Synthesis of Bis[μ-bis(diphenylphosphino)methane]-tri-μ-carbonyl-tricarbonyl-*triangulo*-trirhodium(1+) Perchlorate, $[Rh_3(CO)_3(\mu\text{-}CO)_3(\mu\text{-}dppm)_2]ClO_4$. An Unusual 46-Electron Cluster possessing the A-Frame Structure with a Bridging $Rh(CO)_3$ Fragment

Samitha P. Deraniyagala and Kevin R. Grundy *
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

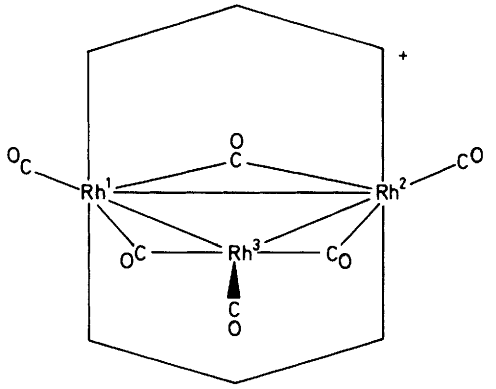
The A-frame complexes $[Rh_2(\mu\text{-}OR)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (R = H, Me, or Et; dppm = $Ph_2PCH_2PPh_2$) react under carbon monoxide to give the 46-electron, trinuclear cluster $[Rh_3(CO)_3(\mu\text{-}CO)_3(\mu\text{-}dppm)_2]ClO_4$ whose structure resembles that of an A-frame complex with a bridging $Rh(CO)_3$ group. The unique terminal carbonyl on the bridging rhodium atom undergoes rapid exchange with ^{13}CO and is readily substituted by tertiary phosphines PR_3 (R_3 = $MePh_2$, Et_3, or Ph_3; PR_3 = dppm). Unlike the parent cluster, the phosphine-substituted complexes $[Rh_3(CO)_2(\mu\text{-}CO)_3(PR_3)(\mu\text{-}dppm)_2]ClO_4$ undergo rapid exchange of the 1,3 and 2,3 bridging carbonyl groups only. In addition, $[Rh_3(CO)_2(\mu\text{-}CO)_3(dppm)(\mu\text{-}dppm)_2]ClO_4$ is fluxional, showing relatively rapid flipping between one donor atom and the other in the diphosphine. All complexes have been characterized on the basis of i.r., ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy. The structure of $[Rh_3(CO)_3(\mu\text{-}CO)_3(\mu\text{-}dppm)_2]ClO_4$ is discussed and a rationale proposed for the stability of the 46-electron cluster by comparison to the expected 48-electron species $[Rh_3(CO)_7(\mu\text{-}dppm)_2]^+$.

In a recent publication dealing with the electronic structure of molecular A frames, Hoffman and Hoffmann[1] employed the isolobal analogy between CH_2, C_{2v} d^{10} ML_2, and d^8 ML_4 metal fragments to predict the existence of trimetallic clusters based upon the A-frame structure with bridging ML_n groups.

In principle, the synthesis of such molecules should be straightforward, requiring only the interaction of a metal–metal bonded dimer, such as $[Rh_2(CO)_2(\mu\text{-}dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$)[2] or $[M_2Cl_2(\mu\text{-}dppm)_2]$ (M = Pd or Pt)[3] with an appropriate 14- or 16-electron metal fragment. The difficulty, of course, is in generating appropriate electron-deficient species under suitably mild conditions, which are not stabilized by ligands so bulky that steric interactions severely destabilize the product. Work in our laboratory aimed at generating trinuclear clusters in this manner has so far met with limited success. However, we now report the serendipitous discovery of a reaction between the A-frame complexes $[Rh_2(\mu\text{-}OR)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ (R = H, Me, or Et)[4] and carbon monoxide under pressure yielding the unusual cluster $[Rh_3(CO)_3(\mu\text{-}CO)_3(\mu\text{-}dppm)_2]ClO_4$, which can be regarded as the carbon monoxide adduct of the A-frame complex generated by combination of $[Rh_2(CO)_2(\mu\text{-}dppm)_2]$ with the planar 14-electron fragment $[Rh(CO)_3]^+$.

Results and Discussion

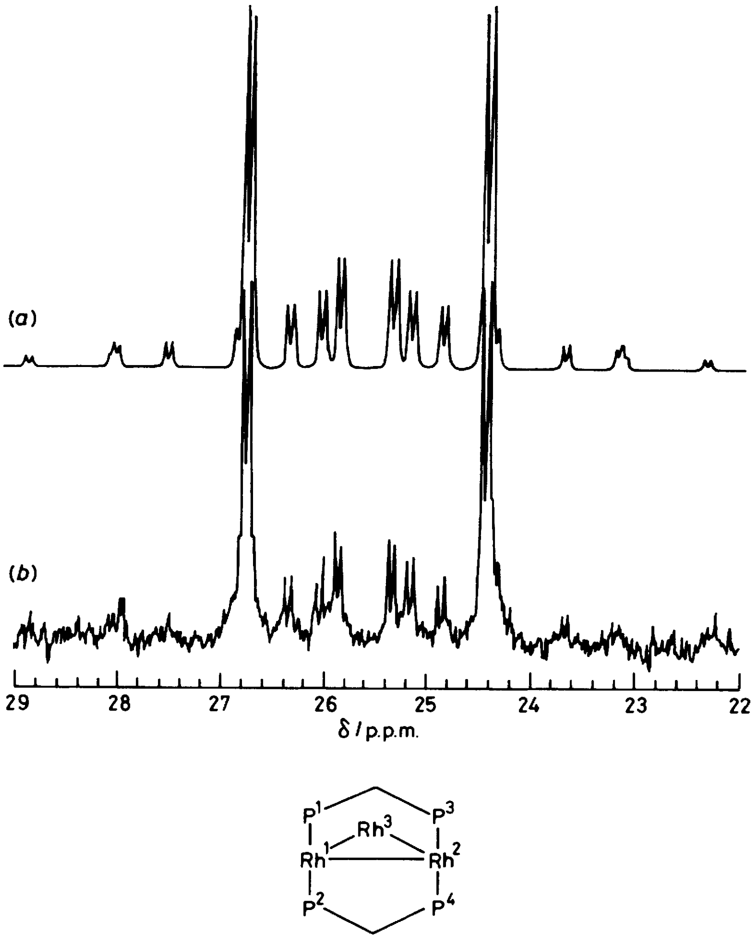
At room temperature and pressure, the O-bridged A-frame complexes $[Rh_2(\mu\text{-}OH\cdots Cl)(CO)_2(\mu\text{-}dppm)_2]$ and $[Rh_2(\mu\text{-}OR)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ show no tendency to react with carbon monoxide. Under CO pressure, however, $[Rh_2(\mu\text{-}OH\cdots Cl)(CO)_2(\mu\text{-}dppm)_2]$ reacts to give *trans*-$[Rh_2Cl_2(CO)_2(\mu\text{-}dppm)_2]$ in a reaction thought to involve removal of the bridging oxygen atom in the form of CO_2.[5] The reaction of the other O-bridged species differs dramatically from this. Subjecting a solution of $[Rh_2(\mu\text{-}OR)(CO)_2(\mu\text{-}dppm)_2]ClO_4$ to 2.1 MPa (30 lbf in^{-2}) of CO results in a colour change from yellow to red-brown and the deposition of an orange crystalline material after approximately 2 h. This complex has been characterized by the usual spectroscopic techniques† as a trinuclear cluster, $[Rh_3(CO)_3(\mu\text{-}CO)_3(\mu\text{-}dppm)_2]ClO_4\cdot CH_2Cl_2$ (1). Consistent with the assigned structure, in the solid-state i.r. spectrum of the cluster six bands can be identified at 2 035m, 2 000 (sh), 1 998vs, 1 924w, 1 869 (sh), and 1 858s cm^{-1}. Labelling studies with ^{13}CO (see below) have established that the three bands at higher frequencies are those associated with the terminal carbonyls. In dichloromethane solution the high-frequency shoulder on the most intense band can no longer be distinguished and the absorptions occur at 2 032m, 2 008vs, 1 929w, 1 872 (sh), and 1 869 cm^{-1}. It should be noted here that the ^1H n.m.r. spectrum of complex (1) is clear to *ca.* -50 p.p.m., indicating an absence of terminal or bridging hydride ligands.



