

Synthetic and structural studies on metal cluster compounds

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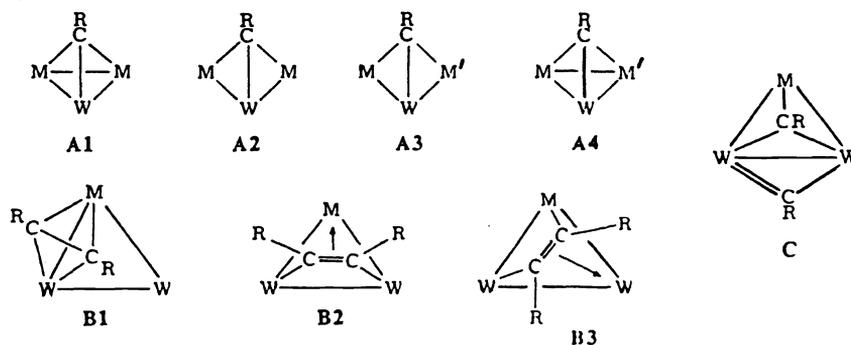
Abstract - The complex $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = C_6H_4Me-4$) is a useful precursor for the synthesis of heteronuclear metal cluster compounds. Dimetal species have been prepared in which tungsten is bonded to Ti, Zr, Cr, Re, Mn, Fe, Co, Rh, Ir, Pt or Cu, with the metal-metal bonds bridged by a tolylmethylidyne group. The dimetal compounds can serve as reagents for the preparation of trimetal complexes in which the alkylidyne ligand triply bridges a triangle of metal atoms. The core structures of these species may be of the trimetallatetrahedrane variety or of the 'butterfly' type in which a $\mu-C-W$ group transversely bridges a metal-metal vector with two non-tungsten metal atoms occupying wingtip positions. Another class of trimetal compound has a linear or near linear MW_2 ($M = Pt, Pd, Ni, Au^+,$ or Ag^+) spine with a $\mu-CR$ group edge-bridging each $M-W$ bond. The paradigm is $[PtW_2(\mu-CR)_2(CO)_4(\eta-C_5H_5)_2]$, an unsaturated species which may be used as a building block in the synthesis of cluster compounds with chains, *e.g.* $[Pt_3W_4(\mu_2-CR)_2(\mu_3-CR)_2(CO)_8(\eta-C_5H_5)_4]$, or rings of metal atoms, *e.g.* $[Pt_4W_4(\mu_2-CR)(\mu_3-CR)_3(CO)_8(\eta-C_5H_5)_4]$. In other work, the dimetal species $[ReM(\equiv CR)(CO)_9]$ ($M = Cr, Mo$ or W) and $[CoW(\equiv CR)(CO)_8]$ have been used as starting complexes for the preparation of 'mixed-metal' cluster compounds, such as $[Co_2MRe(\mu_3-CR)(CO)_{15}]$, $[Co_2Re(\mu_3-CR)(CO)_{10}]$, $[ReMFe(\mu_3-CR)(\mu-CO)(CO)_{11}]$, $[CoFe_2(\mu_3-CR)(\mu-CO)(CO)_9]$, and $[M'M_2Re_2(\mu_2-CR)_2(CO)_{18}]$ ($M' = Ni$ or Pt , $M = Cr$ or W).

EARLY WORK

It was in 1979 that we first reported (ref. 1) that the compound $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = C_6H_4Me-4$), discovered by Fischer *et al* (ref. 2), would displace ethylene from the platinum complexes $[Pt(C_2H_4)(PR'_3)_2]$ ($R' =$ alkyl or aryl) to give dimetal species $[PtW(\mu-CR)(CO)_2-(PR'_3)_2(\eta-C_5H_5)]$ with bridging tolylmethylidyne ligands. Subsequently it was demonstrated that this synthesis was of very general applicability since numerous metal-ligand fragments will combine with the alkylidyne tungsten compound $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ to afford dimetal compounds containing 'dimetallacyclopropene' rings (Scheme 1). The results fall within the framework of the isolobal model, relating the frontier orbitals of metal-ligand fragments with those of organic groups (ref. 3). The $W(CO)_2(\eta-C_5H_5)$ moiety in the molecule $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ is isolobal with CR , and the ML_n fragments of Scheme 1 are isolobal with the methylene group (ref. 4).

