Reversible Skeletal Rearrangement in a Carbido Carbonyl Cluster induced by Ligand Substitution. Synthesis and Crystal Structure of the Anion $[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^-$ ‡

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The mixed-metal carbido carbonyl cluster anion $[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^-$ has been obtained by reaction of $[Rh_{12}C_2(CO)_{24}]^{2-}$ with $[Au(PPh_3)Cl]$. It is an intermediate species in the previously reported reaction producing the two related clusters $[Rh_{10}C_2(CO)_{18}(AuPPh_3)_4]$ and $[Rh_{10}C_2(CO)_{20}(AuPPh_3)_4]$ and reacts with CO regenerating the starting dianion. The molecular structure of the $[NEt_4]^+$ salt has been determined by X-ray diffraction analysis [monoclinic, space group $P2_1/n$, $Z = 4$, $a = 13.499(2)$, $b = 32.789(3)$, $c = 14.923(3)$ Å, $\beta = 101.26(2)°$]. The loss of a CO ligand and the addition of the gold fragment result in major rearrangements in the $Rh_{12}C_2$ cluster yielding an unprecedented layered aggregation in which three fused trigonal prisms (two containing the carbide atoms) are recognizable. The $Au(PPh_3)^+$ fragment bridges a Rh_4 butterfly-shaped face of the Rh-atom skeleton. Phosphorus-31 NMR spectra at low temperature show that the solution structure is somewhat different with the gold bonded to a $Rh_ARh_BRh_B$ face. The CO ligands are distributed in such a way as to achieve a regular charge distribution among the metal atoms.

We have previously reported the synthesis and structural characterization in solution and/or the solid state of several mixed-metal carbido carbonyl clusters obtained from the reaction of the cluster anions $[Rh_6C(CO)_{15}]^{2-}$ [1] or $[Rh_6C(CO)_{13}]^{2-}$ [2,3] (having, respectively, a trigonal-prismatic and an octahedral metal skeleton) with electrophilic Group 11 metal fragments. In all these species the Group 11 atoms bind to the rhodium polyhedron, the geometry of which is essentially preserved, exclusively by capping of one or two triangular faces and yielding respectively products of general formula $[Rh_6C(CO)_{15}E]^-$ or $[Rh_6C(CO)_{15}E_2]$ or $[Rh_6C(CO)_{13}E]^-$ and $[Rh_6C(CO)_{13}E_2]$ [E = $M(PPh_3)$, M = Cu, Ag or Au;[4,5] M(NCMe), M = Cu or Ag;[4,6] or Ag[7]]. More recently, we attempted the same kind of reactions with the high-nuclearity dianion $[Rh_{12}C_2(CO)_{24}]^{2-}$ [8] and obtained, by reaction with an excess of $[Au(PPh_3)Cl]$, the two related species $[Rh_{10}C_2(CO)_{20}(AuPPh_3)_4]$ and $[Rh_{10}C_2(CO)_{18}(AuPPh_3)_4]$.[9] On that occasion, there was also some evidence for a substitution-labile intermediate product. The present paper deals with the isolation and characterization of such an intermediate, the anion $[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^-$.

Results and Discussion

Synthesis and Chemical Characterization.—The first stage of the reaction of $K_2[Rh_{12}C_2(CO)_{24}]$ with $[Au(PPh_3)Cl]$ can be represented by equilibrium (1). When the reaction is performed

$$[Rh_{12}C_2(CO)_{24}]^{2-} + [Au(PPh_3)Cl] \rightleftharpoons [Rh_{12}C_2(CO)_{23}(AuPPh_3)]^- + Cl^- + CO \quad (1)$$

under nitrogen in tetrahydrofuran (thf) or propan-2-ol, with the reagents in 1:1 molar ratio, there is IR evidence of the new species $[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^-$ **1**, together with a major amount of unreacted $[Rh_{12}C_2(CO)_{24}]^{2-}$. The starting dianion disappears and the monoanion **1** becomes the unique species in solution, only when the Rh_{12}:$[Au(PPh_3)Cl]$ molar ratio is in the range 1:1.5–2. Similar equilibrium reactions which need an excess of $[Au(PPh_3)Cl]$ to proceed have been reported.[4,5] However, at these molar ratios, another process becomes evident, that is partial decomposition of the rhodium cluster with formation, as previously reported, of $[Rh(CO)_2Cl_2]^-$ and insoluble $[Rh_{10}C_2(CO)_{20}(AuPPh_3)_4]$.[9] This further reaction is complete when another 3 mol of $[Au(PPh_3)Cl]$ are added to the products of equilibrium (1), according to equation (2).

$$[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^- + Cl^- + CO + 3[Au(PPh_3)Cl] \longrightarrow [Rh_{10}C_2(CO)_{20}(AuPPh_3)_4] + 2[Rh(CO)_2Cl_2]^- \quad (2)$$

Besides Cl^-, CO is also an active participant in equilibrium (1) and in fact a carbon monoxide atmosphere (1 atm, *ca.* 100 kPa) severely hinders the reaction, so that no $[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^-$ is detected in solution by IR spectroscopy. However with $[Au(PPh_3)Cl]$ in excess the reaction evolves in any case as under nitrogen to give $[Rh_{10}C_2(CO)_{20}(AuPPh_3)_4]$ and $[Rh(CO)_2Cl_2]^-$, apparently directly from the dianion $[Rh_{12}C_2(CO)_{24}]^{2-}$.

