 7 Average interatomic CO distances/Ru-O vectors (Å)

$Ru_3(CO)_{11}(PPh_3)$ (16c)			$Ru_3(CO)_{11}(PCy_3)$ (16f)		
Distances	C-O(ax.)	= 1.145	Distances	C-O(ax.)	= 1.135(5)
	C-O(eq.)	= 1.149		C-O(eq.)	= 1.134(4)
Vectors	Ru-O(ax.)	= 3.083	Vectors	Ru-O(ax.)	= 3.073
	Ru-O(eq.)	= 3.040		Ru-O(eq.)	= 3.044

$Ru_3(CO)_{10}[P(OMe)_3]_2$ (17h)

Distances	C-O(ax.)	= 1.135(8)
	C-O(eq.)	= 1.159(5)
Vectors	Ru-O(ax.)	= 3.071
	Ru-O(eq.)	= 3.059

$Ru_3(CO)_9(PMe_3)_3$ (18a)

Distances	C-O(ax.)	= 1.141(2)
	C-O(eq.)	= 1.142(3)
Vectors	Ru-O(ax.)	= 3.061
	Ru-O(eq.)	= 3.011

$Ru_3(CO)_8[P(OMe)_2Ph]_4$ (19i)

Distances	C-O(ax.)	= 1.139(4)
	C-O(eq.)	= 1.132(7)
Vectors	Ru-O(ax.)	= 3.057
	Ru-O(eq.)	= 3.021

$Ru_3(CO)_{11}(CNBu^t)$ (1)			$Ru_3(CO)_{10}(CNBu^t)_2$ (2)		
Distances	C-O(ax.)	= 1.124(5)	Distances	C-O(ax.)	= 1.148
	C-O(eq.)	= 1.120(1)		C-O(eq.)	= 1.177
Vectors	Ru-O(ax.)	= 3.070	Vectors	Ru-O(ax.)	= 3.088
	Ru-O(eq.)	= 3.098		Ru-O(eq.)	= 3.087

of CO (a good π-acceptor) with PR_3 (a good σ donor). There is no apparent correlation with basicity of phosphine (or phosphite), nor with degree of substitution. The range of Ru-P distances from 2.265(2) Å to 2.330(1) Å observed falls in the order $PCy_3 > PPh_3 > PMe_3 > P(OMe)_2Ph > P(OMe)_3$, which follows the general trend expected on the basis of cone angles.[150] Interestingly, one Ru-P distance in $Ru_3(CO)_{10}[P(OMe)_3]_2$ (17h) is 2.265(2) Å, which is at the lower limit of all Ru-P distances observed.[49] The reason for the two large differences in Ru-$P(OMe)_3$ distances is not apparent.

The Ru-CO bond lengths of the various phosphine substituted clusters show little variation. In all complexes, the Ru-CO(eq) distances are shorter than the Ru-CO(ax) distances by 0.04-0.05 Å. In $Ru_3(CO)_{12}$[331] the difference in averaged values is 0.02 Å. Similarly, the equatorial R---O vectors are shorter than the axial Ru---O vectors (see Table 7).[376]

It is interesting that the introduction of the Group V ligand results in the peripheral atom polyhedra of these complexes moving away from the anticuboctahedron found in $Ru_3(CO)_{12}$ towards the icosahedron found for $Fe_3(CO)_{12}$. This change is generally accompanied by concerted twist distortions about the Ru-Ru bonds. Where the combined steric bulk of the entering Group V ligands exceeds that which may be accommodated by concerted twist distortions of CO groups, semi-bridging or bridging CO ligands result. Hence, $Ru_3(CO)_8[P(OMe)_2Ph]_4$ (19i) has a structure and ligand envelope analogous to $Fe_3(CO)_{12}$.

Several other clusters are reported to have disordered structures involving different orientations of the metal core within the same ligand polyhedron; they include $[H_6Re_4(CO)_{12}^{2-}]$,[378] $Fe_3As_2(CO)_9$,[379] $Os_3(CO)_{11}(\mu^2\text{-}CH_2)$[380] and $Ir_4(CO)_{12}$.[381] To the best of my knowledge,

however, this is the first occasion that this disorder has been resolved in cluster complexes containing such disparate ligands.

The rationale for these observations is that the particular crystalline form of a molecule, existing in two or more conformations, is largely determined by crystal packing interactions. Generally, one form is more stable than the other(s), and an ordered lattice results from all molecules having the same conformation. Crystal packing interactions are determined by intermolecular contacts of the peripheral atoms of the molecule, so that if two or more conformations have the same arrangement of peripheral atoms, random occupation of lattice sites will result. In the special instance of symmetry-related sites in the polyhedron, half-occupancy may occur [*e.g.* $M_3(CO)_{10}L_2$, see Figures 13, 16(ii), 18(ii)].

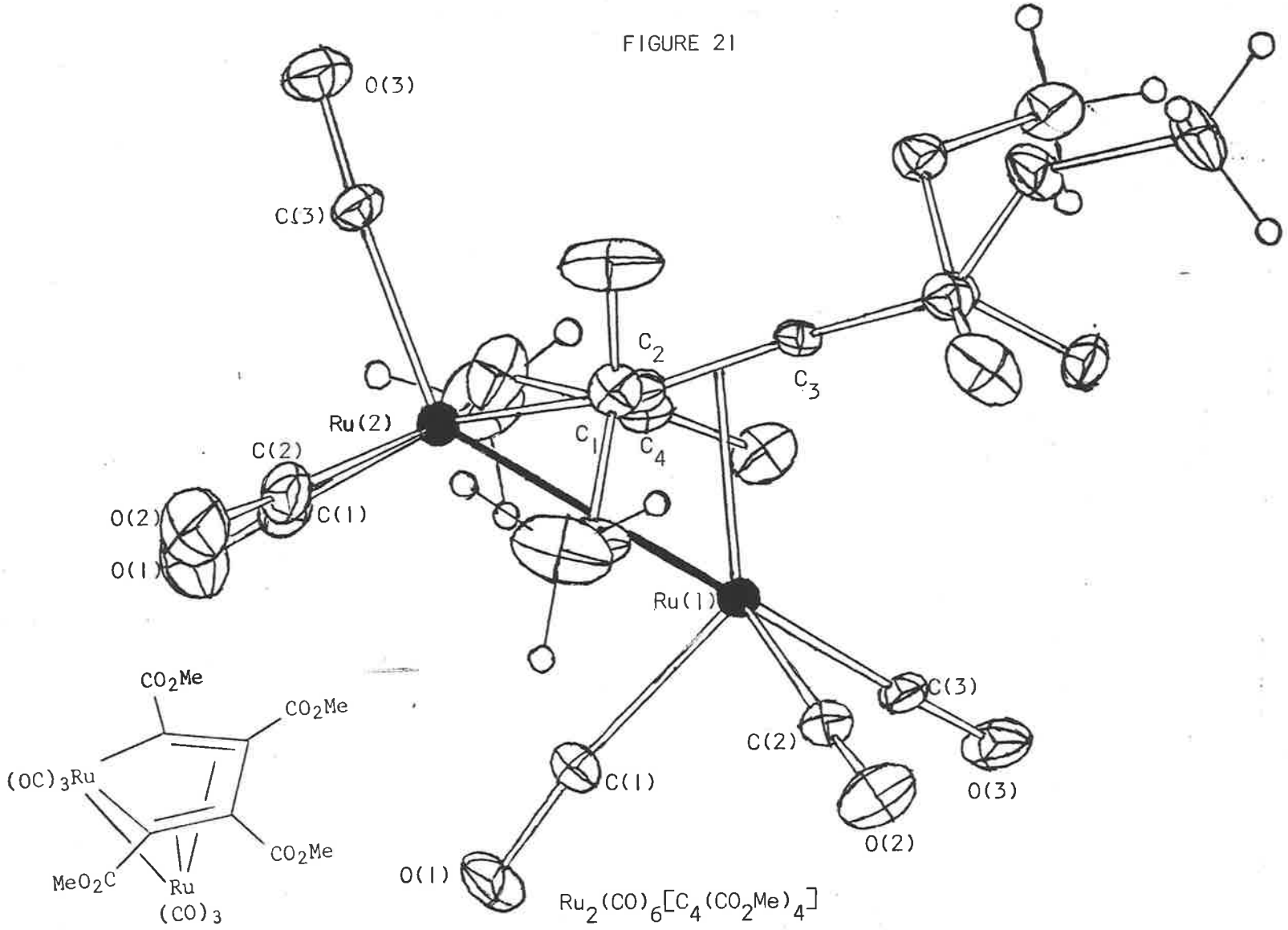
(d) Miscellaneous Reactions of $Ru_3(CO)_{12}$ and its Substituted Derivatives

(i) Reaction of $Ru_3(CO)_{12}$ with dimethylacetylenedicarboxylate[384]

Reactions between $Ru_3(CO)_{12}$ and $C_2(CO_2Me)_2$ readily afford at least fourteen complexes, two of which can be separated easily by chromatographic methods, to give deep red $Ru_3(CO)_7[C_2(CO_2Me)_2]_4$ (55) and yellow $Ru_2(CO)_6[C_4(CO_2Me)_4]$ (56) (Figure 21). The former complex probably has an open-chain ligand formed by oligomerisation of the alkyne, and may be similar to complexes obtained with 1-alkynes such as HC_2Bu^t.

Complex (56) is obtained as well-formed crystals. The composition was indicated by analysis, the $\nu(CO)$ spectrum, which was characteristic of an $M_2(CO)_6$ system, and by the ^1H n.m.r. spectrum, which contained two singlets for the two pairs of CO_2Me groups. In addition, the mass spectrum contained a molecular ion centred on *m/e* 654, and fragment ions formed by the loss of the six CO ligands. Further breakdown of

FIGURE 21



$Ru_2(CO)_6[C_4(CO_2Me)_4]$

FIGURE 21: Selected Bond Lengths and Angles

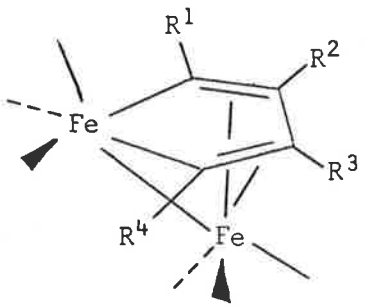
Ru(1)-Ru(2)	2.744				
Ru(1)-C(1)	1.933	C(1)-O(1)	1.121		
Ru(1)-C(2)	1.913	C(2)-O(2)	1.135		
Ru(1)-C(3)	1.899	C(3)-O(3)	1.135		
Ru(1)-C1	2.251				
Ru(1)-C2	2.244				
Ru(1)-C3	2.246				
Ru(1)-C4	2.225				
Ru(2)-C(1)	1.963	C(1)-O(1)	1.121		
Ru(2)-C(2)	1.955	C(2)-O(2)	1.131		
Ru(2)-C(3)	1.869	C(3)-O(3)	1.131		
Ru(2)-C1	2.073				
Ru(2)-C4	2.059				
C1-C2	1.410	C2-C3	1.424	C3-C4	1.428

Angles	
Ru(2)-C1-C2	117.2(5)
C1-C2-C3	114.5(6)
C2-C3-C4	113.2(6)
C3-C4-Ru(1)	117.3(5)

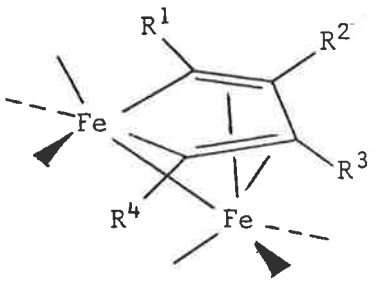
the $[Ru_2C_4(CO_2Me)_4]^+$ ion occurred by loss of OMe and CO fragments. The structure determination confirms the assignment of the molecular formula.

The tricarbonylferracyclopentadiene-$Fe(CO)_3$ moiety (see Figure 22) is a common feature of many complexes obtained from reactions between alkynes and iron carbonyls: structural studies of eleven examples have been reported.[385-395] The osmium analogue is found in a reaction product from $Os_3(CO)_{12}$ and 2,3 dimethylbutadiene, and the bicyclic derivative $Os_2(CO)_6(C_8H_6)$[396,397] Few ruthenium complexes of this type have been previously described, though $Ru_3(CO)_{12}$ reacts with $HC \equiv CCR_2OH$ (where R = H, Me or Et)[398,399] to form complexes of similar structure to $Ru_2(CO)_6[C_4(CO_2Me)_4]$ (56).

FIGURE 22



(a)



(b)

	R^1	R^2	R^3	R^4
(1)	OH	Me	Me	OH
(2)	OH	Et	Et	OH
(3)	$CHPh_2$	H	OMe	OMe
(4)	Ph	Ph	Ph	Ph

The $Fe_2(CO)_6$(ligand) structure has been theoretically examined by extended Hückel methods. The $Fe_2(CO)_6$ moiety may adopt the sawhorse geometry (Figure 22a), or an alternative in which the $Fe(CO)_3$ group π-bonded to the carbons is rotated by 60°, as in Figure 22b. In this instance, one CO group is positioned to interact with the second iron atom, forming a semi-bridging CO group, which has been rationalised as enabling the electron-deficient ferrole metal atom to recover some electron density. Energy differences between these two arrangements are calculated as only 0.2 eV in the parent compound, favouring the structure shown in Figure 22b; experimental results confirm that there is only a low energy difference, since $Fe_2(CO)_6[C_4(OH)_2Me_2]$ adopts structure (b), whereas the corresponding ethyl derivative is found to have structure (a). Of the known structures of iron complexes of this type, only two [Figure 22(2) and 22(3)] adopt conformation (a); on the other hand, both osmium complexes (***vide supra***) have this conformation. Complex (56) is also of this structural type [Figure 21 compared with Figure 22(a)].

The molecular structure of (56) closely resembles the archetypal $Fe_2(CO)_6(C_4H_4)$ molecule,[387] with a tetrasubstituted tricarbonylruthenacyclopentadiene ligand π-bonded to the second $Ru(CO)_3$ group. The environment of both ruthenium atoms can be considered to be six-coordinate, although interaction of Ru(B) with the semi-bridging CO group gives that atom *pseudo*-seven coordination. The C_4 skeleton of the $[C_4(CO_2Me)_4]^{2-}$ ligand is almost planar, with all carboxyl groups tilted well out of the C_4 plane. The structure indicates that Ru(B) lies appreciably out of the C_4 plane, away from Ru(A). The CO ligands on Ru(A) are staggered with respect to those on Ru(B). The Ru(B)-CO(3) distance of 1.872(10), 1.866(8)Å is found to be shorter than the other two, as found for the iron complexes. This is a result of increased back-bonding to ruthenium as a partial compensation for its electron deficiency.

It is of some interest that the two crystallographically independent molecules differ significantly in the disposition of the three CO groups about Ru(A), and of the semi-bridging CO group towards Ru(B). This underlines the conclusion of Thorn and Hoffmann[15] that a delicate balance of forces affects the choice of conformation, and suggests that the steric constraints associated with the packing of molecules of (56) into the crystal lattice are sufficient to perturb the minimum energy geometry.

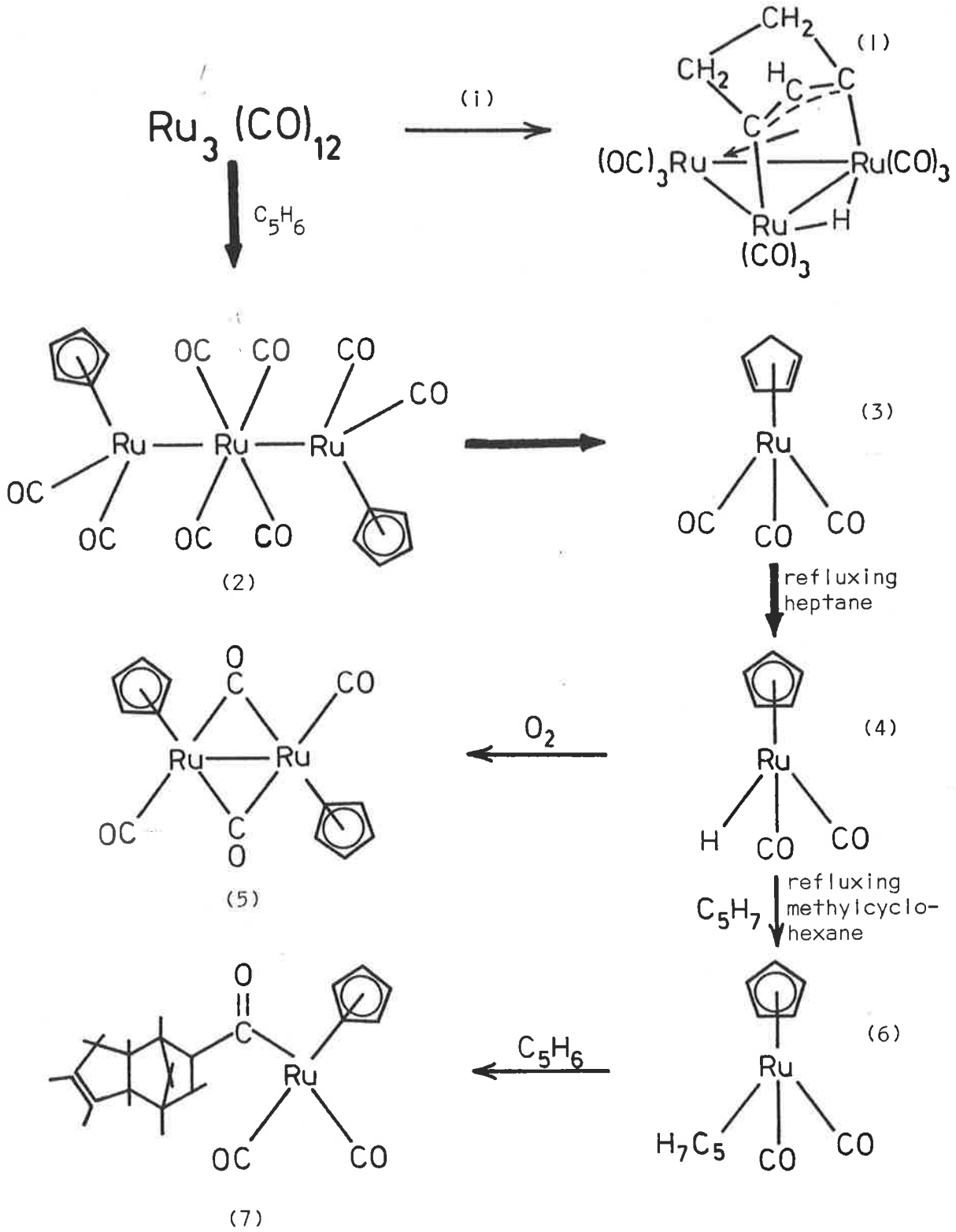
(ii) Reactions of $Ru_3(CO)_{10}(PPh_3)_2$ and $Ru_3(CO)_9L_3$ (Where L = PPh_3, PMe_3)

The reactions of $Ru_3(CO)_9L_3$ (where L = PPh_3, PMe_3) require more forcing conditions than reactions using $Ru_3(CO)_{12}$, though the final products are generally analogous. This indicates that $Ru_3(CO)_9L_3$ is more chemically inert than $Ru_3(CO)_{12}$, as the phosphine ligands sterically inhibit further reactivity toward incoming reagents. Where sufficient thermal activation is supplied, however, the reaction mechanism does not appear to differ significantly from that of analogous $Ru_3(CO)_{12}$ reactions. The complex, $Ru_3(CO)_{10}(PPh_3)_2$, undergoes initial CO substitution to give $Ru_3(CO)_9(PPh_3)_2X$ (X = 2 electron donor) before displaying similar reactivity patterns to that of $Ru_3(CO)_9L_3$.

Reaction of $Ru_3(CO)_9(PMe_3)_3$ with Cyclopentadiene

The reaction of $Ru_3(CO)_{12}$ with cyclopentadiene results in cluster degradation, the major product being $HRu(CO)_2(\eta\text{-}C_5H_5)$ (Figure 23).[400-403] An alternative reaction path gives $HRu_3(CO)_9(\eta\text{-}C_5H_5)$ in low yield, which can be obtained in 67% yield, however, by reacting $Ru_3(CO)_{12}$ with penta-1,3-diene in refluxing heptane.[400] This result is consistent with the observed reaction of isoprene (2 methylbuta-1,3-diene) and $Ru_3(CO)_{12}$, where the same type of product is isolated.[404] The reaction of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ with cyclopentadiene[405-408] gives products resulting from metal-metal bond rupture. The greater metal-metal bond strength of

FIGURE 23



(main reaction path thick arrows)

(i) C_5H_6 produces (1) in 2% yield

(i) penta-1,3-diene produces (1) in 67% yield

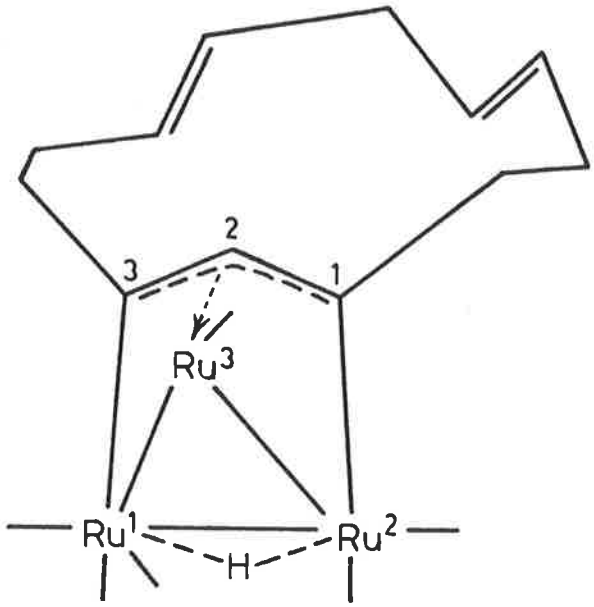
$Os_3(CO)_{12}$ [compared with $Ru_3(CO)_{12}$ or $Fe_3(CO)_{12}$][161-168] is shown by its long reaction time with cyclopentadiene (20 days) to produce $HOs(CO)_2(\eta\text{-}C_5H_5)$.[400]

When reacted with cyclopentadiene, $Ru_3(CO)_9(PMe_3)_3$ is less prone to cluster degradation. The major products all retain at least one Ru-Ru bond; {*i.e.*$[Ru(CO)(PMe_3)(\eta\text{-}C_5H_5)]_2$ (57); $HRu_3(CO)_6(PMe_3)(\eta\text{-}C_5H_5)$ (58) and $Ru_3(CO)_5(PMe_3)_3(\eta\text{-}C_5H_5)_2$ (59)}. Traces of $HRu(CO)(PMe_3)(\eta\text{-}C_5H_5)$ (60) and $Ru(CO)_2(PMe_3)(\eta^4\text{-}C_5H_6)$ (61) were also observed. The products are phosphine substituted analogues of the $Ru_3(CO)_{12}$ reaction with cyclopentadiene (refer to Figure 23). All products are readily characterised by mass spectroscopy; producing a molecular ion with subsequent loss of carbonyl groups. Insufficient sample prevented the location of the hydride ligand in the ^1H n.m.r. of $HRu(CO)(PMe_3)(\eta\text{-}C_5H_5)$ (60), but multiple scanning of the molecular ion in the mass spectrometer consistently produced the highest *m/e* = 272. Its dicarbonyl analogue, $HRu(CO)_2(\eta\text{-}C_5H_5)$, was the major product when $Ru_3(CO)_{12}$ reacted with cyclopentadiene.[400-403] In fact, the products obtained from the $Ru_3(CO)_9(PMe_3)_3$ reaction are phosphine substituted analogues of (1), (2), (3), (4) and (5) [Figure 23]. No products analogous to (6) or (7) were seen and higher reaction temperatures resulted only in increasing amounts of metal.

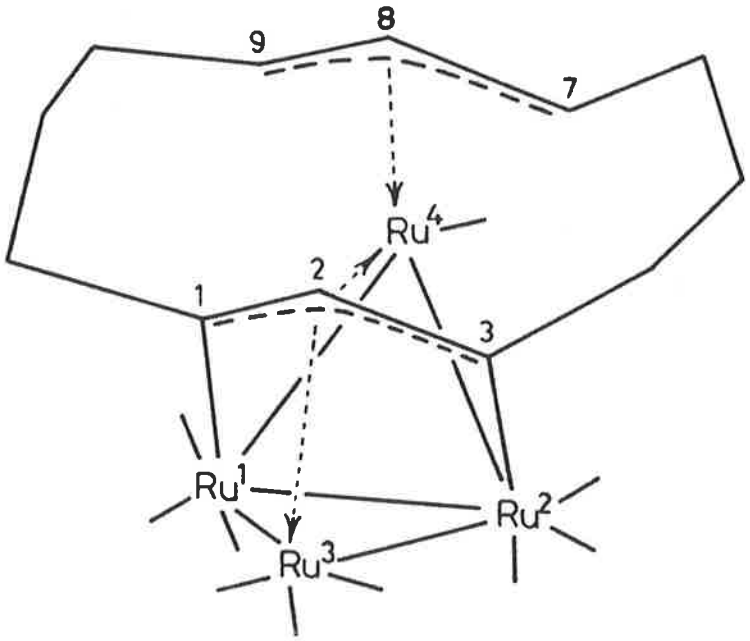
Reaction of $Ru_3(CO)_9(PMe_3)_3$ with Cyclododecatriene

Reaction of cyclododecatrienes with $Ru_3(CO)_{12}$ yields $HRu_3(CO)_9(C_{12}H_{15})$, $Ru_4(CO)_{10}(C_{12}H_{16})$, $HRu_3(CO)_9(C_{12}H_{17})$ and $HRu_3(CO)_7(C_{24}H_{34})$;[409-411] the first two have been structurally characterised (Figure 24).[412,413] The analogous reaction with $Fe(CO)_5$ causes ring closure, the product being tricarbonylbicyclo[6,4,0]dodeca-9,11-dieneiron.[414] The complex $HRu_3(CO)_9(C_{12}H_{17})$ reacts with phosphines to give the substituted products $HRu_3(CO)_{9-n}L_n(C_{12}H_{17})$ [L = $P(OMe)_3$, $P(OCH_2)_3CEt$, PMe_2Ph; n = 1-3].[411]

FIGURE 24



$HRu_3(CO)_9(C_{12}H_{15})$ and (62)



$Ru_4(CO)_{10}(C_{12}H_{16})$ and (64)

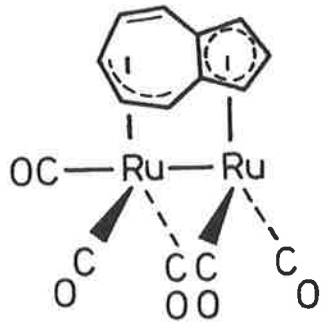
Cyclododecatriene reacts with $Ru_3(CO)_9(PMe_3)_3$ to give $HRu_3(CO)_6(PMe_3)_3(C_{12}H_{15})$ (62), $HRu_3(CO)_4(PMe_3)_3(C_{24}H_{33})$ (63) and $Ru_4(CO)_7(PMe_3)_4(C_{12}H_{16})$ (64). These are the phosphine substituted analogues of the $Ru_3(CO)_{12}$ reaction (*vide supra*).[411] No complex corresponding to $HRu_3(CO)_6(PMe_3)_3(C_{12}H_{17})$ could be recovered. All products may be easily identified by their mass spectra, which show the molecular ion followed by subsequent CO loss. All spectra recorded are consistent with those discussed for the $Ru_3(CO)_{12}$ analogue[411] (the PMe_3 resonance in the ^1H n.m.r. spectrum is obscured by the massive cyclododecatriene resonance in the region δ = 3.0-1.0 ppm).

Reaction of $Ru_3(CO)_9(PMe_3)_3$ with Azulene

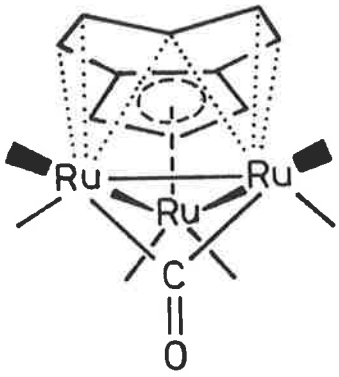
Several azulene complexes of metal carbonyls have been previously described.[415-423] Both $Ru_3(CO)_{12}$[430-434] and iron carbonyls [$Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$][424-429] react with azulene (or substituted azulenes) to give the complexes $M_2(CO)_6$(azulene) and $M_4(CO)_{10}$(azulene) [Figure 25], where M = Ru, Fe. Reaction of azulene with $Ru_3(CO)_{12}$ in refluxing heptane gives $Ru_3(CO)_7(C_{10}H_8)$ [Figure 25] in high yield.[432,433] Not surprisingly, $Ru_3(CO)_9(PMe_3)_3$ reacts with azulene to give $Ru_2(CO)_3(PMe_3)_2(C_{10}H_8)$ (64), $Ru_3(CO)_4(PMe_3)_3(C_{10}H_8)$ (65) and $Ru_4(CO)_6(PMe_3)_4(C_{10}H_8)$ (66); each complex displaying a characteristic molecular ion followed by CO loss in the mass spectrum. The infra-red spectrum of (64) shows one terminal and one bridging CO absorption. Steric factors would favour a terminal PMe_3 (and terminal CO) ligand on each Ru atom, with a bridging CO group located across the Ru-Ru bond. No such bridging CO absorptions are observed in the i.r. spectrum of $Ru_2(CO)_6(C_{10}H_8)$. A molecular ion at *m/e* = 568 together with the analytical data confirms the proposed formula. Spectroscopic data for $Ru_3(CO)_4(PMe_3)_3(C_{10}H_8)$ (65) and $Ru_4(CO)_6(PMe_3)_4(C_{10}H_8)$ (66) are consistent with the structures determined for the azulene ruthenium carbonyl analogues (Figure 25).[430,432] Contrary to other

results,[435] the phosphine substitution products are more air and moisture sensitive than their carbonyl analogues; this explains the low yields recovered after chromatographic separation.

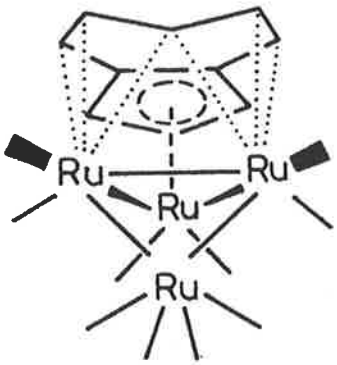
FIGURE 25



$Ru_2(CO)_5(C_{10}H_8)$



$Ru_3(CO)_7(C_{10}H_8)$ or (65)



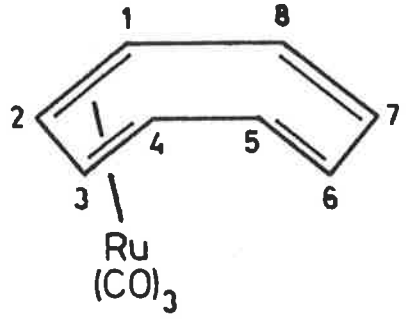
$Ru_4(CO)_{10}(C_{10}H_8)$ or (66)

Azulene derivatives of $Ru_3(CO)_{12}$

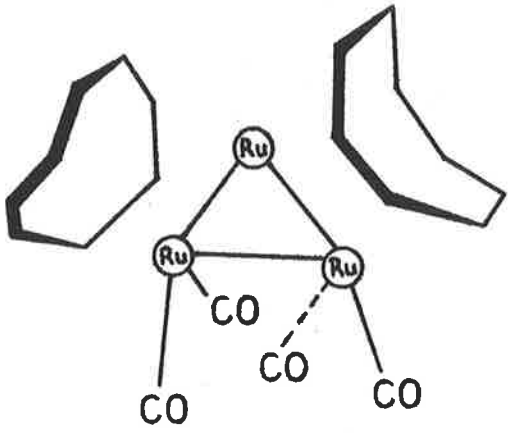
Reaction of $Ru_3(CO)_9(PMe_3)_3$ with Cycloocta-1,3,5,7-tetraene(COT)

The reactions of cyclooctatetraenes with iron carbonyls have been extensively studied,[436-486] largely as a result of the fluxional behaviour of the products. Ruthenium analogues of the $Fe_x(CO)_y(COT)$ complexes have been obtained.[441,463,473,479,480,482,483,487-514] The major products from the reaction of $Ru_3(CO)_{12}$ with COT are: $Ru(CO)_3(C_8H_8)$, $Ru_2(CO)_5(C_8H_8)$, $Ru_2(CO)_6(C_8H_8)$ and $Ru_3(CO)_{11}(C_8H_8)$ (see Figure 26).[487-491] The reactions of COT with iron or ruthenium carbonyls, even under very mild conditions, gives a number of products (some very minor), which are very dependent on the reaction conditions. Thus, in almost every

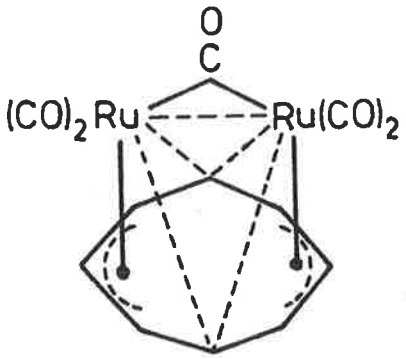
FIGURE 26



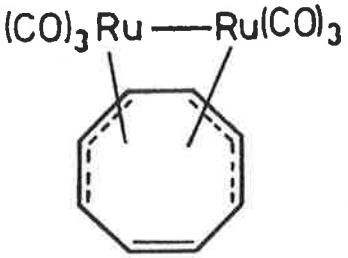
$Ru(CO)_3(C_8H_8)$



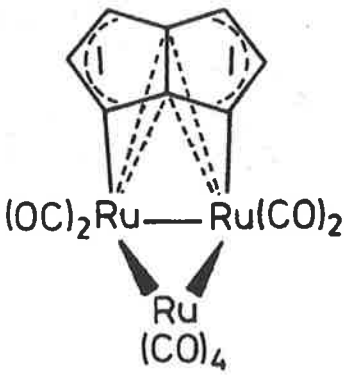
$Ru_3(CO)_4(C_8H_8)_2$



$Ru_2(CO)_5(C_8H_8)$



$Ru_2(CO)_6(C_8H_8)$



$Ru_3(CO)_8(C_8H_6)$

Cyclooctatetrene derivatives of $Ru_3(CO)_{12}$

case, chromatography is necessary. The reactions of osmium carbonyls with COT have not been as thoroughly investigated.[485,514-516]

The complex $Ru_3(CO)_9(PMe_3)_3$ reacts with COT to form the characterised products: $Ru(CO)_2(PMe_3)(C_8H_8)$ (67), $Ru_2(CO)_4(PMe_3)_2(C_8H_8)$ (68), $Ru_2(CO)_3(PMe_3)_2(C_8H_8)$ (69) and $Ru_3(CO)_5(PMe_3)_3(C_8H_6)$ (70). A previous attempt to form phosphine/COT substituted ruthenium carbonyl complexes from $Ru(CO)_3(C_8H_8)$ failed, because COT is displaced by the incoming phosphine or phosphite.[491] Hence, use of $Ru_3(CO)_9(PR_3)_3$ as a starting material provides a way of incorporating both phosphine and COT on a metal carbonyl fragment. The yields of the complexes obtained, however, are very low. Moreover, the number of products generated in the reaction makes isolation difficult. Column chromatography using Florisil or silica, though enabling a good overall recovery of products, was far less selective than alumina, which, however, showed greater decomposition. All products show characteristic molecular ions (M^+) in their mass spectra; with subsequent CO loss. ^1H n.m.r. data on the phosphine-substituted products are consistent with the ruthenium carbonyl analogues, and hence imply analogous structures (Figure 26).

Interestingly, $Ru_3(CO)_8(C_8H_6)$ is only formed as a very minor product in the reaction of $Ru_3(CO)_{12}$ with COT,[497,507] yet (70) is isolated in 16% yield as the major product in the reaction of $Ru_3(CO)_9(PMe_3)_3$ with COT. Cyclooctatrene and (70) react further after prolonged heating in toluene to give $Ru_3(CO)(PMe_3)_3(C_8H_6)(C_8H_8)$ (71). This complex shows only one $\nu(CO)$ vibration at 1711 cm^{-1}, a frequency consistent with a face-bridging CO group. The ^1H n.m.r. confirms the existence of a pentalene ring system[485] (formed *via* transannular cyclisation of COT - Figure 26) as well as showing a resonance at δ = 3.63 assigned to a COT ring [Note: the complex $Ru_3(CO)_4(C_8H_8)$ shows a single

resonance at δ = 3.74 at 35° C[487,496]. The mass spectrum shows a molecular ion at *m/e* = 768, but no subsequent CO loss. Furthermore, the PMe_3 resonance in the ^1H n.m.r. spectrum is a doublet, implying that one PMe_3 group is attached to each Ru atom. The exact nature of this complex is unknown and suitable crystals for structural characterisation have not been grown to this point.

Reaction of $Ru_3(CO)_9(PMe_3)_3$ with t-Butyl Isocyanide

The complex $Ru_3(CO)_9(PMe_3)_3$ reacts with *t*-butyl isocyanide (*t*-BuNC) to give the complexes $Ru_3(CO)_8(CNBu^t)(PMe_3)_3$ (72), $Ru_3(CO)_7(CNBu^t)_2(PMe_3)_3$ (73) and $Ru_3(CO)_6(PMe_3)_3(CNBu^t)$ (74). The complexes (72) and (73) are formed by straightforward CO substitution by the isocyanide. Interestingly, these complexes could not be obtained by the radical anion initiated method described earlier. Both of the isocyanide substituted complexes contain bridging CO absorptions in their infra-red spectra. This arrangement allows an easing of the increased steric forces introduced by substitution of CO for *t*-BuNC; presumably forming the most stable ligand envelope around the Ru_3 triangle. Complex (74) is thought to have the isocyanide ligand acting as a six electron donor. This is consistent with micro-analytical data, a low ν(CN) value in the infra-red spectrum (1715 cm^{-1}) and the molecular ion at *m/e* = 785 in the mass spectrum. Though the reaction mixture was stable under an inert atmosphere, chromatography, even under nitrogen, resulted in extensive decomposition, hence enabling isolation of products only in low yields.

Reaction of $Ru_3(CO)_9(PPh_3)_3$ with t-Butyl Isocyanide

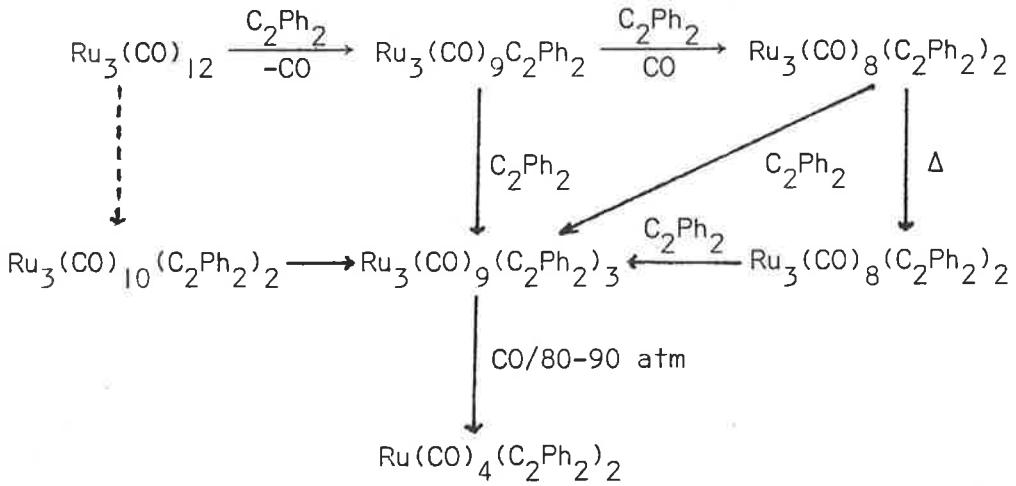
The complex $Ru_3(CO)_9(PPh_3)_3$ reacts with *t*-butyl isocyanide (*t*-BuNC) to give a host of products, from which only $Ru_3(CO)_8(CNBu^t)(PPh_3)_3$ (75) and $Ru_3(CO)_7(CNBu^t)_2(PPh_3)_3$ (76) could be characterised. These complexes are formed in low yield and are extremely air sensitive. Their

i.r. spectra in the carbonyl region resemble those of the analogous PMe_3 derivatives (*vide supra*). On standing in solution (CH_2Cl_2, acetone, diethyl ether; 1-2 days) a murky grey precipitate [no ν(CO) absorptions] results, indicating decomposition. No evidence for *t*-BuNC acting as a six electron donor was found in any of the products. Easing of the steric forces associated with substituting *t*-BuNC for CO apparently occurs through cluster degradation, resulting finally in formation of the insoluble grey precipitate.

Reaction of $Ru_3(CO)_9(PR_3)_3$ with Dimethylacetylenedicarboxylate (DMA)

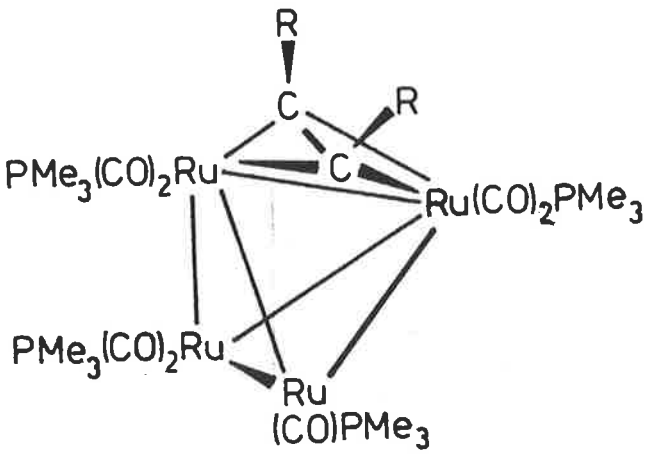
A thorough study has been made of the reactions of disubstituted alkynes with $Fe_3(CO)_{12}$,[385-395,517-519] $Ru_3(CO)_{12}$[84,263,384,404,520-532] or $Os_3(CO)_{12}$.[396-398,532-537] A greater number of trinuclear acetylene-substituted products are formed when $Ru_3(CO)_{12}$ reacts with diphenylacetylene than is the case for $Fe_3(CO)_{12}$.[520-522] The following Reaction Scheme was established by varying the conditions of the reaction.[522]

REACTION SCHEME 2



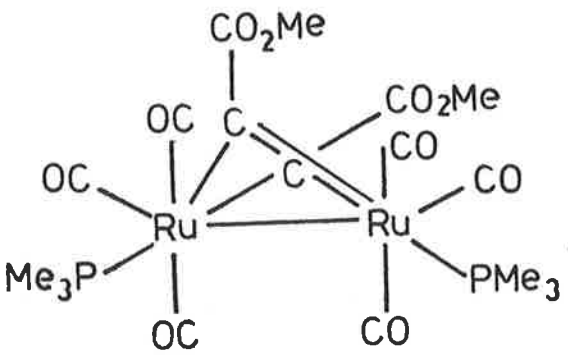
The complexes $Ru_3(CO)_9(PR_3)_3$ (where R = Ph or Me) react to give a variety of products, which in most cases retain the Ru_3 triangle. On the basis of spectroscopic evidence, particularly the easy identification of an accurate molecular ion in the mass spectrum, the following products were characterised from the reaction of $Ru_3(CO)_9(PMe_3)_3$ with DMA: $Ru_2(CO)_6[\eta\text{-}C_2(CO_2Me)_2](PMe_3)_2$ (77), $Ru_3(CO)_7[\eta\text{-}C_2(CO_2Me)_2](PMe_3)_3$ (78), $Ru_3(CO)_6[\eta\text{-}C_2(CO_2Me)_2](PMe_3)_3$ (79) and $Ru_4(CO)_8[\eta\text{-}C_2(CO_2Me)_2](PMe_3)_4$ (80). Complexes (79) and (80) can be related to complexes illustrated in the Reaction Scheme above. Complex (80) is analogous to the tetranuclear Ru_4C_2 clusters obtained in low yield by heating $Ru_3(CO)_{12}$ and R_2C_2 (R = Ph, Me, Et, CH_3OCH_2) at reflux in hexane.[523] Its probable structure is shown in Figure 27. The first complex (77) has no known analogue, but on the basis of its spectroscopic evidence a plausible structure can be assigned (Figure 27).

FIGURE 27



(80)

$Ru_4(CO)_7(PMe_3)_4(C_2R_2)$



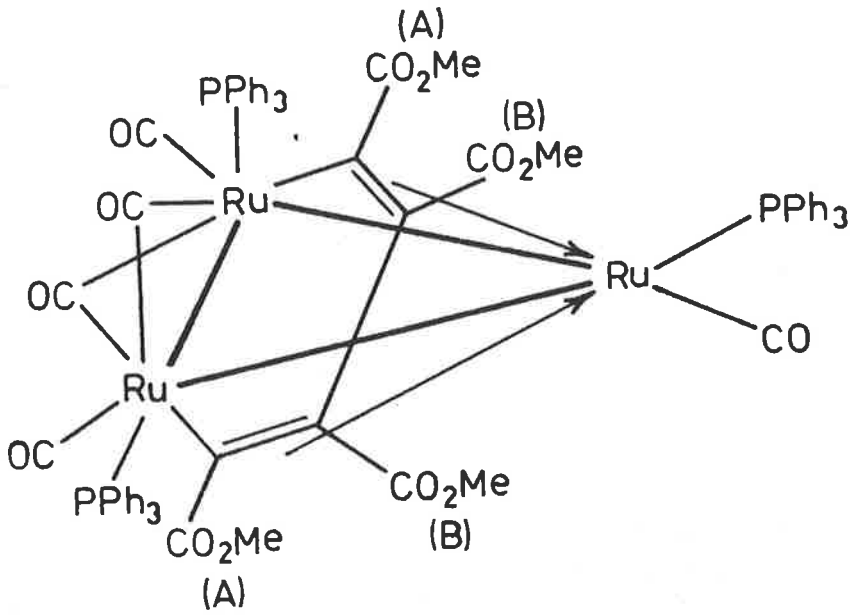
(77)

$Ru_2(CO)_6(PMe_3)_2[C_2(CO_2Me)_2]$

The complex $Ru_3(CO)_9(PPh_3)_3$ reacts with DMA to give $Ru_3(CO)_7[\eta\text{-}C_2(CO_2Me)_2](PPh_3)_3$ (81), $Ru_3(CO)_6[\eta\text{-}C_2(CO_2Me)_2](PPh_3)_3$ (82), $Ru_3(CO)_5(PPh_3)_3[\eta\text{-}C_4(CO_2Me)_4]$ (83) and $Ru_4(CO)_8[\eta\text{-}C_2(CO_2Me)_2](PPh_3)_4$ (84). Of these complexes only (83) has no analogue in the reaction of DMA with $Ru_3(CO)_9(PMe_3)_3$. The complex $Ru_3(CO)_5(\eta\text{-}C_2Ph_2)(PPh_3)_3$ has been isolated,[521] and the ν(CO) absorptions in its infra-red spectrum are almost

identical with those of (83), except that the DMA product is consistently 3-11 cm^{-1} higher in energy. Both complexes have five terminal CO and three bridging CO absorptions, which is unusual for complexes possessing only five CO groups. The ^1H n.m.r. indicates two different types of CO_2Me moieties; consistent with A and B in the proposed structure of $Ru_3(CO)_5(PPh_3)_3[\eta\text{-}C_4(CO_2Me)_4]$ (83) (Figure 28). The remaining characterised products show carbonyl infra-red spectra very similar, in both band position and intensity, to the well characterised PMe_3 substituted adducts (*vide ante*).

FIGURE 28



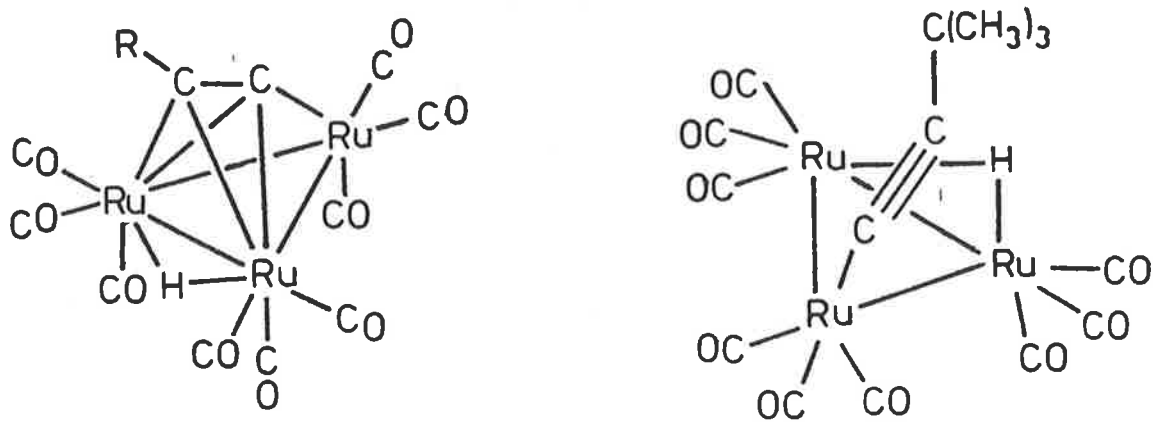
(83)

$Ru_3(CO)_5(PPh_3)_3[C_4(CO_2Me)_4]$

Reactions of $Ru_3(CO)_{12-n}L_n$ (where L = PMe_3, n = 3; L = PPh_3, n = 1-3) with t-Butyl Acetylene (HC_2Bu^t)

A reaction of $Ru_3(CO)_{12}$ and *t*-butylacetylene in heptane gave $HRu_3(CO)_9(\eta\text{-}C_2Bu^t)$ in good yield.[538-542] The reactions of this product have been extensively investigated.[539,543-550] The complex reacts with PPh_3 to give $HRu_3(CO)_8(PPh_3)(\eta\text{-}C_2Bu^t)$ and $HRu_3(CO)_7(PPh_3)_2(\eta\text{-}C_2Bu^t)$ in low yield.[539] Variable-temperature ^{13}C and ^1H n.m.r. studies indi-

FIGURE 29



$HRu_3(CO)_9(C_2Bu^t)$: two perspectives

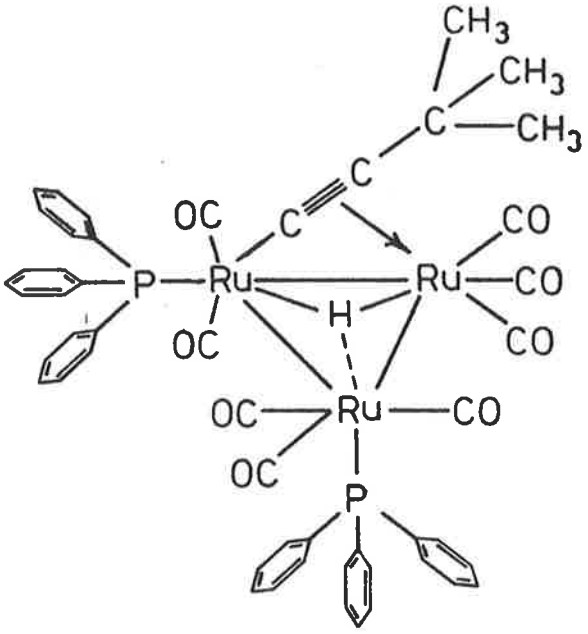
cate that initial phosphine substitution of a CO group occurs only on the ruthenium atoms having a σ bond with the organic ligand.[539]

The reaction of $Ru_3(CO)_{11}(PPh_3)$ with an equimolar amount of HC_2Bu^t gave $HRu_3(CO)_8(PPh_3)(\eta\text{-}C_2Bu^t)$ (85) in 73% yield together with a small amount of $HRu_3(CO)_6(PPh_3)(\eta\text{-}C_{12}H_{19})$ (86). The major product was identified by comparison with literature data.[539] The minor product was tentatively postulated to contain a dimerised acetylene moiety. The disubstituted complex $Ru_3(CO)_{10}(PPh_3)_2$ reacts with an equimolar amount of HC_2Bu^t to give three major products: $HRu_3(CO)_8(PPh_3)_2(\eta\text{-}C_2Bu^t)$ (87), $HRu_3(CO)_7(PPh_3)_2(\eta\text{-}C_2Bu^t)$ (88) and $HRu_3(CO)_5(PPh_3)_2(\eta\text{-}C_2Bu^t)$ (89). Complex (88) was formed in the greatest yield (42%) and was readily identified by comparison with literature spectroscopic data [see Figure 30(2)].[539] The ^1H n.m.r. spectrum of $HRu_3(CO)_8(PPh_3)_2(\eta\text{-}C_2Bu^t)$ (87) displays two broad hydride signals, but these integrate for only one proton; the exact nature of the complex still remains to be determined. A molecular formula was elucidated from vapour pressure osmometric and analytical data. The ^1H n.m.r. spectrum of $HRu_3(CO)_8(PPh_3)(\eta\text{-}C_5H_7)$, formed by reacting $Ru_3(CO)_{12}$ with 1,3 pentadiene followed by subsequent reaction

with PPh_3,[404,539] also contains two hydride signals (both doublets).[539] No bridging CO ligands were observed in the i.r. spectrum of $HRu_3(CO)_8(PPh_3)_2(\eta\text{-}C_2Bu^t)$. An electron count of the $Ru_3(CO)_{10}(PPh_3)_2$ fragment totals 44 cluster valence electrons.[551-553] Thus, the hydride and the C_2Bu^t contribute four electrons to the total number of 48 cluster valence electrons predicted for a Ru_3 cluster.[551-553] A hydride is generally a one electron donor. This suggests a $\sigma + \pi$ interaction for the C_2Bu^t moiety, probably bridging a Ru-Ru bond (in an analogous way to the isoelectronic semibridging CO groups[196]). Literature data indicates a preference for the $M \xrightarrow{\sigma} CCBu^t$ bond to form at a Ru centre with a coordinated PPh_3 group,[539] and a tendency for the acetylene-Ru π interaction to occur at the sterically less demanding Ru centre (containing no coordinated PPh_3). Hence, the structure shown in Figure 30(1) is the most feasible. The other complex isolated, $HRu_3(CO)_5(PPh_3)_3(C_2Bu^t)$, (89) shows five ν(CO) absorptions in its i.r. spectrum, (two that can be associated with terminally bound CO groups and three that can be associated with bridging or semi-bridging CO groups[554]). The ^1H n.m.r. spectrum indicates the presence of a hydride ligand, two PPh_3 ligands and a tertiary butyl group associated with the initial acetylene reagent.

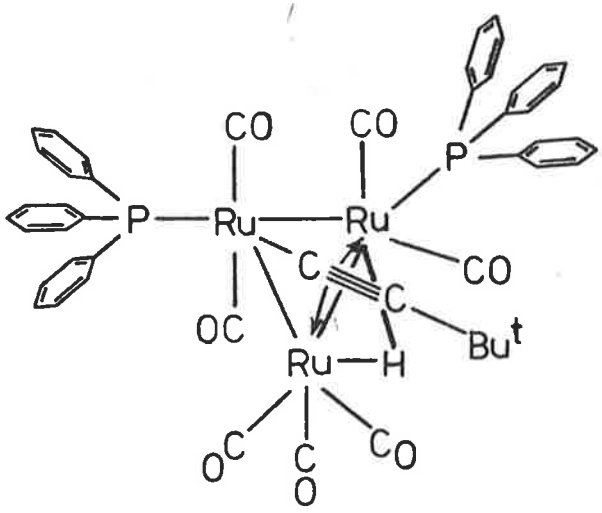
The $M \xrightarrow{\sigma} CCBu^t$ bond is likely to form at a Ru centre with coordinated PPh_3(*vide supra*), thus the structure shown in Figure 30(3) is proposed. This means that the major products isolated differ empirically only in the number of CO groups they possess. This suggests (in the absence of any *ortho*-metalation of the PPh_3 groups) that the bonding of the C_2Bu^t moiety and to a minor extent the hydride ligand must compensate for the steric as well as electronic factors associated with a $Ru_3(CO)_n(PPh_3)_2$ entity. Only X-ray crystallographic data will reveal the nature of bonding in these complexes.

