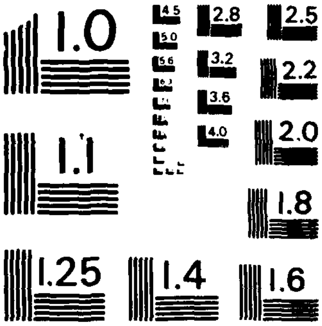
AD-A170 923   COMPOUNDS CONTAINING HETERONUCLEAR METAL-METAL BONDS   1/1
(U) BRISTOL UNIV (ENGLAND) DEPT OF INORGANIC CHEMISTRY
F G STONE 31 MAR 86 AFOSR-TR-86-0510 AFOSR-82-0070
UNCLASSIFIED   F/G 7/4   NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AFOSR-TR- 86-0510

(2)

AFOSR-82-0070

AD-A170 923

COMPOUNDS CONTAINING HETERONUCLEAR METAL-METAL BONDS

F. Gordon A. Stone
Department of Inorganic Chemistry
The University
Bristol BS8 1TS
ENGLAND

31 March 1986

Approved for public release,
distribution unlimited

Final Scientific Report, 01 Mar 82 - 28 Feb 86

Prepared for the Air Force Office of Scientific Research (AFSC),

Bolling Air Force Base, D.C. 20332

and the

European Office of Aerospace Research and Development (LNM),

223/231 Old Marylebone Road, London NW1 5TH, England.

DTIC FILE COPY

DTIC
S ELECTE D
AUG 1 4 1986
B

86 8 13 072

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release;
distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR- 86-0510

6a. NAME OF PERFORMING ORGANIZATION Department of Inorganic Chemistry

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION European Office of Aerospace Research and Development/LNM.

6c. ADDRESS *(City, State and ZIP Code)*
University of Bristol,
Bristol BS8 1TS, United Kingdom.

7b. ADDRESS *(City, State and ZIP Code)*
223/231 Marylebone Road
London NW1 5TH, U.K.

8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR

8b. OFFICE SYMBOL *(If applicable)* NC

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-82-0070

8c. ADDRESS *(City, State and ZIP Code)*
Building 410 Bolling AFB
Washington DC 20332

10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
61102F	2303	B2	

11. TITLE *(Include Security Classification)* COMPOUNDS CONTAINING Heteronuclear Metal-metal Bonds

12. PERSONAL AUTHOR(S) F. Gordon A. Stone

13a. TYPE OF REPORT FINAL

13b. TIME COVERED FROM 01.Mar.82 TO 28 Feb86

14. DATE OF REPORT *(Yr., Mo., Day)* 86 March 31

15. PAGE COUNT 21

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Synthesis
Gold-ruthenium
heteronuclear cluster compounds

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

This Report describes the synthesis and structural characterisation of several gold-ruthenium cluster compounds, as well as the discovery of the first trimetallic complexes containing the hexanuclear core structures $MM'Ru_4$ ($M = Ag$, $M' = Cu$; $M = Au$, $M' = Cu$; $M = Au$, $M' = Ag$). Using variable temperature $^{31}P-\{^1H\}$ nuclear magnetic resonance spectroscopy we have observed polytopal rearrangements of these clusters in solution. Also described are new heteronuclear cluster compounds containing bonds between iridium and osmium or platinum. In a further study the first mixed-metal clusters involving osmium and platinum with interstitial carbido ligands are reported.

Rational synthetic routes have been developed for preparing cluster compounds containing chains and rings of metal atoms in which the metal-metal bonds are bridged by alkylidyne groups. This work has led to the characterisation, via X-ray diffraction and n.m.r. studies, of novel compounds with core structures having eight metal atoms (Pt_4W_4 or $Ni_2Pt_2W_4$) in a ring in the shape of a 'star'.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐

21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL Professor F. Gordon A. Stone

22b. TELEPHONE NUMBER *(Include Area Code)* 272-303674

22c. OFFICE SYMBOL

TABLE OF CONTENTS

Page No.

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMITTAL TO DTIC
This technical report has been reviewed and is
approved for public release IAW AFR 190-12.
Distribution is unlimited.
MATTHEW J. KERPER
Chief, Technical Information Division

Acce
NT ✓
D
Un
J
PER CALL JC
Di
A-1

QUALITY INSPECTED 1

INTRODUCTION

This report describes work carried out under Grant Number AFOSR 82-0070 during the period 01 Mar 82 - 28 Feb 86. We have previously submitted through the European Office of Aerospace Research and Development three Interim Reports, as well as reprints and preprints of various scientific journal articles resulting from work carried out under the Grant.

In addition to the Principal Investigator, the persons listed below have been associated with the research program during the last four years for various periods of time. Generally postdoctoral fellows worked with the group for one year or less, whereas graduate students carried out research for longer periods. In the majority of cases stipends for these workers were provided by matching funds.

Senior Research Personnel

Dr. D.L. Davies
Dr. D.G. Evans
Dr. J.A.K. Howard
Dr. J.C. Jeffery
Dr. A.N.M. Jelfs
Dr. A.G. Orpen

Junior Research Personnel

G.P. Elliott
L.J. Farrugia
M.J. Freeman
A.D. Miles
R.M. Mills
T. Mise
C.M. Nunn
I.D. Salter
C. Sambale
M.F. Schmidt

The project was greatly assisted by collaboration with the X-ray crystallographic group at Bristol (Drs. J.A.K. Howard, J.C. Jeffery, A.G. Orpen, M.J. Freeman, Miss R.M. Mills, and Miss C.M. Nunn). Some of the results obtained as a result of the Grant were presented by the Principal Investigator at the ACS Meeting in Miami, April 1985 ('Inorganic Chemistry'

Award Address) and at the XII International Conference on Organometallic Chemistry in Vienna, September 1985 (Plenary Lecture).

RESEARCH OBJECTIVES

As described in our original proposal (Feb. 81) the objective of the research was to devise new systematic syntheses of polynuclear metal complexes containing bonds between metal atoms of different transition elements. Cluster compounds constitute an almost marginal state of molecular matter, and heteronuclear species offer exciting possibilities for new chemistry in relation to selective activation of different substrates at different metal centres, differing redox character of individual metal atoms, and the preparation of polymetallic crystallites of importance to heterogeneous catalysis. We proposed to establish the molecular structures of the new species produced, investigate any dynamic behaviour, and study reactions of the cluster frameworks with substrate moelcules in order to discover new reactivity patterns. In practice, over the four year period the research program closely followed the original plan.

RESEARCH PROGRESS.*

1. Polynuclear Ruthenium Carbonyl Complexes Containing Gold, Silver, and Copper.

Compounds in which gold-containing groups are bonded to transition elements were first obtained about twenty years ago. However, it became

---

* Reference numbers in text refer to cumulative list of journal articles on pages 19 - 21.

apparent[*] that an isolobal relationship exists between the groups CH_3, H and $AuPR_3$. This prompted us to design a rational synthesis of polynuclear metal species containing $AuPPh_3$ groups. The strategy involved treatment of a polynuclear transition metal hydride complex with $[AuMe(PPh_3)]$. Methane is eliminated and the $AuPPh_3$ group replaces H in the structure.

