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ACRONYM: HETERONUCLEAR METAL CLUSTER COMPOUNDS

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HETERONUCLEAR METAL CLUSTER COMPOUNDS
SYNTHESIS AND REACTIVITY

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) This Final Report describes the synthesis and characterisation of compounds containing metal-metal bonds between dissimilar transition elements. The new compounds reported include species with chains or rings of metal atoms, involving tungsten or molybdenum bonded to the elements nickel, platinum, rhodium, or iridium. The Report also describes numerous mixed-metal compounds in which the metal-metal bonds are bridged by the carbaborane group $C_2B_9H_9R_2$ (R = H or Me). A variety of unprecedented molecular structures have been identified by X-ray crystallographic studies.					
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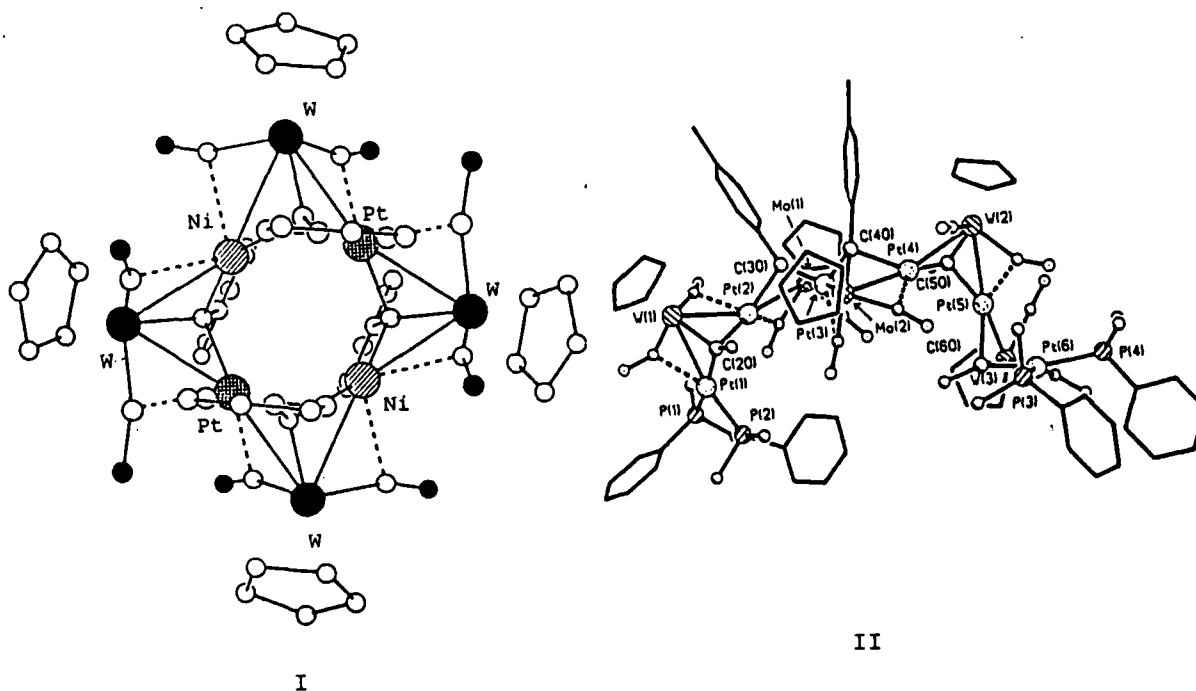
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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

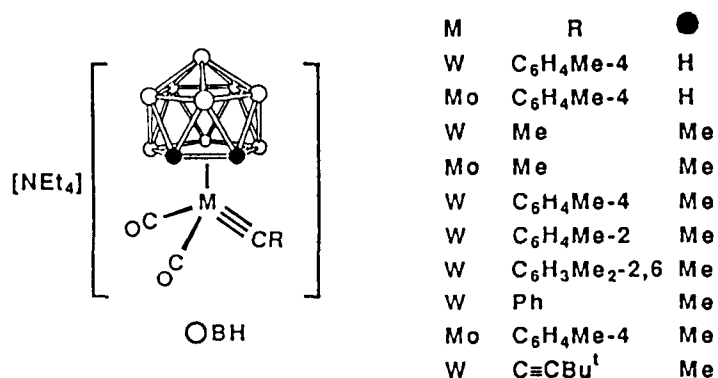
The objectives of the research program were to develop rational syntheses of polynuclear metal compounds containing bonds between different transition elements, to determine the structures and properties of the new metal complexes obtained, and to investigate their reactivity. It was anticipated that the metal-metal bonds would be bridged by alkylidyne groups, and that the compounds would be unsaturated. The latter property would be expected to lead to enhanced reactivity. Compounds containing heteronuclear metal-metal bonds, so-called 'mixed-metal' complexes, are of considerable interest both in the context of new materials, and through studies on their reactivity increasing our understanding of the activation of small organic molecules at metal centres.

The results from the research have been especially significant in two areas. Firstly, we have successfully prepared metallacycles containing eight metal atoms (I), and also polynuclear metal complexes containing up to eleven metal atoms in the chain (II). Secondly, we have



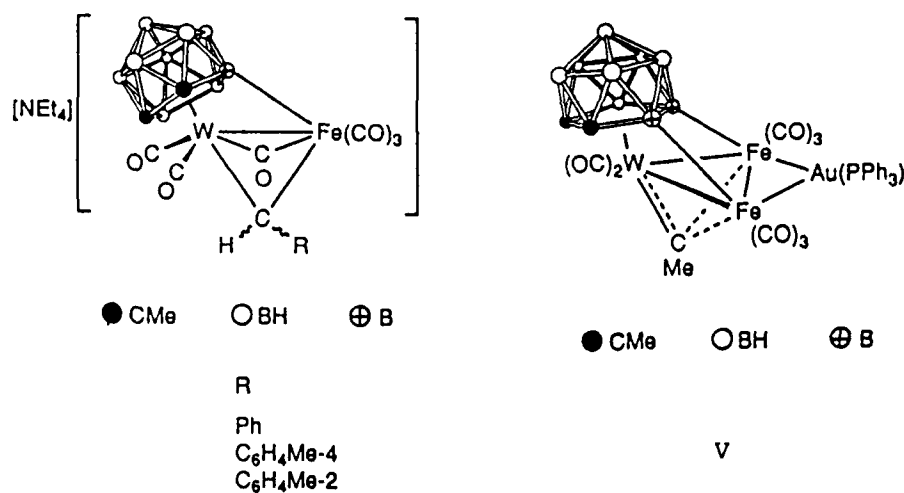
employed the alkylidyne(carbaborane)-tungsten and -molybdenum reagents (III) as synthons for preparing polynuclear metal compounds. The novelty of this work lies in the frequently displayed 'non-spectator' role of the carbaborane cage. Consequently, many of the products

obtained have unprecedented molecular structures such as IV and V shown below. These species are representative of a new area of metal cluster chemistry wherein a carbaborane cage



In some reactions use of [N(PPh₃)₂]⁺, [PPh₄]⁺, or [P(CH₂Ph)Ph₃]⁺ salts is advantageous.

III



is associated with a di- or tri-nuclear metal fragment involving bonding between different transition elements and between the metal atoms and the cage.

INTRODUCTION

Work began on the project on 1 March 1986, and research progress has been summarised in three Interim Scientific Reports submitted in April 1987, 1988, and 1989, respectively. This Final Scientific Report covers the period 1 March 86 through 31 July 90.

