The Chemistry of Stabilized Clusters

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The chemistry of stabilized clusters

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The complexes $[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_9]$ (**1**) and $[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)(CO)_8]$ (**2**) have been prepared in high yields from, respectively, the reaction of $[Ru_3(CO)_{12}]$ with $PhPH_2$ and the reaction of $[Mn_2(CO)_{10}]$ with Ph_2PH. Complexes **1** and **2** undergo a range of reactions without fragmentation into mononuclear species. Thus **1**, after treatment with Me_3NO, reacts with a wide range of two-electron donor ligands, L, to give the substitution products $[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8L]$. It also undergoes oxidative addition reactions with addenda XY to give the complexes $[Ru_3(\mu_2\text{-}H)_2(X)(Y)(\mu_3\text{-}PPh)(CO)_9]$ (**3**), $[Ru_3(\mu_2\text{-}H)_2(Y)(\mu_2\text{-}X)(\mu_3\text{-}PPh)(CO)_8]$ (**4**) and $[Ru_3(\mu_2\text{-}H)_2(\mu_2\text{-}Y)(\mu_2\text{-}X)(\mu_3\text{-}PPh)(CO)_7]$ (**5**) (**3**, X = Y = Cl or Br; **4**, X = Y = Cl or Br; X = Cl, Y = HgCl; **5*a***, X = Y = Cl or Br; **5*b***, X = Cl, Y = HgCl). $[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)(CO)_8]$ (**2**) undergoes substitution reactions to give complexes of formula $[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)(CO)_{8-n}L_n]$ ($n = 1$, 2 or 4) and reacts with alkynes, $RC\vdots CR'$, to give the complexes $[Mn_2(\mu_2\text{-}\eta^2\text{-}RC{:}C(H)R')(\mu_2\text{-}PPh_2)(CO)_7]$, which themselves react further with electron donor molecules such as R_3P and H^- to give μ_2-carbene complexes. Complexes **1** and **2** react with Na/Hg to give, respectively, the anions $[Ru_3(\mu_2\text{-}H)(\mu_3\text{-}PPh)(CO)_9]^-$ and $[Mn_2(\mu_2\text{-}PPh_2)(CO)_8]^-$, which react with neutral or cationic complexes of other metals to give a variety of mixed-metal clusters.

Introduction

Studies of the chemistry of metal cluster complexes and, in particular, their reactions with small organic molecules, have been confined to relatively few systems. Among the reasons for this are:

(i) not many clusters are easily synthesized in high yields;

(ii) their reactions often give a multitude of products that are difficult to separate and characterize;

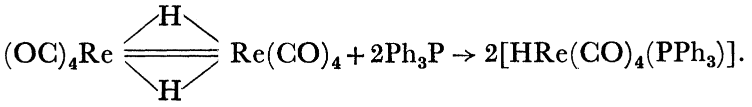
(iii) the conditions required to bring about reactions often lead to fragmentation of the cluster into lower nuclearity (often mononuclear) species.

One cluster whose chemistry has been extensively studied is $[Os_3H_2(CO)_{10}]$. This can be synthesized in high yields from $[Os_3(CO)_{12}]+H_2$ (Knox *et al.* 1975) and reacts readily under mild conditions with a wide range of electron-donor molecules by virtue of its coordinative unsaturation (Shapley *et al.* 1975; Deeming & Hasso 1976; Adams & Golembeski 1979). Formally, one may consider that a metal–metal double bond is present, which is reduced to a single bond on coordination of an additional two-electron donor ligand such as an organophosphine. The presence of metal–hydrogen bonds in this cluster and the cluster's ability to coordinate organic substrates enable it to undergo a wide variety of insertion reactions, leading to products that may be regarded as intermediates in the reduction of organic molecules by clusters (Deeming & Hasso 1975; Keister & Shapley 1975).

RESULTS AND DISCUSSION

Our interest in this area began with a study of the interaction of $[Os_3H_2(CO)_{10}]$ with various fluorocarbon molecules in an attempt to delineate cyclic reduction processes by using clusters. In some cases, such as the hydrogenation of an alkyne to an alkene, cyclic processes can be completed (Dawoodi *et al.* 1982). In other examples, such as the attempted hydrogenation of a nitrile, the stability of an intermediate complex prevents completion of the cycle (Banford *et al.* 1982).