Our method proved to be very successful, particularly in the preparation of gold— ruthenium clusters.[3,4,7] Some examples of compounds prepared and fully characterised by X-ray diffraction studies are given in Figures 1- 5. When more than one $AuPPh_3$ group is introduced into the cluster Au — Au bonds form (Figures 3 and 4). The compound $[Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}\text{-}(PPh_3)_3]$ is interesting in that it contains seven metal atoms.[7]

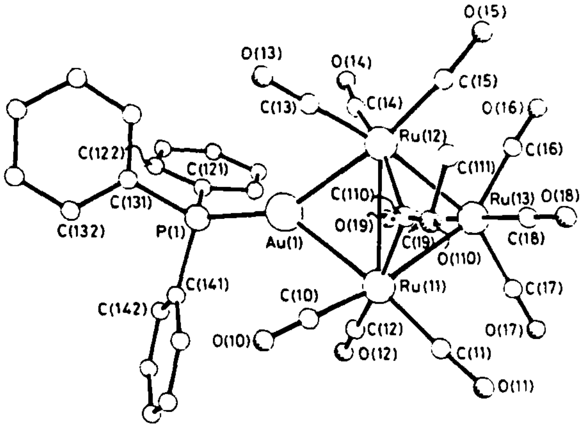


Figure 1. Molecular structure of $[AuRu_3(\mu\text{-}COMe)(CO)_{10}(PPh_3)]$.

---

[*] (a) R. Hoffmann, Angew.Chem., Int.Ed.Engl., 1982, 21, 711; (b) K. Wade, in 'Transition Metal Clusters', ed. B.F.G. Johnson, Wiley, New York, 1980, ch. 3; (c) D.G. Evans and D.M.P. Mingos, J.Organomet.Chem., 1982, 232, 171.

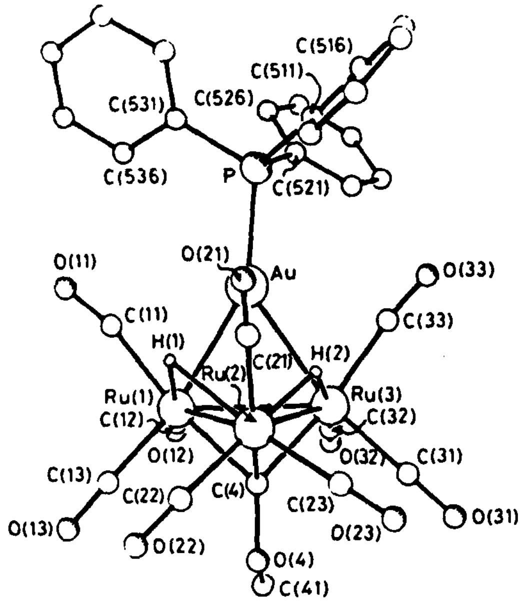


Figure 2. Molecular structure of [$AuRu_3(\mu\text{-}H)_2(\mu_3\text{-}COMe)(CO)_9(PPh_3)$]

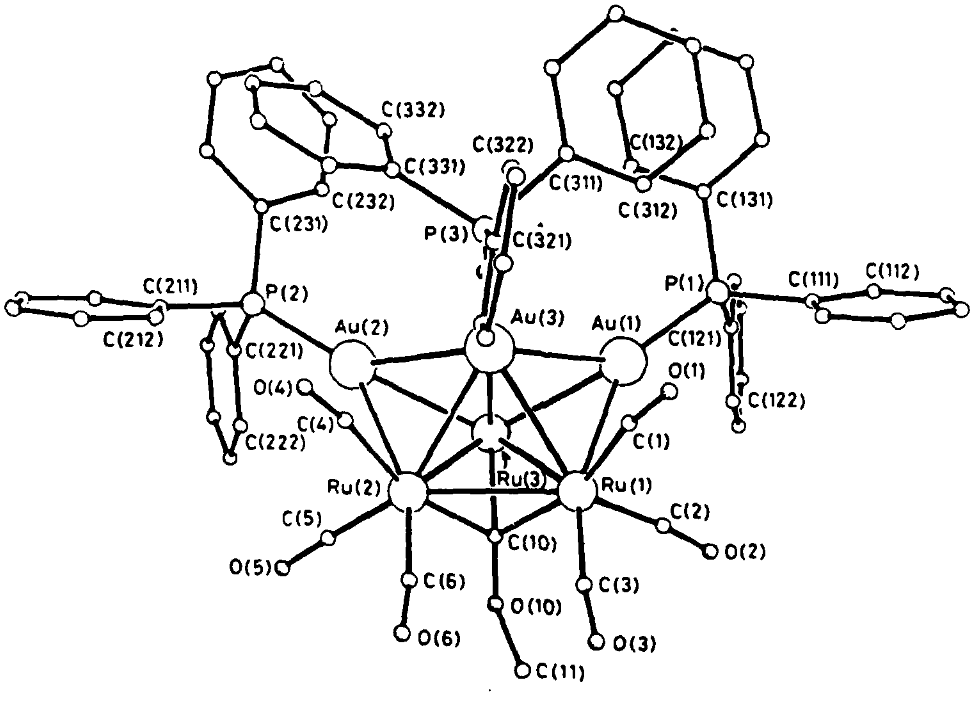


Figure 3. Molecular structure of [$Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3$]. Three carbonyl ligands on Ru(3), labelled (7), (8), and (9), have been omitted because they are obscured by the bonds Ru(3)-Au(3), Ru(3)-Ru(1), and Ru(3)-Ru(2), respectively.

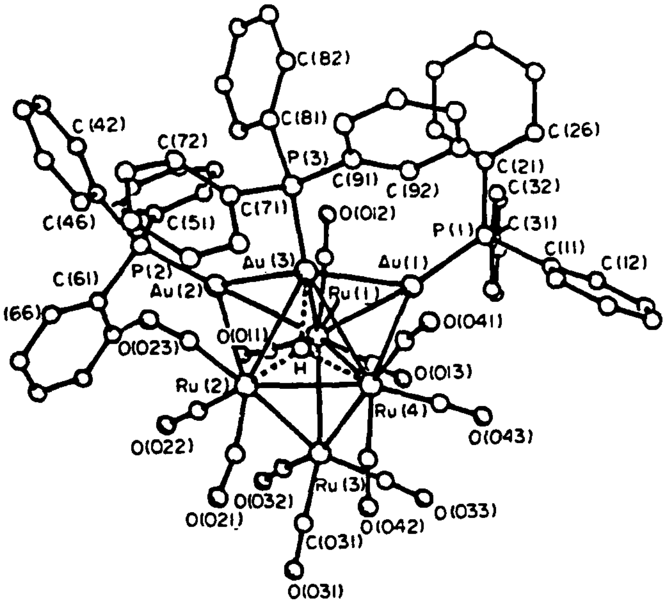


Figure 4. The molecular structure of $[Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3]$.