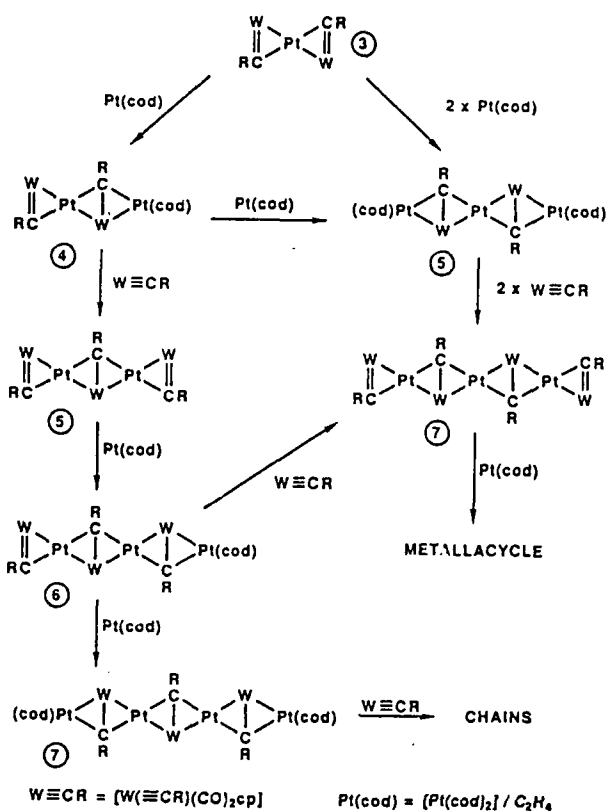
Twenty six scientific publications have resulted from the Grant, and these articles are listed at the end of this Report. All carry acknowledgements to AFOSR support. Reference numbers in the cursive text which follows refer to these papers.

Over the period of the Grant (53 months) several persons (undergraduates, postgraduates, and postdoctoral) carried out the research under the supervision of the Principal Investigator. However, most of these workers were supported by matching funds, as stipulated in the Grant proposal. A full list of persons associated with the project is given below:

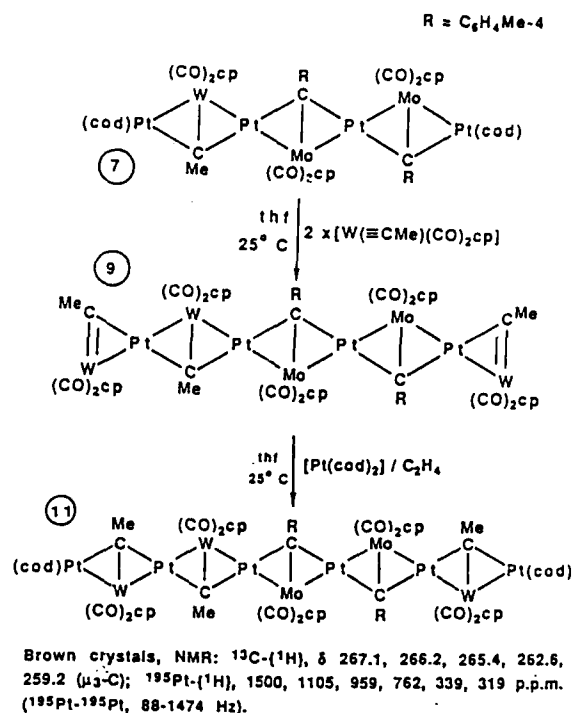
M.J. Attfield*	M.C. Gimeno†	T. Mise†
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F-E. Baumann†	I.J. Hart ^Δ	C.M. Nunn ^Δ
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* Undergraduate research worker (duration 6 months). † Postdoctoral worker. ^Δ Graduate student.

Significant assistance was given by Drs. J.A.K. Howard and J.C. Jeffery of the Department's X-ray diffraction laboratory.



Scheme 1

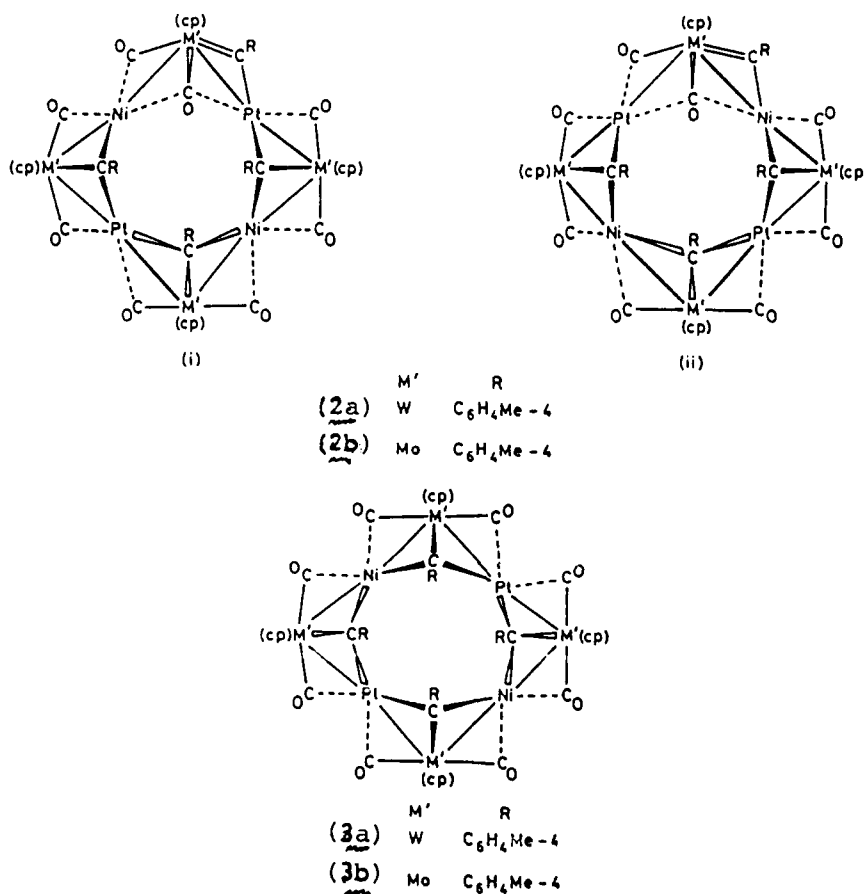


Scheme 2

Chain molecules containing seven metal atoms and having terminal $C=M$ groups have been shown to react with Ni or Pt atoms, derived from labile complexes of these metals, to give eight-membered ring metallacycles, and further chain growth does not occur. However, we have successfully developed a method for preparing metal chain complexes containing as many as eleven metal atoms. Cyclisation processes have been avoided by using as precursors seven metal atom chain complexes with terminal $Pt(cod)$ (cod = cyclo-octa-1,5-diene) groups (Schemes 1 and 2).^{15,20} An X-ray diffraction study established the structure of the eleven metal atom cluster $[Mo_2W_3Pt_6(\mu_3-CMe)_3(\mu_3-CC_6H_4Me-2)_2(CO)_{10}(PMe_2Ph)_4(\eta-C_5H_5)_5]$ (see II on page 1). This study has placed the new synthetic procedures on a firm structural basis.

Several metallacycles have also been prepared.^{4,13} For example, the reaction between (1a) and an excess of $[Ni(cod)_2]$ affords the octanuclear metal complex $[Ni_2Pt_2W_4(\mu-CC_6H_4Me-4)(\mu_3-CC_6H_4Me-4)_3(\mu-CO)(CO)_7(\eta-C_5H_5)_4]$ (2a), formed as a mixture of two isomers. In one isomer (i) a *p*-tolylmethyldiene ligand edge-bridges a $W-Pt$ bond, and in the

other (ii) a W-Ni bond. At reflux temperatures, in tetrahydrofuran, the two isomers are converted to the symmetrical species $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_4(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$ (3a) in which all four alkylidyne ligands occupy triply bridging sites. The molybdenum analogue (3b) has been similarly prepared.



