Adducts of Trigonal-Prismatic and Octahedral Metal Clusters containing Interstitial Atoms (Nitrogen or Carbon) with $[Au(PPh_3)]^+$

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Spectroscopic evidence indicates that the anion $[Rh_6N(CO)_{15}]^-$ reacts with $[Au(PPh_3)Cl]$ to afford $[Rh_6N(CO)_{15}\{Au(PPh_3)\}]$, but there is no evidence that a similar reaction with either CF_3CO_2H or $HBF_4{\cdot}Et_2O$ leads to $[Rh_6(H)N(CO)_{15}]$. Addition of $[Au(PPh_3)Cl]$ to $[Rh_6C(CO)_{13}]^{2-}$ at −80 °C gives $[Rh_6C(CO)_{13}\{Au(PPh_3)\}]^-$, in which there is complete migration of the $Au(PPh_3)$ group and all the carbonyls around the Rh_6 octahedron even at −80 °C. At higher temperatures, $[Rh_6C(CO)_{13}\{Au(PPh_3)\}]^-$ loses CO and forms $[Rh_6C(CO)_{12}\{Au(PPh_3)\}]^-$, which has been characterised by a variety of multinuclear NMR measurements. Spectroscopic evidence is presented to suggest that a related 84-electron octahedral cluster $[Rh_6N(CO)_{12}]^-$ is formed, rather than the 86-electron cluster $[Rh_6N(CO)_{13}]^-$, on heating $[Rh_6N(CO)_{15}]^-$.

There are now many adducts of metal carbonyls with the $[M(PPh_3)]^+$ group (M = Cu, Ag or Au). This group is isolobal with H^+ and, as a result, much effort has been associated with establishing whether H^+ and the $[M(PPh_3)]^+$ group occupy similar sites in metal clusters. The structures of these adducts have recently been reviewed.[1]

There is now an extensive class of carbide and some nitride clusters $[M_6E(CO)_x]^{n-}$ (M = Co or Rh, x = 13 or 15; E = N, n = 1; E = C, n = 2) with the nitrogen or carbon at the centre of the trigonal-prismatic (x = 15) or octahedral (x = 13) homo- or hetero-metallic polyhedron.[2-9] It has already been shown that the trigonal-prismatic cluster $[Rh_6C(CO)_{15}]^{2-}$ adds electrophiles, such as $[M(PR_3)]^+$ (M = Cu, Ag or Au; R = Ph or Et), $[Cu(NCMe)]^+$,[5,10,11,12] Ag^+ [12] or H^+ [13] to the trigonal Rh_3 face. It was of interest to extend these reactions to the isostructural nitride cluster, $[Rh_6N(CO)_{15}]^-$, and to the octahedral cluster $[Rh_6C(CO)_{13}]^{2-}$. The results form the basis of this paper.

Results and Discussion

Addition of $[Au(PPh_3)Cl]$ to a solution of $[N(PPh_3)_2][Rh_6N(CO)_{15}]$ in CH_2Cl_2 in the presence of acid ($HBF_4{\cdot}OEt_2$) produced $[Rh_6N(CO)_{15}\{Au(PPh_3)\}]$ **1** which has been characterised by multinuclear NMR measurements and shown to be isostructural with the analogous carbide derivative.[11] Unlike $[Rh_6C(CO)_{15}]^{2-}$, further addition of $[Au(PPh_3)Cl]$ (up to three equivalents) to $[Rh_6N(CO)_{15}]^-$ does *not* result in the formation of the bis-gold adduct. It is important to note that formation of the mono-gold adduct only occurs in the presence of acid. This rather surprising result probably stems from the fact that $[N(PPh_3)_2]^+$, salts are often found to be much less reactive than salts with smaller cations (*e.g.* Na^+) and the enhanced reactivity of $[N(PPh_3)_2][Rh_6N(CO)_{15}]$ in the presence of acid undoubtedly stems from cation exchange. It should also be noted that we have no NMR evidence (^1H or ^{13}C) for the formation of $[Rh_6(H)N(CO)_{15}]$ on addition of either CF_3CO_2H or $HBF_4{\cdot}OEt_2$ (10-fold excess) to $[N(PPh_3)_2][Rh_6N(CO)_{15}]$ over a range of temperatures (−80 to + 25 °C). The lack of formation of $[Rh_6(H)N(CO)_{15}]$ must be associated with the monoanionic charge on the cluster $[Rh_6N(CO)_{15}]^-$, inducing a weaker electrostatic attraction for H^+ compared to $[Rh_6C(CO)_{15}]^{2-}$ which readily forms $[Rh_6(H)C(CO)_{15}]^-$.[13]

