New Carbide Clusters in the Cobalt Subgroup. Part 12.[1] Synthesis and *X*-Ray Characterization of the Tetradecanuclear Carbido-carbonyl Cluster $[Rh_{14}C_2(\mu\text{-}CO)_{21}(CO)_{12}]^{2-}$ †

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The compound $[Rh_{14}C_2(\mu\text{-}CO)_{21}(CO)_{12}]^{2-}$ has been synthesized by reaction of $[Rh_6C(CO)_{15}]^{2-}$ with $[Rh(CO)_2(MeCN)_2]^+$. Its molecular structure has been determined by single-crystal *X*-ray crystallography: monoclinic, space group $C2/m$, with $a = 13.496(1)$, $b = 37.175(2)$, $c = 15.858(1)$ Å, $\beta = 113.9(1)°$, and $Z = 4$. The structure has been solved from 3 460 reflections collected by counter methods and refined by least-squares calculations to $R = 0.042$. The dianion has idealized D_{3h} symmetry and contains two Rh_7C moieties related by a crystallographic mirror plane. Each unit is a C_{3v} monocapped trigonal prism. The two halves are linked by a Rh–Rh bond between the capping atoms and by three bridging carbonyl ligands. The remaining 30 CO groups are distributed 15 on each Rh_6 prism, the geometry of the parent $[Rh_6C(CO)_{15}]^{2-}$ anion being retained. The Rh–Rh bond between the two Rh_7 units is remarkably short, 2.570(2) Å. Other relevant (average) bond distances are as follows: Rh–Rh 2.778, Rh–C(carbide) 2.14; Rh–C and C–O for terminal and bridging ligands 1.89 and 1.14 and 2.07 and 1.17 Å, respectively. A comparison is made with the clusters $[Rh_8C(CO)_{19}]$, $[Cu_2Rh_6C(CO)_{15}(MeCN)_2]$, and $[Ag\{Rh_6C(CO)_{15}\}_2]^{3-}$.

We have recently obtained mixed-metal carbonyl carbido-clusters by reactions of the dianion[2] $[Rh_6C(CO)_{15}]^{2-}$ with metal cations of Group 1B. First some copper derivatives were isolated among which the structure of $[Cu_2Rh_6C(CO)_{15}(MeCN)_2]$ was determined in detail.[3] A whole family of silver derivatives was subsequently prepared and the *X*-ray structure of the monosilver adduct $[Ag\{Rh_6C(CO)_{15}\}_2]^{3-}$ was determined, while a series of polysilver oligomers was characterized in solution by n.m.r. techniques.[4] The silver atoms in these species are sandwiched between $Rh_6C(CO)_{15}$ prismatic units. Similar gold derivatives have also been isolated and are under investigation. In all these compounds the entering metal atoms have been found to be bonded on the triangular faces of the Rh_6 prismatic units, indicating some localization of negative charge on these faces.

However, our previous work on the oxidation products of the $[Rh_6C(CO)_{15}]^{2-}$ anion had yielded the neutral cluster $[Rh_8C(CO)_{19}]$,[5] which is formally derived from the condensation of two $Rh(CO)_2{}^+$ fragments on the hexanuclear dianion. The structure of this compound showed the two extra Rh atoms to be bonded to the Rh_6 prism, one bridging an edge of a triangular face and the other capping a square face.[5] Such a situation, being in contrast with what is observed in all Group 1B mixed-metal derivatives, induced us to investigate the analogous reaction between the cation $[Rh(CO)_2(MeCN)_2]^+$ and the anion $[Rh_6C(CO)_{15}]^{2-}$ in order to determine the observed structural difference between heteronuclear and homonuclear addition products on the Rh_6 prism. This study has led to the isolation and structural characterization of the new dianion $[Rh_{14}C_2(CO)_{33}]^{2-}$ and to the demonstration that it is chemically related to $[Rh_8C(CO)_{19}]$.