FIGURE 30



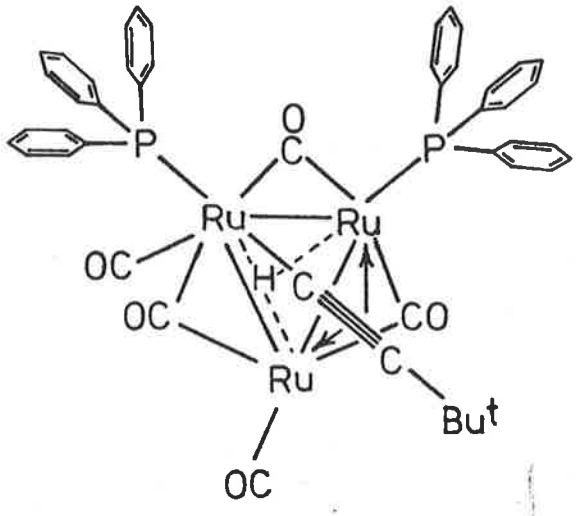
(1)

$HRu_3(CO)_8(PPh_3)_2(C_2Bu^t)$ (87)



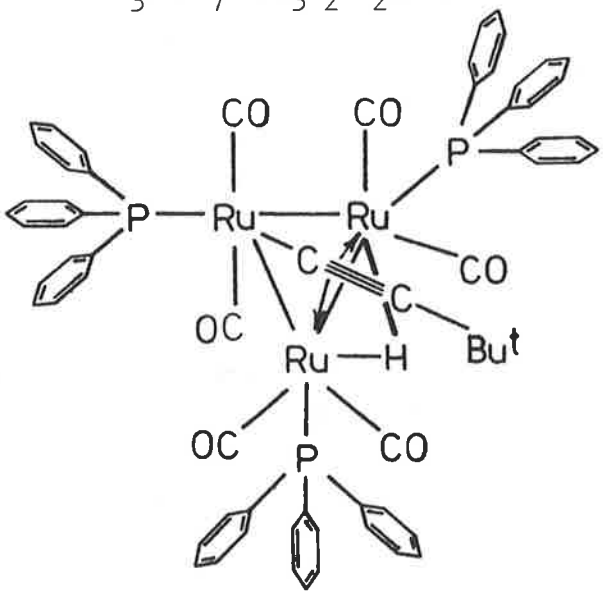
(2)

$HRu_3(CO)_7(PPh_3)_2(C_2Bu^t)$ (88)



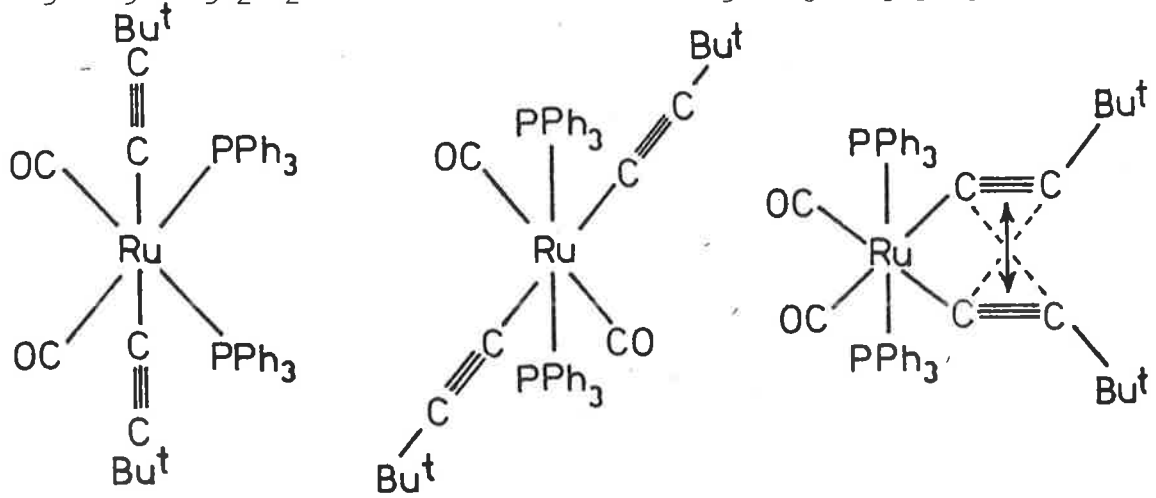
(3)

$HRu_3(CO)_5(PPh_3)_2(C_2Bu^t)$ (89)



(4)

$HRu_3(CO)_6(PPh_3)_3(C_2Bu^t)$ (93)



(5a) (5b) (5c)

$Ru(CO)_2(PPh_3)_2(C\equiv C\text{-}Bu^t)_2$ (92)

Tertiary butyl acetylene reacts with $Ru_3(CO)_9(PR_3)_3$ (R = Ph or Me) to give the major product $HRu_3(CO)_6(PR_3)_3(C_2Bu^t)$ in low yield. The spectral data associated with these complexes indicate that a phosphine-substituted analogue of $HRu_3(CO)_9(C_2Bu^t)$ [see Figure 30(4) for R = PPh_3] is formed. When R = Me, the reaction resulted in the formation of a host of minor products, of which $Ru_3(CO)_5(PMe_3)_3(C_2Bu^t)_3$ could be identified by its molecular ion at *m/e* = 917 in the mass spectrum. The infra-red spectrum indicated that bridging CO ligands were present. Trimerisation of the acetylene to give products with Ru_3 cores in low yield is consistent with previous reports.[544, 548, 555] When R = Ph, the complexes $Ru(CO)_2(PPh_3)_2(C_2Bu^t)_2$ (92), $HRu_3(CO)_5(PPh_3)_2(C_{12}H_{19})$ (94) and $HRu_3(CO)_4(PPh_3)_2(C_{18}H_{29})$ (95) could also be isolated. It appears that $HRu_3(CO)_6(PPh_3)_3(C_2Bu^t)$ initially forms, followed by dimerisation or trimerisation of the organic ligand with excess HC_2Bu^t. This further reaction is easily detected in the ^1H n.m.r. spectrum by the appearance of low field signals (δ = 5.40-6.40), resulting from the incorporation of the acetylenic hydride of the dimerisation/trimerisation adducts. The structural nature of these final complexes, as indicated by Sappa and coworkers,[555] must await X-ray crystallographic studies. The only cluster degradation product isolated is $Ru(CO)_2(C_2Bu^t)_2(PPh_3)_2$ (92). The presence of only one $\nu(C\equiv C)$ and one $\nu(CO)$ absorption in the i.r. spectrum implies an equivalent environment for both CO groups and both C_2Bu^t groups. Three possible structures for complex (92) are given in Figure 30(5).

Reaction of $Ru_3(CO)_{10}(PPh_3)_2$ with t-Butyl Isocyanide or PMe_3

Tertiary butyl isocyanide and $Ru_3(CO)_{10}(PPh_3)_2$ react in refluxing n-hexane to form $Ru_3(CO)_9(CNBu^t)(PPh_3)_2$ (96) in good yield. Likewise, $Ru_3(CO)_{10}(PPh_3)_2$ reacts with an equimolar amount of PMe_3 under gentle heating to afford $Ru_3(CO)_9(PMe_3)(PPh_3)_2$ (97) in good yield. This is

consistent with the prevalence of tri-substituted complexes in the thermal substitution chemistry of $Ru_3(CO)_{12}$.[77-91]

Brief Summary

The following observations are made on the reactions described above:

i) $Ru_3(CO)_{11}L$ and $Ru_3(CO)_{10}L_2$ preferentially undergo CO substitution reactions until substitution has occurred on each ruthenium centre.

ii) $Ru_3(CO)_9L_3$ can undergo cluster degradation, but this is not the major reaction mode.

iii) When $Ru_3(CO)_{12-n}L_n$ ($L = PR_3$, $n = 0-3$) is reacted with unsaturated organic molecules, the yield decreases with increasing substitution.

iv) The number of products obtained using $Ru_3(CO)_{12-n}L_n$ ($L = PR_3$, $n = 0-3$) increases with increasing substitution.

v) *Ortho*-metalation of aryl phosphine derivatives is not observed on heating.

vi) $Ru_3(CO)_9(PPh_3)_3$ can lose a PPh_3 ligand when reacting with acetylenes.

vii) Steric interactions determined by phosphine cone angles[150] predominate in deciding the nature and yields of the products.

viii) Acetylenes can dimerise or trimerise on the Ru_3 triangle and this type of reaction is apparently unaffected by the presence of phosphine[555] (though it only occurs to a minor extent).

Effect of Chromatographic Adsorbents and/or Water on $Ru_3(CO)_9(PR_3)_3$

The water sensitivity of many of the reaction products of $Ru_3(CO)_9(PMe_3)_3$ emerged during their isolation. Unlike $Ru_3(CO)_9(PPh_3)_3$, $Ru_3(CO)_9(PMe_3)_3$ does react with water in various refluxing ether solvents to give at least five uncharacterised products. The yield and number of products isolated by chromatography is dependent on the particular ether solvent used, which can be linked to their particular

boiling points. In all cases (diethyl ether, di-n-butyl ether, thf, dimethoxyethane) a reaction takes place which, given sufficient time (2-9 days), results in the complete disappearance of the starting material. No reaction is observed using strictly anhydrous solvents. Unexpectedly, no molecular ions could be located for the reaction products of $Ru_3(CO)_9(PMe_3)_3$ (highest *m/e* = 76). The ^1H n.m.r. spectra of several products show resonances between δ = 3.85 and 7.80, which are of much lower field than might be expected from the nature of the reagents. Furthermore, the PMe_3 region (δ = 1.00-2.20) shows numerous peaks (as many as eleven) which cannot be accounted for at this stage. Unfortunately, consistent analytical data could not be obtained. The reactivity of $Ru_3(CO)_9(PMe_3)_3$ toward water is much lower in acetone or dimethylformamide (greater than 90% starting complex recovered after 1 week of heating at reflux point). Heating $Ru_3(CO)_9(PMe_3)_3$ at reflux point in dry octane for 14 days resulted in no detectable reaction. Previous studies[556,557] have shown that water will react with $M_3(CO)_{12}$ (M = Ru, Os) to give hydrido carbonyl clusters. Initial ^1H n.m.r. studies of the reaction products of $Ru_3(CO)_9(PMe_3)_3$ with water, however, have failed to reveal any such metal hydrides. Lack of suitable crystals prevented X-ray crystallographic characterisation of the products.

Both $Ru_3(CO)_9(PMe_3)_3$ and $Ru_3(CO)_9(PPh_3)_3$ react with chromatographic adsorbents (silica gel, alumina, florisil) at room temperature over prolonged periods. The products were obtained in very low yields, as the majority of the starting complex was recovered. Furthermore, the reaction is sensitive to the type of adsorbent and whether solvent is present. The products obtained from both complexes show consistent analytical data considerably higher in both carbon and hydrogen content than either of the respective starting complexes. Considerable difficulty is experienced in chromatographic separation

of products. The two products obtained when $Ru_3(CO)_9(PMe_3)_3$ reacts with silica required elution through four feet of silica gel (*ca.* 8 h) to enable effective separation. On isolation, these two products were indistinguishable spectroscopically, or on the basis of analytical data. The ^1H n.m.r. data indicate that the PMe_3 ligands are present in two separate environments in the ratio 2:1. It was not possible to chromatographically separate the products obtained when $Ru_3(CO)_9(PPh_3)_3$ absorbed onto alumina. Suitable crystals could not be obtained from these reactions for X-ray structural studies.

Catalysis by metal clusters is being actively investigated, as they may be valid models for metal surfaces and may also be good catalysts themselves.[178-185,558,559] Anchoring metal clusters onto supports offers obvious advantages for catalysis, such as ease of separation, lack of corrosion, stabilization.[560] The preparation and catalytic activity of supported iron, ruthenium or osmium clusters has been extensively investigated.[561-581] The nature of the complexes formed on the actual support is, however, still speculative. Furthermore, not one of the proposed structures from these studies[561-581] agrees with the high hydrogen and carbon content observed in the products made on binding $Ru_3(CO)_9(PR_3)_3$ (R = Me, Ph) to a solid support. The emerging importance of this area of research demands new attempts be made to solve the structural character of these complexes.

Reaction of $Ru_3(CO)_9(PR_3)_3$ (R = Me, Ph) with Dihydrogen

The complexes $Ru_3(CO)_9(PR_3)_3$ (R = Me or Ph) react with H_2 at high temperatures to give the complexes: $H_4Ru_4(CO)_{10}(PR_3)_2$, $H_4Ru_4(CO)_9(PR_3)_3$ (R = Me, Ph) and $H_4Ru_4(CO)_8(PMe_3)_4$ (100) among many other uncharacterised products. The characterised products agree with the available data (R = Ph, previously reported;[287] R = Me previously uncharacterised

but good comparative CO absorptions with respect to other $H_4Ru_4(CO)_{12-n}(PR_3)_n$ derivatives[80,87,287,288,582,583] and are consistent with the formation of $H_4Ru_4(CO)_{12}$ from $Ru_3(CO)_{12}$ and H_2.[584,585] Interestingly, the products characterised have generally less than one phosphine ligand per Ru atom, unlike the corresponding reagent complexes. No trace of phosphine was detected during or after the reaction. The phosphine may then be either associated with the other uncharacterised derivatives produced, or be associated with the complexes that decomposed on chromatography.

Reactions of $Ru_3(CO)_{11}(CNBu^t)$

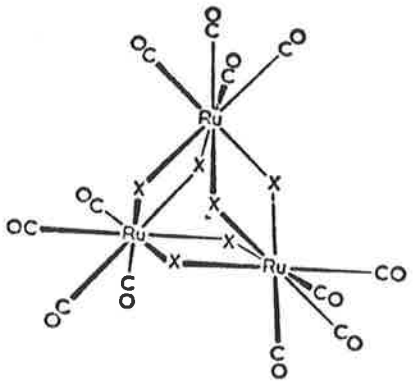
Two equivalents of PCy_3 readily react with $Ru_3(CO)_{11}(CNBu^t)$ in thf heated at reflux point to give an excellent yield of $Ru_3(CO)_9(CNBu^t)(PCy_3)_2$ (101). The CO absorptions in the i.r. spectrum showed the presence of at least one bridging CO ligand; otherwise its spectral and analytical data were as anticipated.

The complex $Ru_3(CO)_{11}(CNBu^t)$ also reacts with cyclopentadiene, cyclododecatriene and nickelocene to give a wide variety of uncharacterised products. Initial ^1H n.m.r. data indicate that some interaction occurs between the isocyanide ligand and the unsaturated organic moiety of the reagents, but further decoupling and/or labelling studies, together with structural data, are needed to understand the course of this unusual reaction type.[586]

Iodine also reacts with $Ru_3(CO)_{11}(CNBu^t)$ to yield $Ru_3I_2(CO)_9(CNBu^t)$ (102) in good yield and $Ru_3I_7(CO)_{11}(CNBu^t)$ (103) in poor yield. The former complex is most probably the result of CO substitution by I_2. The empirical formula of complex (103) is established by analytical data. The parent carbonyl, $Ru_3(CO)_{12}$, reacts with halogens to yield

$Ru_3X_6(CO)_{12}$ (X = halogen).[169,587] The chloride is most conveniently prepared by direct chlorination of $Ru_3(CO)_{12}$ in refluxing chloroform.[169,587] These trinuclear derivatives (see Figure 31) are thought to have no Ru-Ru bonds and are stable for short periods as solids.[169,587] Complex (163) presumably has a similar structure, although the interaction of an extra iodine is not understood at this stage. No formation of $[RuI_2L_2]_n$ (L = CO or $CNBu^t$) was observed,[169] presumably due to the low temperature used in the reaction. The lower reaction temperature may also assist in formation of the major product, $Ru_3I_2(CO)_9(CNBu^t)$ (102), as insufficient thermal energy is present to facilitate Ru-Ru bond breaking to any major extent.

FIGURE 31



$Ru_3X_6(CO)_{12}$

EXPERIMENTAL

General Experimental Conditions

All preparations and reactions were carried out in an atmosphere of dry nitrogen. All compounds were stored in the dark.

Elemental microanalyses were determined by the Australian Microanalytical Service (Melbourne), the Canadian Microanalytical Service (Vancouver), or at the South Australian Institute of Technology.

Infra-red spectra were recorded using Perkin Elmer 457, Perkin Elmer 683 or Jasco IRA-2 double-beam Grating Infrared Spectrophotometers in the range 4000-600 cm^{-1} and were calibrated with polystyrene (1583.1 cm^{-1}). The Perkin Elmer 457 instrument has incorporated into it a scale changing mechanism at 2000 cm^{-1}, which produces a discontinuity in the spectrum, thus interfering with any absorptions near this wavenumber (CO, CN, CC). The Perkin Elmer 683 or Jasco instrument has a smooth scale changing mechanism, which does not interfere with the recording of the spectra. These stretching frequencies were, if possible, recorded in solution between NaCl plates using a standard solution cell.

Proton n.m.r. spectra were recorded relative to TMS on a Varian T60 spectrometer at 60 MHz. Fourier transformed ^{1}H spectra were recorded on computer-equipped Bruker HX-90E or WP-80DS spectrometers, at 90 and 80 MHz respectively. Carbon n.m.r. spectra were also recorded on the Bruker WP-80DS. The spectra were determined in deuterated solvents, usually deutero-chloroform, in 10 mm tubes. Deuterated solvents were required for the deuterium resonance lock. Concentrations of the samples were in the range 0.01-1.0 ***M*** solutions. ***Mass spectra*** were recorded on an AEI-GEC MS 3074 spectrometer (mass, with 70 eV ionizing energy). ***Solution molecular weights*** were obtained using

a Knauer Vapour Pressure Osmometer with attached Universal Temperature Measuring Instrument.

For osmometric work, samples were weighed on a Cahn Model G2 electrobalance. For routine preparative work, weighings were done on a Mettler H16 balance weighing to 0.01 mg.

Chromatography was routinely carried out on columns of alumina (BDH, Fluka or Ajax), Florisil (Strem) or silica gel (Merck, Fluka or Ajax) initially packed in light petroleum. Thin layer chromatography was carried out using silica (Merck or Camag: Kieselgel G, Kieselgel H or Kieselgel F_{254}).

All solvents were dried using (i) sodium (diethyl ether, tetrahydrofuran, all petroleum fractions, benzene, toluene), (ii) magnesium (methanol, ethanol), (iii) calcium chloride (dichloromethane, chloroform) or (iv) Linde 4 Å molecular sieves (d-chloroform, d^6-acetone, d^6-benzene). Light petroleum refers to a fraction of b.p. 40-60° C.

High purity nitrogen was obtained from Commonwealth Industrial Gases (CIG) Limited and carbon monoxide from Matheson Gas Products; both were used as received.

Ligands were commercial products and were used as received. *t*-Butyl isocyanide was prepared by methods analogous to that of other isocyanides.[588-590]

High pressure reactions were carried out in a stainless steel autoclave (Baskerville and Lindsay), internal volume 1000 ml, equipped with a removable glass liner.

$H_4Ru_4(CO)_{12}$,[585] $H_4Os_4(CO)_{12}$[585] and $HRu_3(CO)_9(C_2Bu^t)$[539] were prepared according to published procedures. $RuCl_3$, xH_2O and OsO_4 were used as received (Johnson Matthey).

Preparation of $Ru_3(CO)_{12}$

A solution of $RuCl_3.xH_2O$ (4 g) in methanol (300 ml), in an autoclave, was pressurized to 40 atmospheres with CO. The solution was heated at 125° for 20 h, the working CO pressure increasing to approximately 55 atmospheres. The reaction mixture was allowed to cool, the CO vented, and the bright orange *crystals* of $Ru_3(CO)_{12}$ were collected (2.6 g). Hydrated ruthenium trichloride (2.6 g) was added to the mother liquor and the reaction repeated to yield 2.4 g of the ruthenium carbonyl cluster. The latter procedure was followed two more times, total yield of $Ru_3(CO)_{12}$ being 9.84 g (from 11.44 g of ruthenium trichloride), m.p. 144-145° (dec.) (Found: C - 22.4%; *M* (mass spectrometry) - 641. $C_{12}O_{12}Ru_3$ requires C - 22.5%; *M* - 641). Infrared (C_6H_{12}): ν(CO) = 2062vs, 2030s and 2004m cm^{-1}.

Another series of experiments was carried out using six consecutive 7.0 g charges of $RuCl_3.xH_2O$ in methanol (700 ml), with an initial CO pressure of between 53 and 60 atm, and heating at 125° for between 16.0 and 18.5 h, to give a total yield of 38.4 g $Ru_3(CO)_{12}$; on another occasion, 45.5 g $RuCl_3.xH_2O$ was similarly converted to 42.4 g $Ru_3(CO)_{12}$ (each charge in 700 ml methanol, initial pressure 60-65 atm, heating at 125° for 17 h).

The three sets of experiments described (*vide supra*) result in a virtually quantitative conversion of $RuCl_3.xH_2O$ to $Ru_3(CO)_{12}$; however, the yield from the first charge is often only moderate to good. The actual overall yields are *ca.* 91-99% based on the trihydrate.

Reactions of $Ru_3(CO)_{12}$ with isocyanides

(a) t-Butyl isocyanide, $CNBu^t$

i) A mixture of ruthenium carbonyl (706 mg, 1.10 mmol) and *t*-butyl isocyanide (100 mg, 1.20 mmol) was heated at reflux point in cyclohexane (110 ml) for 2 h. Evaporation of solvent and chromatography (Florisil) afforded two fractions. A yellow band was eluted with light petroleum. Crystallisation (light petroleum) then afforded orange *crystals* of $Ru_3(CO)_{12}$ (114 mg, 16%). The second fraction, an orange-red band, was eluted with light petroleum. Crystallisation (light petroleum) then afforded red *crystals* of $Ru_3(CO)_{11}(CNBu^t)$ (1) (576 mg, 82%), m.p. 114-116° [Found: C - 27.6, H - 1.3, N - 1.9%, *M* (mass spectrometry) - 696; $C_{16}H_9NO_{11}Ru_3$ requires C - 27.7, H - 1.3, N - 2.0%, *M* - 696]. Infra-red (C_6H_{12}): ν(CN) = 2170w; ν(CO) = 2093w, 2047s, 2040s, 2016m, 1998m and 1995m cm^{-1}. ^1H n.m.r. δ($CDCl_3$) = 1.53s, CMe_3. ^{13}C n.m.r. δ($CDCl_3$) = 201.1s, CO, 59.0s, CMe_3, 30.1s, CMe_3. Mass spectrum (most intense ion of cluster): *m/e* 696m, 667vw, 640m, 609m, 584s, 556s, 528s, 500s, 470s, 444s, 416s, 386s, 357s, 329s, 305s.

ii) A suspension of ruthenium carbonyl (500 mg, 0.78 mmol) and *t*-butyl isocyanide (130 mg, 1.56 mmol) in petroleum spirit (80 mmol) was heated at reflux point for 30 min. The solvent was removed, and the residue was chromatographed (Florisil). An orange-red band was eluted with petroleum spirit. Crystallisation (light petroleum) then afforded red *crystals* of $Ru_3(CO)_{11}(CNBu^t)$ (1) (80 mg, 15%). A second fraction, a red-orange band, was eluted with petroleum spirit. Crystallisation from light petroleum gave deep red *crystals* of pure $Ru_3(CO)_{10}(CNBu^t)_2$ (2) (410 mg, 70%), m.p. 90-91° [Found: C - 31.5, H - 2.4, N - 3.7%, *M* (mass spectrometry) - 751; $C_{20}H_{18}N_2O_{10}Ru_3$ requires C - 32.0, H - 2.4, N - 3.7%, *M* - 751]. Infra-red (C_6H_{12}): ν(CN) = 2155w; ν(CO) = 2065w, 2020s, 2007m,

1996w, 1990m and 1986 cm^{-1}. ^{1}H n.m.r. $\delta(CDCl_3)$ = 1.54s, CMe_3. ^{13}C n.m.r. $\delta(CDCl_3)$ = 204.0s, CO, 144.1s, C≡N, 58.3s, CMe_3, 30.2s, CMe_3. Mass spectrum (most intense ion of cluster): *m/e* 751m, 723vw, 694m, 666m, 640s, 611s, 582s, 556s, 526s, 498s, 467s, 441s, 413s, 386s, 357s, 330s, 305s.

iii) A mixture of $Ru_3(CO)_{10}(CNBu^t)_2$ (48 mg, 0.06 mmol) and *t*-butyl isocyanide (5 mg, 0.06 mmol) was warmed in cyclohexane (30 ml) for 10 min. The tri-substituted complex $Ru_3(CO)_9(CNBu^t)_3$ (3) was identified spectroscopically. Infra-red (C_6H_{12}): ν(CN) = 2189m; ν(CO) = 2040m, 1998s and 1971s cm^{-1}. ^{1}H n.m.r. $\delta(C_6D_6)$ = 1.04s, CMe_3. ^{13}C n.m.r. $\delta(C_6D_6)$ = 208.0s, CO, 57.8s, CMe_3, 30.0s, CMe_3.

(b) Cyclohexyl isocyanide, CNCy

A mixture of ruthenium carbonyl (650 mg, 1.02 mmol) and cyclohexyl isocyanide (130 mg, 1.19 mmol) was heated in tetrahydrofuran (100 ml) at 70°C for 135 min. Evaporation of the solvent and column chromatography on Florisil afforded four fractions. An orange band was eluted with light petroleum. Crystallisation (light petroleum) afforded orange *crystals* of $Ru_3(CO)_{12}$ (320 mg, 49%) identified by infra-red spectroscopy. A second fraction, an orange band, was eluted with light petroleum. Crystallisation (light petroleum) afforded orange *crystals* of $Ru_3(CO)_{11}(CNCy)$ (4) (161 mg, 22%), m.p. 139-141° [Found: C - 30.0, H - 1.5, N - 1.9%, *M* (mass spectrometry) - 722; $C_{18}H_{11}NO_{11}Ru_3$ requires C - 30.0, H - 1.5, N - 1.9%, *M* - 722]. Infra-red (C_6H_{12}) ν(CN) = 2155w; ν(CO) = 2092w, 2071vw, 2062w, 2049s, 2041vs, 2019m, 1999m and 1992 cm^{-1}. ^{1}H n.m.r. $\delta[(CD_3)_2CO]$ = 1.14m, Cy. Mass spectrum (most intense ion of cluster): *m/e* 722s, 700vw, 686m, 666w, 641s, 613s, 582s, 555s, 529s, 501s, 471s, 442s, 417s, 389s, 361s, 329s, 305s. A red fraction, in very low yield, was eluted with light petroleum. The infra-red in cyclohexane: ν(CN) = 2165m; ν(CO) = 2071m, 2046m, 2037sh, 2023vs, 1994s, 1984s and 1975s cm^{-1}. The fourth

fraction eluted with diethyl ether afforded pink translucent *crystals* (14 mg), m.p. 80-83° (Found: C - 42.6, H - 5.1, N - 3.4%). Infra-red (C_6H_{12}): ν(CN) = 2167w; ν(CO) = 2073m, 2060w, 2048s, 2040s, 2026vs, 1995s, 1987m and 1968m cm^{-1}. ^1H n.m.r. δ[$(CD_3)_2CO$] = 1.14m, Cy. The latter two products were not further identified.

(c) 4-Methoxyphenyl isocyanide, CNC_6H_4OMe-p

i) A mixture of ruthenium carbonyl (200 mg, 0.31 mmol) and *p*-methoxyphenyl isocyanide (60 mg, 0.45 mmol) in thf (100 ml) was vigorously stirred at 65° for 3 h. Evaporation of the solvent and chromatography (Florisil) afforded three fractions. A yellow-orange band was eluted with light petroleum. Crystallisation (light petroleum) afforded orange *crystals* of $Ru_3(CO)_{12}$ (62 mg, 31%) identified by infra-red spectroscopy. This was followed by a yellow band and crystallisation (light petroleum) afforded a yellow *powder* of $Ru_3(CO)_{11}(CNC_6H_4OMe\text{-}p)$ (5) (45 mg, 23%). m.p. 147-148° (Found: C - 30.8, H - 0.8, N - 1.9; $C_{19}H_7NO_{12}Ru_3$ requires C - 30.7, H - 0.9, N - 1.9%). Infra-red (C_6H_{12}): ν(CN) = 2155w; ν(CO) = 2092w, 2071vw, 2062w, 2049s, 2041vs, 2019m, 1999m and 1992 cm^{-1}. ^1H n.m.r. δ($CDCl_3$) = 7.56, 7.38, 7.10 and 6.82m (4), C_6H_4; 5.83s (3), OMe. A third light red fraction was eluted with light petroleum/diethyl ether (1:1). Crystallisation from light petroleum/diethyl ether (the complex is both heat and air sensitive, decomposing above 50° to an insoluble black residue) afforded a light red *powder* of $Ru_3(CO)_{10}(CNC_6H_4OMe\text{-}p)_2$ (6) (32 mg, 16%) [Found: C - 37.0, H - 2.3, N - 2.8%, *M* (acetone) - 889; $C_{26}H_{14}N_2O_{12}Ru_3$ requires C - 36.8, H - 1.7, N - 3.3%, *M* - 851]. Infra-red (C_6H_{12}): ν(CN) = 2154m; ν(CO) = 2093w, 2066m, 2048s, 2040s, 2030vs, 2022s, 1997s and 1990s cm^{-1}.

ii) A mixture of $Ru_3(CO)_{12}$ (526 mg, 0.82 mmol) and CNC_6H_4OMe-*p* (379 mg, 2.85 mmol) in thf (90 ml) was heated at reflux point, with vigorous stirring, for 3 h. Evaporation of the solvent and chromatography (Florisil) afforded three fractions. A yellow fraction, eluted with light petroleum, was crystallised (light petroleum) affording yellow ***crystals*** of $Ru_3(CO)_{11}(CNC_6H_4OMe\text{-}p)$ (98 mg, 16%) identified by infra-red spectroscopy. A red fraction, eluted with diethyl ether, was crystallised (light petroleum/ diethyl ether) affording a light red ***powder*** of $Ru_3(CO)_{10}(CNC_6H_4OMe\text{-}p)_2$ (361 mg, 52%) identified by infra-red spectroscopy. A third brown fraction was eluted with methanol. Collected brown product (117 mg), m.p. 121°. Infra-red (CH_2Cl_2): ν(CO) = 2054m, 2031s and 1969s(br) cm^{-1}. This product is believed to be the decomposition product of the disubstituted complex.

(d) 4-Toluenesulphonylmethylisocyanide (tosmic), $CNCH_2SO_2C_6H_4Me$-p

i) A mixture of ruthenium carbonyl (160 mg, 0.25 mmol) and tosmic (49 mg, 0.25 mmol) was heated at reflux point in benzene (40 ml) for 12 h. Chromatography (Florisil) afforded two fractions. An orange band was eluted with light petroleum and crystallisation (light petroleum) yielded orange ***crystals*** of $Ru_3(CO)_{12}$ (85 mg, 53%). The second band, purple-brown in colour, was eluted with methanol. Crystallisation acetone/light petroleum afforded purple-brown ***crystals*** of $Ru_3(CO)_9(CNCH_2SO_2C_6H_4Me\text{-}p)_3$ (7) (80 mg, 28%) (Found: C - 36.9, H - 2.9, N - 3.8; $C_{36}H_{27}N_3O_{15}Ru_3S_3$ requires C - 37.9, H - 2.4, N - 3.7%). Infra-red (Nujol): ν(CN) = 2168m; ν(CO) = 1980s cm^{-1}.

ii) A mixture of ruthenium carbonyl (160 mg, 0.25 mmol) and tosmic (147 mg, 0.75 mmol) was heated at reflux point in benzene (40 ml) for 12 h. The solution was allowed to cool, and the purple-

brown crystals that deposited were recrystallised (acetone/light petroleum) to afford $Ru_3(CO)_9(CNCH_2SO_2C_6H_4Me\text{-}p)_3$ (7) (175 mg, 61%); identical with the product obtained above.

Reactions of $Ru_3(CO)_{11}(CNBu^t)$

(a) With CO

Carbon monoxide was passed *via* a glass frit into a solution of $Ru_3(CO)_{11}(CNBu^t)$ (100 mg, 0.14 mmol) in cyclohexane (20 ml) and heated at reflux point for 75 min. After cooling, solvent was removed, and the residue chromatographed (Florisil). Light petroleum eluted

i) $Ru_3(CO)_{12}$ (10 mg, 11%), identified by its infra-red spectrum;

ii) recovered $Ru_3(CO)_{11}(CNBu^t)$ (60 mg, 60%); and

iii) $Ru_3(CO)_{10}(CNBu^t)_2$ (2) (15 mg, 14%), also identified by its infra-red spectrum.

(b) With PPh_3

A mixture of triphenylphosphine (70 mg, 0.27 mmol) and $Ru_3(CO)_{11}(CNBu^t)$ (186 mg, 0.27 mmol) dissolved in $CDCl_3$ was heated, the course of the reaction being followed by ^1H and ^{13}C n.m.r. After 8 h at *ca.* 35°, separation by preparative t.l.c. afforded

i) $Ru_3(CO)_{12}$ (5 mg, 3%);

ii) recovered $Ru_3(CO)_{11}(CNBu^t)$ (1) (60 mg, 32%);

iii) $Ru_3(CO)_{11}(PPh_3)$ (10 mg, 6%)

(all three compounds being identified by their infra-red spectra)

iv) $Ru_3(CO)_{10}(CNBu^t)(PPh_3)$ (8), as a burnt-orange *powder*, (75 mg, 45%) (Found: C - 43.6, H - 2.9, N - 1.4; $C_{33}H_{24}NO_{10}PRu_3$ requires C - 42.7, H - 2.6, N - 1.5%). Infra-red (C_6H_{12}): ν(CN) = 2162m; ν(CO) = 2069m, 2026vs, 2003s, 1990s(br), 1977(sh) cm^{-1}. ^1H n.m.r.: $\delta(CDCl_3)$ = 1.48s (9), Bu^t; 7.39m (15), PPh_3.

In another experiment, a reaction between $Ru_3(CO)_{11}(CNBu^t)$ (100 mg, 0.14 mmol) and excess PPh_3 (150 mg, 0.57 mmol) in cyclohexane (20 ml) at reflux point gave purple $Ru_3(CO)_9(PPh_3)_3$ (140 mg, 75%), identified by comparison with an authentic sample.

(c) With $P(C_6H_4Me\text{-}p)_3$

A mixture of tri-*p*-tolylphosphine (110 mg, 0.36 mmol) and $Ru_3(CO)_{11}(CNBu^t)$ (250 mg, 0.36 mmol) was heated at reflux point in light petroleum (60 ml) for 30 min. Chromatography on Florisil gave

i) $Ru_3(CO)_{12}$ (15 mg, 7%);

ii) recovered $Ru_3(CO)_{11}(CNBu^t)$ (110 mg, 44%); and

iii) $Ru_3(CO)_{11}[P(C_6H_4Me\text{-}p)_3]$ (40 mg, 22%). Infra-red (C_6H_{12}): ν(CO) = 2093w, 2043s, 2029(sh), 2013s, 1987(sh) and 1974w cm^{-1}; ^1H n.m.r.: δ ($CDCl_3$) = 2.39s (9), Me; 7.32m (12), C_6H_4.

A second reaction was carried on for 2 h, and similarly gave

i) recovered $Ru_3(CO)_{11}(CNBu^t)$ (80 mg, 35%) and

ii) $Ru_3(CO)_{10}(CNBu^t)[P(C_6H_4Me\text{-}p)_3]$ (9) as an orange-red powder (120 mg, 51%) (Found: C - 42.9, H - 3.3, N - 1.7%, M^+ - 972; $C_{36}H_{30}NO_{10}PRu_3$ requires C - 44.5, H - 3.1, N - 1.4%, M - 972). Infra-red (C_6H_{12}): ν(CN) = 2164w; ν(CO) = 2068m, 2027vs, 2002vs, 1976(sh) cm^{-1}; ^1H n.m.r.: δ ($CDCl_3$) = 1.49s (9), Bu^t; 2.36s (9), C_6H_4Me; 7.26m (12), C_6H_4; ^{13}C n.m.r.: δ ($CDCl_3$) = 21.3s, C_6H_4Me; 30.0s, CMe_3; 128.7-140.3m, C_6H_4; 205.5s, CO. A third, minor purple product, was not fully characterised [Infra-red (C_6H_{12}): ν(CN) = 2148w; ν(CO) = 2041w, 1997ms, 1988vs, 1981sh cm^{-1}] but may have been $Ru_3(CO)_9(CNBu^t)[P(C_6H_4Me\text{-}p)_3]_2$.

The reaction of $Ru_3(CO)_{11}(CNBu^t)$ (100 mg, 0.14 mmol) with three equivalents of the tertiary phosphine, when heated at reflux point in cyclohexane (50 ml) for 30 min. gave purple *crystals* of $Ru_3(CO)_9[P(C_6H_4Me\text{-}p)_3]_3$ (170 mg, 83%), identified by comparison with an authentic sample.

(d) With PCy_3

A mixture of tricyclohexylphosphine (80 mg, 0.28 mmol) and $Ru_3(CO)_{11}(CNBu^t)$ (200 mg, 0.29 mmol) was heated at 45° in benzene (55 ml) for 3 h. Chromatography (alumina) gave

i) a yellow, highly air-sensitive product (22 mg) which has not yet been identified. [Infra-red (C_6H_{12}): ν(CN) = 2168w; ν(CO) = 2097w, 2065s, 2050s, 2043s, 2034s, 2011s, 2001m, 1993m, 1979w cm^{-1}];

ii) $Ru_3(CO)_{10}(CNBu^t)(PCy_3)$ (10) as a red *powder* (81 mg, 30%), m.p. 210°(dec.) [Found: *M*(acetone) - 711; calculated *M* - 745]; (Found C - 42.60, H - 5.07, N - 1.37%; $C_{33}H_{42}O_{10}NPRu_3$ requires C - 41.86, H - 4.47, N - 1.48%); with infra-red (C_6H_{12}): ν(CN) = 2168m; ν(CO) = 2066m, 2034(sh), 2022vs, 2008s, 1996s, 1990s, 1971s, 1949s, 1922m, 1904m cm^{-1}; ^1H n.m.r.: δ [$(CD_3)_2CO$] = 1.05m (33), Cy, 1.65s (9), Bu^t. All attempts to recrystallise this material led to the formation of an insoluble yellow powder, so far unidentified [Infra-red (Nujol): ν(CN) = 2172m; ν(CO) = 2062s, 2020vs, 1974m(br) cm^{-1}].

iii) A third fraction, eluted with 1/1 light petroleum-diethyl ether, contained $Ru_3(CO)_{11}(PCy_3)$ (19 mg, 7%), identified by comparison with an authentic sample and by analysis (Found: C - 38.7, H - 5.6; $C_{29}H_{33}O_{11}PRu_3$ requires C - 39.1, H - 5.8%).

(e) With $AsPh_3$

After heating at reflux point in cyclohexane (40 ml) for 90 min., a mixture of $Ru_3(CO)_{11}(CNBu^t)$ (112 mg, 0.16 mmol) and triphenylarsine (50 mg, 0.16 mmol), showed no further change in the infra-red spectrum. Chromatography (Florisil) gave three minor fractions (total 30 mg), followed by

i) $Ru_3(CO)_{10}(AsPh_3)_2$ (48 mg, 25%), obtained as a toluene solvate, m.p. 170-172°, from heptane-toluene (Found: C - 49.6, H - 3.2; $C_{46}H_{30}As_2O_{10}Ru_3.C_7H_8$ requires C - 49.4, H - 2.95%). Infra-red (CH_2Cl_2): ν(CO) = 2099w, 2073w, 2046w, 2025s, 2014s, 1995s, 1979(sh), 1954(sh) cm^{-1}; ^1H n.m.r.: δ ($CDCl_3$) = 2.02s (3), Ph*Me*, 7.43m (35), $AsPh_3$ + *Ph*Me.

ii) $Ru_3(CO)_{10}(CNBu^t)(AsPh_3).C_6H_{12}$ (11), as a purple solid (14 mg, 9%), m.p. 113-115°, from cyclohexane-toluene (Found: C - 43.9, H - 4.4, N - 1.7; $C_{33}H_{24}AsNO_{10}Ru_3.C_6H_{12}$ requires C - 44.3, H - 3.4, N - 1.3%). Infra-red ($CHCl_3$): ν(CN) = 2180m; ν(CO) = 2098w, 2074s, 2057s, 2040vs, 2000vs, 1995(sh), 1981(sh), 1923w cm^{-1}; ^1H n.m.r.: δ ($CDCl_3$) = 1.43m (12), C_6H_{12}, 1.65s (9), Bu^t, 7.43m (15), $AsPh_3$.

(f) With $SbPh_3$

A mixture of $Ru_3(CO)_{11}(CNBu^t)$ (89 mg, 0.13 mmol) and triphenylstibine (50 mg, 0.14 mmol) was heated at reflux point in cyclohexane (35 ml) for 7 h. Chromatography (Florisil) afforded

i) recovered $Ru_3(CO)_{11}(CNBu^t)$ (17 mg, 19%);

ii) yellow-orange $Ru_3(CO)_{10}(CNBu^t)(SbPh_3)$ (12), recrystallised from hexane (37 mg, 35%), m.p. 195-197° (Found: C - 37.5, H - 2.7, N - 1.2; $C_{33}H_{24}NO_{10}Ru_3Sb$ requires C - 38.3, H - 2.4, N - 1.4%). Infra-red (C_6H_{12}): ν(CN) = 2188w; ν(CO) = 2099w, 2064m, 2053vs, 2002s(br), 1976(sh) cm^{-1}; ^1H n.m.r.: δ($CDCl_3$) = 1.50s (9), Bu^t, 7.32m (15), $SbPh_3$,

iii) an unidentified green fraction;

iv) a small amount (17 mg) of a brown compound, eluted with methanol, which may be $Ru_3(CO)_9(CNBu^t)(SbPh_3)_2$ (13). Infra-red ($CHCl_3$): ν(CN) = 2156w; ν(CO) = 2099w, 2061(sh), 2036s, 1976(sh) cm^{-1}; ^1H n.m.r.: δ ($CDCl_3$) = 1.50s (9), Bu^t, 7.32m (30), $SbPh_3$.

Reaction between $Ru_3(CO)_{11}(PCy_3)$ and $CNBu^t$

A mixture of *t*-butyl isocyanide (100 mg, 1.2 mmol) and $Ru_3(CO)_{11}(PCy_3)$ (526 mg, 0.59 mmol) was heated at reflux point in tetrahydrofuran (100 ml) for 2 h, the reaction being followed by t.l.c. Removal of solvent, and chromatography (Florisil) of a diethyl ether extract afforded $Ru_3(CO)_{10}(CNBu^t)(PCy_3)$ (10) as the only identifiable product, being eluted with 95/5 light petroleum-diethyl ether (164 mg, 29%). This compound was identical with the product obtained from reaction *(d)* above. Unidentified carbonyl-containing compounds were eluted with light petroleum (red, 66 mg), light petroleum-ether mixtures [after (10), purple, 28 mg], and methanol (yellow-brown, 61 mg). Much decomposition of the material adsorbed on the column was evident.

Pyrolysis of $Ru_3(CO)_{11}(CNBu^t)$

A solution of $Ru_3(CO)_{11}(CNBu^t)$ (1) (500 mg, 0.72 mmol) in acetone (30 ml), in a 250 ml round-bottomed flask, was evaporated, leaving a film of complex (1) on the glass surface. The flask, under a nitrogen pressure of *ca.* 0.5 atmospheres, was heated in an oil bath, at 120°, for 16 h. The reaction product was extracted with acetone (4 x 20 ml), leaving a grey metallic residue of *ca.* 180 mg. The extracts were combined, concentrated and chromatographed on a preparative t.l.c. plate (Kieselgel G adsorbent; light petroleum developer). Five bands were obtained. Band one, yellow in colour, with R_f = 0.8, afforded orange *crystals* of $Ru_3(CO)_{12}$ (10 mg, 2%). Band two, orange in colour,

with R_f = 0.7, afforded red *crystals* of $Ru_3(CO)_{11}(CNBu^t)$ (1) (30 mg, 6%). The third band, orange in colour, with R_f = 0.6, afforded red *crystals* of $Ru_3(CO)_{10}(CNBu^t)_2$ (2) (10 mg, 2%). The fourth band was purple in colour with R_f = 0.3. The product was crystallised from light petroleum as purple *crystals* (20 mg, 3%) and identified tentatively as $Ru_5(CO)_{14}(CNBu^t)_2$ (14) [Found: C - 27.6, H - 1.5, N - 2.6%, *M* (mass spectrometry) - 1068; $C_{24}H_{10}N_2O_{14}Ru_5$ requires C - 27.1, H - 1.7, N - 2.6%, *M* - 1068]. Infra-red (C_6H_{12}): ν(CN) = 2158vw; ν(CO) = 2073w, 2044s, 2028m, 1999s, and 1995sh cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 1.38s, CMe_3. ^{13}C n.m.r. δ ($CDCl_3$) = 223.0s, CO, 30.3s and 29.4s, CMe_3. The fifth band, purple in colour, with R_f = 0.2 was a minor fraction, which was tentatively identified as $Ru_6(CO)_{14}(CNBu^t)_2$ (15) on the basis of mass spectrometric evidence [Found: *M* (mass spectrometry) - 1168, $C_{24}H_{18}N_2O_{14}Ru_6$ requires *M* - 1168]. Infra-red (C_6H_{12}): ν(CN) = 2149w; ν(CO) = 2058w, 2032s, 2022s, 1996vs, 1977w, and 1967sh cm^{-1}.

Radical Initiated Substitutions

Tables 8-11 list yields, melting points, analytical and spectroscopic data for the products. Postulated structures are indicated in Figure 7 (*vide supra*). Reaction details are given following the Tables.

Preparation of sodium diphenylketyl solution

Benzophenone (19 mg, 0.5 mmol) was dissolved in thf (20 ml) in a Schlenk tube and finely cut sodium metal was added. The mixture was stirred for two hours. The resulting deep purple solution was assumed to be *ca.* 0.025 mmol/ml in $[Ph_2CO]^{\cdot-}$.

LIGANDS USED (TABLES 8-11)

a	PMe_3	
b	PMe_2Ph	
c	PPh_3	
d	$P(C_6H_4Me\text{-}p)_3$	
e	$P(C_6H_4Me\text{-}o)_3$	
f	PCy_3	
g	$P(CH_2CH_2CN)_3$	
h	$P(OMe)_3$	
i	$PPh(OMe)_2$	
j	$P(OC_6H_4Me\text{-}p)_3$	
k	$P(OCH_2)_3CEt$	
l	$AsPh_3$	
m	$SbPh_3$	
n	$CNBu^t$	
o	CNCy	
p	R-(+)-CNCHMePh	
q	$CH_2(PPh_2)_2$	(dppm)
r	$CH_2(AsPh_2)_2$	(dpam)
s	$Ph_2AsCH_2CH_2AsPh_2$	(dpae)
t	$CNCH_2SO_2C_6H_4Me\text{-}p$	
u	$Ph_2PCH_2CH_2PPh_2$	(dppe)
v	$P(OPh)_3$	

TABLE 8 Preparations and analytical data for complexes $Ru_3(CO)_{12-n}(L)_n$

Complex	L	Colour	n	Yield (%)[a]	m.pt. (°C)	Found (calculated) C	H	Other	M	Notes
16a	PMe_3	red	1	75 (15)	dec 132	24.64	2.21		689	
						(24.46)	(1.32)		(689)	
17a	PMe_3	red	2	60 (60)	192-193	26.12	2.17		737	
						(26.13)	(2.46)		(737)	
18a	PMe_3	red	3	76 (90)	168-171	27.34	3.45		785	
						(27.59)	(3.47)		(785)	
19a	PMe_3	deep red	4	-(0.3)	-	29.38	3.83		833	
						(28.89)	(4.36)		(833)	
16b	PMe_2Ph	red-orange	1	76 (3)	104-106	30.26	1.23			
						(30.46)	(1.48)			
16c	PPh_3	orange	1	81 (37)	131-133	40.86	1.80			
						(39.87)	(1.73)			
17c	PPh_3	deep red	2	96 (76)	199-201	50.11	2.53			
						(49.86)	(2.73)			
18c	PPh_3	purple-red	3	85 (98)	178-181	57.49	3.71			
						(56.38)	(3.38)			

16d	$P(C_6H_4Me\text{-}p)_3$	deep orange	1	79	185-186	42.47	2.13			
						(41.97)	(2.31)			
18d	$P(C_6H_4Me\text{-}p)_3$	purple	3	87 (88)	184-185					*b*
16e	$P(C_6H_4Me\text{-}o)_3$	red	1	37	>300	42.29	2.33			
						(41.97)	(2.31)			
16f	PCy_3	red	1	89 (42)	177-179	38.84	3.61			
						(39.06)	(3.73)			
17f	PCy_3	yellow	2	55 (80)	211-213	47.21	5.51			
						(48.24)	(5.81)			
17g	$P(CH_2CH_2CN)_3$	orange	2	91	157-158	35.61	2.49	(N) 7.96		
						(34.68)	(2.49)	(8.67)		
18g	$P(CH_2CH_2CN)_3$	orange-red	3	72	dec 180	38.07	3.34	(N) 10.96		
						(38.10)	(3.19)	(11.11)		
16h	$P(OMe)_3$	orange	1	81 (43)	61-63	23.04	0.74		737	
						(22.87)	(1.23)		(737)	
17h	$P(OMe)_3$	red	2	81 (35)	72-73	23.02	1.78		833	
						(23.12)	(2.18)		(833)	
18h	$P(OMe)_3$	red	3	70 (15)	111-114	22.87	2.82		929	
						(23.31)	(2.93)		(929)	
16i	$PPh(OMe)_2$	orange-red	1	74	93.5-95	35.41	2.46			*c*
						(34.93)	(1.99)			

17i	$PPh(OMe)_2$	red	2	63 (14)	120-122	38.13	3.21		c
						(38.37)	(2.81)		
18i	$PPh(OMe)_2$	red	3	44 (7)	106-108	37.07	2.93		
						(37.19)	(3.12)		
19i	$PPh(OMe)_2$	purple	4	91 (57)	165-168				b
16j	$P(OC_6H_4Me\text{-}p)_3$	red	1	64		39.31	1.92	(P) 3.32	
						(39.88)	(2.20)	(3.21)	
17j	$P(OC_6H_4Me\text{-}p)_3$	red	2	26		47.85	3.41	(P) 4.60	
						(48.49)	(3.29)	(4.81)	
18j	$P(OC_6H_4Me\text{-}p)_3$	red	3	66	153	54.33	4.18	(P) 5.73	
						(53.32)	(3.90)	(5.81)	
16k	$P(OCH_2)_3CEt$	orange	1	50	135-137	26.78	1.24		
						(26.40)	(1.24)		
17k	$P(OCH_2)_3CEt$	tan	2	57	197-199	34.26	2.65		
						(34.11)	(2.86)		
18k	$P(OCH_2)_3CEt$	yellow-brown	3	92	>200	31.89	3.45		c
						(31.10)	(3.19)		
16l	$AsPh_3$	orange-brown	1	66		42.88	2.15		
						(42.23)	(2.12)		
17l	$AsPh_3$	deep red	2	48 (1.5)					b

(3)

16m	$SbPh_3$	orange	1	44		92-93	36.49	1.31	(Sb) 10.88		
							(36.12)	(1.57)	(12.62)		
16n	$CNBu^t$	red	1	78	(86)	114-116	27.46	1.17	(N) 1.36	696	
							(27.55)	(1.31)	(2.02)	(696)	
17n	$CNBu^t$	red	2	61	(41)	90-91				751	*b*
										(751)	
16o	CNCy	red	1	89	(80)	122-125	29.83	1.11	(N) 1.36	722	
							(30.01)	(1.54)	(1.94)	(722)	
16p	R-(+)-CNCHMePh	deep red	1	33		61	32.57	0.77	(N) 1.96		
							(32.37)	(1.22)	(1.96)		
17†	$CNCH_2SO_2C_6H_4Me$-*p*	red	2	87		dec 132	33.70	2.46	(N) 4.73	975	
							(34.84)	(1.86)	(2.88)	(975)	
20q	dppm	red	1	90	(28)	174-176	43.76	2.05			
							(43.44)	(2.29)	-		
21q	dppm	dark red-brown	2	26	(12)	178-180	53.46	2.94	(N) 10.00		
							(53.75)	(3.42)	(9.56)		
22q	dppm	orange-red	0.5	98		169-170	39.58	2.97			
							(40.54)	(3.01)			
20r	dpam	red	1	53	(75)	172-173	44.23	2.67			*d*
							(43.95)	(2.63)			
21r	dpam	red	2	8	(21)	>300	47.78	3.65			
							(47.33)	(3.01)			
20s	dpae	red	1	78	(60)	dec 172	39.76	2.96			
							(40.43)	(2.26)			

[a] From radical-ion initiated reactions; values in parentheses from thermally induced reactions. In neither case have yields been optimised.

[b] Identified by comparison with literature values.

[c] C_6H_6 solvate.

[d] PhMe solvate.

TABLE 9 Preparations and analytical data for mixed ligand complexes

Complex	Ligand	Colour	Yield (%)	m.pt (°C)	Found (calculated) C	H	Other	M	Notes
(a) $Ru_3(CO)_{12-n}L_n$									
26ah	PMe_3	red	87	102-104	26.95	2.50		785	*a*
	$P(OMe)_3$				(26.06)	(2.91)		(785)	
26bn	PMe_2Ph	red	42	128-132	33.82	2.37	(N) 1.59		
	$CNBu^t$				(34.33)	(2.51)	(1.74)		
26dl	$P(C_6H_4Me\text{-}p)_3$	deep red	39	154-156	50.33	3.17			
	$AsPh_3$				(49.30)	(3.04)			
26dn	$P(C_6H_4Me\text{-}p)_3$	red	88	dec 151	44.51	3.35	(N) 1.04		
	$CNBu^t$				(44.54)	(3.11)	(1.44)		
26kl	$P(OCH_2)_3CEt$	red	9	-	37.33	2.59			
	$AsPh_3$				(37.34)	(2.39)			
26no	$CNBu^t$	deep red	85	dec 130	34.03	3.07	(N) 3.81		
	CNCy				(34.07)	(2.60)	(3.61)		
27ach	PMe_3	deep red	41	>300	38.70	3.66			
	PPh_3				(38.95)	(3.26)			
	$P(OMe)_3$								
30au	PMe_3	deep red	81	dec 252	47.41	3.82			
	dppe				(47.70)	(3.54)			
30hr	$P(OMe)_3$	bright red	51	dec 223	41.40	2.99			
	dpam				(42.00)	(3.03)			
27kln	$P(OCH_2)_3CEt$	deep red	22	-	39.86	2.86	(N) 1.94	(P) 3.66	
	$AsPh_3$				(39.72)	(3.07)	(1.22)	(2.70)	
	$CNBu^t$								
30kn	$P(OCH_2)_3CEt$	deep red	37	-	32.15	3.26	(N) 0.99		
	$P(OCH_2)_3CEt$				(32.44)	(3.24)	(1.45)		
	$CNBu^t$								
(b) $H_4Ru_4(CO)_{12-n}(L)_n$ (by B.K. Nicholson)									
28bk	PMe_2Ph	golden yellow	66	136-137	40.53	2.96			
	$P(OC_6H_4Me\text{-}p)_3$				(39.74)	(3.08)			
28hi	$P(OMe)_3$	red	60	oil					*b*
	$PPh(OMe)_2$								
29bhi	PMe_2Ph	red	75	oil	30.78	3.23			
	$P(OMe)_3$				(31.63)	(3.02)			
	$PPh(OMe)_2$								
29bjk	PMe_2Ph	bright yellow	64	153-155	40.25	3.61	(P) 5.98		
	$P(OCH_2)_3CEt$				(40.25)	(3.61)	(7.08)		
	$P(OC_6H_4Me\text{-}p)_3$								

[a] Et_2O solvate.

[b] Identified from IR and NMR spectra only.