There is a small number of polynuclear transition metal complexes related to $[Os_3H_2(CO)_{10}]$ in that metal–hydrogen and multiple metal–metal bonds (in the same sense as in $[Os_3H_2(CO)_{10}]$) are present. In general, however, these complexes are more difficult to synthesize in high yield than $[Os_3H_2(CO)_{10}]$ and, more significantly, they decompose readily into lower nuclearity fragments on treatment with electron-donor ligands (Andrews *et al.* 1977):



$$(OC)_4Re\overset{H}{\underset{H}{=\!=\!=}}Re(CO)_4 + 2Ph_3P \rightarrow 2[HRe(CO)_4(PPh_3)].$$

We have sought to prepare complexes of this type containing bridging ligands and, for example, in the complexes $[Re_2(\mu_2\text{-}H)_2(CO)_6(LL)]$ (LL = $Ph_2PCH_2PPh_2$ or $(EtO)_2POP(OEt)_2$), we have found that such ligands do stabilize the dinuclear unit with respect to the above decomposition (Mays *et al.* 1980). With suitable organic substrates, insertion reactions, analogous to those of $[Os_3H_2(CO)_{10}]$, can then be observed (figure 1).

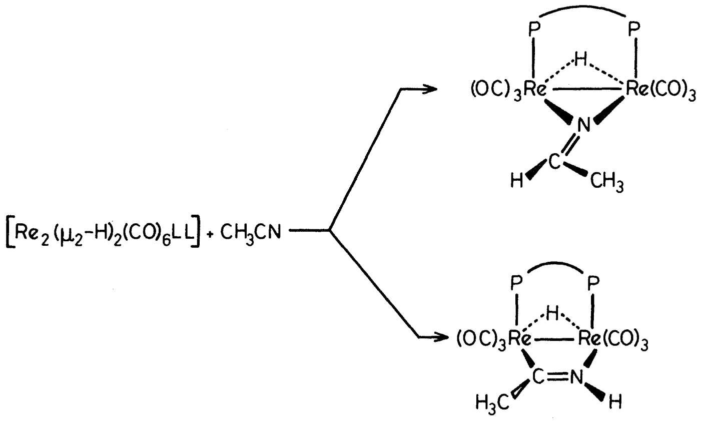


FIGURE 1. The reaction of $[Re_2(\mu_2\text{-}H)_2(CO)_6(LL)]$ with CH_3CN (LL = $Ph_2PCH_2PPh_2$ or $(EtO)_2POP(OEt)_2$).

The above examples of insertion reactions involve coordinatively unsaturated polynuclear complexes, and in the course of the reaction a formal hydrogen-bridged metal–metal bond of order two is reduced to a single bond, which presumably facilitates the initial coordination of the organic substrate. Recent work by, for example, Huttner *et al.* (1979) shows, however, that the coordination of electron-donor ligands to clusters can also be achieved by a reduction of metal–metal bond order from one to zero, in particular for clusters containing first-row transition metals. This suggests that apparently coordinatively saturated 'stabilized' clusters containing hydrogen-bridged metal–metal bonds might react with electron donor ligands in a similar way (figure 2). To examine this possibility we have investigated the reactions of some complexes of this type, concentrating on those for which we have been able to devise high-yield syntheses. One such complex is $[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_9]$ (**1**), which may be obtained in 50% yield from the reaction of $[Ru_3(CO)_{12}]$ with $PhPH_2$ in refluxing hexane (Iwasaki *et al.* 1981). Treatment of this complex with electron donor ligands, however, does not result in fission of the metal–metal or hydrogen-bridged metal–metal bonds. Thus, under a pressure of 50 atm (1 atm ≈ 133 Pa) CO at 100 °C in heptane solution, no change in the infrared spectrum of the cluster is observed. With phosphorus donor ligands (L) the substitution products, $[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8L]$ rather than simple adducts, are obtained on refluxing in cyclohexane. A much wider range of substitution products (table 1) can be obtained in high yield by treatment of **1** with Me_3NO in CH_2Cl_2 at room temperature followed by addition of the ligand.