Results and Discussion

Synthesis and Chemical Characterization.—The dianion $[Rh_{14}C_2(CO)_{33}]^{2-}$ has been synthesized from the reaction under a carbon monoxide atmosphere of $K_2[Rh_6C(CO)_{15}]$ in aqueous acidic solution with $[Rh(CO)_2(MeCN)_2]BF_4$ in acetonitrile. The resulting yellow-brown precipitate was separated by extraction with CH_2Cl_2. Slow diffusion of toluene into the extract under a CO atmosphere yields black crystals of the $[Rh(CO)_2(MeCN)_2]^+$ salt of the new dianion together with minor amounts of the corresponding K^+ salt and traces of $[Rh_6(CO)_{16}]$. The latter is probably formed by reduction of $[Rh(CO)_2(MeCN)_2]^+$ by OH^-/CO. Acidic conditions have been used to suppress this side reaction, but in the CH_2Cl_2 extract only traces of the original acid are probably present. Crystals suitable for *X*-ray analysis were found in the crude product. The mixture of the $[Rh(CO)_2(MeCN)_2]^+$ and K^+ salts can be converted into the $[N(PPh_3)_2]^+$ salt by metathesis with $[N(PPh_3)_2]_2SO_4$ in propan-2-ol. For this purpose halide salts of $[N(PPh_3)_2]^+$ must be avoided (see later).

The $[N(PPh_3)_2]^+$ salt can be crystallized as long fine dark violet needles by the slow-diffusion technique from tetrahydrofuran (thf) and n-hexane. Both solid $[N(PPh_3)_2]^+$ and $[Rh(CO)_2(MeCN)_2]^+$ salts are stable in air for some days, while the deep violet solutions in thf or acetone are slowly oxidized. Solutions of the $[Rh(CO)_2(MeCN)_2]^+$ salt in these solvents undergo slow decomposition also under nitrogen.

The i.r. spectrum of a Nujol mull of selected crystals of the $[Rh(CO)_2(MeCN)_2]^+$ salt is shown in Figure 1; characteristic are the bands at 2 330 and 2 300 cm^{-1} of the MeCN co-ordinated to the cation. The presence of $[Rh_6(CO)_{16}]$ would have been revealed by a band at 1 800 cm^{-1} due to its triply bridging carbonyls. The i.r. spectrum of the $[N(PPh_3)_2]^+$ salt in thf solution in the carbonyl-stretching region shows bands at 2 047s, 2 035s, 2 026s, 1 920w, 1 893s, and 1 866m cm^{-1} (Figure 2).

The rather unusual method used to carry out the condens-

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† Tri-μ-carbonyl-bis{[μ_6-carbido-nona-μ-carbonyl-*cyclo*-hexa-(carbonylrhodio)(3 *Ru*–*Ru*)]rhodate}(*Ru*–*Ru*)(2 –).

Supplementary data available (No. SUP 23923, 24 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

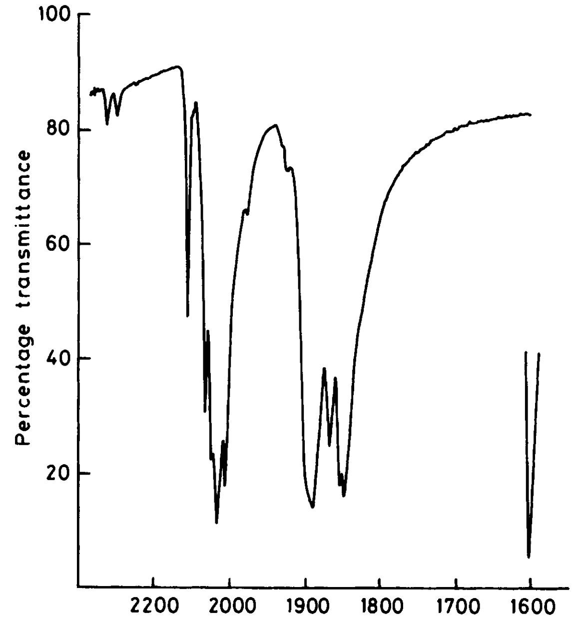


Figure 1. The i.r. spectrum of $[Rh(CO)_2(MeCN)_2]_2[Rh_{14}C_2(CO)_{33}]$ in Nujol mull