The dimetallacyclopropene complexes have proven to be versatile reagents for preparing trimetal compounds, since many of these species will react further, either with a second metal-ligand fragment or with $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ (Scheme 2). The resulting cluster compounds

Scheme 3

TABLE Some Trimetal Compounds Derived from $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = C_6H_4Me-4$).

$[W_3(\mu_3-CR)(CO)_6(\eta-C_5H_5)_3]^a$	$[FeCoW(\mu_3-CR)(\mu-CO)(CO)_5(\eta-C_5H_5)(\eta-C_5Me_5)]^d$
$[Mo_2W(\mu_3-CR)(CO)_6(\eta-C_5H_5)_3]^a$	$[FeRhW(\mu_3-CR)(\mu-CO)(CO)_5(\eta-C_5H_5)(\eta-C_9H_7)]^d$
$[Fe_2W(\mu_3-CR)(\mu-CO)(CO)_8(\eta-C_5H_5)]^b$	$[FePtW(\mu_3-CR)(CO)_5(PMePh_2)_2(\eta-C_5H_5)]^f$
$[Co_2W(\mu_3-CR)(CO)_8(\eta-C_5H_5)]^c$	$[CuPtW(\mu_3-CR)(CO)_2(PMe_3)_2(\eta-C_5H_5)(\eta-C_5Me_5)]^g$
$[Ni_2W(\mu_3-CR)(CO)_2(\eta-C_5H_5)_3]^d$	$[Cu_2W(\mu_3-CR)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2]^g$
$[Re_2W(\mu_3-CR)(CO)_{10}(\eta-C_5H_5)]^e$	$[AuPtW(\mu_3-CR)(CO)_2(PMe_3)_3(\eta-C_5H_5)] [PF_6]^h$
$[ReW_2(\mu-Br)(\mu-CO)(\mu_2-CR)(\mu_3-CR)(CO)_3(\eta-C_5H_5)_2]^e$	$[FeW_2(\mu_3-RC_2R)(CO)_6(\eta-C_5H_5)_2]^b$
$[Rh_2W(\mu_3-CR)(acac)_2(\mu-CO)(CO)_2(\eta-C_5H_5)]^c$	$[RuW_2(\mu_3-RC_2R)(CO)_7(\eta-C_5H_5)_2]^i$
$[Rh_2W(\mu_3-CR)(\mu-CO)(CO)_2(\eta-C_5H_5)(\eta-C_5Me_5)_2]^d$	$[OsW_2(\mu_3-RC_2R)(CO)_7(\eta-C_5H_5)_2]^i$
$[Rh_2W(\mu_3-CR)(\mu-CO)(CO)_2(\eta-C_5H_5)(\eta-C_9H_7)_2]^d$	

^a Ref. 6b. ^b Ref. 7. ^c Ref. 8. ^d Ref. 6a. ^e Ref. 9. ^f Ref. 10.

^g Ref. 11. ^h Ref. 12. ⁱ Ref. 13.

METAL ATOM RINGS AND CHAINS

In 1981 we reported (ref. 14) the preparation of the novel trimetal compound $[PtW_2(\mu-CR)_2(CO)_4(\eta-C_5H_5)_2]$ (1) which was obtained by treating $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ with $[Pt(C_2H_4)_3]$ in pentane at $-40^\circ C$. The molecular structure is shown in Figure 1, from which it will be seen that the platinum atom is in a distorted tetrahedral environment, ligated by two $C \equiv W$ groups. The related species (3) - (6) (Scheme 4) were also prepared (refs. 14 and 15). Compound (1) is unsaturated at the $C = W$ bonds, and it was, therefore, thought possible to use this species as a building block for the preparation of clusters with chains of metal atoms (Scheme 5). This strategy has proved successful and interesting results have been obtained.