TABLE 10 IR and NMR spectroscopic data for complexes $Ru_3(CO)_{12-n}(L)_n$

L	Complex	ν(CO), cm^{-1} (solvent)		δ		
(a) n = 1						
PMe_3	16a	2086w, 2066(sh), 2056m, 2040s, 2023s, 2011vs, 1990(sh), 1978(sh), 1943m	(C_6H_{12})	1.60d (J 11)		[$(CD_3)_2CO$]
PMe_2Ph	16b	2096m, 2044s, 2028s, 2016s, 2000w, 1987w	(C_6H_{12})	1.97d (J 10) 7.52m	Me Ph	($CDCl_3$)
PPh_3	16c	2097m, 2047s, 2031(sh), 2026(sh), 2017s, 2001w, 1986w	(C_6H_{12})	7.48m		($CDCl_3$)
$P(C_6H_4Me\text{-}p)_3$	16d	2098m, 2063m, 2048s, 2032ms, 2017vs, 2001m, 1989m, 1977sh, 1955m	(C_6H_{12})	2.35s 7.28m	Me C_6H_4	($CDCl_3$)
$P(C_6H_4Me\text{-}o)_3$	16e	2099m, 2045s, 2030s, 2016vs, 2000m, 1989m, 1955(sh)	(CH_2Cl_2)	2.45s 7.30m	Me C_6H_4	($CDCl_3$)
PCy_3	16f	2099m, 2082m, 2047m, 2026s, 2016vs, 1996s, 1985s, 1970m, 1945m	(C_6H_{12})	0.53, 1.42, 1.58, 2.23m(br)		($CDCl_3$)
$P(OMe)_3$	16h	2104m, 2064w, 2051vs, 2038s, 2019vs, 2001s, 1997s, 1984m	(C_6H_{12})	3.68d (J 12)		($CDCl_3$)
$PPh(OMe)_2$	16i	2103m, 2051s, 2035s, 2020s, 2002ms, 1997ms, 1990(sh), 1978(sh), 1967(sh)	(C_6H_{12})	3.62d (J 12.0) 7.51m	OMe Ph + C_6H_6	($CDCl_3$)
$P(OC_6H_4Me\text{-}p)_3$	16j	2104m, 2088w, 2050s, 2038s, 2020vs, 2003s, 1990m	(C_6H_{12})	2.33s 7.03m	Me C_6H_4	($CDCl_3$)

$P(OCH_2)_3CEt$	16k	2106w, 2051s, 2043m, 2023s, 2002m, 1990w	(C_6H_{12})	0.84, 1.19 Et 4.25d (J 5) OCH_2		($CDCl_3$)
$AsPh_3$	16l	2100w, 2048m, 2038(sh), 2018vs, 2000m, 1990(sh)	(C_6H_{12})	7.45m		($CDCl_3$)
$SbPh_3$	16m	2101m, 2050s, 2032m, 2019vs, 2000w, 1989w, 1976m, 1965m	(C_6H_{12})	7.40m		($CDCl_3$)
$CNBu^t$	16n	2093m, 2047s, 2040s, 2016s, 1998m, 1995m ν(CN) 2170m	(C_6H_{12})	1.53s		($CDCl_3$)
CNCy	16o	2090m, 2048m, 2038vs, 2032s, 2024m, 2011m, 2003m, 1994(sh) ν(CN) 2175m	(C_6H_{12})	1.78m(br) -		$[(CD_3)_2CO]$
CNCHMePh	16p	2095m, 2047s, 2041s, 2022m, 2006m, 2001m ν(CN) 2175w	(C_6H_{12})			
½(dppm)	22q	2094m, 2054(sh), 2046m, 2012(sh), 1998(sh), 1978s, 1969s, 1946(sh), 1912vw	(C_6H_{12})	4.24t (J 12) CH_2 7.36m Ph		($CDCl_3$)
(b) n = 2						
PMe_3	17a	2076m, 2046w, 2019vs, 1998vs, 1976s, 1955m	(C_6H_{12})	1.80d (J 10)		$[(CD_3)_2CO]$
PPh_3	17c	2072w, 2060w, 2047m, 2034(sh), 2024s, 1990s, 1968s, 1950m	(C_6H_{12})	7.50m		($CDCl_3$)
PCy_3	17f	2077s, 2059w, 2045s, 2001s, 1989m, 1979m, 1941w	(C_6H_{12})	0.75, 1.32, 1.50, 1.88m		($CDCl_3$)
$P(CH_2CH_2CN)_3$	17g	2076w, 2056w, 2022m, 2000s, 1988vs, 1950m, 1937m ν(CN) 2162w	(CH_2Cl_2)	1.39(br)		$[(CD_3)_2CO]$
$P(OMe)_3$	17h	2088w, 2050w, 2034s, 2008vs, 1991m, 1980(sh)	(C_6H_{12})	3.66d (J 12)		($CDCl_3$)
$PPh(OMe)_2$	17i	2081w, 2058w, 2005s, 1986s, 1971(sh)	(C_6H_{12})	3.57d (J 11) OMe 7.41m		

$P(OC_6H_4Me\text{-}p)_3$	17j	2088w, 2036m, 2010s, 1993m, 1980(sh)	(C_6H_{12})	2.29s 7.10m	Me C_6H_4	$[(CD_3)_2CO]$
$P(OCH_2)_3CEt$	17k	2092w, 2053(sh), 2038s, 2022(sh), 2010vs, 1988(sh,br)	(CH_2Cl_2)	0.81m, 1.14m 4.20m 7.36s	Et OCH_2 C_6H_6	
$AsPh_3$	17l	2080m, 2050w, 2026s, 1997vs(br), 1980(sh)	(CH_2Cl_2)	7.42m		$(CDCl_3)$
$CNBu^t$	17n	2065m, 2020vs, 2007(sh), 1996m, 1990s, 1986s ν(CN) 2155m	(C_6H_{12})	1.55s		$[(CD_3)_2CO]$
$CNCH_2SO_2C_6H_4Me\text{-}p$	17t	2095w, 2069m, 2022vs, 2005m, 1996m, 1990s, 1982s ν(CN) 2160m	(C_6H_{12})			
dppm	20q	2083m, 2023w, 2013s, 2003s, 1987w, 1966m, 1964(sh), 1961m	(C_6H_{12})	4.29t (J 10.5) 7.35m	CH_2 Ph	$(CDCl_3)$
dpam	20r	2083m, 2067m, 2024m, 2009vs, 1990(sh), 1964m, 1944w	(C_6H_{12})	2.26s 4.11s 7.36m	PhMe CH_2 Ph	$(CDCl_3)$
dpae	20s	2082m, 2066w, 2048m, 2022(sh), 2013vs, 2002vs, 1986s, 1964s, 1950(sh)	(C_6H_{12})	4.32m 7.40m	CH_2 Ph	$(CDCl_3)$
PMe_3 $P(OMe)_3$	26ah	2081m, 2061w, 2047m, 2024s, 2002vs, 1966s, 1958(sh), 1935w	(C_6H_{12})	1.69d (J 12) 2.40q, 1.71t 3.66d (J 12)	PMe_3 (Et_2O) $P(OMe)_3$	$(CDCl_3)$
PMe_2Ph $CNBu^t$	26bn	2098w, 2068w, 2045m, 2029s, 2016s, 2004m, 1986w ν(CN) 2168w	(C_6H_{12})	1.49s 1.86d (J 9) 7.42m	CMe_3 PMe Ph	$(CDCl_3)$
$P(C_6H_4Me\text{-}p)_3$ $AsPh_3$	26dl	2077w, 2062m, 2047w, 2024s, 1998vs, 1989(sh), 1979s, 1957s, 1908m	(C_6H_{12})	2.42s 7.51m	Me Ph + C_6H_4	$(CDCl_3)$

(3)

$P(C_6H_4Me\text{-}p)_3$	26dn	2066m, 2024s, 1996s, 1978m		1.53s	CMe_3	
$CNBu^t$		ν(CN) 2164w		2.38s	Me	
				7.50m	C_6H_4	$[(CD_3)_2CO]$
$P(OCH_2)_3CEt$	26kl	2078w, 2057w, 2038s, 2027m, 2014vs, 1990m		0.83t (J 6)	Me	
$AsPh_3$			(C_6H_{12})	1.33q (J 7)	CH_2Me	
				4.23t (J 2)	OCH_2	
				7.38m	Ph	$(CDCl_3)$
$CNBu^t$	26no	2097w, 2065m, 2022vs, 2001m, 1995m, 1990(sh), 1985w		1.55s,	CMe_3	$(CDCl_3)$
CNCy		ν(CN) 2166w, 2159(sh)	(C_6H_{12})	1.65(br)	Cy	

(c) n = 3

PMe_3	18a	2044w, 2015(sh), 1997(sh), 1975vs, 1943s	(C_6H_{12})	1.80d (J 10)		$[(CD_3)_2CO]$
PPh_3	18c	2044m, 1978(sh), 1967(br)	(C_6H_{12})	7.43m		$(CDCl_3)$
$P(C_6H_4Me\text{-}p)_3$	18d	2039vw, 2017vw, 1977(sh), 1965s		2.36s	Me	
			(C_6H_6)	7.25m	C_6H_4	$(CDCl_3)$
$P(CH_2CH_2CN)_3$	18g	2087m, 2025vs, 1991vs, 1920w ν(CN) 2166m	(CH_2Cl_2)	1.40m(br)		$[(CD_3)_2CO]$
$P(OMe)_3$	18h	2062w, 2032m, 2005vs, 1993vs, 1964(sh)	(C_6H_{12})	3.64d (J 12)		$(CDCl_3)$
$PPh(OMe)_2$	18i	2054w, 2034w, 1999s, 1988vs, 1968m, 1959(sh)		3.60d (J 11)	P(OMe)	$(CDCl_3)$
			(C_6H_{12})	7.48m	Ph	
$P(OC_6H_4Me\text{-}p)_3$	18j	2062m, 2010s, 1998vs, 1976(sh)	(C_6H_{12})	2.27s	Me	$(CDCl_3)$
				7.10m	C_6H_4	
$P(OCH_2)_3CEt$	18k	2058m, 2012s(sh), 1997vs(br), 1975s(sh)	(CH_2Cl_2)	0.80m, 1.13m	Et	
				4.17m	OCH_2	

PMe_3	27ach	2050m, 1980vs, 1957s, 1946(sh)	(C_6H_{12})	1.70d (J 12)	P*Me*	
PPh_3				3.68d (J 11)	PO*Me*	
$P(OMe)_3$				7.50m	Ph	$(CDCl_3)$
PMe_3	30au	2031m, 2009ms, 1995s, 1987s, 1973vs, 1940m	(C_6H_{12})	1.72d (J 12)	PMe	
dppe				2.76s(br)	CH_2CH_2	
				7.46m	Ph	$(CDCl_3)$
$P(OMe)_3$	30hr	2027w, 2012, 2003vs, 1988s, 1967s, 1959(sh),		2.99s	OMe	
dpam		1952(sh)	(C_6H_{12})	5.78s	CH_2	
				7.50m	Ph	$(CDCl_3)$
$P(OCH_2)_3CEt$	27kln	2048m, 1989vs, 1955vs, 1945(sh)	(C_6H_{12})	0.92m, 1.16m	Et	
$AsPh_3$		ν(CN) 2162m		1.99s	Bu^t	
$CNBu^t$				4.22m	OCH_2	
				7.40m	Ph	$(CDCl_3)$
$P(OCH_2)_3CEt$	30kn	2056m, 1992vs, 1960vs, 1955(sh)	(C_6H_{12})	1.05m	Et	
$P(OCH_2)_3CEt$		ν(CN) 2178m		1.92s	Bu^t	
$CNBu^t$				4.19m	OCH_2	$(CDCl_3)$
(d) n = 4						
PMe_3	19a	2072w, 2043w, 2018m, 1990(sh), 1976vs, 1942s, 1897s	(C_6H_{12})	1.82d (J 11) 1.88d (J 11)		$[(CD_3)_2CO]$
$PPh(OMe)_2$	19i	2061w, 2030mw, 2000(sh), 1986vs, 1967vs, 1920m	(C_6H_{12})	3.08d (J 12) 3.56d (J 12)	PO*Me*	
				7.48m	Ph	$(CDCl_3)$
dppm	21q	2056w, 2046w, 2023m, 2012(sh), 1998(sh), 1981vs, 1970s, 1945m	(C_6H_{12})	4.25t (J 11) 7.36m	CH_2 Ph	$(CDCl_3)$
dpam	21r	2054m, 2041w, 2026m, 2011vs, 2006(sh), 1963vs	(C_6H_{12})	4.19s 7.36m	CH_2 Ph	$(CDCl_3)$

TABLE II IR and NMR spectroscopic data for complexes $H_4Ru_4(CO)_{12-n}(L)_n$ *(by B.K. Nicholson)*

L	Complex	ν(CO), cm^{-1} (C_6H_{12} solvent)	δ	
n = 1				
PPh_3	23c	2095m, 2082m, 2068vs, 2059s, 2028vs, 2015m, 2009s, 1969w		
$P(OMe)_3$	23h	2097w, 2069vs, 2060vs, 2031vs, 2018m, 2009m, 1976w		
$CNBu^t$	23n	2104w, 2078s, 2070s, 2042s, 2022s, 2012m, 1998w, 1984w ν(CN) 2178w	-17.97s 1.51s	RuH CMe_3
$P(OPh)_3$	23v	2098m, 2072vs, 2061s, 2036s, 2013s		
$P(OC_6H_4Me\text{-}p)_3$	23j	2098m, 2071s, 2061s, 2036s, 2028w, 2016s, 2000(sh), 1983w	-17.70d (J 7) 2.33s 7.87m	RuH Me C_6H_4
n = 2				
PPh_3	24c	2079m, 2062s, 2052m, 2036m, 2022vs, 2013s, 2003w, 1977w, 1960w		
$P(OMe)_3$	24h			
$CNBu^t$	24n	2092m, 2084w, 2060s, 2034vs, 2020s, 2000s, 1982s ν(CN) 2168m	-17.7s, -18.2s 1.49s	RuH CMe_3
PMe_2Ph	28bj	2082s, 2061vs, 2043w, 2028vs, 2017s, 2002m, 1992w, 1955w	-17.4t (J 7)	RuH
$P(OC_6H_4Me\text{-}p)_3$			1.87d (J 9) 2.30s 7.11s 7.42m	PMe_2 Me C_6H_4 Ph
$P(OMe)_3$ $PPh(OMe)_2$	28hi	2079s, 2058vs, 2032s, 2024vs, 2018(sh), 2000s, 1983w, 1974w, 1966w		
n = 3				
$P(OMe)_3$	25h	2068m, 2036s, 2014m, 1998s, 1985m, 1978s, 1963w		
PMe_2Ph $P(OMe)_3$ $PPh(OMe)_2$	29bhi	2061s, 2031vs, 2010s, 1992s, 1984w, 1971m, 1956w, 1941w	-17.0s(br) 1.78m 3.55d (J 12) 3.57d (J 9) 7.40m	RuH PMe P-OMe P-OMe Ph
PMe_2Ph $P(OCH_2)_3CEt$ $P(OC_6H_4Me\text{-}p)_3$	29bjk	2065s, 2041s, 2009s, 2000m(sh), 1986(br)	-17.3m(br) 0.82m, 1.16m 1.80d (J 10) 2.31s 4.17d (J 5) 7.11m 7.42m	RuH Et PMe_3 Me OCH_2 C_6H_4 Ph

Standard Reaction Procedure

The cluster and the required amount of ligand were dissolved in thf (with warming to ~40°C if necessary for the less soluble clusters) in a side-arm flask. The required amount of initiator solution was added dropwise from a syringe, the extent of reaction being monitored by regular infra-red examination of diluted aliquots. When reaction was complete, thf was pumped off under vacuum and the residue re-crystallised from an appropriate solvent.

Full details for all reactions will not be given, the examples below being typical, and indicative of the simplicity of the method and the high yields usually obtained therefrom.

Reactions of $Ru_3(CO)_{12}$

(a) Dimethylphenylphosphine

The radical ion-initiated reaction between $Ru_3(CO)_{12}$ (250 mg, 0.39 mmol) and PMe_2Ph (55 mg, 0.4 mmol) in thf (8 ml) required 0.1 ml $[Ph_2CO]^{\cdot-}$ solution for complete reaction. Recrystallisation from warm light petroleum gave red-orange (16b) (230 mg, 76%).

(b) Triphenylphosphine

Similarly, $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and PPh_3 (40 mg, 0.15 mmol) in thf (6 ml) afforded orange crystals of (16c) (110 mg, 81%), recrystallised from dichloromethane/light petroleum. Complexes (17c) and (18c) were obtained in 96 and 85% yields as dark-red and purple-red solids, respectively.

(c) Tricyclohexylphosphine

Reactions under the usual conditions between $Ru_3(CO)_{12}$ and PCy_3 in the presence of $Na[Ph_2CO]$, afforded (16f) and (17f) in 89 and 55% yields, respectively, when 1:1 and 1:2 molar proportions were used.

In an attempt to substitute a third CO ligand, a reaction with six-molar excess PCy_3 was carried out. A mixture of $Ru_3(CO)_{12}$ (75 mg, 0.12 mmol) and PCy_3 (200 mg, 0.70 mmol) in thf (25 ml) was treated with $Na[Ph_2CO]$ (*ca.* 1.2 ml). The solution went dark red immediately [the i.r. contained ν(CO) bands of $Ru_3(CO)_{11}(PCy_3)$], then changed to orange-yellow after 10 min. [the i.r. now contained ν(CO) bands of $Ru_3(CO)_{10}(PCy_3)_2$]; after 45 min. at 42° the solution was a cloudy brown. Filtration removed a black solid, and preparative t.l.c. under nitrogen (developing with 3:7 Et_2O/light petroleum) afforded as the only product an off-white powder (26 mg, 11%), dec. >300°, whose analysis is consistent with the formulation $Ru(CO)_2(PCy_3)_3$. Infra-red (Nujol): ν(CO) = 2030vs, 1945vs cm^{-1} (Found: C - 67.36, H - 9.98%; $C_{56}H_{99}O_2P_3Ru$ requires C - 67.74, H - 10.43%).

(d) Triphenylarsine

i) A mixture of $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and $AsPh_3$ (50 mg, 0.16 mmol) in thf (10 ml) was treated with $Na[Ph_2CO]$ (*ca.* 1.1 ml). Recrystallisation from a benzene/light petroleum mixture afforded orange-brown (16m) as a benzene solvate (100 mg, 66%).

ii) Similarly, $Ru_3(CO)_{12}$ (150 mg, 0.24 mmol) and $AsPh_3$ (140 mg, 0.62 mmol) in thf (6 ml) required $Na[Ph_2CO]$ (2.3 ml) for completion of the reaction. Deep red ***crystals*** of (17m) (134 mg, 48%) were obtained from benzene/light petroleum.

(e) R-(+)-α-Methylbenzyl isocyanide

A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and R-(+)-CNCHMePh (43 mg, 0.33 mmol) in thf (10 ml) required 0.1 ml initiator solution for complete reaction. The product is extremely soluble in hexane, from which deep-red well-formed crystals of (16q) (74 mg, 33%) were obtained.

(f) Bis(diphenylphosphino)methane

Complexes (20s) and 21s) were obtained as the sole products in 90 and 26% yields, respectively, in stoichiometric reactions carried out according to the general procedure outlined above, while if the ratio $Ru_3(CO)_{12}$/dppm was 2/1, the complex $[Ru_3(CO)_{11}]_2(\mu$-dppm) (22s) was formed in 98% yield.

Reactions of $H_4Ru_4(CO)_{12}$ *(by B.K. Nicholson)*

In a typical reaction, a mixture of $H_4Ru_4(CO)_{12}$ (185 mg, 0.25 mmol) and PPh_3 (70 mg, 0.27 mmol) in thf (10 ml) required 0.5 ml of $Na[Ph_2CO]$ solution for complete reaction at room temperature. Evaporation and recrystallisation (light petroleum) gave pale orange *crystals* of (23c) (133 mg, 55%).

The following monosubstituted complexes were prepared similarly: light orange $H_4Ru_4(CO)_{11}[P(OMe)_3]$ (23h) (90%); orange $H_4Ru_4(CO)_{11}[P(OPh)_3]$ (23j) (76%) from CH_2Cl_2/light petroleum; bright orange $H_4Ru_4(CO)_{11}(CNBu^t)$ (23o) (63%) from EtOH/benzene. With two molar equivalents of ligand, red $H_4Ru_4(CO)_{10}(PPh_3)_2$ (24c) (53%) from MeOH, and red $H_4Ru_4(CO)_{10}(CNBu^t)_2$ (24o) (34%) from EtOH/benzene were obtained, while a reaction between $H_4Ru_4(CO)_{12}$ (100 mg, 0.13 mmol) and $P(OMe)_3$ (87 mg, 0.7 mmol) gave orange $H_4Ru_4(CO)_9[P(OMe)_3]_3$ (25h) (65 mg, 47%) from light petroleum. All complexes have been described previously, and were characterised by comparison either with authentic samples, or with the literature values.

Preparation of ruthenium carbonyl derivatives containing different ligands

(a) $Ru_3(CO)_9[P(OMe)_3]$ (dpam)

A mixture of $Ru_3(CO)_{10}$(dpam) (20r) (100 mg, 0.09 mmol) and $P(OMe)_3$ (16 mg, 0.13 mmol) in thf (10 ml) was heated to 42°, and treated with the initiator solution (0.35 ml). After 30 min, solvent was removed

(rotary evaporator) and the residue recrystallised (benzene/EtOH) to give bright red crystals of $Ru_3(CO)_9[P(OMe)_3]$(dpam) (30hu) (56 mg, 51%).

(b) $Ru_3(CO)_9(PMe_3)$(dppe)

Similarly, a mixture of $Ru_3(CO)_{10}$(dppe) (150 mg, 0.15 mmol) and PMe_3 (19 mg, 0.25 mmol) in thf (9 ml) was treated with 10 drops of $Na[Ph_2CO]$ solution at room temperature. Effervescence occurred, and the solution darkened in colour. After 15 min., the solvent was removed and the product recrystallised (benzene/EtOH) to give deep red $Ru_3(CO)_9(PMe_3)$(dppe) (30at) (127 mg, 81%).

(c) $Ru_3(CO)_9(PMe_3)(PPh_3)[P(OMe)_3]$

A mixture of $Ru_3(CO)_{11}[P(OMe)_3]$ (16h) (100 mg, 0.14 mmol) and PMe_3 (19 mg, 0.25 mmol) in thf (9 ml) was treated with 8 drops of initiator solution. After 10 min. gas evolution had ceased, and the i.r. spectrum indicated that reaction was complete. Solvent was then removed, and the product was recrystallised (Et_2O/pentane) to give pure $Ru_3(CO)_{10}(PMe_3)[P(OMe)_3] \cdot Et_2O$ (26ah) (93 mg, 87%). Isolation of the intermediate complex is not necessary: addition of PPh_3 (32 mg, 0.12 mmol) to the product in thf (8 ml), warming to 47°, and addition of $Na[Ph_2CO]$ solution (0.95 ml) gave, after 40 min., deep red $Ru_3(CO)_9(PMe_3)[P(OMe)_3](PPh_3)$ (27ach) (50 mg, 41%), which was recrystallised from an EtOH/benzene/heptane mixture.

(d) $H_4Ru_4(CO)_9(PMe_2Ph)[P(OMe)_3][PPh(OMe)_2]$ **(by B.K. Nicholson)**

Addition of 0.1 ml initiator solution to $H_4Ru_4(CO)_{11}[P(OMe)_3]$ (13h) (246 mg, 0.29 mmol) and $PPh(OMe)_2$ (50 mg, 0.29 mmol) was sufficient to complete the reaction. The product formed a red oil (from light petroleum) (170 mg, 60%), and was identified as $H_4Ru_4(CO)_{10}[P(OMe)_3][PPh(OMe)_2]$ (28hi) from its i.r. and ^1H n.m.r. spectra. Further reaction of (28hi) (169

mg, 0.17 mmol) with PMe_2Ph (25 mg, 0.18 mmol) in thf (3 ml) occurred after addition of 0.3 ml initiator solution. Evaporation of a warm light petroleum extract of the residue afforded a red oil which slowly solidified, shown to be $H_4Ru_4(CO)_9(PMe_2Ph)[P(OMe)_3][PPh(OMe)_2]$ (29bhi) (140 mg, 75%).

(e) $H_4Ru_4(CO)_9(PMe_2Ph)[P(OC_6H_4Me\text{-}p)_3][P(OCH_2)_3CEt]$ **(by B.K. Nicholson)**

A mixture of $H_4Ru_4(CO)_{11}[P(OC_6H_4Me\text{-}p)_3]$ (23k) (735 mg, 0.69 mmol) and PMe_2Ph (95 mg, 0.69 mmol) in thf (6 ml) reacted after addition of 0.12 ml initiator solution. Recrystallisation (hexane) gave golden *needles* of $H_4Ru_4(CO)_{10}(PMe_2Ph)[P(OC_6H_4Me\text{-}p)_3]$ (28bk) (540 mg, 66%). This complex (330 mg, 0.28 mmol) reacted with $P(OCH_2)_3CEt$ (45 mg, 0.28 mmol) in thf (4 ml), requiring 3 ml of $Na[Ph_2CO]$ solution. Evaporation and recrystallisation (benzene/light petroleum) gave bright yellow *microcrystals* of $H_4Ru_4(CO)_9(PMe_2Ph)[P(OC_6H_4Me\text{-}p)_3][P(OCH_2)_3CEt]$ (29bkl) (230 mg, 64%).

Thermally induced reactions of $Ru_3(CO)_{12}$

(a) Trimethylphosphine

i) PMe_3 (55 mg, 0.72 mmol) was distilled into a solution of $Ru_3(CO)_{12}$ (450 mg, 0.70 mmol) in benzene (65 ml). After 9 h at room temperature, chromatography (neutral alumina) gave recovered $Ru_3(CO)_{12}$ (379 mg, 84%) and red (16a) (72 mg, 15%), both eluted with light petroleum.

ii) Similarly, a mixture of $Ru_3(CO)_{12}$ (150 mg, 0.23 mmol) and PMe_3 (76 mg, 1.0 mmol) in benzene (65 ml) after 4.5 h at room temperature gave $Ru_3(CO)_{12}$ (50 mg, 33%), red (16a) (75 mg, 43.5%) (eluted with 5:95 Et_2O/light petroleum) and red (17a) (29 mg, 16%) (eluted with 1:1 Et_2O/light petroleum).

iii) The reaction between $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and PMe_3 (25 mg, 0.33 mmol) in benzene (50 ml) afforded $Ru_3(CO)_{12}$ (26 mg, 26%), (16a) (9 mg, 8.4%) and (17a) (69 mg, 60%).

iv) A mixture of $Ru_3(CO)_{12}$ (1750 mg, 2.74 mmol) and PMe_3 (822 mg, 10.8 mmol) was heated at reflux point in degassed pentane to give (18a) (1930 mg, 90%) and (19a) (7 mg, 0.3% (eluted with 1:1 Et_2O/light petroleum).

(b) Triphenylphosphine

i) $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and PPh_3 (41 mg, 0.16 mmol) were heated in hexane (50 ml) at 45° for 1 h. Chromatography (silica gel) gave recovered $Ru_3(CO)_{12}$ (36 mg, 36%), (16c) (50 mg, 36.6%) and (17c) (40 mg, 23%), eluted with light petroleum or benzene.

ii) $Ru_3(CO)_{12}$ (900 mg, 1.41 mmol) and PPh_3 (740 mg, 2.82 mmol) in cyclohexane (500 ml) at 55° for 4 h afforded (16c) (90 mg, 7.3%), (17c) (1190 mg, 76.3%) and (18c) (186 mg, 9.8%).

iii) $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and PPh_3 (120 mg, 0.46 mmol) in hexane (50 ml) at reflux point for 2 h gave, after cooling, an insoluble purple solid, which was filtered off to give (18c) (205 mg, 97.7%).

(c) Tris(p-tolyl)phosphine

The reaction between $Ru_3(CO)_{12}$ (356 mg, 0.56 mmol) and $P(C_6H_4Me\text{-}p)_3$ (462 mg, 1.52 mmol) in hexane at reflux point for 3 h gave purple (18d) (727 mg, 88%) after recrystallisation (CH_2Cl_2/hexane).

(d) Tricyclohexylphosphine

i) After 2.5 h in hexane (70 ml) at reflux point, a mixture of $Ru_3(CO)_{12}$ (211 mg, 0.33 mmol) and PCy_3 (282 mg, 1.01 mmol) was chromatographed (neutral alumina) to give:

i) yellow (17f) (301 mg, 80%), eluted with light petroleum;

ii) red (16f) (38 mg, 13%), eluted with 3:7 dichloromethane/diethyl ether;

iii) a small amount of an unidentified green complex, eluted with 1:1 CH_2Cl_2/Et_2O; Infra-red ($CHCl_3$): ν(CO) = 2094m, 2075w, 2055s, 2033(sh), 1988vs, 1960(sh) cm^{-1}.

ii) A similar reaction between $Ru_3(CO)_{12}$ (202 mg, 0.32 mmol) and PCy_3 (95 mg, 0.34 mmol) in heptane (50°, 1 h) afforded:

i) recovered $Ru_3(CO)_{12}$ (71 mg, 35%);

ii) complex (17f) (22 mg, 6%);

iii) complex (16f) (118 mg, 42%).

(e) Trimethyl phosphite

i) A mixture of $Ru_3(CO)_{12}$ (400 mg, 0.63 mmol) and $P(OMe)_3$ (70 mg, 0.56 mmol) in hexane (150 ml) was heated (50°, 3 h), and the products separated by chromatography (Florisil) to give:

i) recovered $Ru_3(CO)_{12}$ (78 mg, 20%);

ii) orange (16h) (198 mg, 43%);

iii) red (17h) (92 mg, 18%), eluted successively with light petroleum.

ii) A similar reaction between $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and $P(OMe)_3$ (70 mg, 0.56 mmol) in hexane (100 ml) at 50° for 5 h afforded:

i) recovered $Ru_3(CO)_{12}$ (10 mg, 5%);

ii) complex (16h) (67 mg, 29%);

iii) complex (17h) (91 mg, 35%);

iv) red (18h) (43 mg, 15%), eluted with 1:3 Et_2O/light petroleum.

iii) A third experiment used $Ru_3(CO)_{12}$ (400 mg, 0.63 mmol) and $P(OMe)_3$ (220 mg, 1.77 mmol); heating in cyclohexane at reflux point for 3 h resulted in deposition of some dark-coloured material. Chroma-

tography of the filtered reaction mixture gave only complex (18h) (81 mg, 14%).

(f) Bis(diphenylphosphino)methane

The reaction between $Ru_3(CO)_{12}$ (480 mg, 0.75 mmol) and dppm (600 mg, 1.56 mmol) in cyclohexane (200 ml) at reflux point for 16 h afforded the following compounds by chromatography (alumina) of the filtered solution:

i) recovered $Ru_3(CO)_{12}$ (42 mg, 9%);

ii) red (20q), eluted with light petroleum, and obtained as a toluene solvate (201 mg, 28%) from toluene/light petroleum;

iii) dark red-brown (21q) (82 mg, 12%), eluted with 95:5 Et_2O/C_6H_6.

A yellow solid deposited during the reaction was shown to be $Ru_3(\mu_3\text{-}PPh)(\mu\text{-}CHPPh_2)(CO)_7(dppm)$ (220 mg, 25%) by comparison with the literature.[188]

(g) Bis(diphenylarsino)methane

i) A reaction between $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and dpam (76 mg, 0.16 mmol) in toluene (20 ml) at reflux point for 1.5 h gave, after chromatography (Florisil):

i) recovered $Ru_3(CO)_{12}$ (11 mg, 11%);

ii) red (20r) (123 mg, 75%).

ii) Similarly, $Ru_3(CO)_{12}$ (400 mg, 0.63 mmol) and dpam (610 mg, 1.29 mmol) in toluene (50 ml) at reflux point for 24 h afforded:

i) complex (20r) (291 mg, 44%), obtained as a toluene solvate from toluene/octane;

ii) red (21r) (196 mg, 21%), eluted with benzene;

iii) an unidentified deep red complex (41 mg), eluted with MeOH.

Infra-red (CH_2Cl_2): $\nu(CO)$ = 2020s, 1995(sh), 1975vs, 1946(sh) cm^{-1}.

(h) 1,2-Bis(diphenylarsino)ethane

Chromatography (alumina) of the mixture obtained by heating $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and dpae (76 mg, 0.16 mmol) in toluene (75 ml) at reflux point for 23 h gave:

i) recovered $Ru_3(CO)_{12}$ (29 mg, 29%), eluted with light petroleum;

ii) red (20s) (100 mg, 60%), eluted with light petroleum.

Reactions of $Os_3(CO)_{12}$

(a) Triphenylphosphine

A mixture of $Os_3(CO)_{12}$ (122.4 mg, 0.135 mmol) and PPh_3 (51.0 mgs, 0.194 mmol) in thf (10 ml) reacted after addition of 0.65 ml of initiator solution. The solvent was removed *in vacuo* and chromatography using preparative t.l.c. (Kieselgel GF_{254} adsorbent, n-hexane developer) gave 4 bands as follows:

i) yellow $Os_3(CO)_{12}$ (48 mg, 39%), identified by comparison with an authentic sample.

ii) yellow $Os_3(CO)_{11}(PPh_3)$ (31) (37 mgs, 24%); m.p. 178°C. Infra-red (C_6H_{12}): ν(CO) = 2108w, 2058m, 2038vs, 2005m, 1998m, 1988m, 1979m cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 7.51m, PPh_3; identified by comparison with literature.[159,591]

iii) yellow $Os_3(CO)_{10}(PPh_3)_2$ (32) (39 mgs, 21%); m.p. 198-201°C. Infra-red (CCl_4): ν(CO) = 2088w, 2072vw, 2056w, 2032s, 2012m, 2002vs, 1997sh, 1969m, 1955w cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 7.51 m, PPh_3; identified by comparison with literature.[159]

iv) orange-yellow $Os_3(CO)_9(PPh_3)_3$ (33) (35 mgs, 16%); m.p. 189-192°C. Infra-red (CCl_4): ν(CO) = 2070sh, 2056w, 2040sh, 2030w, 1994sh, 1969m, 1950s cm^{-1}; ^1H n.m.r. δ($CDCl_3$) = 7.50 m, PPh_3; identified by comparison with literature.[159]

(b) Tertiary butyl isocyanide

A mixture of $Os_3(CO)_{12}$ (103 mgs, 0.114 mmol) and t-BuNC (17 mgs, 0.204 mmol) in thf (10 ml) reacted after addition of 0.74 ml of initiator solution. The solvent was removed *in vacuo* and preparative t.l.c. (Kieselgel GF_{254} adsorbent, n-hexane developer) gave 8 bands, of which the following could be characterised:

i) yellow $Os_3(CO)_{12}$ (37 mg, 36%), identified by comparison with an authentic sample.

ii) yellow $Os_3(CO)_{11}(CNBu^t)$ (34) (19 mgs, 17%); m.p. 163-165°C. Infra-red (C_6H_{12}): ν(CN) = 2175 m; ν(CO) = 2100m, 2054s, 2039s, 2019vs, 2005s, 1988s, 1985sh cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 1.58s Me. [*M* (mass spectrometry) = 961; $C_{16}H_9O_{11}NOs_3$ requires *M* - 961]; identified by comparison with literature.[232,591]

iii) yellow $Os_3(CO)_{10}(CNBu^t)_2$ (35) (12 mgs, 10%); m.p. 236-238°C. Infra-red (C_6H_{12}): ν(CN) = 2162m; ν(CO) = 2069m, 2026sh, 2024s, 2003sh, 1996sh, 1987s, 1973s, 1966s cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 1.58s Me. [*M* (mass spectrometry) = 1016; $C_{20}H_{18}O_{10}N_2Os_3$ requires *M* - 1016]; identified by comparison with literature.[232]

iv) yellow $Os_3(CO)_9(CNBu^t)_3$ (36) (10 mgs, 8%); d. 305°C. Infra-red (C_6H_{12}): ν(CN) = 2154m; ν(CO) = 2065m, 2050m, 2035m, 2010s, 1985m cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 1.58s Me. [*M* (mass spectrometry) = 1071; $C_{24}H_{27}O_9N_3Os_3$ requires *M* - 1071]; identified by comparison with literature.[232]

v) yellow $Os_3(CO)_8(CNBu^t)_4$ (37) (3 mgs, 2%); m.p. >305°C. Infra-red (C_6H_{12}): ν(CN) = 2138s; ν(CO) = 2042sh, 2034m, 2013m, 1997s, 1992m, 1971s, 1955s, 1943s, 1933s cm^{-1}; [*M* (mass spectrometry) = 1126; $C_{28}H_{36}O_8N_4Os_3$ requires *M* - 1126]; identified by comparison with literature.[232]

(c) Trimethylphosphite

A mixture of $Os_3(CO)_{12}$ (160 mg, 0.176 mmol) and $P(OMe)_3$ (56 mg, 0.451 mmol) in thf (15 ml) reacted after addition of 1.2 ml of initiator solution. The solvent was removed *in vacuo* and preparative t.l.c. (Kieselgel GF_{254}, 30% diethyl ether: cyclohexane developer) gave 5 bands, of which the following were characterised:

i) yellow $Os_3(CO)_{11}[P(OMe)_3]$ (38) (30mg, 17%); m.p. 52-54°C. Infra-red (C_6H_{12}): ν(CO) = 2110m, 2055s, 2039m, 2021s, 2002w, 1992m, 1981w, 1967w cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 3.78d [J_{P-H} = 10.5 Hz] $P(OMe)_3$. [Found C - 17.29, H - 1.00%, *M* (mass spectrometry) = 1002; $C_{14}H_9O_{14}POs_3$ requires C - 16.77, H - 0.90%, *M* - 1002]; identified by comparison with literature.[591]

ii) yellow $Os_3(CO)_{10}[P(OMe)_3]_2$ (39) (33 mg, 16%); m.p. 63-64°C. Infra-red (C_6H_{12}): ν(CO) = 2071m, 2055mw, 2038w, 2018s, 1994vs, 1981sh, 1957m, 1948 sh cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 3.78d [J_{P-H} = 11.0 Hz] $P(OMe)_3$. [Found C - 17.93, H - 1.50%, *M* (mass spectrometry) = 1098; $C_{16}H_{18}O_{16}P_2Os_3$ requires C - 17.49, H - 1.65%, *M* - 1098].

iii) yellow $Os_3(CO)_9[P(OMe)_3]_3$ (40) (23 mg, 10%); m.p. 126-127°C. Infra-red (C_6H_{12}): ν(CO) = 2070w, 2058w, 2026s, 2000vs, 1967m, 1962sh, 1949sh, 1930w cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 3.78d [J_{P-H} = 11.0 Hz] $P(OMe)_3$. [Found C - 18.13, H - 1.84%, *M* (mass spectrometry) = 1.194; $C_{18}H_{27}O_{18}P_3Os_3$ requires C - 18.09, H - 2.28%, *M* - 1194].

(d) Triphenylphosphite

A mixture of $Os_3(CO)_{12}$ (190 mg, 0.210 mmol) and $P(OPh)_3$ (130 mg, 0.419 mmol) in thf (25 ml) reacted after addition of 1.3 ml of initiator solution. The solvent was removed *in vacuo* and preparative t.l.c.

(Kieselgel GF_{254}, 30% diethyl ether: cyclohexane developer) gave 7 bands, of which the following were characterised:

i) yellow $Os_3(CO)_{11}[P(OPh)_3]$ (41) (22 mg, 9%); m.p. 181-183°C. Infra-red (C_6H_{12}): ν(CO) = 2114m, 2061s, 2046s, 2026vs, 2007m, 1998s, 1992m, 1981m, 1954vw cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 7.60m, $P(OPh)_3$. [Found C - 29.55, H - 1.89%, *M* (mass spectrometry) = 1156; $C_{29}H_{15}O_{14}POs_3$ requires C - 29.30, H - 1.27%, *M* - 1156].

ii) yellow $Os_3(CO)_{10}[P(OPh)_3]_2$ (42) (96 mg, 31%); m.p. 210-214°C. Infra-red (C_6H_{12}): ν(CO) = 2080m, 2060m, 2044s, 2025s, 2015vs, 2002sh, 1986s, 1977sh, 1960sh cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 7.61m, $P(OPh)_3$. Found C - 37.56, H - 2.28%; $C_{46}H_{30}O_{16}P_2Os_3$ requires C - 37.55, H - 2.05%).

iii) yellow $Os_3(CO)_9[P(OPh)_3]_3$ (43) (22 mg, 6%); m.p. >280°C. Infra-red (C_6H_{12}): ν(CO) = 2070m, 2048s, 2024s, 2016vs, 2004sh, 1987s cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 7.60m, $P(OPh)_3$. (Found C - 43.47, H - 2.91%; $C_{63}H_{45}O_{18}P_3Os_3$ requires C - 43.15, H - 2.58%).

Reactions of $H_4Os_4(CO)_{12}$

(a) Triphenylphosphine

A mixture of $H_4Os_4(CO)_{12}$ (105 mg, 0.095 mmol) and PPh_3 (25 mg, 0.95 mmol) in thf (15 ml) reacted after addition of 0.45 ml of initiator solution. The solvent was removed *in vacuo* and preparative t.l.c. (Kieselgel GF_{254}, 40% diethyl ether: cyclohexane developer) gave 12 bands, of which the following could be characterised:

i) yellow $H_4Os_4(CO)_{11}(PPh_3)$ (44) (13 mg, 10%). Infra-red (C_6H_{12}): ν(CO) = 2098w, 2070vs, 2060s, 2038s, 2024s, 2004m, 1990w, 1971w cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 7.48m (15), PPh_3, -20.29d (4) [J_{P-H} = 4 Hz], H [Found C -

26.34, H - 2.36%, $C_{29}H_{19}O_{11}POs_4$ requires C - 26.09, H - 1.43%).

ii) yellow $H_4Os_4(CO)_{10}(PPh_3)_2$ (45) (7 mg, 5%). Infra-red (C_6H_{12}): ν(CO) = 2079s, 2070m, 2061s, 2051s, 2037s, 2020vs, 2011s, 2001s, 1985m, 1957m cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 7.48m (30), PPh_3, -20.50t (4) [J_{P-H} = 8 Hz], H. (Found C - 35.32, H - 3.33%; $C_{46}H_{34}O_{10}P_2Os_4$ requires C - 35.20, H - 2.18%).

iii) yellow $H_4Os_4(CO)_9(PPh_3)_3$ (46) (9 mg, 5%). Infra-red (C_6H_{12}): ν(CO) = 2088m, 2066s, 2051m, 2037m, 2028vs, 2002s, 1984m, 1967s, 1949m cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 7.50m (45), PPh_3, -20.61q (4) [J_{P-H} = 9 Hz], H. (Found C - 41.54, H - 2.94%; C - 41.95, H - 2.74%).

iv) yellow-brown $H_4Os_4(CO)_8(PPh_3)_4$ (47) (6 mg, 3%). Infra-red (C_6H_{12}): ν(CO) = 2069s, 2060s, 2049m, 2023vs, 2006m, 2001m, 1983m, 1976w cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 7.50m (66), PPh_3, -20.60qu (4) [J_{P-H} = 9 Hz], H. (Found C - 48.36, H - 3.32%; $C_{80}H_{64}O_8P_4Os_4 \cdot C_6H_6$ requires C - 48.81, H - 3.33%).

(b) Trimethylphosphite

A mixture of $H_4Os_4(CO)_{12}$ (102 mg, 0.093 mmol) and $P(OMe)_3$ (36 mg, 0.290 mmol) in thf (10 ml) reacted after addition of 0.68 ml of initiator solution. The solvent was removed *in vacuo* and preparative t.l.c. (Kieselgel GF_{254}, 50% diethyl ether: cyclohexane developer) gave 7 bands, of which the following could be characterised:

i) pale yellow $H_4Os_4(CO)_{11}[P(OMe)_3]$ (48) (18 mg, 16%). Infra-red (C_6H_{12}): ν(CO) = 2099w, 2072s, 2060vs, 2022s, 2000s, 1991w cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 3.79d (9) [J_{P-H} = 13 Hz], $P(OMe)_3$, -20.38d (4) [J_{P-H} = 4 Hz], H. [*M* (mass spectrometry) = 1196; $C_{14}H_{13}O_{14}POs_4$ requires *M* - 1196]; identified by comparison with literature.[294]

ii) pale yellow $H_4Os_4(CO)_{10}[P(OMe)_3]_2$ (49) (6 mg, 5%). Infra-red (C_6H_{12}): ν(CO) = 2080m, 2069m, 2060m, 2050m, 2039s, 2024vs, 2016s, 2004s, 1991m, 1960sh cm^{-1}. [*M* (mass spectrometry) = 1292, $C_{16}H_{22}O_{16}P_2Os_4$ requires *M* 1292]; identified by comparison with authentic sample.[592]

iii) yellow $H_4Os_4(CO)_9[P(OMe)_3]_3$ (50) (8 mg, 6%). Infra-red (C_6H_{12}): ν(CO) = 2086m, 2066s, 2042w, 2021vs, 1999vs, 1986m, 1959w cm^{-1}. [*M* (mass spectrometry) = 1388, $C_{18}H_{31}O_{18}P_3Os_4$ requires *M* - 1388]; identified by comparison with authentic sample.[592]

iv) yellow-brown $H_4Os_4(CO)_8[P(OMe)_3]_4$ (51) (4 mg, 3%). Infra-red (CH_2Cl_2): ν(CO) = 2069m, 2050m, 2022vs, 2000s, 1982sh, 1950sh, 1924sh cm^{-1}. [*M* (mass spectrometry) = 1484, $C_{20}H_{40}O_{20}P_4Os_4$ requires *M* - 1484]; identified by comparison with authentic sample.[592]

Reactions of $HRu_3(CO)_9(C_2Bu^t)$

(a) Triphenylphosphine

A mixture of $HRu_3(CO)_9(C_2Bu^t)$ (104 mg, 0.163 mmol) and PPh_3 (46 mg, 0.175 mmol) in thf (6 ml) reacted after addition of 0.550 ml of initiator solution. The solvent was removed *in vacuo* and preparative t.l.c. (Kieselgel GF_{254}, cyclohexane developer) gave 8 bands, of which only the following red band could be characterised: red $HRu_3(CO)_8(PPh_3)(C_2Bu^t)$ (52) (41 mg, 29%). Infra-red (C_6H_{12}): ν(CO) = 2092m, 2064s, 2017vs, 2005s, 1996s, 1953m, 1948sh cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 7.50m (15), PPh_3, 1.29s (9), Bu^t, -19.8s (1), H; identified by comparison with literature.[539]

(b) Tertiary butyl isocyanide

A mixture of $HRu_3(CO)_9(C_2Bu^t)$ (113 mg, 0.177 mmol) and t-BuNC (0.200 mmol - standard 1 mmol/ml solution: 0.2 ml) in thf (10 ml)

reacted after addition of 0.65 ml of initiator solution. The solvent was removed *in vacuo* and preparative t.l.c. (Kieselgel GF_{254}: cyclohexane developer) gave 6 bands, of which only the following deep red band could be characterised: red $HRu_3(CO)_8(t\text{-BuNC})(C_2Bu^t)$ (53) (39 mg, 32%). Infra-red (CH_2Cl_2): ν(CN) = 2161m; ν(CO) = 2044s, 1980vs,br cm^{-1}; ^1H n.m.r. δ [$(CD_3)_2CO$] = 1.17s (9), $CNCMe_3$, 1.50s (9), C_2Bu^t, -21.2d (1) [J_{P-H} = 3 Hz], H. [Found C - 32.07, H - 2.01, N - 1.92%, *M* (mass spectrometry) = 694, $C_{19}H_{19}O_8NRu_3$ requires C - 32.95, H - 2.26, N - 2.02%, *M* - 694].

Preparation of $Ru_6(CO)_{18}^{2-}$

$Ru_3(CO)_{12}$ (250 mg, 0.391 mmol) in 25 ml of thf had injected dropwise 0.42 ml of initiator solution at 42° Effervescence was noted and the solution gradually darkened (45 mins.). The infra-red spectrum of this solution confirmed the existence of $Ru_6(CO)_{18}^{2-}$ (54). [Infra-red (CH_2Cl_2): ν(CO) = 2003vs, 1982ms, 1925sh cm^{-1}], identified by comparison with literature.[298] The product could be isolated in best yield (94%) as its tetraphenyl phosphonium salt. The solution containing the anionic product can be used for subsequent reactions without prior isolation and purification.

Miscellaneous Reactions

Reaction between $Ru_3(CO)_{12}$ and $C_2(CO_2Me)_2$

Isolation of $Ru_2(CO)_6[C_4(CO_2Me)_4]$

A mixture of $Ru_3(CO)_{12}$ (600 mg, 0.94 mmol) and $C_2(CO_2Me)_2$ (400 mg, 2.82 mmol) in tetrahydrofuran (50 ml) was heated at reflux point for 5 h. Evaporation and separation of the products by thin layer chromatography (adsorbent: Kieselgel H; developed in 85:15 ethyl acetate/acetone) gave the following fractions:

i) a yellow band which moved with the solvent front;

ii) an orange band (R_f = 0.79) which afforded $Ru_3(CO)_7[C_2(CO)_2Me)_2]_4$ (55) (45 mg, 4.4%), purified by recrystallisation from hexane/dichloromethane mixtures [Found: C - 35.13, H - 2.93%, *M* (acetone) - 1110; $C_{31}H_{24}O_{23}Ru_3$ requires: C - 34.86, H - 2.25%, *M* - 1067]. Infra-red (CH_2Cl_2): ν(CO) = 2111m, 2085s, 2058vs, 2042vs, 2020s, 1986(sh) cm^{-1} ;

iii) an orange band (R_f = 0.22), presently unidentified [31 mg. Infra-red (CH_2Cl_2): ν(CO) = 2104(sh), 2087m, 2050vs, 1982vs cm^{-1}].

The brown baseline (144 mg) also contained metal carbonyl complexes. Further separation of fraction (i) (using 70:30 cyclohexane/acetone) gave $Ru_3(CO)_{12}$ (21 mg, 3.5%) and a pale yellow fraction (R_f = 0.48) which afforded pure $Ru_2(CO)_6[C_4(CO_2Me)_4]$ (56) (5; 78 mg, 13%) from hexane or on sublimation (65°/0.01 mm) [Found: C - 33.29, H - 1.59%, *M* (mass spectrometry) - 654; $C_{18}H_{12}O_{14}Ru_2$ requires: C - 33.04, H - 1.85%, *M* - 654]. Infra-red (cyclohexane): ν(CO) = 2114m, 2090vs, 2050s, 2038s, 2021vs cm^{-1}.

$Ru_3(CO)_9(PMe_3)_3 + C_5H_5$

Cyclopentadiene (100 mg, 1.53 mmol) was added to $Ru_3(CO)_9(PMe_3)_3$ (250 mg, 0.319 mmol) and heated in toluene (70 ml) at reflux point for 15 h. The reaction was followed by t.l.c. The solvent was removed *in vacuo*, and preparative t.l.c. (Kieselgel HF_{254} adsorbent, 30% diethyl ether:cyclohexane developer) isolated the following products:

i) yellow $[Ru(CO)(PMe_3)(\eta\text{-}C_5H_5)]_2$ (57) (37 mg, 21%), R_f = 0.11, recystallised from isopentane, m.p. 121°. Infra-red (C_6H_{12}): ν(CO) = 2023s, 1865sh, 1850vs cm^{-1}. [Found: C - 39.81, H - 5.85%, *M* (mass spectrometry) = 542; $C_{18}H_{28}O_2P_2Ru_2$ requires C - 40.00, H - 5.22%, *M* - 542]; ^1H n.m.r.: δ ($CDCl_3$) = 4.73s (10), C_5H_5, 1.80d [J_{P-H} = 11 Hz] (18), PMe_3;

ii) orange $HRu_3(CO)_6(PMe_3)_3(\eta\text{-}C_5H_5)$ (58) (72 mg, 29%), R_f = 0.28, recrystallised from CH_2Cl_2/isopentane, m.p. = 142-146°. Infra-red (C_6H_{12}): ν(CO) = 2033m, 2005w, 1982m, 1970w, 1957w, 1932vs cm^{-1}. [Found: C - 32.02, H - 4.43%, *M* (mass spectrometry) = 767; $C_{20}H_{33}O_6P_3Ru_3$ requires C - 31.38, H - 4.34%, *M* - 767]; ^1H n.m.r. δ ($CDCl_3$) = 5.19s (5), C_5H_5, 1.90d [J_{P-H} = 12 Hz] (27), PMe_3 -15.93s (1), H;

iii) white $HRu(CO)(PMe_3)(\eta\text{-}C_5H_5)$ (60) (9 mg, 10%), R_f = 0.60, recrystallised from isopentane/isopropanol. Infra-red (C_6H_{12}): ν(CO) = 1911m(br) cm^{-1}. [Found: C - 39.15, H - 5.86%, *M* (mass spectrometry) = 272; $C_9H_{15}OPRu$ requires C - 39.85, H - 5.57%, *M* - 272];

iv) yellow $Ru(CO)_2(PMe_3)(\eta\text{-}C_5H_6)$ (61) (10 mg, 10%), R_f = 0.82 recrystallised from CH_2Cl_2/n-hexane. Infra-red (C_6H_{12}): ν(CO) = 1987s, 1967s cm^{-1}. [Found: C - 40.80, H - 5.56%, *M* (mass spectrometry) = 300; $C_{10}H_{15}O_2PRu$ requires C - 40.13, H - 5.05%, *M* - 300];

v) orange brown $Ru_3(CO)_5(PMe_3)(\eta\text{-}C_5H_5)_2$ (59) (43 mg, 17%), R_f = 0.00, [Baseline extracted with diethyl ether, further preparative t.l.c. in 50% acetone/cyclohexane yielded orange-brown band R_f = 0.72] recrystallised from acetone/isopropanol. Infra-red (CH_2Cl_2): ν(CO) = 2000w, 1980vs, 1970s, 1962sh, 1947m cm^{-1}. [Found: C - 36.63; H - 5.04%, *M* (mass spectrometry) = 804; $C_{24}H_{37}O_5P_3Ru_3$ requires C - 35.96, H - 4.65%, *M* - 804]; ^1H n.m.r. δ ($CDCl_3$) = 5.39s (5), C_5H_5, 4.96s (5), C_5H_5, 1.83d [J_{P-H} = 11 Hz] (27), PMe_3.

$Ru_3(CO)_9(PMe_3)_3$ + Cyclododecatriene (CDT)

Cyclododecatriene [300 mg, 1.85 mmol (2:1 - cis:trans isomeric mixture)] was added to $Ru_3(CO)_9(PMe_3)_3$ (300 mg, 0.383 mmol) in benzene (120 ml) and heated at reflux point for 3 days. Preparative t.l.c. of

the resultant solution on Kieselgel GF_{254} in 30% acetone/cyclohexane isolated the following products:

i) clear cyclododecatriene - R_f = 0.98 (identified by mass spectroscopy);

ii) red $HRu_3(CO)_6(PMe_3)_3$ ($C_{12}H_{15}$) (62) (145 mg, 44%); R_f = 0.53, recrystallised from benzene/n-heptane, m.p. 149-151°. Infra-red (C_6H_{12}): ν(CO) = 2070vw, 2044m, 2025m, 1999sh, 1969vs, 1940s cm^{-1}. [Found: C - 37.64, H - 5.13%, *M* (mass spectrometry) = 862; $C_{27}H_{43}O_6P_3Ru_3$ requires C - 37.72%, H - 5.04%, *M* - 862]; ^1H n.m.r. δ ($CDCl_3$) = 6.42d (1), 5.34m (2), 7.0-9.0m,br (39), $C_{12}H_{15}$ + PMe_3, -21.56t (1), H;

iii) red $HRu_3(CO)_4(PMe_3)_3(C_{24}H_{33})$ (63) (42 mg, 10%); R_f = 0.35, recrystallised from benzene/n-heptane, m.p. = 293-302°. Infra-red (C_6H_{12}): ν(CO) = 2012s, 1994s, 1965vs, 1955sh cm^{-1}. [Found: C - 48.85; H - 6.24%, *M* (mass spectrometry) = 968; $C_{37}H_{61}O_4P_3Ru_3 \cdot C_6H_6$ requires C - 49.47, H - 6.46%, *M* - 968]; ^1H n.m.r. δ ($CDCl_3$) = 6.43m (1), 6.21s (2), 4.34s (2), 3.0-1.4m,br (55), $C_{24}H_{33}$ + PMe_3, -24.01s (1), H;

iv) orange $Ru_4(CO)_7(PMe_3)_4(C_{12}H_{16})$ (64) (19 mg, 5%); R_f = 0.11, recrystallised from CH_2Cl_2/ethanol, m.p. = 212°. Infra-red (CH_2Cl_2): ν(CO) = 2050m, 2025s, 1985vs, 1957sh cm^{-1}. [Found: C - 34.11, H - 4.21, O - 10.31%, *M* (mass spectrometry) = 1067; $C_{31}H_{52}O_7P_4Ru_4$ requires C - 34.96, H - 4.92, O - 10.52%, *M* - 1067]; ^1H n.m.r. δ ($CDCl_3$) = 5.80s (1), 4.01s (1), 3.0-1.0m,br (50), $C_{12}H_{16}$ + PMe_3;

v) brown baseline, 35 mg, extracted with boiling acetone, then boiling ethyl acetate, recrystallised from isopropanol/acetone. Infra-red (CH_2Cl_2): ν(CO) = 2050s, 1980vs, 1957sh cm^{-1}; product was not characterised further.

$Ru_3(CO)_9(PMe_3)_3$ + Azulene

Azulene (100 mg, 0.78 mmol) was added to $Ru_3(CO)_9(PMe_3)_3$ (600 mg, 0.766 mmol) in toluene (200 ml) and heated at reflux point for 5.25 h. The solvent was then removed *in vacuo* and the residue chromatographed under nitrogen on dried Florisil. The reaction residue was air and moisture sensitive, while on the column, and no products are recovered if care is not taken. Elution with 30% CH_2Cl_2/n-hexane gave 23 mg (5.3%) of deep red $Ru_2(CO)_3(PMe_3)_2(C_{10}H_8)$ (64), m.p. = 343°(dec) [Found: C - 40.15, H - 4.29%, *M* (mass spectrometry) = 568; $C_{19}H_{26}O_3P_2Ru_2$ requires C - 40.28, H - 4.62%, *M* - 568]. Infra-red (CH_2Cl_2): ν(CO) = 1990s, 1789vs cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 5.42d [J = 2 Hz] (2), 5.01s (1), 4.90m (2), 4.47m (1), 3.60m (2), azulene; 1.83d [J_{P-H} = 12 Hz] (18), PMe_3. Further elution with 50% CH_2Cl_2/n-hexane gave 29 mg (3.8%) of black $Ru_4(CO)_6(PMe_3)_4(C_{10}H_8)$ (66), m.p. = 253-255° [Found: C - 33.72, H - 4.80%, *M* (mass spectrometry) = 1007; $C_{28}H_{44}O_6P_4Ru_4$ requires C - 33.46, H - 4.41%, *M* - 1007]. Infra-red (CH_2Cl_2): ν(CO) = 2042m, 1994sh, 1959vs cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 5.81d [J = 3 Hz] (2); 4.91d [J = 3 Hz] (1); 4.20m (2), 3.83m (2), 3.01m (1), azulene; 1.95d [J = 11 Hz] (36), PMe_3; recrystallisation of sample from CH_2Cl_2/benzene gave the complex as its benzene solvate (Found: C - 37.89, H - 4.40, P - 12.18%; $C_{28}H_{44}O_6P_4Ru_4 \cdot C_6H_6$ requires C - 37.71, H - 4.65, P - 11.44%): the solvent molecule is readily detected in the ^1H n.m.r. spectrum at δ = 7.52m (6). Further elution with 50% CH_2Cl_2 / n-hexane gave 55 mg (9.3%) of red-black $Ru_3(CO)_4(PMe_3)_3(C_{10}H_8)$ (65), m.p. >320° [Found: C - 36.04, H - 3.83%, *M* (mass spectrometry) = 773; $C_{23}H_{35}O_4P_3Ru_3$ requires C - 35.80, H - 4.47%, *M* - 773.] Infra-red (CH_2Cl_2): ν(CO) = 1998m, 1962sh, 1856vs cm^{-1}; ^1H n.m.r. δ[$(CD_3)_2CO$] = 5.45d [J = 2 Hz] (2), 5.15m (1), 4.95m (2), 4.61m (1), 3.43m (2), azulene; 1.87d [J = 10 Hz] (27), PMe_3.

$Ru_3(CO)_9(PMe_3)_3$ + Cycloocta-1,3,5,7-tetraene

i) A mixture of freshly distilled cycloocta-1,3,5,7-tetraene (COT) (200 mg, 1.92 mmol) and $Ru_3(CO)_9(PMe_3)_3$ (1.06 gm, 1.35 mmol) in toluene (250 ml) was heated at 80-85° for 38 h. The solution was then filtered and chromatographed on an alumina column. Elution with 15% toluene/cyclohexane gave pale orange *crystals* of $Ru(CO)_2(PMe_3)(C_8H_8)$ (67) (48 mg, 10.5%); m.p. = 156-161° [Found: C - 45.56, H - 5.26, P - 8.37%, *M* (mass spectroscopy) = 338; $C_{13}H_{17}O_2PRu$ requires C - 46.29, H - 5.07, P - 9.18%, *M* - 338.] Infra-red (C_6H_{12}): ν(CO) = 2015s, 1968s cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 5.01s (8), C_8H_8, 1.81d [J_{P-H} = 11.5 Hz] (9), PMe_3. Further elution with 35% toluene/cyclohexane gave 35 mg (4.5%) of yellow $Ru_2(CO)_4(PMe_3)_2(C_8H_8)$ (68); m.p. = 179°(dec) [Found: C - 37.99, H - 4.37%, *M* (mass spectrometry) = 572; $C_{18}H_{26}O_4P_2Ru_2$ requires C - 37.90; H - 4.59%, *M* - 572.] Infra-red (C_6H_{12}): ν(CO) = 2050s, 2032vs, 2001vs, 1969s, 1959sh cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 5.66m (2), 4.25m (4), 2.80m (2), cyclooctatetrene; 1.89d [J = 12 Hz] (18), PMe_3. Continued elution with 35% toluene/cyclohexane gave yellow $Ru_2(CO)_3(PMe_3)_2(C_8H_8)$ (69) (52 mg, 7.1%); m.p. = 129°(dec) [Found: C - 44.99, H - 4.88, P - 10.22%, *M* (mass spectrometry) = 544; $C_{17}H_{26}O_3P_2Ru_2 \cdot C_6H_6$ requires C - 44.52, H - 4.88, P - 9.98%, *M* - 544.] Infra-red (C_6H_{12}): ν(CO) = 2030vsu, 2009vs, 2001vs, 1951vs, 1806m cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 7.60m (6), C_6H_6, 4.69s (8), C_8H_8, 1.81d [J_{P-H} = 11 Hz] (18), PMe_3. Elution with 5% CH_2Cl_2/toluene gave 31 mg of a red complex (which remained uncharacterised), followed by another red complex - 22 mg (also uncharacterised), and by 169 mg (16.1%) of crimson $Ru_3(CO)_5(PMe_3)_3(C_8H_6)$ (70); m.p. = 278-280° [Found C - 33.79, H - 3.71, O - 10.30%, *M* (mass spectrometry) = 779; $C_{22}H_{33}O_5P_3Ru_3$ requires C - 34.16, H - 4.30, O - 10.34%, *M* -

779.] Infra-red (C_6H_6): ν(CO) = 2015s, 1978m, 1923vs,br cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 6.15m (2), 4.75m (4), cyclooctatetrene; 1.78d [J_{P-H} = 11 Hz] (27), PMe_3. Elution with increasing proportions of CH_2Cl_2/toluene eluted a further 12 complexes all in minor amounts (less than 20 mg), and these complexes remain uncharacterised.

ii) A mixture of freshly distilled cycloocta-1,3,5,7-tetraene (COT) (35 mg, 0.34 mmol) and (70) (120 mg, 0.75 mmol) in toluene (75 ml) was heated at reflux point for 8 days. The resulting solution was filtered (paper) and chromatographed on an alumina column. Elution with 75% CH_2Cl_2/benzene gave crimson-black $Ru_3(CO)(PMe_3)(C_8H_6)(C_8H_8)$ (71) (36 mg, 32%); m.p. >320° [Found: C - 39.93, H - 4.80%, *M* (mass spectrometry) = 768; $C_{26}H_{41}OP_3Ru_3$ requires C - 40.65, H - 5.64%, *M* - 768.] Infra-red (CH_2Cl_2): ν(CO) = 1711m cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) = 6.15m (2), 4.75 (4), C_8H_6; 3.63s,br (3), C_8H_8; 1.75d [J_{P-H} = 11 Hz] (27), PMe_3. This complex decomposes slowly in chloroform (*ca.* 5 days) and is mildly air sensitive.