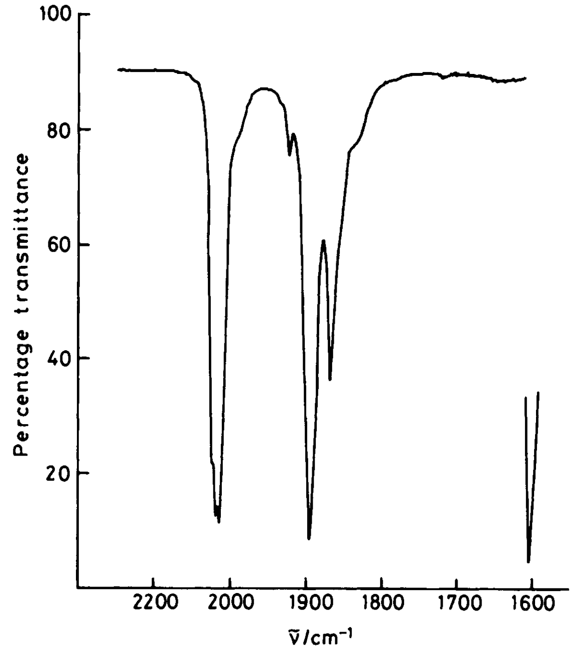
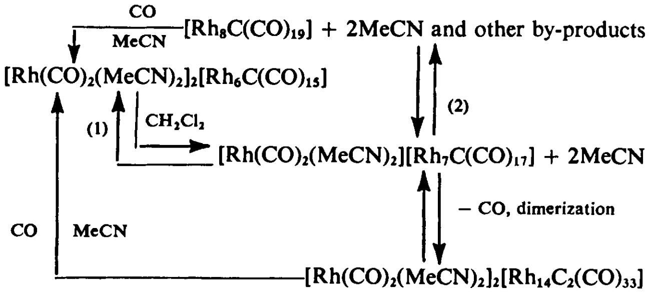


Figure 2. The i.r. spectrum of $[N(PPh_3)_2]_2[Rh_{14}C_2(CO)_{33}]$ in thf solution

ation between $[Rh(CO)_2(MeCN)_2]^+$ and $[Rh_6C(CO)_{15}]^{2-}$ needs some explanation. Direct condensation in the usual solvents (MeCN, thf, and acetone) does not take place under an atmosphere of CO, while under nitrogen other as yet uncharacterized products are formed.

After the structure of this new dianion had been elucidated (see next section) it became apparent that a heptanuclear species is an intermediate in the synthesis of the dimeric dianion. The same kind of intermediate had been postulated in the synthesis of $[Rh_8C(CO)_{19}]$.[5] In fact the latter was originally obtained by leaving under a CO atmosphere a CH_2Cl_2 solution of the products of reaction of $[Rh_6C(CO)_{15}]^{2-}$ with iron(III) salts in water. It was supposed that the oxidant produced some reactive rhodium(I) fragment which added to the unreacted dianion.



Scheme.

In order to demonstrate a possible connection between $[Rh_{14}C_2(CO)_{33}]^{2-}$ and $[Rh_8C(CO)_{19}]$ we attempted to synthesize $[Rh_8C(CO)_{19}]$ directly from the rhodium(I) species instead of generating the latter by oxidation. When $[Rh(CO)_2(MeCN)_2]BF_4$ and $K_2[Rh_6C(CO)_{15}]$ are mixed in water there is instantaneous formation of a yellow-brown precipitate, similar to that observed in the reaction with iron(III) salts. I.r. spectroscopic analysis of this precipitate indicates that it consists mainly of the $[Rh(CO)_2(MeCN)_2]^+$ salt of $[Rh_6C(CO)_{15}]^{2-}$, therefore the condensation process takes place subsequently in CH_2Cl_2. We have also observed that when $[Rh(CO)_2(MeCN)_2]BF_4$ is placed in the reaction vessel as a concentrated solution in MeCN, rather than as a solid or aqueous solution, the new anion $[Rh_{14}C_2(CO)_{33}]^{2-}$ is formed (see above) instead of $[Rh_8C(CO)_{19}]$. From these findings we infer that both species are formed from the same Rh_7 intermediate and that the amount of MeCN present in the CH_2Cl_2 solution has a key role in determining the final product. A tentative rationalization of the condensation processes which occur in CH_2Cl_2 is summarized in the Scheme.