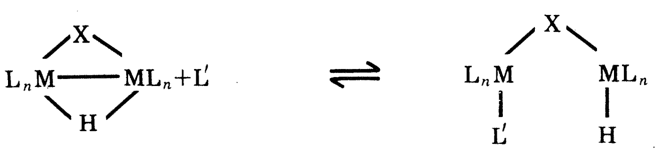


FIGURE 2. Suggested mode of reaction of complexes containing hydrogen-bridged metal–metal bonds with electron donor ligands, L′ (X is a bridging ligand).

TABLE 1. SUBSTITUTION PRODUCTS DERIVED FROM $[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_9]$

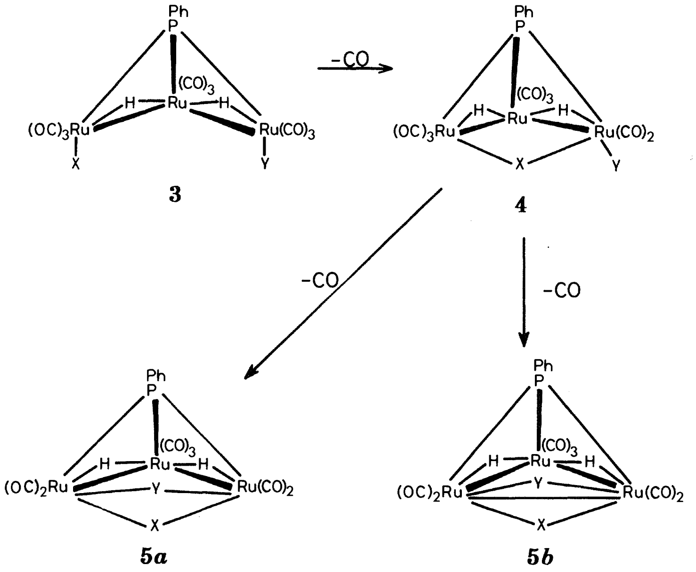
compound†	$\nu(CO)/cm^{-1}$‡	^1H n.m.r.§
$[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PPh_3)]$	2073m, 2043s, 2036s, 2003s, 1989s, 1980m, 1967w	7.53(m, 20H, Ph), −18.54(d of d, $^2J_{PH}$ = 16 Hz, $^2J_{P'H}$ = 10 Hz, 2H, RuH)
$[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PH_2Ph)]$	2077m, 2048s, 2041s, 2009s, 2001m, 1993m, 1978w	7.70(m, 10H, Ph), 5.97 (d, J_{PH} = 354 Hz, 2H, Ph), −19.02 (d of d, $^2J_{PH}$ = 14 Hz, $^2J_{P'H}$ = 15 Hz, 2H, RuH)
$[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(CNBu^t)]$	2072m, 2046s, 2036s, 2004s, 1995m, 1981m, 1969w	7.50(m, 5H, Ph), 1.33(s, 9H, Bu^t) −18.88(d, $^2J_{PH}$ = 16 Hz, 2H, RuH)
$[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(NCMe)]$	2076m, 2043s, 2035s, 2002s, 1992m, 1979m, 1967w	
$[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(\mu_2\text{-}CH_2)]$	2087m, 2056s, 2035s, 2010m, 1987m, 1968w, 1767w, br	7.55(m, 5H, Ph), 5.96(m, 1H, CH_2), 4.18(m, 1H, CH_2), −17.45(br d, $^2J_{PH}$ = 15 Hz, 2H, RuH)

† Molecular ion peaks observed in mass spectra of all compounds except $[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(NCMe)]$.
‡ Recorded in cyclohexane solution.
§ In millionths relative to $SiMe_4$ and recorded in CD_2Cl_2 solution at −70°C.