$Ru_3(CO)_9(PMe_3)_3$ + *t*-butyl isocyanide (*t*-BuNC)

A mixture of *t*-BuNC (34 mg, 0.41 mmol) and $Ru_3(CO)_{12}$ (200 mg, 0.26 mmol) in toluene (70 ml) was heated at 55° for 3 h. The solvent was then removed *in vacuo*, and the residue chromatographed under nitrogen on Florisil. Elution with 15% benzene/heptane gave deep crimson $Ru_3(CO)_8(CNBu^t)(PMe_3)_3$ (72) (29 mg, 13%); m.p. >300° [Found: C - 32.07, H - 4.01, N - 1.92%, *M* (mass spectrometry) = 841; $C_{22}H_{36}O_8NP_3Ru_3$ requires C - 31.51, H - 4.32, N - 1.67%, *M* - 841.] Infra-red (C_6H_{12}): ν(CN) = 2156m; ν(CO) = 2055m, 2030w, 2020m, 1975vs, 1938s, 1885vs, 1845w cm^{-1}; ^1H n.m.r. δ [$(CD_3)_2CO$] = 1.84d [J_{P-H} = 11 Hz] (27), PMe_3, 1.44s (9), Bu^t. Further elution with 75% benzene/heptane gave deep

crimson $Ru_3(CO)_7(CNBu^t)_2(PMe_3)_3$ (73) (54 mg, 29%); m.p. >300° [Found: C - 39.82, H - 6.01, N - 2.68%, *M* (mass spectrometry) = 896; $C_{26}H_{45}O_7N_2P_3Ru_3 \cdot C_6H_6$ requires C - 39.55, H - 5.28, N - 2.88%, *M* - 896.] Infra-red (C_6H_6): ν(CN) = 2145vw; ν(CO) = 2023m, 1981m, 1940vs, 1821w cm^{-1}; ^1H n.m.r. δ [$(CD_3)_2CO$] = 7.60m (6), C_6H_6, 1.84d [J_{P-H} = 12 Hz] (27), PMe_3, 1.51s (18), Bu^t. Elution with benzene gave red-black $Ru_3(CO)_6(PMe_3)_3(CNBu^t)$ (74) (18 mg, 9%); m.p. >300° [Found C - 30.24, H - 4.38, N - 1.19, *M* (mass spectrometry) = 785; $C_{20}H_{36}O_6NP_3Ru_3$ requires C - 30.69, H - 4.63, N - 1.79%, *M* - 785.] Infra-red (CH_2Cl_2): ν_{CN} = 1715w; ν(CO) = 2001m, 1982s, 1965m, 1942m, 1935sh cm^{-1}; ^1H n.m.r. δ [$(CD_3)_2CO$] = 1.88d [J = 12 Hz] (27), PMe_3, 1.60s (9), Bu^t.

$Ru_3(CO)_9(PPh_3)_3$ + t-BuNC

A mixture of t-BuNC (19 mg, 0.23 mmol) and $Ru_3(CO)_9(PPh_3)_3$ (175 mg, 0.130 mmol) in benzene (100 ml) was heated at reflux point for 6 h. The reaction was monitored by t.l.c. The solvent was removed *in vacuo* and preparative t.l.c. (Kieselgel H adsorbent; 30% diethyl ether/ cyclohexane developer) under nitrogen resulted in separation of eight products, leaving a dark brown baseline.

i) dark red $Ru_3(CO)_8(CNBu^t)(PPh_3)_3$ (75) (27 mg, 15%); R_f = 0.68, recrystallised from n-hexane. Infra-red (C_6H_{12}): ν(CN) = 2158m; ν(CO) = 2061m, 2040m, 2032sh, 2024m, 2003vs, 1976vs, 1888vs, 1865s cm^{-1}. (Found: C - 57.90, H - 3.74, N - 1.27%; $C_{67}H_{54}NO_8P_3Ru_3$ requires C - 57.59, H - 3.89, N - 1.00%); ^1H n.m.r. δ[$(CD_3)_2CO$] = 7.55m (45), PPh_3, 1.49s (9), Bu^t;

ii) crimson $Ru_3(CO)_7(CNBu^t)_2(PPh_3)_3$ (76) (42 mg, 25%); R_f = 0.54, recrystallised from n-hexane. Infra-red (C_6H_{12}): ν(CN) = 2158m; ν(CO) = 2028m, 2005m, 1999sh, 1988vs, 1944vs, 1939sh, 1867s, 1833sh cm^{-1} (Found: C - 59.17, H - 4.16, N - 2.19%; $C_{71}H_{63}N_2O_7P_3Ru_3$

requires C - 58.71, H - 4.37, N - 1.93%); ^{1}H n.m.r. δ [$(CD_3)_2CO$] = 7.53m (45), PPh_3, 1.52s (18), Bu^t.

iii) six other bands and a baseline were only partially characterised.

$Ru_3(CO)_9(PMe_3)_3$ + Dimethylacetylenedicarboxylate (DMA)

A mixture of dimethylacetylenedicarboxylate (600 mg, 4.22 mmol) and $Ru_3(CO)_9(PMe_3)_3$ (790 mg, 1.01 mmol) in toluene (200 ml) was heated at reflux point for 15 days. The solvent was then removed *in vacuo* and preparative t.l.c. (Keiselgel HF_{254} adsorbent, 75% benzene/hexane developer) isolated the following products:

i) yellow $Ru_2(CO)_6[\eta\text{-}C_2(CO_2Me)_2](PMe_3)_2$ (77) (61 mg, 10%); R_f = 0.88, recrystallised from benzene/n-hexane; m.p. = 272-274°. Infra-red (C_6H_{12}): ν(CO) = 2034s, 2009vs, 1981s, 1966sh, 1690vs cm^{-1}. [Found: C - 38.79, H - 4.38%, *M* (mass spectrometry) = 666; $C_{18}H_{24}O_8P_2Ru_3 \cdot C_6H_6$ requires C - 38.81, H - 4.07%, *M* - 666]; ^{1}H n.m.r. δ ($CDCl_3$) = 7.53m (6), C_6H_6, 3.12s (6), Me, 1.89d [J_{P-H} = 10 Hz] (18), PMe_3;

ii) red $Ru_3(CO)_7[\eta\text{-}C_2(CO_2Me)_2](PMe_3)_3$ (78) (31 mg, 4%); R_f = 0.70, recrystallised from CH_2Cl_2/n-pentane; m.p. = 147-148°. Infra-red (CH_2Cl_2): ν(CO) = 2051m, 1988s, 1890sh, 1875w, 1725s cm^{-1}. [Found: C - 30.15, H - 3.70%, *M* (mass spectrometry) = 872; $C_{22}H_{33}O_{11}P_3Ru_3$ requires C - 30.39, H - 3.82%, *M* - 872]; ^{1}H n.m.r. δ ($CDCl_3$) = 2.96s (6), Me, 1.85d [J_{P-H} = 10 Hz] (27), PMe_3.

iii) red $Ru_3(CO)_6[\eta\text{-}C_2(CO_2Me)_2](PMe_3)_3$ (79) (97 mg, 12%); R_f = 0.44, recrystallised from CH_2Cl_2/n-hexane; m.p. = 180-181°. Infra-red (CH_2Cl_2): ν(CO) = 2052m, 2017s, 2010sh, 1991m, 1961s, 1710s cm^{-1}. [Found: C - 29.58; H - 4.26, P - 11.86%, *M* (mass spectrometry) = 844; $C_{21}H_{33}O_{10}P_3Ru_3$ requires C - 29.96, H - 3.95, P - 11.04%, *M* - 844]; ^{1}H n.m.r. δ ($CDCl_3$) = 3.01s (6), Me, 1.82d [J_{P-H} = 10 Hz] (27), PMe_3.

iv) brown $Ru_4(CO)_8[\eta\text{-}C_2(CO_2Me)_2](PMe_3)_4$ (80) (38 mg, 4%); R_f = 0.19, recrystallised from ethanol/benzene; m.p. >300°. Infra-red (CH_2Cl_2): ν(CO) = 2090m, 2080m, 2035vs, 1974vs, 1710vs cm^{-1}. [Found: C - 28.77; H - 3.01%, *M* (mass spectrometry) = 1077; $C_{26}H_{42}O_{12}P_4Ru_4$ requires C - 29.06, H - 3.93%, *M* - 1077]; ^1H n.m.r. δ [$(CD_3)_2CO$] = 2.75s (6), Me, 1.91d [J_{P-H} = 12 Hz] (36), PMe_3;

v) seven other bands were observed but remained uncharacterised.

$Ru_3(CO)_9(PPh_3)_3$ + Dimethylacetylenedicarboxylate (DMA)

A mixture of dimethylacetylenedicarboxylate (120 mg, 0.844 mmol) and $Ru_3(CO)_9(PPh_3)_3$ (400 mg, 0.298 mmol) in benzene (100 ml) was heated at reflux point for two days. The solvent was then removed *in vacuo*, and preparative t.l.c. (Kieselgel GF_{254} adsorbent, 30% diethyl ether/cyclohexane developer) isolated the following products:

i) orange-red $Ru_3(CO)_7[\eta\text{-}C_2(CO_2Me)_2](PPh_3)_3$ (81) (30 mg, 7%); R_f = 0.61, recrystallised from CH_2Cl_2/n-hexane; m.p. = 304-307°. Infra-red (CH_2Cl_2): ν(CO) = 2046s, 1979vs, 1875vw, 1710s cm^{-1}. (Found: C - 55.87, H - 4.03%; $C_{67}H_{51}O_{11}P_3Ru_3$ requires C - 56.34, H - 3.60%); solution M.Wt = 1381 (acetone), required M.Wt = 1,428; ^1H n.m.r. δ($CDCl_3$) = 7.55m (45), PPh_3, 3.16s (6), Me;

ii) red $Ru_3(CO)_6[\eta\text{-}C_2(CO_2Me)_2](PPh_3)_3$ (82) (62 mg, 15%); R_f = 0.44, recrystallised from CH_2Cl_2/n-hexane; m.p. >300°. Infra-red (CH_2Cl_2): ν(CO) = 2046m, 2013s, 2009sh, 1988m, 1952s, 1711s cm^{-1}. (Found: C - 56.62, H - 3.91, P - 6.47%; $C_{66}H_{51}O_{10}P_3Ru_3$ requires C - 56.66, H - 3.67, P - 6.63%); solution M.Wt = 1433 (acetone), requires M.Wt = 1,400; ^1H n.m.r. δ ($CDCl_3$) = 7.56m (45), PPh_3, 3.21s (6), Me;

iii) dark crimson $Ru_3(CO)_5[\eta\text{-}C_2(CO_2Me)_2]_2(PPh_3)_3$ (83) (62 mg, 14%); R_f = 0.40, recrystallised from CH_2Cl_2/n-hexane; m.p. >300°.

Infra-red (CH_2Cl_2): ν(CO) = 2062m, 2023s, 2019sh, 1999m, 1970s, 1890m, 1865m, 1832m, 1720s cm^{-1}. (Found: C - 55.12, H - 3.99%; $C_{71}H_{57}O_{13}P_3Ru_3$:0.5$CH_2Cl_2$ requires C - 55.16, H - 3.75%); solution M.Wt = 1,498 (acetone), required M.Wt = 1,514; ^{1}H n.m.r. δ [$(CD_3)_2CO$] = 7.54m (45), PPh_3, 3.73s (1), CH_2Cl_2, 2.84s (6), 2.62s (6), Me;

iv) brown $Ru_4(CO)_8[\eta$-$C_2(CO_2Me)_2](PPh_3)_4$ (84) (38 mg, 7%); R_f = 0.10, recrystallised from ethanol/benzene; m.p. = 232-236°. Infra-red (CH_2Cl_2): ν(CO) = 2110m, 2090m, 2043vs, 1981vs, 1726sh, 1710vs cm^{-1}. (Found: C - 57.91, H - 4.35%; $C_{86}H_{66}O_{12}P_4Ru_4$:$C_6H_6$ requires C - 58.23, H - 3.82%); solution M.Wt = 1961 (acetone), required M.Wt = 1898; ^{1}H n.m.r. δ [$(CD_3)_2CO$] = 7.60m (66), PPh_3, 2.82s (6), Me;

v) six other bands were observed but remained uncharacterised.

$Ru_3(CO)_9(PMe_3)_3$ + $HC\equiv C\text{-}Bu^t$

A mixture of tertiary butyl acetylene (270 mg, 3.29 mmol) and $Ru_3(CO)_9(PMe_3)_3$ (300 mg, 0.383 mmol) in benzene (150 ml) was heated at reflux point for 5 days. The solvent was then removed *in vacuo* and preparative t.l.c. (Kieselgel G adsorbent, 25% acetone/cyclohexane developer) gave 12 brightly coloured bands, from which the following products could be characterised:

i) red $HRu_3(CO)_6(PMe_3)_3(C_2Bu^t)$ (90) (57 mg, 19%); R_f = 0.71, recrystallised from n-hexane. Infra-red (CH_2Cl_2): ν(CO) = 2048m, 2012m, 1981vs, 1968sh, 1956sh cm^{-1}. [Found: C - 32.44, H - 4.64, *M* (mass spectrometry) = 784; $C_{21}H_{37}O_6P_3Ru_3$ requires C - 32.27, H - 4.77%, *M* - 784]; ^{1}H n.m.r. δ [$(CD_3)_2CO$] = 1.95d [J_{P-H} = 12.5 Hz] (27), PMe_3, 1.41s (9), Bu^t, -21.9m (1), H;

ii) brown $Ru_3(CO)_5(PMe_3)_3(C_2Bu^t)_3$ (91) (18 mg, 5.1%); R_f = 0.21, recrystallised from CH_2Cl_2/n-hexane. Infra-red (CH_2Cl_2): ν(CO) = 2054s, 2023s, 1981vs, 1954, 1821vw cm^{-1} [Found: C - 42.46, H -

5.88%, *M* (mass spectrometry) = 917; $C_{32}H_{54}O_5P_3Ru_3$ requires C - 42.01, H - 5.94%, *M* - 917].

$Ru_3(CO)_9(PPh_3) + HC\equiv C\text{-}Bu^t$

A mixture of tertiary butylacetylene (40 mg, 0.487 mmol) and $Ru_3(CO)_9(PPh_3)_3$ (200 mg, 0.149 mmol) in benzene (75 ml) was heated at reflux point for 3.5h. The solvent was then removed *in vacuo*, and preparative t.l.c. of the residue (20% diethyl ether/cyclohexane developer, Kieselgel H adsorbent) resolved 5 brightly coloured bands, together with a brown baseline:

i) yellow $Ru(CO)_2(PPh_3)_2(C_2Bu^t)_2$ (92) (16 mg, 13%); R_f = 0.96, recrystallised from n-pentane. Infra-red (C_6H_{12}): $\nu(C_2)$ = 2096 vw cm^{-1}; $\nu(CO)$ = 1942m cm^{-1}. (Found C - 71.04, H - 5.37%; $C_{50}H_{48}O_2P_2Ru$ requires C - 71.16, H - 5.73%); ^1H n.m.r. δ ($CDCl_3$) = 7.56m (30), PPh_3, 1.36s (18), Bu^t;

ii) red $HRu_3(CO)_6(PPh_3)_3(C_2Bu^t)$ (93) (39 mg, 20%); R_f = 0.69, recrystallised from n-hexane. Infra-red (C_6H_{12}): $\nu(CO)$ = 2080m, 2023m, 2001vs, 1972m, 1955sh cm^{-1}. (Found C - 58.46, H - 4.50%; $C_{66}H_{55}O_6P_3Ru_3$ requires C - 59.15, H - 4.13%); solution M.Wt = 1301 (acetone), required M.Wt = 1340; ^1H n.m.r. δ [$(CD_3)_2CO$] = 7.48m (45), PPh_3, 1.38s (9), Bu^t, -22.1m (1), H;

iii) red-orange $HRu_3(CO)_5(PPh_3)_2(C_{12}H_{19})$ (94) (13 mg, 8%); R_f = 0.37, recrystallised from ethanol/benzene. Infra-red (CH_2Cl_2): $\nu(CO)$ = 2060s, 2011vs, 1985m, 1932w, 1850 vw cm^{-1}. (Found: C - 56.82, H - 4.22%; $C_{53}H_{50}O_5P_2Ru_3$ requires C - 56.23, H - 4.45%); ^1H n.m.r. δ [$(CD_3)_2CO$] = 7.50m (30), PPh_3 5.48s (1), 1.36s (18), $C_{12}H_{19}$, -21.7m (1), H;

iv) crimson $HRu_3(CO)_4(PPh_3)_2(C_{18}H_{29})$ (95) (18 mg, 7%); R_f = 0.08, recrystallised from ethanol/benzene. Infra-red (CH_2Cl_2): $\nu(CO)$ =

1995vs, 1984s, 1957s, 1930m cm^{-1}. (Found: C - 58.56, H - 6.00%; $C_{58}H_{60}O_4P_2Ru_3$ requires C - 58.73, H - 5.09%); ^1H n.m.r. δ [$(CD_3)_2CO$] = 7.51m (30), PPh_3, 6.35s (1), 5.72s (1), 1.36s (27), $C_{18}H_{29}$, -19.1m (1), H;

v) yellow uncharacterised band observed at R_f = 0.75.

$Ru_3(CO)_{10}(PPh_3)_2 + HC\equiv C\text{-}Bu^t$

A mixture of HC_2Bu^t (22 mg, 0.268 mmol) and $Ru_3(CO)_{10}(PPh_3)_2$ (200 mg, 0.181 mmol) in n-hexane (75 ml) was heated at reflux point for 1 h. The reaction was followed by t.l.c. The solvent was then removed *in vacuo*, and preparative t.l.c. (20% diethyl ether/cyclohexane developer, Kieselgel G adsorbent) gave nine brightly coloured bands, of which the following were characterised:

i) orange $HRu_3(CO)_8(PPh_3)_2(C_2Bu^t)$ (87) (62 mg, 30%); R_f = 0.62, recrystallised from diethyl ether/ n-pentane; m.p. = 163°. Infra-red (C_6H_{12}): ν(CO) = 2075s, 2054s, 2043w, 2012vs, 2004s, 1994sh, 1975m, 1950m cm^{-1}. (Found: C - 53.19, H - 3.57, P - 5.59%; $C_{50}H_{40}O_8P_2Ru_3$ requires C - 53.21, H - 3.64, P - 5.60%); solution M.Wt = 1198 (acteone), 1141 (benzene), required M.Wt = 1134; ^1H n.m.r. δ [$(CD_3)_2CO$] = 7.50m (30), PPh_3, 1.38s (9), Bu^t, -20.8s (0.5), -21.15s (0.5), H;

ii) orange $HRu_3(CO)_7(PPh_3)_2(C_2Bu^t)$ (88) (85 mg, 42%); R_f = 0.56, recrystallised from diethyl ether/n-pentane. Infra-red (C_6H_{12}): ν(CO) = 2049s, 2008s, 1985vs, 1950m, 1932m, 1923m cm^{-1}; ^1H n.m.r. δ($CDCl_3$) = 7.50m (30), PPh_3, 1.38s (9), Bu^t, -21.5m (1), H. Identified by comparison with literature sample.[539]

iii) red $HRu_3(CO)_5(PPh_3)_2(C_2Bu^t)$ (89) (40 mg, 21%); R_f = 0.36, recrystallised from diethyl ether/n-pentane. Infra-red (C_6H_{12}): ν(CO) = 2076m, 2054vs, 1893vs, 1885s, 1846m cm^{-1}. (Found: C - 54.11, H - 4.06, P - 5.53%; $C_{47}H_{40}O_5P_2Ru_3$ requires C - 53.71,

H - 3.93, P - 5.89%); solution M.Wt = 1003 (acetone), 1021 (benzene), required M.Wt = 1050; ^{1}H n.m.r. δ[$(CD_3)_2CO$] = 2.55m (30), PPh_3, 1.40s (9), Bu^t, -21.1m (1), H;

iii) six other bands (trace quantities) remain uncharacterised.

$Ru_3(CO)_{11}(PPh_3)$ + $HC\equiv C\text{-}Bu^t$

A mixture of tertiary butylacetylene (16 mg, 0.195 mmol) and $Ru_3(CO)_{11}(PPh_3)$ (150 mg, 0.72 mmol) in n-hexane (55 ml) was heated at reflux point for 1.5 h. The reaction was followed by t.l.c. The solvent was then removed *in vacuo*, and preparative t.l.c. (Kieselgel GF_{254} adsorbent, 15% diethyl ether/cyclohexane developer) gave six bands, of which the following were characterised:

i) red $HRu_3(CO)_8(PPh_3)(C_2Bu^t)$ (85) (109 mg, 73%); R_f = 0.75, recrystallised from n-hexane. Infra-red (C_6H_{12}): ν(CO) = 2091s, 2072s, 2015vs, 1998s, 1984sh, 1960sh cm^{-1}. (Found: C - 43.23, H - 2.90%; $C_{32}H_{25}O_8PRu_3$ requires C - 44.09, H - 2.89%); solution M.Wt = 855 (acetone), 879 (benzene), required M.Wt = 872; ^{1}H n.m.r. δ ($CDCl_3$) = 7.51m (15), PPh_3, 1.32s (9), Bu^t, -21.2d [J_{P-H} = 2.5 Hz], (1), H. Checked by comparison with literature sample.[539]

ii) orange-red $HRu_3(CO)_6(PPh_3)(C_{12}H_{19})$ (86) (8 mg, 6%); R_f = 0.52, recrystallised from diethyl ether. Infra-red (C_6H_{12}): ν(CO) = 2089s, 2056s, 2018vs, 2001sh, 1971m cm^{-1}. (Found: C - 46.72, H - 3.65%; $C_{36}H_{35}O_6PRu_3$ requires C - 46.82, H - 3.92%); solution M.Wt = 901 (acetone), required M.Wt - 898.

iii) four other bands (trace quantities) remained uncharacterised.

$Ru_3(CO)_{10}(PPh_3)_2$ + *t*-BuNC

A mixture of *t*-BuNC (10 mg, 0.12 mmol) and $Ru_3(CO)_{10}(PPh_3)_2$ (108 mg, 0.097 mmol) in n-hexane (100 ml) was heated at reflux point for 20

min. The solvent was removed *in vacuo*, and preparative t.l.c. (Kieselgel H, 30% diethyl ether/ cyclohexane) of the residue gave one major product and four minor products (remaining uncharacterised). Deep red $Ru_3(CO)_9(CNBu^t)(PPh_3)_2$ (96) (69 mg, 61%); R_f = 0.79, recrystallised from n-hexane. Infra-red (C_6H_{12}): ν(CN) = 2141m cm^{-1}; ν(CO) = 2078m, 2068m, 2042s, 2004vs, 1993s, 1988s, 1977sh, 1958sh cm^{-1}. (Found: C - 51.54, H - 3.59, N - 1.30%; $C_{50}H_{39}NO_9P_3Ru_3$ requires C - 51.64, H - 3.38, N - 1.20%); ^1H n.m.r. δ [$(CD_3)_2CO$] = 7.50m (30), PPh_3, 1.51s (9), Bu^t.

$Ru_3(CO)_{10}(PPh_3)_2 + PMe_3$

A mixture of PMe_3 (35 mg, 0.46 mmol) and $Ru_3(CO)_{10}(PPh_3)_2$ (100 mg, 0.90 mmol) in benzene (45 ml) was heated at 40-43°C for 16 h. The reaction was followed by infra-red spectroscopy. Chromatography on alumina resulted in extensive decomposition, though $Ru_3(CO)_9(PPh_3)_2(PMe_3)$ (97) was eluted with n-hexane. The crude product was recrystallised from diethyl ether/n-hexane to give (97) (71 mgs, 68%). Infra-red (C_6H_{12}): ν(CO) = 2053w, 2005sh, 1991sh, 1969vs, 1950sh cm^{-1}. (Found: C - 50.05, H - 3.52%; $C_{48}H_{39}O_9P_3Ru_3$ requires C - 49.87, H - 3.40%); ^1H n.m.r. δ ($CDCl_3$) = 2.54m (30), PPh_3, 1.82d [J = 12 Hz] (9), PMe_3.

$Ru_3(CO)_9(PMe_3)_3 + H_2O$

A solution of $Ru_3(CO)_9(PMe_3)_3$ (100 mg, 0.13 mmol) in dimethoxyethane (50 ml) and water (3 ml) was heated at reflux point for 3.5 days. The solvent was removed *in vacuo*, and preparative t.l.c. of the residue (Kieselgel H adsorbent, 30% acetone/diethyl ether developer) separated 5 brightly coloured bands, including a brown baseline. Severe decomposition occurred on chromatography. No products could be characterised, but the following spectral information enables easy identification of the products:

i) Band one - yellow; R_f = 0.95. Infra-red (C_6H_{12}): ν(CO) = 2063m, 2022s, 1999s, 1992sh, 1987s, 1967sh, 1957vs, 1949m cm^{-1}; ^1H n.m.r. δ (C_6F_6) = 4.10d [J = 7 Hz] (1), 2.2-0.8m (45); 35 mg.

ii) Band two - yellow; R_f = 0.67. Infra-red (C_6H_{12}): ν(CO) = 2073w, 2050s, 1987vs, 1942w cm^{-1}; ^1H n.m.r. δ [$(CD_3)_2CO$] = 7.80s (1), 4.18m (1), 2.0-1.0m (44); 27 mg.

iii) Band three - orange brown; R_f = 0.44. Infra-red (C_6H_{12}): ν(CO) = 2068m, 2037s, 1982sh, 1957vs cm^{-1}; 12 mg.

iv) Band four - black; R_f = 0.11. Infra-red (C_6H_{12}): ν(CO) = 2050m, 2036sh, 1951vs cm^{-1}; 7 mg.

v) Baseline - brown; 18 mg.

$Ru_3(CO)_9(PPh_3)_3$ + Alumina

i) A mixture of $Ru_3(CO)_9(PPh_3)_3$ (1·062 gm, 0.791 mmol) and 25 gm of alumina (Fluka, pH = 7.0 ± 0.5, 100-200 mesh, Type 507C) in benzene (65 ml) was stirred for 4 days. Chromatography of this mixture gave two bands:

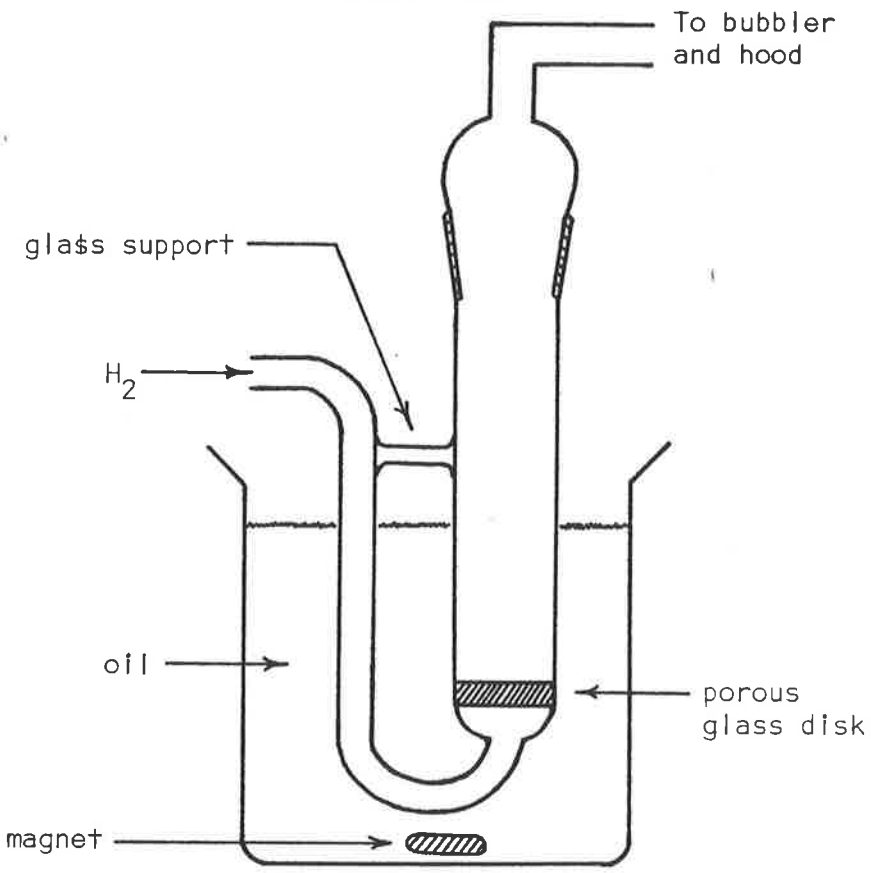
i) red $Ru_3(CO)_9(PPh_3)_3$ (889 mg, 84%) eluted with benzene

ii) yellow unknown - 49 mg (eluted with methanol). Infra-red (C_6H_{12}): ν(CO) = 2063s, 2052sh, 2034m, 2016m, 1987vs, 1958s, 1910w cm^{-1}; recrystallisation from diethyl ether/n-hexane initially gave a white powder with yellow flakes, further cooling of the solution to -78°C (4 days) produced some very small orange crystals as well. Further chromatography could not separate this product mixture.

ii) The complex $Ru_3(CO)_9(PPh_3)_3$ (506 mg, 0.375 mmol) in CH_2Cl_2 (60 ml) was adsorbed onto 15 gm of alumina by slowly removing the solvent *in vacuo*. The resulting solid residue was allowed to stand at room temperature for 43 days. Chromatography on neutral alumina recovered 72% $Ru_3(CO)_9(PPh_3)_3$. A further yellow fraction was eluted with methanol (*vide supra*) - 73 mg.

$Ru_3(CO)_9(PPh_3)_3 + H_2$

FIGURE 32



Apparatus for the hydrogenation of metal clusters

The complex $Ru_3(CO)_9(PPh_3)_3$ (100 mg, 0.075 mmol) in xylene (100 ml) was heated at 130°C for 2 h with H_2 vigorously bubbling through the solution (see Figure 32). Chromatography on Florisil gave $H_4Ru_4(CO)_{10}(PPh_3)_2$[50] (24c) (22mg, 24%) eluted with n-hexane. Infra-red (C_6H_{12}): ν(CO) = 2079m, 2062s, 2052m, 2036m, 2022vs, 2013s, 2003w, 1977w, 1960w cm^{-1}. (Found: C - 45.57, H - 2.18%; $C_{46}H_{34}O_{10}P_2Ru_4$ requires C - 45.55, H - 2.82%); ^1H n.m.r. δ ($CDCl_3$) = 7.54m (30), PPh_3, -16.4m (4), H; followed by $H_4Ru_4(CO)_9(PPh_3$[50] (98) (43 mg, 48%); eluted with n-hexane. Infra-red (C_6H_{12}): ν(CO) = 2068s, 2024vs, 2003s, 1993s, 1987sh, 1963s, 1945sh, 1940m cm^{-1} (Found C - 52.67, H - 4.44%; $C_{63}H_{49}D_9P_3Ru_4$ requires C - 52.28, H - 3.41%); ^1H n.m.r. δ ($CDCl_3$) = 7.55m (45), PPh_3, 26.6m (4),. H. Two other fractions were eluted with n-hexane (*vide infra*), but remain uncharacterised. One further fraction was eluted with acetone (also uncharacterised).

i) yellow fraction. Infra-red (C_6H_{12}): ν(CO) = 2082w, 2077sh, 2061m, 2048vs, 2033s, 2017vs, 1993s, 1987s, 1966s, 1953m, 1950sh cm^{-1} (eluted with n-hexane);

ii) orange-red fraction. Infra-red (C_6H_{12}): ν(CO) = 2062m, 2048m, 2038s, 2019m, 1987s, 1964vs, 1950sh cm^{-1} (eluted with n-hexane);

iii) brown. Infra-red (C_6H_{12}): ν(CO) = 2072m, 2063m, 2040m, 1990sh, 1963vs cm^{-1} (eluted with acetone).

$Ru_3(CO)_9(PMe_3)_3 + H_2$

The complex $Ru_3(CO)_9(PMe_3)_3$ (250 mg, 0.319 mmol) in n-octane (180 ml) was heated at reflux point for 2.5 h with H_2 vigorously bubbling through the solution (see Figure 32). Chromatography on Florisil resulted in some decomposition, but the following products were isolated:

i) orange $H_4Ru_4(CO)_{10}(PMe_3)_2$ (99) (29 mg, 11%); eluted with n-hexane. Infra-red (C_6H_{12}): ν(CO) = 2082m, 2061s, 2042w, 2023vs, 2005s, 1975w cm^{-1}. [Found: C - 22.82, H - 2.64%, *M* (mass spectrometry) = 843; $C_{16}H_{22}O_{10}P_2Ru_4$ requires C - 22.86, H - 264%, *M* - 843]; ^{1}H n.m.r. δ (C_6F_6) = 1.80d [J = 11 Hz] (18), PMe_3, -17.82t (4), H;

ii) red-orange $H_4Ru_4(CO)_9(PMe_3)_3$ (99) (38 mg, 13%); eluted with n-hexane. Infra-red (C_6H_{12}): ν(CO) = 2065m, 2035vs, 2017s, 2000s, 1988m, 1977m, 1966sh cm^{-1}. [Found: C - 24.54, H - 3.40%, *M* (mass spectrometry) = 891; $C_{18}H_{31}O_9P_3Ru_4$ requires C - 24.33, H - 3.51%, *M* - 891]; ^{1}H n.m.r. δ (C_6F_6) = 1.82d [J = 11 Hz] (27), PMe_3, -17.86q (4), H;

iii) red $H_4Ru_4(CO)_8(PMe_3)_4$ (100) (58 mg, 19%); eluted with n-hexane. Infra-red (C_6H_{12}): ν(CO) = 2021vs, 1991m, 1972s cm^{-1}. [Found: C - 25.22, H - 4.53%, *M* (mass spectrometry) = 939; $C_{20}H_{40}O_8P_4Ru_4$ requires C - 24.33, H - 3.51%, *M* - 939]; ^{1}H n.m.r. δ (C_6F_6) = 1.81d [J = 11 Hz] (36), PMe_3, -17.99qu (4), H;

iv) yellow unknown eluted with n-hexane. Infra-red (C_6H_{12}): ν(CO) = 2103m, 2087m, 2078s, 2068vs, 2034vs, 2020s, 2009s, 1999m, 1991sh, 1987w, 1981w cm^{-1};

v) orange unknown eluted with diethyl ether; m.p. = 185-186°. Infra-red (C_6H_{12}): ν(CO) = 2087m, 2070s, 2062m, 2043m, 2038w, 2022vs, 2013s, 1999m, 1997sh, 1991w, 1981m cm^{-1}.

$Ru_3(CO)_9(PMe_3)_3$ + Silica gel

The complex $Ru_3(CO)_9(PMe_3)_3$ (1.132 gm, 1.445 mmol) and 100 gm of Silica gel (Ajax, 100-200 mesh, Grade 12) in benzene (175 ml) was stirred overnight. Chromatography (4 foot column) on Silica gel (100-200 mesh) gave $Ru_3(CO)_9(PMe_3)_3$ (1.089 gm, 96.2%); eluted with 5% benzene/:n-hexane. Further chromatography with 50% benzene/n-hexane gave two pale red products, both eluted almost simultaneously:

i) Infra-red (CH_2Cl_2): ν(CO) = 2050vw, 1975vs, 1942m cm^{-1}; ^1H n.m.r. δ (CD_2Cl_2) = 1.95d [J = 12 Hz] (9), 1.82d [J = 12 Hz] (18), PMe_3 (Found: C - 40.80%, H - 5.56%), 19 mg;

ii) Infra-red (CH_2Cl_2): ν(CO) = 2050vw, 1976vs, 1942m cm^{-1}; ^1H n.m.r. δ (CD_2Cl_2) = 1.93d [J = 10 Hz] (9), 1.81d [J = 12 Hz] (18), PMe_3 (Found: C - 40.89%, H - 5.74%), 23 mg.

$Ru_3(CO)_{11}(CNBu^t)$ + $2PCy_3$

A mixture of $Ru_3(CO)_{11}(CNBu^t)$ (495 mg, 0.713 mmol) and PCy_3 (404 mg, 1.440 mmol) in thf (125 ml) was heated at reflux point for 3 h. The reaction was followed by t.l.c. The solution was cooled, filtered (paper), and the solvent removed *in vacuo*. The residue was taken up in n-hexane and chromatographed on Florisil to give purple *crystals* of $Ru_3(CO)_9(CNBu^t)(PCy_3)_2$ (101) (782 mg, 91%); eluted with 5% diethyl ether/n-hexane; m.p. = 263-265°. Infra-red (C_6H_{12}): ν(CN) = 2150w, ν(CO) = 2058m, 2033s, 2021s, 2009s, 1993vs, 1987vs, 1964m, 1926m, 1864w cm^{-1}. (Found: C - 50.21, H - 6.63, N - 1.54, P - 6.31%;

$C_{50}H_{75}O_9NP_2Ru_3$ requires C - 50.04, H - 6.30, N - 1.17, P - 5.09%); solution M.Wt = 1212 (acetone), 1221 (benzene), 1190 ($CHCl_3$), required M.Wt = 1199; ^1H n.m.r. δ [$(CD_3)_2CO$] = 2.0-0.6m, PCy_3 + Bu^t.

$Ru_3(CO)_{11}(CNBu^t)$ + I_2

A mixture of $Ru_3(CO)_{11}(CNBu^t)$ (160 mg, 0.230 mmol) and I_2 (400 mg, 1.58 mmol) in benzene (40 ml) was stirred for 2 h. The solvent was removed *in vacuo* and the products extracted with boiling n-hexane (2 x 50 ml). Slow evaporation of this n-hexane solution gave orange *microcrystals* of $Ru_3I_2(CO)_9(CNBu^t)$ (102) (121 mg, 59%); m.p. >300°. Infra-red (C_6H_{12}): ν(CN) = 2122m; ν(CO) = 2099w, 2079vs, 2070s, 2050s, 2037w, 2026m, 2021sh, 2010w cm^{-1}. (Found: C - 18.61, H - 2.07, N - 0.80, O - 13.89, I - 27.35%; $C_{14}H_9O_9NI_2Ru_3$ requires C - 18.84, H - 1.02, N - 1.57, O - 16.14, I - 28.44%); ^1H n.m.r. δ ($CDCl_3$) = 1.69s, Bu^t; solution M.Wt = 845 (acetone), 887 (benzene), required M.Wt = 892. Further evaporation of the n-hexane solution gave a mixture of products. The remaining solution had the solvent removed *in vacuo* and recrystallisation by slow diffusion of isopentane into a diethyl ether solution of the residue gave orange-brown $Ru_3I_7(CO)_{11}(CNBu^t)$ (103) (28 mg, 7.7%); m.p. >300°. Infra-red (C_6H_{12}): ν(CN) = 2156w; ν(CO) = 2089m, 2056m, 2044vs, 2011s, 1993s, 1982s, 1950m cm^{-1}. (Found: C - 14.06, H - 0.82, N - 0.96, I - 58.75%; $C_{16}H_9O_{11}NI_7Ru_3$ requires C - 12.14, H - 0.57, N - 0.88, J - 57.12%); ^1H n.m.r. δ ($CDCl_3$) = 1.68s (2), 1.60s (1), Bu^t.

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CHAPTER TWO

REACTIONS BETWEEN $Ru_3(CO)_{11}(CNBu^T)$ AND $Pt(\eta\text{-}C_2H_4)(PPh_3)_2$ AND RELATED CHEMISTRY

INTRODUCTION

Some years ago, it was observed that the complexes $Pt(PR_3)_4$ or $Pt(\eta^2\text{-}PhHC=CHPh)(PPh_3)_2$ react with $Fe_2(CO)_9$, $Ru_3(CO)_{12}$ or $H_2Os(CO)_4$ to give a variety of heteronuclear trimetal complexes (see Figure 1).[1-6] Generally, the yields of the trimetal species from these reactions are very low, the major products being tertiary phosphine-substituted derivatives of iron, ruthenium or osmium carbonyls. These results can be attributed to two factors

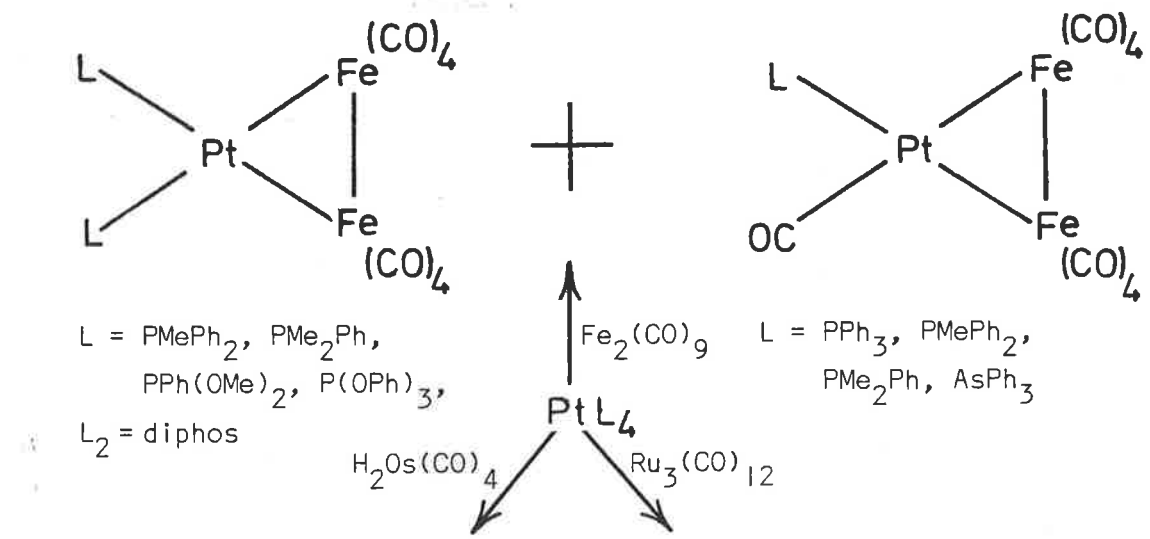
i) the well established stability of the $M_3(CO)_{12}$ triangle (M = Ru, Os; *cf.* Chapter I), and

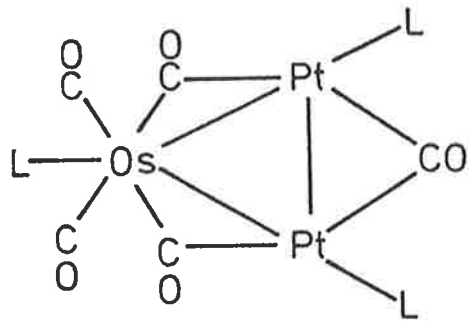
ii) the presence of PR_3, produced by dissociation of $Pt(PR_3)_4$, resulting in preferential formation of $M_3(CO)_{12-n}(PR_3)_n$, rather than the desired heterometallic clusters.

A more favourable route to heterometallic clusters containing platinum[7,8] became available with the discovery of the complexes $Pt(\eta\text{-}C_2H_4)(PR_3)_2$,[9-14] $Pt(\eta\text{-}C_2H_4)_2PR_3$[15,16] and $Pt(\eta\text{-}C_2H_4)_3$.[16] The $Pt(\eta\text{-}C_2H_4)(PR_3)_2$ complexes are stable in the solid state, although loss of ethylene together with oxidative addition to $Pt(PR_3)_2$ occurs on treatment with a variety of reagents.[11,17-21] These zerovalent platinum-ethylene reagents do not suffer the disadvantage of tertiary phosphine dissociation as do the $Pt(PR_3)_4$ complexes.[22] Hence, $FeCl(CO)_2(\eta\text{-}C_5H_5)$ reacts with $Pt(\eta\text{-}C_2H_4)(PPh_3)_2$ to give a reasonable yield of $FePtCl(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)$.[19]

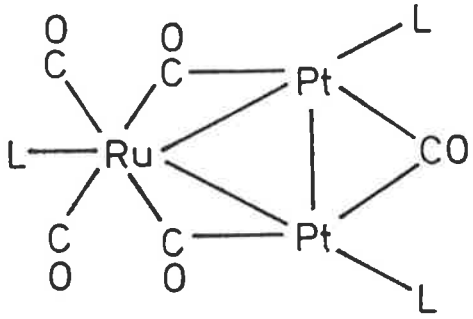
Stone *et al.* have utilized the 46-electron complex $H_2Os_3(CO)_{10}$, which formally contains an Os = Os bond,[23] to generate the 58-electron *closo*-tetrahedral clusters $H_2Os_3Pt(CO)_{10}(PR_3)$ (see Figure 2) on reaction with $Pt(\eta\text{-}C_2H_4)_2(PR_3)$.[24] Similarly, $H_2Os_3(CO)_{10}$ reacts with $Pt(\eta\text{-}C_2H_4)(PR_3)_2$ to give $H_2Os_3Pt(CO)_{10}(PR_3)_2$ (see Figure 2), a 60-electron, *nido*, "butterfly"

FIGURE I

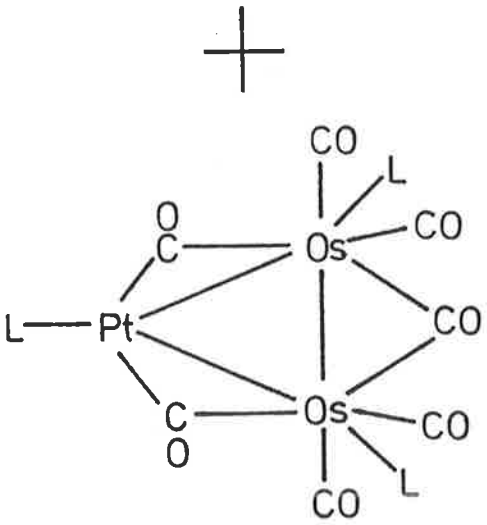




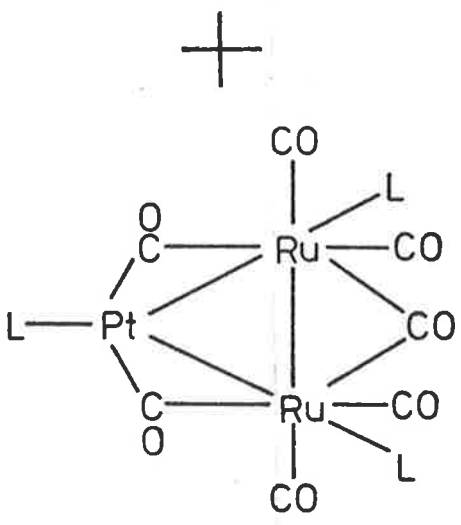
L = PPh_3,[a] $PMePh_2$



L = PPh_3, $PMePh_2$, PMe_2Ph, $AsPh_3$



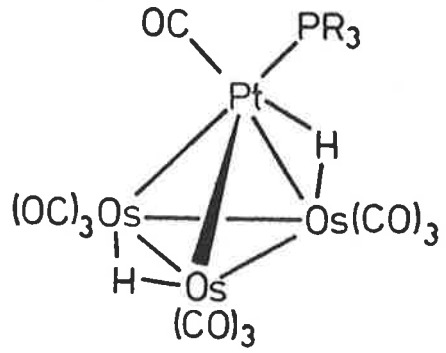
L = $PMePh_2$



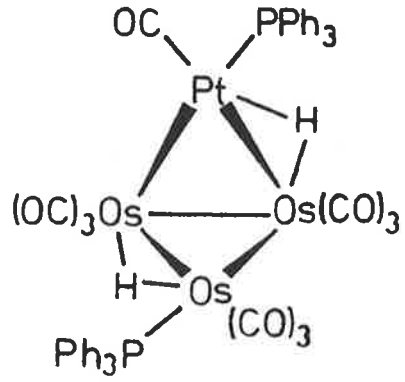
L = PMe_2Ph

[a] $Pt(PPh_3)_2(C_2H_4)$ was used in this experiment.

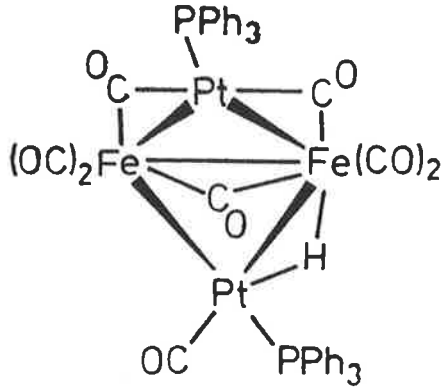
FIGURE 2



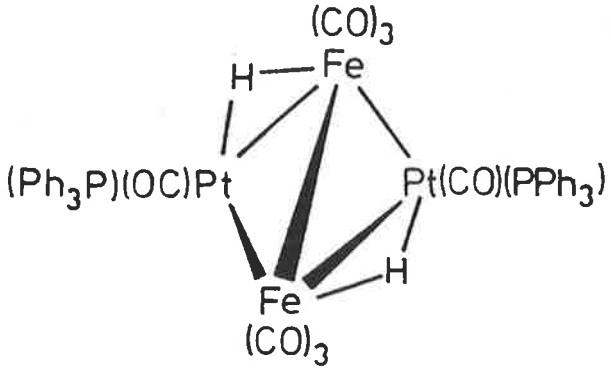
(1) $H_2Os_3Pt(CO)_{10}PR_3$



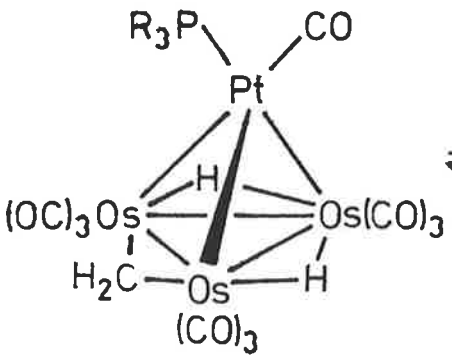
(2) $H_2Os_3Pt(CO)_{10}(PPh_3)_2$



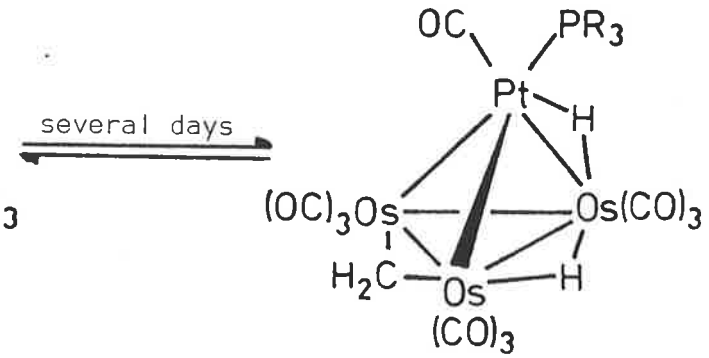
(3) $HFe_2Pt_2(CO)_8(PPh_3)_2$



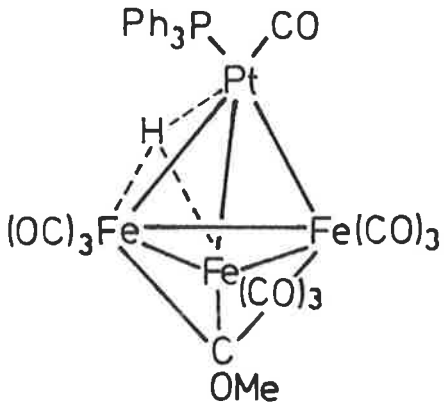
(4) $H_2Fe_2Pt_2(CO)_8(PPh_3)_2$



(5) $H_2Os_3Pt(CO)_{10}(PR_3)(\mu\text{-}CH_2)$



(6) $H_2Os_3Pt(CO)_{10}(PR_3)(\mu\text{-}CH_2)$



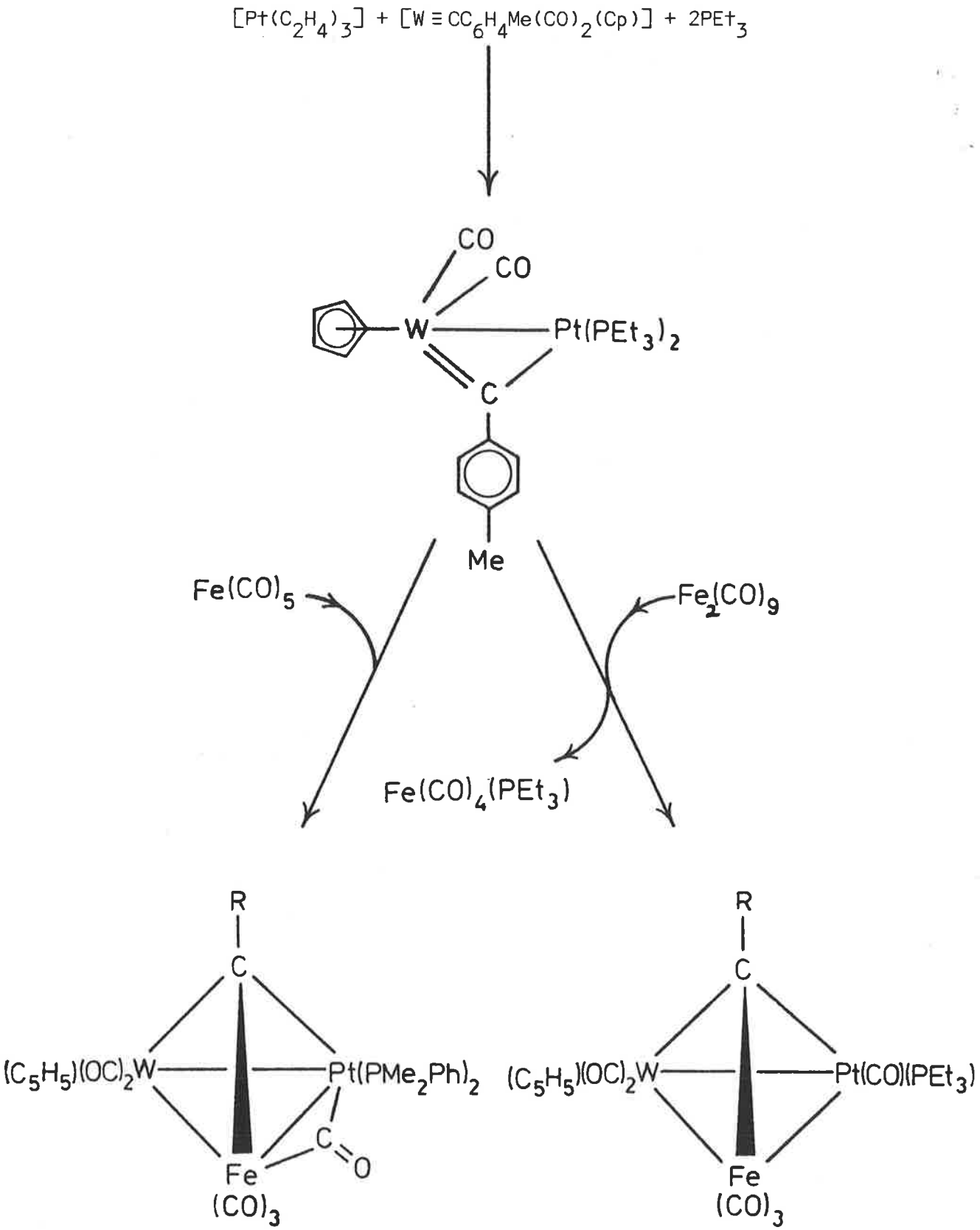
(7) $HFe_3Pt(CO)_{10}(PPh_3)(\mu_3\text{-}COMe)$

cluster, which is also formed by reacting the unsaturated $H_2Os_3Pt(CO)_{10}(PR_3)$ with an equimolar amount of PR_3.[25,26] The readiness with which the Pt(0) complexes [particularly $Pt(\eta\text{-}C_2H_4)_2(PR_3)$] bond a CO ligand makes it possible to synthesize a variety of platinum-containing cluster compounds by reaction of the Pt(0) species with coordinatively and electronically saturated metal carbonyls. The reaction involves the transfer of a CO ligand to a platinum atom, which then inserts into the molecular framework.[8] Thus, $Pt(\eta\text{-}C_2H_4)_2(PPh_3)$ reacts with the anions $[HFe_2(CO)_8]^-$ or $[HFe_3(CO)_{11}]^-$ to give the anions $[HFe_2Pt_2(CO)_8(PPh_3)_2]^-$ and $[HFe_3Pt(CO)_{11}(PPh_3)]^-$, respectively.[27] Protonation of $[HFe_2Pt_2(CO)_8(PPh_3)_2]^-$ affords $H_2Fe_2Pt_2(CO)_8(PPh_3)_2$ (see Figure 2), in which the CO ligands are all terminally bound.[27]

Similar transfer of CO from a metal carbonyl derivative to platinum occurs in the reactions of $H_2Os(CO)_4$ with $Pt(\eta\text{-}C_2H_4)_2(PR_3)$. The products are the diosmium-diplatinum complexes $H_2Os_2Pt_2(CO)_8(PPh_3)_2$ (see Figure 2).[28] Treatment of the unsaturated complex $H_2Os_3Pt(CO)_{10}(PCy_3)$[24] with diazomethane affords, under kinetic control, a single isomer, $H_2Os_3Pt(CO)_{10}(\mu\text{-}CH_2)(PCy_3)$, which isomerises over several days to a second isomer (see Figure 2).[29] In an elegant stepwise synthesis, Stone *et al.*[30] have formed the complexes $FeWPt(CO)_6(PEt_3)_n(\mu_3\text{-}C_6H_4Me\text{-}p)(\eta\text{-}C_5H_5)$ (n = 1, 2; Scheme 1). The reaction of $Pt(\eta\text{-}C_2H_4)(PPh_3)$ with $HFe_3(CO)_{10}(\mu\text{-}COMe)$ was shown to give $HFe_3Pt(CO)_{10}(\mu_3\text{-}COMe)(PPh_3)$.[31]

Recently, treatment of $H_2Os_3Pt(CO)_{10}(PCy_3)$ with either H_2 or CO resulted in the 1:1 adducts $H_4Os_3Pt(CO)_{10}(PCy_3)$ and $H_2Os_3Pt(CO)_{11}(PCy_3)$, respectively, being formed.[32] Both these products revert to the starting complex under nitrogen purge.[32] Reports have appeared on the catalytic activity [33,34] of many of the heterometallic complexes synthesized.

SCHEME I


[Pt(C2H4)3] + [W≡CC6H4Me(CO)2(Cp)] + 2PEt3
CO
CO
W
Pt(PEt3)2
C
Me
Fe(CO)5
Fe2(CO)9
Fe(CO)4(PEt3)
R
C
(C5H5)(OC)2W
Pt(PMe2Ph)2
C=O
Fe
(CO)3
R
C
(C5H5)(OC)2W
Pt(CO)(PEt3)
Fe
(CO)3

Initial correlations between n.m.r. and structural data of some of these complexes have also been investigated.[35]

Platinum readily forms compounds having metal-metal bonds.[36,37] The heterometallic cluster anions $[Fe_3Pt_3(CO)_{15}]^{2-}$, $[Fe_3Pt_3(CO)_{15}]^{-}$, $[Fe_4Pt_6(CO)_{22}]^{2-}$ and $[Fe_4Pt(CO)_{16}]^{2-}$ discovered by Longoni and his coworkers,[38–40] are good examples of the tendency of platinum in this respect. Square planar isonitrile or pyridine complexes, $PtCl_2L_2$, also react with various carbonyl metallate anions to form linear trimetallic complexes, such as $Pt(CNR)_2[Fe(CO)_3NO]_2$.[41-47]

In view of the number of complexes containing Fe/Pt or Os/Pt cluster units thus far characterised, it is somewhat surprising to see the dearth of Ru/Pt clusters synthesized. This has largely been due to the inaccessibility of a suitable ruthenium cluster reagent.