It is important to stress that, in order to promote dimerization to Rh_{14}, the MeCN concentration must be low enough to allow reaction (1) to take place to some extent, but not so low as to favour equilibrium (2), which requires further MeCN elimination. The concentration of MeCN extracted by CH_2Cl_2 (*ca.* 5%) seems to be just that needed for the Rh_{14} formation. Dichloromethane is the best solvent for this kind of condensation, as it is not able to stabilize the rhodium(I) cation, as does MeCN, thus favouring the condensation and allowing its control through the CH_2Cl_2 : MeCN ratio. In the absence of MeCN, $[Rh_8C(CO)_{19}]$ is formed,[6] while when $[Rh_8C(CO)_{19}]$ or $[Rh_{14}C_2(CO)_{33}]^{2-}$ is dissolved in pure MeCN under a CO atmosphere both species are completely converted back into the rhodium(I) cation and $[Rh_6C(CO)_{15}]^{2-}$ anion. In other solvents, such as thf or acetone, this decomposition is more difficult, but becomes instantaneous in the presence of halide ions which remove the rhodium(I) as stable $[Rh(CO)_2X_2]^-$ complexes. Further, treatment of $[Rh_8C(CO)_{19}]$ with a solution of MeCN in CH_2Cl_2 (*ca.* 5%) under a CO atmosphere and addition of toluene as above results in formation of a significant amount of $[Rh_{14}C_2(CO)_{33}]^{2-}$.

The structure of the Rh_7 intermediate, the precursor of both Rh_8 and Rh_{14} species, could be pictured as a Rh_6 prism bearing a $Rh(CO)_3$ unit on a basal edge. Such a species could either afford $[Rh_{14}C_2(CO)_{33}]^{2-}$ by isomerization to a C_{3v} capped prism followed by dimerization, or undergo further condensation with $[Rh(CO)_2(MeCN)_2]^+$ on a rectangular face to give $[Rh_8C(CO)_{19}]$.

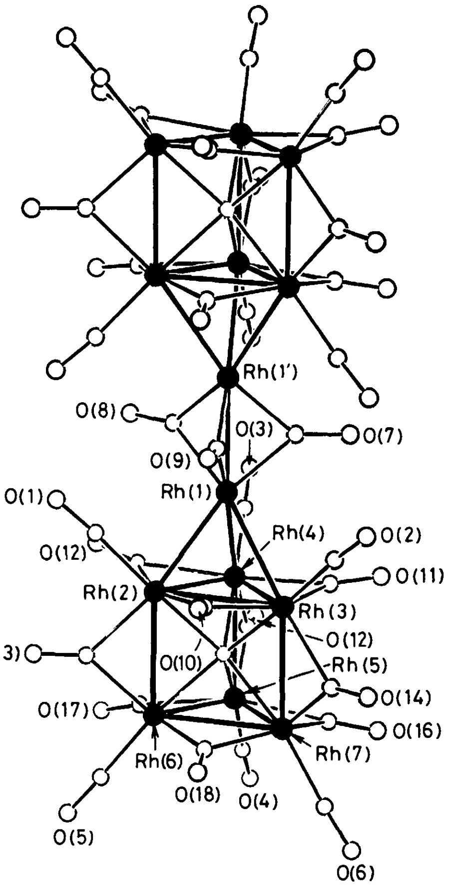


Figure 3. The anion $[Rh_{14}C_2(CO)_{33}]^{2-}$ showing the atom labelling. The carbon atoms of the CO ligands, not labelled, bear the same numbers as the corresponding oxygens