The two cluster compounds with five metal atom chains, *viz.* $[Pt_3W_2(\mu_3-CR)_2(CO)_4(cod)_2(\eta-C_5H_5)_2]$ (Figure 2) and $[Pt_2W_3(\mu_2-CR)_2(\mu_3-CR)(CO)_6(\eta-C_5H_5)_3]$ (Figure 3) can be prepared in good yield (Ref. 16). Treatment of $[Pt_3W_2(\mu_3-CR)_2(CO)_4(cod)_2(\eta-C_5H_5)_2]$ with two equivalents of $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ affords a seven metal atom chain compound $[Pt_3W_4(\mu_2-CR)_2(\mu_3-CR)_2(CO)_8(\eta-C_5H_5)_4]$ (ref. 17). The latter forms as a mixture of isomers in solution, which is not surprising in view of the bent and twisted nature of the chains, allowing different conformations probably differing little in energy. The compound crystallised as one isomer however, and an X-ray diffraction study was carried out confirming the nature of the complex.

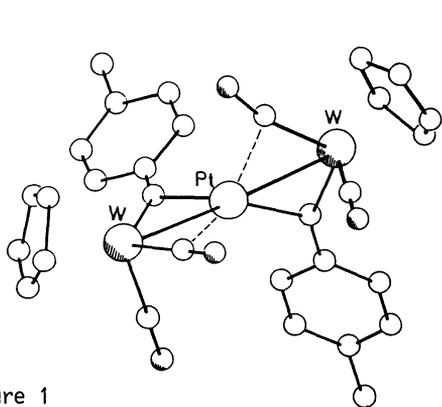


Figure 1

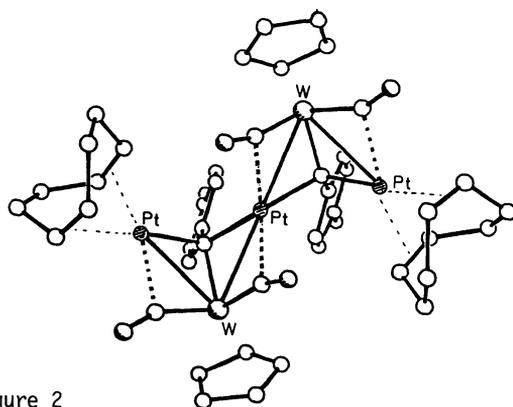
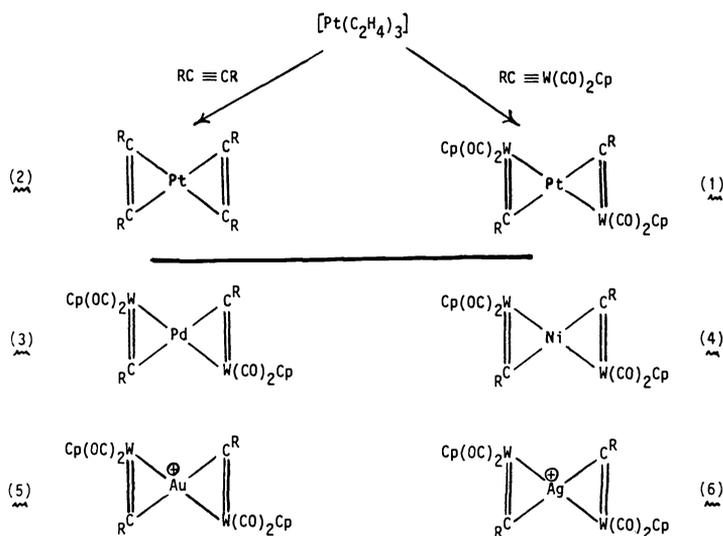
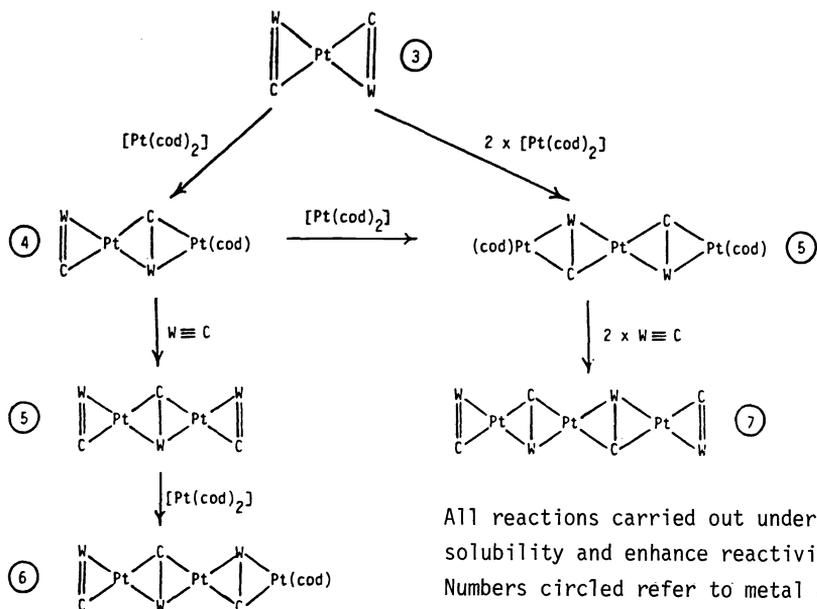