(1)

---

† The many attempts to get crystals of complex (1) of *X*-ray quality all gave needles consisting of bundles of rods of poor diffracting ability. An *X*-ray crystallographic study of one such crystal was undertaken, however, with results of predictably insufficient accuracy to warrant publication. Nevertheless, the basic structural features were confirmed: cell parameters a = 19.413(16), b = 15.050(7), c = 20.501(16) Å, β = 100.90(6)°, Z = 4, space group $C2/c$ (monoclinic). Further details of the data set, its solution and refinement, may be obtained from Professor T. S. Cameron of this Department. Efforts to obtain crystals of (1) (or a derivative) of suitable quality are continuing but with little promise so far.



$J(P^1P^2) = 429{\cdot}6$, $J(P^1P^3) = 81{\cdot}5$, $J(P^1P^4) = 33{\cdot}8$,
$J(Rh^1P^1) = 95{\cdot}2$, $J(Rh^2P^1) = -1{\cdot}5$, $J = (Rh^3P^1) = 2{\cdot}5$, $J(Rh^1Rh^2) = J(Rh^1Rh^3) = J(Rh^2Rh^3) = 0$

Figure 1. Calculated (*a*) and observed (*b*) ^{31}P-$\{^1H\}$ n.m.r. spectra of $[Rh_3(CO)_3(\mu\text{-}CO)_3(\mu\text{-dppm})_2]ClO_4$ (**1**). Derived coupling constants (Hz) are shown

The only reasonable assignment of the terminal CO bands was that at 2 032 cm^{-1} due to ν(CO) of the unique carbonyl and the pair at 2 000, 1 998 cm^{-1} due to the symmetric and asymmetric stretch of the remaining carbonyl groups. In keeping with this assignment, the band envelope of this pair of absorptions closely resembles those of other A-frame complexes. Of the bridging carbonyl absorptions, the band at 1 924 cm^{-1} is attributable to the symmetric stretch of the equivalent bridging carbonyls. Relative intensities would suggest that the band at 1 872 cm^{-1} arises from the unique bridging carbonyl.

Exposing dichloromethane solutions of complex (**1**) to ^{13}CO results in the rapid exchange of only the unique terminal carbonyl group. No evidence is seen for exchange of the bridging carbonyls, as observed for the phosphine derivatives (see below). The medium-intensity band at 2 032 cm^{-1} is replaced by another of medium intensity at 1 980 cm^{-1} and no other changes are apparent within experimental error. The ^{13}C-$\{^1H\}$ n.m.r. spectrum of this species exhibits only a simple doublet centred at 185.7 p.p.m. with ^1J(C–Rh) = 90.0 Hz, verifying that it is the unique carbonyl that undergoes exchange. These facts establish unequivocally the presence of only a single carbonyl group on Rh^3. The presence of two terminal carbonyls on Rh^3 would necessarily give rise to two i.r. absorptions since the possibility of such carbonyls being *trans* to one another can be eliminated on steric grounds (see below). On leaving solutions of labelled (**1**) for *ca.* 12 h it was apparent that the labelled carbonyl was slowly introduced into the two adjacent bridging positions. Along with the appearance of a high-energy shoulder on the band at 2 008 cm^{-1} and a decrease in intensity of the band at 1 980 cm^{-1}, a new low-energy shoulder appears on the band at 1 869 cm^{-1}. In addition to the doublet at 185.7 p.p.m., the ^{13}C-$\{^1H\}$ n.m.r. spectra of these aged solutions exhibit a doublet of broad complex second-order multiplets centred at 242.2 p.p.m. (with a separation of *ca.* 54 Hz) arising from coupling with the rhodium and phosphorus nuclei, as well as the ^{13}C nuclei in the other two sites. The ^{31}P-$\{^1H\}$ n.m.r. spectrum of the cluster (**1**) is shown in Figure 1, along with the simulated spectrum and the derived coupling constants.* The spectrum analyses quite readily as an AA′A″A‴MXX′ spin system which gives rise to the typical A-frame AA′A″A‴XX′ pattern in which each line is split into a doublet by coupling with nucleus M, the bridging rhodium atom. We saw no evidence in the ^{31}P-$\{^1H\}$ n.m.r. of aged solutions of (**1**) to suggest significant decomposition was occurring, leading us to believe that the i.r. and ^{13}C n.m.r.

---

* Simulation performed by Professor J. T. Mague, Tulane University, New Orleans.