Description of the Structure.—The crystal comprises discrete dianions $[Rh_{14}C_2(CO)_{33}]^{2-}$ (Figure 3) and cations $[Rh(CO)_2(MeCN)_2]^+$. The cations are in general positions while the anions have C_s-*m* crystallographic symmetry. The mirror plane relates two Rh_7 moieties consisting of C_{3v} monocapped prisms. The prisms contain the $Rh_6C(CO)_{15}$ unit with a geometry almost identical to that of the parent dianion. The two Rh_7 units are linked by a Rh–Rh bond between the capping atoms and by three bridging CO ligands. The overall idealized molecular symmetry is D_{3h}. There are three metal–metal bonds in the outer triangular faces and four in the inner ones and between the capping atoms. All these Rh–Rh distances but one are in the range 2.771—2.830(1), average 2.778 Å. Average values for symmetry-equivalent sets are as follows: outer base, 2.779(4); inter-base, 2.825(6); inner base, 2.742(3); and base–cap, 2.765(4) Å. These values can be compared with those found in the related species $[Rh_6C(CO)_{15}]^{2-}$ (base, 2.776; inter-base, 2.817 Å),[2] $[Cu_2Rh_6C(CO)_{15}(MeCN)_2]$ (base, 2.765; inter-base, 2.810 Å),[3] and $[Ag\{Rh_6C(CO)_{15}\}_2]^{3-}$ (outer base, 2.780; inter-base, 2.826; inner base, 2.781 Å).[4] The small but significant variations in bond distances observed above show that, taking as reference the dianion $[Rh_6C(CO)_{15}]^{2-}$, the silver derivative contains the least disturbed Rh_6 system, followed by the dicopper derivative in which some shrinkage of the distances is observed, and finally the present species which exhibits wider ranges of bond distances. Increasing integration of the capping atoms in the molecular orbitals of the prismatic unit can be inferred from this trend. This is at a minimum in the case of the silver–rhodium interaction, which has more ionic character, and at a maximum for the homonuclear system.

The bond between the capping atoms is remarkably short, 2.570(2) Å, one of the shortest observed for rhodium. The presence of the three bridging carbonyl ligands could account for this. In order to verify whether the value is entirely attributable to the well known shortening effect of bridging ligands a comparison can be made with the iron–iron distances in $[Fe_3(CO)_{12}]$ [7] and $[Fe_2(CO)_9]$ [8] in which unbridged, doubly bridged, and triply bridged Fe–Fe bonds are present. In the trinuclear species the unbridged and doubly bridged edges are 2.68 and 2.56 Å long, in the binuclear molecule the triply bridged bond is 2.52 Å long. The maximum shortening is therefore 0.16 Å. In the present case the shortening with respect to the average rhodium–rhodium bond length is 0.21 Å. An electron count based on localized electron-pair bonds shows that the capping atoms have only 16 electrons. Even though such counts are oversimplifications, they never give values far from 18 if the metal–metal bonds are properly taken into account. Therefore both the bond length and electron count support a Rh(1)–Rh(1′) bond order higher than unity.

The average Rh–C(carbide) distance, 2.14(1) Å, is coincident with the value in the parent dianion. The carbide atom, on the other hand, is not equidistant from the two faces, being 0.03 Å nearer to the outer atoms.