Figure 2

Scheme 4



Scheme 5



All reactions carried out under C_2H_4 to increase solubility and enhance reactivity of $[\text{Pt}(\text{cod})_2]$. Numbers circled refer to metal atoms in chain.

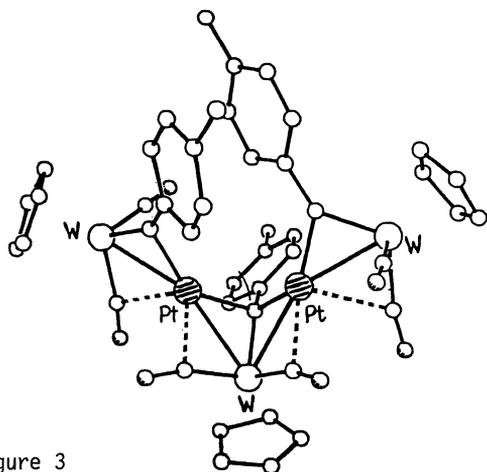


Figure 3

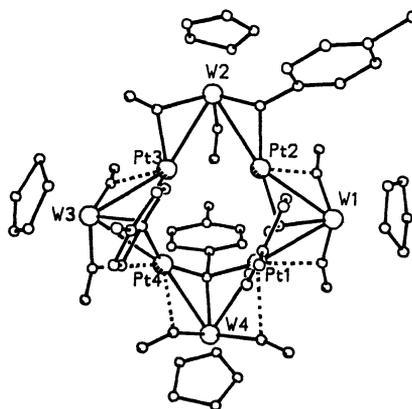


Figure 4

With increasing chain length there is the possibility of cyclisation occurring, leading to ring formation. We have recently observed such cyclisation reactions. Addition of one equivalent of $[\text{Pt}(\text{C}_2\text{H}_4)_3]$, in tetrahydrofuran at 0°C , to $[\text{Pt}_3\text{W}_4(\mu_2\text{-CR})_2(\mu_3\text{-CR})_2(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$ gives the cluster compound $[\text{Pt}_4\text{W}_4(\mu_2\text{-CR})(\mu_3\text{-CR})_3(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$, formed as a single isomer (ref. 17). The $^{195}\text{Pt}\text{-}\{^1\text{H}\}$ and $^{13}\text{C}\text{-}\{^1\text{H}\}$ n.m.r. spectra revealed that the four platinum atoms were in different chemical environments, and that one of the alkyldiene groups was edge-bridging a metal-metal bond while three triply-bridge metal centres. An X-ray diffraction study established the remarkable structure shown in Figure 4. In principle it should be possible to replace the tungsten or platinum atoms in the chains or rings by other metallic elements isoelectronic with these metals. We have begun studies with this objective, using bis(cyclo-octa-1,5-diene)nickel to introduce nickel atoms in place of platinum. Treatment of compound (1) (Scheme 4) with $[\text{Ni}(\text{cod})_2]$ in tetrahydrofuran at room temperature affords $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_2\text{-CR})(\mu_3\text{-CR})_3(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$. Examination of the $^{195}\text{Pt}\text{-}\{^1\text{H}\}$ and $^{13}\text{C}\text{-}\{^1\text{H}\}$ n.m.r. spectrum of this product showed that it was formed as a 1:1 mixture of two isomers. Four $^{195}\text{Pt}\text{-}\{^1\text{H}\}$ resonances are observed at δ 1725 and 1138 p.p.m. [$J(\text{PtPt})$ 410 Hz], and at 1640 and 1001 p.p.m. [$J(\text{PtPt})$ 234 Hz]. Eight $^{13}\text{C}\text{-}\{^1\text{H}\}$ signals for the alkyldiene ligated-carbon nuclei are seen at δ 326.4, 314.0 ($\mu_2\text{-C}$) and 297.6, 297.2, 290.8, 288.2, 288.0 and 284.8 ($\mu_3\text{-C}$) p.p.m. Fortunately, suitable crystals were available for an X-ray diffraction study (ref. 17), and the structure is shown in Figure 5. The tungsten sites are not disordered, but the nickel and platinum are disordered with a 50 % site occupancy as shown. Molecules of both isomers are thus present in equal amounts in the crystal. The distinction between the two isomers is best revealed in Figure 6. In one isomer the edge-bridging tolylmethylidyne ligand spans a Ni—W bond whereas in the other isomer this group bridges a Pt—W bond.