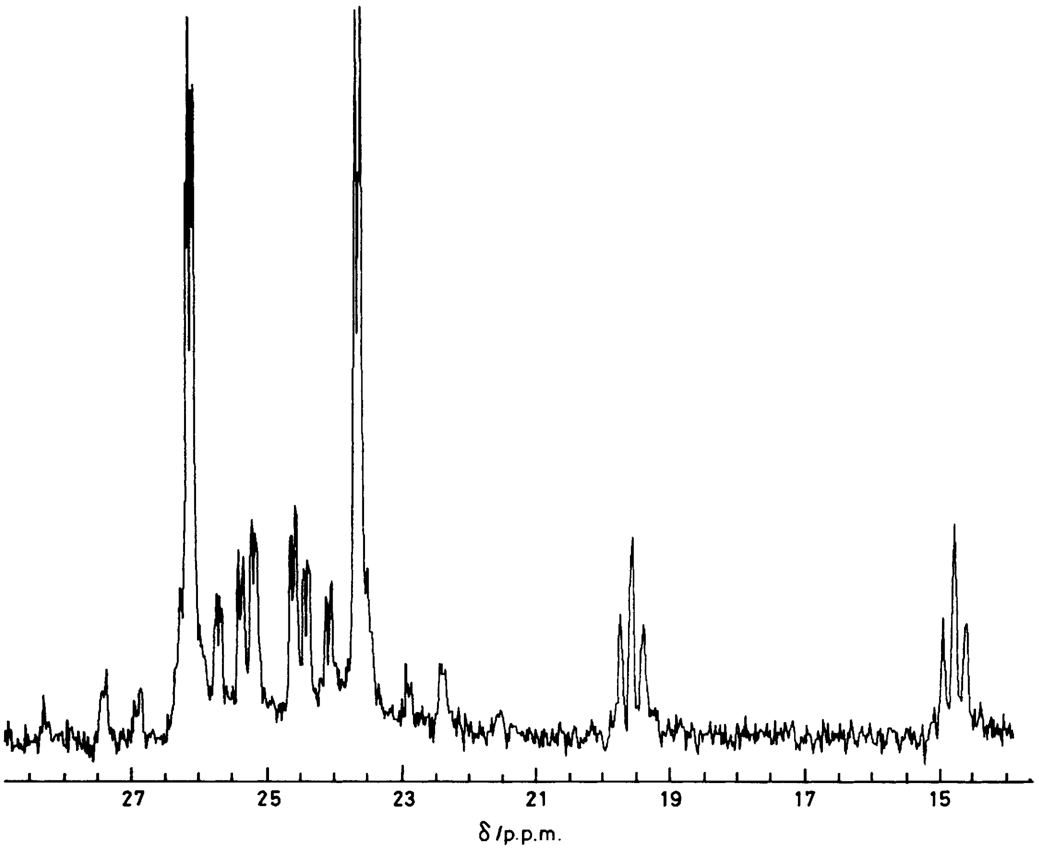


Figure 2. Observed $^{31}P-\{^{1}H\}$ n.m.r. spectrum of $[Rh_3(CO)_2(\mu-CO)_3(PMePh_2)(\mu-dppm)_2]ClO_4$. See Table for data

spectroscopic changes described above do, in fact, result from redistribution of ^{13}CO.

Considering the ease with which the unique terminal carbonyl underwent exchange, it was of interest to see whether or not this carbonyl was also substitutionally labile. Treatment of dichloromethane suspensions of the cluster with tertiary phosphines, PR_3, resulted in immediate dissolution of the starting material along with gas evolution. As expected, the products of these reactions were identified as $[Rh_3(CO)_2(\mu-CO)_3(PR_3)(\mu-dppm)_2]ClO_4$ [R_3 = $MePh_2$ (**2**), R = Ph (**3**) or Et (**4**), PR_3 = dppm (**5**)]. The $^{31}P-\{^{1}H\}$ n.m.r. spectra establish the site of substitution as Rh^3. Thus the spectrum of complex (**2**) in the dppm region (Figure 2) exhibits a symmetrical second-order pattern virtually identical to that of the parent cluster, except that each line appears to be further split as a result of coupling with the remote phosphorus nucleus, although this splitting of *ca.* 1.1 Hz was only resolved in the low-field region of the spectrum. The signal due to the $PMePh_2$ ligand occurs as a doublet of 1:2:1 triplets at 17.11 p.p.m. with $^{1}J(Rh-P)$ = 200.8 Hz and $^{2}J(Rh-P)$ = 6.9 Hz. The lines forming this multiplet were broad as a result of unresolved coupling with the dppm phosphorus atoms. A similar spectrum was observed for complex (**4**) with the PEt_3 signal centred at 24.54 p.p.m., $^{1}J(Rh-P)$ = 185.6 Hz, and $^{2}J(Rh-P)$ = 6.2 Hz.

The i.r. spectra of complexes (**2**) and (**4**) are also consistent with substitution of the unique terminal CO. In the solid state, ν(CO) maxima occur at *ca.* 1 990, 1 975, 1 920, 1 850, and 1 830 cm^{-1} (see Table). In solution, the two terminal carbonyl bands coalesce to a principal band at *ca.* 1 990 with a high-energy shoulder at *ca.* 2 000 cm^{-1}. A similar situation holds also for the bridging carbonyl bands which appear as a maximum at *ca.* 1 850 cm^{-1} with a low-energy shoulder at *ca.* 1 840 cm^{-1}. Identical spectra are obtained when the ^{13}CO-labelled complex (**1**) is treated with the appropriate phosphine further verifying that it is the Rh^3 carbonyl that is substituted. The triphenylphosphine cluster (**3**) is essentially insoluble in most organic solvents and its characterization was limited. The solid-state i.r. spectrum exhibits ν(CO) at 1 993m, 1 977vs, 1 934mw, 1 849s, and 1 840s cm^{-1}. The close similarity of these values with those of complexes (**2**) and (**4**), and the method of synthesis of (**3**), leaves little doubt as to its formulation, however.