There are 18 independent carbonyl ligands in the anion, 12 of which are edge-bridging and six terminal. The three ligands bridging the inter-unit Rh–Rh bond lie in the mirror plane and have average Rh–C and C–O distances of 1.99(2) and 1.18(3) Å, respectively. The groups bridging the prism edges belong to three non-equivalent sets with the following average bond distances: inner base, 2.12(2) and 1.16(1); inter-base, 2.05(2) and 1.18(2); and outer base, 2.13(2) and 1.15(1) Å. These values compare well with those in the parent dianion $[Rh_6C(CO)_{15}]^{2-}$ [base, 2.12(1) and 1.14(2); inter-base, 2.04(1) and 1.17(2) Å]. There is a correlation between the metal–metal and metal–bridging carbonyl distances, *i.e.* the shorter are the former the shorter are the latter. The six independent terminal ligands are bonded to the prism atoms and belong to two non-equivalent sets. The bond distances are not discernibly different, average Rh–C and C–O distances being 1.89(1) and 1.14(1) Å, respectively. The average Rh–C–O angles for inner and outer ligands, 175 and 176°, are not significantly different. The inner ligands show a contact with the capping atom, 3.08 Å, similar to that found in the capped derivatives $[Cu_2Rh_6C(CO)_{15}(MeCN)_2]$ and $[Ag\{Rh_6C(CO)_{15}\}_2]^{3-}$. The most significant effect of the capping process on the ligands is the outward displacement of the inner terminal carbonyls, as shown by the average Rh–Rh–CO angles, 134.1(2) and 142.2(2)° for inner and outer ligands, respectively.

We can now try to explain why the addition of rhodium fragments on the Rh_6 prism does not give species structurally equivalent to the copper and silver derivatives. A rhodium atom on a triangular face would require three terminal ligands to be co-ordinatively saturated and such a $Rh(CO)_3$ fragment would produce considerable ligand overcrowding. This unfavourable situation is alleviated by adopting a looser geometry in the case of $[Rh_8C(CO)_{19}]$ and through dimerization in $[Rh_{14}C_2(CO)_{33}]^{2-}$. In the latter three CO groups are still bonded to the capping atoms but, being shared between these atoms, they are moved away from the prismatic units thus reducing the inter-ligand interactions.

The $[Rh(CO)_2(MeCN)_2]^+$ cations show *cis* square-planar co-ordination and, interestingly, form parallel pairs with rhodium–rhodium contacts of 3.27 Å. This is indicative of some bonding interaction, probably because the rhodium atoms have two electrons less than the noble-gas configuration.

Table 1. Final positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	1 685(1)	346(1)	3 079(1)	C(11)	3 208(11)	911(4)	4 534(10)
Rh(2)	726(1)	956(1)	2 080(1)	O(11)	3 896(8)	854(3)	5 257(7)
Rh(3)	2 911(1)	954(1)	3 142(1)	C(12)	− 122(10)	914(3)	2 943(9)
Rh(4)	1 477(1)	956(1)	3 969(1)	O(12)	−996(8)	869(3)	2 892(8)
Rh(5)	1 478(1)	1 713(1)	3 983(1)	C(13)	−211(11)	1 351(4)	1 184(11)
Rh(6)	706(1)	1 717(1)	2 074(1)	O(13)	−958(9)	1 356(3)	433(8)
Rh(7)	2 927(1)	1 715(1)	3 138(1)	C(14)	4 045(9)	1 354(3)	3 143(9)
Rh(8)	757(1)	3 558(1)	−586(1)	O(14)	4 888(7)	1 345(2)	3 124(6)
C(0)	1 702(8)	1 345(3)	3 062(8)	C(15)	1 448(12)	1 355(4)	4 891(11)
C(1)	−92(11)	604(4)	1 247(10)	O(15)	1 489(11)	1 344(4)	5 642(10)
O(1)	−635(9)	402(3)	694(8)	C(16)	3 202(11)	1 785(3)	4 533(10)
C(2)	3 915(11)	591(4)	3 190(10)	O(16)	3 877(8)	1 846(3)	5 239(8)
O(2)	4 539(8)	394(3)	3 171(7)	C(17)	− 129(11)	1 768(4)	2 942(10)
C(3)	1 328(11)	603(4)	4 774(10)	O(17)	−992(8)	1 832(3)	2 876(7)
O(3)	1 265(9)	413(3)	5 304(8)	C(18)	2 020(11)	1 802(4)	1 698(10)
C(4)	1 332(12)	2 112(4)	4 655(11)	O(18)	2 175(8)	1 905(3)	1 077(8)
O(4)	1 277(10)	2 342(3)	5 117(9)	C(19)	1 586(10)	3 200(4)	123(10)
C(5)	−7(13)	2 118(4)	1 354(11)	O(19)	2 084(8)	2 964(3)	557(7)
O(5)	−489(11)	2 353(4)	917(9)	C(20)	1 728(11)	3 875(4)	249(9)
C(6)	3 818(10)	2 112(4)	3 158(10)	O(20)	2 234(9)	4 079(3)	749(9)
O(6)	4 361(9)	2 344(3)	3 148(8)	N(1)	− 192(9)	3 960(3)	−1 414(8)
C(7)	1 890(15)	0	2 219(4)	C(21)	−788(10)	4 127(3)	−1 973(9)
O(7)	2 018(11)	0	1 505(11)	C(22)	−1 554(11)	4 348(4)	−2 732(10)
C(8)	531(16)	0	3 015(14)	N(2)	−294(8)	3 214(4)	−1 546(8)
O(8)	−363(11)	0	2 989(10)	C(23)	−897(10)	3 046(4)	−2 157(9)
C(9)	2 638(15)	0	4 054(14)	C(24)	−1 694(11)	2 850(4)	−2 901(10)
O(9)	3 350(11)	0	4 753(10)	C(25)	3 006(8)	0	77(8)
C(10)	2 046(10)	909(3)	1 691(10)	Cl(1)	4 258(5)	0	860(4)
O(10)	2 221(8)	845(3)	1 054(7)	Cl(2)	2 856(5)	0	−1 043(4)