An alternative approach to bond breaking is to treat the complex with reducing agents. Reaction of **1** with sodium amalgam at room temperature, however, gives the anion $[Ru_3H(CO)_9PPh]^-$ in quantitative yield:

$$[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_9] \xrightarrow{Na/Hg} [Ru_3(\mu_2\text{-}H)(\mu_3\text{-}PPh)(CO)_9]^- + \tfrac{1}{2}H_2.$$

Oxidative addition can also lead to bond fission in polynuclear complexes and treatment of **1** with suitable addenda does lead to initial cleavage of the lone metal–metal bond, although the hydrogen-bridged metal–metal bonds remain intact. Thus if a solution of **1** in CH_2Cl_2 at room temperature is allowed to react with Cl_2 or Br_2 a mixture of complexes (**3**, **4** and **5*a***) is obtained after a few seconds (figure 3). With $HgCl_2$ the initial products are presumably analogous to **3** and **4**, but the major product observed even at room temperature is **5*b***, in which the ruthenium–ruthenium bond has reformed. A product analogous to **4** has been isolated by Adams (1982) from the reaction of $[Ru_3(\mu_2\text{-}H)_2(CO)_9S]$ with $SnCl_4$, and type **5*b*** complexes have been obtained previously from the reaction of $[Ru_3H(CO)_9C_6H_9]$ with PhHgX (X = Br, I) (Fahmy *et al.* 1980).



3	**4**	**5*a***	**5*b***
X=Y=Cl or Br	X=Y=Cl or Br X=Cl, Y=HgCl	X=Y= Cl or Br	X=Cl, Y=HgCl

FIGURE 3. Proposed structures for oxidative addition products from reaction of $[Ru_3(\mu_2\text{-}H)_2(\mu_3\text{-}PPh)(CO)_9]$ with addenda XY.

Previous studies indicate that metal–metal bonds involving first row transition metals are more easily broken than those involving second and third row transition elements, and it seemed likely that the same would be true of hydrogen-bridged metal–metal bonds. We have therefore also studied the reactivity of the complex $[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)(CO)_8]$ (**2**). This was first prepared by Green & Moelwyn-Hughes (1962) in 2% yield as a by-product from the reaction of Ph_2PCl with $[Mn(CO)_5]^-$ and subsequently by Hayter (1964) in 12% yield from the reaction of $[Mn_2(CO)_{10}]$ with Ph_4P_2. We have now synthesized **2** in 80% yield by treatment of $[Mn_2(CO)_{10}]$ with Ph_2PH in undried decalin at 150 °C. As with **1**, however, high-pressure infrared studies in heptane solution reveal that **2** is unaffected by CO even at pressures of 50 atm and temperatures of 200 °C. Reaction of **2** with other two-electron donor ligands such as organophosphines, nitriles or isonitriles in refluxing cyclohexane or on u.v. irradiation in pentane solution results in the formation of substitution products of general formulae $[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)(CO)_{8-n}L_n]$ (n = 1, 2 or 4) (table 2). No simple 1:1 addition products corresponding to fission of the hydrogen-bridged metal–metal bond could be identified.

With alkynes, RC⋮CR′, a reaction takes place under thermal or photolytic conditions, which is in many ways analogous to that of $[Os_3H_2(CO)_{10}]$ with acetylene. The complexes

Table 2. Substitution products derived from $[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)(CO)_8]$

compound	$\nu(CO)/cm^{-1}$†	^1H n.m.r.‡
$[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)(CNBu^t)(CO)_7]$	2074m, 2020s, 2000s, 1974s, 1953s, 1947m, 1927m	7.46(m, 10H, Ph), 4.29(s, 9H, Bu^t), –15.06(d, $^2J_{PH}$ = 34.9 Hz, 1H, MnH)
$[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)(PPh_3)(CO)_7]$	2073m, 2023m, 1989s, 1953s, 1940m, 1917m	7.78(m, 25H, Ph), –15.82 (t, $^2J_{PH}$ = 30.8 Hz, 1H, MnH)
$[Mn_2(\mu_2\text{-}H)(\mu\text{-}PPh_2)P(OMe)_3(CO)_7]$	2075m, 2034m, 1992s, 1950s, 1926m	7.70(m, 10H, Ph), 3.89(d, $^3J_{PH}$ = 12.0, 9H, OMe), –16.46(t, $^2J_{PH}$ = 30.6, 1H, MnH)
$[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)(CNBu^t)_2(CO)_6]$	2016m, 2004s, 1950s, 1944w, 1924s	7.67(m, 10H, Ph), 0.99(s, 18H, Bu^t)' – 16.38(d, $^2J_{PH}$ = 36.6 Hz, 1H, MnH)
$[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)\{(EtO)_2POP(OEt)_2\}(CO)_6]$	2034s, 2003s, 1959m, 1925s	7.89(m, 10H, Ph), 4.11(m, 20H, Et)' – 17.11(q, $^2J_{PH}$ = 28.9 Hz, 1H, MnH)
$[Mn_2(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)\{(EtO)_2POP(OEt)_2\}_2(CO)_4]$	2075m, 2029m, 1989vs, 1945s, 1929sh	7.69(m, 10H, Ph), 4.22(m, 40H, Et), –16.72(m, 1H, MnH)