Monoanion **1** is decomposed by air but is indefinitely stable in solution under a nitrogen atmosphere. Addition of a halide

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[‡] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Selected bond lengths (Å) and angles (°) for the anion $[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^-$

Rh(2)–Rh(1)	2.910(1)	Rh(7)–C(24)	2.11(1)	Rh(1)–Au	2.710(1)	Rh(7)–C(7)	2.02(1)
Rh(3)–Rh(1)	2.750(1)	Rh(9)–C(24)	2.165(9)	Rh(2)–Au	2.822(1)	Rh(9)–C(7)	2.03(1)
Rh(4)–Rh(1)	2.834(1)	Rh(12) ••• C(24)	2.83(1)	Rh(4)–Au	3.105(1)	C(7)–O(7)	1.16(1)
Rh(5)–Rh(1)	2.871(1)	C(25) ••• C(24)	2.86(2)	Rh(5)–Au	3.016(1)	Rh(8)–C(8)	2.05(1)
Rh(6)–Rh(1)	2.708(1)	Rh(1)–C(25)	2.00(1)	Au–P	2.273(3)	Rh(10)–C(8)	1.99(1)
Rh(11)–Rh(1)	2.784(1)	Rh(3)–C(25)	2.09(1)	C(26)–P	1.817(8)	C(8)–O(8)	1.18(2)
Rh(12)–Rh(1)	2.625(1)	Rh(5)–C(25)	2.14(1)	C(32)–P	1.792(7)	Rh(3)–C(9)	2.05(1)
Rh(4)–Rh(2)	2.859(1)	Rh(6)–C(25)	2.40(1)	C(38)–P	1.816(8)	Rh(5)–C(9)	2.02(1)
Rh(5)–Rh(2)	2.928(1)	Rh(8)–C(25)	2.04(1)	Rh(1)–C(24)	2.096(9)	C(9)–O(9)	1.14(2)
Rh(9)–Rh(2)	2.725(1)	Rh(10)–C(25)	2.09(1)	Rh(2)–C(24)	2.09(1)	Rh(2)–C(10)	2.04(1)
Rh(5)–Rh(3)	2.831(1)	Rh(5)–C(1)	2.02(1)	Rh(4)–C(24)	2.17(1)	Rh(4)–C(10)	2.02(1)
Rh(10)–Rh(3)	2.712(1)	Rh(8)–C(1)	2.05(1)	Rh(6)–C(24)	2.12(1)	C(10)–O(10)	1.15(2)
Rh(11)–Rh(3)	2.783(1)	C(1)–O(1)	1.17(2)	Rh(4)–C(11)	1.90(1)	Rh(4)–C(18)	2.53(2)
Rh(7)–Rh(4)	2.764(1)	Rh(2)–C(2)	2.05(1)	C(11)–O(11)	1.14(2)	Rh(12)–C(18)	1.90(2)
Rh(12)–Rh(4)	2.923(1)	Rh(9)–C(2)	2.02(1)	Rh(2)–C(12)	1.92(1)	C(18)–O(18)	1.14(2)
Rh(8)–Rh(5)	2.742(1)	C(2)–O(2)	1.17(2)	C(12)–O(12)	1.13(2)	Rh(3)–C(19)	1.94(2)
Rh(7)–Rh(6)	2.823(1)	Rh(3)–C(3)	2.06(1)	Rh(9)–C(13)	1.90(1)	C(19)–O(19)	1.12(2)
Rh(8)–Rh(6)	2.951(1)	Rh(10)–C(3)	1.99(1)	C(13)–O(13)	1.15(2)	Rh(5)–C(20)	1.88(2)
Rh(9)–Rh(6)	2.728(1)	C(3)–O(3)	1.17(2)	Rh(6)–C(14)	1.86(1)	C(20)–O(20)	1.14(2)
Rh(10)–Rh(6)	2.826(1)	Rh(4)–C(4)	2.08(1)	Rh(9)–C(14)	2.62(1)	Rh(11)–C(21)	1.96(1)
Rh(11)–Rh(6)	2.716(1)	Rh(7)–C(4)	2.03(1)	C(14)–O(14)	1.15(2)	Rh(12)–C(21)	2.13(1)
Rh(12)–Rh(6)	2.936(1)	C(4)–O(4)	1.14(1)	Rh(11)–C(15)	1.87(1)	C(21)–O(21)	1.16(2)
Rh(9)–Rh(7)	2.807(1)	Rh(6)–C(5)	1.99(1)	C(15)–O(15)	1.13(2)	Rh(8)–C(22)	1.91(1)
Rh(12)–Rh(7)	2.782(1)	Rh(11)–C(5)	2.08(2)	Rh(12)–C(16)	1.86(1)	C(22)–O(22)	1.11(2)
Rh(9)–Rh(8)	2.880(1)	C(5)–O(5)	1.18(2)	C(16)–O(16)	1.14(2)	Rh(10)–C(23)	1.87(2)
Rh(10)–Rh(8)	2.841(1)	Rh(1)–C(6)	1.89(1)	Rh(7)–C(17)	1.92(1)	C(23)–O(23)	1.12(2)
Rh(11)–Rh(10)	2.823(1)	Rh(3)–C(6)	2.53(1)	C(17)–O(17)	1.12(2)		
Rh(12)–Rh(11)	2.760(1)	C(6)–O(6)	1.17(2)				
Rh(5)–C(1)–O(1)	136(1)	Rh(2)–C(10)–O(10)	134(1)	Rh(11)–C(5)–O(5)	132(1)	Rh(7)–C(17)–O(17)	177(1)
Rh(8)–C(1)–O(1)	139(1)	Rh(4)–C(10)–O(10)	137(1)	Rh(1)–C(6)–O(6)	162(1)	Rh(4)–C(18)–O(18)	125(1)
Rh(2)–C(2)–O(2)	137(1)	Rh(4)–C(11)–O(11)	175(1)	Rh(3)–C(6)–O(6)	122(1)	Rh(12)–C(18)–O(18)	154(1)
Rh(9)–C(2)–O(2)	139(1)	Rh(2)–C(12)–O(12)	176(1)	Rh(7)–C(7)–O(7)	136(1)	Rh(3)–C(19)–O(19)	176(1)
Rh(3)–C(3)–O(3)	136(1)	Rh(9)–C(13)–O(13)	178(1)	Rh(9)–C(7)–O(7)	136(1)	Rh(5)–C(20)–O(20)	176(1)
Rh(10)–C(3)–O(3)	140(1)	Rh(6)–C(14)–O(14)	165(1)	Rh(8)–C(8)–O(8)	134(1)	Rh(11)–C(21)–O(21)	144(1)
Rh(4)–C(4)–O(4)	135(1)	Rh(9)–C(14)–O(14)	123(1)	Rh(10)–C(8)–O(8)	137(1)	Rh(12)–C(21)–O(21)	131(1)
Rh(7)–C(4)–O(4)	140(1)	Rh(11)–C(15)–O(15)	178(1)	Rh(3)–C(9)–O(9)	135(1)	Rh(8)–C(22)–O(22)	174(1)
Rh(6)–C(5)–O(5)	144(1)	Rh(12)–C(16)–O(16)	176(1)	Rh(5)–C(9)–O(9)	136(1)	Rh(10)–C(23)–O(23)	173(2)