The i.r. spectra of $[Rh_3(CO)_2(\mu-CO)_3(dppm)(\mu-dppm)_2]ClO_4$ (**5**) also establish the close similarity of this complex to its analogues (**2**) and (**4**). The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of cluster (**5**), however, differs from that of its analogues in that a fluxional process exchanging the ends of the dppm-*P* ligand is operative. At room temperature the ^{31}P n.m.r. spectrum is remarkably similar in form to that of the parent cluster (**1**). On cooling to −40 °C, however, separate signals for the free and co-ordinated ends of the dppm-*P* ligand could be identified at −25.15 and 27.23 p.p.m. respectively. The signal at −25.15 p.p.m. occurs as a doublet [$^{2}J(P_aP_b)$ = 103 Hz] and that at 27.23 as a doublet of doublets [$^{2}J(P_aP_b)$ = 102 Hz, $^{1}J(Rh_bP_b)$ = 201.7 Hz]. At this temperature, crystallization of the solute occurred with the result that the spectrum was too broadened to allow resolution of further rhodium-phosphorus couplings as seen for complexes (**2**) and (**4**). This fluxional behaviour was also reflected in the ^{1}H n.m.r. spectrum which showed a triplet for the dppm-*P* methylene protons at 3.17 p.p.m. [$^{2}J(HP)$ = 5.1 Hz] at room temperature. At −35 °C, however, a poorly resolved complex multiplet was observed, consistent with now differing phosphorus environments. Fluxional behaviour of this type with dppm-*P* ligands has ample precedent.[6–9]

Surprisingly, treatment of the phosphine-substituted clusters

Table. I.r. and n.m.r. (${}^1H$, ${}^{31}P\text{-}\{{}^1H\}$, and ${}^{13}C\text{-}\{{}^1H\}$) data of $[Rh_3(\mu\text{-}CO)_3(CO)_3(\mu\text{-dppm})_2]ClO_4\cdot CH_2Cl_2$ and its phosphine derivatives

Compound	$\tilde{\nu}(CO)^a$/cm^{-1}	N.m.r.^{b}
(**1**) $[Rh_3(CO)_3(\mu\text{-}CO)_3(\mu\text{-dppm})_2]ClO_4\cdot CH_2Cl_2$	2 032m, 2 008vs, 1 929w, 1 872 (sh), 1 869s [2 035m, 2 000 (sh), 1 998vs, 1 924w, 1 869 (sh), 1 858s]	${}^{31}P$: 25.60 [m, dppm, $\lvert {}^1J(Rh–P) + {}^xJ(Rh–P)\rvert$ = 93.7, ${}^2J(Rh_b–P)$ = 2.5] ${}^1H$: 7.37 (m, 40 H, Ph), 5.32 (s, CH_2Cl_2), 3.65, 3.36 (m, 4 H, CH_2 dppm)^c
(**1a**) $[Rh_3(CO)_2({}^{13}CO)(\mu\text{-}CO)_3(\mu\text{-dppm})_2]ClO_4\cdot CH_2Cl_2$	2 008vs, 1 980m, 1 929w, 1 872 (sh), 1 869s	${}^{13}C$: 185.7 [d, ${}^1J(Rh_b–C)$ = 90.0]
(**2**) $[Rh_3(CO)_2(\mu\text{-}CO)_3(PMePh_2)(\mu\text{-dppm})_2]ClO_4$	2 003 (sh), 1 993vs, 1 920mw, 1 853s, 1 845 (sh) [1 992m, 1 982 (sh), 1 975vs, 1 919mw, 1 855s, 1 837 (sh)]	${}^{31}P$: 24.82 [m, dppm, $\lvert {}^1J(Rh–P) + {}^xJ(Rh–P)\rvert$ = 100.6], 17.11 [dt, $PMePh_2$, ${}^1J(Rh_b–P_b)$ = 200.8, ${}^2J(Rh–P_b)$ = 6.9] ${}^1H$: 7.21 (m, 50 H, Ph), 3.65 (m, 4 H, CH_2 dppm), 1.92 [dd, 3 H, $PMePh_2$, ${}^2J(P_b–H)$ = 8.0, ${}^3J(Rh_b–H)$ = 1.8]^d
(**2a**) $[Rh_3(CO)_2(\mu\text{-}CO)(\mu\text{-}{}^{13}CO)_2(PMePh_2)(\mu\text{-dppm})_2]ClO_4$	2 003 (sh), 1 993vs, 1 877mw, 1 853m, 1 811s	${}^{13}C$: 245.7 (dm, J 55)
(**3**) $[Rh_3(CO)_2(\mu\text{-}CO)_3(PPh_3)(\mu\text{-dppm})_2]ClO_4$	[1 993m, 1 977vs, 1 934mw, 1 849s, 1 840s]	
(**4**) $[Rh_3(CO)_2(\mu\text{-}CO)_3(PEt_3)(\mu\text{-dppm})_2]ClO_4$	2 002 (sh), 1 991vs, 1 919mw, 1 850s, 1 841 (sh) [1 990s, 1 974vs, 1 919mw, 1 850s, 1 841 (sh)]	${}^{31}P$: 23.31 [m, dppm, $\lvert {}^1J(Rh–P) + {}^xJ(Rh–P)\rvert$ = 101.2], 24.54 [dt, PEt_3, ${}^1J(Rh_b–P_b)$ = 185.6, ${}^2J(Rh–P_b)$ = 6.2] ${}^1H$: 7.26 (m, 40 H, Ph), 3.71 (m, 4 H, CH_2 dppm), 1.68 (m, 6 H, CH_2 PEt_3), 1.13 (m, 9 H, CH_3 PEt_3)
(**4a**) $[Rh_3(CO)_2(\mu\text{-}CO)(\mu\text{-}{}^{13}CO)_2(PEt_3)(\mu\text{-dppm})_2]ClO_4$	2 002 (sh), 1 991vs, 1 880mw, 1 850m, 1 811s	${}^{13}C$: 247.0 (dm, J 53)
(**5**) $[Rh_3(CO)_2(\mu\text{-}CO)_3(dppm)(\mu\text{-dppm})_2]ClO_4\cdot 0.5CH_2Cl_2$	2 003 (sh), 1 995vs, 1 919mw, 1 850s, 1 845 (sh) [1 995 (sh), 1 978vs, 1 921mw, 1 849 (sh), 1 844s]	${}^{31}P$: 24.87 [m, dppm, $\lvert {}^1J(Rh–P) + {}^xJ(Rh–P)\rvert$ = 99.7], 27.23 [dd, dppm-P, ${}^2J(P_a–P_b)$ = 102, ${}^1J(Rh_b–P_b)$ = 201.7]^e, −25.15 [d, dppm-P, ${}^2J(P_a–P_b)$ = 103]^e ${}^1H^c$: 7.17 (m, 60 H, Ph), 5.32 (s, CH_2Cl_2), 3.90, 3.61 (m, 4 H, CH_2 dppm), 3.17 [t, 2 H, dppm-P, ${}^2J(P–H)$ = 5.1]
(**5a**) $[Rh_3(CO)_2(\mu\text{-}CO)(\mu\text{-}{}^{13}CO)_2(dppm)(\mu\text{-dppm})_2]ClO_4$	2 003 (sh), 1 995vs, 1 880 (sh), 1 850m, 1 810s	${}^{13}C$: 246.7 (dm, J 57.4)