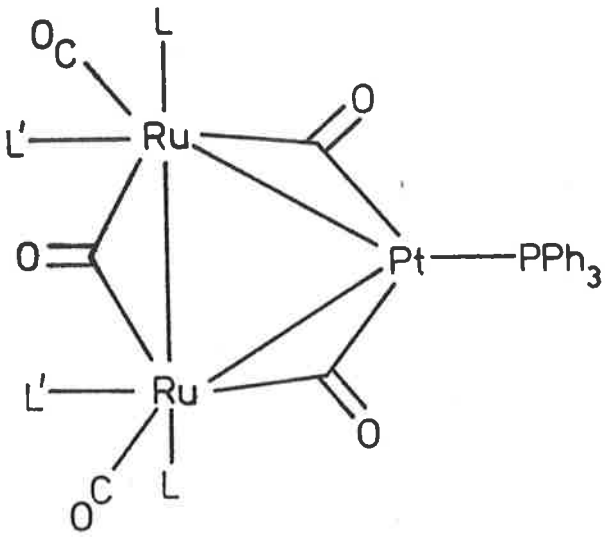
RESULTS AND DISCUSSION[48]

Isocyanide complexes of $Ru_3(CO)_{12}$ have proved to be unusually reactive sources of polynuclear ruthenium carbonyl moieties.[49] In contrast to the reactions of $[Ru_3(CO)_{12}]$, those between $[Ru_3(CO)_{11}(CNBu^t)]$ and platinum (0) complexes proceed instantaneously at room temperature. If the reactants are mixed at -30°, and the solution allowed to warm to -20°, a crimson colour develops; thin layer chromatography (t.l.c.) indicates that this is one compound, but its rapid decomposition above -10°C has prevented a definitive characterisation of this complex. In the following account, I use the descriptor "complex A" for this intermediate. If the solution is allowed to warm to room temperature, at least 13 distinct products can be separated by t.l.c. methods. It became apparent that many of these complexes are formed by complex disproportionation reactions. Simpler reaction mixtures were obtained if the crimson intermediate complex is reacted with other 2e-donor ligands. Further reactions with CO, Bu^tNC and tertiary phosphines have resulted in the isolation of twelve more complexes. It is more convenient to discuss these reactions first, and then to return to a description of the transformation products of the intermediate complex A.

Reaction with carbon monoxide

Interaction of $[Ru_3(CO)_{11}(CNBu^t)]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (molar ratio 1:2) at -20° gave a crimson solution; passage of CO into the solution for 30 minutes resulted in a colour change to orange-yellow. Separation of the products by preparative t.l.c. gave several fractions. The first, orange band was further separated into the known complex $[Ru_3(CO)_{11}(PPh_3)]$ (4) and $[RuPt_2(CO)_6(CNBu^t)(PPh_3)]$ (5) (see Figure 3). The latter was characterised on the basis of elemental analyses and from its spectra (see Experimental section), in particular, the

FIGURE 3

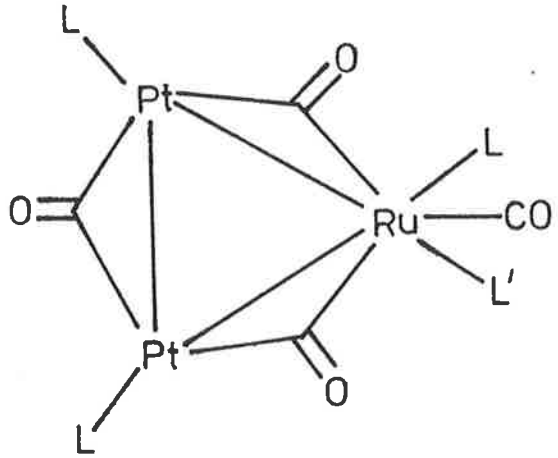


(1) L = PPh_3, L' = CO

(8) L_2L_2' = $\{(CO)(CNBu^t)_3\}$

(9) L = PPh_3, L_2' = $\{(CNBu^t)(PMe_3)\}$

(16) L = PPh_3, L_2' = $\{(CNBu^t)(PPh_3)\}$



(2) L = PPh_3, L' = CO

(3) L = $PMePh_2$, L' =CO

(5) L_3L' = $\{(CNBu^t)(PPh_3)(CO)_2\}$

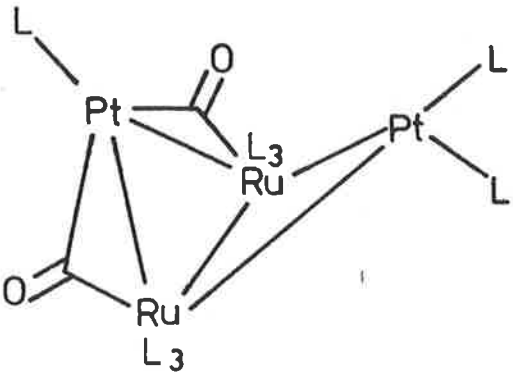
(7) L = PPh_3, L' = $CNBu^t$

(12) L = PPh_3, L' = $P(OMe)_3$

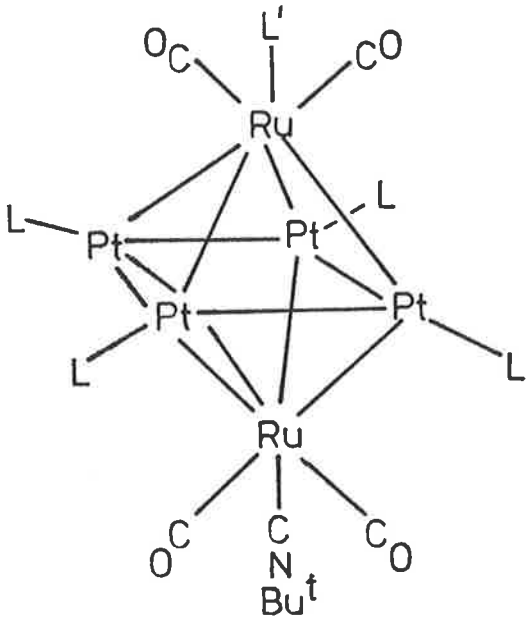
(13) L_3L' = $\{(CNBu^t)(PPh_3)_2[P(OMe)_3]\}$

(19) L_3L' = $\{(CNBu^t)(PPh_3)_2(CO)\}$

(20) L = L' = $P(C_6H_4Me\text{-}p)_3$

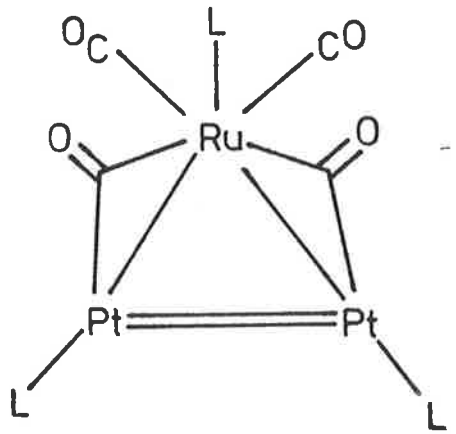


(6) L_9 = $\{(CO)_7(CNBu^t)(PPh_3)\}$



(17) L = PPh_3, L' = CO

(18) L = L' = PPh_3



(A) L = PPh_3

mass spectrum, which contained a parent ion at *m/e* 1004, together with fragment ions consistent with the presence of six CO groups (lost stepwise), as well as Bu^tNC and PPh_3 ligands. As with many of the complexes to be described, the molecular weight was confirmed osmometrically (further indication that the mass spectrum is that of the complex, and not of some product formed by pyrolysis in the mass spectrometer). A second, red fraction was tentatively identified as the tetranuclear complex $[Ru_2Pt_2(CO)_9(CNBu^t)(PPh_3)]$ (6) mainly from mass spectrometric data (parent ion at *m/e* 1190, and appropriate fragment ions), and ^1H n.m.r. spectra (which confirmed the ratio of tertiary phosphine to isocyanide ligands). A possible structure for (6) is based on an open "butterfly" Ru_2Pt_2 skeleton (see Figure 3), which requires a total of 22 electrons to be donated by the ligands to achieve the usual electron count. (In many related complexes, the platinum atoms have an effective atomic number of 16). The major product from this reaction, isolated in 35% yield, is $[RuPt_2(CO)_5(PPh_3)_3]$ (2), which has been described previously.[3] This compound is a yellow solid, and was identified from its infra-red and ^1H n.m.r. spectra; the single-crystal X-ray structure has also been determined (*vide infra*). A small amount of the complex $[Ru_2Pt(CO)_7(PPh_3)_3]$ (1) (see Figure 3) is found in the fraction of R_f 0.35; the analogous complex $[Ru_2Pt(CO)_7(PMe_2Ph)_3]$, also described earlier,[3] has a very similar infra-red spectrum. One other slower-moving fraction remains unidentified; it is also found in the room-temperature "decomposition" products of complex A. In all of these reactions, a dark brown product, which is soluble only in the more polar solvents, and which has not yet been adequately purified, is formed. It is likely that clusters of higher nuclearity remain in this fraction.

Reaction with t-butyl isocyanide

A similar reaction was carried out using $[Ru_3(CO)_{11}(CNBu^t)]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (molar ratio 1:2.4) at -20°C; addition of Bu^tNC resulted in a change in colour of the solution to red, followed by a slow precipitation of an orange powder, which was identified as the benzene solvate of $[RuPt_2(CO)_4(CNBu^t)(PPh_3)_3]$ (7) (see Figure 3) by elemental analysis and spectroscopic methods. On chromatography, the mother liquor gave only two fractions, one orange and containing more (7), the other dark brown and remaining at the origin. There was some evidence of decomposition on chromatography, to give material which would not be removed from the adsorbent. Complex (7) is slightly air-sensitive, and not surprisingly, solutions in $CHCl_3$ decompose over several hours.

Another reaction in which excess Bu^tNC was added to the crimson intermediate gave a dark orange, rather air-sensitive material, which was tentatively identified as the benzene solvate of $[Ru_2Pt(CO)_6(CNBu^t)_3(PPh_3)]$ (8) (see Figure 3) by elemental analysis and from its ^1H n.m.r. spectrum. In neither case were satisfactory mass spectra obtained.

Reaction with trimethylphosphine

Addition of PMe_3 to the crimson solution obtained from $[Ru_3(CO)_{11}(CNBu^t)]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (molar ratio 1:2.4) at -20° resulted in no apparent change in colour. Separation of the products by preparative t.l.c. gave three complexes. The first of these was identified as orange $[Ru_2Pt(CO)_5(CNBu^t)(PMe_3)PPh_3)_3]$ (9) (see Figure 3), obtained as a cyclohexane solvate, for which appropriate analytical, osmometric and spectroscopic data are listed in the Experimental section; the ^1H n.m.r. spectrum confirms the presence of the isocyanide and four tertiary phosphine ligands, as well as the cyclo-

hexane solvate molecule. The second fraction contained red $[Ru_3(CO)_{10}(PMe_3)PPh_3]$ (10); the similarity between the infra-red spectra of (10) and other $[Ru_3(CO)_{10}(L)_2]$ complexes, together with the ^1H n.m.r. spectra, which contained resonances consistent with the presence of each tertiary phosphine ligand, confirms the formulation proposed on the basis of the analytical results. Also isolated from this reaction was $[RuPt_2(CO)_5(PPh_3)_3]$ (2), obtained as a benzene solvate, as first revealed by the X-ray study (*vide infra*).

Reaction with tri-*p*-tolylphosphine

The only complex identified out of the four fractions separated from the reaction between the intermediate complex A and tri-*p*-tolylphospine was $[Ru_3(CO)_{10}(CNBu^t)\{P(C_6H_4Me\text{-}p)_3\}]$ (11), identified by comparison with an authentic sample obtained directly from $[Ru_3(CO)_{11}(CNBu^t)]$ and $P(C_6H_4Me\text{-}p)_3$.[49]

Reaction with trimethyl phosphite

The instantaneous reaction between complex A and trimethyl phosphite at -40° (indicated by an immediate change in colour on mixing the reactants) afforded two $RuPt_2$ complexes on workup. The first was identified as $[RuPt_2(CO)_4(PPh_3)_3\{P(OMe)_3\}]$ (12) (see Figure 3) by analytical and spectroscopic methods; the infra-red spectrum was markedly simpler than those of the penta-, hexa- or hepta-carbonyl complexes, containing only four ν(CO) absorptions. A small amount of $[RuPt_2(CO)_4(CNBu^t)(PPh_3)_2\{P(OMe)_3\}]$ (13) (see Figure 3) was obtained as its toluene solvate; this was one of the few complexes which gave a mass spectrum which contributed to deciding its formulation, rather than being consistent with a previously proposed composition. In addition to the parent ion (at *m/e* 1335), ions resulting from competitive

loss of $CNBu^t$, $P(OMe)_3$ and PPh_3 ligands were present; in this instance CO groups were seen to fragment from the resulting $[RuPt_2(CO)_4]^+$ ion at *m/e* 604. A third product from this reaction was the monosubstituted $[Ru_3(CO)_{11}\{P(OMe)_3\}]$ (14), identified by comparison with an authentic sample.[53]

Thermal behaviour of the "crimson intermediate" (complex A)

The results described above showed that the crimson complex, obtained initially from $[Ru_3(CO)_{11}(CNBu^t)]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$, is itself quite reactive, and affords further complexes on reaction with 2e-donor ligands such as CO, $CNBu^t$ or tertiary phosphines. If the two reagent complexes were mixed together, a yellow solid slowly precipitated, which was shown to be $RuPt_2(CO)_5(PPh_3)_3$ (1). At -40°, a mixture of $[Ru_3(CO)_{11}(CNBu^t)]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ in toluene or tetrahydrofuran is orange-red; on warming to -20°C, the solution takes on an intense crimson colour. Examination by t.l.c. showed the formation of this intermediate, which ran as one spot, was best achieved with a Ru:Pt ratio of 3:2. The intermediate complex decomposes rapidly above -10°, and is also air-sensitive; the nature of the products obtained on warming to room temperature is discussed below. At low temperatures (*ca.* -78°C), a deep crimson powder can be obtained by slowly distilling either isobutane or methylcyclohexane into a toluene solution. On warming, the solid changes colour to dark red-orange, and thus far suitable crystals for a structure determination have not been obtained.

Extensive studies of the reaction products obtained on warming the solution of the crimson intermediate, or by carrying out the reaction at room temperature, have shown that there are about fourteen different complexes formed, together with the usual dark brown material left at the origin on a t.l.c. plate. Several of these are obtained in

only low yield, and identification is necessarily tentative in some cases. The usual combination of elemental analysis with spectroscopic methods, and both osmometric and mass spectrometric molecular weight determinations (all of which are detailed in the Experimental section), are consistent with the identification (see Figure 3) of the following products (in order of decreasing R_f values):

i) a rapidly moving orange fraction which could be further separated into unreacted $[Ru_3(CO)_{11}(CNBu^t)]$, $[Ru_3(CO)_{11}(PPh_3)]$ (4) and $[RuPt_2(CO)_6(CNBu^t)(PPh_3)]$ (5);

ii) a red band, shown to contain $[Ru_3(CO)_{10}(CNBu^t)(PPh_3)]$ (15) by comparison with an authentic sample obtained from $[Ru_3(CO)_{11}(CNBu^t)]$ and PPh_3;

iii) red $[Ru_2Pt_2(CO)_9(CNBu^t)(PPh_3)]$ (6), as found in the reaction with CO;

iv) $[Ru_2Pt(CO)_7(PPh_3)_3]$ (1);

v) $[RuPt_2(CO)_5(PPh_3)_3]$ (2);

vi) seven other products obtained in yields ranging from 1-4%.

While identical infra-red and ^1H n.m.r. spectra were obtained for similar fractions obtained from several experiments, no further characterisation of these has yet proved possible.

If a mixture of $[Ru_3(CO)_{11}(CNBu^t]$ and $[Pt(\eta-C_2H_4)(PPh_3)_2]$ is heated overnight in benzene at reflux point, a dark brown solution is formed, from which four fractions were obtained. None of these contained the Ru_2Pt complex (1) or the $RuPt_2$ complex (2), although one is probably $[Ru_2Pt(CO)_5(CNBu^t)(PPh_3)_4]$ (16). Combined analytical and osmometric measurements are consistent with two of the products being the hexanuclear complexes $[Ru_2Pt_4(CO)_5(CNBu^t)(PPh_3)_4]$ (17) and $[Ru_2Pt_4(CO)_4(CNBu^t)(PPh_3)_5]$ (18).

Other reactions

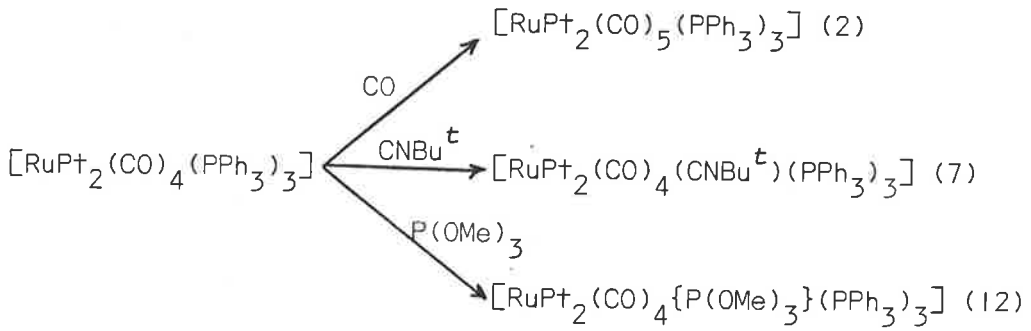
In the hope of obtaining one or more hydrido complexes, we treated the intermediate complex A with dihydrogen. The only product characterised was $[RuPt_2(CO)_5(CNBu^t)(PPh_3)_2]$ (19) (see Figure 3), although other complexes were shown as present by t.l.c.; some of these were unstable at room temperature.

On reacting $[Ru_3(CO)_{11}(CNBu^t)]$ with $[Pt\{P(C_6H_4Me\text{-}p)_3\}_4]$, the toluene solution turned deep red at -17°, and workup afforded yellow $[RuPt_2(CO)_4\{P(C_6H_4Me\text{-}p)_3\}_4]$ (20) (see Figure 3), which had an infrared spectrum similar to that of complex (7), as well as analytical and ^1H n.m.r. spectral data consistent with the proposed formulation. The disubstituted complex $[Ru_3(CO)_{10}\{P(C_6H_4Me\text{-}p)_3\}_2]$ (21) was also isolated.

The benzene solvate of $[RuPt_2(CO)_5(CNBu^t)(PPh_3)_2]$ (19) was the only complex isolated from the reaction between $[Ru_3(CO)_{10}(CNBu^t)_2]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$. The mother liquors were quite air-sensitive, suggesting that the product(s) contained more than one $CNBu^t$ ligand.[54]

The crimson complex A also reacted instantly with $Co_2(CO)_8$ or $Fe_2(CO)_9$ to give a host of products, all in low yield. Though these products all produced definite fragmentation patterns in the mass spectrometer, difficulty in isolating pure samples by chromatography prevented their characterisation. Cyclopentadiene also reacted with the crimson intermediate to give $RuPt_2(CO)_4(PPh_3)_2(\eta\text{-}C_5H_5)$ (22) in 30% yield. This compound is readily characterised on the basis of spectral and analytical data. No hydride resonances in the high field ^1H n.m.r. spectrum have been located thus far. The present formulation of (22) suggests an odd-electron count for the cluster. Further studies are in progress to verify this result.[61]

It is quite evident from the foregoing discussion that the reaction between $[Ru_3(CO)_{11}(CNBu^t)]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ proceeds much more rapidly than those described earlier between $[Ru_3(CO)_{12}]$ and related platinum (0) complexes.[3] In several cases the products retain the isocyanide ligand, but none have a complexed olefin ligand. The initial reaction between these two complexes generates a crimson material which appears to be the source of many of the other complexes I have isolated. Its subsequent reactions suggest that it is a new member of the class of "unsaturated" metal clusters, reacting by addition of ligands, rather than by substitution. Although not fully characterised, this intermediate appears to be one species (by t.l.c.), and subsequent reactivity suggests it is $[RuPt_2(CO)_4(PPh_3)_3]$; the major products of reactions with ligands, L, being the adducts $[RuPt_2(CO)_4(PPh_3)_3(L)]$:



In several cases, the presence of excess ligand results in further reaction to substitute either CO or PPh_3, to give, for example, $[RuPt_2(CO)_4(CNBu^t)_3(PPh_3)]$ with Bu^tNC. As found in other instances, isocyanide-rich clusters tend to be more air-sensitive.[54]

Several structures may be written for the intermediate. I suggest that a triangular $RuPt_2$ cluster is formed, containing a metal-metal double bond; the intense colour of this complex suggests a stronger metal-metal interaction than found in the Ru_2Pt (yellow) or $RuPt_2$ (red) complexes. One possible arrangement is shown in Figure 3(A).

Evidence for further cluster disproportionation, over that required to form the $RuPt_2$ complexes from Ru_3 and Pt components, is given by the isolation of the Ru_2Pt complex (1) in reasonable yield, particularly when CO is added to the reaction mixture. This type of redistribution reaction has a growing importance in cluster chemistry,[7,8] and the example of Co_2Rh_2 complexes being formed in the reactions between $[Co_3Rh(CO)_{12}]$ and $P(OMe)_3$[55] also suggests that this reaction is facilitated by the presence of free donor ligands. The complete breakdown of the cluster carbonyls, such as $[Ru_3(CO)_{12}]$, to mononuclear complexes by reaction with excess CO or tertiary phosphines has, of course, long been known.[56]

The spectroscopic data obtained is not sufficient to enable a definitive characterisation of the trinuclear $RuPt_2$ and Ru_2Pt complexes, insofar as the precise distribution of the various ligands on the different metal atoms cannot be determined. However, the general similarity of these complexes to (1), (2) and (3), of known structure, suggests that they contain similar structural features. Thus, it seems reasonable to suggest that complexes (7), (9), (12), (16) and (20) contain one triarylphosphine ligand attached to each metal atom, and that in complexes (8), (13) and (19), the triarylphosphine ligand is attached to platinum. There is no evidence for hydrogen-platinum coupling to the POMe resonance in the ^1H n.m.r. spectra of (12) or (13), suggesting that the trimethylphosphite ligand is attached to ruthenium.

The formation and structure of the tetranuclear cluster described herein is, unfortunately, not yet corroborated by any structural studies. However, the formation of tetranuclear Os_2Pt_2 clusters is well documented.[3,7,8,25,26,28] The apparent preference for "butterfly" structures found for homo- and hetero-metallic clusters containing platinum,[7,8] leads me to suggest structure (6) for this complex. No

high-field signals from metal-bonded protons were located in the ^1H n.m.r. spectra of any of the complexes described above. Similarly, the hexanuclear complexes (17) and (18), obtained from the reaction carried out in benzene heated to reflux point, have been formulated only on the basis of analytical and spectroscopic data. The proposed formulations are consistent with the presence of an octahedral Ru_2Pt_4 core, which requires the associated ligands to donate 20 electrons, allowing the metal atoms to attain the usual 16e (Pt) or 18e (Ru) configurations.

The Ru_3 complexes isolated from these reactions apparently arise by substitution of either CO or $CNBu^t$ in $[Ru_3(CO)_{11}(CNBu^t)]$ by tertiary phosphine. Previous work indicates that both reactions proceed competitively.[49] The mono- and di-substituted complexes $[Ru_3(CO)_{12-n}(PR_3)_n]$ (n = 1 or 2) were also first isolated from reactions between $[Ru_3(CO)_{12}]$ and $[Pt(PR_3)_4]$.[3] In a similar way, $Ru_3(CO)_{12}$ reacts with $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ to yield the mono- and di-substituted complexes. The more reactive platinum reagent used in the latter reaction reduces the reaction time from 1 week [using $Pt(PR_3)_4$][3] to only 25 min.

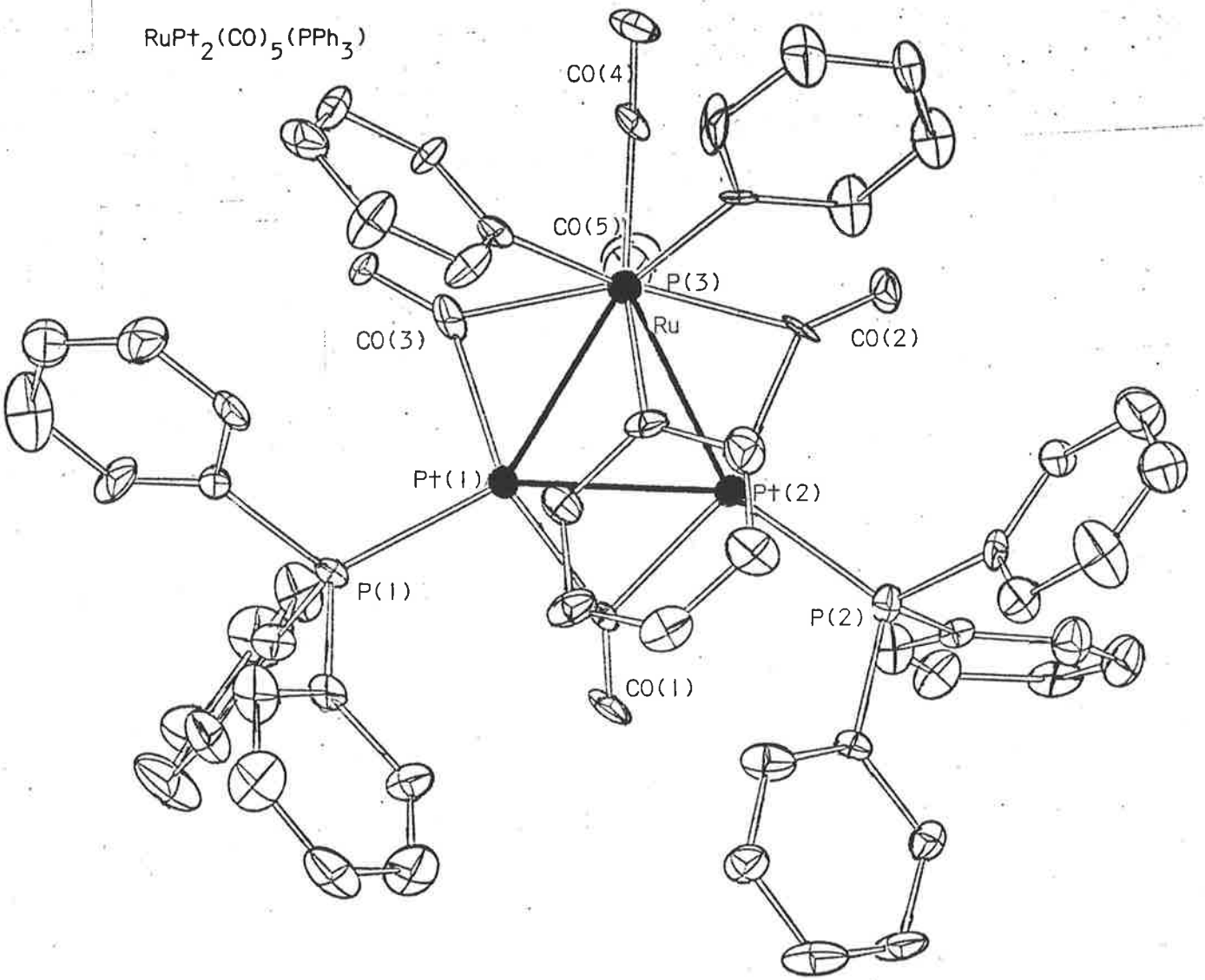
Crystal and Molecular Structure of $[RuPt_2(CO)_5(PPh_3)_3]$ (2)

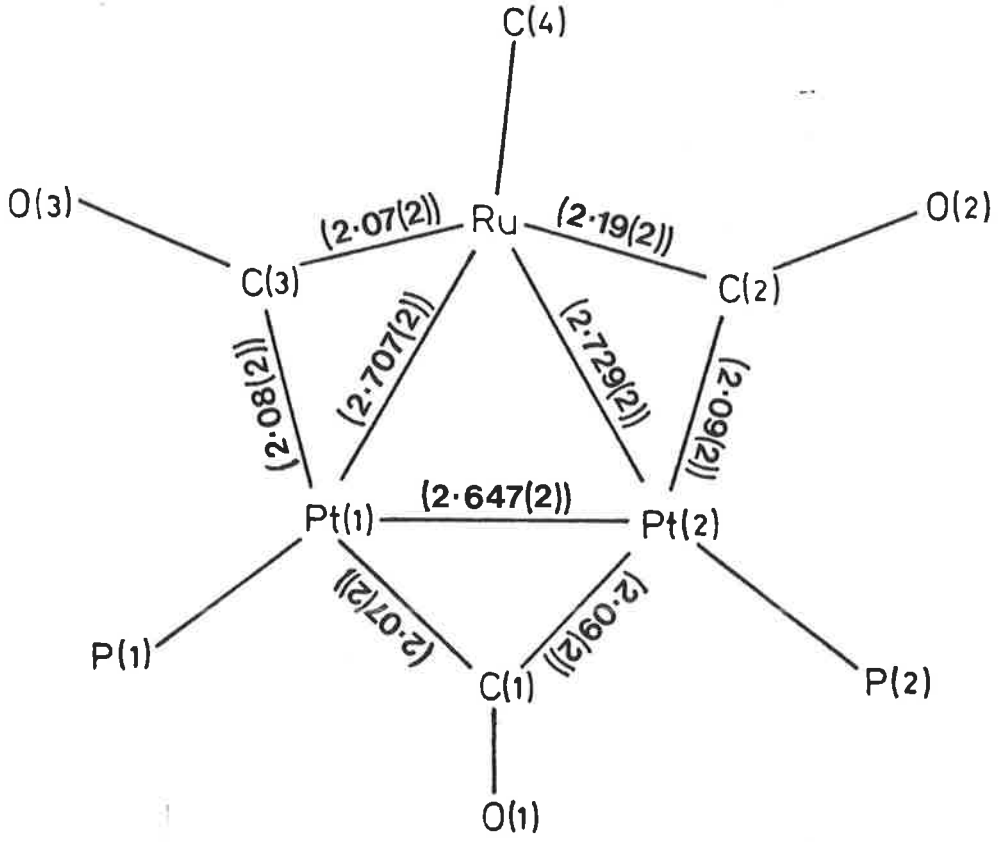
An earlier structure determination of $RuPt_2(CO)_5(PMe_2Ph)_3$ showed the phosphine ligand attached to the Ru atom to lie normal to the plane of the metal atom triangle.[6] This is in complete contrast to the preferential equatorial substitution of phosphines on $Ru_3(CO)_{12}$,[50] or with the equatorial ("in-plane") substitution of phosphite on the Fe atom of $FePt_2(CO)_5[P(OPh)_3]_3$.[51,52]

The molecular structure of $[RuPt_2(CO)_5(PPh_3)_3]$ (2) is shown in Figure 4. The coordination disposition of the ligands about the $RuPt_2$

FIGURE 4

$RuPt_2(CO)_5(PPh_3)$





core in (2) is the same as in $[RuPt_2(CO)_5(PMePh_2)_3]$ (3).[6] The increased bulk of the ligands in complex (2) results in diminished distortions of the angular geometry about the $RuPt_2$ core. In complex (2) the angles P(3)-Ru-Pt(1,2) are all increased relative to those of complex (3), indicating that the phosphine ligand lies outward from the core of the molecule, as a consequence of the increased steric effect (cone angle for PMe_2Ph = 136° *vs.* cone angle for PPh_3 = 145°[57]].

The angular geometries about Pt(1,2) indicate that, in spite of the lower coordination numbers of the platinum (*cf.* the ruthenium) the increased steric crowding has a noticeable effect. Carbonyl (1) bridges both platinum atoms symmetrically. In complex (3), however, differences in the angles P(1)-Pt(1)-C(1,3), P(2)-Pt(2)-C(1,2) were minor, whereas in complex (2) they are pronounced, and of opposite disposition on the two platinum atoms, P(1) lying toward carbonyl (1), while P(2) is bent towards carbonyl (2).

The introduction of the bulkier ligand does have considerable consequence, in terms of the ligand atom deviations from the molecular plane.[48] This is particularly so in respect of the bridging carbonyl groups (1,2), here seen to be considerably twisted out of the $RuPt_2$ plane. The distortion of carbonyl (2) and carbonyl (1) is due to interactions with phenyl moieties [attached to P(3) and P(2), respectively]; these being bent out of the plane in the opposite direction. Comparison of the $RuPt_2$ triangle in both complexes also shows a small increase in the Ru-Pt vector when $PMePh_2$ in complex (3) is replaced by the more bulky PPh_3 in complex (2). The C-O distances in the terminal carbonyl groups are collectively shorter than their counterparts in the bridging groups.

EXPERIMENTAL

General experimental conditions

Spectroscopic instrumentation is as outlined in Chapter 1. A nitrogen atmosphere was used routinely during the formation and reactions of the crimson intermediate, which were carried out in conventional Schlenk tubes. Solvents were dried and distilled before use, and solutions of reagents were degassed (freeze-thaw) before mixing. Trimethylphosphine was used as obtained from Strem Chemicals Co. (Danvers, Mass.). Literature methods were used to prepare $[Ru_3(CO)_{11}(CNBu^t)]$,[58] $[Ru_3(CO)_{10}(CNBu^t)_2]$,[58] $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$[12] and $[Pt\{P(C_6H_4Me\text{-}p)_3\}_4]$ (by a method analogous to that used for $[Pt(PPh_3)_4]$, but using $P(C_6H_4Me_3\text{-}p)_3$ in place of PPh_3).[59] Reactions were monitored by t.l.c. using Kieselgel G/HF_{254} (2:1) on microscope slides. Preparative t.l.c. was carried out on 20 x 20 cm plates coated with 1 mm thick Kieselgel 60G (Merck).

Reactions between $[Ru_3(CO)_{11}(CNBu^t)]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$

Several reactions were carried out to investigate the effect of variations in molar ratio, temperature and solvent. Three typical experiments are given below:

(a) Molar ratio 1:1, benzene, room temperature

Solutions of $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (230 mg, 0.31 mmol) and $[Ru_3(CO)_{11}(CNBu^t)]$ (210 mg, 0.3 mmol) in benzene (total volume, 50 ml) were mixed, and the colour changed to deep red within 5 seconds. After stirring at room temperature for 5 min., solvent was removed *in vacuo*. The reaction product was chromatographed on a preparative t.l.c. plate [3:7 acetone/light petroleum (b.p. 40-60°) developer]. Thirteen brightly-coloured bands were obtained, which on further purification (t.l.c. and recrystallisation) afforded

fifteen products. A summary of R_f, yield and identification is included in Table I, and further details of analyses, spectroscopic properties, *etc.*, are given below.

(b) Molar ratio 1:2, tetrahydrofuran, -20°C

Solutions of $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (300 mg, 0.4 mmol) and $[Ru_3(CO)_{11}(CNBu^t)]$ (140 mg, 0.2 mmol) in tetrahydrofuran (total volume, 60 ml) were mixed at -40° to give a red-orange solution. On warming to -20°, the colour changed to deep crimson within five minutes; examination by t.l.c. showed the presence of only one fraction (R_f 0.5, 3:7 Et_2O/cyclohexane). This solution was allowed to warm up to room temperature, when examination by t.l.c. showed the formation of a similar complex mixture of reaction products (Table I).

Attempts to isolate the crimson intermediate were made

i) by running the reaction in toluene solution at -20°, followed by evaporation of solvent until solid material began to separate. Cooling to -78° afforded a deep crimson solid;

ii) a similar solid material was obtained by adding either isobutane or methylcyclohexane to the cooled toluene solution. The product was thermally unstable, and decomposed rapidly to an orange solid, consisting of a mixture of products (*vide infra*).

(c) Molar ratio 3:5, benzene, 80°

A solution of $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (305 mg, 0.41 mmol) in benzene (20 ml) was added to $[Ru_3(CO)_{11}(CNBu^t)]$ (160 mg, 0.23 mmol) in benzene (20 ml) and heated to reflux point. The resulting deep brown mixture was heated at reflux point under nitrogen for 18 h. Preparative t.l.c. (1:1 cyclohexane/diethyl ether) gave four bands, and some material remained on the baseline. Three of these were identified as

i) yellow $[Ru_2Pt(CO)_5(CNBu^t)(PPh_3)_4]$ (16) (37 mg, 8%), R_f 0.81 (Found: C - 59.1, H - 5.0, N - 0.56%; $C_{82}H_{69}NO_5P_4PtRu_2$ requires C - 59.0, H - 4.2, N - 0.84%). Infra-red (C_6H_{12}): ν(CN) = 2155m; ν(CO) = 2061s, 2044(sh), 2000vs, 1977s, 1952m cm^{-1}; ^1H n.m.r.: δ $[(CD_3)_2CO]$ = 1.79s (9), CMe_3; 7.40m (60), PPh_3;

ii) brown $[Ru_2Pt_4(CO)_5(CNBu^t)(PPh_3)_4] \cdot C_6H_6$ (17) (169 mg, 21%), R_f 0.49 (Found: C - 44.8, H - 3.45, N - 0.45%; *M* (acetone) - 2308; $C_{82}H_{69}NO_5P_4Pt_4Ru_2 \cdot C_6H_6$ requires C - 45.3, H - 3.25, N - 0.6%; *M* - 2331). Infra-red (C_6H_6): ν(CN) = 2160m; ν(CO) = 2060(sh), 2016(sh), 1995vs, 1967m, 1945m cm^{-1}; ^1H n.m.r.: δ $[(CD_3)_2CO]$ = 1.71s (9), CMe_3; 7.89m (66), $PPh_3 + C_6H_6$;

iii) brown $[Ru_2Pt_4(CO)_4(CNBu^t)(PPh_3)_5] \cdot C_6H_6$ (18) (88 mg, 10%), R_f 0.38 (Found: C - 48.9, H - 3.5, N - 0.4%; *M* (acetone) - 2585; $C_{99}H_{84}NO_4P_5Pt_4Ru_2 \cdot C_6H_6$ requires C - 49.1, H - 3.5, N - 0.55%; *M* - 2567). Infra-red (C_6H_6): ν(CN) = 2156m; ν(CO) = 2036s, 1999(sh), 1995vs, 1972vs cm^{-1}; ^1H n.m.r.: δ $[(CD_3)_2CO]$ = 1.70s (9), CMe_3; 7.56m (81), $PPh_3 + C_6H_6$.

Characterisation and properties of products from reactions between $[Ru_3(CO)_{11}(CNBu^t)]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (Table 1)

Band (2a): $[Ru_3(CO)_{11}(CNBu^t)]$ - Identified by comparison of infra-red and mass spectra.

Band (2b): $[RuPt_2(CO)_6(CNBu^t)(PPh_3)]$ (5) - Found: C - 34.61, H - 3.30, N - 1.59%; *M* (methyl ethyl ketone) - 989; $C_{29}H_{24}NO_6PPt_2Ru$ requires: C - 34.66, H - 2.39, N - 1.39%; *M* -1004. Infra-red (C_6H_{12}): ν(CN) = 2166m; ν(CO) = 2061m, 2014s, 1999(sh), 1810m cm^{-1}; ^1H n.m.r.: δ $[(CD_3)_2CO]$ = 1.63s (9), CMe_3; 7.37m (15), PPh_3.

Band (2c): $[Ru_3(CO)_{11}(PPh_3)]$ (4) - Infra-red (C_6H_{12}): ν(CO) = 2099m, 2046s, 2029(sh), 2025(sh), 2016s, 1996(sh), 1986m, 1970(sh), 1958(sh) cm^{-1} [literature[50,60] values: 2097m, 2046s, 2030(sh), 2023(sh), 2014s, 1996(sh), 1986m, 1972(sh), 1960(sh) cm^{-1}].

Band (3): $[Ru_3(CO)_{10}(CNBu^t)(PPh_3)]$ (15) - Identified by analysis (Found: C - 43.6, H - 2.85, N - 1.4; $C_{33}H_{24}NO_{10}PRu_3$ requires: C - 42.7, H - 2.6, N - 1.5%) and by comparison with an authentic sample.[49]

Band (4): $[Ru_2Pt_2(CO)_9(CNBu^t)(PPh_3)]$ (6) - Tentative identification only from mass spectrum (Found: M^+ at *m/e* - 1190, calculated *M* - 1190); ions formed by loss of Bu^tNC (*m/e* - 1108), stepwise loss of nine CO groups (*m/e* - 1080, 1052, 1032, 1004, 976, 948, 920, 892, 864), and of PPh_3 (*m/e* - 602). Found: *M* (acetone), 1197. Infra-red (C_6H_{12}): ν(CN) = 2166m; ν(CO) = 2095vw, 2067s, 2046m, 2026vs, 1998vs, 1991(sh), 1981(sh), 1967s cm^{-1}; ^1H n.m.r.: δ (C_6D_6) = 1.55s (9), CMe_3; 7.13m (15), PPh_3.

Band (5): $[Ru_2Pt(CO)_7(PPh_3)_3]$ (1) - m.p. 211-212.5°, identified by analysis [Found: C - 53.3, H - 3.4, P - 6.6, Pt - 14.6%; *M* (butan-2-one) - 1318; $C_{61}H_{45}O_7P_3PtRu_2$ requires: C - 53.1, H - 3.3, P - 6.7, Pt - 14.14%; *M* - 1379]. Infra-red (C_6H_{12}): ν(CO) = 2025vs, 1965vs, 1952(sh), 1859w, 1797s, 1783(sh); ^1H n.m.r.: δ(C_6D_6) = 7.29m, PPh_3. The highest ion in the mass spectrum is at *m/e* - 912.

Band (6): $[RuPt_2(CO)_5(PPh_3)_3]$ (2) - Identified by analysis [Found: C - 50.8, H - 3.2%, *M* (butan-2-one) - 1444; $C_{59}H_{45}O_5P_3Pt_2Ru$ requires C - 50.0, H - 3.2%; *M* - 1417], mass spectrum (M^+ at *m/e* - 1418, loss of five CO groups at *m/e* - 1390, 1362, 1334, 1306, and 1278, and loss of PPh_3 at *m/e* - 1156), and by comparison with literature values: m.p. 220-221° (literature[3] value 220-221°). Infra-red

(C_6H_{12}): ν(CO) = 2020s, 1953vs, 1848w, 1791s, [literature[3] values (C_6H_6) 2020s, 1948s, 1845w, 1788s cm^{-1}]; ^1H n.m.r.: δ (C_6D_6) = 7.42m, PPh_3. The identity of this complex was confirmed by the X-ray structural analysis (*vide supra*).

Bands (7)-(14) inclusive were not identified.

Reactions of the crimson intermediate

(a) With CO

Toluene solutions of $[Ru_3(CO)_{11}(CNBu^t)]$ (140 mg, 0.2 mmol, in 20 ml) and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (311 mg, 0.42 mmol, in 35 ml) were mixed at -20° to form a solution of the crimson intermediate (within eight min. verified by t.l.c.). Carbon monoxide was then bubbled through this solution for 30 min., maintaining the temperature at -20°. During this time, the colour of the solution changed slowly to yellow-orange. Separation of the products by preparative t.l.c. (3:7 Et_2O/cyclohexane developer) gave the following products (in order of decreasing R_f):

i) an orange band, R_f 0.61 (86 mg, 19%), further separated into $[Ru_3(CO)_{11}(PPh_3)]$ (4) and $[RuPt_2(CO)_6(CNBu^t)(PPh_3)]$ (5);

ii) $[Ru_2Pt_2(CO)_9(CNBu^t)(PPh_3)]$ (6), R_f 0.52 (36 mg, 8%);

iii) $[RuPt_2(CO)_5(PPh_3)_3]$ (2), R_f 0.49 (158 mg, 35%);

iv) $[Ru_2Pt(CO)_7(PPh_3)_3]$ (1), R_f 0.35, (45 mg, 10%).

Dark brown fractions at R_f 0.08 and remaining on the baseline amounted to 91 mg (*ca.* 20%).

(b) With $CNBu^t$

The crimson intermediate, prepared from $[Ru_3(CO)_{11}(CNBu^t)]$ (98 mg, 0.14 mmol) and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (252 mg, 0.34 mmol) in toluene (47 ml) at -20° was treated with Bu^tNC (15 mg, 0.18 mmol). Within five mins., the colour changed to red, and an orange powder precipitated over 3.5 h. at -38°. Filtration afforded 94 mg of

TABLE 1 Reactions between $Ru_3(CO)_{11}(CNBu^t)$ and $Pt(\eta\text{-}C_2H_4)(PPh_3)_2$

		$Ru_3(CO)_{11}(CNBu^t)$ mg/mmol		210/0.3		101/0.15		165/0.24		101/0.15	
		$Pt(\eta\text{-}C_2H_4)(PPh_3)_2$ mg/mmol		230/0.3		248/0.33		95/0.13		163/0.22	
		solvent (°C/min)		C_6H_6(25°/5)		C_6H_6(25°/30)		C_6H_6(25°/120)		MeCy[a](25°/120)	
No.	Colour	Identity	R_f[b]	mg	%	mg	%	mg	%	mg	%
1	yellow		0.80	4	1			6	2		
2a	orange	$Ru_3(CO)_{11}(CNBu^t)$						64	25		
2b	orange	$RuPt_2(CO)_6(CNBu^t)(PPh_3)$	0.60[c]	101	23					44	17
2c	orange	$Ru_3(CO)_{11}(PPh_3)$									
3	red	$Ru_3(CO)_{10}(CNBu^t)(PPh_3)$	0.56	94	21	85	25	52	20	86	33
4	red	$Ru_2Pt_2(CO)_9(CNBu^t)(PPh_3$	0.53	58	13	50	14	29	11	16	6
5	red	$Ru_2Pt(CO)_7(PPh_3)_3$	0.51	27	6	54	16			13	5
5a	green		0.51					16	6		
6	yellow	$RuPt_2(CO)_5(PPh_3)_3$	0.49	44	10					50	19
7	dark brown		0.46	9	2	20	6	11	4		
8	light brown		0.45	4	1						
8a	brown		0.43					15	6		
9	yellow		0.37	9	2						
10	orange-red		0.33	17	4						
11	pale brown		0.31	4	1						
12	dark brown		0.24	14	3	25	7			3	1
13	brown		0.08					24	9	16	6
14	dark brown		0.0	26	6	10	3	10	4	13	5

[a] methylcyclohexane

[b] in 3:7 Et_2O/cyclohexane

[c] This band was resolved into its components by further t.l.c. (2a, R_f = 0.37; 2b, R_f = 0.30; 2c, R_f = 0.25; cyclohexane).

$[RuPt_2(CO)_4(CNBu^t)(PPh_3)_3] \cdot C_6H_6$ (7). A further 67 mg were obtained by t.l.c. of the mother liquor, from an orange band (R_f 0.75; 1:1 acetone/cyclohexane) (total yield, 62%). Found: C - 53.5, H - 3.8, N - 1.1%; *M* (acetone) - 1492; $C_{69}H_{60}NO_4P_3Pt_2Ru$ requires C - 53.4, H - 3.9, N - 0.9%; *M* - 1550. Infra-red (CH_2Cl_2): ν(CN) = 2147m; ν(CO) = 2012w, 1986m, 1979s(br), 1830s cm^{-1}. ^1H n.m.r.: δ $[(CD_3)_2CO]$ = 1.54s (9), CMe_3; 7.45m (51), $PPh_3 + C_6H_6$. This complex is slightly air-sensitive, and decomposes after several hours in chloroform solution.

Another experiment, in which the crimson intermediate from $[Ru_3(CO)_{11}(CNBu^t)]$ (51 mg, 0.07 mmol) and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (124 mg, 0.17 mmol) in toluene (25 ml) at -20° was treated with Bu^tNC (70 mg, 0.84 mmol), gave a red solution, from which a pale orange-red powder deposited over several hours. Filtration afforded a dark orange powder (37 mg, 21%), which was purified by preparative t.l.c. (R_f 0.82, 3:2 acetone/cyclohexane) to give $[Ru_2Pt(CO)_6(CNBu^t)_3(PPh_3)] \cdot C_6H_6$ (8) [Found: C - 46.8, H - 4.5, N - 3.2, O - 9.65%; *M* (butan-2-one) - 1053; $C_{45}H_{48}N_3O_6PPtRu_2$ requires C - 46.8, H - 4.2, N - 3.6, O - 9.7%; *M* - 1154]. Infra-red (CH_2Cl_2): ν(CN) = 2168(sh), 2151(sh), 2147s; ν(CO) = 2048(sh), 2035m, 2012(sh), 1979m, 1942vs, 1879w cm^{-1}. ^1H n.m.r.: δ $[(CD_3)_2CO]$=1.54s (27), CMe_3; 7.45m (45), PPh_3. As in the first experiment, the dark brown material which remained on the baseline could not be re-extracted into any solvent.

(c) With PMe_3

Solid $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (253 mg, 0.34 mmol) was added to $[Ru_3(CO)_{11}(CNBu^t)]$ (98 mg, 0.14 mmol) dissolved in toluene (50 ml) at -40°. After warming to -20°, PMe_3 (11 mg, 0.15 mmol) was distilled into the crimson solution. After 3 h., solvent was removed, and the products were separated by preparative t.l.c. (3:7 acetone/cyclohexane developer) to give the following fractions (in order of decreasing R_f value):

i) $[Ru_2Pt(CO)_5(CNBu^t)(PMe_3)(PPh_3)_3] \cdot C_6H_{12}$ (9), R_f 0.59, orange (39 mg, 11%) from cyclohexane. Found: C - 55.9, H - 6.25, N - 0.5%; *M* (acetone) - 1590; $C_{73}H_{75}NO_5P_4PtRu_2$ requires C - 55.9, H - 4.8, N - 0.9%; *M* - 1566. Infra-red (C_6H_{12}): ν(CN) = 2196w; ν(CO) = 2042m, 2014s, 2000vs, 1993s, 1965m, 1811w cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) = 1.43br (12), C_6H_{12}; 1.72s (9), CMe_3; 1.90d (9), PMe_3; 7.45m (45), PPh_3;

ii) $[Ru_3(CO)_{10}(PMe_3)(PPh_3)] \cdot C_5H_{12}$ (10); R_f 0.54, red (67 mg, 19%), from n-pentane. Found: C - 43.5, H - 3.6; $C_{36}H_{36}O_{10}P_2Ru_3$ requires C - 43.5, H - 3.65%. Infra-red (C_6H_{12}): ν(CO) = 2085w, 2060m, 2047(sh), 2037s, 2012vs, 2002(sh), 1996s, 1985(sh), 1968(sh) cm^{-1}. ^1H n.m.r.: δ ($CDCl_3$) = 0.92 1.32m (12), C_5H_{12}; 2.21d (9), PMe_3; 7.33m (15), PPh_3;

iii) $[RuPt_2(CO)_5(PPh_3)_3] \cdot C_6H_6$ (2), R_f 0.52 (81 mg, 23%) from benzene/n-pentane. Found: C - 51.75, H - 3.8,) - 7.1; $C_{65}H_{51}O_5P_3Pt_2Ru$ requires C - 52.2, H - 3.4, O - 5.2%. The identity of this complex was confirmed by the X-ray structural determination (*vide supra*). The dark brown fractions (R_f 0.43 and baseline) afforded 88 mg (*ca.* 25%) unidentified material.

(d) With $P(C_6H_4Me\text{-}p)_3$

Tri-*p*-tolylphosphine (47 mg, 0.15 mmol) in toluene (10 ml) cooled to -40° was added to a solution of the crimson intermediate prepared from $[Ru_3(CO)_{11}(CNBu^t)]$ (101 mg, 0.15 mmol) and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (163 mg, 0.22 mmol) and held at -40°. On warming to -25°, reaction commenced, and was allowed to go to completion in 75 mins. (followed by t.l.c.). During this time, the colour of the solution lightened to red. Filtration under nitrogen and workup by preparative t.l.c. (3:7 diethyl ether/cyclohexane) afforded four fractions; the only one identified was the major component, R_f 0.58, which afforded

$[Ru_3(CO)_{10}(CNBu^t)\{P(C_6H_4Me\text{-}p)_3\}]$ (11) as an orange-red solid (51 mg, 36%), identified by analysis (Found: C - 43.8, H - 3.5, N - 1.5; $C_{36}H_{30}NO_{10}PRu_3$ requires C - 44.5, H - 3.1, N - 1.4%) and by comparison with an authentic sample.[49]

(e) With P(OMe)$_3$

The reaction of the crimson intermediate, prepared from $[Ru_3(CO)_{11}(CNBu^t)]$ (102 mg, 0.15 mmol) and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (250 mg, 0.33 mmol) in toluene (25 ml), with trimethyl phosphite (50 mg, 0.4 mmol) occurred instantaneously at -40°. Isopentane (15 ml) was distilled into the solution at -30°, to precipitate a yellow solid, which was recrystallised (benzene/isopentane) to give pure $[RuPt_2(CO)_4(PPh_3)_3\{P(OMe)_3\}]$ (12) (63 mg) [Found: C - 48.4, H - 3.6, O - 6.5 ; *M* (acetone) - 1535; $C_{61}H_{54}O_7P_4Pt_2Ru$ requires C - 48.4, H - 3.6, O - 7.4%; *M* - 1514). Infra-red (CH_2Cl_2): ν(CO) = 2029s, 1998vs, 1961m, 1945(sh) cm^{-1}. ^1H n.m.r.: δ $[(CD_3)_2CO]$ = 3.64d (9), $P(OMe)_3$; 7.33m (45), PPh_3. Preparative t.l.c. of the remaining solution gave four bands, one of which (R_f 0.24) contained more of the above complex (35 mg, total yield 15%). The first band was identified as $[Ru_3(CO)_{11}\{P(OMe)_3\}]$ (14) from its infra-red [(C_6H_{12}: ν(CO) = 2096w, 2031s, 2018m, 1991w, 1960vs cm^{-1}], ^1H n.m.r. [δ ($CDCl_3$) = 3.63d, Me] and mass spectra ($[P]^+$ at *m/e* - 737, and ions formed by stepwise loss of eleven CO groups). The second, yellow-brown band (R_f 0.57) afforded $[RuPt_2(CO)_4(CNBu^t)(PPh_3)_2\{P(OMe)_3\}]\cdot C_7H_8$ (13) (29 mg, 5%) on recrystallisation from toluene/isopentane (Found: C - 47.6, H - 5.3, N - 0.5; $C_{55}H_{56}NO_7P_3Pt_2Ru$ requires C - 46.3, H - 3.9, N - 1.0%). Infra-red (CH_2Cl_2): ν(CO) = 2010w, 1991m, 1981vs, 1945s, 1797w cm^{-1}. ^1H n.m.r.: δ $[(CD_3)_2CO]$ = 1.42s (3), Ph*Me*; 1.71s (9), CMe_3; 3.67d (9), $P(OMe)_3$; 7.39m (38), PPh_3 + *Ph*Me. Mass spectrum: *m/e* - 1335 (P^+), 1252 ($[P\text{-}CNBu^t]^+$), 1211 ($[P\text{-}P(OMe)_3]^+$), 1128 ($[P\text{-}CNBu^t\text{-}P(OMe)_3]^+$),

990 ([P-CNBu^t-PPh_3]$^+$), 866 ([P-CNBu^t-$P(OMe)_3$-PPh_3]$^+$), 604 ([867-PPh_3]$^+$); ions formed by stepwise loss of four CO groups from *m/e* -604 occur at *m/e* - 576, 548, 520 and 492.

(f) With dihydrogen

Dihydrogen was bubbled through a solution of the crimson intermediate {from $[Ru_3(CO)_{11}(CNBu^t)]$ (95 mg, 0.14 mmol) and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (159 mg, 0.22 mmol) in toluene (25 ml)} for 3 h. at -30°. After this time, warming to -5° afforded an unstable yellow solid, which darkened at room temperature. The remaining solution afforded two major products by preparative t.l.c., one of which (R_f 0.58, 35:65 acetone/cyclohexane) was shown to be $[RuPt_2(CO)_5(CNBu^t)(PPh_3)_2]$ (19) (65 mg, 17%) (Found: C - 44.7, H - 3.8, N - 1.1; $C_{46}H_{39}NO_5P_2Pt_2Ru$ requires C - 44.6, H - 3.2, N - 1.1%). Spectral data were the same as found for the benzene solvate of this complex isolated from the reaction between $[Ru_3(CO)_{10}(CNBu^t)_2]$ and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (*vide infra*).

(g) With cyclopentadiene

Cyclopentadiene (35 mg, 0.53 mmol) was added to a solution of the crimson intermediate prepared from $Ru_3(CO)_{11}(CNBu^t)$ (100 mg, 0.14 mmol), and the mixture was stirred at -21° for 4 h. During this time a yellow powder separated; filtration and recrystallisation (toluene/isopentane) afforded $RuPt_2(CO)_4(PPh_3)_2(\eta\text{-}C_5H_5)\cdot C_7H_8$ (22) (97 mg). [Found: C - 49.3, H - 4.3, N - 0.0, P - 4.9%; *M* (acetone) - 1210; $C_{52}H_{43}O_4P_2Pt_2Ru$ requires C - 48.6, H - 3.5, N - 0.0, P - 4.8%; *M* - 1284]. Infra-red (C_6H_{12}): ν(CO) = 2029vs, 1958s, 1812s, 1806 vs cm^{-1}. ^1H n.m.r. δ [$(CD_3)_2CO$] = 1.39s (3), Ph*Me*; 5.19s (5), C_5H_5; 7.35m (35), PPh_3 + *Ph*Me. Workup of the remaining solution by preparative t.l.c. afforded seven products, most of which were obtained in small yield (≤10%) and not identified. However, more of the above complex (22) was obtained from a band with R_f 0.62 (29 mg, total yield 30%).

Reaction between $[Ru_3(CO)_{11}(CNBu^t)]$ and $[Pt\{P(C_6H_4Me\text{-}p)_3\}_4]$

A mixture of $[Ru_3(CO)_{11}(CNBu^t)]$ (114 mg, 0.16 mmol) and $[Pt\{P(C_6H_4Me\text{-}p)_3\}_4]$ (400 mg, 0.28 mmol) in toluene (25 ml) at -40° was allowed to warm slowly. At -17°, a deep red colour developed; the solution was kept at this temperature for 3 h., and then allowed to reach ambient temperature. Addition of isopentane precipitated a yellow powder, which was recrystallised (benzene/isopentane) to give pure $[RuPt_2(CO)_4\{P(C_6H_4Me)_3\}_4]$ (20) (134 mg, 27%) [Found: C - 57.1, H - 4.5, O - 5.5%, *M* (acetone) - 1888; $C_{88}H_{84}O_4P_4Pt_2Ru$ requires C - 58.1, H - 4.6, O - 3.5%; *M* - 1,819]. Infra-red (CH_2Cl_2): ν(CO) = 2018vs, 1994s, 1978m, 1952m cm^{-1}. ^1H n.m.r. δ [$(CD_3)_2CO$] = 1.35s (36), Me; 7.33m (48), C_6H_4. Preparative t.l.c. (30% diethyl ether/cyclohexane) of the remaining solution afforded red $[Ru_3(CO)_{10}\{P(C_6H_4Me\text{-}p)_3\}_2]$ (21) (R_f 0.72), tentatively identified from its infra-red [(C_6H_{12}): ν(CO) = 2060w, 2046m, 2030(sh), 2022vs, 1990s, 1960s, 1950m cm^{-1}] and ^1H n.m.r. spectra [δ ($CDCl_3$) 2.37s (9), Me; 7.25m (12), Ph].