X^- as the salt $[NEt_4]Cl$, $[N(PPh_3)_2]Cl$ or $[NEt_4]Br$ decomposes the product, extracting the $[Au(PPh_3)]^+$ moiety and yielding an unknown product; excesses of halides eventually induce further cluster fragmentation with formation of $[Rh(CO)_2X_2]^-$ and other unknown anions. For these reasons, the separation of the monoanion from the reaction mixture by precipitation as a salt of bulky cations must be done by metathesis with salts having a non-co-ordinating anion such as $[NEt_4][BF_4]$ or $[N(PPh_3)_2][BF_4]$. A good alternative is the use of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) which directly precipitates the [K(18-crown-6)]$^+$ salt. Exposure to CO of pure $[NEt_4][Rh_{12}C_2(CO)_{23}(AuPPh_3)]$ in MeCN causes dissociation of the $[Au(PPh_3)]^+$ moiety and reinsertion of CO to give back $[Rh_{12}C_2(CO)_{24}]^{2-}$. The same reaction, performed in thf, yields an IR spectrum reminiscent of that of the parent dianion but shifted to higher wavenumbers by *ca.* 20 cm^{-1}, possibly due to formation of ion pairs. These solutions are quite unstable and decompose with precipitation of insoluble material.

Spectroscopic Measurements.—The infrared spectrum of $[NEt_4][Rh_{12}C_2(CO)_{23}(AuPPh_3)]$ in thf solution is shown in Fig. 1. The bands (± 2 cm^{-1}) are at 2066w, 2036s, 1968w, 1930w 1867s and 1851m cm^{-1}. Spectra of salts of different cations are similar both in thf and propan-2-ol, but in MeCN show a shift to lower wavenumbers: K$^+$ (propan-2-ol), 2067w, 2037s, 1970w, 1930w, 1870s and 1854m; [K(18-crown-6)]$^+$ (thf), 2065w, 2034s, 1965w, 1928w, 1868s and 1851m; $[NEt_4]^+$ (MeCN), 2057 (sh), 2020s, 1861s and 1839m cm^{-1}.

The ^{31}P NMR spectra of $[NEt_4][Rh_{12}C_2(CO)_{23}(AuPPh_3)]$ were recorded in acetone + 20% $(CD_3)_2CO$. The singlet observed at 297 K (δ 48.12) gradually, on cooling, transformed into a five-line multiplet which was best resolved at about 200 K; further cooling to 179 K resulted in poorer resolution. A temperature dependence of the chemical shift, which moved to δ 46.48 at 179 K, was also observed. The relative intensities of 1:2:2:2:1 identify the multiplet more correctly as a doublet [J(P–Rh$_A$) *ca.* 12 Hz] of triplets [J(P–Rh$_B$) *ca.* 6 Hz]. This