Experimental

General.—The solvents were distilled and dried by the usual methods and stored under nitrogen. All the operations were carried out under CO or nitrogen atmospheres as specified. The salts $K_2[Rh_6C(CO)_{15}]$ and $[Rh(CO)_2(MeCN)_2]BF_4$ were prepared as described.[9,10] Infrared spectra were recorded on a Perkin-Elmer model 781 spectrometer.

Synthesis of the $[Rh_{14}C_2(CO)_{33}]^{2-}$ *Salts*.—A solution of $[Rh(CO)_2(MeCN)_2]BF_4$ (0.208 g, 0.63 mmol) in acetonitrile (4 cm^3) was quickly added dropwise under a CO atmosphere and with vigorous stirring to a solution of $K_2[Rh_6C(CO)_{15}]\cdot$3thf (0.34 g, 0.25 mmol) and Na_2SO_4 (10 g) in 0.1 mol dm^{-3} aqueous sulphuric acid (100 cm^3) presaturated with CO. A yellow-brown precipitate formed immediately and was quickly extracted with CH_2Cl_2 (10 cm^3). The brown-violet extract was quickly syringed off and transferred under CO to another Schlenk tube (100 cm^3). Toluene (40 cm^3) was carefully added with a syringe as a layer over the CH_2Cl_2 solution and the whole system was left for a few days under CO until completion of the solvent diffusion. The crystals which separated were washed with toluene, dried under vacuum, and kept under nitrogen. The product consisted mainly of the $[Rh(CO)_2(MeCN)_2]^+$ salt of $[Rh_{14}C_2(CO)_{33}]^{2-}$ together with some K^+ salt and, sometimes, traces of $[Rh_6(CO)_{16}]$. To calculate the yields the above salts were transformed into the $[N(PPh_3)_2]^+$ salt by extraction under nitrogen of the soluble salts with methanol, filtration, and precipitation on dropwise addition of a propan-2-ol solution of $[N(PPh_3)_2]_2SO_4$ (3.6%, 5 cm^3) to the stirred methanolic solution. The precipitate was filtered off, washed three times with propan-2-ol (10 cm^3), twice with water (5 cm^3), and again twice with propan-2-ol (10 cm^3), and vacuum dried. Yields were 25—30%. This product can be recrystallized by the slow-diffusion technique from tetrahydrofuran-n-hexane (Found: C, 36.3; H, 2.40; N, 0.90; Rh, 42.9. Calc. for $C_{107}H_{60}N_2O_{33}P_4Rh_{14}$: C, 37.05; H, 1.75; N, 0.80; Rh, 41.6%). The $[N(PPh_3)_2]^+$ salt is soluble in thf and acetone. Solutions of the $[Rh(CO)_2(MeCN)_2]^+$ salt are unstable and give, on standing, products as yet uncharacterized.