† Recorded in cyclohexane solution.
‡ In millionths relative to $SiMe_4$ and recorded in CD_2Cl_2 solution at room temperature.

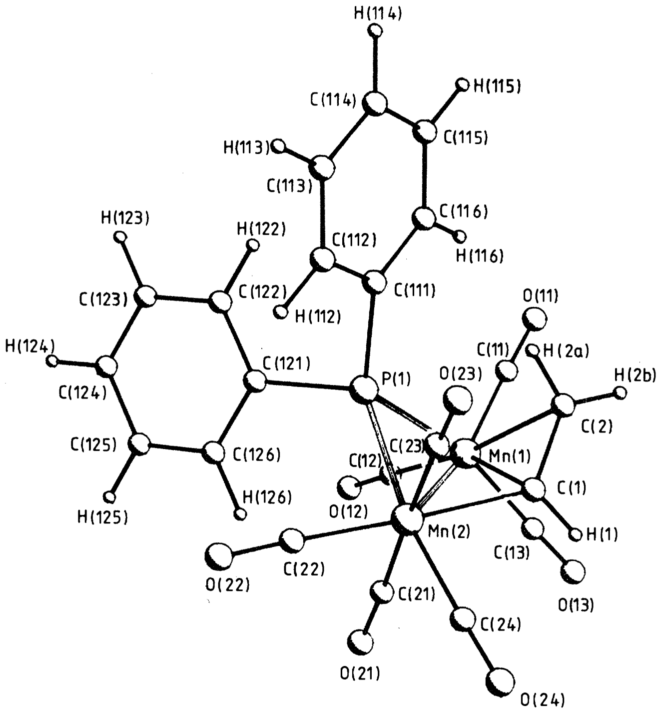
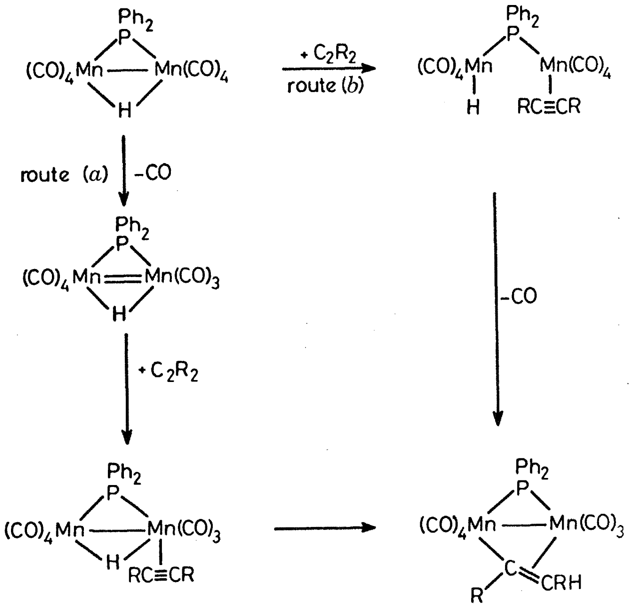


Figure 4. The molecular structure of $[Mn_2(\mu_2\text{-}\eta^2\text{-}HC{:}CH_2)(\mu_2\text{-}PPh_2)(CO)_7]$, including the atom numbering scheme with some bond parameters: Mn(1)–Mn(2), 2.750(1) Å; Mn(1)–C(1), 2.086(3) Å; Mn(1)–P(1), 2.253(2) Å; Mn(1)–C(2), 2.263(4) Å; Mn(2)–P(1), 2.369(1) Å; Mn(2)–C(1), 2.057(6) Å; C(1)–C(2), 1.372(7) Å; angle Mn(1)–P(1)–Mn(2), 73.0(1)°. (1 Å = 10^{-10} m = 10^{-1} nm.)