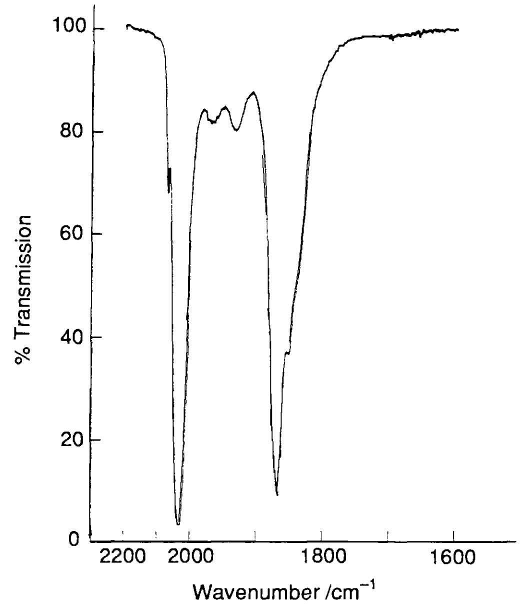

Fig. 1 The IR spectrum of $[NEt_4][Rh_{12}C_2(CO)_{23}(AuPPh_3)]$ in thf

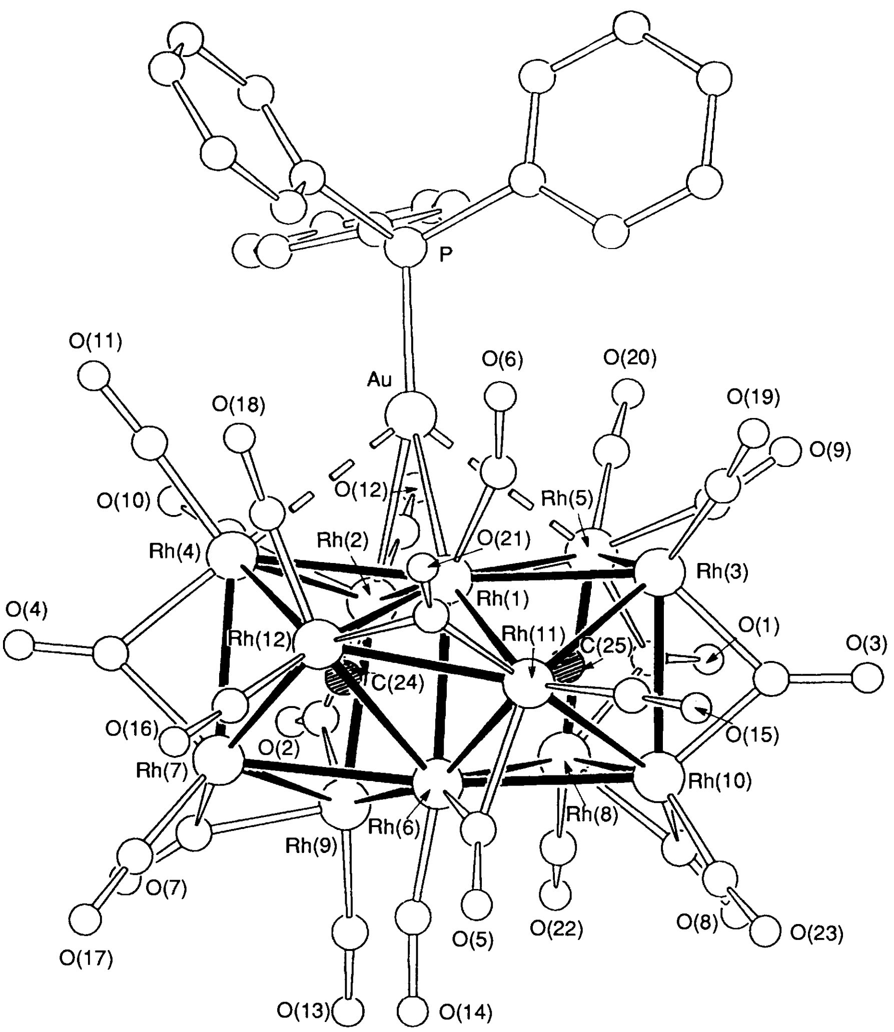

Fig. 2 The molecular stereogeometry of the anion $[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^-$. Carbon atoms of the CO groups bear the same numbering as the O atoms

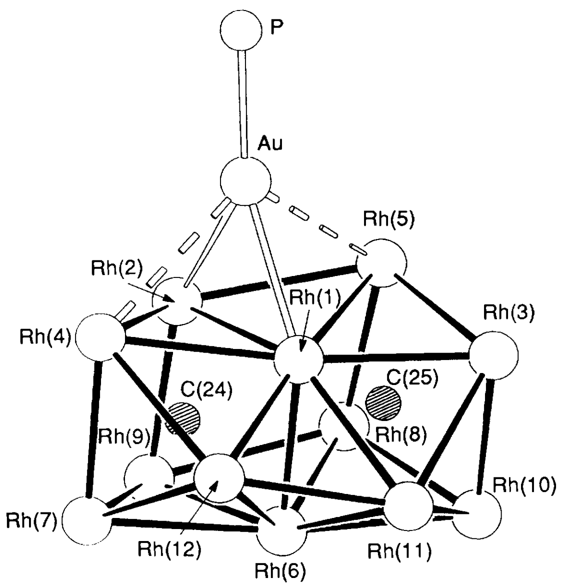

Fig. 3 View of the heavy-atom skeleton showing the prismatic cavities defined by the Rh atoms

indicates that, in solution, the interaction of the Au(PPh$_3$) moiety with the rhodium cluster is different from that observed in the solid state, which should give a triplet of triplets. The actual pattern is consistent with the capping of a rhodium triangular face comprising a unique Rh$_A$ and two equivalent Rh$_B$ (possibly the face 1,2,4 in Fig. 2). A natural-abundance ^{13}C NMR spectrum of $[NEt_4][Rh_{12}C_2(CO)_{23}(AuPPh_3)]$ in thf + 10% $[^2H_8]$thf did not yield, at room temperature (297 K), significant signals in the carbonyl region (δ 150–250).