Reaction between $[Ru_3(CO)_{10}(CNBu^t)_2]$ and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$

A solution of $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (163 mg, 0.22 mmol) in toluene (25 ml) was added to $[Ru_3(CO)_{10}(CNBu^t)_2]$ (76 mg, 0.1 mmol) in toluene (25 ml) at -50°. The mixture was stirred for 5 h. at -26°, when it was dark red-brown, addition of isopentane (30 ml) gave a dark red precipitate, which was filtered and recrystallised (benzene/isopentane) to give $[RuPt_2(CO)_5(CNBu^t)(PPh_3)_2]\cdot C_6H_6$ (19) (54 mg, 13%) [Found: C - 47.3, H - 3.6, N - 1.1, O - 7.7%; *M* (butan-2-one) - 1291; $C_{52}H_{45}NO_5P_2Pt_2Ru$ requires C - 47.4, H - 3.4, N - 1.1, O - 6.1%; *M* - 1316]. Infra-red (C_6H_{12}): ν(CN) = 2181m; ν(CO) = 2049m, 2035vs, 2004s, 1997s, 1994s(br) cm^{-1}. ^1H n.m.r.: δ [$(CD_3)_2CO$] = 1.69s, (9), CMe_3; 7.35m (36), $PPh_3 + C_6H_6$. This complex, and the remaining solution, were air-sensitive; no tractable materials were obtained by preparative t.l.c.

Reaction of $Ru_3(CO)_{12}$ with $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$

A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.313 mmol) and $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$ (240 mg, 0.321 mmol) in benzene (60 ml) was stirred for 24 min. under nitrogen. The reaction was followed by t.l.c. The solvent was removed *in vacuo* and preparative t.l.c. (30% diethyl ether:cyclohexane) separated six brightly coloured bands (in order of decreasing R_f):

i) orange $Ru_3(CO)_{12}$, R_f 0.96 (42 mg, 21%);

ii) red $Ru_3(CO)_{11}(PPh_3)$, R_f 0.71 (48 mg, 18%);

iii) red-purple $Ru_3(CO)_{10}(PPh_3)_2$, R_f 0.56 (18 mg, 5%);

iv) red $[Ru_2Pt(CO)_7(PPh_3)_3]$ (1), R_f 0.49 (42 mg, 10%);

v) orange $[RuPt_2(CO)_5(PPh_3)_3]$ (2), R_f 0.40 (94 mg, 20%);

(The above five products were identified by comparison with authentic samples).

vi) a pink uncharacterised band, R_f = 0.25. Infra-red (C_6H_{12}):
ν(CO) = 2105w, 2080w, 2058m, 2040sh, 2032m, 2019s, 1997m, 1992m, 1960vs, 1800vw cm^{-1};

vii) a brown baseline.

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CHAPTER THREE

SYNTHESIS OF GROUP IB PHOSPHINE ACETYLIDE COMPLEXES

INTRODUCTION

Many transition metal σ-acetylide complexes are known, but little of their chemistry has been investigated.[1-4] The chief synthetic methods in preparing σ-acetylide complexes are

i) oxidative addition of an acetylene to a metal complex;[5,6]

ii) metathesis reaction of metal complexes with other metal acetylide complexes;[7-9,55]

iii) reactions between anionic metal complexes and halo-acetylenes;[10]

iv) reaction of a metal halide complex in triethylamine solution with a terminal acetylene and CuI as a catalyst;[11]

v) deprotonation of isolated or non-isolated vinylidene complexes.[12-28]

Alkynylgold (I) complexes[7,8,29,36,39,51-53,55] have been known since 1866, when the explosive gold (I) acetylide was reported.[49] Both the copper and the silver acetylide complexes are also well known.[30-35,37,38] Studies of these complexes indicate that they are polymeric, containing metal-alkyne π bonds. Infra-red spectra show that the metal-alkyne π bond is weak, and the polymers are easily broken down by addition of other ligands.[31,33,39-44,50] In this way, the Group IB phosphine acetylide complexes were first prepared.[31,33,39] For example, phenylethynyl gold reacts directly with one equivalent of triphenylphosphine to form $Au(C_2Ph)PPh_3$.[39] An alternative preparative route involves cleavage of a methylgold bond by a terminal alkyne [equation (1)].[45-47]

$$AuMePPh_3 + PhC{\equiv}CH \longrightarrow Au(C_2Ph)PPh_3 + CH_4 \qquad (1)$$

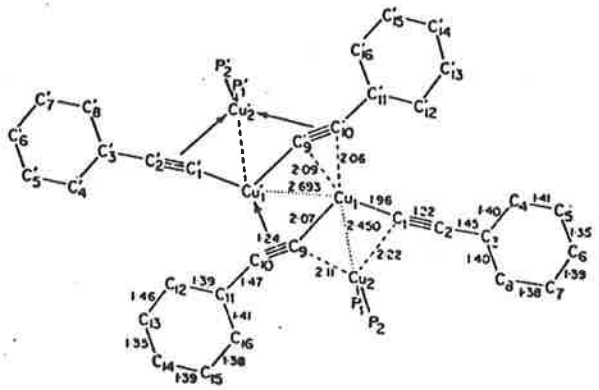
Crystallographic studies of $Cu(C_2Ph)PMe_3$[41] and $Ag(C_2Ph)PMe_3$[48] revealed that formally the structures are built up of $[M(C_2Ph)_2]^-$ and $[M(PMe_3)_2]^+$ (M = Cu, Ag) units with the ethynyls linking adjacent metal atoms (see Figure 1). Hence, the molecular formulae of these complexes are best written as $\{[Cu(PMe_3)_2][Cu(C_2Ph)_2]\}_2$ and $\{[Ag(PMe_3)_2][Ag(C_2Ph)_2]\}_n$.

FIGURE I

STRUCTURES OF GROUP IB ACETYLIDES

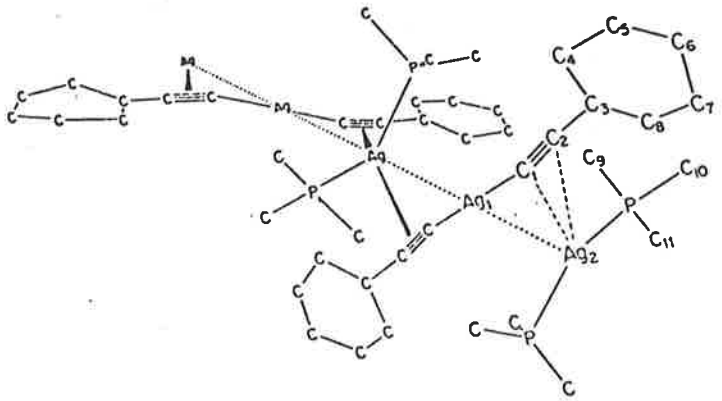
$[(PhC{\equiv}C)Cu(PMe_3)]_4$ or

$[\{Cu(PMe_3)_2\}\{Cu(C{\equiv}CPh)_2\}]_2$

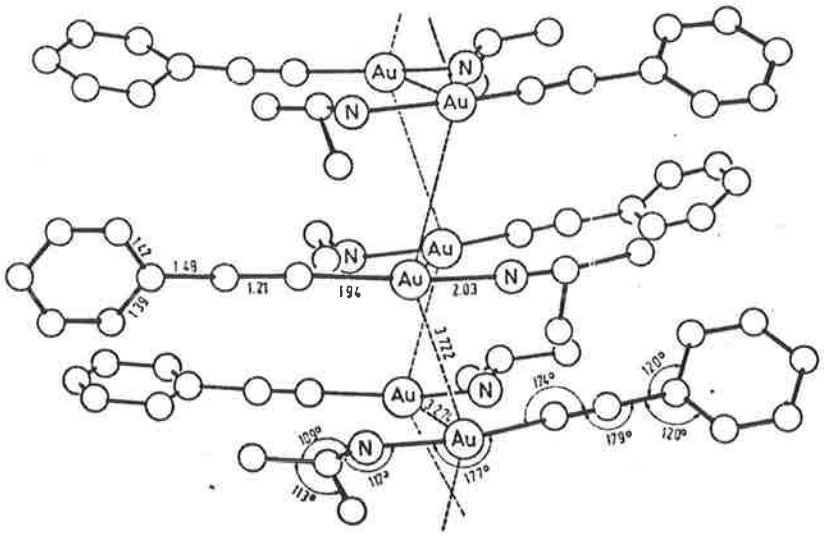


$[(PhC{\equiv}C)Ag(PMe_3)]_n$ or

$[\{Ag(PMe_3)_2\}\{Ag(C{\equiv}CPh)_2\}]_n$



A perspective view of the crystal structure of $C_6H_5C{\equiv}CAuNH_2CH(CH_3)_2$



No comparable crystallographic studies have been made for analogous gold complexes. However, an X-ray crystallographic structure for $Au(C_2Ph)NH_2CHMe_2$ (see Figure 1),[54] shows that the gold atoms lie in infinite zig-zag chains, extending along the direction of the C axis. The gold-gold distances between the chains are 3.27 Å. The complex may be viewed as built from monomers with discrete gold-gold contacts (Au-Au-Au angles of 153°). The NH_2 groups appears to be engaged in hydrogen bonding with the ethynyl group.[54]

RESULTS AND DISCUSSION

The σ-acetylide complexes $M(C_2R)PR'_3$ (M = Au, Ag, Cu) have been optimally formed by one of three synthetic routes:

a) Reaction of $MClPR'_3$ (M = Au, Ag) with the appropriate terminal alkyne HC_2R in di- or tri-ethylamine solution. The reaction commenced only after the addition of CuCl as a catalyst. This suggests the formation of a copper acetylide complex, which undergoes a metathesis reaction with $MClPR'_3$ (M = Au, Ag). This synthetic route allows the isolation of $M(C_2R)PR'_3$ (R = aryl ligand) in optimum yield.

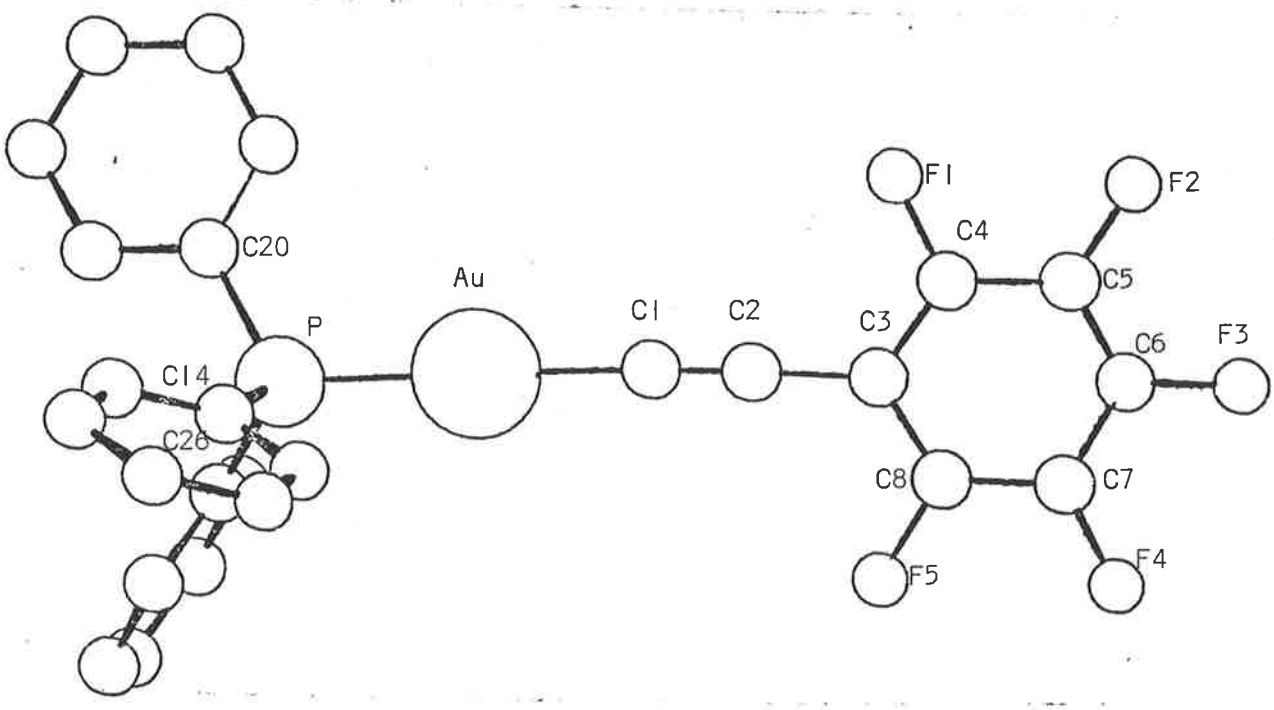
b) Reaction of $MClPR'_3$ (M = Au, Ag, Cu) with the appropriate terminal alkyne HC_2R in sodium methoxide solution. This synthetic route allows the isolation of $M(C_2R)PR'_3$ (R = alkyl or ester ligand) in optimum yield.

c) Reaction of $MClPR'_3$ (M = Au, Ag, Cu) with the appropriate terminal alkyne, HC_2R, in the presence of sodium hydroxide. This synthetic route allows the isolation of $M(C_2R)PR'_3$ (R = alcohol ligand).

The basic medium used in reactions (a)-(c) was needed to act as a proton "sponge." Ligand exchange reactions between phosphines and $M(C_2R)PPh_3$ were unsuccessful.

An X-ray crystal structure of $Au(C_2C_6F_5)PPh_3$ (I) establishes the complex to be monomeric (see Figure 2). The P-Au-C(1) ≡ C(2)-C(3) chain is almost linear, with only a slight distortion [P-Au-C(1) angle of 177.9° (3) and Au-C(1) ≡ C(2) angle of 175.4° (10)] rising as a result of crystal packing forces. No Au-Au interaction (>5.0Å) is observed. The simplicity of the observed structure is in complete contrast to the zwitterionic forms of copper and silver phosphine acetylide complexes (Figure 1).

FIGURE 2



$Au(C_2C_6F_5)PPh_3$

Selected Bond Lengths (Å) and Angles (°)

Au-P	2.274 (3)
Au=C(1)	1.993 (14)
C(1)-C(2)	1.197 (16)
C(2)-C(3)	1.442 (20)
P-C(14)	1.830 (7)
P-C(20)	1.814 (6)
P-C(26)	1.836 (9)
C(1)-Au'-P	177.9 (3)
C(1)-C(2)-C(3)	178.4 (12)
C(2)-C(1)-Au	175.4 (10)
Au-P-C(14)	111.8 (2)
Au-P-C(20)	114.1 (3)
Au-P-C(26)	113.8 (3)

The orbitals with a predominance of d orbital character for MPR_3 (M = Au, Ag, Cu) fragments are filled, and the bonding characteristics of these fragments are determined primarily by the degenerate pair of metal p_x and p_y orbitals.[56-58] The p_x and p_y orbitals for MPR_3 (M = Cu, Ag) are of lower energy than those for $AuPR_3$, and consequently can accept additional electron density more effectively.[56] The hy(s-z) orbital, directed linearly away from the MPR_3 fragment, is responsible for the two-coordinate nature of Au(I) compounds,[57,59,60] and forms the Au $\overset{\sigma}{—}$ C(1) bond in $Au(C_2C_6F_5)PPh_3$ (I) (Figure 2).

The phosphine gold, silver and copper acetylide complexes were identified by their spectral and microanalytical data. All complexes showed a characteristic $\nu(C\equiv C)$ absorption in the infra-red spectrum. The $\nu(C\equiv C)$ band energy increases down the group (Cu < Ag < Au, Table I), and reflects the decreasing M $\overset{\pi}{—}$ C_2R association (compare Figures I and 2), as the HOMO p_x and p_y orbitals also increase in energy down the same group. The complex, $Au(C_2Ph)PPh_3$ (10), was identified by comparing its spectral and physical data with literature values[39] (see Experimental section).

EXPERIMENTAL

General experimental conditions have been described in Chapter I. Although $AuClPPh_3$ can be prepared by several synthetic routes, from a variety of reagents,[61-70,72-84] the method of Kowala and Swan[71] was chosen for its simplicity and yield. $AgClPPh_3$,[85,89] $CuClPPh_3$[68] and $AuClSMe_2$[71,86,87] were prepared according to literature methods. Acetylenes were prepared according to methods outlined in the literature.[91,92]

Preparation of $AuClPMe_3$ (21)

The complex was prepared, with the following modifications, from a literature preparation.[69] Trimethylphosphine (918 mg, 12.06 mmol) was distilled into a solution of chloroauric acid (2.000 gm, 5.886 mmol) in ethanol (100 ml) at 0° and mixed for 2.5 h. under a nitrogen atmosphere. The initial orange solution slowly decolourised, resulting in the formation of a white precipitate. The solvent was removed *in vacuo*, the residue taken up in CH_2Cl_2 (50 ml), and dried over anhydrous $MgSO_4$. After filtration (scintered glass; under nitrogen), the solvent was reduced to half its volume, and diethyl ether (50 ml) was added. The resulting precipitate of $AuClPMe_3$ was recrystallised from acetone/methanol to afford fine white needles (1.65 g, 91%), m.p. = 226-228° (literature:[69] m.p. = 231-233°). ^1H n.m.r. δ [$(CD_3)_2CO$] = 1.96d, J_{PH} = 14 Hz. The product is extremely light-sensitive, and exposure to light should be kept to a minimum during the preparation. The product is also mildly air-sensitive, but can be handled for brief periods in air.

Preparation of $AuCl[P(OMe)_2Ph]$ (22)

A solution of $AuClSMe_2$ (160 mg, 0.543 mmol) and $P(OMe)_2Ph$ (95 mg, 0.558 mmol) in CH_2Cl_2 (20 ml) was mixed at room temperature for 1.5 h. The solvent was removed *in vacuo*, and the residue recrystallised from CH_2Cl_2/n-pentane to give white $AuCl[P(OMe)_2Ph]$ (22) (210 mg, 96%). ^1H

n.m.r. δ ($CDCl_3$) = 7.21m (5), $P(OMe)_2Ph$, 3.11d (6), J_{PH} = 13 Hz, $P(OMe)_2Ph$. Complex (22) could also be prepared in 69% yield by adding $P(OMe)_2Ph$ to an ether solution containing chloroauric acid and PCl_3, a method similar to that used by Nyholm and workers.[88]

Preparation of $AgC{\equiv}C\text{-}C_6F_5$ (23)

Silver nitrate (100 mg, 0.589 mmol) in a 1:1 concentrated ammonia/water solution (40 ml) was mixed with $HC_2C_6F_5$ (120 mg, 0.625 mmol) in ethanol (20 ml). Filtration of the white precipitate afforded $AgC_2C_6F_5$ (23) (141 mg, 80%), identified by comparison with literature data.[90]

Preparation of Group IB Phosphine Acetylides

The synthetic routes (a)-(c) (*vide supra*) were used. Some illustrative examples of each synthetic route are given below. A comprehensive summary of the spectral and physical data, synthesis and yields is given in Table 1.

Synthetic Route (a)

Preparation of $Au(C_2C_6F_5)PPh_3$ (1)

A mixture of $AuClPPh_3$ (495 mg, 1.00 mmol) and $HC_2C_6F_5$ (208 mg, 1.08 mmol) in diethylamine (40 ml) was mixed under a nitrogen atmosphere. To this mixture was added a catalytic amount (<8 mg) of CuCl, and stirring was maintained for 2.5 h. The solvent was then removed *in vacuo*. Water (30 ml) was added to the residue, and the product then extracted with benzene (3 x 30 ml). The resultant benzene solution was dried over $MgSO_4$ overnight, filtered (paper), and the solvent removed *in vacuo*. The resulting solid was washed with diethyl ether (30 ml) and recrystallised from toluene/n-octane, to afford white crystalline $Au(C_2C_6F_5)PPh_3$ (1) (419 mg, 64%).

TABLE I Group IB Phosphine Acetylides

Compound	Synthesis[a]	Yield	m.p.	Analytical data Found (calculated)	$\nu(C\equiv C)$ cm^{-1} (Nujol)	M^+ (mass spectrum)	^1H n.m.r. δ ($CDCl_3$)
$Au(C_2C_6F_5)PPh_3$ (1)	(a)	64%	235-236°	C - 48.04, H - 2.34% (C - 48.02, H - 2.32%)	2130	650	7.35m,PPh_3
	(d)	0%					
$Au(C_2Me)PPh_3$ (2)	(a)	45%	173-175°	C - 49.55, H - 3.45% (C - 50.62, H - 3.64%)	2130	498	7.49m (15),PPh_3 1.10s (3),Me
	(b)	77%					
$Cu(C_2Ph)PPh_3$ (3)	(d)	80%		C - 73.39, H - 4.84% (C - 73.14, H - 4.72%)	2043		7.43m,PPh_3 + Ph
	(b)	92%					
$Ag(C_2Ph)PPh_3$ (4)	(d)	52%		C - 66.14, H - 3.98% (C - 66.26, H - 4.27%)	2075		7.32m,PPh_3 + Ph
	(b)	95%					
$Au(C_2CMe_3)PPh_3$ (5)	(a)	67%	181-182°	C - 52.32, H - 4.39% (C - 53.34, H - 4.48%)	2140	540	7.41m (15),PPh_3 1.39s (9),CMe_3
	(b)	93%					
	(d)	0%					
$Au(C_2CO_2Me)PPh_3$ (6)	(b)	60%	239-240°	C - 48.37, H - 3.21% (C - 48.72, H - 3.34%)	2100	542	7.50m (15),PPh_3 2.47s (3),CO_2Me
	(a)	0%					
$Au(C_2CMe_3)PMe_3$ (13)	(b)	81%	183-186°	C - 30.79, H - 5.25% (C - 30.52, H - 5.12%)	2115	354	1.80d (9),PMe_3, (J_{PH} = 12 Hz) 1.39s (9),CMe_3
$Au(C_2Me)PMe_3$ (14)	(b)	28%	123°(dec.)	C - 22.90, H - 3.32% (C - 23.09, H - 3.87%)	2120	312	1.80d (9),PMe_3, (J_{PH} = 12 Hz) 1.10s (3),Me
$Au(C_2Ph)P(OMe)_2Ph$ (15)	(b)	68%	212-215°	C - 40.19, H - 3.36% (C - 41.04, H - 3.44%)	2110	468	7.56m (10),C_2***Ph*** + $P(OMe)_2$***Ph*** 3.06d (6),$P(O$***Me***$)_2Ph$, (J_{PH} = 13 Hz)
$Ag(C_2C_6F_5)PPh_3$ (16)	(a)	92%		C - 56.01, H - 3.40% (C - 55.64, H - 2.69%)	2097		7.49m,PPh_3
	(b)	87%					
	(d)	82%					
$Cu(C_2C_6F_5)PPh_3$ (17)	(b)	87%		C - 58.57, H - 2.70% (C - 58.46, H - 2.50%)	2064		7.48m,PPh_3
$Ag(C_2Pr^n)PPh_3$ (18)	(b)	71%		C - 62.85, H - 4.39% (C - 63.18, H - 5.07%)	2070		7.50m (15),PPh_3 1.60-0.70m (15),Pr^n
	(a)	41%					
$Ag(C_2Me)PPh_3$ (19)	(b)	86%		C - 61.13, H - 4.04% (C - 61.64, H - 4.43%)	2072		7.39m (15),PPh_3 0.99s (3),Me
	(a)	12%					
$Cu(C_2Me_3)PPh_3$ (20)	(b)	62%		C - 70.89, H - 5.58% (C - 70.83, H - 5.94%)	2055		7.40m (15),PPh_3 1.55s (9),CMe_3

[a](a)-(c) refer to synthetic methods so designated in text (Results and Discussion); (d) refers to the method of Coates and Parkin (Reference 39).

Preparation of $Ag(C_2C_6F_5)PPh_3$ (16)

A mixture of $AgClPPh_3$ (250 mg, 0.616 mmol) and $HC_2C_6F_5$ (131 mg, 0.680 mmol) in triethyl amine (28 ml) was mixed under a nitrogen atmosphere. To this mixture was added a catalytic amount (<8 mg) of CuCl, and mixing was maintained for 6 h. The solvent was removed *in vacuo*. Water (15 ml) was added to the residue, and the product then extracted with benzene (4 x 25 ml). The resultant benzene solution was dried over $MgSO_4$ overnight, filtered (paper), and the solvent removed *in vacuo*. The resulting solid was washed with a 1:1 mixture of diethyl ether/n-pentane (30 ml), and recrystallised from CH_2Cl_2/ n-pentane. White crystalline $Ag(C_2C_6F_5)PPh_3$ (16) (318 mg, 92%).

Synthetic Route (b)

Preparation of $Au(C_2CO_2Me)PPh_3$ (6)

To a solution of $AuClPPh_3$ (200 mg, 0.404 mmol) in methanol (45 ml), was added a small piece (50-75 mg) of sodium. After hydrogen evolution had ceased, a solution containing HC_2CO_2Me (34 mg, 0.404 mmol) in methanol (1.5 ml) was added dropwise over 15 min. The resultant mixture was stirred under a nitrogen atmosphere for 3 h. The solvent was then removed *in vacuo* at 15°. The residue was recrystallised from methanol/diethyl ether to give light-sensitive, microcrystalline $Au(C_2CO_2Me)PPh_3$ (6) (131 mg, 60%). The product is unstable in chlorinated solvents, depositing colloidal gold.

Preparation of $Cu(C_2C_6F_5)PPh_3$ (17)

A mixture of $CuClPPh_3$ (500 mg, 1.38 mmol) and $HC_2C_6F_5$ (269 mg, 1.40 mmol) in methanol (35 ml) was stirred under a nitrogen atmosphere. To this mixture was added a small piece of sodium (50-75 mg) and, after hydrogen evolution had ceased, the solution was again degassed under nitrogen. Stirring was maintained for 1 h. The product precipitated as yellow granules, and was collected by filtration (scintered glass).

After washing with methanol (50 ml), water (20 ml), methanol (20 ml) and diethyl ether (25 ml), the product was dried *in vacuo* for 17 h., to afford $Cu(C_2C_6F_5)PPh_3$ (17) as a yellow powder (625 mg, 87%).

Synthetic Route (c)

Preparation of $Au(C_2CH_2OH)PPh_3$ (9)

A mixture of $AuClPPh_3$ (100 mg, 0.202 mmol) and HC_2CH_2OH (15 mg, 0.224 mmol) in methanol (15 ml) was stirred under a nitrogen atmosphere. To this mixture was added, dropwise, a solution of KOH (80 mg, 1.43 mmol) in warm methanol (50 ml, 40°). Addition was discontinued on noticing the formation of a pale orange colour. Stirring was maintained for an additional 0.5 h. The solvent was removed *in vacuo*, and the residue extracted with toluene (25 ml). Slow diffusion of n-octane into this toluene solution afforded crystals of $Au(C_2CH_2OH)PPh_3$ (9) (56 mg, 54%).

Preparation of $Au(C_2CH_2CH_2OH)PPh_3$ (8)

A mixture of $AuClPPh_3$ (200 mg, 0.404 mmol) and $HC_2CH_2CH_2OH$ (30 mg, 0.428 mmol) in methanol (30 ml) was stirred under a nitrogen atmosphere. To this mixture was added, dropwise, a solution of KOH (80 mg, 143 mmol) in warm methanol (50 ml, 40°). Addition was discontinued on the first appearance of a pale orange-red colour. Stirring was maintained for an additional 1 h. The solvent was then removed *in vacuo*, and the residue recrystallised from toluene/n-octane, to afford $Au(C_2CH_2CH_2OH)PPh_3$ (8) (89 mg, 42%).

Synthetic Route (d)

Preparation of $Ag(C_2C_6F_5)PPh_3$ (16)

A mixture of $Ag(C_2C_6F_5)$ (23) (141 mg, 0.738 mmol) and PPh_3 (185 mg, 0.705 mmol) in ethanol (40 ml) was heated at reflux point for 30 min. Dichloromethane (40 ml) was added to the cooled solution, the solution

filtered (paper), and the volume reduced by half *in vacuo*. Filtration (scintered glass) and washing with cold diethyl ether (8 ml) gave $Ag(C_2C_6F_5)PPh_3$ (16) (243 mg, 92%).

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CHAPTER FOUR

SYNTHESIS AND REACTIVITY OF GROUP IB PHOSPHINE ACETYLIDE COMPLEXES WITH $H_2Os_3(CO)_{10}$

INTRODUCTION

The first complexes containing transition metal-gold bonds were described twenty-one years ago.[145] Since that time, the synthesis of Group IB heterometallic complexes has increased to incorporate most of the transition elements (see Table I: Appendix I). The early work of Nyholm and Lewis showed that stable gold-osmium clusters could be obtained by oxidative addition of $AuX(PR_3)$ (X = halide, R = alkyl, aryl) to osmium carbonyl clusters.[55,56,152] Over the last three years, the number of heteronuclear metal clusters incorporating gold atoms in the metal core has increased rapidly (see Table I and 2, following).[153] The current interest in these compounds was facilitated by the recognition that the $AuPR_3$ moiety is isolobal[154] with H.[75,155-158]

Lauher's demonstration that the $Au(PPh_3)$ moiety in $AuCo_3Fe(CO)_{12}(PPh_3)$[75] occupies a similar Co_3-face-bridging position to that of H in $HCo_3Fe(CO)_{12}$,[159-161] was quickly followed by structural studies with other gold-containing clusters.[71] Likewise, the $Au(PPh_3)$ moiety is seen to occupy an analogous edge-bridging position in $AuRu_3(CO)_9(PPh_3)(C_2Bu^t)$[125,126] to that of H in $HRu_3(CO)_9(C_2Bu^t)$.[162,163] Hydrogen bonds to a transition metal by using its 1s orbital, while gold primarily used its 6s orbital.[164] Gold forms polar bonds with transition metal anions.[29-31] This is reflected in the carbonyl infra-red spectra, which indicate that the electron density on the transition metal tends to be intermediate between that of the free anion and its hydride.[152] It should be possible, then, to prepare gold phosphine analogues of most transition-metal hydrides.

Heterometallic gold clusters have generally been synthesized by one of four preparative methods (see Table I):

i) Oxidative addition of $AuXPR_3$ (X = halide) to a transition metal carbonyl cluster.

ii) Addition of $AuXPR_3$ (X = halide) to a cluster carbonyl anion in the presence of $TlPF_6$ (removes X^- from solution as TlX).

iii) Addition of $AuPR_3$ to a hydrido-carbonyl cluster by displacement of methane from the $AuMePPh_3$ reagent.

iv) Reaction of $[(AuPPh_3)_3O]BF_4$ with cluster carbonyl anions, resulting in the incorporation of up to three $AuPPh_3$ moieties into the cluster framework.

Method (ii) is the most synthetically useful route for the introduction of an $AuPR_3$ moiety to a carbonyl cluster, largely because the heterometallic cluster is formed in near quantitative yields. Few cluster anion precursors with three or more negative charges are known, although three PR_3Au moieties can be added to the anions $M(CO)_4^{3-}$ (M = Mn,Re)[36,37] and $V(CO)_5^{3-}$,[39] to form $Au_3M(CO)_n(PPh_3)$ (M = Mn, Re, n = 4; M = V, n = 5). Recently, Stone[76,81] has prepared several trigold metal clusters from reactions between $AuMePPh_3$ and cluster hydride precursors, which proceed by elimination of methane. The number of $AuPR_3$ moieties introduced thus depends on the number of metal bound hydrides in the reagent cluster. A far more versatile reagent is $[(AuPPh_3)_3O]BF_4$,[165] which can be used as a vehicle for the introduction of up to six[166] gold atoms into metal cluster anions. Structural studies of the polygold clusters[76,79-81,142,143,151] reveal that the isolobal analogy between H and $AuPR_3$ no longer exists for these complexes.

The observed geometries of gold heterometallic clusters can be rationalised as follows. The first $AuPR_3$ group occupies a position analogous to that occupied by H in the corresponding cluster hydride. This may be either edge-bridging or face-capping, and it is in this case that the isolobal relationship between the H and $AuPR_3$ moieties is important. However, the second and third $AuPR_3$ moieties occupy face-capping sites, which develop the maximum number of tetrahedral units with Au-Au edges. This results from the necessity to maximise

the interactions between *p* orbitals of neighbouring gold atoms,[155,167] which thus play a steric role in developing the geometry of the resulting poly-gold clusters. These interactions are relatively weak, as shown by the wide range of observed Au-Au separations,[151] and also by the ability of the Au_n fragment to accommodate steric interactions between peripheral ligands.[151]

Synthesis of silver heterometallic clusters is generally accomplished (Table 1) by the addition of Ag^+ (from $AgNO_3$[75,93] or $AgBF_4$[112]) to a cluster carbonyl anion. However, unlike gold heterometallic clusters, there is a dearth of structural information on silver heterometallic clusters. The only structurally characterised silver heterometallic cluster, $AgFe_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}CHC(NHCH_3)C_6H_5]^+$, shows the silver atom to be coordinated to only two iron atoms.[123,124]

Heterometallic carbonyl clusters containing copper are generally synthesized by reacting $Cu(CNMe)_4^+$ or $CuClPPh_3$ with cluster carbonyl anions (see Table 1). Recently, however, treatment of copper (I) chloride with LiC_5Me_5 in tetrahydrofuran gave a reagent which has proved a useful source of the $Cu(\eta\text{-}C_5Me_5)$ fragment in the synthesis of heterometallic clusters.[137,168] Structural information on heterometallic clusters containing copper is limited to five studies,[5,89,121,130,138] and of these, only $Cu_2Ru_6C(CO)_{16}(CNMe)_2$[121] and $CuOs_{10}C(CO)_{24}(NCMe)$[138] contain carbonyl ligands. The recent upsurge of interest in this field should provide further data on the bonding of not only copper, but also silver, in heterometallic carbonyl clusters.

TABLE I Heterometallic Clusters containing Copper, Silver or Gold

Group IB reagent	Other reagent	Product	Heterometallic Bond Lengths (average in Å)	Yield	Reference(s)
CuC_2R	$IrCl(CO)(PPh_2R')_2$	$Ir_2Cu_4(C_2R)_8(PPh_2R')_2$			
R = Ph	R′ = Ph		2.870	61%	4, 5, 6
R = C_6H_4Me-*p*	R′ = Ph			73%	4
R = C_6H_4F-*p*	R′ = Ph			65%	4
R = C_6F_5	R′ = Ph			63%	4
R = Ph	R′ = Me			90%	4
R = C_6F_5	R′ = Me			9%	4
$Cu(C_2Ph)(PMePh_2)$	R′ = Ph	$Ir_2Cu_4(C_2Ph)_8(PMePh_2)_2$		11%	4
CuC_2R	$RhCl(CO)(PPh_2R')_2$	$Rh_2Cu_4(C_2R)_8(PPh_2R')_2$			
R = Ph	R′ = Ph			7%	4
R = C_6H_4Me-*p*	R′ = Ph			4%	4
R = C_6H_4F-*p*	R′ = Ph			17%	4
R = C_6F_5	R′ = Ph			40%	4
R = Ph	R′ = Me			29%	4
R = C_6H_4Me-*p*	R′ = Me			25%	4

Group IB reagent	Other reagent	Product	Heterometallic Bond Lengths (average in Å)	Yield	Reference(s)
$AgNO_3$	$Co_2(CO)_8$	$AgCo_2(CO)_8 \cdot H_2O$		65%	49, 51, 52
$Ag_2(N_2C_{12}H_8)$	$H_2Fe(CO)_4$	$Ag_2Fe(CO)_4(N_2C_{12}H_8)$			49
$Cu(NH_3)_2$	$H_2Fe(CO)_4$	$Cu_2Fe(CO)_4(NH_3)_2$			49
$AuClPPh_3$	$Os(CO)_4^{2-}$	$Au_2Os(CO)_4(PPh_3)_2$		39%	54
$AuXPPh_3$	$Os_3(CO)_{12}$	$AuOs_3(CO)_{10}(PPh_3)X$		54%(Cl)	55, 56
X = Cl,Br,I,SCN				10%(Br)	55, 56
				8%(I)	55, 56
			2.761	7%(SCN)	55, 56, 71, 73
$(AuPPh_3)_2^5$	$Os_3(CO)_{12}$	$Au_2Os_3(CO)_{10}(PPh_3)_2S_2$		4%	55, 56
$AuCl[P(C_6H_4Me\text{-}p)_3]$	$Os_3(CO)_{12}$	$AuOs_3(CO)_{10}[P(C_6H_4Me\text{-}p)_3]Cl$		50%	55, 56
$CuClPPh_3$	$NaCo(CO)_3(PBu_3)$	$CuCo_2(CO)_6(PBu_3)_2(PPh_3)_2$			59
$AuClPPh_3$	$HOs_3(CO)_{11}^-/TlPF_6$	$HAuOs_3(CO)_{10}(PR_3)$ R = Et,Ph	2.755(Ph)	64%(R = Ph)	71, 73, 77
				62%(R = Et)	
$AuClPPh_3$	$HOs_4(CO)_{13}^-/TlPF_6$	$HAuOs_4(CO)_{13}(PR_3)$ R = Et,Ph	2.777(Et)	60-65%	71, 82
$AuClPPh_3$	$HFeOs_3(CO)_{13}^-/TlPF_6$	$HAuFeOs_3(CO)_{13}(PR_3)$ R = Et,Ph		60-65%	71, 82
$AuClPPh_3$	$H_3Os_4(CO)_{12}^-/TlPF_6$	$H_3AuOs_4(CO)_{12}(PR_3)$ R = Et, Ph	2.793(Et)	45-50%	71, 82
$AuClPPh_3$	$H_3Ru_4(CO)_{12}^-/TlPF_6$	$H_3AuRu_4(CO)_{12}(PR_3)$ R = Et,Ph		80%	71, 82

Group IB reagent	Other reagent	Product	Heterometallic Bond Lengths (average in Å)	Yield	Reference(s)
$AuClPEt_3$	$Os_5(CO)_{15}^{2-}/H^+/TlPF_6$	$HAuOs_5(CO)_{15}(PEt_3)$		40-60%	71, 82
$AuMePPh_3$	$H_4Os_4(CO)_{12}$	$H_3AuOs_4(CO)_{12}(PR_3)$ R = Et,Ph			71, 74
$AuPPh_3^+NO_3^-$	$FeCo_3(CO)_{12}^-$	$AuFeCo_3(CO)_{12}(PPh_3)$	2.714		75
PPh_3AuMe	$H_2Os_3(CO)_{10}$	$HAuOs_3(CO)_{10}(PPh_3)$			76, 117, 118
$AuClPR_3$ (R = Et,Ph)	$HOs_3(CO)_{11}^-/TlPF_6$	$Au_2Os_3(CO)_{10}(PR_3)_2$ R = Ph,Et	2.761 (R = Et)	80%	77
$AuClPEt_3$	$Os_3(CO)_{10}(OEt)_2/TlPF_6$	$AuOs_3(CO)_{10}(PEt_3)(OEt)$		22%	77
$[(AuPPh_3)_3O][BF_4]$	$PPN[CoRu_3(CO)_{13}]$	$Au_3CoRu_3(CO)_{12}(PPh_3)_3$	2.836	55%	79
$AuClPPh_3$	$Na[CoRu_3(CO)_{13}]$	$AuCoRu_3(CO)_{13}(PPh_3)$		45%	79
$[(AuPPh_3)_3O][BF_4]$	$HCoRu_3(CO)_{13}$	$HAu_2CoRu_3(CO)_{12}(PPh_3)_2$			79
$[(AuPPh_3)_3O][BF_4]$	$H_3Ru_4(CO)_{12}^-$	$H_3AuRu_4(CO)_{12}(PPh_3)$		10%	79, 80, 82
$[(AuPPh_3)_3O][BF_4]$	$H_3Ru_4(CO)_{12}^-$	$H_2Au_2Ru_4(CO)_{12}(PPh_3)_2$		3%	79, 80
$[(AuPPh_3)_3O][BF_4]$	$H_3Ru_4(CO)_{12}^-$	$HAu_3Ru_4(CO)_{12}(PPh_3)_3$	2.881	15%	79, 80
$AuMePPh_3$	$H_4Ru_4(CO)_{12}$	$HAu_3Ru_4(CO)_{12}(PPh_3)_3$	2.880	55%	81
$AuMePPh_3$	$H_3Ru_3(CO)_9(\mu_3\text{-}COMe)$	$H_2AuRu_3(CO)_9(PPh_3)(\mu_3\text{-}COMe)$	2.745	27%	81
$AuMePPh_3$	$H_3Ru_3(CO)_9(\mu_3\text{-}COMe)$	$HAuRu_3(CO)_9(PPh_3)_2(\mu_3\text{-}COMe)$		21%	81
$AuMePPh_3$	$H_3Ru_3(CO)_9(\mu_3\text{-}COMe)$	$Au_3Ru_3(CO)_9(PPh_3)_3(\mu_3\text{-}COMe)$	2.844	12%	81

Group IB reagent	Other reagent	Product	Heterometallic Bond Lengths (average in Å)	Yield	Reference(s)
$AuClPPh_3$	$Na[RuCo_3(CO)_{12}]$	$AuRuCo_3(CO)_{12}(PPh_3)$	2.721		84
$AuClPR_3$	$H_2Os_4(CO)_{12}^{2-}$	$H_2Au_2Os_4(CO)_{12}(PR_3)_2$ R = Et,Ph	2.890		85
$AuClPR_3$	$Fe_4(CO)_{13}^{2-}/TlPF_6/HBF_4$	$HAuFe_4C(CO)_{12}(PR_3)$ R = Et,Ph	2.867	47%	86
$AuClPR_3$	$HAuFe_4C(CO)_{12}(PR_3)/NEt_3/HBF_4$	$Au_2Fe_4C(CO)_{12}(PR_3)_2$ R = Et,Ph	2.917	90%	86
$[AgIPEt_3]_4$	$HRu_3(CO)_9(\mu_3\text{-}PPh)^-$	$HAgRu_3(CO)_9(PEt_3)(\mu_3\text{-}PPh)$			87
$[CuIPEt_3]_4$	$HRu_3(CO)_9(\mu_3\text{-}PPh)^-$	$HCuRu_3(CO)_9(PEt_3)(\mu_3\text{-}PPh)$			87
$[Au(PPh_3)_2][PF_6]$	$HRu_3(CO)_9(\mu_3\text{-}PPh)^-$	$HAuRu_3(CO)_9(PEt_3)(\mu_3\text{-}PPh)$			87
$[Au(PMe_2Ph)_2](PF_6]$	$HRu_3(CO)_9(\mu_3\text{-}PPh)^-$	$HAuRu_3(CO)_9(PMe_2Ph)(\mu_3\text{-}PPh)$	2.757		87
$CuCl_2$	Cs_2WOS_3/PPh_3	$[Cu_3WS_3Cl(PPh_3)_3O]$	2.738		89
$AgNO_3$	$Na[Cr(CO)_3(\eta\text{-}C_5H_5)]$	$[AgCr_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$		80%	93
$AgNO_3$	$Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$	$[AgMo_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$		90%	93, 262
$AgNO_3$	$Na[W(CO)_3(\eta\text{-}C_5H_5)]$	$[AgW_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$		90%	93, 262
CuCl	$Na[Cr(CO)_3(\eta\text{-}C_5H_5]$	$[CuCr_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$		90%	93, 262
CuCl	$Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$	$[CuMo_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$		85%	93
CuCl	$Na[W(CO)_3(\eta\text{-}C_5H_5)]$	$[CuW_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$		85%	93, 262
AgBr	$Cu(NMe_2Ph)$	$Ag_2Cu(NMe_2Ph)_4Br_2$		70%	104, 107, 108
CuBr	$Ag(C_6H_4NMe\text{-}o)$	$Ag_4Cu_4(C_6H_4NMe\text{-}o)_4Br_2$		80%	106

Group IB reagent	Other reagent	Product	Heterometallic Bond Lengths (average in Å)		Yield	Reference(s)
$Cu(CF_3SO_3)$	$Au(C_6H_4NMe\text{-}o)$	$Au_2Cu_4(C_6H_4NMe\text{-}o)_4(CF_3SO_3)_2$			95%	107, 108
$Ag(CF_3SO_3)$	$Au(C_6H_4NMe\text{-}o)$	$Au_2Ag_4(C_6H_4NMe\text{-}o)_4(CF_3SO_3)_2$			91%	108
$AgBF_4$	$[Ni_9(CO)_{18}]^{2-}$	$[AgNi_9(CO)_{18}]^-$			50%	112
$Cu(NCMe)_4^+$	$Rh_6C(CO)_{15}^{2-}$	$Cu_2Rh_6C(CO)_{15}(NCMe)_2$	2.660		70%	114
$Au_8(PPh_3)_7^{2+}$	$Li[Co(CO)_4]$	$Au_6Co_2(CO)_8(PPh_3)_4$	2.46			116
$Cu(NCMe)_4^+$	$Ru_6C(CO)_{16}^{2-}$	$Cu_2Ru_6C(CO)_{16}(NCMe)_2$	2.654		77%	121
$AuClPPh_3$	$Ru_5C(CO)_{15}$	$AuRu_5C(CO)_{15}(PPh_3)Cl$	2.798			122
$AuClPPh_3$	$Ru_5C(CO)_{15}$	$AuRu_5C(CO)_{14}(PPh_3)Cl$	2.742			122
$AgClO_4$	$Fe_2(CO)_6[\mu\text{-}CHC(NRR')(C_6H_5)](\mu\text{-}PPh_2)$	$AgFe_2(CO)_6[\mu CHC(NRR')(C_6H_5)]$-$(\mu PPh_2)$ R = H, R′ = CH_3, C_2H_5, $CH(CH_3)_2$, $C\text{-}C_6H_{11}$; R = R′ = C_2H_5	2.694	R = H R′ = CH_3	85-92%	123, 124
$AuClPPh_3$	$Ru_3(CO)_9(C_2Bu^t)^-$	$AuRu_3(CO)_9(PPh_3)(C_2Bu^t)$	2.760		80%	125, 126
$Cu(NCMe)_4^+$	$[Fe_5C(CO)_{14}]^{2-}$	$[CuFe_5C(CO)_{14}(NCMe)]^-$				127-129
$Cu(NCMe)_4^+$	$[Fe_4C(CO)_{12}]^{2-}$	$[CuFe_4C(CO)_{12}(NCMe)]^-$				127-129
$CuCl_2$	Cs_2WS_4/PPh_3	$[Cu_3WS_3Cl(PPh_3)_3S]$	2.717			130
$Cu(C_5Me_5)$	$Rh_2(CO)_2(C_5Me_5)_2$	$CuRh_2(CO)_2(\eta\text{-}C_5Me_5)_3$				137
$Cu(NCMe)_4^+$	$Os_{10}C(CO)_{24}^{2-}$	$CuOs_{10}C(CO)_{24}(NCMe)$	2.637			138

Group IB reagent	Other reagent	Product	Heterometallic Bond Lengths (average in Å)	Yield	Reference(s)
$AuClPPh_3$	$Os_{10}C(CO)_{24}^{2-}$	$AuOs_{10}C(CO)_{24}(PPh_3)$	2.816		138
$AuClPPh_3$	$Ru_6C(CO)_{14}(NO)_2$	$AuRu_6C(CO)_{15}(PPh_3)(NO)$	2.908		139
$AuClPPh_3$	$Ru_3(CO)_9(PPhCH_2PPh_2)^-$	$AuRu_3(CO)_9(PPh_3)(PPhCH_2PPh_2)$		74%	140
$AgPPh_3[C_5(CO_2Me)_5]$	$Ru_3(CO)_9(PPhCH_2PPh_2)^-$	$AgRu_3(CO)_9(PPh_3)(PPhCH_2PPh_2)$		82%	141
$CuClPPh_3$	$Ru_3(CO)_9(PPhCH_2PPh_2)^-$	$CuRu_3(CO)_9(PPh_3)(PPhCH_2PPh_2)$		81%	140
$AuClPPh_3$	$Ru_3(CO)_9(AsPhCH_2AsPh_2)^-$	$AuRu_3(CO)_9(PPh_3)$-$(AsPhCH_2AsPh_2)$		75%	140
$AuClPPh_3$	$Ru_3(CO)_9(PPhCH_2CH_2PPh_2)^-$	$AuRu_3(CO)_9(PPh_3)$-$(PPhCH_2CH_2PPh_2)$		10%	140
$[(AuPPh_3)_3O]BF_4$	$Ru_3(CO)_9(C_2Bu^t)^-$	$Au_2Ru_3(CO)_9(PPh_3)_2(C_2Bu^t)$		24%	142
$[(AuPPh_3)_3O]BF_4$	$Ru_3(CO)_9(\mu_3\text{-}S)^{2-}$	$Au_2Ru_3(CO)_9(PPh_3)_2(\mu_3\text{-}S)$		19%	143
$AuClPPh_3$	$HRu_3(CO)_9(\mu_3\text{-}S)^-/TlPF_6$	$HAuRu_3(CO)_9(PPh_3)(\mu_3\text{-}S)$		28%	126
$[(AuPPh_3)_3O]BF_4$	$Ru_3(CO)_9(C_{12}H_{15})$	$Au_3Ru_3(CO)_8(PPh_3)_3(C_{12}H_{15})$		19%	143
$AuClPPh_3$	$HRu_3(CO)_9(\mu_3\text{-}SBu^t)^-/TlPF_6$	$AuRu_3(CO)_9(PPh_3)(\mu_3\text{-}SBu^t)$		27%	126
$AuClPPh_3$	$HRu_3(CO)_9(\mu_3\text{-}SBu^t)^-/TlPF_6$	$HAuRu_3(CO)_9(PPh_3)(\mu_3\text{-}SBu^t)$			126
$AuClPPh_3$	$Ru_3(CO)_9(\mu_3\text{-}SBu^t)^{2-}/TlPF_6$	$Au_2Ru_3(CO)_9(PPh_3)(\mu_3\text{-}SBu^t)$			126
$AuClPPh_3$	$[Fe_3(CO)_9(\mu_3\text{-}HC=NBu^t)]^-$	$AuFe_3(CO)_9(PPh_3)(\mu_3\text{-}HC=NBu^t)$		63%	151

Group IB reagent	Other reagent	Product	Heterometallic Bond Lengths (average in Å)	Yield	Reference(s)
$AuMePPh_3$	$H_2Re_2(CO)_8$	$HAuRe(CO)_9(PPh_3)$			265

TABLE 2 Reactivity of Heterometallic Compounds Containing Copper Silver or Gold

Reagent	Heterometallic Reagent	Product	Yield	Reference(s)
$Fe_2(CO)_9$	$Ir_2Cu_4(C_2R)_8(PPh_3)_2$	$Ir_2Cu_4Fe_2(C_2R)_8(CO)_8(PPh_3)_2$		
	R = Ph		63%	4
	R = C_6H_4Me-*p*		53%	4
L = (PPh_3, $AsPh_3$, py)	$AuMn(CO)_5(PPh_3)$	$AuMn(CO)_4(PPh_3)L$	30%	25
$P(OPh)_3$	$AuMn(CO)_5(PPh_3)$	$AuMn(CO)_4(PPh_3)[P(OPh)_3]$	30%	25, 26
PPh_3	$AuFe(CO)_3(NO)(PPh_3)$	$AuFe(CO)_2(NO)(PPh_3)_2$	80%	43
$P(OPh)_3$	$AuFe(CO)_3(NO)(PPh_3)$	$AuFe(CO)_2(NO)[P(OPh)_3](PPh_3)$	55%	43
Bipyridyl	$AgCo_2(CO)_8$	$AgCo(CO)_4$(bipyridyl)	88%	49, 261
PPh_3	$[AuCo(CO)_4(C_6F_5)_3]^-$	$[AuCo(CO)_3(C_6F_5)_3(PPh_3)]^-$	87%	63
$P(OPh)_3$	$[AuCo(CO)_4(C_6F_5)_3]^-$	$\{AuCo(CO)_3(C_6F_5)_3[P(OPh)_3]\}^-$	72%	63
PEt_3	$AuPt(PPh_3)_3(C_6Cl_5)$	$AuPt(PPh_3)_2(PEt_3)(C_6Cl_5)$	95%	67
$PPhEt_2$	$AuPt(PPh_3)_3(C_6Cl_5)$	$AuPt(PPh_3)_2(PPhEt_2)(C_6Cl_5)$	95%	67
PPh_2Et	$AuPt(PPh_3)_2(C_6Cl_5)$	$AuPt(PPh_3)_2(PPh_2Et)(C_6Cl_5)$	95%	67
CN^-	$CuMoS_4(NH_4)$	$[CuMoS_4(CN)]^-$		70
		(Cu-Mo = 2.624 Å)		
$AuMePPh_3$	$H_3AuOs_4(CO)_{12}(PPh_3)$	$H_2Au_2Os_4(CO)_{12}(PPh_3)_2$		71, 74

$AuMePEt_3$	$H_3AuOs_4(CO)_{12}(PPh_3)$	$H_2Au_2Os_4(CO)_{12}(PEt_3)(PPh_3)$		71, 74
$[N(PPh_3)_2]Cl$	$HAuOs_3(CO)_{10}(PPh_3)$	$[H_2AuOs_6(CO)_{20}][N(PPh_3)_2]$ (Average Au-Os = 2.808 Å		71, 88
CO	$HAuOs_3(CO)_{10}(PPh_3)$	$HAuOs_3(CO)_{11}(PPh_3)$		71, 77
$CNBu^t$	$HAuOs_3(CO)_{10}(PEt_3)$	$HAuOs_3(CO)_{10}(CNBu^t)(PPh_3)$		71
heat	$HAuOs_3(CO)_{10}(PR_3)$	$H_3AuOs_4(CO)_{12}(PR_3)$; R = Ph,Et	1%	71, 82
heat	$HAuOs_3(CO)_{10}(PR_3)$	$HAuOs_5(CO)_{15}(PR_3)$; R = Ph,Et	8%	71, 82
$AuClPPh_3$	$AuOs_3(W)_{11}(PPh_3)^-$	$Au_2Os_3(CO)_{11}(PPh_3)_2$		77, 78
$AuClPEt_3$	$AuOs_3(CO)_{11}(PEt_3)^-$	$Au_2Os_3(CO)_{11}(PEt_3)_2$		77, 78
heat/CO	$Au_2Os_3(CO)_{11}(PPh_3)_2$	$Au_2Os_3(CO)_{10}(PPh_3)_2$		77
heat/CO	$Au_2Os_3(CO)_{11}(PEt_3)_2$	$Au_2Os_3(CO)_{10}(PEt_3)_2$		77
NEt_3	$Au_2Os_3(CO)_{11}(PEt_3)_2$	$Au_2Os_3(CO)_{10}(NEt_3)(PEt_3)_2$		77
PPh_3	$Au_2Os_3(CO)_{11}(PEt_3)_2$	$Au_2Os_3(CO)_{10}(PEt_3)_2(PPh_3)$		77
heat	$HAuOs_3(CO)_{10}(PR_3)$	$HAuOs_5(CO)_{15}(PR_3)$; R = Ph,Et	21-24%	82
1,10 phen	$[CuCr(CO)_3(\eta\text{-}C_5H_5)]_n$	$[CuCr(CO)_3(\eta\text{-}C_5H_5)(phen)]$	50%	93
$W(CO)_3(\eta\text{-}C_5H_5)^-$	$[AgMo(CO)_3(\eta\text{-}C_5H_5)]_n$	$[AgMoW(CO)_6(\eta\text{-}C_5H_5)_2]^-$		93
$W(CO)_3(\eta\text{-}C_5H_5)^-$	$[CuMo(CO)_3(\eta\text{-}C_5H_5)]_n$	$[CuMoW(CO)_6(\eta\text{-}C_5H_5)_2]^-$		93
phen	$[CuM_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$ (M = Cr,Mo,W)	$[CuM_2(CO)_6(\eta\text{-}C_5H_5)_2(phen)]^-$	95%	93

phen	$[AgM(CO)_3(\eta\text{-}C_5H_5)]_n$ (M = Cr,Mo,W)	$[AgM(CO)_3(\eta\text{-}C_5H_5)(phen)]_n$	95%	93	
phen	$[CuM(CO)_3(\eta\text{-}C_5H_5)]_n$ (M = Cr,Mo,W)	$[CuM(CO)_3(\eta\text{-}C_5H_5)(phen)]_n$	95%	93	
L = phen, bipy	$[MCo(CO)_4]_n$ (M = Ag,Cu)	$MCo(CO)_4L$		93	
L = phen, bipy	$MCo(CO)_3(PBu^t_3)$ (M = Ag,Cu)	$MCo(CO)_3(PBu^t_3)L$		93	
L = phen, bipy	$AgFe(CO)_2[P(OPh)_3](NO)$	$AgFe(CO)_2[P(OPh)_3](NO)L$		93	
dppe	$AgCo(CO)_3(PBu^t_3)$	$AgCo(CO)_3(PBu^t_3)(dppe)$		93	
PPh_3	$[CuM_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$ (M = Cr,Mo,W)	$[(PPh_3)_4Cu][CuM_2(CO)_6(\eta\text{-}C_5H_5)_2]$	70%	93	
KCN	$[MMo_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$ (M = Cu,Ag)	$[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$	100%	93	
$Et_2O \cdot BF_3$	$[AgM_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$	$[AgM(CO)_3(\eta\text{-}C_5H_5)]_n$	60%	93	
KSPh	$[CuMoS_4(CN)]^{2-}$/MeCN	$[CuMoS_4(SPh)]^{2-}$ (Cu-Mo = 2.636 Å)	45%	98	
KSPh	$[Cu_2MoS_4(CN)_2]^{2-}$/MeCN	$[Cu_2MoS_4(SPh)_2]^{2-}$ (Cu-Mo = 2.632 Å)	50%	98	

$KSPh^-$	$[Cu_2MoS_4(PPh_3)_3]$/MeCN	$[Cu_2MoS_4(SPh)_2]^{2-}$	60%	98
HBF_4	$AuFe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_3R)(PPh_3)$ ($R = H, Cl, OCH_3, CH_2NMe_2$)	$Au_2Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_3R)(PPh_3)_2$ (Au-Fe = 2.82 Å	96%	109-111, 263, 264
Standing in soln.	$Ag_2WS_4(PPh_2Me)_4$	$Ag_4W_2S_8(PPh_2Me)_4$ (Ag-W = 3.002 Å)	22%	119, 120

RESULTS AND DISCUSSION

Preliminary Remarks

In triosmium cluster chemistry, the addition reactions of $H_2Os_3(CO)_{10}$ with a wide range of nucleophiles (related to the formal unsaturation[169,170] of the hydrido-bridged Os=Os bond[171,172]) has been of enormous synthetic utility.[173] The reaction of $H_2Os_3(CO)_{10}$ with ethylene[174-176] or acetylene[177-179] gives the product $HOs_3(CO)_{10}(\mu_3\text{-}C{=}CH_2)$ (Scheme I). The vinylidene complex $H_2Os_3(CO)_{10}(\mu_3\text{-}C{=}CH_2)$ is formed by pyrolysis of $HOs_3(CO)_{10}(\mu\text{-}CH{=}CH_2)$.[175] Further reaction of the complex $HOs_3(CO)_{10}(\mu\text{-}CH{=}CH_2)$ with acetylene[174,175,178] leads to a complex mixture, the major component being $Os_3(CO)_{10}(\mu_3\text{-}CH{=}CH)$ (Scheme I). A minor product isolated from this mixture is the metalocycle $Os_3(CO)_9(C_4H_4)$, containing two coupled acetylene molecules. The structure of the analogous complex, $Os_3(CO)_9(C_4Ph_4)$, has been determined by an X-ray crystallographic study.[180] The symmetric saturated ethylidyne complex $H_3Os_3(CO)_9(\mu_3\text{-}CCH_3)$ is formed by

i) hydrogenation of $H_2Os_3(CO)_9(CCH_2)$[181,182] or

ii) hydrogenation of $Os_3(CO)_{10}(\mu_3\text{-}CH{=}CH)$ *via* the intermediate $HOs_3(CO)_9(\mu_3\text{-}C_2H)$.[183]