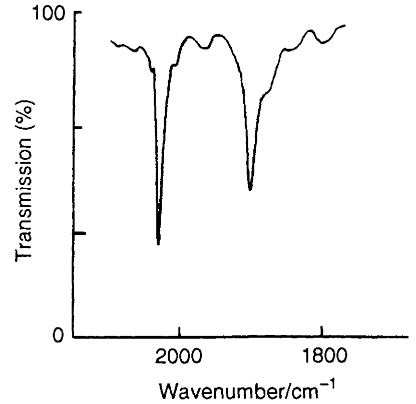

Fig. 1 IR spectrum of $[Rh_6N(CO)_{15}\{Au(PPh_3)\}]$ **1** in thf

Small yellow crystals of compound **1** could be obtained from either CH_2Cl_2 or tetrahydrofuran (thf) but unfortunately they were not suitable for X-ray structural analysis. However, there can be little doubt about the structure of **1** from the following spectroscopic measurements.

The IR spectrum of compound **1** in thf (Fig. 1) shows bands in the carbonyl stretching region at 2080(sh), 2050s, 2000(sh), 1895m and 1870m cm^{-1} and is very similar to the IR spectrum of $[Rh_6C(CO)_{15}\{Au(PPh_3)\}]^-$ [5] except for the expected shift of the bands to higher frequency as a result of the reduced charge on the cluster.

The $^{31}P-\{^1H\}$ NMR spectrum of compound **1** in $[^2H_8]$thf both at 25 and −80 °C is a quartet [δ(P) +59.4, ^2J(Rh-P) 5.6 Hz] which is consistent with the $Au(PPh_3)$ group capping the trigonal face, Fig. 2.

Consistent with the structure shown in Fig. 2, the $^{13}C-\{^1H\}$ NMR spectrum of **1** in thf at 25 °C consists of three equally intense triplets due to the three bridging carbonyl groups CO^c, CO^d and CO^e at δ 212.9, 224.4 and 216.8 and two equally intense doublets due to two sets of inequivalent terminal carbonyls CO^a and CO^b, at δ 191.5 and 190.8 respectively. It should be noted that the triplet at δ 224.4 arises from accidental equivalence of $^1J(Rh_x{-}CO^d)$ and $^1J(Rh_y{-}CO^d)$. These assignments follow from specific $^{13}C-\{^{103}Rh\}$ measurements and the NMR data for compound **1** are compared to those reported previously for $[Rh_6C(CO)_{15}\{Au(PPh_3)\}]^-$ in Table 1.

Table 1 Comparison of NMR data for mono-gold adducts of $[Rh_6N(CO)_{15}]^-$ and $[Rh_6C(CO)_{15}]^{2-}$ in $[^2H_8]$thf solution at room temperature. Figures in parentheses are the data of the parent carbide and nitride clusters. Labelling as in Fig. 2.