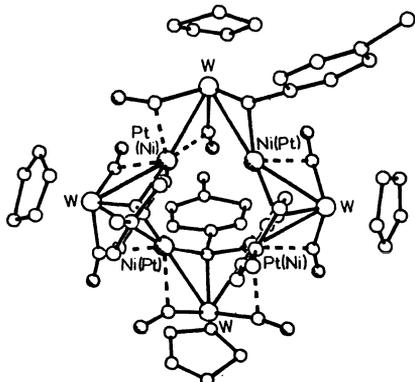


Figure 5

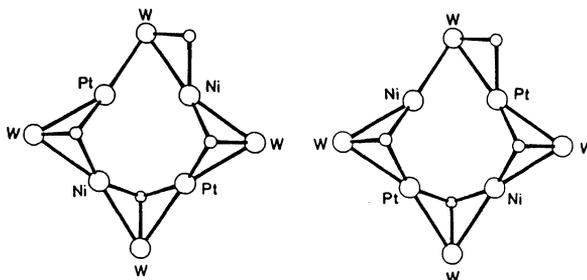


Figure 6. The metal atom core structures and arrangement of the bridging alkyldiene groups in the two isomers of $[\text{Ni}_2\text{Pt}_2\text{W}_4(\mu_2\text{-CR})(\mu_3\text{-CR})_3\text{-}(\text{CO})_8(\eta\text{-C}_5\text{H}_5)_4]$.

HETERONUCLEAR CLUSTERS FROM DIMETAL SPECIES WITH TERMINAL CARBYNE LIGANDS

The compounds $[\text{ReM}(\equiv\text{CR})(\text{CO})_9]$ ($\text{M} = \text{Cr}, \text{Mo}$ or W ; $\text{R} = \text{C}_6\text{H}_4\text{Me}-4$) and $[\text{CoW}(\equiv\text{CR})(\text{CO})_8]$ (ref. 18) contain $\text{C}\equiv\text{M}$ groups, and it seemed likely that these species would also be useful in the synthesis of heteronuclear metal clusters. It was anticipated that metal-ligand fragments would bond with the $\text{C}\equiv\text{M}$ groups, and that in suitable circumstances initially formed complexes might undergo further reaction, affording more condensed species.