[a] Recorded in dichloromethane solution. Solid-state values in square brackets. [b] Chemical shifts (in p.p.m.) relative to tetramethylsilane (${}^1H$ and ${}^{13}C$) and 85% phosphoric acid (${}^{31}P$), positive downfield, J values in Hz. All spectra run in CD_2Cl_2, ${}^{31}P$ at 40 or 140 MHz, ${}^1H$ at 80 MHz unless otherwise stated, and ${}^{13}C$ at 90 MHz. Rh_b = bridging rhodium atom, *i.e.* Rh^3; P_b = phosphorus attached to bridging rhodium atom. [c] Run at 360 MHz. At 80 MHz these dppm methylene multiplets overlap at 3.40 p.p.m. Similar behaviour was observed for the other complexes examined in this study and has been observed for other A-frame complexes.[4] [d] Couplings assigned by comparison to data quoted for *trans*-$[RhCl(CO)(PMePh_2)_2]$ (B. E. Mann, C. Masters, and B. L. Shaw, *J. Chem. Soc. A*, 1971, 1104). [e] At −40 °C. Broad lines with width at half-height *ca.* 40 Hz.

(**2**), (**4**), and (**5**) with ${}^{13}CO$ resulted in the relatively rapid exchange [10 min for (**2**)] of the two equivalent bridging carbonyls. No evidence was seen for replacement of the phosphine ligand and, in fact, carbonylation of the phosphine cluster (**2**) to regenerate (**1**) was found to take over 80 h at room temperature under 2.1 MPa (30 lbf in^{-2}) of carbon monoxide. Similarly, no evidence was seen for initial exchange of the unique bridging carbonyl and the terminal carbonyl groups, although it was apparent that scrambling of the label to the terminal positions can occur very slowly when the complexes are left in solution. Infrared and ${}^{13}C\text{-}\{{}^1H\}$ n.m.r. spectroscopy together establish the site of exchange. Thus, on exposure to ${}^{13}CO$, complex (**2**) exhibits solution i.r. maxima at 2 003 (sh), 1 993vs, 1 877mw, 1 853m and 1 811s cm^{-1}, where only the original bands at 1 920 and 1 845 cm^{-1} have shifted, indicating that they arise from the symmetric and antisymmetric stretching modes of the two equivalent bridging carbonyls. The ${}^{13}C\text{-}\{{}^1H\}$ n.m.r. spectrum of labelled (**2**) shows a doublet of multiplets centred at 245.7 p.p.m. with a separation of *ca.* 55 Hz, similar to that observed for (**1**). This eliminates the possibility of exchange of the 1,2-bridging carbonyl since a pattern consisting of a triplet of quintets would be expected.[10] An entirely analogous situation pertains for clusters (**4**) and (**5**). The occurrence of a double multiplet rather than a double double multiplet for the bridging carbonyl signals of (**2**), (**4**), and (**5**) must mean that one of the Rh–C (bridging) coupling constants is considerably smaller than the other of *ca.* 55 Hz. This could imply significant asymmetry in the bridging mode of these carbonyls. The *X*-ray analysis referred to earlier certainly seems to suggest that the carbonyls bridging Rh^1 and Rh^3, and Rh^2 and Rh^3, are of the semi-bridging type, although we have no further evidence in support of this.

Any attempt to explain the formation of the cluster (**1**) must at some point invoke a reduction step to account for the +1/3 formal oxidation state of the rhodium atoms in the cluster. This is most likely achieved through reduction of the bridging ligand by carbon monoxide (in the case of the μ-OH complex) or an α- or β-hydride elimination (in the case of the μ-OR dimers) followed in both cases by H^+ elimination. The OR ligands in the A-frame complexes employed in this synthesis are known to be acid labile[4] and hence the $Rh(CO)_3{}^+$ fragment may originate from further carbonylation of a complex such as $[Rh_2(CO)_4(\mu\text{-dppm})_2]^{2+}$. Evaporating the filtrate to dryness after isolating the cluster does result in the isolation of an amorphous, ionic mustard coloured material (80—90 mg) with ν(CO) at 1 991 cm^{-1} (CH_2Cl_2) which suggests a complex of rhodium(I). All attempts to characterize this complex, however, have failed primarily due to our inability to isolate a pure crystalline sample. It is quite obvious that the mechanism of cluster formation involves more than the simple combination of a dimer with a monomeric fragment, a fact borne out by our inability to improve upon the yield of (**1**) by performing the carbonylation