As part of our work we investigated the reaction between $[AuMe(PPh_3)]$ and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9]$ and in this manner prepared the compounds $[AuRu_3(\mu\text{-}H)(\mu_3\text{-}S)(CO)_8(PPh_3)L]$ and $[Au_2Ru_3(\mu_3\text{-}S)(CO)_8(PPh_3)_2L]$ (L = CO or PPh_3). These are the first examples of cluster complexes containing gold, ruthenium and sulphur. Of particular significance was the observation _via_ $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy of dynamic behaviour in solution for these compounds, involving site exchange of the gold atoms.[3] The molecular structure of $[Au_2Ru_3(\mu_3\text{-}S)(CO)_8(PPh_3)_3]$ is shown in Figure 5. The probable

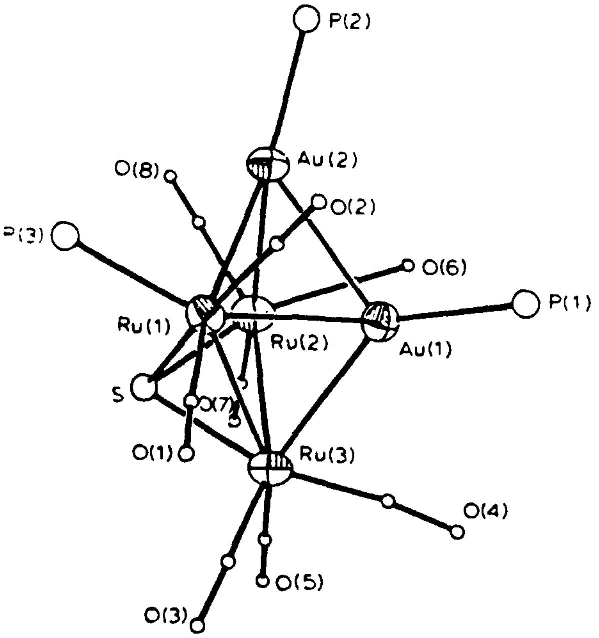


Figure 5. Molecular structure of $[Au_2Ru_3(\mu_3\text{-}S)(CO)_8(PPh_3)_3]$, phenyl groups have been omitted for clarity.

mechanism for rearrangement of the latter complex is shown schematically in Figure 6.

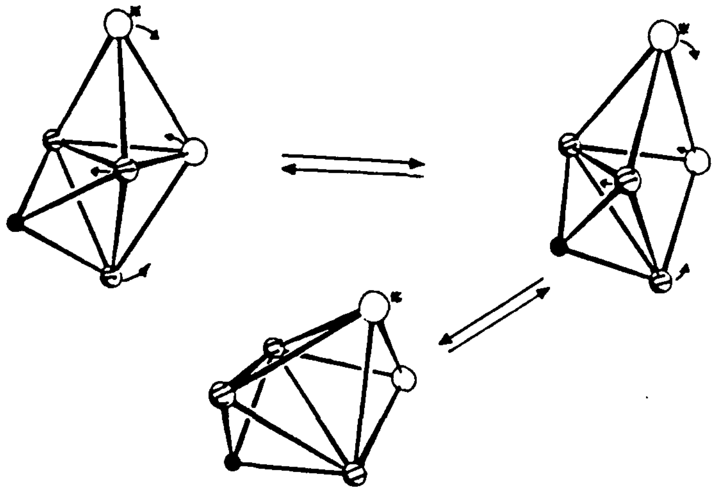
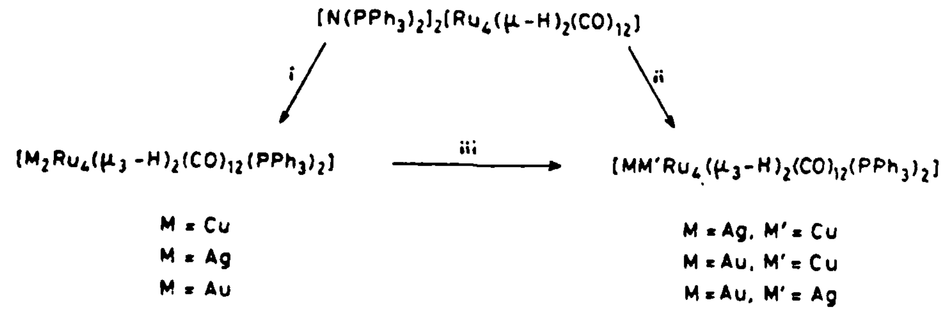


Figure 6. Polytopal site-exchange of Au and Ru sites in $[Au_2Ru_3(\mu_3\text{-}S)(CO)_8(PPh_3)_3]$ observed in solution via $^{31}P\text{-}\{^1H\}$ n.m.r. studies (see ref. 3). The process involves a restricted Berry pseudo-rotation.

○ = Au, ⊜ = Ru, ● = S

We have also prepared a series of hexanuclear metal clusters $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (M = M′ = Cu, Ag or Au; M = Ag or Au, M′ = Cu; M = Au, M′ = Ag) by treating the dianion $[Ru_4(\mu\text{-}H)_2(CO)_{12}]^{2-}$ with the complexes $[MX(PPh_3)]$ (M = Au or Cu, X = Cl; M = Ag, X = I) in the presence of $TlPF_6$ (see Scheme below).[5] A novel alternative synthesis involves metathesis of the two appropriate bimetallic species as in reaction (iii) of the Scheme.



Scheme i, $[MX(PPh_3)]$ (M = Au or Cu, X = Cl; M = Ag, X = I) (2 equiv.) and $TlPF_6$; ii, $[MX(PPh_3)]$ (1 equiv.) and $[M'X(PPh_3)]$ (1 equiv.), with $TlPF_6$; iii, $[M'_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (1 equiv.) in CH_2Cl_2.

The structures of the clusters with the metal cores Cu_2Ru_4, Ag_2Ru_4 and $AgCuRu_4$ have been established by X-ray diffraction, thereby determining all the metal — metal separations (see Figures 7 and 8).

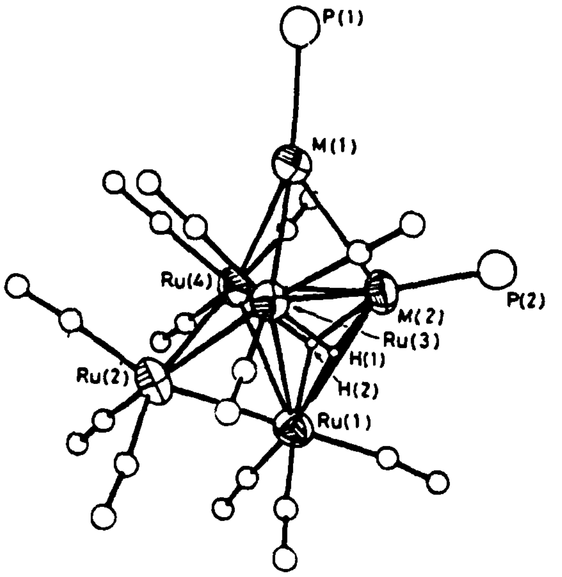


Figure 7. Molecular structure of the compounds $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$, with phenyl ligands on phosphorus omitted for clarity.

M(1) = Cu, M(2) = Cu;

M(1) = Ag, M(2) = Ag,

M(1) = Ag, M(2) = Cu.