	$[Rh_6N(CO)_{15}\{Au(PPh_3)\}]$	$[Rh_6C(CO)_{15}\{Au(PEt_3)\}]^-$
$\delta(CO^a)$	191.5(192.7)	193.7(196.9)
$\delta(CO^b)$	190.8(192.7)	193.1(196.9)
$\delta(CO^c)$	212.9(219.2)	218.7(224.0)
$\delta(CO^d)$	224.4(228.3)	230.6(235.4)
$\delta(CO^e)$	216.8(219.2)	223.6(224.0)
$^1J(Rh_X–CO^a)$/Hz	84.7(85.5)	77.2(79.3)
$^1J(Rh_Y–CO^b)$/Hz	82.7(85.5)	74.2(79.3)
$^1J(Rh_X–CO^c)$/Hz	30.2(30.0)	30.8(30.5)
$^1J(Rh_Y–CO^d)$/Hz	46.4(48.1)	46.9(51.4)
$^1J(Rh_X–CO^d)$/Hz	46.1(48.1)	46.9(51.4)
$^1J(Rh_Y–CO^e)$/Hz	26.3(30.0)	27.3(30.5)
$\delta(Rh_X)$	−296.0(−223.0)	−272(−313)
$\delta(Rh_Y)$	−447.5(−223.0)	−433(−313)
$\delta(P)$	59.4	55.5
$^2J(P–Rh)$/Hz	5.6	5.8
Ref.	This work (14)	13(13)

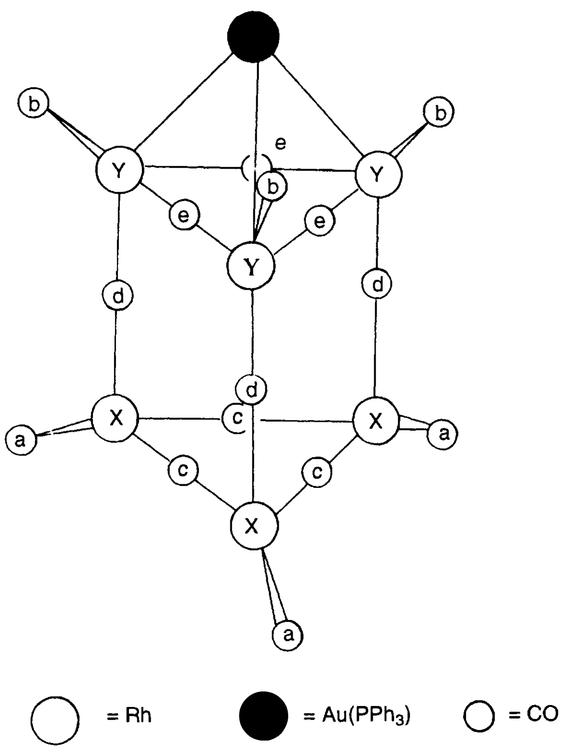

Fig. 2 Schematic representation of $[Rh_6N(CO)_{15}\{Au(PPh_3)\}]$ **1** (the interstitial nitride has been omitted for clarity)

Addition of $[Au(PPh_3)Cl]$ to $[Rh_6C(CO)_{13}]^{2-}$ (1:1) in thf at −78 °C produces $[Rh_6C(CO)_{13}\{Au(PPh_3)\}]^-$ **2**, which loses CO on warming to between −50 and −10 °C to give $[Rh_6C(CO)_{12}\{Au(PPh_3)\}]^-$ **3**. The latter has been formulated on the basis of multinuclear NMR measurements (see later). Addition of $[Au(PPh_3)Cl]$ to $[Rh_6C(CO)_{13}]^{2-}$ in a 2:1 molar ratio at room temperature produces $[Rh_6C(CO)_{13}\{Au(PPh_3)\}_2]$ **4**. We determined the crystal structure of **4** but while this work was in progress the structure was published[15] and shown to be identical to our structural determination with the two $Au(PPh_3)$ groups occupying *cis* faces on the Rh_6 octahedron with an identical distribution of carbonyl groups.

We now report a complete NMR study on **2** and compare the data with those found previously for **4**. Detailed NMR measurements on **3** have allowed us to establish precisely the carbonyl distribution without being able to obtain crystals suitable for an X-ray structural analysis; however it has not been possible to establish unambiguously the exact bonding mode of the $Au(PPh_3)$ group in **3** (see later).