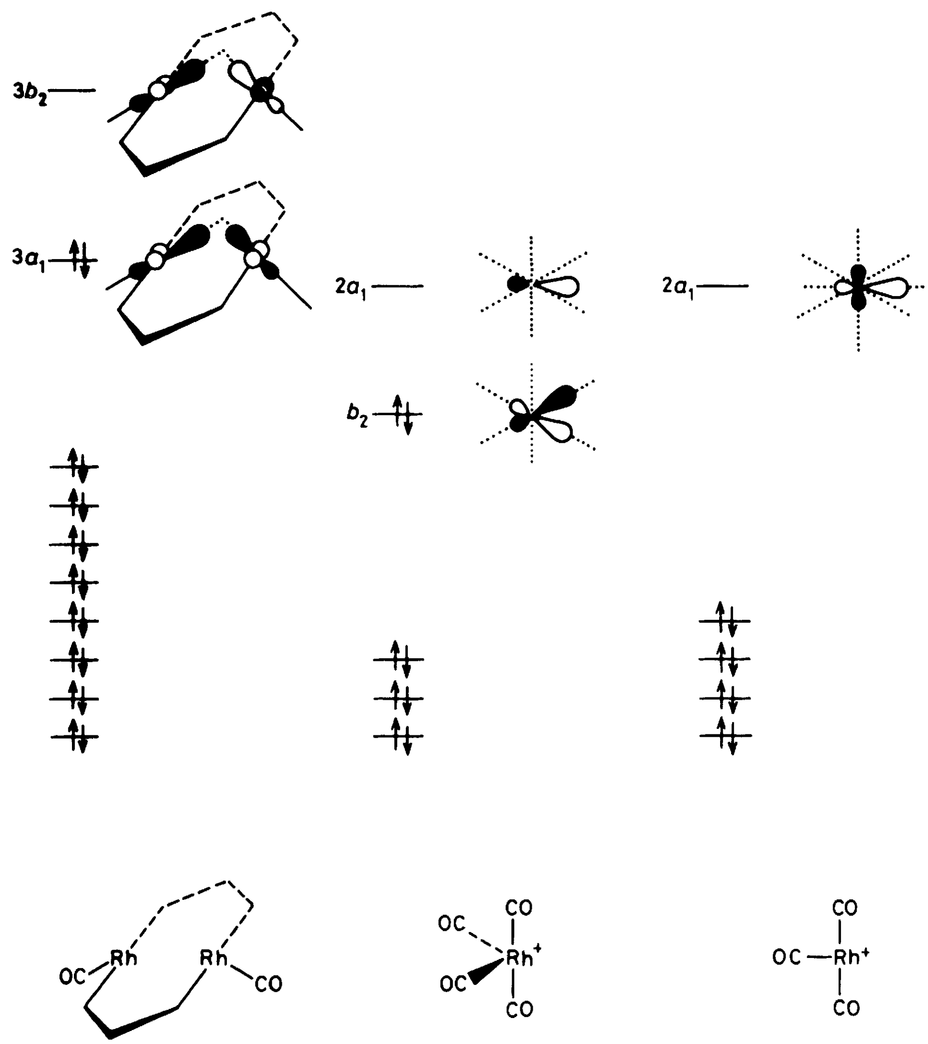


Figure 3. Frontier molecular orbitals of the metal fragments $Rh_2(CO)_2(\mu\text{-dppm})_2$, $Rh(CO)_4^+$, and $Rh(CO)_3^+$. The energy levels are not to scale

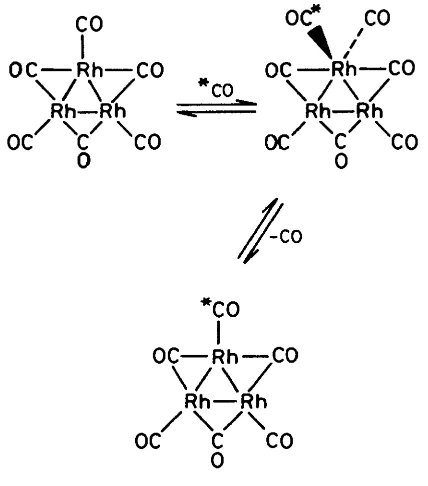
in the presence of stoicheiometric amounts of monomers or monomer precursors such as $[Rh_2Cl_2(CO)_4]$, $[Rh(cod)(PPh_3)_2]^+$ (cod = cyclo-octa-1,5-diene), and [Rh(cod)(acac)] (acac = acetylacetonate). The complex $[Rh_2Cl_2(CO)_4]$, like $[Ir_2Cl_2(cod)_2]$ merely generated $[Rh_2(\mu\text{-Cl})(CO)_2(\mu\text{-dppm})_2]ClO_4$ as the only isolable dimer and the other rhodium monomers merely gave the cluster with no change in yield.

Undoubtedly, the most interesting feature of the clusters (**1**)—(**5**) is their unsaturation, especially so for (**1**) which is formed under CO. The factors contributing to this unsaturation can most readily be appreciated by regarding (**1**) and its derivatives as further examples of A-frame complexes in which the bridging group is an $Rh(CO)_2L$ fragment. Concentrating for the moment on the parent cluster (**1**), a qualitative molecular-orbital picture can easily be drawn by utilizing the approach developed by Hoffman and Hoffmann.[1] This approach consists of examining the combination of frontier oribitals for a suitable d^9–d^9 M_2L_6 fragment [in this case $Rh_2(CO)_2(\mu\text{-dppm})_2$] (Figure 3) with the frontier orbitals of appropriate bridging groups. It should be pointed out here that this approach is a first approximation only in this case since the effect of the three carbonyl bridges is not being given full consideration. While we cannot easily gauge the effect of the carbonyl bridges between Rh^3 and the Rh^1 and Rh^2 atoms, it seems reasonable to assume that the effect of including the third bridging carbonyl group on the arguments to follow will be slight. Sufficient examples of A-frame complexes and their carbonyl adducts are now known to suggest that whereas there is an apparent lengthening of the bonds to the apex ligand upon forming a carbonyl adduct (apparently as much as result of increased steric pressures as any other factor),[11,12] there do not appear to be any major changes in the nature of the frontier orbitals of the binuclear fragment upon adduct formation.

To appreciate the reasons for the unsaturation of complex (**1**) it is instructive to examine the combination of the M_2L_6 fragment with d^8 $Rh(CO)_3^+$ and $Rh(CO)_4^+$ moieties, both of C_{2v} symmetry, the frontier orbitals of which are also depicted in Figure 3.* For the $Rh(CO)_3^+$ fragment the dominant bonding interaction will be between the filled M_2L_6 $3a_1$ level and the empty $Rh(CO)_3^+$ $2a_1$ orbital. Further but much weaker interactions can be expected between the empty M_2L_6 $3b_2$ orbital and either of the lower-lying b_1 or b_2 orbitals of the $Rh(CO)_3^+$ fragment, depending on whether the $Rh(CO)_3$ plane is coplanar with or perpendicular to the Rh_3 plane. These latter interactions will be of approximately the same magnitude, allowing steric and other factors (such as the

---

* The frontier orbitals for $Rh(CO)_3^+$ and $Rh(CO)_4^+$ fragments of C_{2v} symmetry will be analogous to those derived earlier for $[PtCl_3]^-$ and $[Fe(CO)_4]$ respectively.[11]

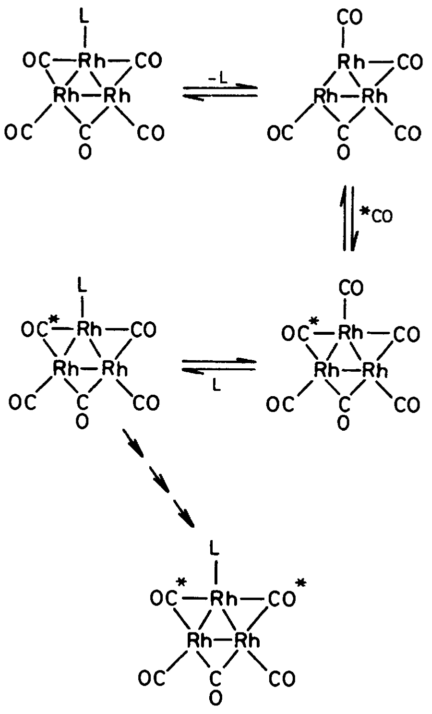


Scheme 1.

formation of carbonyl bridges) to determine the orientation of the bridging group. Hence, coplanarity of the Rh$_3$ plane with all terminal and bridging carbonyls is to be expected in complex (**1**).