Reactions of $H_2Os_3(CO)_{10}$ with substituted acetylenes (or substituted alkenes) have produced a whole series of complexes related to those shown in Scheme I, together with some interesting new ones.[184-187] With substituted alkynes, $H_2Os_3(CO)_{10}$ affords bridging vinyl complexes $HOs_3(CO)_{10}(\mu\text{-}CRCHR')$ (see Figure I), and although four isomeric types are possible, only one is observed.[178] Further reaction of $HOs_3(CO)_{10}(\mu\text{-}CRCHR')$ (R = H, R' = Me) leads to increased formation of $Os_3(CO)_{10}(\mu_3\text{-}CRCR')$ (see Figure 1).[174,175] Heating $HOs_3(CO)_{10}(\mu\text{-}CRCHR')$ results in decarbonylation and removal of hydrogen from the ligand to give $H_2Os_3(CO)_9(\mu_3\text{-}CCRR')$ and $H_2Os_3(CO)_9(\mu_3\text{-}CRCR')$ (see Figure I).[175]

SCHEME I

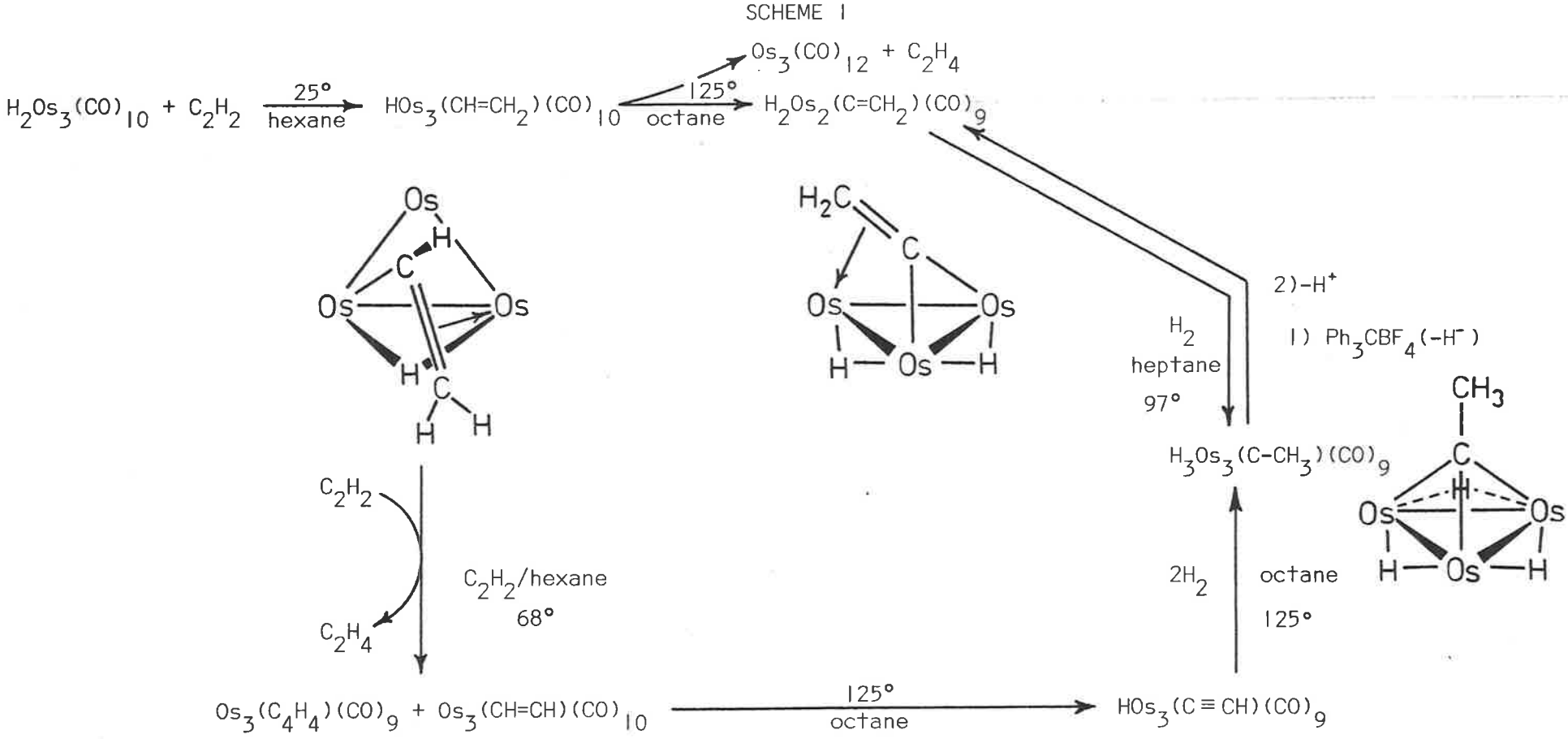
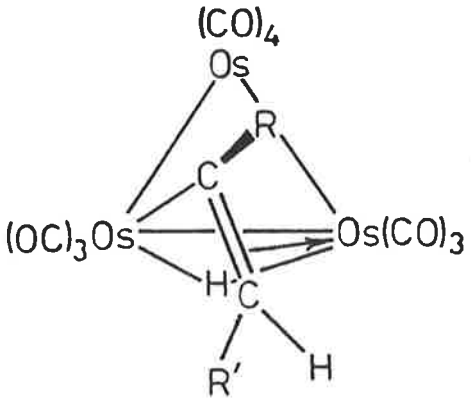
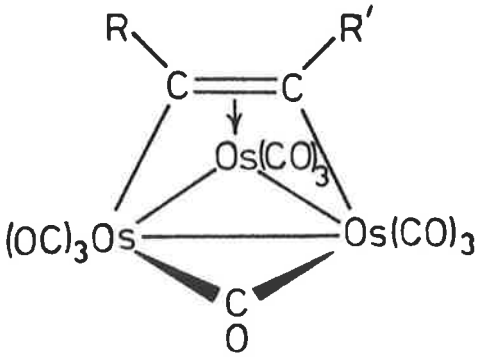

$H_2Os_3(CO)_{10} + C_2H_2$
25°
hexane
$HOs_3(CH=CH_2)(CO)_{10}$
125°
octane
$Os_3(CO)_{12} + C_2H_4$
$H_2Os_2(C=CH_2)(CO)_9$
C_2H_2
C_2H_4
C_2H_2/hexane
68°
$Os_3(C_4H_4)(CO)_9 + Os_3(CH=CH)(CO)_{10}$
125°
octane
$HOs_3(C\equiv CH)(CO)_9$
H_2
heptane
97°
2)-H^+
1) $Ph_3CBF_4(-H^-)$
$H_3Os_3(C-CH_3)(CO)_9$
$2H_2$
octane
125°

FIGURE I



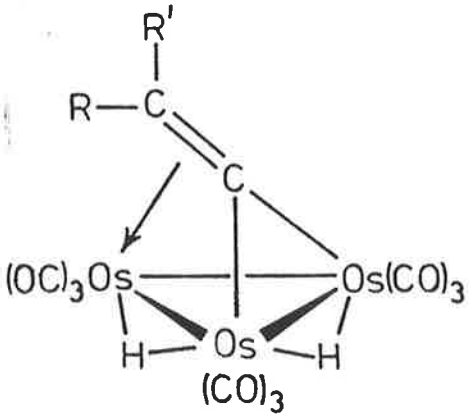
(1)

$HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CRCHR')$



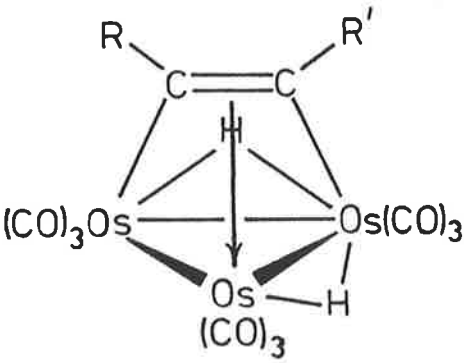
(2)

$Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}CRCR')$



(3)

$H_2Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CCRR')$



(4)

$H_2Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CRCR')$

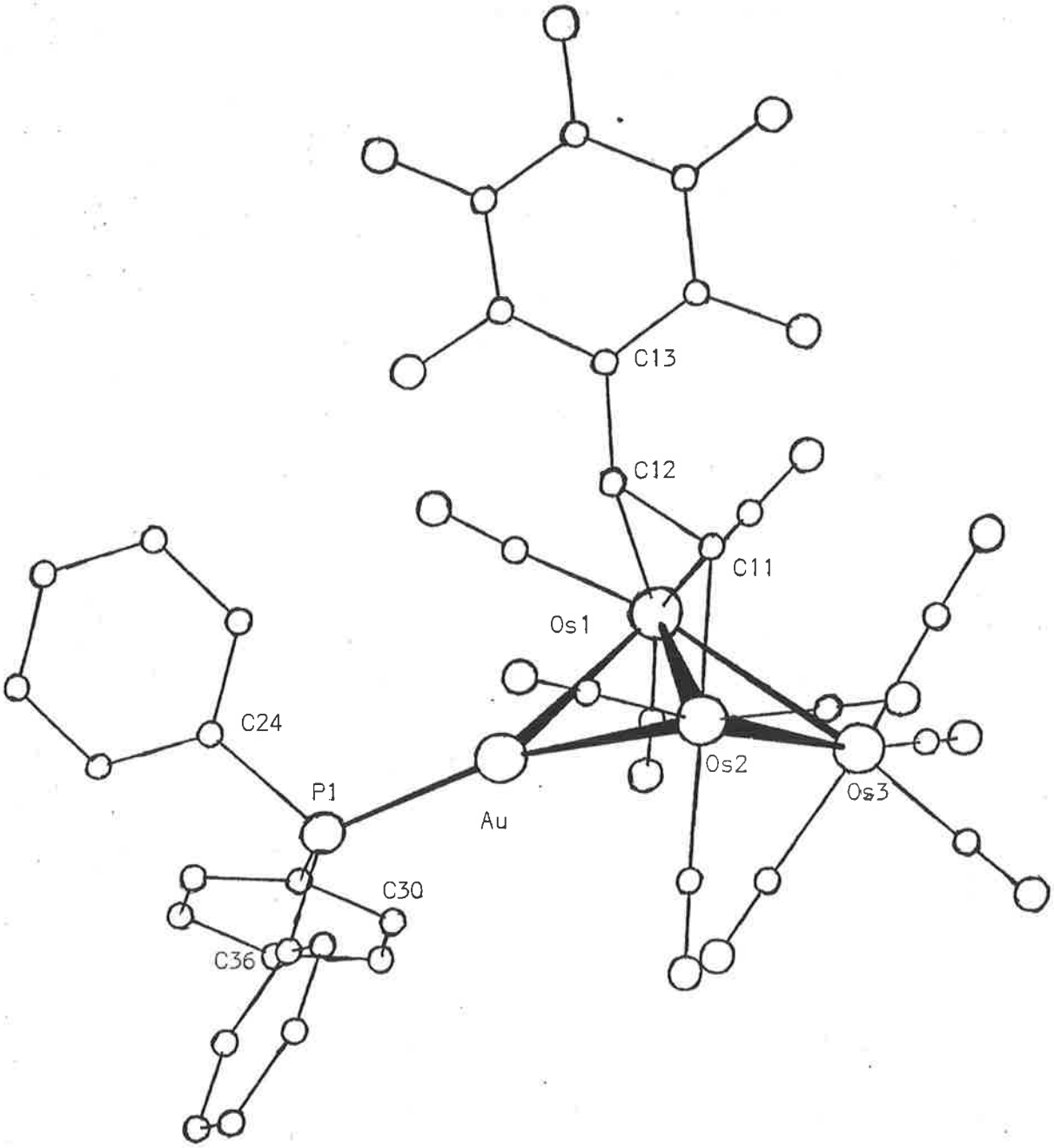
The electron deficient complex, $H_2Os_3(CO)_{10}$, has also proven a useful precursor in forming heteronuclear clusters.[76,188-198] For example, the complex $AuMePPh_3$ reacts with $H_2Os_3(CO)_{10}$ to give the unsaturated product $HAuOs_3(CO)_{10}(PPh_3)$,[76] which can reversibly add CO to form $HAuOs_3(CO)_{11}(PPh_3)$.[71,77] Heteronuclear clusters provide a new aspect of reactivity in cluster chemistry with potential interaction at each metal centre. For the gold complexes, two of the p orbitals in the valence shell still remain unoccupied, the gold utilising an sp hybrid bonding mode.[155] Hence, these empty p orbitals are a potential point of attack for nucleophiles. Johnson and Lewis, note, however, that many of the wide range of reactions observed for $H_2Os_3(CO)_{10}$, with acetylenes, alkenes, azides and diazocompounds, do not seem to occur with the gold complexes $HAuOs_3(CO)_{10}(PR_3)$ or $HAuOs_3(CO)_{11}(PR_3)$, even though $HAuOs_3(CO)_{10}(PR_3)$, like $H_2Os_3(CO)_{10}$, is electron deficient.[71,199,200]

The gold phosphine acetylide complexes, $Au(C_2R)PR'_3$, are isolobal with HC_2R.[155] Similarly, the isolobal concept can be extended to the analogous copper and silver complexes, $M(C_2R)PR'_3$ (M = Ag, Cu), though the p'_x and p_y orbitals of the copper and silver moieties are of lower energy than those of gold,[155] and, consequently, the resulting additional bonding interactions can cause structural variations[201-222] (see also Chapter 3). It was, therefore, of some interest to investigate the reactivity of $M(C_2R)PR'_3$ (M = Au,Ag,Cu) with $H_2Os_3(CO)_{10}$, and determine the extent of the isolobal analogy.

Reactions of $H_2Os_3(CO)_{10}$ with $M(C_2C_6F_5)PPh_3$

In toluene at -11°, $H_2Os_3(CO)_{10}$ and $Au(C_2C_6F_5)PPh_3$ reacted rapidly to give $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (I) in quantitative yield. The structure of (I) has been determined by X-ray diffraction, and is shown in Figure 2 (see also Table 3).

FIGURE 2



$AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$

TABLE 3 Selected Bond Lengths and Angles

$AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$		$AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$	
Au(1)-Os(1)	2.766(1)	Au(1)-Os(1)	2.738(1)
Au(1)-Os(2)	2.777(1)	Au(1)-Os(2)	2.795(1)
Os(1)-Os(2)	2.894(1)	Os(1)-Os(2)	2.882(1)
Os(1)-Os(3)	2.922(1)	Os(1)-Os(3)	2.924(1)
Os(2)-Os(3)	2.054(1)	Os(2)-Os(3)	2.864(1)
Au-P	2.315(2)	Au-P	2.307(4)
Os(2)-C(11)	2.133(8)	Os(2)-C(11)	2.107(15)
Os(1)-C(11)	2.276(6)	Os(1)-C(11)	2.251(14)
Os(1)-C(12)	2.403(7)	Os(1)-C(12)	2.448(16)
C(12)-C(13)	1.488(12)	C(12)-C(13)	1.393(24)
P-C(24)	1.823(6)	P-C(24)	1.800(13)
P-C(30)	1.807(6)	P-C(30)	1.809(9)
P-C(36)	1.809(6)	P-C(36)	1.812(10)
CO Ligands		*CO Ligands*	
Os-C (eq.)	1.908 (ave.)	Os-C (eq.)	1.907 (ave.)
C-O (eq.)	1.139 (ave.)	C-O (eq.)	1.134 (ave.)
Os-C (ax.)	1.915 (ave.)	Os-C (ax.)	1.918 (ave.)
C-O (ax.)	1.143 (ave.)	C-O (ax.)	1.144 (ave.)
Angles		*Angles*	
Os(2)-Au-Os(1)	63.0(1)	Os(2)-Au-Os(1)	62.8(1)
Os(2)-Os(1)-Au	58.7(1)	Os(2)-Os(1)-Au	59.6(1)
Os(3)-Os(1)-Au	97.7(1)	Os(3)-Os(1)-Au	100.0(1)
Os(1)-Os(2)-Au	58.3(1)	Os(1)-Os(2)-Au	57.7(1)
Os(3)-Os(2)-Au	99.0(1)	Os(3)-Os(2)-Au	100.1(1)
Os(3)-Os(1)-C(11)	80.3(2)	Os(3)-Os(1)-C(11)	78.6(4)
Os(3)-Os(1)-C(12)	114.9(2)	Os(3)-Os(1)-C(12)	112.7(4)
Os(3)-Os(2)-C(11)	84.2(2)	Os(3)-Os(2)-C(11)	82.2(5)
Os(2)-Os(1)-C(11)	46.9(2)	Os(2)-Os(1)-C(11)	46.5(4)
Os(1)-C(11)-Os(2)	82.0(3)	Os(1)-C(11)-Os(2)	82.7(5)
Os(2)-Os(1)-C(12)	70.5(2)	Os(2)-Os(1)-C(12)	70.6(4)
Os(1)-Os(2)-C(11)	51.1(2)	Os(1)-Os(2)-C(11)	50.8(4)
Os(1)-C(12)-C(11)	67.8(4)	Os(1)-C(12)-C(11)	65.2(9)
Os(2)-C(11)-C(12)	120.3(6)	Os(2)-C(11)-C(12)	123.3(10)

The PLUTO plot (Figure 2) shows that the metal framework approximates a *nido*[223-227] butterfly configuration with Au and Os(3) on the wing tips and with Os(1) and Os(2) as the hinge atoms. The dihedral angle between the wings is 98.3°. The alkyne is coordinated as a μ-η^2-ligand on the opposite side of the plane (formed by the three osmium atoms) to that of the $AuPPh_3$ moiety. The C(11)-C(12) bond has double bond character (1.396Å), with the C_6F_5 group located on C(12) *trans* to Os(2). Although not located directly, the structural parameters support the *trans* addition of the bridging hydrides, associated with the Os=Os bond in $H_2Os_3(CO)_{10}$ (see Figure 1 and Table 3), to the acetylide moiety. It is apparent that the gold-acetylide bond has been cleaved, leaving the acetylide to bond in a $\sigma+\pi$ manner across an Os-Os bond. The $AuPPh_3$ fragment then bridges this same Os-Os bond.

The *trans* addition of the two hydride ligands across the C≡C bond is unusual, as *cis* addition of dihydrogen is observed when unsaturated organic moieties are hydrogenated on metal surfaces or clusters.[228-231] The bridging vinyl complex, $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CRCHR')$ (Figure 1), formed when $H_2Os_3(CO)_{10}$ reacts with substituted alkynes, is similar to (I). Complex (I) is structurally analogous to the bridging vinyl complex $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}CRCHR')$, where the $AuPPh_3$ moiety is replaced by the isolobal metal hydride. From this perspective, the reactivity of $Au(C_2C_6F_5)PPh_3$ with $H_2Os_3(CO)_{10}$ is similar to the reactivity of $HC_2C_6H_5$ with $H_2Os_3(CO)_{10}$. (Reaction products illustrated in Figure 1.) The high electronegativity of gold,[232] concomitant with its incomplete valency shell, favours the formation of the gold-metal bonds.[71]

The formation of (I) can be understood in terms of (a) the propensity of gold to form heterometallic bonds, and (b) the presence of

an unsaturated organic moiety, able to accommodate two hydrogens from the electron deficient $H_2Os_3(CO)_{10}$ reagent.

The ^1H n.m.r. spectrum of (1) confirms the existence of the *trans* isomer in solution (δ = 1.37d, J = 14 Hz, CH = $CH^*C_6F_5$; δ = 4.43d, J = 14 Hz, CH* = CHC_6F_5). The ^{13}C n.m.r. spectrum at room temperature shows ten distinct carbonyl resonances (Table 5), indicating that the complex is not fluxional. The alkene carbons were coupled to the *trans* hydrogens (δ = 108.8d J_{H-C} = 41 Hz, CH = $C^*HC_6F_5$; δ = 100.8d, J_{H-C} = 43 Hz, C*H = CHC_6F_5).

In toluene below 0°, $Ag(C_2C_6F_5)PPh_3$ or $Cu(C_2C_6F_5)PPh_3$ react with the electron deficient complex $H_2Os_3(CO)_{10}$ to form $AgOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (2) and $CuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (3), respectively. The copper (3) and silver (2) heterometallic products showed similar spectral characteristics to (1) (see Tables 4 and 5). However, in both (2) and (3) the carbonyl ligands were completely fluxional at room temperature. The positions and relative intensities of the ν(CO) absorptions show a close correspondence for (1), (2) and (3). The high energy ν(CO) band (*ca.* 2100-2087 cm^{-1}) is lowered as follows: Cu > Ag > Au (see Table 4). A weak ν(C=C) absorption was also found in all derivatives, suggesting that the molecular structures of (2) and (3) are similar to (1).

Reactions of $H_2Os_3(CO)_{10}$ with $M(C_2Ph)PR_3$

The reactions of Group IB phosphine phenyl acetylide complexes with $H_2Os_3(CO)_{10}$ were not as specific as those of $M(C_2C_6F_5)PPh_3$. A host of products is produced, even at low temperatures. Complexes of the following types were isolated: $HMOs_3(CO)_{10}(PR_3)$, $MOs_3(CO)_{10}(PR_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$, $MOs_3(CO)_9(PR_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$,

TABLE 4 Comparative IR Spectral Data for $MOs_3(CO)_{10}(PR_3)(\mu\text{-}\eta^2\text{-}CHCHR')$

Compound	ν(CO) - cyclohexane solution (cm^{-1})										ν(C=C)
M = Au, R = Ph, R' = F (I)	2094s	2072m	2063m	2040vs	2037vs	2017vs	1992s	1987s	1971s	1960s	1618w
M = Au, R = Ph, R' = H (5)	2087m	2068m	2058s	2045vs	2040vs	2017m	1998s	1985s	1971sh	1960m	1604w
M = Au, R = Me, R' = H (II)	2090m	2070m	2060s	2047s	2041vs	2020m	1999s	1989s		1963m	1610w
M = Ag, R = Ph, R' = F (2)	2097w	2078w	2063vs		2033m	2013m	1998m		1979m	1958m	1602w
M = Ag, R = Ph, R' = H (15)	2096w	2070m	2055s	2046vs	2037vs	2018s	2006s	1996sh	1979m	1961m	1615w
M = Cu, R = Ph, R' = F (3)	2099w	2076s	2063sh	2055vs	2033vs	2018s	2003s	1985m	1977m	1948vw	1608w
M = Cu, R = Ph, R' = H (20)	2100w	2071m	2059s	2048vs	2040vs	2020s	2005s	1996sh	1980m	1966sh	1621w

TABLE 5 Comparative NMR spectra in $[(CD_3)_2CO]$

Compound	^{1}H n.m.r. (δ p.p.m.)[c]				^{13}C n.m.r. (δ p.p.m.)		
$MOs_3(CO)_{10}(PR_3)(\mu\text{-}\eta^2\text{-}CHCHR')$	CH = CH*$C_6R'_5$	PR_3*/$C_6R'_5$*	CH* = $CHC_6R'_5$	*CO	C_6*R'_5	CH = C*$C_6R'_5$	C*H = $CHC_6R'_5$
M = Au, R = Ph, R' = F (1)	8.63d (1) J = 14 Hz	7.51m (15)	5.57d (1) J = 14 Hz	*a,d*	130.8m[a,e]	108.8d[a] J = 41 Hz	100.8d[a] J = 43 Hz
M = Au, R = Ph, R' = H (5)	*b*	7.61m (21)	5.27d (1) J = 14 Hz	176.5s	131.1m[e]	101.2s	92.4s
M = Au, R = Me, R' = H (11)	*b*	7.55m (6)/ 8.31d (9) with J(P-H) = 12 Hz	5.11d (1) J = 13 Hz				
M = Ag, R = Ph, R' = F (2)	8.42d (1) J = 14.5 Hz	7.35m (15)	5.51d (1) J = 14.2 Hz	176.7s	130.5m[e]	109.9s	104.1s
M = Ag, R = Ph, R' = H (15)	7.91d (1) J = 14 Hz	7.48m (20)	5.38d (1) J = 14 Hz	174.7s	132.4m[e]	122.0s	105.1s
M = Cu, R = Ph, R' = F (3)	8.41d (1) J = 15.5 Hz	7.26m (5), 6.87m (10)	5.41d (1) J = 14.7 Hz	176.2s[a]	130.0m[a,e]	150.2d[a] J = 20 Hz	142.1d[a] J = 20 Hz
M = Cu, R = Ph, R' = H (20)	8.19d (1) J = 10 Hz	7.25m (20)	4.30d (1) J = 9 Hz	169.2s	133.8m[e]	127.0s	115.9s

[a]The ^{13}C n.m.r. was an off resonance spectrum showing carbon-hydrogen coupling (all other spectra are broad band showing no carbon-hydrogen coupling).

[b]This proton resonance occurred within the phenyl resonance (as indicated by the integration of the phenyl region).

[c]All values in parentheses are integral ratios of their associated chemical shifts.

[d]CO values at δ = 205.2, 187.1, 185.8, 184.9, 184.1, 183.5, 176.8, 175.5, 174.4, 173.8.

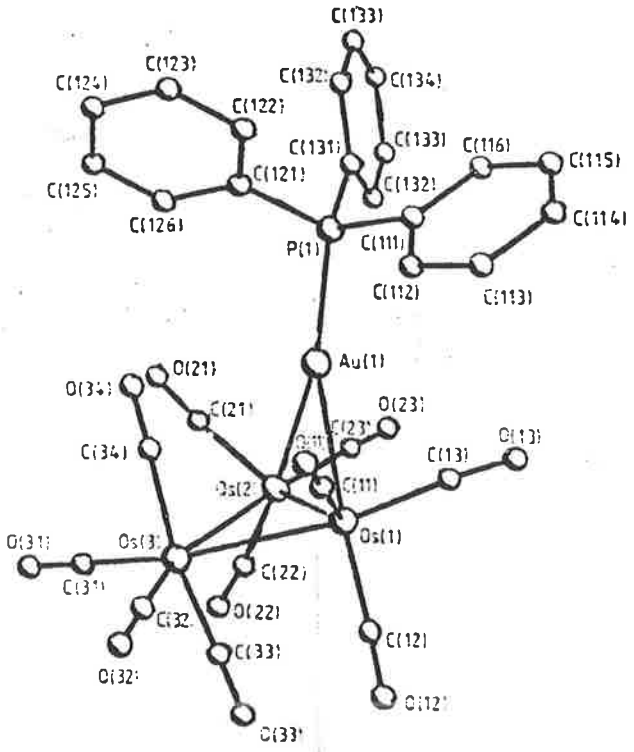
[e]Average (p.p.m.) chemical shift given.

$HMOs_3(CO)_8(CHCPh)$ and $MOs_3(CO)_9(PR_3)_2(CHCHPh)$ (M = Au,Ag,Cu; R = Ph,Me). It is convenient to discuss their probable structures individually.

(a) $HMOs_3(CO)_{10}(PR_3)$ (M = Au, R = Ph, Me; M = Ag, Cu, R = Ph)

The complexes $HMOs_3(CO)_{10}(PR_3)$ [M = Au, R = Ph(4), Me(10); M = Ag(14), Cu(19), R = Ph] were isolated in low yield and contain characteristic ν(CO) absorptions in their infra-red spectra (Table 6). The mass spectrum of $HAuOs_3(CO)_{10}(PMe_3)$ (10) showed a characteristic molecular ion at *m/e* = 1124, followed by subsequent carbonyl loss. The complex, $HAuOs_3(CO)_{10}(PPh_3)$, was identified by comparison with the literature,[75,76] and its X-ray structure is shown in Figure 3.[76] The ^1H n.m.r. spectra of all complexes contain metal-hydride resonances at high field.

FIGURE 3



$HOs_3Au(CO)_{10}(PPh_3)$

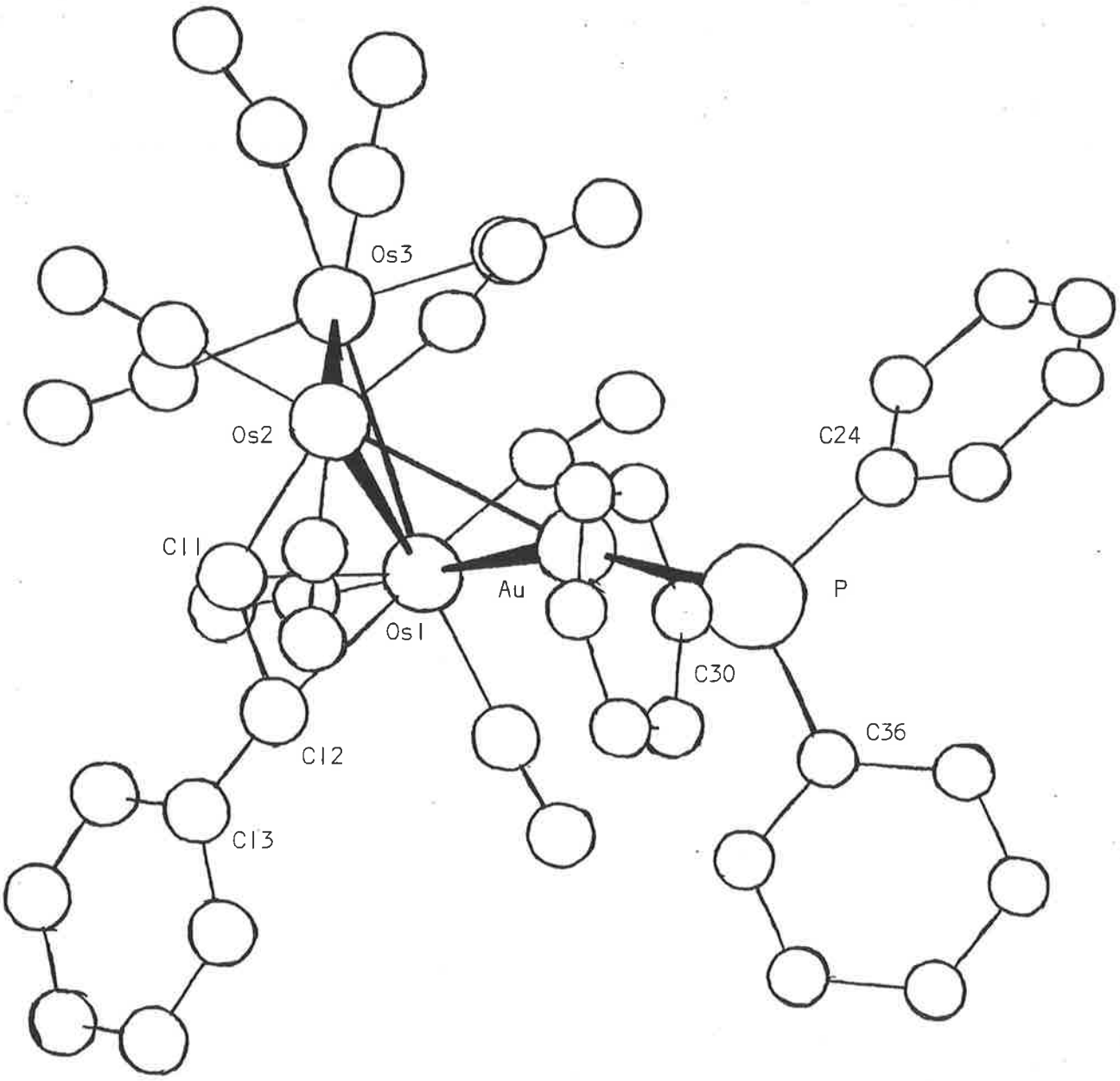
(b) $MOs_3(CO)_{10}(PR_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$ *(M = Au, R = Ph, Me; M = Ag, Cu, R = Ph)*

The complexes $MOs_3(CO)_{10}(PR_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$ [M = Au, R = Ph(5), Me(11); M = Ag(15), Cu(20), R = Ph] were formed as the major products of the reaction. The infra-red spectra [ν(CO) absorptions] of these complexes show close similarity to those of (1), (2) and (3) (see Table 4). A weak ν(C=C) absorption was also found in all derivatives. The ^1H and ^{13}C n.m.r. spectra (see Table 5) confirmed the *trans* migration of hydrides from $H_2Os_3(CO)_{10}$ to the alkyne moiety (*vide supra*). The complexes all showed fluxional CO ligands in the ^{13}C n.m.r. spectrum. A molecular ion at *m/e* = 1227 was observed in the mass spectrum of $AuOs_3(CO)_{10}(PMe_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$ (11). An X-ray crystal structure determination of $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$ (5) is shown in Figure 4. The structure is analogous to that of (1) (see Table 3).

(c) $MOs_3(CO)_9(PR_3)_2(\mu\text{-}\eta^2\text{-}CHCHPh)$ *(M = Au, R = Ph, Me; M = Ag, Cu, R = Ph)*

The complexes $MOs_3(CO)_9(PR_3)_2(\mu\text{-}\eta^2\text{-}CHCHPh)$ [M = Au, R = Ph(8), Me(13); M = Ag(18) Cu(22), R = Ph] were isolated as minor products. The ν(CO) absorptions in their i.r. spectra show close correspondence (see Table 7). All compounds show (^1H n.m.r. data) *trans* association of two hydrides across the C≡C bond. A molecular ion at *m/e* = 1275 was observed in the mass spectrum of $AuOs_3(CO)_9(PMe_3)_2(\mu\text{-}\eta^2\text{-}CHCHPh)$ (13). It is very likely that the complexes (8), (13), (18) and (22) are the tertiary phosphine substituted analogues of (1), (2) and (3). As the only source of phosphine is the $AuPPh_3$ moiety, this implies that the Au-P bond is cleaved during the reaction. It is significant that these products are not formed when the reaction is warmed above 30°.

FIGURE 4



$AuOs_3(CO)_{10}(PPh_3)(\mu-\eta^2-CHCHPh)$

(d) $MOs_3(CO)_9(PR_3)(CHCHPh)$ (M = Au, R = Ph, Me; M = Ag, R = Ph)

The ν(CO) and ν(C=C) absorptions in the infra-red spectra of the complexes $MOs_3(CO)_9(PR_3)(CHCHPh)$ [M = Au, R = Ph(6), Me(12); M = Ag, R = Ph(17)] are listed in Table 6. The ^1H n.m.r. spectra for these complexes are consistent with the presence of a μ-η^2-benzyl moiety. The mass spectrum of $AuOs_3(CO)_9(PMe_3)(CHCHPh)$ showed a molecular ion at *m/e* = 1199, followed by subsequent CO loss. As the $AuPR_3$ moiety can contribute only one electron to the bonding of the cluster, the complexes (6), (12) and (17) are electron deficient, and may possess a metal=metal bond within the cluster framework. The formation of electron deficient clusters incorporating both gold and osmium has been observed recently.[71,73,76,77]

(e) $HMOs_3(CO)_8(CHCPh)$ (M = Au, Ag, Cu)

The ν(CO) and ν(C=C) absorptions in the infra-red spectra of the complexes $MOs_3(CO)_8(CHCPh)$ [M = Au(7), Ag(16), Cu(21)] are listed in Table 7. The ^1H n.m.r. spectra of (7), (16), and (21) all show high field resonances (δ = -17.0 ↔ -22.0) consistent with the presence of a bridging metal hydride.[233-236] The spectra also contain a single resonance at δ = 4.5-5.5, which can be assigned to =C*H*, where the carbon atom is σ bonded to the cluster (compare values in Table 5). Presumably, the original acetylide group is now bonding in a 2σ + π mode to the Os_3 triangle; in a way similar to that postulated for $Os_3(CO)_{10}(CRCR')$ (see Figure 1) or shown to exist in the isoelectronic complex $Rh_3(CO)(alkyne)(\eta\text{-}C_5H_5)_3$.[237,238] The Group IB metal probably occupies an edge or face bridging position in the metal core. The absence of a phosphine is interesting, and indicates that the M-P (M = Au, Ag, Cu) bond can be cleaved. The resulting vacant coordination site may be occupied by a carbonyl ligand, as a high energy ν(CO) band is observed in the infra-red spectrum. The infra-red spectrum also indicates the presence of a bridging

TABLE 6 Comparative IR data

$HMOs_3(CO)_{10}(PR_3)$	$\nu(CO)$ - cyclohexane solution (cm^{-1})					
M = Au, R = Ph (4)	2090w	2047s	2040m	2008s	1996m	1977m
M = Au, R = Me (10)	2095m	2050s	2047m	2015s	2001s	1981m
M = Ag, R = Ph (14)	2092w	2052m	2046m	2012s	2000ms	1986m
M = Cu, R = Ph (19)	2094w	2052m	2047m	2015s	2001m	1986m

$MOs_3(CO)_9(PR_3)(CHCHC_6H_5)$	$\nu(CO)$ - cyclohexane solution (cm^{-1})									$\nu(C=C)$
M = Au, R = Ph (6)	2095m	2073s	2069vs	2044vs		2017vs	1999s	1983s	1943m	1561vw
M = Au, R = Me (12)	2091m	2077m	2063vs	2046s	2037m	2018s	2009vs		1892m	1607m
M = Ag, R = Ph (17)	2094w	2072s	2066vs	2045vs		2018vs	2001s	1985s	1949m	1592w

TABLE 7 Comparative IR data

$HMOs_3(CO)_8(CHCPh)$	$\nu(CO)$ - cyclohexane solution (cm^{-1})							$\nu(C=C)$
M = Au (7)	2116w	2070vs	2054w	2037s	2023m	2015m	1800m	1513mw
M = Ag (16)	2120w	2076vs	2058m	2040s	2025m	2019m	1825m	1540m
M = Cu (21)	2121w	2077vs	2060m	2043s	2029m	2021m	1817m	1542w

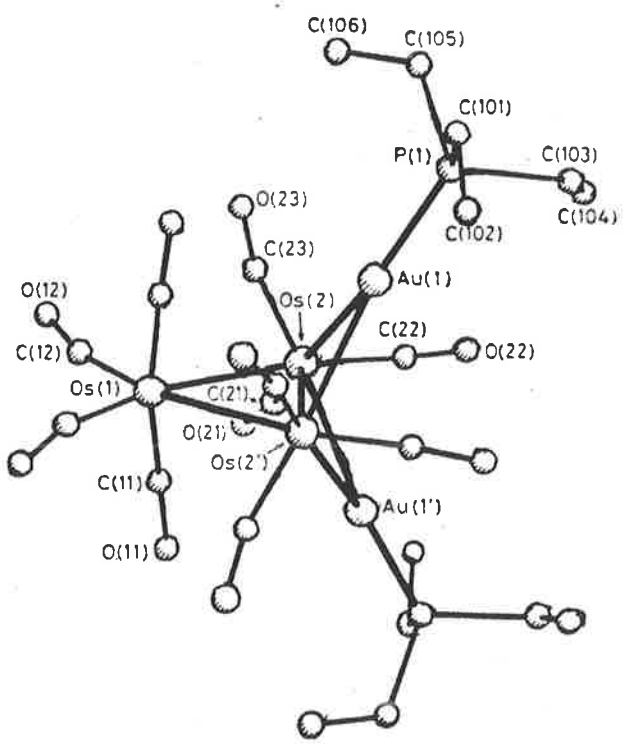
$MOs_3(CO)_9(PR_3)_2(CHCHC_6H_5)$	$\nu(CO)$ - cyclohexane solution (cm^{-1})									$\nu(C=C)$
M = Au, R = Ph (8)	2094m	2075m	2066s	2055m		2038s	2015s	1985vs	1945m	1604w
M = Au, R = Me (13)	2092m	2073m	2065s	2050s	2047vs	2040s	2020m	1997s	1972m	1563w
M = Ag, R = Ph (18)	2094w	2072s	2066vs	2045vs	2040vs	2036s		1985s	1949m	1617w
M = Cu, R = Ph (22)	2090w		2069vs	2049s	2041s	2037s	2017vs	1988sh	1955sh	1681w

CO ligand, a feature also common to $Os_3(CO)_{10}(CHCH)$[233] and $Rh(CO)(alkyne)(\eta\text{-}C_5H_5)_3$.[237,238] The molecular formula of the final product, $HMOs_3(CO)_{10}(CHCPh)$, is derived from analytical data and osmometric molecular weight determinations, and is formally electron deficient. Suitable crystals for an X-ray structure determination have not yet been obtained.

(f) $Au_2Os_3(CO)_{10}(PPh_3)_2$

The acetylide complex, $Au(C_2Ph)(PPh_3)$, reacts with $H_2Os_3(CO)_{10}$ in benzene heated at reflux point, to form a low yield of $Au_2Os_3(CO)_{10}(PPh_3)_2$ (9), together with the complexes (4), (5), (6), (7) and (8). The molecular structure of (9) (see Figure 5) has recently been communicated,[77] and the spectral characteristics of this compound are consistent with the literature data.

FIGURE 5



$Au_2Os_3(CO)_{10}(PEt_3)_2$

TABLE 8 Comparative IR data

$MRu_3(CO)_9(PPh_3)(C_2Ph)$	*IR data: ν(CO) cyclohexane solution in cm^{-1}*						
M = Au (24)	2074m	2052vs	2039vs	1997vs	1981sh	1968m	
M = Ag (29)	2074s	2057s	2032vs	1999vs	1984m		
M = Cu (32)	2069s	2052m	2029s	2003vs	1989m		
$AuRu_3(CO)_9(PPh_3)(C_2Bu^t)$	2074m	2051s	2036vs	1996vs		1968m	
$M_2Ru_3(CO)_7(PPh_3)_2(C_2Ph)_2$	*IR data: ν(CO) cyclohexane solution in cm^{-1}*						
M = Au (25)	2083m	2068m	2062m	2058m	2042vs	2012m	1999vs	1992sh
M = Ag (30)	2098m	2070w		2054s	2045sh	2015w	2002sh	1970w
M = Cu (33)	2091m	2072m	2065m	2060sh	2043vs	2015m	2001vs	1995m

$H_xMRu_3(CO)_{10}(PPh_3)$	*IR data: ν(CO) cyclohexane solution in cm^{-1}*				
M = Au, x = 0 (23)	2083m	2066vs	2032s	2013m	1967w
M = Ag, x = 0 (28)	2082m	2061vs	2026vs	2014m	1994m
M = Cu, x = 1 (31)	2089m	2060s	2038vs	2010s	1985m

Reactions of $Ru_3(CO)_{12}$ with $M(C_2Ph)PPh_3$

Reactions of $M(C_2Ph)PPh_3$ (M = Au, Ag, Cu) with $Ru_3(CO)_{12}$ afford a complex mixture of products. Higher reaction temperatures are required than those needed for reactions with $H_2Os_3(CO)_{10}$. The products $MRu_3(CO)_9(PPh_3)(C_2Ph)$ and $M_2Ru_3(CO)_7(PPh_3)_2(C_2Ph)_2$ (M = Au, Ag, Cu) were isolated from all reactions; $MRu_3(CO)_{10}(PPh_3)$ (where M = Au, Ag) and $HCuRu_3(CO)_{10}(PPh_3)$ were also found. The infra-red spectra within each general class of compounds had similar ν(CO) band patterns (see Table 8). The complex $AuRu_3(CO)_9(PPh_3)(C_2Bu^t)$ has been characterised previously,[125] and its spectral characteristics are very similar to those of $MRu_3(CO)_9(PPh_3)(C_2Ph)$ (M = Au, Ag, Cu; see Table 8). The ^1H n.m.r. spectrum of $HCuRu_3(CO)_{10}(PPh_3)$ (31) showed a high field hydride resonance at δ = -17.1, though attempts to find similar hydride resonances for $HAuRu_3(CO)_{10}(PPh_3)$ (33) or $HAgRu_3(CO)_{10}(PPh_3)$ (28) failed. The complexes $HRu_3(CO)_9(C_2Ph)$ (26) and $Ru_3(CO)_{11}(PPh_3)$ were also obtained as minor products from the reaction between $Ru_3(CO)_{12}$ and $Ag(C_2Ph)PPh_3$, and were identified by comparison with the literature.[239-243] The isolation of these minor products indicates that Ag-P as well as Ag-C_2Ph bond cleavage can occur during the reaction. Similar derivatives were not detected in reactions of $Cu(C_2Ph)PPh_3$ or $Au(C_2Ph)PPh_3$ with $Ru_3(CO)_{12}$.

Reactivity of $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$

On heating (I) in n-octane (120°), a slow colour change from deep red to bright yellow is observed. This colour change is due to the formation of $HAuOs_3(CO)_8(PPh_3)(CHCHC_6F_5)$ (34), which was isolated in 83% yield. The ^1H n.m.r. spectrum of (34) confirmed that the *trans* alkene moiety of (I) remained unchanged on pyrolysis. However, the spectrum also revealed the presence of a high field signal at δ = -22.10. Osmometric molecular weight determinations and analytical data suggest the loss of two CO ligands from (I) in forming (34). The ^{13}C n.m.r.

spectrum indicated that all CO ligands were now completely fluxional at room temperature. An X-ray crystallographic structural determination is currently under way to elucidate the structure of this unusual compound.[255] Pyrolysis of (34) by heating diglyme to reflux point caused a colour change from yellow to deep brown, and deposition of a brown-grey precipitate. Soxhlet extraction with ethyl acetate gave a low yield of an uncharacterised product, with only one signal at $\delta = -19.8$s in the ^{1}H n.m.r. spectrum. The absence of any phenyl resonances suggests a polynuclear osmium cluster. However, a check of the literature[244-253] precludes any such known cluster. Analytical data are consistent with a molecular formula of $H_4Au_2Os_4(CO)_{13}$, but lack of suitable crystals has prevented complete characterisation.

On stirring $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (1) with two equivalents of *K*-Selectride [$K(HBBu^s_3)$] in thf, the deep red solution gradually changed to purple (*ca.* 1 h.). Addition of $[NEt_4]Br$ enabled the isolation of $[NEt_4]_2[H_2AuOs_3(CO)_9(CHCHC_6F_5)]$ (37) in 63% yield. The ^{1}H n.m.r. spectrum showed that the *trans* benzyl moiety of (1) remained intact, and also a high field resonance at -21.6 consistent with a bridging hydride ligand.[233-236] *K*-Selectride [$K(HBBu^s_3)$] is well known as a source of H^-.[254] The dianionic nature of (37) was confirmed by the relative intensity of the NEt_4^+ peaks in the ^{1}H n.m.r. spectrum. Acidification (H_3PO_4) of the product obtained from (1) and *K*-Selectride results in a 40% recovery of (1), together with other uncharacterised derivatives. Addition of $[(AuPPh_3)_3O][BF_4]$ to a solution of (37) (*vide supra*) gives (1) (20%), together with $Au_3Os_3(CO)_7(PPh_3)_3(CHCHC_6F_5)$ (38) and $Au_3Os_3(CO)_6(PPh_3)_3(CHCHC_6F_5)$ (39). Crystals of (39) have been submitted for an X-ray structure determination.[255] The ability of $[(AuPPh_3)_3O][BF_4]$ to incorporate up to three $Au(PPh_3)$ fragments into anionic clusters has been reported previously.[79,80,82,142,143] A complex

tentatively identified as $Au_6Os_3(CO)_7(PPh_3)_6$ (40) was also isolated in the reaction.

Complex (1) reacts with an excess of Me_3NO to generate an extremely unstable product (*ca.* 52% yield). The instability of the product prevented characterisation. However, by bubbling acetylene through a solution of (1) with excess Me_3NO, the product, $AuOs_3(CO)_7(PPh_3)(C_4H_4)(CHCHC_6F_5)$ (42), was obtained in 46% yield. The molecular formula of (42) was assigned on the basis of analytical and spectral data (see Experimental section). An X-ray crystallographic study of (42) is now in progress.[255] No reaction of (1) is observed with acetylene in the absence of Me_3NO. Furthermore, (1) did not react with H_2 (80atm/60°), CO (100atm/60°), C_2H_4 or PPh_3.

Interestingly, pyrolysis of $AgOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (2) in refluxing benzene (*ca.* 15 min.) gave a very light sensitive product. This was initially identified as $AgOs_3(CO)_8(CHCC_6F_5)$ (36), by comparison of its infra-red data with those of the general class of compound $MOs_3(CO)_8(CHCPh)$ (M = Au, Ag, Cu) (see Table 7). All other data obtained are consistent with the proposed formula.

EXPERIMENTAL

General experimental conditions have been described in Chapter 1. The reagent $H_2Os_3(CO)_{10}$ was prepared as described in the literature,[256] using the apparatus shown in Figure 32 (Chapter 1). The preparation of gold, silver or copper phosphine acetylides is described in Chapter 3, while the preparation of $Ru_3(CO)_{12}$ is described in Chapter 1.

Preparation of $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (1)

A mixture of $H_2Os_3(CO)_{10}$ (500 mg, 0.586 mmol) and $Au(C_2C_6F_5)PPh_3$ (380 mg, 0.584 mmol) in toluene (10 ml) at -11° was stirred for 15 min. The solvent was removed *in vacuo*, and recrystallisation of the residue from toluene/n-octane gave an initial crop of red crystals (755 mg). Addition of n-hexane to the mother liquor afforded a further 123 mg of red $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (1) (878 mg, 98%). Spectral data are listed in Tables 4 and 5. Analysis: C - 28.67, H - 0.90, P - 2.83, F - 5.44%; *M* (acetone) - 1489, *M* (benzene) - 1482; $C_{36}H_{17}O_{10}PF_5AuOs_3$ requires C - 28.77, H - 1.14, P - 2.06, F - 6.32%, *M* - 1501.

Preparation of $AgOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (2)

A mixture of $H_2Os_3(CO)_{10}$ (50 mg, 0.059 mmol) and $Ag(C_2C_6F_5)PPh_3$ (33 mg, 0.059 mmol) in toluene (30 ml) at 0° was stirred for 45 min. The solvent was then removed *in vacuo*, and the residue recrystallised from toluene/n-octane. Two subsequent crystallisations also gave red crystalline $AgOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (2) (83 mg, 99%). Spectral data are listed in Tables 4 and 5. Analysis: C - 29.80, H - 1.49%; *M* (acetone) - 1410, *M* (benzene) - 1399; $C_{36}H_{17}O_{10}PF_5AgOs_3$ requires C - 30.58, H - 1.21%; *M* - 1414.

Preparation of $CuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (3)

A mixture of $H_2Os_3(CO)_{10}$ (50 mg, 0.059 mmol) and $Cu(C_2C_6F_5)PPh_3$ (20 mg, 0.059 mmol) in toluene (30 ml) was stirred at -23° for 2 h. The solvent was then removed *in vacuo*, and the residue recrystallised from toluene/n-octane. Addition of further n-octane to the resulting filtrate gave $CuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (3) (80 mg 98%). Spectral data are listed in Tables 4 and 5. Analysis: C - 31.64, H - 0.68%; *M* (acetone) - 1382, *M* (benzene) - 1369; $C_{36}H_{17}O_{10}PF_5CuOs_3$ requires C - 31.57, H - 1.25%; *M* - 1370.

Reaction between $H_2Os_3(CO)_{10}$ and $Au(C_2Ph)PPh_3$

i) A mixture of $H_2Os_3(CO)_{10}$ (203 mg, 0.238 mmol) and $Au(C_2Ph)PPh_3$ (133 mg, 0.237 mmol) in toluene (50 ml) was stirred at -18° for 30 min. The solvent was then removed *in vacuo*. Preparative t.l.c. (15% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent gave the following bands:

i) green $HAuOs_3(CO)_{10}(PPh_3)$ (4) (28 mg, 9%), R_f - 0.61, m.p. = 169-172°. Recrystallised from benzene/n-pentane as its benzene solvate. Infra-red spectral data are listed in Table 6. ^1H n.m.r. δ ($CDCl_3$) = 7.52m (21) Ph, -22.1s (1) H. Analysis: C - 29.33, H - 1.12%; $C_{28}H_{16}O_{10}PAuOs_3 \cdot C_6H_6$ requires C - 29.40, H - 1.59%.

ii) red $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$ (5) (118 mg, 35%), R_f - 0.56, m.p. = 66-69°. Recrystallised from toluene/n-octane. Spectral data are recorded in Tables 4 and 5. Analysis: C - 30.55, H - 1.38, P - 2.37%; *M* (acetone) - 1425, *M* (benzene) - 1392; $C_{36}H_{22}O_{10}PAuOs_3$ requires C - 30.58, H - 1.57, P - 2.19%; *M* - 1413.

iii) yellow-brown $AuOs_3(CO)_9(PPh_3)(CHCHPh)$ (6) (23 mg, 7%), R_f - 0.52, m.p. = 130°(dec.). Recrystallised from toluene/n-octane. Infra-red spectral characteristics are listed in

Table 6. ^{1}H n.m.r. δ [$(CD_3)_2CO$] = 8.12d (1), J = 14 Hz, CHC*H*Ph; 7.43m (20), Ph; 5.24d (1), J = 14 Hz, C*H*CHPh. Analysis: C - 30.15, H - 1.50%; *M* (acetone) - 1369, *M* (benzene) - 1380; $C_{35}H_{22}O_9PAuOs_3$ requires C - 30.35, H - 1.60%; *M* - 1357.

iv) yellow $HAuOs_3(CO)_8(CHCPh)$ (7) (13 mg, 5%), R_f - 0.49, m.p. = 186°(dec.). Recrystallised from acetone/n-pentane. Infra-red spectral characteristics are listed in Table 7. ^{1}H n.m.r. δ [$(CD_3)_2CO$] = 7.58m (5), CHC*Ph*; 5.10s (1), C*H*CPh; -21.6s (1) H. Analysis: C - 17.85, H - 0.92, O - 11.55%; *M* (acetone) - 1125, *M* (benzene) - 1131; $C_{16}H_7O_8AuOs_3$ requires C - 17.55, H - 0.64, O - 11.69%; *M* - 1095.

v) yellow uncharacterised derivative, R_f - 0.75. Infra-red (C_6H_{12}): ν(CO) = 2106m, 2086s, 2078vs, 2069m, 2052vs, 2022m, 2009m, 2000m, 1985w cm^{-1}.

vi) yellow uncharacterised derivative, R_f - 0.68. Infra-red (C_6H_{12}): ν(CO) = 2108m, 2080vs, 2056vs, 2034s, 2014s, 1987m, 1967w cm^{-1}.

vii) light red uncharacterised derivative, R_f - 0.36. Infra-red (C_6H_{12}): ν(CO) = 2069s, 2057m, 2045s, 2018vs, 2002sh, 1999s, 1982m, 1963w, 1955w, 1721m cm^{-1}.

ii) A mixture of $H_2Os_3(CO)_{10}$ (102 mg, 0.120 mmol) and $Au(C_2Ph)PPh_3$ (65 mg, 0.120 mmol) in benzene (50 ml) was heated at reflux point for 18 h. The solvent was removed *in vacuo*, and preparative t.l.c. (15% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent) separated the following products:

i) green $HAuOs_3(CO)_{10}(PPh_3)$ (4) (3 mg, 2%), R_f - 0.61.

ii) red $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$ (5) (61 mg, 36%), R_f - 0.56.

iii) yellow-brown $AuOs_3(CO)_9(PPh_3)(CHCHPh)$ (6) (5 mg, 3%), R_f - 0.52.

iv) yellow $HAuOs_3(CO)_8(CHCPh)$ (7) (17 mg, 13%), R_f - 0.49.

v) purple $AuOs_3(CO)_9(PPh_3)_2(\mu\text{-}\eta^2\text{-}CHCHPh)$ (8) (12 mg, 6%), R_f - 0.40, m.p. = 130°(dec.). Recrystallised from benzene/n-hexane as its benzene solvate. Infra-red spectral characteristics are listed in Table 7. ^1H n.m.r. δ $[(CD_3)_2CO]$ = 8.16d (1), J = 14 Hz, CHC*H*Ph; 7.44m (36), Ph; 5.26d (1), J = 14 Hz, C*H*CHPh. Analysis: C - 41.17, H - 2.22%; *M* (acetone) - 1592, *M* (benzene) - 1629; $C_{53}H_{37}O_9P_2AuOs_3 \cdot C_6H_6$ requires C - 41.08, H - 2.51%; *M* - 1647.

vi) red-black $Au_2Os_3(CO)_{10}(PPh_3)_2$ (9) (6 mg, 3%), R_f - 0.18. Recrystallised from CH_2Cl_2/n-hexane. Infra-red (C_6H_{12}): ν(CO) = 2067m, 2055sh, 2015vs, 1988sh, 1979s, 1967m, 1943w cm^{-1}. ^1H n.m.r. δ $[(CD_3)_2CO]$ = 7.71m, Ph. Analysis: C - 30.81, H - 1.55%, *M* (acetone) - 1812; $C_{46}H_{30}O_{10}P_2Au_2Os_3$ requires C - 31.23, H - 1.71%; *M* - 1769. Complex (8) was also identified by comparison with the literature.[77]

vii) five other products were observed in trace quantities only.

Reaction between $H_2Os_3(CO)_{10}$ and $Au(C_2Ph)PMe_3$

A mixture of $H_2Os_3(CO)_{10}$ (200 mg, 0.235 mmol) and $Au(C_2Ph)PMe_3$ (176 mg, 0.497 mmol) in benzene (20 ml) was stirred at room temperature for 16 h. The solvent was then removed *in vacuo*, and preparative t.l.c. (45% diethyl ether/cyclohexane developer, Kieselgel H adsorbent) separated the following complexes:

i) green $HAuOs_3(CO)_{10}(PMe_3)$ (10) (11 mg, 4%), R_f - 0.89. Recrystallised from benzene/n-octane as its benzene solvate. Infra-red spectral data are recorded in Table 6. ^1H n.m.r. δ ($CDCl_3$) = 7.58s (6), Ph; 1.71d (9), J_{PH} = 12 Hz, PMe_3; -15.3s (1), H. Analysis: C - 18.54, H - 1.87%; *M* (mass spectrometry) - 1124; $C_{13}H_{10}O_{10}PAuOs_3 \cdot C_6H_6$ requires C - 18.97, H - 1.34%; *M* - 1124.

ii) red $AuOs_3(CO)_{10}(PMe_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$ (11) (78 mg, 27%), R_f - 0.73, m.p. = 59-62°. Recrystallised from dichloromethane/cyclohexane. Spectral characteristics are recorded in Tables 4 and 5. Analysis: C - 19.83, H - 1.63%; *M* (mass spectrometry) - 1227; $C_{21}H_{16}O_{10}PAuOs_3$ requires C - 20.56, H - 1.31%; *M* - 1227.

iii) yellow $HAuOs_3(CO)_9(PMe_3)(CHCPh)$ (12) (8 mg, 3%), R_f - 0.66. Infra-red (C_6H_{12}): ν(CO) = 2091m, 2077m, 2063vs, 2046s, 2037m, 2018s, 2009s, 1892m; ν(C=C) = 1607m cm^{-1}. ^1H n.m.r. $\delta[(CD_3)_2CO]$ = 2.52m (5), CHC*Ph*; 5.02s (1), C*H*CPh; 1.74d (9), J_{PH} = 12 Hz, PMe_3; -17.6s (1) H. Analysis: C - 19.46, H - 1.95%; *M* (mass spectrometry) - 1199; $C_{20}H_{16}O_9PAuOs_3$ requires C - 20.04, H - 1.34%; *M* - 1199.

iv) deep crimson $AuOs_3(CO)_9(PMe_3)_2(\mu\text{-}\eta^2\text{-}CHCHPh)$ (13) (18 mg, 6%), R_f - 0.39. Recrystallised from benzene/n-heptane. Infra-red spectral data are listed in Table 7. ^1H n.m.r. δ ($CDCl_3$) = 7.99d (1), J = 14 Hz, CHC*H*Ph; 7.59m (5), CHCH*Ph*; 5.09d (1), J = 14 Hz, C*H*CHPh; 1.75d (18), J_{PH} = 12 Hz, PMe_3. Analysis: C - 21.93, H - 2.14%; *M* (mass spectrometry) - 1275; $C_{23}H_{25}O_9P_2AuOs_3$ requires C - 21.67, H - 1.97%, *M* - 1275.