As reported previously for $[Rh_6C(CO)_{13}\{Au(PPh_3)\}_2]$ **4**,[15] there is also fast exchange of both the carbonyls and the $Au(PPh_3)$ group in $[Rh_6C(CO)_{13}\{Au(PPh_3)\}]^-$ **2** over the Rh_6 octahedron, even at −80 °C. Thus, the ^{31}P and both the ^{13}CO and the ^{13}C-carbide resonances all appear as symmetrical septets due to coupling with six equivalent rhodium atoms which also give rise to a single rhodium resonance [$\delta(Rh)$ at −755]. Comparison of the NMR data for $[Rh_6C(CO)_{13}\{Au(PPh_3)\}_x]^{n-}$ ($x = 0, n = 2; x = 1, n = 1; x = 2, n = 0$) in Table 2 show that there is a systematic shift of all the resonances each of which have similar coupling constant values.

Previous work has provided evidence for facile carbonyl rearrangements in metal clusters and NMR studies have also provided evidence for restricted rearrangements of bis-gold fragments over metal polyhedra.[17–19] However, the recent report by Fumagalli *et al.*[15] and our work show that there is complete intramolecular migration of both the mono- and bis-gold fragments over the entire Rh_6 octahedron with concomittant carbonyl interexchange. Lewis and co-workers[20] have also recently shown that the mercury fragment HgX in $[Os_{10}C(CO)_{24}(HgX)]^-$ (X = Cl, Br, I or CF_3) is highly mobile on the surface of the Os_{10} cluster core and such metal skeletal rearrangements may be much more widespread than has hitherto been realised.

On warming from −80 to −50 °C, **2** loses one carbonyl group to give **3** which is static at low temperatures so an almost complete structural characterisation has been possible from NMR measurements.

The direct ^{103}Rh NMR spectrum of $[Rh_6C(CO)_{12}\{Au(PPh_3)\}]^-$ **3** in $[^2H_8]$thf at −50 °C consists of five resonances $\delta(Rh_A)$ +355, $\delta(Rh_B)$ +75, $\delta(Rh_C)$ +164, $\delta(Rh_D)$ −194 and $\delta(Rh_{E,F})$ −253 in the ratio 1:1:1:1:2 with the resonance at δ + 75 appearing as a doublet [$^2J(Rh_B–P)$ 14 Hz]; the ^{31}P resonance (δ 33.6) is a doublet of doublets (14 and 3 Hz) due to two- and three-bond couplings to rhodium atoms. The $^{31}P-\{^{103}Rh\}$ measurements confirm that the two-bond coupling is due to interaction with Rh_B but, because of the small value of the three-bond coupling, it is difficult to be sure as to which rhodium is responsible for this. However, because of the large difference in the values of the Rh–P coupling constants, we feel this is more likely to be due to two- and three-bond couplings arising from the presence of a terminal $Au(PPh_3)$ group rather than due to the presence of an asymmetric bridging $Au(PPh_3)$ group.

Carbon-13 NMR measurements on **3** at low temperature clearly show that there are twelve inequivalent carbonyls [Fig. 3(*f*)] and $^{13}C-\{^{103}Rh\}$ measurements [Fig. 3(*a*)–(*e*)] have allowed their connectivities to be established. Thus, there are six bridging carbonyls CO(1)–CO(6), at δ 240.2, 235.4, 231.5, 225.1, 218.5 and 212.4 respectively and six equally intense

Table 2 Comparison of NMR data for $[Rh_6C(CO)_{13}\{Au(PPh_3)\}_x]^{n-}$ at room temperature

	$x = 0, n = 2^{16}$	$x = 1, n = 1$	$x = 2, n = 0^{15}$
δ(CO)	217.7*	214.7	209.0
J(Rh–CO)/Hz	—	18.0	13.1
$\delta(C_{carbide})$	472.0	465.7	452.5
$^1J(Rh–C_{carbide})$/Hz	11.0	18.0	16.8
δ(P)	—	53.1	56.3
J(Rh–P)/Hz	—	3.65 ± 0.33	3.81 ± 0.63

* Mean value.