Complicated isomeric mixtures of octanuclear metal clusters, with one edge-bridging and three triply-bridging alkylidyne ligands (see Figure next page) have been obtained from reactions between the complexes $[\text{PtM}'\text{M}''(\mu\text{-CR})(\mu\text{-CR}')(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ (1e) – (1g) and $[\text{Ni}(\text{cod})_2]$. Refluxing these products in tetrahydrofuran afford compounds $[\text{Ni}_2\text{Pt}_2\text{M}_2'\text{W}_2(\mu_3\text{-CR})_2(\mu_3\text{-CR}')_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_4]$ ($\text{M}' = \text{W}$, $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$, $\text{R}' = \text{Me}$ (4a); $\text{M}' = \text{Mo}$, $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$, $\text{R}' = \text{C}_6\text{H}_4\text{Me-4}$ (4b) or $\text{R} = \text{Ph}$, $\text{R}' = \text{C}_6\text{H}_4\text{Me-4}$ (4c)) in which all four alkylidyne groups are triply bridging. Two isomers exist for each species. For (4a) the isomerism depends on the two possible orientations of the $\mu_3\text{-CMe}$ and $\mu_3\text{-CC}_6\text{H}_4\text{Me-4}$ groups with respect to each

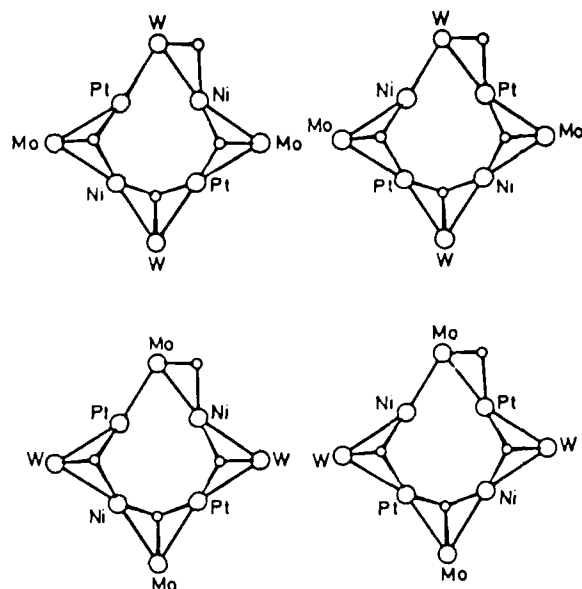
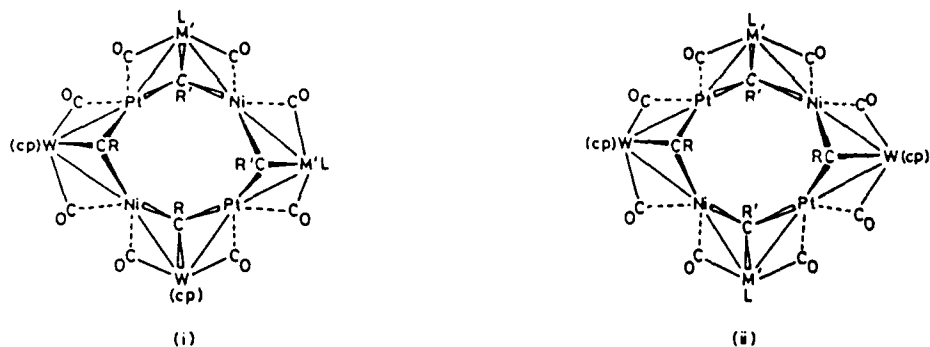


Figure. The metal atom core structures and arrangements of the bridging alkylidyne-carbon atom in the four 'asymmetric' isomers of $[\text{Ni}_2\text{Pt}_2\text{Mo}_2\text{W}_2(\mu\text{-CR})(\mu_3\text{-CR})_3(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$ having the metal atom sequence MoPtWNiMoPtWNi . The alternative metal atom sequence MoNiWPtWNiMoPt also gives rise to four asymmetric isomers depending on whether the $\mu\text{-CR}$ group bridges a W-Ni , W-Pt , Mo-Ni , or Mo-Pt bond

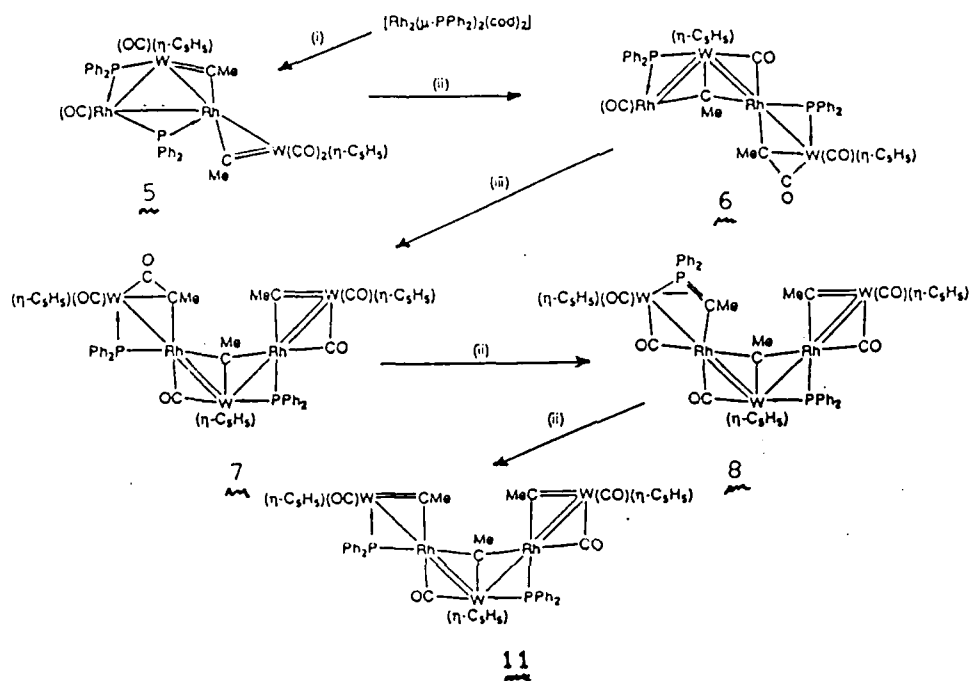


	M'	R	R'	L
(4a)	W	$\text{C}_6\text{H}_4\text{Me}-4$	Me	$\eta\text{-C}_5\text{H}_5$
(4b)	Mo	$\text{C}_6\text{H}_4\text{Me}-4$	$\text{C}_6\text{H}_4\text{Me}-4$	$\eta\text{-C}_5\text{H}_5$
(4c)	Mo	Ph	$\text{C}_6\text{H}_4\text{Me}-4$	$\eta\text{-C}_5\text{H}_5$

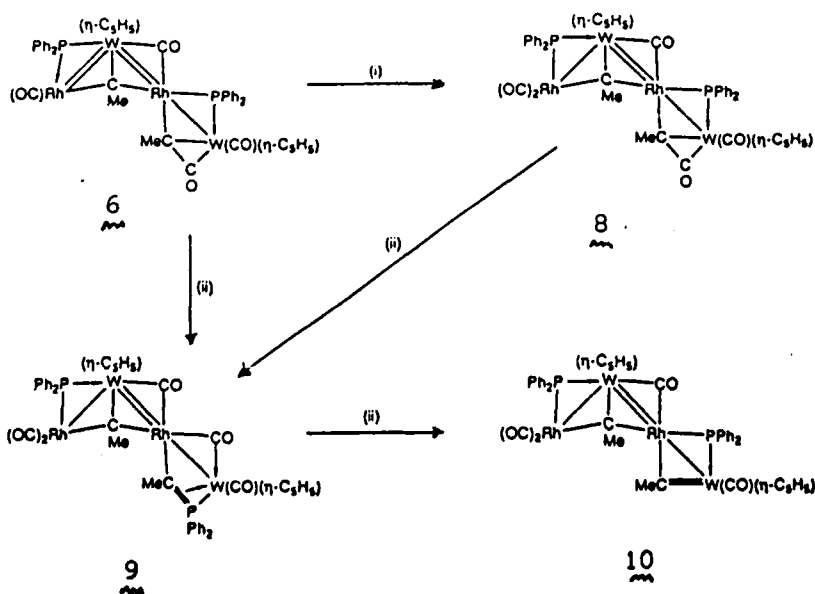
other, while for (4b) and (4c) different metal atom sequences (viz. $\text{Mo.Ni.Mo.Pt.W.Ni.W.Pt}$ and $\text{Mo.Ni.W.Pt.Mo.Ni.W.Pt}$) lead to the existence of two isomers. The term 'star clusters' has been proposed to describe these metallacycles, since they are a new class of metal cluster compound.