At first glance, using this approach, a bridging Rh(CO)$_4$$^+$ moiety might appear to be favoured because of the occurrence of two strong bonding interactions between the $3a_1$ and $3b_2$ orbitals of M$_2$L$_6$ and the $2a_1$ and b_2 orbitals of Rh(CO)$_4$$^+$. Overlap between the $3b_2$ and b_2 orbitals, however, can be achieved only when the Rh(CO)$_4$$^+$ fragment is oriented with the mutually *trans* carbonyls perpendicular to the Rh$_3$ plane. This orientation is strongly disfavoured sterically. A typical feature of the structure of the rhodium A-frame complexes and their adducts is the occurrence of *cis* folding of the dppm methylene groups in order to avoid eclipsing of phenyl rings on the dppm ligands with the equatorial ligands (in this case, the terminal carbonyls attached to Rh^1 and Rh^2).[14] In the case of [Rh$_2$(μ-Cl)(CO)$_2$(μ-dppm)$_2$]$^+$ this folding results in non-bonded contacts of 2.85 and 2.90 Å between the appropriate methylene protons and the bridging chloride group. Quite obviously, severe repulsive interactions would result if the bridging rhodium of the cluster bore carbonyl groups, of *ca.* 3.0 Å in length, perpendicular to the Rh^3 plane. Thus the only favourable orientation for a bridging Rh(CO)$_4$$^+$ fragment in a cluster such as (**1**) would have the mutually *trans* carbonyls in the Rh$_3$ plane in a position suited to the formation of bridges, with the remaining two terminal carbonyls at right angles to this plane and at *ca.* 90° to one another. Considering only the number and type of frontier orbital overlaps, therefore, there seems little to choose between bridging Rh(CO)$_3$$^+$ and bridging Rh(CO)$_4$$^+$ moieties. The observed stoichieometry of (**1**) then, would appear to indicate a somewhat more efficient overlap between the orbitals of the bridging Rh(CO)$_3$$^+$ moiety with those of the Rh$_2$(CO)$_2$(μ-dppm)$_2$ fragment, as well as reflecting a slightly greater degree of steric pressure introduced with a bridging Rh(CO)$_4$$^+$ group.

Another interesting facet of the chemistry of the clusters (**1**)—(**5**) is their selective carbonyl-exchange reactions. In view of the unsaturation of (**1**) and in light of the preceding arguments, an associative mechanism (Scheme 1) seems most likely for the exchange of the unique terminal carbonyl in this cluster. The great facility with which this exchange occurs further suggests that the difference in stability between (**1**) and its 48-electron analogue [Rh$_3$(CO)$_4$(μ-CO)$_3$(μ-dppm)$_2$]ClO$_4$ is not great. For the phosphine clusters (**2**)—(**5**) a similar associative mechanism can be ruled out for two reasons. First, molecular modelling clearly demonstrates the existence of impossible steric pressures in the analogous 48-electron intermediates, and secondly, even in the event that an associative intermediate could be formed, there is no reason to suspect facile interchange between the bridging and terminal carbonyl groups on Rh^3 as required. Instead we favour a dissociative mechanism of the type depicted in Scheme 2.



Scheme 2.

The unsaturation of (**1**) led us to attempt to use the cluster as a homogeneous catalyst for the hydrogenation of olefins. Attempts to hydrogenate 1-hexene and 1-octene were successful, but only after an induction period of 5 h by which time the interior of the vessel was coated with a black deposit. It would, therefore, appear that only heterogeneous catalysis was occurring with rhodium black functioning as the catalyst. Further work aimed at exploiting the co-ordinative unsaturation of complex (**1**) is in progress.

Experimental

Infrared spectra were recorded on Perkin-Elmer 180 or 283B grating spectrophotometers either for Nujol mulls on KBr plates or for CH$_2$Cl$_2$ solutions in NaCl cells. Calibration was achieved with either polystyrene or indene. Proton and ^{13}C n.m.r. spectra were recorded on a Varian Associates CFT20 and the Nicolet 360 MHz spectrometer of the Atlantic Region Magnetic Resonance Centre; SiMe$_4$ (^{1}H) and CD$_2$Cl$_2$ (^{13}C) were used as internal calibrants. Phosphorus-31 n.m.r. spectra were obtained on a Varian Associates XL100 spectrometer of the National Research Council Atlantic Regional Laboratory, whose assistance is gratefully acknowledged. Samples were run either as CD$_2$Cl$_2$ solutions in 5-mm tubes or in CH$_2$Cl$_2$ in 12-mm concentric tubes with CD$_2$Cl$_2$ as lock. In both cases, chemical shifts were determined relative to 85% phosphoric acid as an external standard. Conductivity measurements were made by using an Industrial Instruments conductivity bridge with *ca.* 10^{-3} mol dm^{-3} solutions in dichloromethane or acetone at 25 °C. The cell constant was determined using 0.0100 mol dm^{-3}

KCl solution. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by the Canadian Microanalytical Service Ltd., British Columbia.

Preparation of Complexes.—All reagents were of A.C.S. quality or better and were used without further purification. The solvents were appropriately dried and distilled before being stored over type 4A molecular sieves. All complexes prepared were subjected to vacuum drying prior to the recording of physical and analytical data, unless otherwise stated. Labelling of complexes with ^{13}CO was achieved by subjecting CH_2Cl_2 solutions of the compounds to ^{13}CO (Stohler Isotope Chemicals, 90% ^{13}C) at a partial pressure of *ca.* 250 mmHg (*ca.* 36 kPa) on a standard Toepler line. Under these conditions, exchange is essentially complete within 5 min for 30-mg samples.