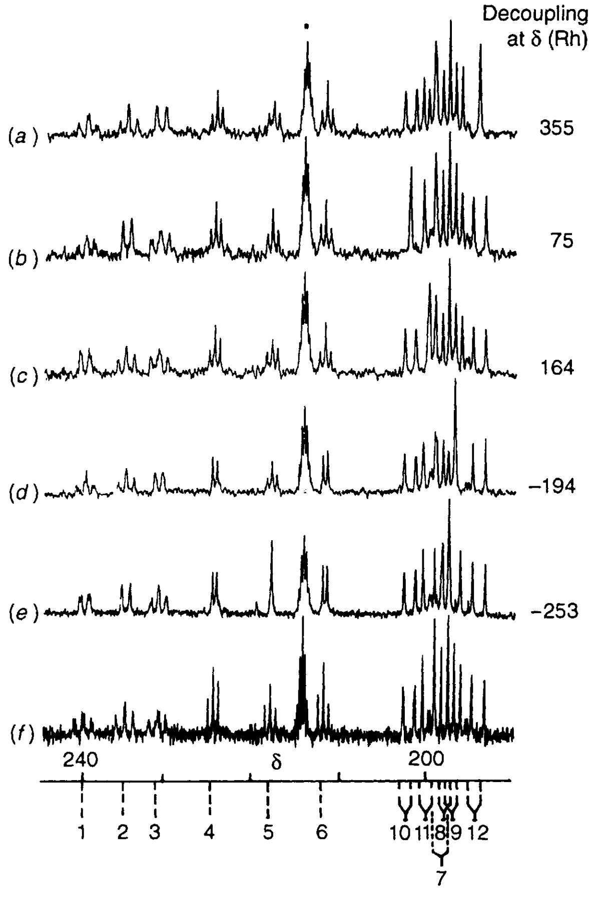

Fig. 3 The $^{13}C-\{^{103}Rh\}$ (*a*)–(*e*) and ^{13}C (*f*) NMR spectra of $[Rh_6C(CO)_{12}\{Au(PPh_3)\}]^-$ **3** (*ca.* 15% ^{13}CO) in $[^2H_8]$thf at −50 °C; * is due to $[Rh_6C(CO)_{13}\{Au(PPh_3)\}]^-$ **2** present as an impurity. The assignments for CO(7) and CO(8) in Fig. 4 may be interchanged

doublets at δ 197.8, 198.6, 197.1, 202.4, 200.1 and 194.2 due to terminal carbonyls which have been assigned as being due to CO(7), CO(8), CO(9), CO(10), CO(11) and CO(12) on $Rh_{E,F}$, Rh_D, Rh_B, Rh_C and Rh_A respectively from $^{13}C-\{^{103}Rh\}$ measurements. Connectivities of the bridging carbonyls can be made similarly. Thus, from Fig. 3: (*a*) decoupling Rh_A in addition to collapsing the doublet at δ 194.2, causes the triplet at δ 231.5 to become a doublet and these CO resonances are assigned to CO(12) and CO(3) respectively, (*b*) decoupling Rh_B, collapses the doublet at δ 202.4 and causes the triplet at δ 235.4 to become a doublet and these resonances are assigned to CO(10) and CO(2) respectively, (*c*) decoupling Rh_C collapses the doublet at δ 200.1 to a singlet and the triplet at δ 240.2 to a doublet due to CO(11) and CO(1) respectively, (*d*) decoupling Rh_D collapses three triplets at δ 231.5, 225.1 and 212.4 to doublets and the doublet at δ 197.0 to a singlet which are assigned to CO(3), CO(4), CO(6) and CO(9) respectively, (*e*) decoupling $Rh_{E,F}$ collapses two doublets at δ 197.8 and 198.6 to two singlets due to CO(7), CO(8) and also collapses three triplets at δ 240.2, 235.4 and 225.1 to doublets, a triplet at δ 218.5 to a singlet and a triplet at δ 212.4 to a doublet; these carbonyl resonances are assigned to CO(1), CO(2), CO(4), CO(5) and CO(6) respectively. It is noteworthy that the collapse of the resonance at δ 212.4 to a singlet arises from a carbonyl bridging Rh_E and Rh_F with the rhodium frequencies of Rh_E and Rh_F being coincident. As expected, the carbide resonance is broad (δ 322.3) due to coupling to all the inequivalent rhodium atoms.