New syntheses have been developed so as to obtain metal chain structures based on rhodium-tungsten bonds.^{18,19} The μ -phosphido-bridged complex $[\text{Rh}_2(\mu\text{-PPh}_2)_2(\text{cod})_2]$ has been used as a precursor. Treatment with the alkylidyne-tungsten complex $[\text{W}(\equiv\text{CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ affords initially the tetranuclear metal compound $[\text{W}_2\text{Rh}_2(\mu\text{-CMe})_2(\mu\text{-PPh}_2)_2]$

$(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2$ (5) shown in Scheme 3. The latter isomerises in thf to give (6) which reacts with additional $[\text{W}(\equiv\text{CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ to give (7), which in turn affords the complex (8) and (11). Compound (6) reacts with CO to give (8) (Scheme 4) which rearranges in tetrahydrofuran to afford (9). Loss of a molecule of CO yields (10) as the final product.



Scheme 3. (i) $[\text{W}(\equiv\text{CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (two equivalents) in thf, (ii) isomerisation in thf, (iii) $[\text{W}(\equiv\text{CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ in thf.



Scheme 4. (i) + CO, (ii) thf reflux

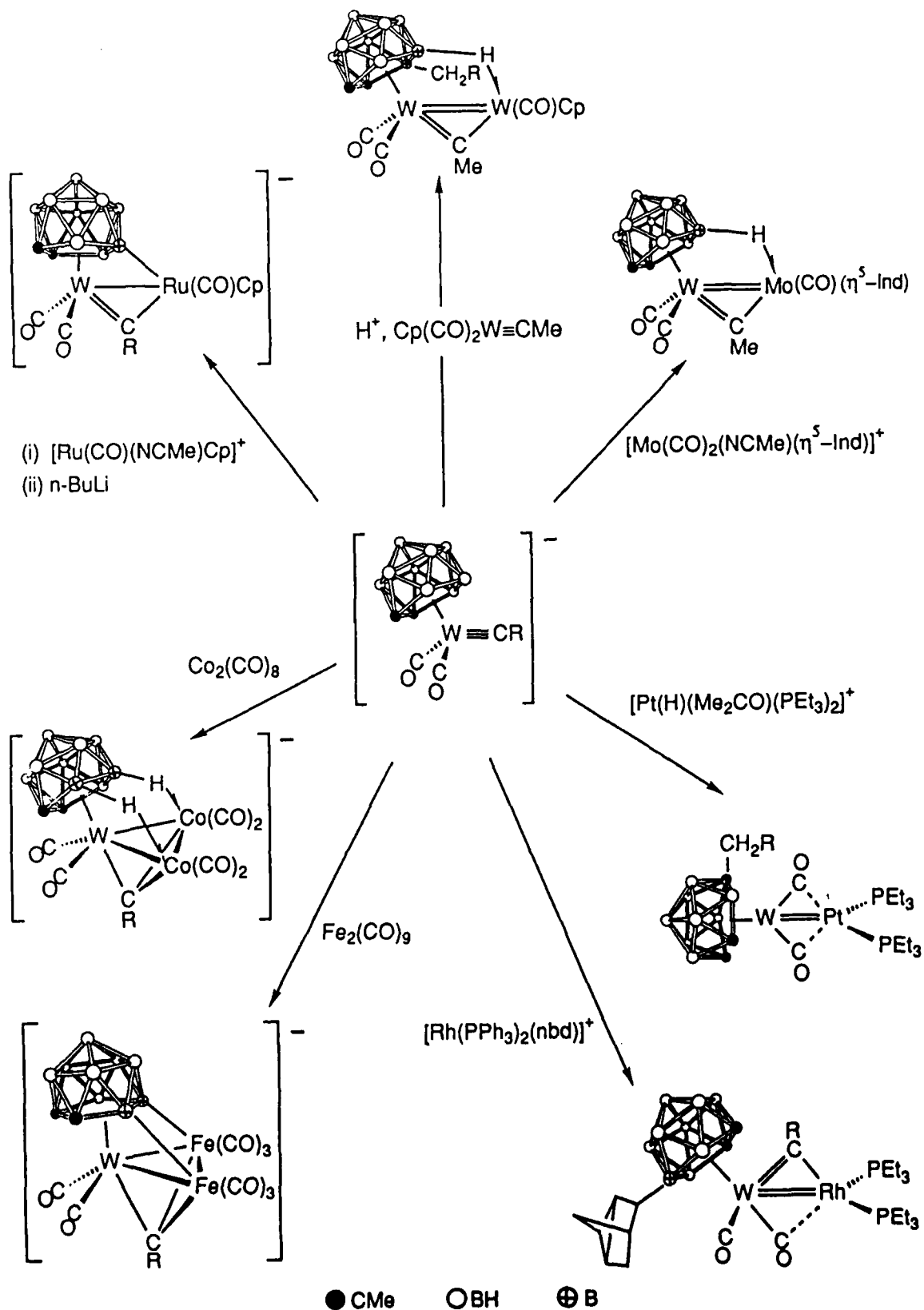
An important aspect of the studies on these rhodium-tungsten clusters is that the research has revealed facile C-C and C-P bond forming processes among the chain compounds. Moreover, species such as (8) and (9) represent the first examples of polynuclear metal compounds where in a λ^5 -phospha-alkyne ligand bridges a dimetal centre. Metal complexes containing $R_2P=CR'$ groups have only recently been discovered.

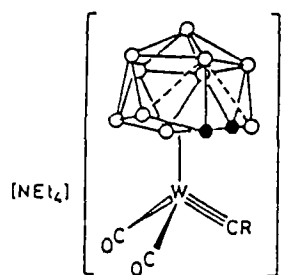
Influence of the Carbaborane Ligands η^5 -C₂B₉H₉Me₂ and η^6 -C₂B₁₀H₁₀Me₂ in the Synthesis of Compounds with Heteronuclear Metal-Metal Bonds.

In our Interim Research Reports we described some novel metal cluster syntheses resulting from reactions between salts of the anions $[W(\equiv CR)(CO)_2(\eta^5-C_2B_9H_9R_2')]^-$ (R = alkyl or aryl; R' = H or Me) (See III page 2) and cationic or neutral metal species. In many of the reactions, the carbaborane ligand, usually η^5 -C₂B₉H₉Me₂, adopts a non-spectator role.^{6-10,12,14,17,26} Our success in this area is indicated by the collage of new compounds illustrated on the next page.

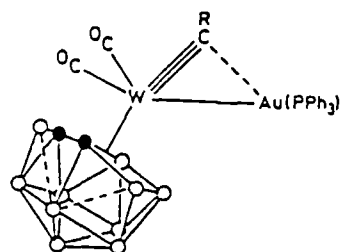
We have extended these studies in several different ways. We have prepared the salts (12) containing the η^6 -C₂B₁₀H₁₀Me₂ ligand, and in a series of reactions using these salts we have characterised several new types of di- and tri-metal compound containing the docosahedral carbaborane ligands, *e.g.* (13) – (16).¹⁶ As with the η^5 -C₂B₉H₉Me₂ group, the η^6 -C₂B₁₀H₁₀Me₂ fragment can adopt a spectator role, as in the gold-tungsten compounds (13), or play a non-spectator role as in the iron-tungsten complexes (14) or (15). Particularly interesting has been the discovery of compounds such as (16) which exist as isomeric mixtures; the isomerism resulting from different bonding modes for the η^6 -C₂B₁₀H₁₀Me₂ moiety.