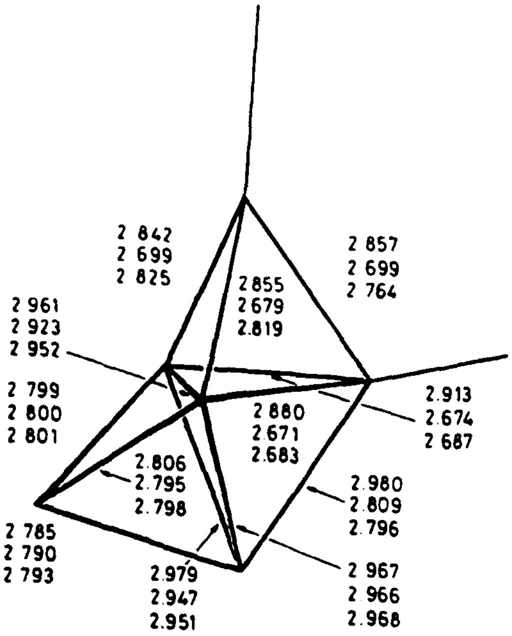


Figure 8. The $M_2Ru_4P_2$ core geometries in (a) $[Cu_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$, (b) $[Ag_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$, and (c) $[AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}\text{-}(PPh_3)_2]$. Distances (in Å) are given for the metal — metal contacts with that for (b) at the top, (a) in the middle and (c) at the bottom.

The metal atom geometry within these hexanuclear metal clusters is bicapped tetrahedral, as found for certain other 84 electron clusters. The Group 1B metals are in close contact and these occupy two distinct sites. One [M(2)] which is in contact with four metal atoms, and a second [M(1)] which is in contact with three. In $[AgCuRu_4(\mu_3\text{-}H)_2(CO)_{12}\text{-}(PPh_3)_2]$ the copper atom occupies the site of higher co-ordination number, and the larger silver atom the other site. The hydrido ligands bridge the $M(2)Ru_2$ faces involving the higher co-ordination number site. No triply-bridging hydrido ligands bonded to Group 1B metals have been previously reported.

For these clusters, $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy established two types of Group 1B metal-exchange. Firstly, an intramolecular mode observable on the n.m.r. time-scale, and secondly an intermolecular mode which is active on the chemical time-scale. The presence of the latter allows cluster formation with predictable stoichiometry and controlled regiochemistry.[5]

2. Heteronuclear Cluster Compounds Containing Bonds Between Iridium and Osmium or Platinum.

Heteronuclear cluster compounds involving iridium are rare, and yet a range of such compounds should exist in view of the facility with which cobalt and rhodium form mixed-metal clusters. At the commencement of our research under the Grant we discovered the cluster complex $[IrOs_3(\mu\text{-}H)_2(\mu\text{-}Cl)\text{-}(CO)_{12}]$.[2] Subsequently we discovered the novel raft-like iridium — platinum cluster $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$. The latter was prepared from the reaction between $[Pt(C_2H_4)_3]$ and $[Ir(CO)_2(\eta\text{-}C_5Me_5)]$.[8] The structure of the hexametal species, which contains two crystallographically independent molecules in the unit cell, is shown in Figure 9. The n.m.r. data reveal that the CO and $\eta\text{-}C_5Me_5$ ligands in this cluster undergo dynamic behaviour in solution.

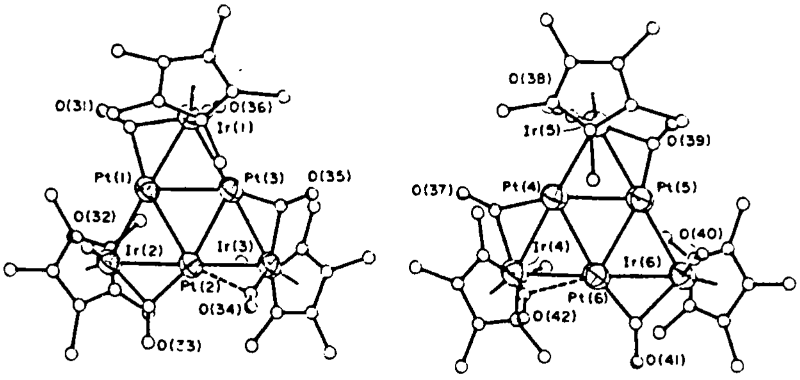


Figure 9. The molecular structures of the two crystallographically independent molecules of $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$ showing the atom numbering scheme.

3. Mixed-metal Clusters of Osmium and Platinum with Carbido Ligands.

There is currently considerable interest in metal cluster compounds containing carbido ligands because the chemistry of such species may relate to the reactivity of carbon on metal surfaces, as in, for example, Fischer-Tropsch chemistry.* We have discovered three new carbido osmium — platinum clusters as a result of studies on the reactions between the compounds $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ and $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$, and between the latter species and $[Os_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$. The structures of the three products $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$, $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\{P(cyclo\text{-}C_6H_{11})_3\}_2]$, and $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)(CO)_9\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ have been established by X-ray crystallography and are shown in Figures 10 - 12.[9]

It is convenient to view the metal framework in $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ as derived from a 'butterfly' arrangement with the Os(1) — Pt bond broken. Thus Os(1) and Os(2) may be viewed as hinge

---

[*] See J.S. Bradley, Adv.Organomet.Chem., 1983, 22, 1, for a review.

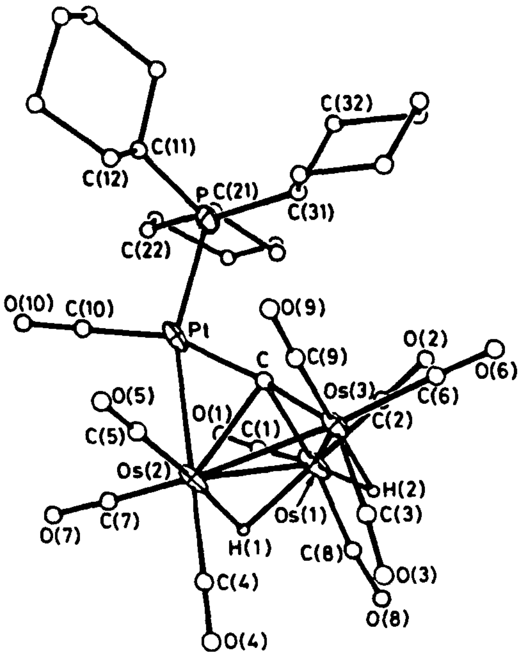


Figure 10.

The molecular structure of $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ showing the crystallographic numbering.

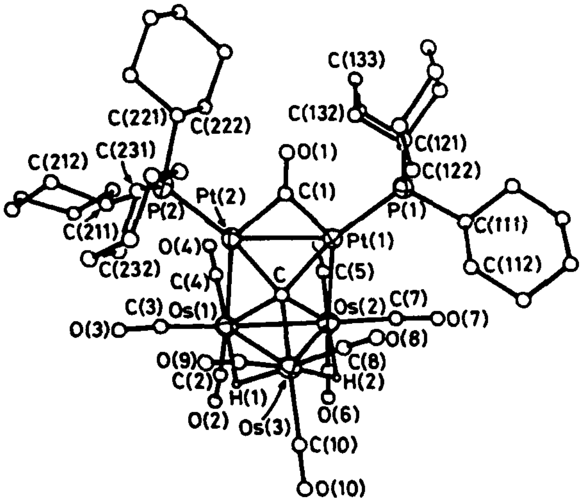


Figure 11.

The molecular structure of $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\text{-}\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ showing the crystallographic numbering.