$[Mn_2(\mu_2\text{-}\eta^2\text{-}RC{:}C(H)R')(\mu_2\text{-}PPh_2)(CO)_7]$ resulting from insertion of the alkyne into a metal–hydrogen bond are the principal products, and an X-ray analysis of the acetylene adduct (Henrick *et al.* 1982) has established its molecular structure (figure 4).

There are two alternative pathways that can be conceived for the insertion reactions we have described, and these are shown in scheme 1. Route (*a*) involves the initial loss of a CO ligand to give the unsaturated species $[Mn_2H(CO)_7PPh_2]$, which can then react with the



SCHEME 1

alkyne in the same manner as proposed for $[Os_2H_2(CO)_{10}]$. Route (*b*) involves the initial co-ordination of the alkyne without CO loss, which presumably involves fission of the hydrogen-bridged metal–metal bond. The results of experiments designed to differentiate between these pathways have so far proved inconclusive. Thus although the fact that the reaction proceeds under photolytic conditions suggests that CO dissociation may be involved, photolysis of **2** in THF or hydrocarbon solvents in the presence of a stream of N_2 to drive off any dissociated CO causes no change either in the infrared spectrum or in the colour of the solution, and subsequent addition of an alkyne does not give the insertion product. Whichever pathway is followed, the alkyne, once coordinated, must undergo insertion rapidly because no simple alkyne adducts (as shown in scheme 1) were isolated from reaction with any of the alkynes studied.

The reaction of electron donor ligands with these vinyl-bridged metal–metal bonded dimers has also been studied. Thus treatment of $[Mn_2(PhC{:}C(H)Ph)(\mu_2\text{-}PPh_2)(CO)_7]$ with $PhMe_2P$ gives the zwitterion complex $[Mn_2^-\{C(Ph)CH(Ph)P^+Me_2Ph\}(\mu_2\text{-}PPh_2)(CO)_7]$, and reaction with H^- ($NaBH_4$) gives the anionic μ_2-carbene complex $[Mn_2\{C(Ph)CH_2Ph\}(\mu_2\text{-}PPh_2)(CO)_7]^-$. The proposed structures for these complexes, based on ^1H n.m.r. data, are shown in figure 5.

Although the focus of this study has been the reactions of stabilized clusters with electron-donor ligands we have also examined the reactions of the ruthenium and manganese complexes with electrophiles: thus **1** on dissolution in trifluoroacetic acid gives the cation $[Ru_3(\mu_2\text{-}H)_3\text{-}$

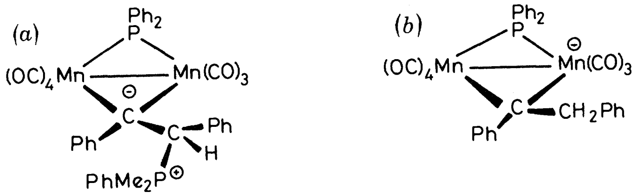


FIGURE 5. Proposed structure for (*a*) $[\mathrm{Mn_2\{C(Ph)CH(Ph)P^+Me_2Ph\}(\mu_2\text{-}PPh_2)(CO)_7}]$ and (*b*) $[\mathrm{Mn_2\{C(Ph)CH_2Ph\}(\mu_2\text{-}PPh_2)(CO)_7}]^-$.