From the above data on $[Rh_6C(CO)_{12}\{Au(PPh_3)\}]^-$ **3**, the rhodium connectivities to all twelve carbonyls and the $Au(PPh_3)$ group are clearly established. The structure consistent with these data is represented schematically in Fig. 4. Since this structure is based on that of an 84-electron Rh_6 octahedron, the implication is that there is some multiple rhodium–rhodium bonding. Although it was impossible to obtain a crystalline sample of **3** for X-ray analysis, analytical data on a solid sample are more consistent with the formulation based on the 84-electron structure rather than the alternative due to the 86-electron cluster, $[NEt_4]_2[Rh_6C(CO)_{12}Cl\{Au(PPh_3)\}]$. Fig. 4(*b*) emphasises the structural similarity of **3** to that adopted by $[Rh_6(CO)_{15}]^{2-}$.[21]

In an attempt to convert the trigonal-prismatic cluster $[Rh_6N(CO)_{15}]^-$ into the octahedral 86-electron cluster $[Rh_6N(CO)_{13}]^-$ by reflux in thf, we have evidence for the formation of a similar unsaturated 84-electron octahedral cluster $[Rh_6N(CO)_{12}]^-$ **5**. Thus, after 7 h all of the IR bands due to the starting material had disappeared and addition of Pr^iOH gave a dark brown solid with the IR spectrum (Fig. 5) containing bands in the carbonyl region at 2005, 1880(sh), 1840m and 1810(sh) cm^{-1}. The direct ^{103}Rh NMR spectrum of **5** at −80 °C consists of a single resonance at δ 184.3 due to six equivalent rhodium atoms and the spectrum does not change with increasing temperature (to +25 °C). The ^{13}C NMR spectrum consists of a doublet at δ 196.2 and a triplet at 212.4 in a *ca.* 1 : 1 ratio (see later). Irradiating at the observed ^{103}Rh frequency causes both the doublet and triplet to collapse to singlets.

From integration of the ^{13}C NMR spectra, it is difficult to be sure whether the ratio of terminal : bridge is 6 : 6 or 6 : 7 as might reasonably be expected from analogues already structurally characterised, *e.g.* $[M_6E(CO)_{13}]^{n-}$ (M = Co or Rh, E = C, *n* = 2;[2,4,9] M = Co, E = N, *n* = 1[8]). However, from the ^{13}C and ^{103}Rh NMR measurements described above, it is impossible to arrive at a symmetrical structure with a formulation based on thirteen carbonyls. As a result, we favour the formulation based on twelve carbonyls, with some multiple rhodium–rhodium bonding present. Such a cluster would then have the structure shown in Fig. 6. Unfortunately good quality crystals of **5** for an X-ray structural analysis could not be obtained.

Experimental

All operations were carried out under a nitrogen atmosphere using Schlenk-tube techniques and ^{13}CO enrichments were carried out using standard vacuum line techniques. The ^{13}C, ^{31}P, $^{13}C-\{^{103}Rh\}$ and $^{31}P-\{^{103}Rh\}$ NMR spectra were