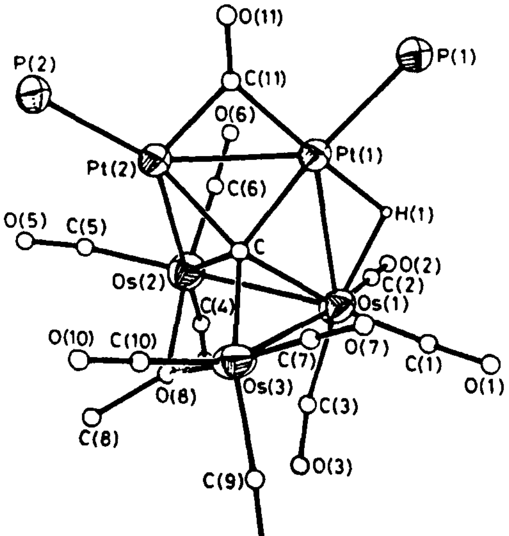


Figure 12.

The molecular structure of $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)\text{-}(CO)_9\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ showing the crystallographic numbering but with the cyclohexyl groups omitted for clarity.

atoms, and Os(3) and Pt as 'wingtip' atoms. The co-ordination mode of the carbido-ligand is irregular and at first sight the rather 'open' metal framework suggests that the carbido-carbon may be sterically accessible and hence reactive. However, as shown in Figure 13, this is not the case.

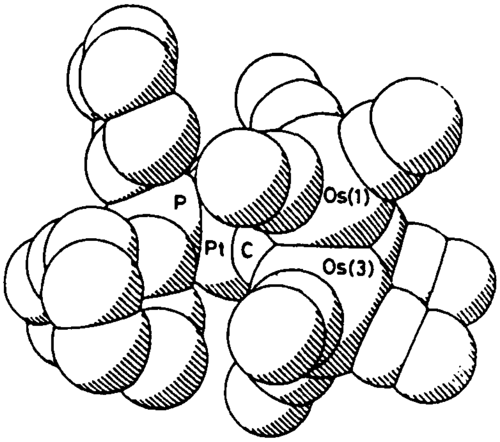


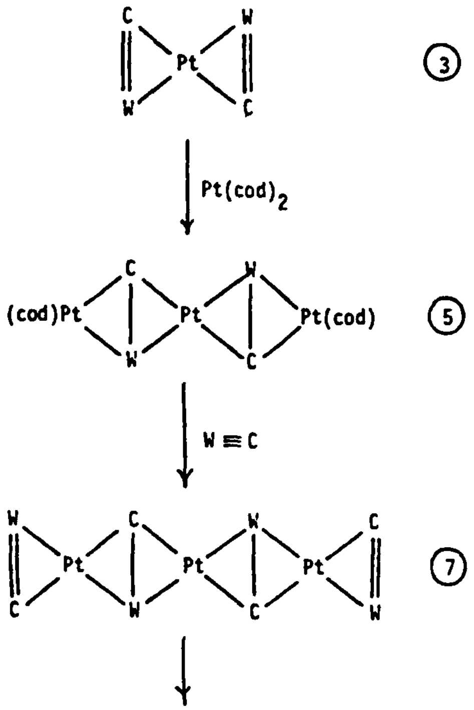
Figure 13. Space-filling diagram of $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ emphasising the protection of the carbido-ligand by the bulky groups surrounding it.

In the compound $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ the metal framework can be viewed as derived from a square pyramid with two Pt — Os bonds having been broken since Pt(1) — Os(3) [3.628(1) Å] and Pt(2) — Os(3) [3.693(1) Å] are too long to be considered bonding (Figure 11). The carbido ligand is essentially of equal distance from all five metal atoms. The compound $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)(CO)_9\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ contains a pentanuclear Os_3Pt_2 core, involving a rather 'buckled' square arrangement of two Pt and two Os atoms with a third, Os(3), bonded to only Os(1) in the square (Figure 12). A methoxy ligand bridges the Os(2) — Os(3) vector. The carbido ligand is essentially equidistant from all five metal atoms and co-ordination about the carbido atom approximates to distorted trigonal bipyramidal.

The mechanism of formation of these compounds has been discussed. They represent hitherto rare examples of heteronuclear metal cluster compounds with carbido ligands.*

4. Compounds Containing Chains or Rings of Platinum or Nickel and Tungsten Atoms.

Some years ago we showed that the alkylidyne — tungsten compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = $C_6H_4Me\text{-}4$) and $[Pt(C_2H_4)_3]$ afforded the trinuclear metal complex $[PtW_2(\mu\text{-}CR)_2(CO)_4(\eta\text{-}C_5H_5)_2]$.** This species with its two spiro trimetallacyclopropene rings is unsaturated, and we have used this feature to prepare polynuclear platinum — tungsten compounds <u>via</u> the stepwise transformation shown in the Scheme below.



Scheme. $W \equiv C$ is $[RC \equiv W(CO)_2\text{-}(\eta\text{-}C_5H_5)]$
R can be $C_6H_4Me\text{-}4$, Ph or Me and $\eta\text{-}C_5H_5$ may be replaced by $\eta\text{-}C_5Me_5$. Numbers in circles refer to number of metal atoms in the chain.

---

* The only other species of this type reported so far have been described by J.W. Kolis, E.M. Holt, J.A. Hriljac, and D.F. Shriver, Organometallics, 1984, 3, 496; J.A. Hriljac, P.N. Swepston, and D.F. Shriver, ibid, 1985, 4, 158.

** T.V. Ashworth, M.J. Chetcuti, J.A.K. Howard, F.G.A. Stone, S.J. Wisbey, and P. Woodward, J.Chem.Soc., Dalton Trans., 1981, 763.

This approach to the synthesis of metal cluster compounds with chains of metal atoms has been very successful, although in this new field progress is likely to be relatively slow since preparative work has to proceed simultaneously with X-ray crystallographic studies. The only satisfactory method of structural analysis is via X-ray diffraction methods. In Figure 14 we show the structure of a new species containing a Pt_3W_4 chain.[11] The twisted backbone is evident and indicates the reason for the existence of isomers and our subsequent discovery of highly novel 'star clusters' with a ring of eight metal atoms as illustrated by