Examples of complexes with $[\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2]^{2-}$ as a "non-spectator" ligand.
 $\text{R}=\text{C}_6\text{H}_4\text{Me-4}$

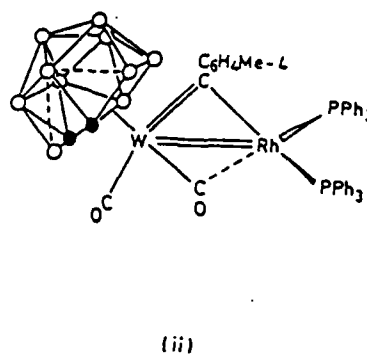
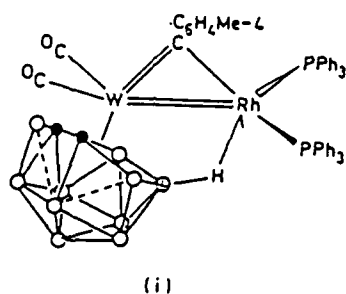
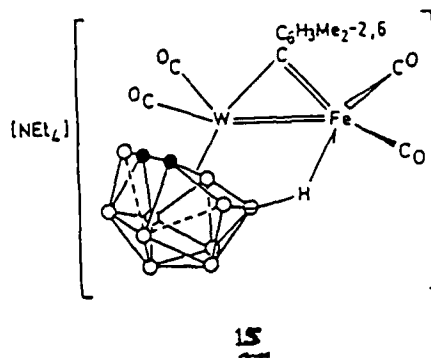
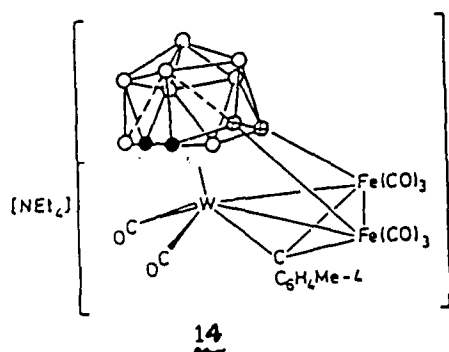




R $\circ$ BH $\bullet$ CMe
12a $\text{C}_6\text{H}_4\text{Me-L}$
12b $\text{C}_6\text{H}_3\text{Me}_2\text{-2,5}$

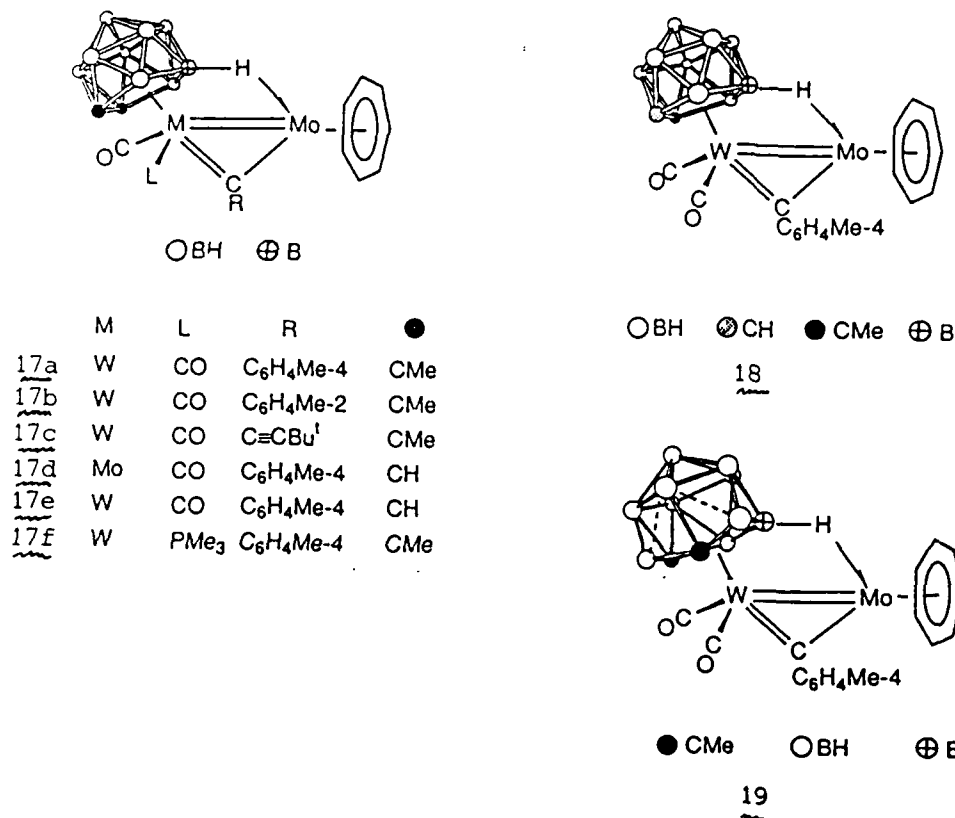


R
13a $\text{C}_6\text{H}_4\text{Me-L}$
13b $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$

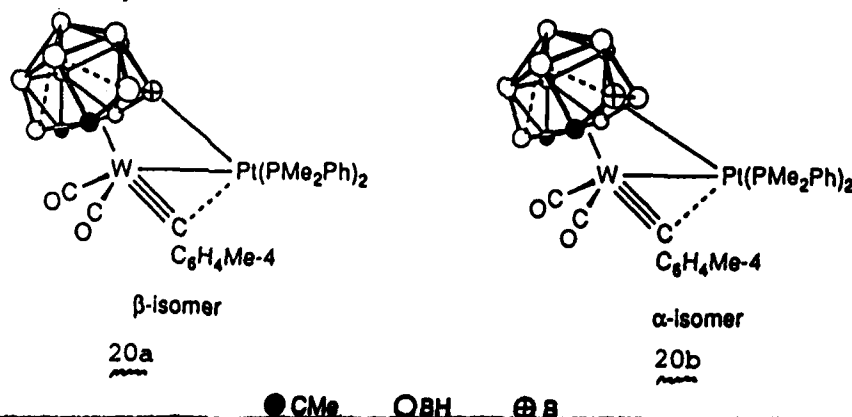


$\circ$ BH $\ominus$ B $\bullet$ CMe
16

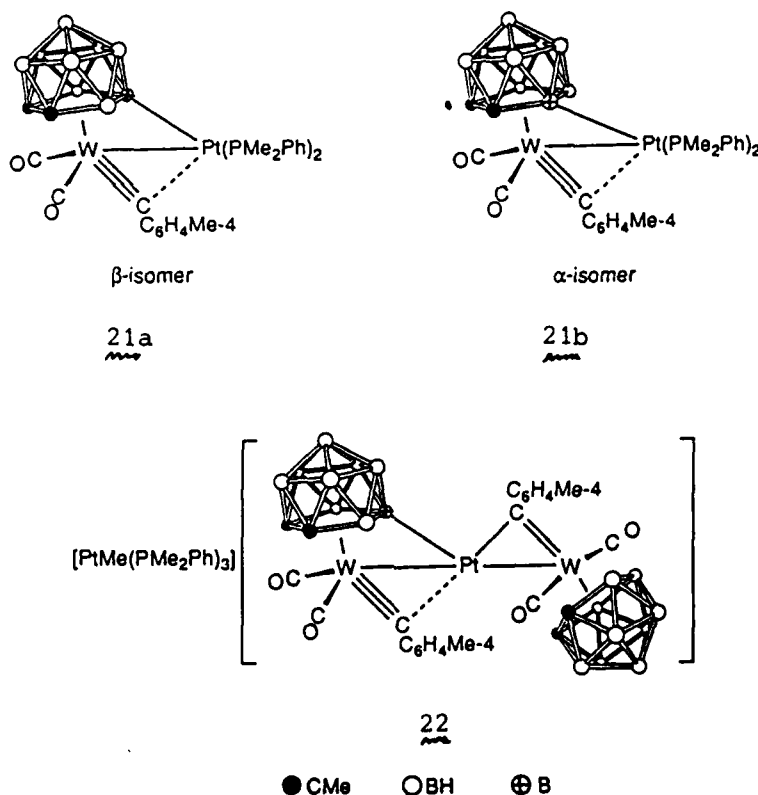
In another new dimension to this area of study we have synthesised a family of molybdenum-tungsten complexes (17) – (19) containing $\text{Mo}(\eta^7\text{-C}_7\text{H}_7)$ groups in which the metal-metal bonds are bridged both by alkylidyne ligands and $\text{B-H}\cdots\text{Mo}$ three-centre two-electron bonds. These compounds are electronically unsaturated and can be expected to display interesting reactivity towards substrate molecules.²⁶