The Molecular Structure of $[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^-$ *as its* $[NEt_4]^+$ *Salt*.—The molecular structure of the ion in the crystalline state is shown in Fig. 2 and the metal-atom skeleton in Fig. 3; relevant bond parameters are reported in Table 1. The $Rh_{12}C_2$ core is quite irregular and only an approximate C_s symmetry can be envisaged. This feature contrasts with the greater regularity of the parent species, in which both the metal-atom polyhedron (Fig. 4) and the ligand coverage conform to an idealized D_{2h} symmetry.[8] It is not simple to elucidate the interconversion mechanism of the two polyhedra but, since the transformation is reversible, it must take place with displacements limited to some of the metal atoms, very probably the capping ones (Fig. 4) loosely bound to the prismatic units.[8]

The Rh_{12} cluster consists of two five-atom triangulated layers [Rh(1) to Rh(5) and Rh(6) to Rh(10)] stacked above each other in an eclipsed configuration so as to form three trigonal-prismatic cavities sharing rectangular faces. Two such cavities contain isolated carbide atoms, the third is empty. The two remaining Rh atoms [Rh(11) and Rh(12)] cap contiguous rectangular faces and are bonded to each other. The rhodium–rhodium co-ordination numbers are as follows: eight atoms are four-, two five- and two seven-connected. The Rh–Rh distances

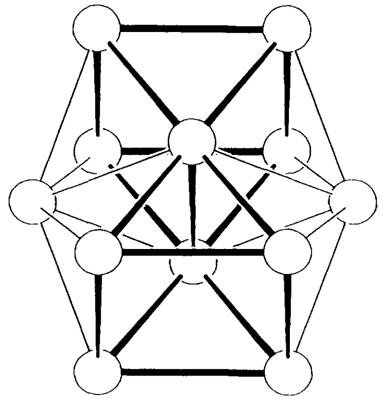

Fig. 4 The $Rh_{12}C_2$ cluster in the parent dianion $[Rh_{12}C_2(CO)_{24}]^{2-}$ viewed as two prisms sharing an edge plus two capping atoms (connected with light lines)[8]

Table 2 Crystal data and details of measurements for $[NEt_4][Rh_{12}C_2(CO)_{23}(AuPPh_3)]$

Formula	$C_{51}H_{35}AuNO_{23}PRh_{12}$
M	2492.56
Crystal size/mm	0.15 × 0.075 × 0.125
System	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	13.499(2)
b/Å	32.789(3)
c/Å	14.923(3)
β/°	101.26(2)
U/Å^3	6477.8
Z	4
D_c/g cm^{-3}	2.56
F(000)	4664
Radiation (graphite monochromated (λ/Å)	Mo-Kα (0.710 67)
μ(Mo-Kα)/cm^{-1}	49.72
Scan mode	ω
θ range/°	2–23
ω Scan width/°	0.8 + 0.35 tanθ
Prescan rate/° min^{-1}	5
Prescan acceptance σ(I)/I	0.5
Required σ(I)/I	0.02
Maximum scan time/s	100
Standard reflections	3, measured periodically
Reflections collected	8188
Unique observed reflections, N_o [$F_o > 4\sigma(F_o)$]	5419
No. of refined parameters, N_p	681
R, R', S[a]	0.037, 0.035, 1.61
K, g[b]	1.75, 4.41 × 10^{-4}

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}$; $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$. [b] $w = K/[\sigma^2(F) + |g|F^2]$.

are not distributed in a manner related to the connectivity, probably because they are influenced by the interactions with the ligands. These distances cover the interval 2.625–2.951(1) Å, mean 2.808 Å. The latter value, averaged over 28 interactions, is a good estimate of the rhodium–rhodium interaction and can usefully be compared to the corresponding average values in the parent dianion $[Rh_{12}C_2(CO)_{24}]^{2-}$ (2.811 Å),[8] in the trianion $[Rh_{12}C_2(CO)_{23}]^{3-}$ (2.830 Å)[10] and in the tetraanion $[Rh_{12}C_2(CO)_{23}]^{4-}$ (2.829 Å).[11] The differences, even though small, are significant and in accord with the expected shrinking of the metal-atom aggregates with decreasing charge. The very small difference between the dianion and monoanion can be attributed to incomplete charge transfer from the $Rh_{12}C_2$ dianion to the attached $Au(PPh_3)^+$ acidic fragment.

The $Au(PPh_3)$ group is bonded perpendicularly to the Rh(1)–Rh(2) edge with quite short Rh–Au distances [2.710, 2.822(1) Å]. Other Rh–Au distances are as follows: 2.826 for $[Rh_{10}C_2(CO)_{18}(AuPPh_3)_4]$,[9] 2.825 for $[Rh_{10}C_2(CO)_{20}(AuPPh_3)_4]$,[9] 2.833 for $[Rh_6C(CO)_{15}(AuPPh_3)_2]$,[4] and 2.804 Å for $[Rh_6C(CO)_{13}\{Au_2(PPh_3)_2\}]$.[5] The Au atom is also in contact with Rh(4) and Rh(5) [3.105, 3.016(1) Å]. The latter interactions, even though weak, are the result of the residual bonding ability of the linearly hybridized gold(I) fragments. Its attractive nature is demonstrated by some folding of the Rh(1), Rh(2), Rh(4), Rh(5) diamond along its short diagonal [dihedral angle 157.3(1)°]. The gold–rhodium interactions can be considered a limiting case of ion pairing with charge transfer from the basic dianion to the acidic gold fragment.