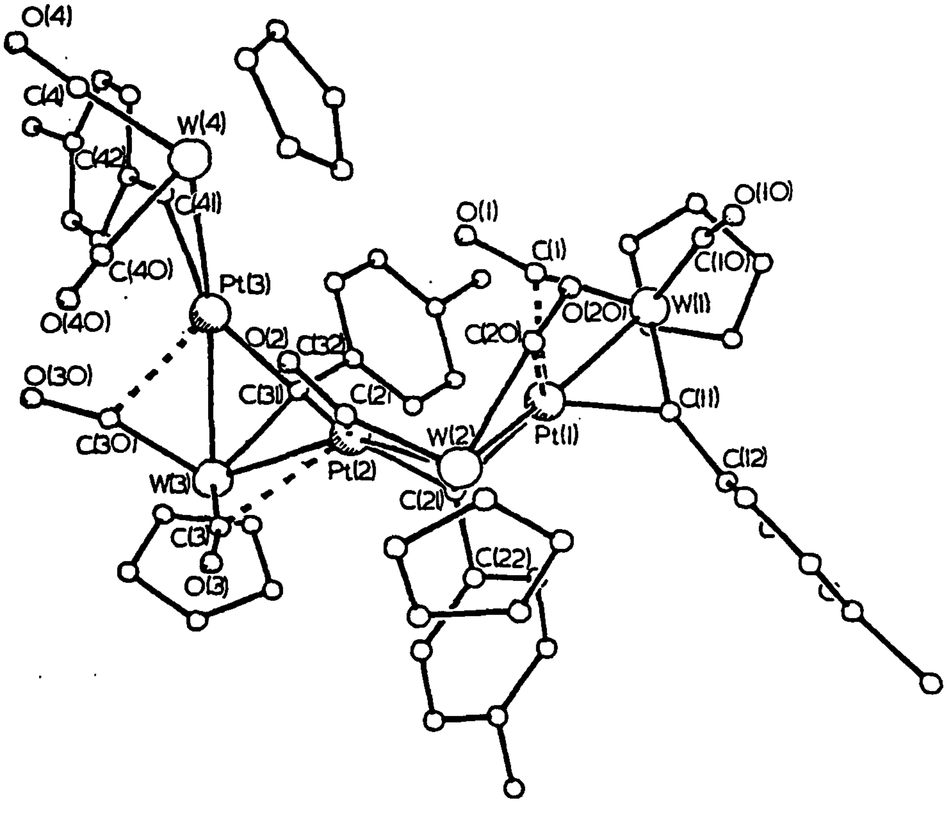


Figure 14. The molecular structure of $[Pt_3W_4(\mu\text{-}CR)_2(\mu_3\text{-}CR)_2(CO)_8(\eta\text{-}C_5H_5)_4]$ (R = C_6H_4Me-4).

the $Ni_2Pt_2W_4$ compound shown in Figure 15.[10]

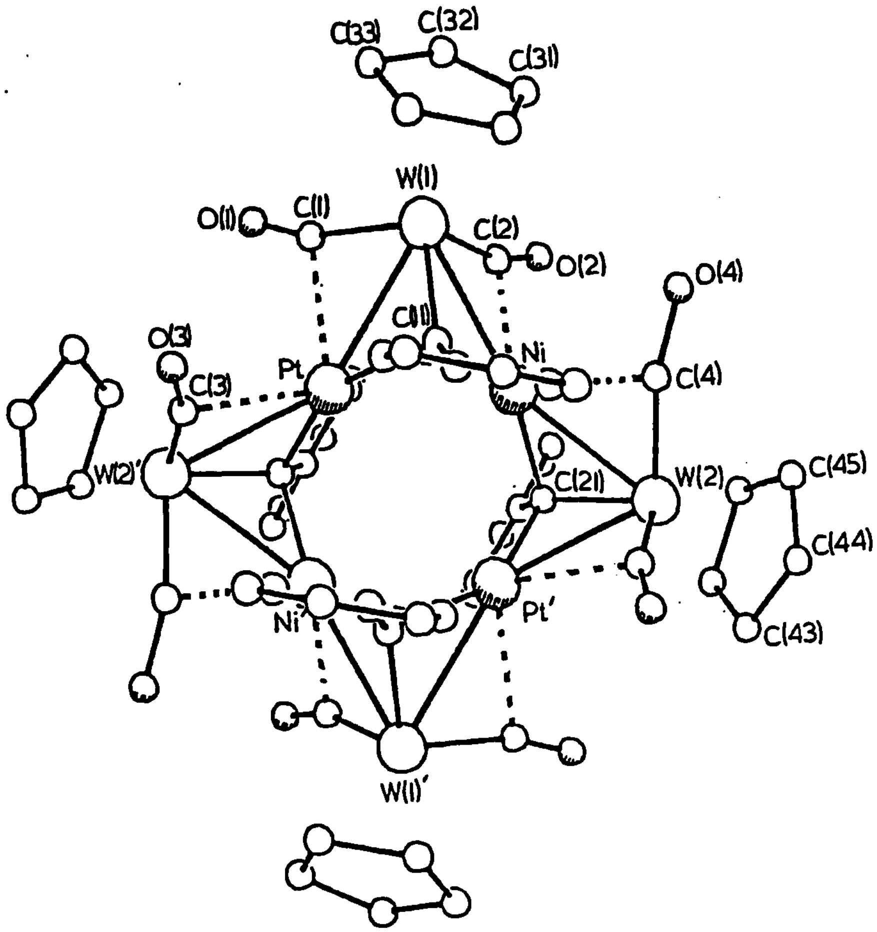


Figure 15. The molecular structure of $[Ni_2Pt_2W_4(\mu_3\text{-}CPh)_4(CO)_8(\eta\text{-}C_5H_5)_4]$.

The compound $[Ni_2Pt_2W_4(\mu_3\text{-}CPh)_4(CO)_8(\eta\text{-}C_5H_5)_4]$ shown in Figure 15 has a symmetrical arrangement of bridging carbyne groups (Figure 16, III, see page 15). Interestingly, unsymmetrical isomers $[Ni_2Pt_2W_4(\mu\text{-}CR)(\mu_3\text{-}CR)_3(CO)_8(\eta\text{-}C_5H_5)_4]$ have been prepared, and identified by X-ray diffraction (see Figure 16, I and II). It will be noted that the isomers I and II differ according to whether the μ-CR group edge bridges a Pt — W or a Ni — W bond.