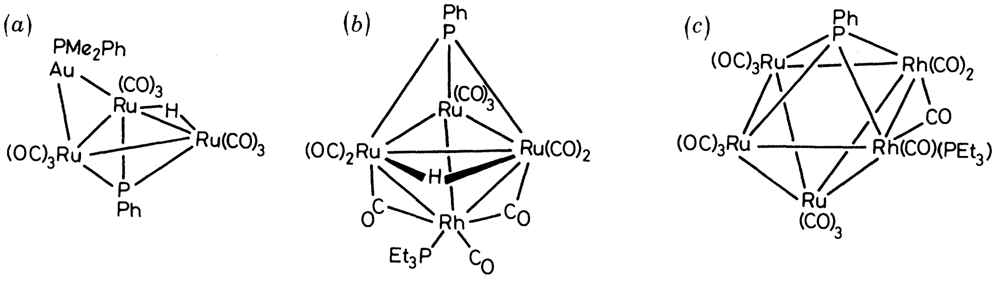


FIGURE 6. Some mixed-metal clusters derived from the anion $[\mathrm{Ru_3H(PPh)(CO)_9}]^-$; (*a*) with $[\mathrm{(PhMe_2P)_2Au}]^+$, (*b*) and (*c*) with $[\mathrm{(Et_3P)_2Rh(CO)_3}]^+$.

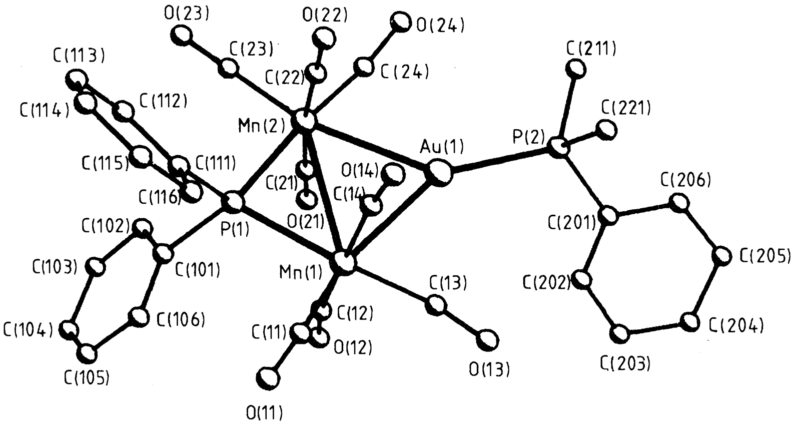


FIGURE 7. The molecular structure of $[\mathrm{Mn_2(\mu_2\text{-}AuPMe_2Ph)(\mu_2\text{-}PPh_2)(CO)_8}]$, including the atom numbering scheme with some bond parameters: Au(1)–Mn(1), 2.696(5) Å; Mn(1)–P(1), 2.297(9) Å; Au(1)–Mn(2), 2.681(5) Å; Mn(2)–P(1), 2.279(9) Å; Mn(1)–Mn(2), 3.066(7) Å; Au(1)–P(2), 2.293(7) Å; angle Mn(1)–Au(1)-Mn(2), 69.5(1)°; angle Mn(1)–P(1)–Mn(2), 84.1(3)°.

$(\mu_3\text{-PPh})(\mathrm{CO})_9]^+$, with addition of a bridging hydride ligand to the third metal–metal bond. An enhanced reactivity towards electrophiles can be engendered by initial deprotonation of the complexes as described earlier for **1**. Complex **2** may be deprotonated in a similar way. In particular we have studied the reactivity of these stabilized anions towards electrophilic attack by neutral and cationic metal complexes, with a view to synthesizing mixed-metal clusters. These so-called redox-condensation reactions (Chini 1978) constitute a general method of synthesis of such clusters (Gladfelter & Geoffroy 1980) and a selection of the mixed-metal complexes containing ruthenium that we have prepared by this route and structurally characterized (Mays *et al.* 1982) are shown in figure 6. It is possible to substitute edge-bridging and face-bridging metal atoms for the proton removed from the starting complex. The second proton can also be substituted by further deprotonation of the mixed-metal species and subsequent reaction with an additional quantity of a cationic metal complex. With the rhodium complex $[(Et_3P)_2Rh(CO)_3]^+$ as the cation, however, a skeletal rearrangement takes place on substitution of the second proton (figure 6*c*). Figure 7 shows the molecular structure of a manganese–gold complex obtained from reaction of the dimanganese anion with $[(PhMe_2P)_2Au]^+$ (Iggo *et al.* 1982). With the exception of the triruthenium–dirhodium species, the complexes shown in figure 6 are obtained in near quantitative yield based on the initial stabilized neutral cluster, and studies of their reactivity towards, for example, organic substrates are therefore also feasible.

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