The 23 CO ligands cover the cluster surface almost uniformly but the overall molecular symmetry is C_1. Thirteen ligands are terminally bonded, one per metal atom except Rh(12) which bears two, but some of these show a tendency towards semibridging geometry. The remaining 10 ligands are bridging and span the edges of two rectangular faces, the edge between the capping atoms Rh(11)–Rh(12) and the edge Rh(6)–Rh(11). Although this geometry appears to be the only one of those accessible in solution that is frozen in the crystal it is not of chemical significance. The regularity of the ligand distribution consists in the triconnection of most Rh atoms, which bear two bridging and one terminal ligand, with the exception of Rh(12) which is connected to two terminal and one bridging group and Rh(1) which bears one unique terminal ligand [bent towards Rh(3)]. The singularity of Rh(1) can be related to the fact that the bridging Au exhibits the shortest contact with this atom [2.710(1) Å]. The efficiency of Au in withdrawing electron density from Rh(1) makes this atom unable to cope with multiple π-back-bonding interactions to the CO ligands.

Conclusion

We have previously reported two cases of reversible rearrangement of a metal skeleton around a pivotal carbido atom: the octahedral polyhedra in $[Rh_6C(CO)_{13}]^{2-}$ [2] and $[Rh_6C(CO)_{13}\{Au_2(PPh_3)_2\}]$[5] are converted into trigonal prismatic in $[Rh_6C(CO)_{15}]^{2-}$ [1] and $[Rh_6C(CO)_{15}\{Au_2(PPh_3)_2\}]$,[4] respectively. The processes are dependent on the variation in the number of CO ligands and, as a consequence, on the cluster valence electrons. It should be noted that additions of $Au(PPh_3)^+$ to both the octahedral and prismatic dianions take place without substantial changes in the Rh_6C cores, in agreement with the d^{10} ML^+ fragments acting purely as acceptors.[12]

In the case of $[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^-$ both these changes, namely loss of a CO group and addition of the electrophilic $Au(PPh_3)^+$, are present and are accompanied by an extensive reorganization of the $Rh_{12}C_2$ core with respect to the parent dianion $[Rh_{12}C_2(CO)_{24}]^{2-}$.[8] In order better to appreciate this phenomenon one should remember that the anions $[Rh_{12}C_2(CO)_{23}]^{n-}$ (n = 3 or 4), which are reduction products of the same parent dianion, do not exhibit variations in the metal anion skeleton. It seems as though neither the loss of a CO nor the addition of a $Au(PPh_3)^+$ group, taken separately, is sufficiently effective in promoting rearrangements of the metal-atom polyhedron. Only the combined action of the two factors confers significant plasticity upon the molecule. This interpretation is in agreement with the ^{31}P NMR data which suggest at low temperature a gold attachment different from that found in the crystal and, at room temperature, extensive fluxionality. The latter phenomenon could provide an efficient mechanism for lowering the activation energy of the process. Both structural and spectroscopic information on this and similar molecules strengthen the feeling that cluster molecules in which the metal-atom polyhedron is not very compact and the surface ligands do not possess a unique regular arrangement of minimum energy are to be considered, at least at room temperature, as highly deformable molecules. These molecules are in continuous evolution among configurations of comparable stabilities and the solid-state structure is a snapshot capturing a configuration of low solubility.

Experimental

All operations were carried out under nitrogen with a standard Schlenk-tube apparatus. Tetrahydrofuran was distilled from sodium–benzophenone and propan-2-ol from aluminium isopropoxide. All other analytical grade solvents were degassed in vacuum and stored under nitrogen. The compounds $K_2[Rh_6C(CO)_{15}]$,[13] $K_2[Rh_{12}C_2(CO)_{24}]$[8] and $[Au(PPh_3)Cl]$[14] were prepared by the published methods. Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer equipped with a data station for spectra elaboration, using 0.1 mm CaF_2 cells previously purged with nitrogen. The ^{31}P NMR spectra were recorded at 81.015 MHz on a Bruker AC200 instrument, with a resolution of ± 1.5 Hz.

Synthesis of $[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^-$ *as its* $[NEt_4]^+$ *or* $[K(18\text{-crown-}6)]^+$ *Salt from* $K_2[Rh_6C(CO)_{15}]$·*ca.* 3thf *and* $[Au(PPh_3)Cl]$.—This is a two-step preparation, where $[Rh_{12}C_2(CO)_{24}]^{2-}$ is first prepared '*in situ*' and then treated with the gold complex. A solution of $K_2[Rh_6C(CO)_{15}]$·*ca.* 3thf (1381.3 mg, 1.03 mmol) in propan-2-ol (25 cm^3) was treated with aqueous H_2SO_4 (0.5 mol dm^{-3}, 1.1 cm^3) and heated under nitrogen at 70 °C; after 1.75 h, IR spectroscopic monitoring showed that the starting product had completely disappeared with formation of a brown solution of $[Rh_{12}C_2(CO)_{24}]^{2-}$. The solution was evacuated for a few seconds to remove all the evolved CO and, when cold, treated with $[Au(PPh_3)Cl]$ (384.1 mg, 0.78 mmol); the mixture was stirred for 4 h and then checked by IR spectroscopy to ensure complete reaction. It was filtered to remove a light brown precipitate which prior to being discarded was washed twice with propan-2-ol (5 cm^3). The solution and the washings were treated with $[NEt_4][BF_4]$ (1.0 g) and water (80 cm^3) was added to induce precipitation of brown flakes. These were filtered from the colourless mother-liquor, washed with water (10 cm^3 × 2) and vacuum dried. The crude product was extracted from the septum with the minimum amount of thf (10 cm^3) and carefully layered with hexane (40 cm^3) to give in a few days crystals suitable for X-ray diffraction; yield 800 mg (62%) {Found: C, 24.25; H, 1.40; N, 0.60. Calc. for $[NEt_4][Rh_{12}C_2(CO)_{23}(AuPPh_3)]$: C, 24.60; H, 1.40; N, 0.55%}.