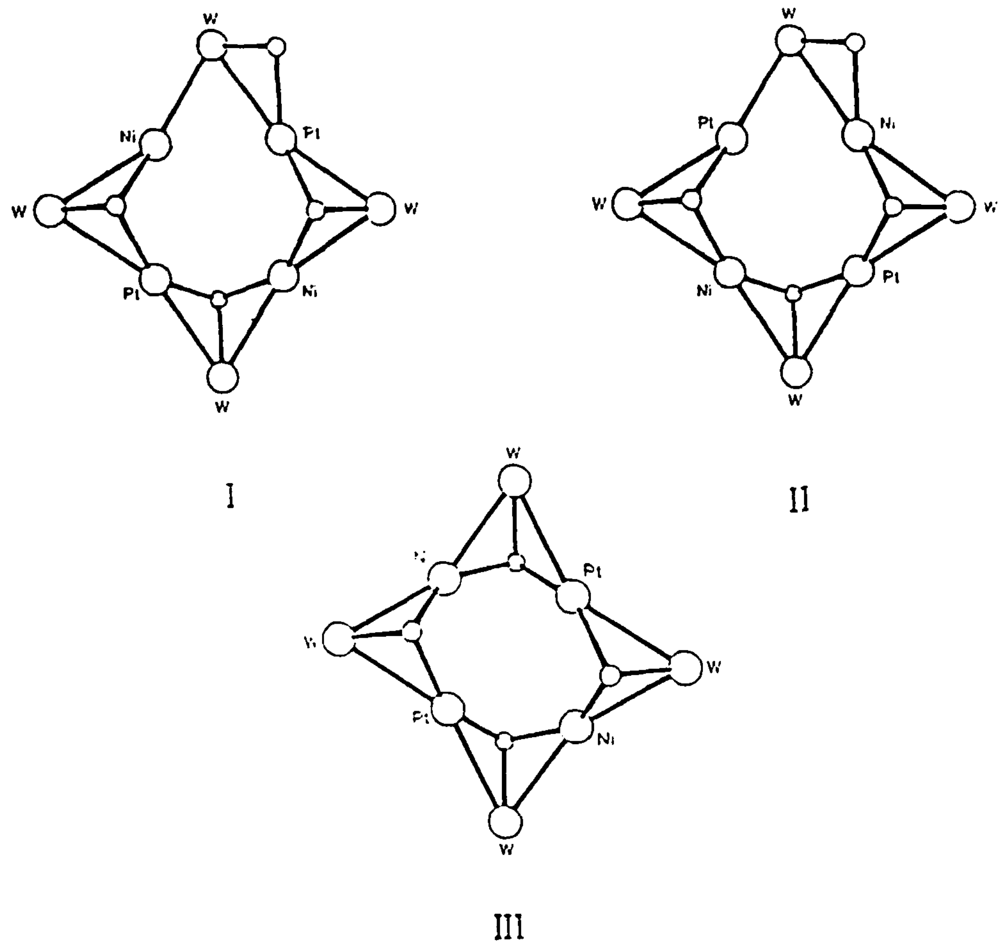
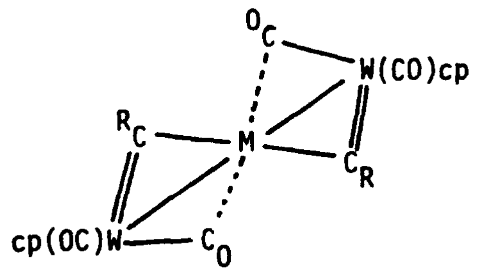
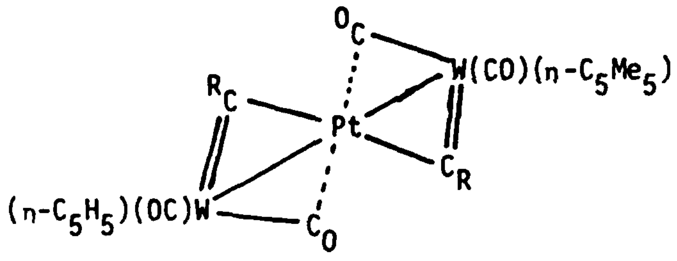


Figure 16. The core structures of the cluster compounds $[Ni_2Pt_2W_4(\mu_2\text{-}CR)(\mu_3\text{-}CR)_3(CO)_8(\eta\text{-}C_5H_5)_4]$ (two isomers, I and II) and $[Ni_2Pt_2W_4(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)_4]$ (III), showing the metal atoms and the ligated carbon atoms of the carbyne groups.

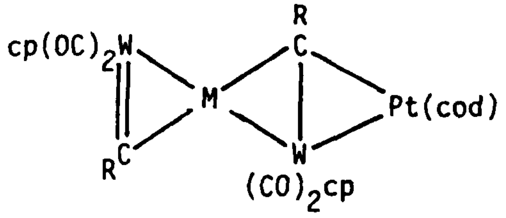
In order to extend this novel area of chemistry, we have recently prepared a substantial number of compounds containing chains of three, four and five metal atoms. These complexes are shown on pages 16 and 17. The importance of these compounds lies in their subsequent use as precursors to larger clusters. The new compounds are either unsaturated with $C = W$ end groups, or they contain the displaceable cyclo-octa-1,5-diene ligand on platinum. The addition of other metal ligand fragments should thus be possible, leading to a rich new area of chemistry.



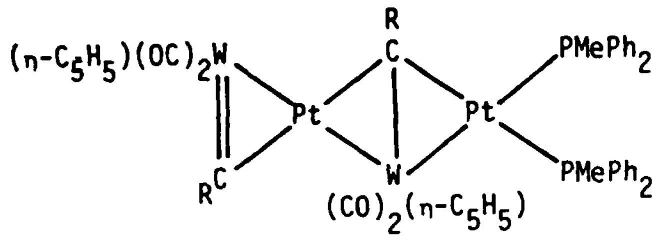
	M	R	cp
(1a)	Pt	C_6H_4Me-4	η-C_5H_5
(1b)	Ni	C_6H_4Me-4	η-C_5H_5
(1c)	Pt	Me	η-C_5H_5
(1d)	Pt	Ph	η-C_5H_5
(1e)	Pt	Me	η-C_5Me_5
(1f)	Pt	Ph	η-C_5Me_5
(1g)	Pt	C_6H_4Me-4	η-C_5Me_5
(1i)	Ni	Me	η-C_5H_5
(1j)	Ni	Ph	η-C_5H_5
(1k)	Ni	Me	η-C_5Me_5
(1l)	Ni	Ph	η-C_5Me_5
(1m)	Ni	C_6H_4Me-4	η-C_5Me_5



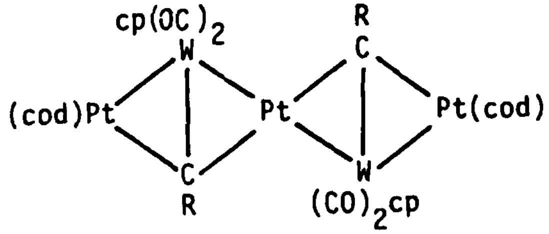
(1h) R = C_6H_4Me-4



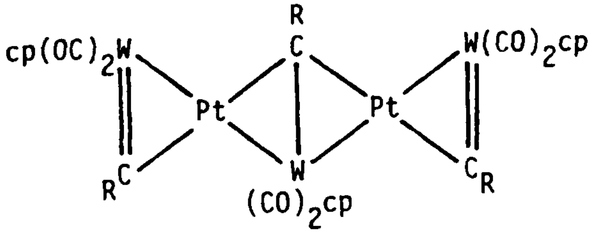
	M	R	cp
(2a)	Pt	C_6H_4Me-4	η-C_5H_5
(2b)	Pt	Me	η-C_5Me_5
(2c)	Pt	C_6H_4Me-4	η-C_5Me_5
(2e)	Ni	C_6H_4Me-4	η-C_5H_5
(2f)	Ni	C_6H_4Me-4	η-C_5Me_5



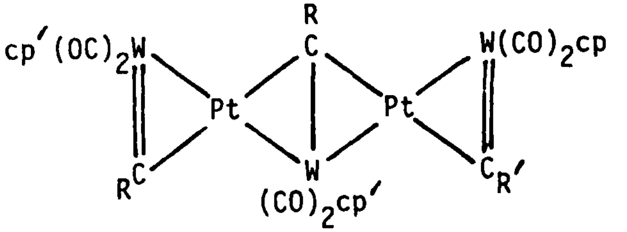
(2d) R = C_6H_4Me-4



	R	cp
(3a)	C_6H_4Me-4	η-C_5H_5
(3b)	Me	η-C_5Me_5



	R	cp
(4a)	C_6H_4Me-4	η-C_5H_5
(4b)	Me	η-C_5Me_5
(4c)	C_6H_4Me-4	η-C_5Me_5



	R	R′	cp	cp′
(5a)	Me	C_6H_4Me-4	η-C_5H_5	η-C_5Me_5
(5b)	C_6H_4Me-4	C_6H_4Me-4	η-C_5H_5	η-C_5Me_5

ACCOMPLISHMENTS

During the four year period of the Grant we have obtained the following results which are especially noteworthy.