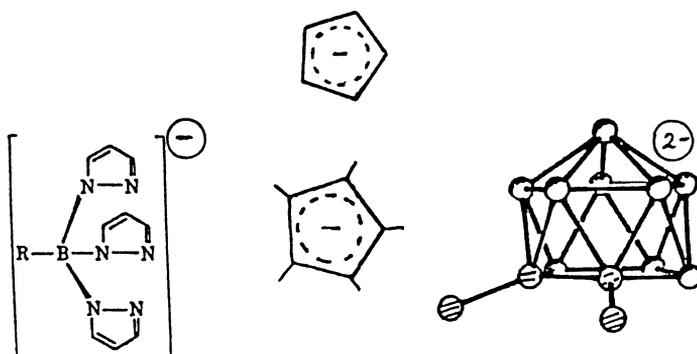
Treatment of the compounds $[\text{ReM}(\equiv\text{CR})(\text{CO})_9]$ with $[\text{Co}_2(\text{CO})_8]$ in light petroleum at room temperature affords the tetranuclear metal complexes $[\text{Co}_2^{\text{MRe}}(\mu_3\text{-CR})(\text{CO})_{15}]$. These compounds have a $\mu_3\text{-CCo}_2\text{M}$ core structure with a pendant $\text{Re}(\text{CO})_5$ group bonded to the sub-Group VI metal. When solutions of these clusters are heated in toluene $[\text{M}(\text{CO})_6]$ is produced, and the compound $[\text{Co}_2\text{Re}(\mu_3\text{-CR})(\text{CO})_{10}]$ is formed (ref. 19).

Diiron enneacarbonyl, $[\text{Fe}_2(\text{CO})_9]$, reacts with $[\text{ReCr}(\equiv\text{CR})(\text{CO})_9]$ to give the cluster compound $[\text{ReCrFe}(\mu_3\text{-CR})(\mu\text{-CO})(\text{CO})_{11}]$; the structure of which has been established by X-ray diffraction (ref. 20). Analogous Mo and W complexes $[\text{ReMFe}(\mu_3\text{-CR})(\mu\text{-CO})(\text{CO})_{11}]$ ($\text{M} = \text{Mo}$ or W) have been prepared. Interestingly these clusters form via species $[\text{ReMFe}(\mu_2\text{-CR})(\text{CO})_{13}]$ ($\text{M} = \text{Mo}$ or W) in which an $\text{Fe}(\text{CO})_4$ fragment is attached to the $\text{M}\equiv\text{C}$ group of the precursors $[\text{ReM}(\equiv\text{CR})(\text{CO})_9]$. The compound $[\text{CoW}(\equiv\text{CR})(\text{CO})_8]$ reacts with $[\text{Fe}_2(\text{CO})_9]$ to yield $[\text{CoFe}_2(\mu_3\text{-CR})(\mu\text{-CO})(\text{CO})_9]$.

A further illustration of employment of the complexes $[\text{ReM}(\equiv\text{CR})(\text{CO})_9]$ in synthesis is provided by reactions of the chromium and tungsten compounds with $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ or $[\text{Ni}(\text{cod})_2]$. The products are $[\text{M}'_2\text{MRe}_2(\mu\text{-CR})_2(\text{CO})_{18}]$ ($\text{M}' = \text{Ni}$ or Pt , $\text{M} = \text{Cr}$ or W), having structures akin to those of the compound shown in Figure 1, with the nickel or platinum atoms sandwiched between two $\text{M}\equiv\text{C}$ groups.

FUTURE DEVELOPMENTS

Use of the compound $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me}-4)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ as a reagent for the synthesis of complexes with heteronuclear metal-metal bonds has opened up a new domain for that area of organo-metallic chemistry concerned with the study of metal clusters. There is wide scope for future developments, because the principles employed (ref. 4) are also applicable to many compounds structurally and electronically related to the tolylmethylidyne-tungsten species. Indeed, only a minor change such as replacement of the $\text{CC}_6\text{H}_4\text{Me}-4$ fragment in the tungsten complex by the CMe group produces major differences in the properties and chemical behaviour of the cluster compounds produced (ref. 21). Particularly interesting discoveries are likely to follow from replacing the $\eta\text{-C}_5\text{H}_5$ anion in $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me}-4$ or Me) by the ligands $\eta\text{-C}_5\text{Me}_5^-$, HBpz_3^- or $\eta\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2^{2-}$, shown below (ref. 22). Isolation of



the salt $[N(PPh_3)_2][W(\equiv CR)(CO)_2(\eta^{-1,2-C_2B_9H_9Me_2})]$, for example, has allowed development of the chemistry indicated in Scheme 6 (refs. 22, 23). Novel structures are being discovered such as those of the molybdenum-tungsten and ruthenium-tungsten complexes shown in Figure 7.