The same procedure may be used to obtain the $[K(18\text{-crown-}6)]^+$ salt: the filtered solution containing $K[Rh_{12}C_2(CO)_{23}(AuPPh_3)]$ was treated with 18-crown-6 (264 mg, 1 mmol) and carefully layered with hexane. A product

Table 3 Fractional atomic coordinates for $[NEt_4][Rh_{12}C_2(CO)_{23}(AuPPh_3)]$

Atom	*x*	*y*	*z*
Rh(1)	0.298 99(6)	0.115 79(2)	0.733 66(6)
Rh(2)	0.081 99(6)	0.110 22(3)	0.666 99(6)
Rh(3)	0.391 58(7)	0.190 82(3)	0.754 65(7)
Rh(4)	0.197 81(7)	0.040 30(3)	0.737 92(6)
Rh(5)	0.178 19(7)	0.188 18(3)	0.727 22(6)
Rh(6)	0.313 20(6)	0.108 21(3)	0.555 91(6)
Rh(7)	0.238 93(6)	0.028 18(3)	0.565 56(6)
Rh(8)	0.168 53(7)	0.176 42(3)	0.543 82(6)
Rh(9)	0.112 39(7)	0.093 37(3)	0.495 63(6)
Rh(10)	0.380 13(8)	0.190 03(3)	0.571 20(7)
Rh(11)	0.483 14(7)	0.126 74(3)	0.679 35(8)
Rh(12)	0.401 20(7)	0.051 14(3)	0.701 44(7)
Au	0.172 07(4)	0.116 85(1)	0.853 66(3)
P	0.130 7(2)	0.121 2(1)	0.993 9(2)
C(24)	0.207 1(7)	0.083 0(3)	0.628 4(6)
C(25)	0.284 4(7)	0.164 5(3)	0.650 8(7)
C(1)	0.108 1(11)	0.219 7(4)	0.616 7(9)
O(1)	0.058 6(10)	0.249 2(4)	0.603 3(7)
C(2)	−0.015 5(10)	0.099 1(4)	0.545 8(8)
O(2)	−0.102 9(7)	0.097 5(3)	0.519 9(7)
C(3)	0.424 9(10)	0.233 4(4)	0.663 6(10)
O(3)	0.451 0(9)	0.267 7(3)	0.667 1(8)
C(4)	0.184 6(8)	−0.010 0(4)	0.651 4(8)
O(4)	0.159 8(6)	−0.043 1(2)	0.655 5(6)
C(5)	0.457 6(10)	0.107 6(4)	0.543 7(11)
O(5)	0.512 8(8)	0.100 0(4)	0.494 0(8)
C(6)	0.379 9(10)	0.127 6(4)	0.849 3(10)
O(6)	0.426 4(8)	0.124 1(3)	0.924 0(7)
C(7)	0.108 3(9)	0.032 3(4)	0.472 6(9)
O(7)	0.057 2(7)	0.009 7(3)	0.424 1(6)
C(8)	0.261 7(11)	0.211 6(4)	0.482 9(9)
O(8)	0.247 4(9)	0.236 1(3)	0.423 9(7)
C(9)	0.283 8(10)	0.226 8(4)	0.795 0(9)
O(9)	0.284 1(8)	0.256 8(3)	0.833 4(8)
C(10)	0.050 5(9)	0.055 9(3)	0.722 4(7)
O(10)	−0.021 5(7)	0.041 9(3)	0.739 9(7)
C(11)	0.184 0(10)	0.008 6(4)	0.841 3(9)
O(11)	0.169 8(10)	−0.012 1(4)	0.899 1(8)
C(12)	−0.028 6(11)	0.135 9(4)	0.708 4(9)
O(12)	−0.097 6(8)	0.149 3(4)	0.730 2(8)
C(13)	0.052 5(9)	0.100 5(4)	0.370 6(9)
O(13)	0.017 8(8)	0.103 8(3)	0.294 5(7)
C(14)	0.278 1(10)	0.101 7(4)	0.430 1(10)
O(14)	0.279 3(9)	0.099 0(4)	0.353 2(7)
C(15)	0.605 6(11)	0.154 9(4)	0.692 7(13)
O(15)	0.679 7(8)	0.171 8(4)	0.697 5(12)
C(16)	0.466 5(9)	0.006 5(4)	0.662 3(10)
O(16)	0.508 9(8)	−0.021 3(3)	0.644 2(10)
C(17)	0.285 5(10)	−0.013 2(5)	0.492 8(10)
O(17)	0.312 0(9)	−0.036 3(3)	0.447 5(8)
C(18)	0.380 3(13)	0.032 4(6)	0.816 7(12)
O(18)	0.406 8(9)	0.020 3(5)	0.889 2(8)
C(19)	0.499 5(12)	0.204 8(4)	0.855 7(13)
O(19)	0.562 9(10)	0.210 4(4)	0.915 2(10)
C(20)	0.089 6(13)	0.207 3(4)	0.800 3(11)
O(20)	0.035 9(10)	0.221 1(4)	0.842 4(9)
C(21)	0.540 5(10)	0.080 8(4)	0.756 3(12)
O(21)	0.608 7(8)	0.070 3(3)	0.812 1(10)
C(22)	0.060 6(12)	0.184 5(4)	0.442 2(10)
O(22)	−0.005 9(9)	0.191 7(3)	0.387 3(8)
C(23)	0.472 1(17)	0.205 2(5)	0.498 2(16)
O(23)	0.534 0(16)	0.214 2(5)	0.462 2(15)
N	0.629 4(9)	0.131 0(4)	0.235 1(10)
C(44)	0.665 4(13)	0.119 2(5)	0.335 4(12)
C(45)	0.699 6(16)	0.152 3(6)	0.396 5(14)
C(46)	0.706 4(11)	0.155 6(5)	0.197 4(13)
C(47)	0.805 3(13)	0.136 8(7)	0.207 7(13)
C(48)	0.615 6(16)	0.089 9(6)	0.189 6(13)
C(49)	0.584 8(17)	0.090 2(7)	0.091 8(13)
C(50)	0.536 1(12)	0.155 7(7)	0.219 7(17)
C(51)	0.450 0(13)	0.138 7(8)	0.253 4(17)
C(26)	0.170 0(6)	0.077 3(2)	1.066 7(5)
C(27)	0.114 3(6)	0.063 9(2)	1.130 5(5)
C(28)	0.150 1(6)	0.031 8(2)	1.189 3(5)
C(29)	0.241 7(6)	0.013 1(2)	1.184 4(5)
C(30)	0.297 5(6)	0.026 5(2)	1.120 6(5)
C(31)	0.261 6(6)	0.058 6(2)	1.061 8(5)
C(32)	−0.003 8(5)	0.124 5(2)	0.981 2(5)
C(33)	−0.061 6(5)	0.090 0(2)	0.951 8(5)
C(34)	−0.166 6(5)	0.092 9(2)	0.929 6(5)
C(35)	−0.213 9(5)	0.130 2(2)	0.936 8(5)
C(36)	−0.156 2(5)	0.164 7(2)	0.966 3(5)
C(37)	−0.051 1(5)	0.161 9(2)	0.988 5(5)
C(38)	0.184 2(6)	0.164 3(2)	1.063 1(5)
C(39)	0.161 6(6)	0.172 2(2)	1.148 7(5)
C(40)	0.204 7(6)	0.205 7(2)	1.199 4(5)
C(41)	0.270 4(6)	0.231 3(2)	1.164 5(5)
C(42)	0.293 0(6)	0.223 4(2)	1.078 8(5)
C(43)	0.249 9(6)	0.189 9(2)	1.028 1(5)