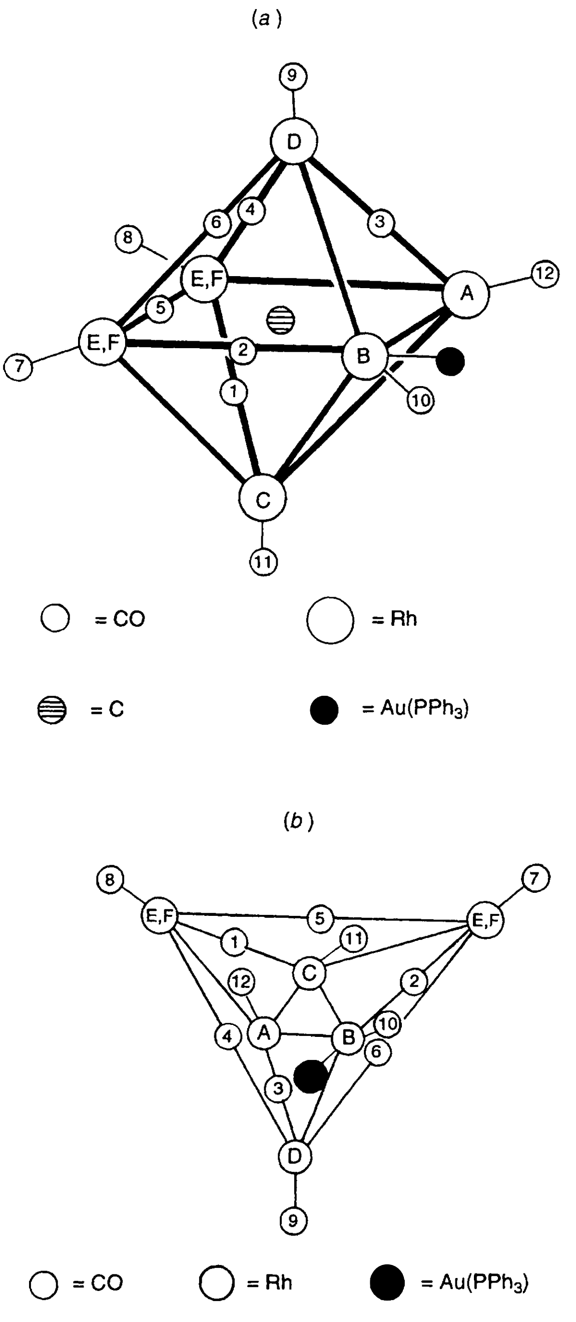

Fig. 4 Schematic representation of (*a*) the structure of $[Rh_6C(CO)_{12}\{Au(PPh_3)\}]^-$ **3** and (*b*) **3** viewed down a pseudo three-fold axis

obtained on either a Bruker WM200 or AMX400 instrument and ^{13}C-$\{^{31}P\}$ NMR spectra were recorded on a Bruker WM250 instrument using 10 mm NMR tubes. Direct ^{103}Rh NMR spectra were obtained on a Bruker WM360 at the University of Edinburgh using 15 mm NMR tubes containing solutions (7 cm^3, *ca.* 0.5 mmol) with added relaxing reagent $[Cr(acac)_3]$ (acac = acetyl acetonate). In the absence of direct ^{103}Rh NMR data, ^{103}Rh frequencies were determined by monitoring the collapse of ^{13}C or ^{31}P multiplets as described previously.[13] All resonances to high frequency of the standard have positive chemical shifts and ^1H, ^{13}C, ^{31}P and ^{103}Rh shifts are referenced to $SiMe_4$, $SiMe_4$, external H_3PO_4 (85% in D_2O) and 6.28 MHz at such a magnetic field that the protons in $SiMe_4$ resonate at exactly 200 MHz respectively. IR spectra were recorded in solution on a Perkin Elmer 252 spectrometer using CaF_2 cells. Solvents were purified using standard procedures and stored under nitrogen.