(i) Development of a rational synthesis of gold — ruthenium clusters *via* reactions of [AuMe(PPh_3)] with polynuclear ruthenium hydrido-(carbonyl) complexes. The discovery of the first trimetallic complexes containing the core structures $MM'Ru_4$ (M = Ag, M′ = Cu; M = Au, M′ = Cu; M = Au, M′ = Ag) and demonstration *via* $^{31}P-\{^1H\}$ n.m.r. spectroscopy of polytopal rearrangements of these clusters in solution.

(ii) Discovery of the first carbido clusters containing two different platinum group metals, *viz* platinum and osmium. The reaction pathways to these species involve novel C — H and C — OMe cleavage reactions by a low-valent platinum — phosphine complex.

(iii) The discovery of a rational route to cluster compounds containing chains and rings of metal atoms in which the metal — metal bonds are bridged by alkylidyne groups. This work has led to the characterisation of cluster compounds with core structures having eight metal atoms (Pt_4W_4 or $Ni_2Pt_2W_4$) in a ring in the shape of a 'star', and as such represent a hitherto unknown type of polynuclear metal species.

CUMULATIVE LIST OF PUBLICATIONS UNDER GRANT 82 —0070.

1. J.C. Jeffery, C. Sambale, M.F. Schmidt, and F.G.A. Stone, Organometallics, 1982, 1, 1597-1604:
   Synthesis and Characterisation of Tungsten —Cobalt, —Rhodium, and —Platinum Compounds and the X-Ray Crystal Structures of $[RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PMe_3)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)]$ and $[PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)\text{-}C(O)\}(CO)(PMe_3)(\eta^4\text{-}C_8H_{12})(\eta\text{-}C_5H_5)]$.
2. L.J. Farrugia, A.G. Orpen, and F.G.A. Stone, Polyhedron, 1983, 2, 171-173:
   A Synthetic Route to Heteronuclear Clusters Containing Iridium and Rhodium; X-Ray Crystal Structures of $[IrOs_3(\mu\text{-}H)_2(\mu\text{-}Cl)(CO)_{12}]$ and $[Ir_2Rh_2(\mu\text{-}CO)(\mu_3\text{-}CO)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$.
3. L.J. Farrugia, M.J. Freeman, M. Green, A.G. Orpen, I.D. Salter, and F.G.A. Stone, J.Organomet.Chem., 1983, 249, 273-288:
   Metal Framework Arrangements in Pentanuclear Gold —Ruthenium Clusters. Crystal Structures of $[Au_2Ru_3(\mu_3\text{-}S)(CO)_8(PPh_3)_3]$ and $[Au_2Ru_3(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_9(PPh_3)_2]$.
4. L.W. Bateman, M. Green, K.A. Mead, R.M. Mills, I.D. Salter, F.G.A. Stone, and P. Woodward, J.Chem.Soc.,Dalton Trans., 1983, 2599-2608:
   Replacement of Hydrido-ligands in Triruthenium Complexes by Triphenylphosphinegold Groups; Crystal Structures of $[AuRu_3(\mu\text{-}COMe)(CO)_{10}\text{-}(PPh_3)]$, $[AuRu_3(\mu\text{-}H)_2(\mu_3\text{-}COMe)(CO)_9(PPh_3)]$, and $[Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9\text{-}(PPh_3)_3]$.

5. M.J. Freeman, M. Green, A.G. Orpen, I.D. Salter, and F.G.A. Stone, J.Chem.Soc.,Chem.Commun., 1983, 1332-1334:

Cluster Complex Metathesis: Synthesis, Structures, and Dynamic Behaviour of Bi- and Tri-metallic Hexanuclear Cluster Complexes $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (M = M' = Cu, Ag, or Au; M = Cu, M' = Ag or Au; M = Ag, M' = Au).

6. I.D. Salter and F.G.A. Stone, J.Organomet.Chem., 1984, 260, C71-C74: Structural Similarities and Differences among Mixed-Metal Clusters Containing a Single $M(PPh_3)$ (M = Cu, Ag, or Au) Fragment.

7. J.A.K. Howard, I.D. Salter, and F.G.A. Stone, Polyhedron, 1984, 3, 567.

Synthesis and Molecular Structure of $[Au_3Ru_4(\mu_3\text{-}H)(CO)_{12}(PPh_3)_3]$.

8. M.J. Freeman, A.D. Miles, A.G. Orpen, and F.G.A. Stone, Polyhedron, 1984, 3, 1093.

Synthesis and X-Ray Crystal Structure of the Hexanuclear Metal Cluster Complex $[Ir_3Pt_3(\mu\text{-}CO)_3(CO)_3(\eta\text{-}C_5Me_5)_3]$.

9. L.J. Farrugia, A.D. Miles, and F.G.A. Stone, J.Chem.Soc., Dalton Trans., 1985, 2437.

Synthesis of Tetra- and Penta-nuclear Platinum—Osmium Carbido- Cluster Complexes from Non-carbido Precursors: X-Ray Structural Studies on $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$, $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)\text{-}(CO)_9\{P(cyclo\text{-}C_6H_{11})_3\}_2]$, and $[Os_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}OMe)(\mu\text{-}CO)(CO)_9\text{-}\{P(cyclo\text{-}C_6H_{11})_3\}_2]$.

10. G.P. Elliott, J.A.K. Howard, T. Mise, C.M. Nunn, and F.G.A. Stone, *Angew.Chem., Int.Ed.Engl.*, 1986, *25* , 190:
'Star Clusters' with Heteronuclear Metal-Metal Bonds; $[Ni_2Pt_2W_4(\mu_3\text{-}CPh)_4(CO)_8(\eta\text{-}C_5H_5)_4]$ and $[Ni_2Pt_2W_4(\mu_2\text{-}CR)(\mu_3\text{-}CR)_3(CO)_8(\eta\text{-}C_5H_5)_4]$ (R = Ph or $C_6H_4Me\text{-}4$).

11. G.P. Elliott, J.A.K. Howard, C.M. Nunn, and F.G.A. Stone, *J.Chem.Soc., Chem.Commun.*, 1986, 431 :
Cyclisation of Metal Chain Complexes: *X*-Ray Crystal Structures of $[Pt_3W_4(\mu\text{-}CR)_2(\mu_3\text{-}CR)_2(CO)_8(\eta\text{-}C_5H_5)_4]$ and $[Pt_4W_4(\mu\text{-}CR)(\mu_3\text{-}CR)_3(CO)_8(\eta\text{-}C_5H_5)_4]$ (R = $C_6H_4Me\text{-}4$).

12. F.G.A. Stone, *Pure Appl.Chem.*, 1986, *58* , 529:
Synthetic and Structural Studies on Metal Cluster Compounds.

13. G.P. Elliott, J.A.K. Howard, T. Mise, I. Moore, C.M. Nunn, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, in press:
Synthesis of Tri-, Tetra- and Penta-heteronuclear Metal Cluster Compounds involving Tungsten with Platinum or Nickel: Crystal Structures of the Compounds $[Pt_3W_2(\mu_3\text{-}CR)_2(CO)_4(cod)_2(\eta\text{-}C_5H_5)_2]$ and $[Pt_2W_3(\mu\text{-}CR)_2(\mu_3\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)_3]$ (R = $C_6H_4Me\text{-}4$, cod = cyclo-octa-1,5-diene).

END

DTIC

9 — 86