composed mostly of black crystals may be recovered after complete diffusion of the solvents.

Synthesis of $[Rh_{12}C_2(CO)_{23}(AuPPh_3)]^-$ *from* $K_2[Rh_{12}C_2(CO)_{24}]$ *and* $[Au(PPh_3)Cl]$.—The salt $K_2[Rh_{12}C_2(CO)_{24}]$,[8] prior to use, must be extracted with thf, which leaves the KCl impurities undissolved. The filtered solution was then evaporated under vacuum to give first a thick black-brown glass, which on heating on a water-bath at 45 °C yielded a black powder still containing *ca.* 2 mol thf per mol product. The reaction with $K_2[Rh_{12}C_2(CO)_{24}]$·*ca.* 2thf was then performed exactly as above in propan-2-ol with *ca.* 1.5 mol $[Au(PPh_3)Cl]$ per mol of cluster compound.

Crystal Structure Determination of $[NEt_4][Rh_{12}C_2(CO)_{23}(AuPPh_3)]$.—Crystal data and details of the data collection are given in Table 2. The diffraction experiments were carried out at room temperature on a fully automated Enraf–Nonius CAD-4 diffractometer. The unit-cell parameters were determined from 25 randomly selected strong reflections by using automatic search, indexing and least-squares routines. Intensity measurements were corrected for Lorentz and polarization effects. A slight crystal decay was observed (3%) and a linear correction was introduced. An empirical absorption correction was applied by using the azimuthal scan method.[15] All calculations were performed using the SHELX 76 package of programs.[16] The metal-atom positions were determined by direct methods and all non-hydrogen atoms located from Fourier difference syntheses. The phenyl groups of the PPh_3 ligand were treated as regular rigid rings (C–C 1.395, C–H 1.08 Å). The structure model was refined by full-matrix least-squares calculations, thermal motion being treated anisotropically for all the atoms except those of the phenyl rings. The hydrogen atoms were assigned fixed thermal parameters of 0.08 Å^2. The final Fourier difference map showed peaks not exceeding 0.85 e Å^{-3} in the vicinity of the Au and Rh atoms. Positional parameters with their estimated standard deviations corresponding to the last least-squares refinement cycle are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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