Scheme 6

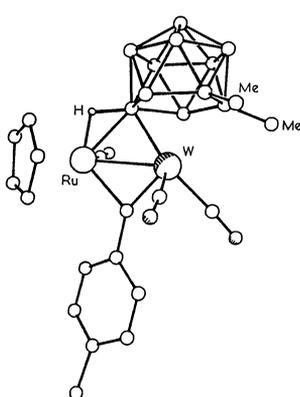
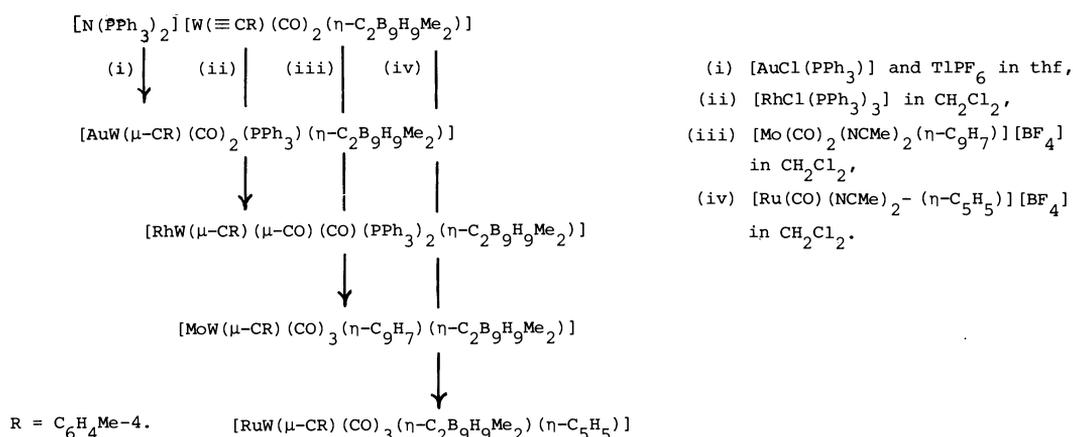


Figure 7

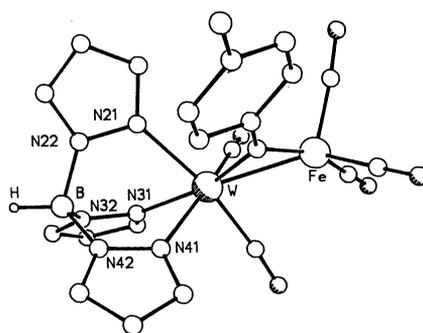
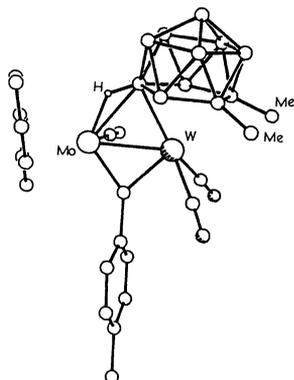


Figure 8

The new tolylmethylidynetungsten complex $[W(\equiv CR)(CO)_2(HBpz_3)]$ is also a ready source of novel species having bonds between tungsten and other transition elements. Figure 8 shows the structure of the 32-valence electron compound $[FeW(\mu-CR)(CO)_5(HBpz_3)]$. The latter reacts with $[Rh(CO)_2(\eta^{-1-C_9H_7})]$ to give $[FeRhW(\mu_3-CR)(\mu-CO)(CO)_5(HBpz_3)(\eta^{-1-C_9H_7})]$, and reversibly adds CO to yield $[FeW(\mu-CR)(CO)_6(HBpz_3)]$. The compounds $[W(\equiv CR)(CO)_2(\eta^{-1-C_5Me_5})]$ ($R = C_6H_4Me-4$ or Me) are also showing a diverse chemistry in reactions with low-valent metal-ligand fragments. The ethylidynetungsten complex $[W(\equiv CMe)(CO)_2(\eta^{-1-C_5Me_5})]$ displays distinct promise as a reagent for the synthesis of platinum-tungsten chain compounds. Substitution of Cr or Mo for W in the various alkylidyne derivatives is also likely to lead to new results reflecting subtle differences in the chemistry of these metals.

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