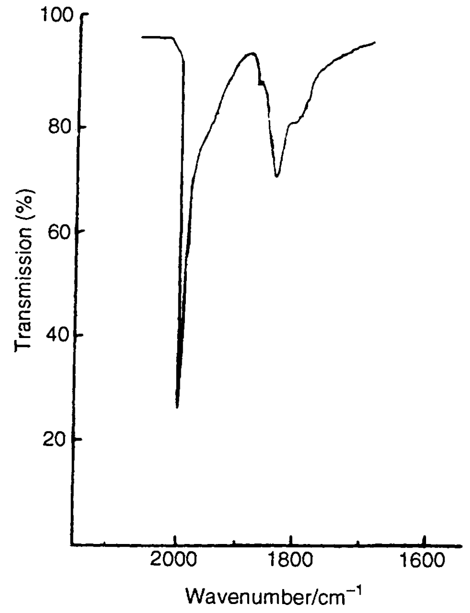

Fig. 5 IR spectrum of $[N(PPh_3)_2][Rh_6N(CO)_{12}]$ in CH_2Cl_2

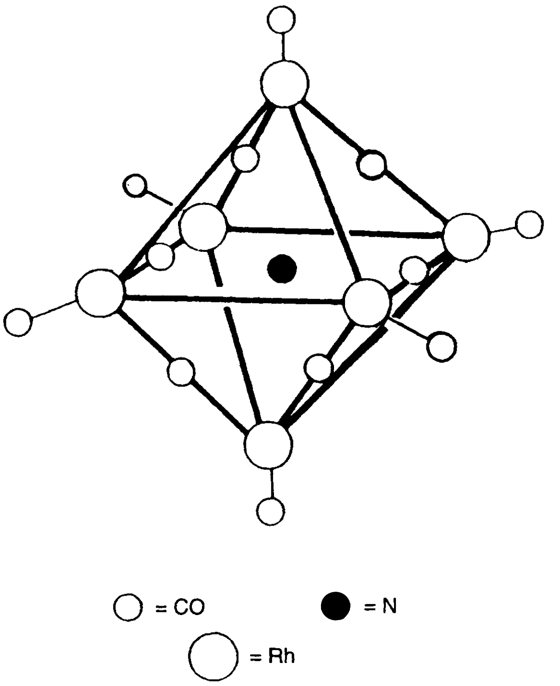

Fig. 6 Schematic representation of the structure proposed for $[Rh_6N(CO)_{12}]^-$ **5**

Synthesis of $[Rh_6N(CO)_{15}\{Au(PPh_3)\}]$ **1**.—To a solution of $[N(PPh_3)_2][Rh_6N(CO)_{15}]$ (0.15 g, 0.09 mmol) in CH_2Cl_2 (5 cm^3) at −78 °C containing $HBF_4{\cdot}Et_2O$ (70 µl) was added $[Au(PPh_3)Cl]$ (0.07 g, 0.14 mmol) in CH_2Cl_2 (3 cm^3). On stirring for 5 min, a yellow precipitate of the product was formed which was filtered off at room temperature and washed with CH_2Cl_2 (2 cm^3). Yield: 0.106 g, 75% (Found: C, 26.80; H, 1.00; N, 0.85. Calc. for $C_{33}H_{15}AuNO_{15}PRh_6$: C, 26.20; H, 1.00; N, 0.90%).

Synthesis of $[NEt_4][Rh_6C(CO)_x\{Au(PPh_3)\}]$ (x = 13 *or* 12).—A solution of $[Au(PPh_3)Cl]$ (0.052 g, 0.11 mmol) in thf (1.5 cm^3) was added to a solution of $[NEt_4]_2[Rh_6C(CO)_{13}]$ (0.133 g, 0.11 mmol) in thf (1.5 cm^3) at −78 °C. Carbon-13 and ^{31}P NMR spectra of this solution at low temperature are consistent with the formation of $[Rh_6C(CO)_{13}\{Au(PPh_3)\}]^-$ **2**.

Warming this solution to −10 °C resulted in the loss of CO and formation of $[Rh_6C(CO)_{12}\{Au(PPh_3)\}]^-$ **3**. Addition of Pr^iOH to the thf solution below −10 °C gave a dark red solid which was recrystallised from a cold (< −10 °C) solution of thf–Pr^iOH to give needle-like crystals of **3** as its $[NEt_4]^+$ salt (Found: C, 29.60; H, 2.20; N, 0.80. Calc. for $C_{39}H_{25}AuNO_{12}PRh_6$: C, 30.30; H, 2.00; N, 0.90%).

Synthesis of $[N(PPh_3)_2][Rh_6N(CO)_{12}]$.—A solution of $[N(PPh_3)_2][Rh_6N(CO)_{15}]$ (0.5 g, 0.31 mmol) in thf (50 cm^3) was refluxed under N_2 for 4 h. The dark brown solution was filtered and, after concentration to (5 cm^3) and slow addition of hexane (40 cm^3), a dark brown crystalline product was obtained which was used directly for NMR studies.

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