The reaction between the compounds [PtCl(Me)(PMe₂Ph)₂], TlBF₄, and [NEt₄][W(≡CC₆H₄Me-4)(CO)₂(η⁶-C₂B₁₀H₁₀Me₂)] in thf (tetrahydrofuran) yields two isomers of a dimetal species [WPt(μ-CC₆H₄Me-4)(μ-σ:η⁶-C₂B₁₀H₉Me₂)(CO)₂(PMe₂Ph)₂] (20).²⁵ The structure of the isomer (20b) formed in greatest yield (*ca.* 70%) was established by X-ray diffraction. The W-Pt bond [2.738(1) Å] is bridged by the alkylidyne group [W-μ-C 1.92(1); Pt-μ-C 2.14(1) Å] and by a C₂B₁₀ fragment. The non-planar $\overline{\text{CBCBBB}}$ face of the latter is η⁶ co-ordinated to the tungsten, but the cage also forms a B-Pt σ bond [2.15(1) Å]. This linkage involves a boron atom of the B₃ group α to a carbon, and correspondingly the other isomer is assigned a structure in which it is the $\overline{\text{CBCBBB}}$ atom of the hexagonal ring which bonds to platinum.

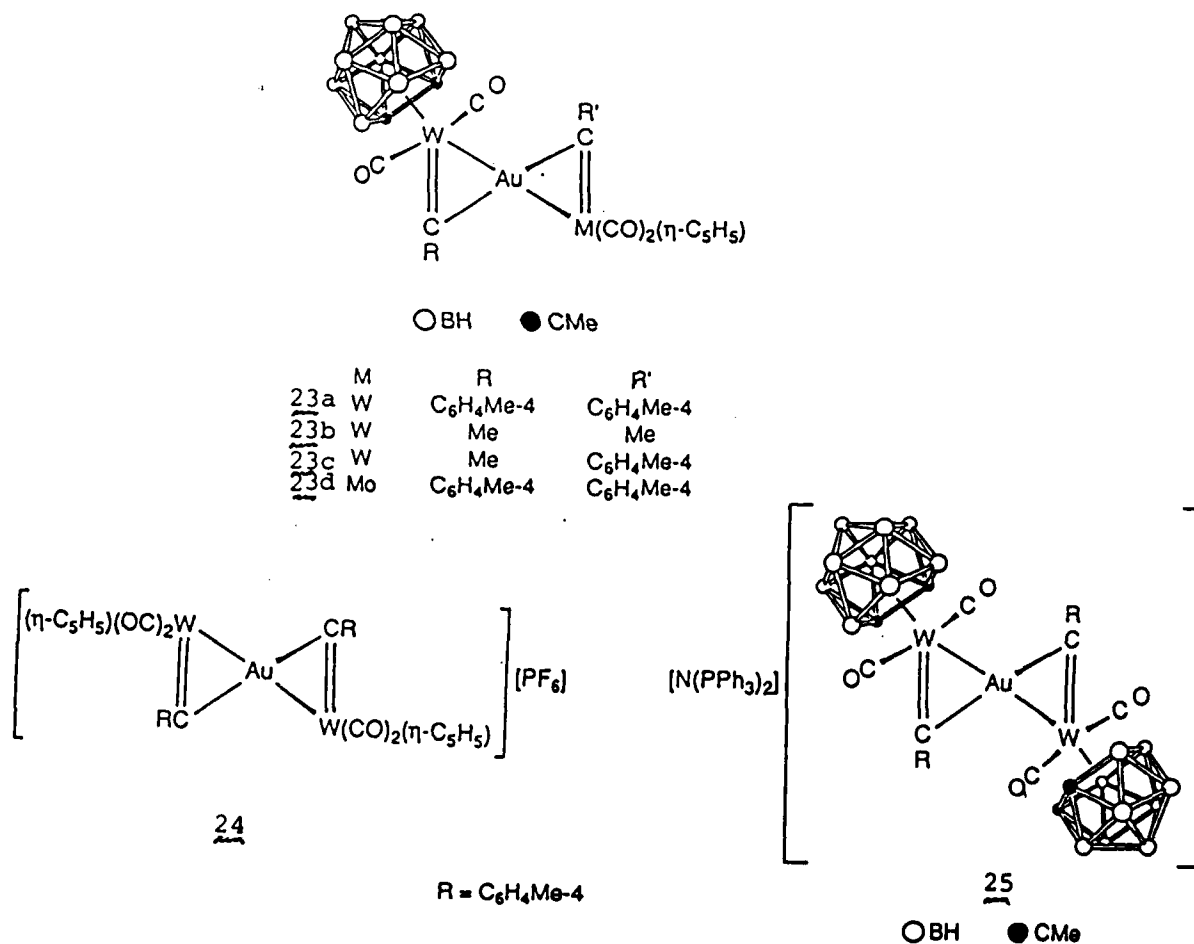


In acetone at ambient temperatures, the reagents $[\text{PtCl}(\text{Me})(\text{PMe}_2\text{Ph})_2]$, TlBF_4 , and $[\text{NEt}_4][\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ afforded $[\text{WPt}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-}\sigma\text{:}\eta^5\text{-C}_2\text{B}_9\text{H}_8\text{Me}_2)(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ (two isomers, **21a** and **21b**), and a small amount of the salt, $[\text{PtMe}(\text{PMe}_2\text{Ph})_3][\text{W}_2\text{Pt}(\mu\text{-C}_6\text{H}_4\text{Me-4})_2(\mu\text{-}\sigma\text{:}\eta^5\text{-C}_2\text{B}_9\text{H}_8\text{Me}_2)(\text{CO})_4(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ (**22**).²⁵ The structure of (**21a**) was determined by X-ray diffraction. The W–Pt bond [2.720(1) Å] is spanned by the p-tolylmethyldyne group [W–μ-C 1.89(1), Pt–μ-C 2.14(1) Å] and by a C₂B₉ fragment. The latter is co-ordinated to the W atom *via* the open pentagonal face of the *nido*-icosahedral cage, and bridges to the Pt atom through an exopolyhedral B–Pt σ bond [2.17(1) Å]. This boron atom is in the β site with respect to the carbon atoms in the $\overline{\text{BBCC}}$ ring. In the other isomer it is the boron α to a carbon atom which forms the B–Pt bond.



Formation of the dimetal compounds (**20**) – (**22**) probably occurs *via* reductive elimination of methane from precursors containing Pt–Me and B–H→Pt bonds. The presence of the B–Pt σ bonds in the final product represents a novel feature of this chemistry.

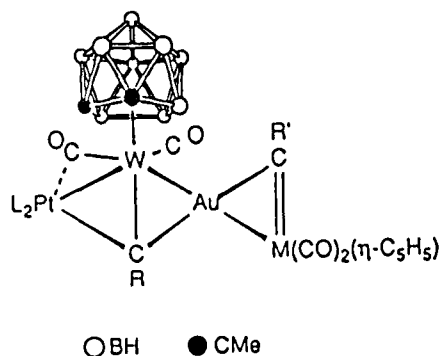
An important development has been the synthesis of the trimetal compounds $[MWAu(\mu-CR)(\mu-CR')(CO)_4(\eta^5-C_5H_5)(\eta^5-C_2B_9H_9Me_2)]$ ($M = Mo$ or W)(23) from reactions between the complexes $[MAuCl(\mu-CR')(CO)_2(\eta^5-C_5H_5)]$ and the reagents $[NEt_4][W(\equiv CR)(CO)_2(\eta^5-C_2B_9H_9Me_2)]$ (see III, page 2). The compounds (23) are neutral species, and are structurally related to the previously prepared salts (24) and (25). However, in (24) the gold atom is part of a cation, whereas in (25) it is part of an anion. The isolobal relationship between the ligands $\eta^5-C_5H_5^-$ and $\eta^5-C_2B_9H_9Me_2^{2-}$ allows for the existence of the *neutral compounds* (23) and prompted their synthesis.²²