Reaction between $H_2Os_3(CO)_{10}$ and $Ag(C_2Ph)PPh_3$

i) A mixture of $H_2Os_3(CO)_{10}$ (210 mg, 0.246 mmol) and $Ag(C_2Ph)PPh_3$ (120 mg, 0.266 mmol) in toluene (50 ml) was stirred at -20° for 2.5 h. The solvent was then removed *in vacuo*, and preparative t.l.c. (15% diethyl ether/cyclohexane developer, Kieselgel H adsorbent, conducted under nitrogen) separated four complexes:

i) red $HAgOs_3(CO)_{10}(PPh_3)$ (14) (21 mg, 7%), R_f - 0.76. Infra-red spectral data are listed in Table 6. ^1H n.m.r. δ (CCl_4) = 7.50m (15), Ph; -14.6s (1) H. Analysis: C - 28.44, H -

1.17%; $C_{28}H_{16}O_{10}PAgOs_3$ requires C - 27.51, H - 1.40%. Complex (14) is light-sensitive and must be isolated with minimal exposure to light.

ii) red $AgOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$ (15) (170 mg, 52%), R_f - 0.60, m.p. = 104°(dec). Complex (15) was recrystallised from benzene/n-hexane. Spectral data are listed in Tables 4 and 5. Analysis: C - 33.72, H - 2.07%; $C_{36}H_{22}O_{10}PAgOs_3$ requires C - 32.66, H - 1.67%. Complex (15) decomposes slowly in light, but can be stored indefinitely in the dark under nitrogen.

iii) orange $HAgOs_3(CO)_8(CHCPh)$ (16) (15 mg, 6%), R_f - 0.51, m.p. = 122°(dec.). Recrystallised from benzene/n-hexane as its benzene solvate. Infra-red spectral data are listed in Table 7. ^1H n.m.r. δ [$(CD_3)_2CO$] = 7.54m (11), CHC*Ph* + C_6H_6; 4.88s (1), C*H*CPh; -19.8s (1) H. Analysis: C - 24.34, H - 1.18%; $C_{16}H_7O_8AgOs_3 \cdot C_6H_6$ requires C - 24.38, H - 1.18%.

iv) dark orange $AgOs_3(CO)_9(PPh_3)(CHCHPh)$ (17) (22 mg, 7%), R_f - 0.47, m.p. = 262°(dec.). Infra-red spectral data are listed in Table 6. ^1H n.m.r. δ [$(CD_3)_2CO$] = 7.98d (1), J = 14 Hz, CHC*H*Ph; 7.55m (26), CHCH*Ph* + PPh_3; 5.09d (1), J = 14 Hz, C*H*CHPh. Analysis: C - 35.71, H - 1.71%; $C_{35}H_{37}O_9PAgOs_3 \cdot C_6H_6$ requires C - 35.84, H - 2.05%.

ii) A mixture of $H_2Os_3(CO)_{10}$ (150 mg, 0.176 mmol) and $Ag(C_2Ph)PPh_3$ (90 mg, 0.199 mmol) in benzene (35 ml) was stirred at room temperature for 15 min. The solvent was then removed *in vacuo*, and preparative t.l.c. (15% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent, under nitrogen) isolated 12 brightly coloured bands:

i) red $HAgOs_3(CO)_{10}(PPh_3)$ (14) (9 mg, 4%), R_f - 0.76.

ii) red $AgOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$ (15) (98 mg, 42%), R_f - 0.61.

iii) orange $HAgOs_3(CO)_8(CHCPh)$ (16) (16 mg, 9%), R_f - 0.51.

iv) orange $AgOs_3(CO)_9(PPh_3)(CHCHPh)$ (17) (9 mg, 4%), R_f - 0.47.

v) crimson $AgOs_3(CO)_9(PPh_3)_2(\mu\text{-}\eta^2\text{-}CHCHPh)$ (18) (16 mg, 6%), R_f - 0.30, m.p. = 251-255°C. Recrystallised from CH_2Cl_2/benzene/n-heptane. Infra-red spectral data are listed in Table 7. ^1H n.m.r. δ ($CDCl_3$) = 8.35d (1), J = 14 Hz, CHC*H*Ph; 7.55m (35), CHCH*Ph* + PPh_3; 5.09d (1), J = 14 Hz, C*H*CHPh. Analysis: C - 39.65, H - 2.39%; *M* (acetone) - 1563, *M* (benzene) - 1529; $C_{53}H_{35}O_9P_2AgOs_3$ requires C - 40.85, H - 2.71%; *M* - 1558.

vi) seven other products were observed, but remain uncharacterised.

Reaction between $H_2Os_3(CO)_{10}$ and $Cu(C_2Ph)PPh_3$

i) A mixture of $H_2Os_3(CO)_{10}$ (100 mg, 0.117 mmol) and $Cu(C_2Ph)PPh_3$ (42 mg, 0.104 mmol) in toluene (60 ml) was stirred at -30° for 3.5 h. The solvent was removed *in vacuo*, and preparative t.l.c. (25% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent) isolated two products:

i) yellow $HCuOs_3(CO)_{10}(PPh_3)$ (19) (18 mg, 13%), R_f - 0.56. Recrystallised from diethyl ether/cyclohexane. Infra-red spectral data are listed in Table 6. ^1H n.m.r. δ ($CDCl_3$) = 7.59m (15), PPh_3; -13.4s (1) H. Analysis: C - 27.67, H - 1.54%; *M* (acetone) - 1204, *M* (benzene) - 1142; $C_{28}H_{16}O_{10}PCuOs_3$ requires C - 28.51, H - 1.54%; *M* - 1178.

ii) yellow $CuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$ (20) (104 mg, 69%), R_f - 0.51, m.p. = 96-99°. Recrystallised from toluene/n-octane. Spectral data are listed in Tables 4 and 5. Analysis: C - 33.00, H - 1.47%; *M* (acetone) - 1296, *M* (benzene) - 1304; $C_{36}H_{22}O_{10}PCuOs_3$ requires C - 33.79, H - 1.73%; *M* - 1280.

ii) A mixture of $H_2Os_3(CO)_{10}$ (100 mg, 0.117 mmol) and $Cu(C_2Ph)PPh_3$ (50 mg, 0.124 mmol) in benzene (40 ml) was stirred at room temperature for 19 h. The solvent was removed *in vacuo*, and preparative t.l.c. (25% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent) separated eight products:

i) yellow $HCuOs_3(CO)_{10}(PPh_3)$ (19) (4 mg, 3%), R_f - 0.56.

ii) yellow $CuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHPh)$ (20) (62 mg, 41%), R_f - 0.51.

iii) yellow $HCuOs_3(CO)_8(CHCPh)$ (21) (9 mg, 8%), R_f - 0.42. Recrystallised from benzene/n-heptane. Infra-red spectral data are listed in Table 7. ^1H n.m.r. δ ($CDCl_3$) = 7.49m (5), CHC*Ph*; 4.69s (1), C*H*CPh; -17.3s (1) H. Analysis: C - 19.50, H - 0.56%; *M* (acetone) - 1003, *M* (benzene) - 1021; $C_{16}H_7O_8CuOs_3$ requires C - 19.99, H - 0.73%; *M* - 961.

iv) orange-red $CuOs_3(CO)_9(PPh_3)_2(\mu\text{-}\eta^2\text{-}CHCHPh)$ (22) (5 mg, 3%), R_f - 0.23. Recrystallised from diethyl ether/n-pentane. Infra-red spectral data are listed in Table 7. ^1H n.m.r. δ ($CDCl_3$) = 8.20d (1), J = 14 Hz, CHC*H*Ph; 7.54m (35), CHCH*Ph* + PPh_3; 5.01d (1), J = 14 Hz, C*H*CHPh. Analysis: C - 42.13, H - 2.86%; *M* (acetone) - 1521, *M* (benzene) - 1490; $C_{53}H_{37}O_9P_2CuOs_3$ requires C - 42.02, H - 2.53%; *M* - 1515.

v) four other products were observed, but remain uncharacterised.

Reaction between $Ru_3(CO)_{12}$ and $Au(C_2Ph)PPh_3$

A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.313 mmol) and $Au(C_2Ph)PPh_3$ (260 mg, 0.481 mmol) in benzene (40 ml) was heated at reflux point for 2.5 h. The solution was allowed to cool, and the solvent removed *in vacuo*.

Preparative t.l.c. (15% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent) separated the following complexes:

i) yellow $AuRu_3(CO)_{10}(PPh_3)$ (23) (23 mg, 7%), R_f - 0.93, m.p. = 201-203°. Recrystallised from n-heptane. Infra-red spectral data are listed in Table 8. ^1H n.m.r. δ ($CDCl_3$) = 7.52m, PPh_3; ^{13}C n.m.r. δ ($CDCl_3$) = 182.9s, CO; 143.1m, PPh_3. Analysis: C - 32.33, H - 1.98%; *M* (acetone) - 1069, *M* (benzene) - 1096; $C_{28}H_{15}O_{10}PAuRu_3$ requires C - 32.26, H - 1.45%; *M* - 1043.

ii) red $AuRu_3(CO)_9(PPh_3)(C_2Ph)$ (24) (59 mg, 17%), R_f - 0.75, m.p. = 224-226°. Recrystallised from n-heptane. Infra-red spectral data are listed in Table 8. ^1H n.m.r. δ ($CDCl_3$) = 7.50m, $PPh_3 + C_2Ph$; ^{13}C n.m.r. δ ($CDCl_3$) = 191.2s, CO; 169.5s, $C{\equiv}CPh$; 120.2s, $C{\equiv}C$-Ph; 134.6m, $C{\equiv}C$-*Ph* + PPh_3. Analysis: C - 37.97, H - 2.09%; *M* (acetone) - 1169, *M* (benzene) - 1093; $C_{35}H_{20}O_9PAuRu_3$ requires C - 37.68, H - 1.80%; *M* - 1116.

iii) deep red $Au_2Ru_3(CO)_7(PPh_3)_2(C_2Ph)_2$ (25) (82 mg, 16%), R_f - 0.45, m.p. >310°. Recrystallised from benzene/n-heptane. Infra-red spectral data are listed in Table 8. ^1H n.m.r. δ ($CDCl_3$) = 7.50m, $PPh_3 + C_2Ph$; ^{13}C n.m.r. δ ($CDCl_3$) = 180.0s (4), 178.1s (2), 176.9s (1), 176.3s (1), CO; 162.4s (1), $C{\equiv}CPh$; 131.7m (24), $PPh_3 + C{\equiv}CPh$; 69.2s (1), $C{\equiv}CPh$. Analysis: C - 43.45, H - 2.58%; *M* (acetone) - 1701, *M* (benzene) - 1680; $C_{59}H_{40}O_7P_2Au_2Ru_3$ requires C - 43.74, H - 2.49%; *M* - 1648.

iv) three other products were observed, but remain uncharacterised.

Reaction between $Ru_3(CO)_{12}$ and $Ag(C_2Ph)PPh_2$

A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.313 mmol) and $Ag(C_2Ph)PPh_3$ (440 mg, 0.975 mmol) in benzene (40 ml) was heated at reflux point for 15 min. A grey precipitate formed. Filtration (paper) removed 49 mg of this insoluble material. The remaining solvent was removed *in vacuo*, and preparative t.l.c. (20% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent) separated the following complexes:

i) pale orange $HRu_3(CO)_9(C_2Ph)$ (26) (10 mg, 5%), R_f - 0.92, m.p. = 101-102°. Recrystallised from benzene/n-hexane as its benzene solvate. Infra-red (C_6H_{12}): ν(CO) = 2099m, 2074vs, 2055vs, 2028sh, 2026vs, 1994m cm^{-1}. ^1H n.m.r. δ ($CDCl_3$) = 7.26m (11), Ph; -21.4s (1) H. Analysis: C - 38.13, H - 2.36; *M* (mass spectrometry) - 658; $C_{17}H_6O_9Ru_3 \cdot C_6H_6$ requires C - 37.56, H - 1.64%; *M* - 658. Confirmed by comparison with the literature.[239]

ii) red $Ru_3(CO)_{11}(PPh_3)$ (27) (16 mg, 6%), R_f - 0.81. Recrystallised from CH_2Cl_2/n-pentane. Identified by comparison with the literature.[240-242]

iii) red $AgRu_3(CO)_{10}(PPh_3)$ (28) (24 mg, 8%), R_f - 0.77, m.p. = 156°(dec.). Recrystallised from benzene. Infra-red spectral data are listed in Table 8. ^1H n.m.r. δ ($CDCl_3$) = 7.40m, PPh_3. Analysis: C - 35.46, H - 1.25%; *M* (acetone) - 949, *M* (benzene) - 935; $C_{28}H_{15}O_{10}PAgRu_3$ requires C - 35.27, H - 1.58%; *M* - 953.

iv) red $AgRu_3(CO)_9(PPh_3)(C_2Ph)$ (29) (32 mg, 10%), R_f - 0.65, m.p. = 209°(dec.). Recrystallised from benzene/n-heptane as its benzene solvate. Infra-red spectral data are listed in Table 8. ^1H n.m.r. δ [$(CD_3)_2CO$] = 7.35m, $PPh_3 + C_2Ph$. Analysis: C - 45.13, H - 2.58%; *M* (acetone) - 998,

M (benzene) - 1003; $C_{35}H_{20}O_9PAgRu_3$ requires C - 44.58, H - 2.37%; *M* - 1027. Complex (29) is very light-sensitive, and was handled in the dark. Chromatography in the presence of light results in extensive decomposition.

v) deep red $Ag_2Ru_3(CO)_7(PPh_3)_2(C_2Ph)_2$ (30) (104 mg, 23%), R_f - 0.50, m.p. = 315°(dec.). Recrystallised from benzene. Infra-red spectral data are listed in Table 8. ^1H n.m.r. δ ($CDCl_3$) = 7.38m, $PPh_3 + C_2Ph$. ^{13}C n.m.r. δ ($CDCl_3$) = 177.4s, CO; 159.7s, *C*CPh; 130.9m, CC*Ph*; 73.6s, C*C*Ph. Analysis: C - 50.94, H - 3.00%; *M* (acetone) - 1401, *M* (benzene) - 1395; $C_{59}H_{40}O_7P_2Ag_2Ru_3 \cdot C_6H_6$ requires C - 51.21, H - 2.99%; *M* - 1442.

vi) five other products were observed, but remain uncharacterised.

Reaction between $Ru_3(CO)_{12}$ and $Cu(C_2Ph)PPh_3$

A mixture of $Ru_3(CO)_{12}$ (75 mg, 0.117 mmol) and $Cu(C_2Ph)PPh_3$ (150 mg, 0.372 mmol) in benzene (50 ml) was stirred at room temperature for 15.5 h. The solution gradually darkened. Filtration (paper) and preparative t.l.c. (10% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent) of the resulting solution separated the following complexes:

i) yellow $HCuRu_3(CO)_{10}(PPh_3)$ (31) (14 mg, 9%), R_f - 0.82, m.p. = 250°(dec.). Recrystallised from n-heptane. Infra-red spectral data are listed in Table 8. ^1H n.m.r. δ ($CDCl_3$) = 7.42m (15), PPh_3; -17.1s (1) H. Analysis: C - 36.49, H - 2.27%; *M* (acetone) - 915, *M* (benzene) - 923; $C_{28}H_{16}O_{10}PCuRu_3$ requires C - 36.95, H - 1.77%; *M* - 910.

ii) orange-yellow $CuRu_3(CO)_9(PPh_3)(C_2Ph)$ (32) (21 mg, 18%), R_f = 0.71, m.p. = 272-273°. Recrystallised from n-heptane. Infra-red spectral data are listed in Table 8. ^1H n.m.r. δ ($CDCl_3$) =

7.43m, $PPh_3 + C_2Ph$. Analysis: C - 42.87, H - 2.49%; *M* (acetone) - 1016, *M* (benzene) - 1018; $C_{35}H_{20}O_9PCuRu_3$ requires C - 42.80, H - 2.05%; *M* - 982.

iii) orange $Cu_2Ru_3(CO)_7(PPh_3)_2(C_2Ph)_2$ (33) (50 mg, 31%), R_f - 0.52, m.p. >310°. Recrystallised from benzene/n-heptane. Infra-red spectral data are listed in Table 8. ^1H n.m.r. δ ($CDCl_3$) = 7.39m, $PPh_3 + C_2Ph$; ^{13}C n.m.r. δ ($CDCl_3$) = 176.9s, CO; 164.1s, *C*CPh; 131.2m, CC*Ph*; 71.2s, C*C*Ph. Analysis: C - 51.39, H - 3.02%; *M* (acetone) - 1317, *M* (benzene) - 1343; $C_{59}H_{40}O_7P_2Cu_2Ru_3$ requires C - 52.18, H - 2.92%; *M* - 1381.

iv) seven other products were observed, but remain uncharacterised.

Pyrolysis of $AgOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (2)

Heating $AgOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (2) (83 mg, 0.059 mmol) in benzene (10 ml) at reflux point for 15 min. results in the formation of a silver mirror. The solution was cooled and filtered under nitrogen, through a short silica gel column. Elution with 50% CH_2Cl_2/cyclohexane gave a crimson band. This was recrystallised from n-hexane to give $HAgOs_3(CO)_8(CHCHC_6F_5)$ (36) (15 mg, 24%), m.p. = 106°(dec.). The product was both light and air sensitive. Infra-red (C_6H_{12}): ν(CO) = 2095w, 2070s, 2055vw, 2044vs, 2027vs, 2014sh, 1986m, 1855w cm^{-1}; ν(C=C) = 1579w cm^{-1}. ^1H n.m.r. δ ($CDCl_3$) = 8.95d (1), J = 14 Hz, CHC*H*C_6F_5; 5.78d (1), J = 14 Hz, C*H*CHC$_6F_5$; -19.8s (1), H. Analysis: C - 17.67, H - 0.32%; $C_{16}H_3O_8F_5AgOs_3$ requires C - 17.54, H - 0.18%. No further products were eluted from the column.

Pyrolysis of $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (1)

Heating $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (1) (100 mg, 0.067 mmol) in n-octane (60 ml) at 120° for 3.5 h. resulted in a gradual colour change from deep red to bright yellow. On cooling, the solvent was

removed *in vacuo*. The residue was recrystallised from toluene/n-octane to give bright yellow crystals of $HAuOs_3(CO)_8(PPh_3)(CHCHC_6F_5)$ (34) (80 mg, 83%). Infra-red (C_6H_{12}): ν(CO) = 2087m, 2065s, 2039vs, 2007s, 1988m, 1972m, 1962m cm^{-1}; ν(C=C) = 1583m cm^{-1}. ^1H n.m.r. δ ($CDCl_3$) = 7.50m (15), PPh_3; 6.28s (1), $CHCHC_6F_5$; 4.71s (1), $CHCHC_6F_5$; ^{13}C n.m.r. δ ($CDCl_3$) = 176.2s, CO; 133.1m, $PPh_3 + C_6F_5$; 106.4s, $CHCHC_6F_5$; 92.1s, $CHCHC_6F_5$. Analysis: C - 27.51, H - 0.78%; *M* (acetone) - 1440; $C_{34}H_{18}O_8PF_5AuOs_3$ requires C - 28.20, H - 1.25%; *M* - 1423.

Pyrolysis of $HAuOs_3(CO)_8(PPh_3)(CHCHC_6F_5)$ (34)

Heating $HAuOs_3(CO)_8(PPh_3)(CHCHC_6F_5)$ (34) (70 mg, 0.049 mmol) in diglyme (45 ml) at reflux point for 6 h. resulted in gradual darkening of the initial yellow solution to a final brown-black colour. The solution was filtered (hot) and the solvent was then removed *in vacuo*. Soxhlet extraction of the residue with ethyl acetate gave a dark brown, partially characterised product (7 mg, 9%). Infra-red (CH_2Cl_2): ν(CO) = 2059m, 2018s, 1991s, 1979sh cm^{-1}. ^1H n.m.r. δ ($CDCl_3$) = -19.8s, H. Analysis: C - 9.74, H - 0.64%; $C_{13}O_{13}H_4Au_2Os_4$ requires C - 10.25, H - 0.26%. The available data is consistent with the molecular formula $H_4Au_2Os_4(CO)_{13}$, but further confirmation is needed from crystallographic studies, before such a formula can be ascribed to this compound.

Reaction between $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ and $K(HBBu^s_3)$

To a stirred solution of $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (1) (50 mg, 0.033 mmol) in thf (25 ml) was added [$K(HBBu^s_3)$] (0.1 ml, 0.5 M thf solution). The reaction solution changed to an intense purple colour instantly. Addition of $(NEt_4)Br$, and removal of solvent *in vacuo*, gave an intense violet residue, which, when recrystallised from benzene/n-octane, gave violet $[H_2AuOs_3(CO)_9(PPh_3)(CHCHC_6F_5][NEt_4]_2$ (37) (38 mg, 63%). Complex (37) was isolated as its benzene solvate.

Infra-red (CH_2Cl_2): ν(CO) = 2095m, 2080m, 2063m, 2036s, 1998vs, 1990s, 1986s, 1982s, 1977s, 1973sh cm^{-1}. ^1H n.m.r. δ [$(CD_3)_2CO$] = 8.69d (1), J = 14 Hz, $CHCHC_6F_5$; 7.53m (21), $PPh_3 + C_6H_6$; 5.62s (1), $CHCHC_6F_5$; 3.13q (16), J = 7 Hz, $(CH_3CH_2)_4N$; 1.51t (24), J = 7 Hz, $(CH_3CH_2)_4N$; -21.6s (2), H. Analysis: C - 32.36, H - 3.16, N - 1.27%; $C_{51}H_{59}O_9N_2PF_5AuOs_3 \cdot C_6H_6$ requires C - 32.42, H - 2.50, N - 1.54%.

Reaction between $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ and (i) $K(HBBu^s_3)$/(ii) H_3PO_4

To a solution of $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (1) (100 mg, 0.067 mmol) in thf (10 ml) was added K-Selectride [$K(HBBu^s_3)$] (0.2 ml, 0.5 M thf solution). To the resultant violet solution was added H_3PO_4 (10 mg, 0.102 mmol), and a deep red colour formed instantly. The solvent was removed *in vacuo*. Extraction of the residue with cyclohexane (69 ml) gave (1) (40 mg, 40%). Further extraction of the residue with dichloromethane yielded a black, highly air-sensitive product (15 mg), which remains uncharacterised. Subsequent extraction with isopropanol yielded an uncharacterised brown complex (28 mg).

Reaction between (1) and $K(HBBu^s_3)/[(AuPPh_3)_3O][BF_4]$

To a solution of $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (1) (200 mg, 0.133 mmol) in thf (10 ml) was added $K(HBBu^s_3)$ (0.4 ml, 0.5 M thf solution). To the resultant violet solution was added $[(AuPPh_3)_3O][BF_4]$ (270 mg, 0.182 mmol). The violet colour dissipated, and an intense red solution resulted. The solvent was removed *in vacuo*, and preparative t.l.c. (35% dichloromethane/isopentane developer, Kieselgel GF_{254} adsorbent) separated twelve brightly coloured bands:

i) recovered (1) (40 mg, 20%), R_f - 0.79.

ii) red $Au_3Os_3(CO)_7(PPh_3)_3(CHCHC_6F_5)$ (38) (34 mg, 11%), R_f - 0.65. Recrystallised from benzene/n-heptane. Infra-red (C_6H_{12}): ν(CO) = 2072m, 2040s, 2022s, 1999sh, 1995vs,

1960sh cm^{-1}; ν(C=C) = 1608m cm^{-1}. ^1H n.m.r. δ ($CDCl_3$) = 8.60d (1), J = 13.7 Hz, $CHCHC_6F_5$; 7.45m (45), PPh_3; 5.16d (1), J = 13.8 Hz, $CHCHC_6F_5$. Analysis: C - 35.12, H - 2.03%; *M* (acetone) - 2398; $C_{69}H_{47}O_7P_3F_5Au_3Os_3$ requires C - 35.45, H - 2.02%; *M* - 2338.

iii) red $Au_3Os_3(CO)_6(PPh_3)_3(CHCHC_6F_5)$ (39) (40 mg, 13%), R_f - 0.62. Recrystallised from benzene/n-heptane. Infra-red (C_6H_{12}): ν(CO) = 2070m, 2046m, 2030s, 2019vs, 1998s, 1969m cm^{-1}; ν(C=C) = 1618w cm^{-1}. ^1H n.m.r. δ ($CDCl_3$) = 8.59d (1), J = 14.1 Hz, $CHCHC_6F_5$; 7.43m (45), PPh_3; 5.13d (1) J = 14.0 Hz, $CHCHC_6F_5$. Analysis: C - 34.61, H - 1.85%; *M* (acetone) - 2292; $C_{68}H_{47}O_6P_3F_5Au_3Os_3$ requires C - 35.36, H - 2.05%; *M* - 2310.

iv) purple-black $Au_6Os_3(CO)_7(PPh_3)_6$ (40) (47 mg, 10%), R_f - 0.32. Recrystallised from dichloromethane/benzene as its benzene solvate. Infra-red (CH_2Cl_2): ν(CO) = 2103m, 2074vs, 2055vs, 2022s, 2005s, 1991sh cm^{-1}. ^1H n.m.r. δ [$(CD_3)_2CO$] = 7.48m $PPh_3 + C_6H_6$. Analysis: C - 40.29, H - 3.19%; *M* (acetone) - 3590; $C_{115}H_{90}O_7P_6Au_6Os_3 \cdot C_6H_6$ requires C - 40.37, H - 2.68%; *M* - 3522.

v) eight other products were observed, but remain uncharacterised.

Reaction between (1) and Me_3NO/C_2H_2

A mixture of $AuOs_3(CO)_{10}(PPh_3)(\mu\text{-}\eta^2\text{-}CHCHC_6F_5)$ (1) (100 mg, 0.67 mmol) and Me_3NO (15 mg, 0.200 mmol) in toluene (25 ml) was stirred at 85° for 2 h. The resultant solution was allowed to cool, and then C_2H_2 was bubbled through a glass frit at 40° for 3 h. The initial black solution slowly became red. Slow diffusion of n-octane into this solution gave bright red microcrystals of $AuOs_3(CO)_7(PPh_3)(C_4H_4)(CHCHC_6F_5)$ (41) (48 mg, 46%) as its n-octane solvate. Infra-red (CH_2Cl_2): ν(CO) =

2094m, 2064m, 2048sh, 2038vs, 2008vs, 1989sh cm^{-1}. ^1H n.m.r. δ $[(CD_3)_2CO]$ = 7.36m (16), PPh_3 + $CHCHC_6F_5$; 7.08d (4), J = 7.6 Hz, C_4H_4; 3.45d (1), J = 12.2 Hz, $CHCHC_6F_5$; 1.9-0.5m,br (18), C_8H_{18}. Analysis: C - 34.14, H - 2.73%; $C_{37}H_{21}O_7PF_5AuOs_3 \cdot C_8H_{18}$ requires C - 34.09, H - 2.48%. The octane solvate can be removed by re-dissolving the crystals in acetone and gently heating the residue to 40° *in vacuo* for 24 h. The ^1H n.m.r. spectrum showed loss of broad bands at δ = 1.9-0.5. Other bands were detected in the infra-red spectrum as follows: (CH_2Cl_2) - 3073m, 3061ms, 3054ms, 3003w, 2995m, 2991sh, 2980w, 2970w, 2688w, 2327w, 2306m, 1716vw cm^{-1}. An X-ray structure determination of (41) is in progress.[255]

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APPENDIX ONE

GROUP IB HETEROMETALLIC COMPOUNDS (NOT CLUSTERS)

TABLE I Heterometallic Compounds Containing Copper, Silver or Gold (Not Clusters)

Group IB reagent	Other reagent	Product	M-M′ Bond Lengths (average in Å)	Yield	References(s)[a]
$AuClPPh_3$	$Me_3SnMn(CO)_5$	$AuMn(CO)_5(PPh_3)$		77%	1,46,47
$AuClPPh_3$	$Me_3SnCo(CO)_4$	$AuCo(CO)_4(PPh_3)$		80%	1,46,47
$Ag(C_2C_6F_5)$	$RhCl(PPh_3)_3$	$RhAg_2(C_2C_6F_5)_5(PPh_3)_3$	3.094	10.5%	2,3,7
$Ag(C_2C_6F_5)$	$RhCl(PPh_3)_3$	$RhAg(C_2C_6F_5)_4(PPh_3)_3$		6.5%	3,7
$Ag(C_2C_6F_5)$	$IrCl(CO)(PPh_3)_2$	$IrAg(C_2C_6F_5)_4(PPh_3)_3$		10%	7
$Cu(C_2C_6F_5)$	$IrCl(CO)(PPh_3)_2$	$IrCu(C_2C_6F_5)_4(PPh_3)_3$		9%	4
$Ag(C_2C_6F_5)$	$IrCl(CO)(PPh_3)_2$	$IrAg(C_2C_6F_5)_4(PPh_3)_3$		10%	7
$AuClPPh_3$	$K[Rh(PF_3)_4]$	$AuRh(PF_3)_4(PPh_3)$		60%	8
$AuClPPh_3$	$K[Ir(PF_3)_4]$	$AuIr(PF_3)_4(PPh_3)$		50%	8
$[CuCl(PMe_3)_2]_2$	$CoZn(\eta\text{-}C_5H_5)(PMe_3)_3Cl_2$	$CuCo(\eta\text{-}C_5H_5)(PMe_3)_4Cl$		100%	9,91
$AgNO_3/PPh_3$	$WS_4(NH_4)_2$	$Ag_2WS_4(PPh_3)_3$	2.971	5%	10
$AgNO_3/PPh_3$	$MoS_4(NH_4)_2$	$Ag_4Mo_2S_8(PPh_3)_4$	2.975	51%	11
$AgNO_3$	$IrCl(CO)(PPh_3)_2$	$AgIr(CO)(PPh_3)_2(NO_3)_2$		60%	12
$[Cu(EtNCHNC_6H_4Me\text{-}p)]$	$IrCl(CO)(PPh_3)_2$	$CuIr(CO)(PPh_3)_2(EtNCHNC_6H_4Me\text{-}p)$		20%	13

Group IB reagent	Other reagent	Product	Bond Length	Yield	Reference(s)[a]
$[Ag(MeNCHNC_6H_4Me\text{-}p)]$	$IrCl(CO)(PPh_3)_2$	$AgIr(CO)(PPh_3)_2(M3NCHNC_6H_4Me\text{-}p)$		95%	13
$[Cu(MeN_3Me)]_4$	$RhCl(CO)(PPh_3)_2$	$CuRh(CO)(PPh_3)_2(MeN_3Me)Cl$	2.730	75%	14,15
$[Cu(O_2CCF_3)]_4$	$Ir(CO)(PPh_3)_2(O_2C_2F_3)$	$CuIr(CO)(PPh_3)_2(O_2C_2F_3)$		80%	14
$Ag(MeN_3Me)$	$RhCl(CO)(PPh_3)_2$	$AgRh(CO)(PPh_3)_2(MeN_3Me)Cl$		50%	16
$Ag(MeN_3Me)$	$IrCl(CO)(PPh_3)_2$	$AgIr(CO)(PPh_3)_2(MeN_3Me)Cl$		90%	16
$AgClO_4$	$Ir(CO)(PPh_3)_2(ClO_4)$	$AgIr(CO)(PPh_3)_2(ClO_4)$		75%	17
$Ag(O_2C_2F_3)$	$IrCl(CO)(PPh_3)_2$	$AgIr(CO)(PPh_3)_2(O_2C_2F_3)_2$		50%	17
$Ag(O_2C_2F_3)$	$RhCl(CO)(PPh_3)_2$	$AgRh(CO)(PPh_3)_2(O_2C_2F_3)_2$		50%	17
$Ag(p\text{-}MeC_6H_4N_3C_6H_4Me\text{-}p)$	$Ir(CO)(PPh_3)_2(O_2C_2F_3)$	$AgIr(CO)(PPh_3)_2(p\text{-}MeC_6H_4N_3C_6H_4Me\text{-}p)(O_2C_2F_3)$		70%	17
$Ag[O_2CCH(CH_3)_2]$	$Ir(CO)(PPh_3)_2[O_2CCH(CH_3)_2]$	$AgIr(CO)(PPh_3)_2[O_2CCH(CH_3)_2]$	2.874	75%	17,18
$Ag[O_2CCH(CH_3)_2]$	$Rh(CO)(PPh_3)_2[O_2CCH(CH_3)_2]$	$AgRh(CO)(PPh_3)_2[O_2CCH(CH_3)_2]$		75%	17
$[Cu(MeN_3Me)]_4$	$IrCl(CO)(PMe_2Ph)_2$	$CuIrCl(CO)(PMe_2Ph)_2(MeN_3Me)$	2.686	75%	14,19
$AuClPPh_3$	$HCr(CO)_3(\eta\text{-}C_5H_5)$	$AuCr(CO)_3(PPh_3)(\eta\text{-}C_5H_5)$		67%	20
$AuClPR_3$ (R = Ph,Cy, OPh)	$HMo(CO)_3(\eta\text{-}C_5H_5)$	$AuMo(CO)_3(PR_3)(\eta\text{-}C_5H_5)$		83%(Ph),74%(Cy), 39%(OPh)	20

Group IB reagent	Other reagent	Product	Bond Length	Yield	Reference(s)[a]
$AuClPPh_3$	$HW(CO)_3(\eta\text{-}C_5H_5)$	$AuW(CO)_3(PPh_3)(\eta\text{-}C_5H_5)$	2.698	75%	20-22,259
$AuClPPh_3$	$NaMn(CO)_5$	$AuMn(CO)_5(PPh_3)$		80%	22,28,29,40
$AuClPPh_3$	$NaCo(CO)_4$	$AuCo(CO)_4(PPh_3)$	2.501	60%	22-24,28,40,42, 145-147,150
CuCl(*o*-triars)	$HMo(CO)_3(\eta\text{-}C_5H_5)$	$CuMo(CO)_3$(*o*-triars)$(\eta\text{-}C_5H_5)$		63%	20
CuCl(*o*-triars)	$HW(CO)_3(\eta\text{-}C_5H_5)$	$CuW(CO)_3$(*o*-triars)$(\eta\text{-}C_5H_5)$		67%	20
$AuClPPh_3$	$NaMn(CO)_4L$ L = PPh_3,$AsPh_3$	$AuMn(CO)_4(PPh_3)L$		80%	25
$AuClPPh_3$	$NaMn(CO)_4[P(OPh)_3]$	$AuMn(CO)_4(PPh_3)[P(OPh)_3]$	2.571	80%	25,26
CuBr(*v*-triars)	$NaMn(CO)_5$	$CuMn(CO)_5$(*v*-triars)		65%	27,28,30
CuBr(*o*-triars)	$NaMn(CO)_5$	$CuMn(CO)_5$(*o*-triars)	2.561	67%	23,27,28
AgBr(*o*-triars)	$NaMn(CO)_5$	$AgMn(CO)_5$(*o*-triars)		67%	27,28
CuBr(*o*-triars)	$NaCo(CO)_4$	$CuCo(CO)_4$(*o*-triars)		100%	27,28
AgBr(*o*-triars)	$NaCo(CO)_4$	$AgCo(CO)_4$(*o*-triars)	2.661	100%	24,27,28
AuCl(*v*-triars)	$NaMn(CO)_5$	$AuMn(CO)_5$(*v*-triars)		80%	30
$AuClPPh_3$	$NaV(CO)_6$	$AuV(CO)_6(PPh_3)$		100%	31-35
CuBr(*o*-triars)	$NaV(CO)_6$	$CuV(CO)_6$(*o*-triars)		100%	31,35
$AuClPPh_3$	$KTa(CO)_6$	$AuTa(CO)_6(PPh_3)$		80%	32,35

Group IB reagent	Other reagent	Product	Bond Length	Yield	Reference(s)[a]
$AuClPPh_3$	$KNb(CO)_6$	$AuNb(CO)_6(PPh_3)$		50%	32,35
$Au(PPh_3)_4^+ClO_4^-$	$KTa(CO)_6$	$AuTa(CO)_6(PPh_3)_3$		60%	32,35
$AuClPPh_3$	$V(CO)_5(PPh_3)(NEt_4)$	$AuV(CO)_5(PPh_3)_2$		40%	32,35
$AuClPPh_3$	$Ta(CO)_5(PPh_3)(NEt_4)$	$AuTa(CO)_5(PPh_3)_2$		28%	32,35
$AuClPPh_3$	$Nb(CO)_5(PPh_3)(AsPh_4)$	$AuNb(CO)_5(PPh_3)_2$		48%	32,35
$AuCl_2(N\Sigma t_4)$	$[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$	$[AuMo_2(CO)_6(\eta\text{-}C_5H_5)_2][\Sigma t_4N]$		65%	41,60
$AuCl_2(N\Sigma t_4)$	$[Mn(CO)_5]^-$	$[AuMn_2(CO)_{10}][\Sigma t_4N]$		65%	41,60
$AuBr_2(N\Sigma t_4)$	$[Co(CO)_4]^-$	$[AuCo_2(CO)_8][\Sigma t_4N]$		65%	41,60
$AuBr_2(NBu^n_4)$	$[Fe(CO)_2(\eta\text{-}C_5H_5]^-$	$[AuFe_2(CO)_4(\eta\text{-}C_5H_5)_2][Bu^n_4N]$		65%	41,60
$AuClPR_3$ (R = OMe, Me, Ph, p-ClC_6H_4, p-MeC_6H_4; also PR_3 = PCy_2Ph, $PCyPh_2$)	$NaFe(CO)_3NO$	$AuFe(CO)_3(NO)(PR_3)$		30-60%	43
$AuClPPh_3$	$NaFe(CO)_2(NO)(AsEt_2Ph)$	$AuFe(CO)_2(NO)(AsEt_2Ph)(PPh_3)$		45%	43
$CuClPPh_3$	$RhCl(CO)(PPh_3)_2$	$CuRhCl_2(CO)(PPh_3)_3$		75%	48,94
$Ag_2(N_2C_{12}H_8)$	$H_2Fe(CO)_4$	$AgFeH(CO)_4(N_2C_{12}H_8)$			49

Group IB reagent	Other reagent	Product	Bond Length	Yield	Reference(s)[a]
$AuClPPh_3$	$Me_6Si_2Ru_2(CO)_8$	$AuRu(CO)_4(PPh_3)(SiMe_3)$		18%	53
$AuClPPh_3$	$[Me_3GeRu(CO)_4]^-$	$AuRu(CO)_4(GeMe_3)(PPh_3)$			57
$AgNO_3$	$Co(CO)_4^-$	$AgCo(CO)_4$		64%	58,93
$CuClPPh_3$	$[Co(CO)_3(PBu^t_3)]Mg(thf)_4$	$CuCo(CO)_3(PBu^t_3)(PPh_3)$			59
$CuCl_2 \cdot 2H_2O$	$MoS_4(NEt_4)_2/PPh_3$	$Cu_3MoS_3(Cl)(PPh_3)_3S$	2.700		61,95
$AgPF_6$	$Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)$	$[AgRh_2(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)_2]PF_6$	2.644	>70%	62
$[Au(C_6F_5)_3(tht)]$	$Co(CO)_4^-$	$[AuCo(CO)_4(C_6F_5)_3]^-$		91%	63
$[Au(C_6F_5)_3(tht)]$	$Mn(CO)_5^-$	$[AuMn(CO)_5(C_6F_5)_3]^-$		70%	63
$[Au(C_6F_5)_3(tht)]$	$[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$	$[AuMo(CO)_3(\eta\text{-}C_5H_5)(C_6F_5)_3]^-$		40%	63
$[Au(C_6F_5)_3(tht)]$	$[W(CO)_3(\eta\text{-}C_5H_5)]^-$	$[AuW(CO)_3(\eta\text{-}C_5H_5)(C_6F_5)_3]^-$		38%	63
$Au(C_6F_5)(tht)$	$Co(CO)_4^-$	$[AuCo(CO)_8]^-$	2.509	46%	63
$Au(C_6F_5)(tht)$	$Mn(CO)_5^-$	$[AuMn(CO)_{10}]^-$		35%	63
$Au(C_6F_5)(tht)$	$[W(CO)_3(\eta\text{-}C_5H_5)]^-$	$[AuW_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$		40%	63
$Au(C_6F_5)(tht)$	$[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$	$[AuMo_2(CO)_6(\eta\text{-}C_5H_5)_2]^-$		42%	63

Group IB reagent	Other reagent	Product	Bond Length	Yield	Reference(s)[a]
$AuClPPh_3$	$OsCC_6H_4Me$-*p*$(CO)(Cl)$-(PPh_3)	$AuOsCC_6H_4Me$-*p*$(CO)(Cl)_2(PPh_3)_2$		>75%	64
AgCl	$OsCC_6H_4Me$-*p*$(CO)(Cl)$-$(PPh_3)_2$	$AgOsCC_6H_4Me$-*p*$(CO)(Cl)_2(PPh_3)_2$	2.799	70%	64
CuCl	$OsCC_6H_4Me$-*p*$(CO)(Cl)$-$(PPh_3)_2$	$CuOsCC_6H_4Me$-*p*$(CO)(Cl)_2(PPh_3)_2$		>75%	64
$AgClO_4/CH_3CN$	$OsCC_6H_4Me$-*p*$(CO)(Cl)$-$(PPh_3)_2$	$AgOsCC_6H_4Me$-*p*$(CO)(PPh_3)_2(ClO_4)$-(MeCN)			64
$AgNO_3$	cis $Pt(NH_3)_2$-$(C_6H_7N_2O_2)_2$	$AgPt_2(NH_3)_4(C_6H_7N_2O_2)_4$	2.867	19%	65
$AgNO_3$	cis $Pt(NH_3)_2$-$(C_6H_7N_2O_2)_2$	$AgPt(NH_3)_2(C_6H_7H_2O_2)_2$		65%	65
$AgPF_6$	$Mo(SCH_2CH_2SCH_2CH_2S)_2$	$AgMo(SCH_2CH_2SCH_2CH_2S)_2$	3.053		66
$AuC_6Cl_5PPh_3$	$Pt(PPh_3)_3$	$AuPt(PPh_3)_3(C_6Cl_5)$	3.26	65%	67-69
$AuMePPh_3$	$Pt(PPh_3)_3$	$AuPt(PPh_3)_3Me$		60%	67
$AuClPPh_3$	$Fe(CO)_3(C_3H_5)Br/Zn$	$AuFe(CO)_3(PPh_3)(C_3H_5)$	2.519	43%	72
$AuClPPh_3$	$Fe(CO)_3(C_6H_5C_3H_5)Br/Mg$	$AuFe(CO)_3(PPh_3)(C_6H_5C_3H_5)$		6%	72
$AuClPPh_3$	$HCr(CO)_5^-/TlPF_6$	$HAuCr(CO)_5(PPh_3)$	2.770	⩾70%	74
$AuClPPh_3$	$HMo(CO)_5^-/TlPF_6$	$HAuCr(CO)_5(PPh_3)$		⩾70%	74

Group IB reagent	Other reagent	Product	Bond Length	Yield	Reference(s)[a]
$AuClPPh_3$	$HW(CO)_5^-/TlPF_6$	$HAuW(CO)_5(PPh_3)$		⩾70%	74
$AgIPMe_3$	$HCr(CO)_5^-/TlPF_6$	$HAgCr(CO)_5(PMe_3)$		⩾70%	74
$AgIPMe_3$	$HW(CO)_5^-/TlPF_6$	$HAgW(CO)_5(PMe_3)$		⩾70%	74
$CuBr(CNBu^t)_3$	$Mo(SBu^t)_4$	$CuMo(SBu^t)_2(CNBu^t)_4Br$	2.615	60%	83
$CuBr(CNBu^t)_3$	$Mo(SBu^t)_2(CNBu^t)_2$	$CuMo(SBu^t)_2(CNBu^t)_4Br$	2.615	31%	83
$AuClPPh_3$	$Ir(CO)_3(PPh_3)^-$	$AuIr(CO)_3(PPh_3)_2$			90,148
$[CuCl(COD)]_2$	$Ti(\eta\text{-}C_5H_5)(SMe)_2$	$[CuTi(\eta\text{-}C_5H_5)(SMe_2)Cl]_2$			92
CuCl	$Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$	$[CuMo(CO)_3(\eta\text{-}C_5H_5) \cdot \frac{1}{2}H_2O \cdot \frac{1}{2}NH_3]_n$		50%	93
$AgNO_3$	$Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$	$[AgMo(CO)_3(\eta\text{-}C_5H_5)]_n$		50%	93
$AgNO_3$	$Na[W(CO)_3(\eta\text{-}C_5H_5)]$	$[AgW(CO)_3(\eta\text{-}C_5H_5)]_n$		50%	93
CuCl	$Na[W(CO)_3(\eta\text{-}C_5H_5)]$	$[CuW(CO)_3(\eta\text{-}C_5H_5) \cdot H_2O]_n$		50%	93
CuCl	$Na[Cr(CO)_3(\eta\text{-}C_5H_5)]$	$[CuCr(CO)_3(\eta\text{-}C_5H_5)]_n$		50%	93
CuCl	$Na[Co(CO)_4]$	$[CuCo(CO)_4 \cdot xH_2O \cdot xNH_3]$		64%	93
$AgNO_3$	$Co_2(CO)_6(PBu^t_3)_2$	$[AgCo(CO)_3(PBu^t_3)]_n$		30%	93
CuCl	$Co_3(CO)_6(PBu^t_3)_2$	$[CuCo(CO)_3(PBu^t_3)]_n$		30%	93
$AgNO_3$	$\{Fe(CO)_2[P(OPh)_3]\text{-}(NO)\}_2Hg$	$\{AgFe(CO)_2[P(OPh)_3](NO)\}_n$		70%	93
$AgNO_3$	$Na[HFe(CO)_4]$	$[HAgFe(CO)_4]_2 \cdot AgNO_3$		40%	93

Group IB reagent	Other reagent	Product	Bond Length	Yield	Reference(s)[a]
CuCl	$V(CO)_6^-$/bipy	$[CuV(CO)_6(bipy)_2]_n$		60%	93
CuCl	$V(CO)_6^-$/phen	$[CuV(CO)_6(phen)_2]_n$		70%	93
$CuCl_2$	$MoS_4(NEt_4)_2/PPh_3$	$Cu_2MoS_4(PPh_3)_3$	2.709		96
$AuClPPh_3$	$[W(\mu\text{-}CHR)(CO)_7(\eta\text{-}C_5H_5)]^-/TlPF_6$ (R = C_6H_4Me-*p*)	$AuW(\mu\text{-}CHR)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)$	2.729		97
CuCN	$MoS_4(PPh_4)_2$	$[CuMoS_4CN][PPh_4]_2$	2.630	60%	99
CuCN	$MoS_4(NMe_4)_2$	$Cu_2MoS_4(CN)_2(NMe_4)_2$		75%	99
$AgNO_3$	$MoS_4(NH_4)_2/PPh_3$	$Ag_2MoS_4(PPh_3)_4$		95%	100
$CuCl_2$	$WO_2S_2(PPh_3Me)_2/PR_3$ (R = C_6H_4Me-*p*)	$Cu_4W_2O_2S_6(PR_3)_4$	2.793	2%	101
$CuCl_2$	$WO_2S_2(PPh_3Me)_2/PR_3$ (R = C_6H_4Me-*p*)	$Cu_4W_2S_8(PR_3)_4$		26%	101
$AgNO_3$	$[Pt_2(NH_3)_4(C_5H_5N_2O_2)_2](NO_3)_2$	$[AgPt_4(NH_3)_8(C_5H_5N_2O_2)_2]^{5+}$	2.787		102
CuI	$Li_2Au_2(C_6H_4CH_2NMe_2\text{-}o)_4$	$Cu_2Au_2(C_6H_4CH_2NMe_2\text{-}o)_4$		75%	103,105
$AuClPPh_3$	$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_3R)]$-Li	$AuFe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_3R)(PPh_3)$ (R = M, Cl, OCH_3, CH_2NMe_2)		100%	109
$CuC_2C_6F_5$	$Re(CO)_3(PPh_3)_2Cl$	$CuRe(CO)_3(PPh_3)_2(C_2C_6F_5)_2$	3.078		113

Group IB reagent	Other reagent	Product	Bond Length	Yield	Reference(s)[a]
$CuCl_2$	WOS_3^{2-}/PPh_3	$Cu_4W_2S_6(PPh_3)_4O_2$	2.780	10%	115
CuS_2	$Mo_7O_{24}(NH_4)_4 \cdot 4H_2O$	$CuMoS_4(NH_4)$	2.70	90%	131
$AgNO_3$	$WS_4(NH_4)_2/PPh_3$	$Ag_2WS_4(PPh_3)_3$	2.971		132
CuS_2	$W_7O_{24}(NH_4)_6$	$CuWS_4(NH_4)$	2.72		133
$AgNO_3$	$MoS_4(NH_4)_2$	$Ag_2MoS_4(PPh_3)_2$	2.945		130,134
$[Au(S_2O_3)_2]^{3-}$	WS_4^{2-}	$[Au_2W_2S_8]^{2-}$	3.169		135
$[Au(S_2O_3)_2]^{3-}$	WOS_3^{2-}	$[AuW_2S_6O_2]^{2-}$	3.221		130
$AgNO_3$	$NiCl_2/SC(Me)_2CH(NH_2)CO_2$	$Ag_8Ni_6[SC(Me)_2CH(NH_2)CO_2]_{12}Cl$			136
CuCl	$NiCl_2/SC(Me)_2CH(NH_2)CO_2$	$Cu_8Ni_6[SC(Me)_2CH(NH_2)CO_2]_{12}Cl$			136
$AgNO_3$	$PdCl_2/SC(Me)_2CH(NH_2)CO_2$	$Ag_8Pd_6[SC(Me)_2CH(NH_2)CO_2]_{12}Cl$			136
$Cu(C_5Me_5)$	$W[=C(OMe)C_6H_4Me\text{-}p](CO)_5$	$CuW[\mu\text{-}C(OMe)C_6H_4Me\text{-}p](\eta\text{-}C_5Me_5)$		51%	137
$Cu(C_5Me_5)$	$PtW(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(PMe_3)_2$	$CuPtW(\mu\text{-}CC_6H_4Me\text{-}p)(CO)_2(PMe_3)_2(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_5)$	2.648		137
$AuClPPh_3$	$Me_6Ge_2Ru_2(CO)_8$	$AuRu(CO)_4(PPh_3)(GeMe_3)$		18%	144
$AuClPPh_3$	$Pt(PPh_3)_2Cl_2$	$AuPt(PPh_3)_3Cl$		15%	149

Group IB reagent	Other reagent	Product	Bond Length	Yield	Reference(s)[a]
$AuClPPh_3$	$Pt(PPh_3)_2Br_2$	$AuPt(PPh_3)_3Br$		15%	149
CuCl	$Ti(SR_2)(\eta\text{-}C_5H_5)_2$	$[CuTiX(SR)_2(\eta\text{-}C_5H_5)_2]_n$ (X = Cl,Br; R = Me,Ph		70%	257
$\{Cu[HB(pz)_3]\}_n$	$H_2Mo(C_5H_5)_2$	$H_2CuMo[HB(pz)_3](\eta\text{-}C_5H_5)$			258
$AuClPPh_3$	$HMo_2(CO)_{10}^-/TlPF_6$	$HAuMo(CO)_5(PPh_3)$		40%	74

[a]References refer to those of Chapter 4.

APPENDIX TWO

RECENT PUBLICATIONS RELEVANT TO WORK DESCRIBED IN THIS THESIS

CHAPTER 1

1. Synthesis, Structure and Photochemistry of Tetracarbonyl (Fulvalene) diruthenium. Thermally Reversible Photoisomerisation Involving Carbon-Carbon Bond Activation at a Dimetal Centre.

   K. Peter, C. Vollhardt and Timothy W. Weidmann, *J. Am. Chem. Soc.*, 1983, 105, 1676.

2. Preparation and Reactivity of a Dimeric Ruthenium μ-Methylene Complex with No-Metal-Metal Bond: Crystal and Molecular Structure of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2(\mu\text{-}CH_2)$.

   Y.C. Lin, J.C. Calabrese and S.S. Wreford, *J. Am. Chem. Soc.*, 1983, 105, 1679.

3. Paramagnetic Organometallic Molecules XIV. Ion-Pair and Steric Effects in Dissociative Electron Transfer Reactions of Metal Cluster Carbonyl Radical Anions.

   Christopher M. Kirk, Barrie M. Peake, Brian H. Robinson and Jim Simpson, *Aust. J. Chem.*, 1983, 36, 441.

4. Paramagnetic Organometallic Molecules XV. Electron Attachment Reactions of Metal Carbonyls.

   Alan S. Huffadine, Barrie M. Peake, Brian H. Robinson and Jim Simpson, *Aust. J. Chem.*, 1983, 36, 613.

5. Radical and Ionic Nucleophilic Substitution Reactions on α-Alkyl-γ-(p-nitrophenyl)allyl Derivatives.

   Steven D. Barker and Robert K. Norris, *Aust. J. Chem.*, 1983, 36, 527.

6. An Equilibrium between Two Isomers of $Ir_4(CO)_{11}PEt_3$ and the Pathway for Carbonyl Scrambling.

   B.E. Mann, C.M. Spencer and A.K. Smith, *J. Organomet. Chem.*, 1983, 244, C17.

7. Reactions of Metal Carbonyl Cluster Complexes with Multidentate Phosphine Ligands; Reactions with Methyltris(dialkylphosphino)-silanes.

   Douglas F. Foster, Barry S. Nicholls and Anthony K. Smith, *J. Organomet. Chem.*, 1983, 244, 159.

8. X-Ray and Neutron Diffraction Studies on $[Ru_4(CO)_8(\mu\text{-}H)_4\{P(OCH_3)_3\}_4]$ at 293 and 20 K: Characterisation of the Vibrational Behaviour of Two-co-ordinate Hydrogen Atoms.

   A. Guy Orpen and Richard K. McMullan, *J. Chem. Soc., Dalton Trans.*, 1983, 463.

Addendum

To Whom It May Concern:

The following two pages of tables were omitted during the typing. The first is the middle of the fold-out of Table 1 - Chapter 3 (page 233). The second is part of Table 1, Chapter 4 (and may be attached to page 252). I apologize for not noting these missing sheets of information sooner.

Yours sincerely,

Janis G. Matisons B.Sc. (Hons.) Dip. Ed.

Corrections

1. page 166 Reference 177 should read:

   see footnote (6) Reference 174.

2. page 250 (References 123, 124 on Table) The product should read:

   $AgFe_2(CO)_6[\mu\text{-}CHC(NRR')(C_6H_5)](\mu\text{-}PPh_2)$

3. page 307 (Reference 13 on Table) The product should read:

   $AgIr(CO)(PPh_3)_2(MeNCHNC_6H_4Me\text{-}p)$

4. page 309 (References 41, 60 on Table) The counter ion for both the Group 1B reagent and the product (lines 6, 7, 8 from top of table) should read:

   (NEt_4) not $(N\Sigma t_4)$ {in all three cases}

Compound	Synthesis[a]	Yield	m.p.	Analytical data Found (calculated)	$\nu(C\equiv C)$ cm^{-1} (Nujol)	M^+ (mass spectrum)	^1H n.m.r. δ ($CDCl_3$)
$Au(C_2C_4H_9)PPh_3$ (7)	(b)	92%	279-281°	C - 53.46%, H - 3.90% (C - 53.34%, H - 4.47%)	2135	564	7.42m (15), PPh_3 1.90-0.50m (9), n-Bu
	(a),(d)	0%					
$Au(C_2CH_2CH_2OH)PPh_3$ (8)	(c)	42%	248-250°	C - 50.20%, H - 3.94% (C - 50.01%, H - 3.81%)	2130	528	7.55m (15), PPh_3 5.046 (1), OH (J = 7 Hz) 3.19m (2), CH_2OH 2.77m (2), CH_2CH_2OH
	(b)	18%					
	(a),(d)	0%					
$Au(C_2CH_2OH)PPh_3$ (9)	(c)	54%	234-235°	C - 49.04%, H - 3.35% (C - 49.04%, H - 3.52%)	2110	514	7.50m (15), PPh_3 5.10t (1), OH (J = 7 Hz) 3.23d (2), CH_2OH (J = 7 Hz)
	(b)	7%					
	(a),(d)	0%					
$Au(C_2Ph)PPh_3$ (10)	(a)	93%	135-138°	C - 54.96%, H - 3.46% (C - 55.73%, H - 3.59%)	2120	560	7.50m, PPh_3 + Ph
	(b)	71%					
	(d)	62%					
$Au(C_2C_3H_7)PPh_3$ (11)	(b)	95%	256-259°	C - 52.99%, H - 4.76% (C - 52.48%, H - 4.21%)	2135	550	7.42m (15), PPh_3 1.90-0.70m (7), n-Pr
$Au(C_2Ph)PMe_3$ (12)	(b)	73%	196-198°	C - 34.38%, H - 3.64% (C - 35.31%, H - 3.77%)	2097	374	7.50m (5), Ph 1.79d (9), PMe_3 (J_{PH} = 12 Hz)

Group 1B reagent	Other reagent	Product	Heterometallic Bond Lengths (average in Å)	Yield	Reference(s)
$AuClPPh_3$	$[Na(HMPA)_x]_3M(CO)_4$	$Au_3M(CO)_4(PPh_3)_3$		20%(M=Mn)	36,37
	M = Mn, Re			6%(M=Re)	
	HMPA = hexamethylphosphoramide				
$AuClPPh_3$	$V(CO)_5^{3-}$	$Au_3V(CO)_5(PPh_3)_3$	2.734	60%	38,39
$AgNO_3$	$Co_2(CO)_8$	$AgCO_2(CO)_8$			50
CuI	$Co_2(CO)_8$	$CuCo_2(CO)_8$		75%	44
AgI	$Co_2(CO)_8$	$AgCo_2(CO)_8$		75%	44
$AuCl(\overset{\frown}{P\quad P})$	$H_2Fe(CO)_4$	$Au_2Fe(CO)_3(\overset{\frown}{P\quad P})$		46%	45
		where $\overset{\frown}{P\quad P} = (m\text{-}PPh_2C_6H_4)_2$			
$[CuCl(PMe_3)_2]_2$	$CpCo(PMe_3)_2$	$CuCoCl(PMe_3)_4(\eta^5\text{-}C_5H_5)$			91