Synthesis of $[Rh_3(CO)_3(\mu\text{-}CO)_3(\mu\text{-dppm})_2]ClO_4{\cdot}CH_2Cl_2$ (**1**).—(*a*) *From* $[Rh_2(\mu\text{-}OR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (R = Me *or* Et). A solution containing $[Rh_2(\mu\text{-}OR)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.20 g, 0.17 mmol) dissolved in dichloromethane (5 cm^3) and ROH (0.5 cm^3) was subjected to a carbon monoxide pressure of 2.1 MPa (30 lbf in^{-2}) at 25 °C for 2 h. During the course of the reaction the colour of the solution changed from yellow to red-brown and an orange precipitate developed. After venting the reaction vessel, diethyl ether was added dropwise to complete the precipitation. The product was collected by filtration, washed with diethyl ether, and recrystallized from dichloromethane–diethyl ether in the form of long orange needles (0.085 g, 52% based on available rhodium), m.p. 146—160 °C (decomp.) (Found: C, 47.85; H, 3.25; P, 9.90. Calc. for $C_{57}H_{46}Cl_3O_{10}P_4Rh_3$: C, 47.85; H, 3.20; P, 8.70%). Evidence for the dichloromethane solvate molecule was obtained from the ^{1}H n.m.r. spectrum in $(CD_3)_2CO$ (5.60 p.p.m., 2 H). $\Lambda_M = 131.7\ \Omega^{-1}$ cm^2 equiv.$^{-1}$ (acetone).

(*b*) *From* $[Rh_2(\mu\text{-}OH)(CO)_2(\mu\text{-dppm})_2]ClO_4$. In a procedure analogous to that described above, but without added alcohol, $[Rh_2(\mu\text{-}OH)(CO)_2(\mu\text{-dppm})_2]ClO_4$ (0.20 g, 0.17 mmol) was subjected to carbon monoxide pressure under identical conditions. Work-up was as described above (0.055 g, 34% based on available rhodium).

Reaction of $[Rh_3(CO)_3(\mu\text{-}CO)_3(\mu\text{-dppm})_2]ClO_4$ *with Phosphines.—Synthesis of* $[Rh_3(CO)_2(\mu\text{-}CO)_3(PMePh_2)(\mu\text{-dppm})_2]\text{-}ClO_4$ (**2**). To $[Rh_3(CO)_3(\mu\text{-}CO)_3(\mu\text{-dppm})_2]\text{-}ClO_4{\cdot}CH_2Cl_2$ (0.10 g, 0.070 mmol) suspended in dichloromethane (5 cm^3) was added a slight excess of $PMePh_2$ (0.016 cm^3, *ca.* 0.080 mmol). The suspended solid immediately dissolved, with slight gas evolution. After stirring for 10 min, diethyl ether was added to the red solution to precipitate an orange solid which was recrystallized from dichloromethane–diethyl ether as red-orange crystals (0.091 g, 86%), m.p. decomp. >165 °C (Found: C, 52.8; H, 3.60; P, 10.05. Calc. for $C_{68}H_{57}ClO_9P_5Rh_3$: C, 53.85; H, 3.80; P, 10.2%). $\Lambda_M = 126.2\ \Omega^{-1}$ cm^2 mol^{-1} (acetone).

Using analogous procedures, the following were obtained: $[Rh_3(CO)_2(\mu\text{-}CO)_3(PPh_3)(\mu\text{-dppm})_2]ClO_4$ (**3**), 94%, orange solid (Found: C, 55.15; H, 3.60; P, 8.80. Calc. for $C_{73}H_{59}\text{-}ClO_9P_5Rh_3$: C, 55.5; H, 3.75; P, 9.80%); $[Rh_3(CO)_2(\mu\text{-}CO)_3\text{-}(PEt_3)(\mu\text{-dppm})_2]ClO_4$ (**4**), 73%, orange crystals (Found: 50.0; H, 3.95; P, 9.40. Calc. for $C_{61}H_{59}ClO_9P_7Rh_3$: C, 51.05; H, 4.15; P, 10.8%), $\Lambda_M = 128\ \Omega^{-1}$ cm^2 mol^{-1} (acetone); $[Rh_3(CO)_2(\mu\text{-}CO)_3(dppm)(\mu\text{-dppm})_2]ClO_4{\cdot}0.5CH_2Cl_2$ (**5**), 90%, red crystals (Found: C, 55.05; H, 3.75; P, 11.4. Calc. for $C_{80.5}H_{67}Cl_2\text{-}O_9P_6Rh_3$: C, 55.4; H, 3.85; P, 10.65%), $\Lambda_M = 124\ \Omega^{-1}$ cm^2 mol^{-1} (acetone), δ_H [solvent $(CD_3)_2CO$, standard $SiMe_4$] 5.60 (1 H, s, CH_2Cl_2).

Acknowledgements

The authors thank N.S.E.R.C. for financial assistance and Johnson Matthey Ltd. for a generous loan of rhodium trichloride. Our thanks are also due to Professor J. Mague for the ^{31}P n.m.r. simulation.

References

1 D. M. Hoffman and R. Hoffmann, *Inorg. Chem.*, 1981, **20**, 3543.
2 C. P. Kubiak, C. Woodcock, and R. Eisenberg, *Inorg. Chem.*, 1982, **21**, 2119.
3 M. P. Brown, J. R. Fisher, S. J. Franklin, R. J. Puddephatt, and M. A. Thompson, *Adv. Chem. Ser.*, 1982, **196**, 231 and refs. therein; A. L. Balch, *ibid.*, p. 243 and refs. therein.
4 S. P. Deraniyagala and K. R. Grundy, *Inorg. Chem.*, 1985, **24**, 50.
5 S. P. Deraniyagala and K. R. Grundy, *Inorg. Chim. Acta*, 1984, **84**, 205.
6 E. E. Isaacs and W. A. G. Graham, *Inorg. Chem.*, 1975, **14**, 2560.
7 M. P. Brown, J. R. Fisher, R. H. Hill, R. J. Puddephatt, and K. R. Seddon, *Inorg. Chem.*, 1980, **19**, 3516.
8 M. M. Olmstead, C. Lee, and A. L. Balch, *Inorg. Chem.*, 1982, **21**, 2712.
9 P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 581.
10 J. T. Mague and A. R. Sanger, *Inorg. Chem.*, 1979, **18**, 2060.
11 M. Cowie and S. K. Dwight, *Inorg. Chem.*, (*a*) 1979, **18**, 858; (*b*) 1980, **19**, 2500.
12 S. P. Deraniyagala and K. R. Grundy, *Inorg. Chim. Acta*, in the press.
13 T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, 1979, **101**, 3801.
14 M. Cowie, *Inorg. Chem.*, 1979, **18**, 286 and refs. therein.

Received 13*th August* 1984; *Paper* 4/1421