These species have considerable potential as starting materials for the synthesis of other polynuclear metal compounds. The structures of the compounds (23) are clearly related to those of the complexes (1) (page 4) which have been successfully used in the preparation of metal-chain and -ring compounds (Scheme 1). The presence of the unsaturated C=W and

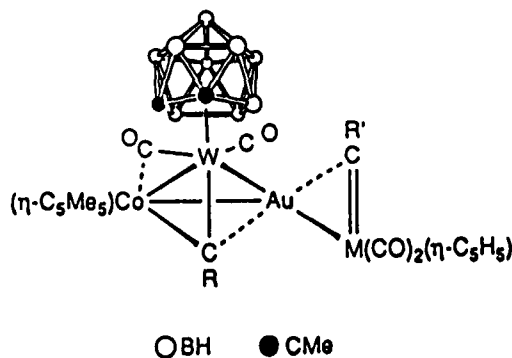
C=M sites in the compounds (23) should serve as points of attack for metal-ligand fragments. Accordingly, we have exploited this idea.

Treatment of the compounds (23) with the reagents $[\text{Pt}(\text{cod})_2]$ or $[\text{Pt}(\text{PMe}_2\text{Ph})_2(\text{nb})]$ (nb = norborene = bicyclo[2,2,1]heptene) affords, respectively the complexes $[\text{W}_2\text{PtAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\text{cod})(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ (26a) and $[\text{MWPtAu}(\mu\text{-CR})(\mu_3\text{-CR})(\text{CO})_4(\text{PMe}_2\text{Ph})_2(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ (26b – 26d). Interestingly, the platinum fragment adds to the C=W linkage rather than the C=M group, indicating a greater activation of the carbon-metal double bond by the $\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2$ cage than by the $\eta\text{-C}_5\text{H}_5$ ligand.



	M	R	R'	L ₂
26a	W	C ₆ H ₄ Me-4	C ₆ H ₄ Me-4	cod
26b	W	C ₆ H ₄ Me-4	C ₆ H ₄ Me-4	PMe ₂ Ph x 2
26c	W	Me	C ₆ H ₄ Me-4	PMe ₂ Ph x 2
26d	Mo	C ₆ H ₄ Me-4	C ₆ H ₄ Me-4	PMe ₂ Ph x 2

A similar reactivity pattern is shown in reactions of $[\text{Co}(\text{C}_2\text{H}_4)_2(\eta\text{-C}_5\text{Me}_5)]$ with the compounds (23), the products being the compounds $[\text{MWCuAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CR})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ (27, M = Mo or W). X-Ray crystallographic studies on (27b) have confirmed the structure of this group of cluster compounds.



	M	R	R'
27a	W	C ₆ H ₄ Me-4	C ₆ H ₄ Me-4
27b	Mo	C ₆ H ₄ Me-4	C ₆ H ₄ Me-4

CUMULATIVE LIST OF PUBLICATIONS

A.F.O.S.R. GRANT 86-0125

Period 1 March 86 – 31 July 90

1. G.P. Elliott, J.A.K. Howard, C.M. Nunn, and F.G.A. Stone, *J.Chem.Soc., Chem.Comm.*, 1986, 431.
Cyclisation of Metal Chain Complexes: X-Ray Crystal Structures of $[\text{Pt}_3\text{W}_4(\mu\text{-CR})_2(\mu_3\text{-CR})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$ and $[\text{Pt}_4\text{W}_4(\mu\text{-CR})(\mu_3\text{-CR})_3(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$).
2. 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.
Heteronuclear 'Star Clusters' $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_3\text{-CPh})_4(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$ and $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu\text{-CR})(\mu_3\text{-CR})_3(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$ ($\text{R} = \text{Ph}$ or $p\text{-C}_6\text{H}_4\text{Me}$).
3. S.J. Davies, G.P. Elliott, J.A.K. Howard, C.M. Nunn, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1987, 2177.
Synthesis of Penta-, Hexa-, and Hepta- Heteronuclear Metal Cluster Compounds Involving Tungsten or Molybdenum With Platinum or Nickel; Crystal Structures of the Chain Compounds $[\text{Pt}_3\text{W}_3(\mu\text{-CMe})(\mu_3\text{-CMe})_2(\text{CO})_6(\text{cod})(\eta\text{-C}_5\text{Me}_5)_3]$ ($\text{cod} = \text{cyclo-octa-1,5-diene}$) and $[\text{Pt}_3\text{W}_4(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$.
4. G.P. Elliott, J.A.K. Howard, T. Mise, C.M. Nunn, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1987, 2189.
Synthesis of Eight Membered Ring Metallacycles; X-Ray Crystal Structures of $[\text{Pt}_4\text{W}_4(\mu\text{-CR})(\mu_3\text{-CR})_3(\mu\text{-CO})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_4]$, $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu\text{-CR})(\mu_3\text{-CR})_3(\mu\text{-CO})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)_4]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$), and $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_3\text{-CPh})_4(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$.
5. D. Barratt, S.J. Davies, G.P. Elliott, J.A.K. Howard, D.B. Lewis, and F.G.A. Stone, *J.Organomet.Chem.*, 1987, 325, 815.
Hydroboration of Carbon-Tungsten Triple Bonds; Crystal Structures of $[\text{W}_2\{\mu\text{-MeCB(H)Et}\}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ and $[\text{W}\{\eta^3\text{-CH(BC}_8\text{H}_{14})\text{C}_6\text{H}_4\text{Me-4}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$.
6. M.J. Attfield, J.A.K. Howard, A.N. de M. Jelfs, C.M. Nunn, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1987, 2219.
Carbaboranetungsten-Platinum Complexes. Polyhedral Rearrangements of a 12-Vertex Cage System. Crystal Structures of $[\text{PtW}(\text{CO})_2(\text{PEt}_3)_2\{\eta^6\text{-C}_2\text{B}_9\text{H}_8(\text{CH}_2\text{C}_6\text{H}_4\text{Me-4})\text{Me}_2\}]$, $[\text{PtW}(\mu\text{-H})\{\mu\text{-}\sigma,\eta^5\text{-C}_2\text{B}_9\text{H}_7(\text{CH}_2\text{C}_6\text{H}_4\text{Me-4})\text{Me}_2\}(\text{CO})_2(\text{PMe}_3)(\text{PEt}_3)_2]$ and Related Compounds.

7. F-E. Baumann, J.A.K. Howard, O. Johnson, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1987, 2917.
Reactions Between Diiron Nonacarbonyl and the Salts $[\text{NEt}_4][\text{W}(\equiv\text{CR})(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ ($\text{R} = \text{Me}$, Ph , or $\text{C}_6\text{H}_4\text{Me-4}$): Crystal Structures of $[\text{NEt}_4][\text{FeW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-}\sigma,\eta^5\text{-C}_2\text{B}_9\text{H}_8\text{Me}_2)(\mu\text{-CO})(\text{CO})_5]$ and $[\text{NEt}_4][\text{Fe}_2\text{W}(\mu_3\text{-CPh})(\mu\text{-}\sigma:\sigma',\eta^5\text{-C}_2\text{B}_9\text{H}_7\text{Me}_2)(\text{CO})_8]$.
8. F-E. Baumann, J.A.K. Howard, R.J. Musgrove, P. Sherwood, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1988, 1879.
Salts of the Anions $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]^-$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-2}$ or $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$) as Reagents for the Synthesis of Compounds with Heteronuclear Metal-Metal Bonds; Crystal Structure of $[\text{NEt}_4][\text{FeW}(\mu\text{-CC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})_5(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$.
9. F-E. Baumann, J.A.K. Howard, R.J. Musgrove, P. Sherwood, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1988, 1891.
Reactions of Dicobalt Octacarbonyl with the Salts $[\text{X}][\text{W}(\equiv\text{CR})(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ ($\text{X} = \text{NEt}_4$ or PPh_4 ; $\text{R} = \text{Me}$, Ph , $\text{C}_6\text{H}_4\text{Me-2}$ or $\text{C}_6\text{H}_4\text{Me-4}$); Crystal Structure of $[\text{PPh}_4][\text{Co}_2\text{W}(\mu_3\text{-CPh})(\text{CO})_8(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$.
10. F-E. Baumann, J.A.K. Howard, R.J. Musgrove, P. Sherwood, M.A. Ruiz, and F.G.A. Stone, *J.Chem.Soc., Chem.Comm.*, 1987, 1881.
The Carbaborane Group $\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2$ as a Spectator and Non-Spectator Ligand in Di- and Tri-metal Complex Chemistry: X-Ray Crystal Structures of $[\text{PPh}_4][\text{Co}_2\text{W}(\mu_3\text{-CPh})(\text{CO})_8(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)] \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$, $[\text{NEt}_4][\text{FeW}(\mu\text{-CC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})_5(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$, and $[\text{IrW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PEt}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$.
11. J.R. Fernandez and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1988, 3035.
Molybdenum and Tungsten Complexes Containing the Alkylidyne Group $\text{C}(\eta^6\text{-C}_6\text{H}_4(\text{OMe-2})\text{Cr}(\text{CO})_3)$.
12. D.D. Devore, J.A.K. Howard, J.C. Jeffery, M.U. Pilotti, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1989, 303.
Carbaboranetungsten-Platinum Complexes having a $\mu\text{-CC}_6\text{H}_3\text{Me}_2\text{-2,6}$ Ligand; Crystal Structures of $[\text{WPt}(\mu\text{-CC}_6\text{H}_3\text{Me}_2\text{-2,6})(\mu\text{-}\sigma,\eta^5\text{-C}_2\text{B}_9\text{H}_8\text{Me}_2)(\text{CO})_n(\text{PEt}_3)]$ ($n = 2$ or 3).
13. S.J. Davies and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1989, 785.
Synthesis of Chain and Ring Compounds Containing Molybdenum.
14. D.D. Devore, C. Emmerich, J.A.K. Howard, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1989, 797.
Alkylidyne(carbaborane)molybdenum-gold, -rhodium and -iron Complexes; Crystal Structure of $[\text{NEt}_4][\text{MoFe}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-}\sigma:\sigma',\eta^5\text{-C}_2\text{B}_9\text{H}_7\text{Me}_2)(\text{CO})_8]$.
15. S.J. Davies, J.A.K. Howard, R.J. Musgrove, and F.G.A. Stone, *Angew.Chem., Int.Ed.Engl.*, 1989, **28**, 624.
Eleven Metal Atom Chain Complexes.

16. S.J. Crennell, D.D. Devore, S.J.B. Henderson, J.A.K. Howard, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1989, 1363.
Docosahedral Carbaborane(alkylidyne)tungsten Complexes as Reagents for the Synthesis of Compounds with Heteronuclear Metal-Metal Bonds; Crystal Structures of $[\text{NEt}_4]\text{-}[\text{W}(\equiv\text{CC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})_2(\eta^6\text{-C}_2\text{B}_{10}\text{H}_{10}\text{Me}_2)]$ and $[\text{NEt}_4][\text{WFe}(\mu\text{-CC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})_4(\eta^6\text{-C}_2\text{B}_{10}\text{H}_{10}\text{Me}_2)]$.
17. J.C. Jeffery, M.A. Ruiz, P. Sherwood, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1989, 1845.
Carbaboranetungsteniridium Compounds; Crystal Structure of the Complex $[\text{WIr}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PEt}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$.
18. S.J. Davies, J.A.K. Howard, M.U. Pilotti, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1989, 1855.
Tetra- and Penta-nuclear Tungsten-Rhodium Complexes: Crystal Structures of $[\text{W}_3\text{Rh}_2(\mu\text{-CO})_2(\mu\text{-CMe})\{\mu\text{-C(Me)C(O)}\}(\mu\text{-PPh}_2)_2(\mu_3\text{-CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_3]$ and $[\text{W}_3\text{Rh}_2(\mu\text{-CO})_3(\mu\text{-CMe})\{\mu\text{-C(Me)PPh}_2\}(\mu\text{-PPh}_2)(\mu_3\text{-CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_3]$.
19. S.J. Davies and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1989, 1865.
Synthesis of the Complexes $[\text{W}_2\text{M}_2(\mu\text{-CMe})_2(\mu\text{-PPh}_2)_2(\text{CO})_4(\text{C}_5\text{H}_5)_2]$ ($\text{M} = \text{Rh}$ or Ir) and Related Tetra- and Penta-nuclear Metal Compounds; Interconversion of Ketenyl and λ^5 -Phospha-alkyne Ligands Bridging Tungsten-Rhodium Bonds.
20. S.J. Davies, J.A.K. Howard, R.J. Musgrove, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1989, 2269.
Synthesis of Heteropolynuclear Metal Compounds with Chains of Seven to Eleven Metal Atoms; Crystal Structure of $[\text{Mo}_2\text{W}_3\text{Pt}_6(\mu_3\text{-CMe})_3(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})_2(\text{CO})_{10}(\text{PMe}_2\text{Ph})_4(\eta\text{-C}_5\text{H}_5)_5]$.
21. S.J. Davies, A.F. Hill, M.U. Pilotti, and F.G.A. Stone, *Polyhedron*, 1989, **8**, 2265.
Synthesis and Crystal Structure of $[\text{Mo}_2\text{FePt}(\mu\text{-}\sigma,\sigma',\sigma'':\eta^5\text{-CC}_5\text{H}_4)_2(\text{CO})_4\{\text{HB(pz)}_3\}_2]$ [$\text{HB(pz)}_3 = \text{hydrotris(pyrazol-1-yl)borate}$].
22. M.C. Gimeno and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1990, **2239**
Tri- and Tetra-nuclear Metal Compounds with Ethylidyne or p-Tolylmethylidyne Groups, and having both Cyclopentadienyl and Carbaborane Ligands.
23. N. Carr, M.C. Gimeno, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1990, **2247**
Synthesis of the Cluster Compounds $[\text{MWCoAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CR})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ ($\text{M} = \text{Mo}$ or W , $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$; $\text{M} = \text{W}$, $\text{R} = \text{Me}$); Crystal Structure of the Complex $[\text{MoWCoAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$.

24. N. Carr, M.C. Gimeno, J.E. Goldberg, M.U. Pilotti, F.G.A. Stone, and I. Topaloğlu, *J.Chem.Soc., Dalton Trans.*, 1990, 2253.
 Synthesis of Mixed-metal Compounds via the Salts $[\text{NEt}_4][\text{Rh}(\text{CO})\text{L}(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{R}_2)]$ ($\text{L} = \text{PPh}_3$, $\text{R} = \text{H}$; $\text{L} = \text{CO}$, $\text{R} = \text{Me}$); Crystal Structures of the Complexes $[\text{WRhAu}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_3(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})]$ and $[\text{WRh}_2\text{Au}_2(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6(\eta\text{-C}_5\text{H}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)_2]$.
25. N. Carr, M.C. Gimeno, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1990, in press.
 Synthesis of the Compounds $[\text{WPt}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{:}\eta^x\text{-C}_2\text{B}_n\text{H}_{n-1}\text{Me}_2)(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ ($x = 5$, $n = 9$; $x = 6$, $n = 10$); Crystal Structures of an Isomer of Each Complex.
26. S.J. Dossett, I.J. Hart, M.U. Pilotti, and F.G.A. Stone, *J.Chem.Soc., Dalton Trans.*, 1990, in press.
 Trimetal Molybdenum and Tungsten Complexes Containing $\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{R}_2'$ ($\text{R}' = \text{H}$ or Me) Ligands; Crystal Structure of $[\text{NEt}_4][\text{Mo}_2\text{W}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\mu\text{-CO})(\text{CO})_7(\text{PMe}_3)(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$.