Crystallography.—*Crystal data*. $C_{47\cdot3}H_{12\cdot6}Cl_{0.6}N_4O_{37}Rh_{16}$, $M = 2\,896.7$, monoclinic, $a = 13.496(1)$, $b = 37.175(2)$, $c = 15.858(1)$ Å, $\beta = 113.9(1)°$, $U = 7\,274$ Å^3, $D_m = 2.7$, $Z = 4$, $D_c = 2.64$ g cm^{-3}, space group $C_{2/m}$ (no. 12), Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 34.4 cm^{-1}, $F(000) = 5\,696$.

Collection and reduction of X-*ray intensity data*. A crystal fragment with average dimensions 0.08 × 0.15 × 0.23 mm was mounted on a Philips PW1100 diffractometer. Diffraction intensities were measured by the ω-scan method in the range $3 < \theta < 26°$, with scan interval 1.0° and speed 2.0° min^{-1}. The background was measured on both sides of the reflections for a total time equal to the peak scanning time. 6 267 Diffraction intensities were collected, 3 460 of which $[F_o > 5\sigma(F_o)]$ were used for the structure solution and refinement. The integrated intensities were reduced to F_o values and an experimental correction for absorption was applied.

Determination of the structure. For all the computations the SHELX package of crystallographic programs was used.[11] The structure was solved by direct methods. The identification of the metal polyhedron geometry in the *E* map was not straightforward due to multiple images and lack of information on the molecular complexity. After various attempts a Rh_7 fragment was recognized close to a crystallographic symmetry plane and bonded to its mirror image, thus generating a Rh_{14} molecular frame. A Fourier map computed after a preliminary refinement of the metal-atom co-ordinates showed the cation and the ligands. A Fourier-difference map, calculated after refinement of the structure model with aniso-

Table 2. Distances (Å) and relevant angles (°) with estimated standard deviations in parentheses

Rh(1)–Rh(1′)	2.570(2)	Rh(3)–C(2)	1.89(1)	Rh(3)–C(14)	2.13(1)	C(12)–O(12)	1.16(2)
Rh(1)–Rh(2)	2.771(1)	Rh(1)···C(2)	3.08(1)	Rh(7)–C(14)	2.02(1)	C(13)–O(13)	1.21(2)
Rh(1)–Rh(3)	2.779(1)	Rh(4)–C(3)	1.90(2)	Rh(4)–C(15)	2.10(2)	C(14)–O(14)	1.15(2)
Rh(1)–Rh(4)	2.745(2)	Rh(1)···C(3)	3.07(2)	Rh(5)–C(15)	1.97(2)	C(15)–O(15)	1.17(2)
Rh(2)–Rh(6)	2.829(1)	Rh(5)–C(4)	1.88(2)	Rh(5)–C(16)	2.15(1)	C(16)–O(16)	1.15(2)
Rh(3)–Rh(7)	2.830(1)	Rh(6)–C(5)	1.89(2)	Rh(7)–C(16)	2.11(2)	C(17)–O(17)	1.15(2)
Rh(4)–Rh(5)	2.816(1)	Rh(7)–C(6)	1.89(7)	Rh(5)–C(17)	2.14(1)	C(18)–O(18)	1.15(2)
Rh(2)–Rh(3)	2.739(1)	Rh(1)–C(7)	1.97(2)	Rh(6)–C(17)	2.11(2)	C(7)···C(9)	2.67
Rh(2)–Rh(4)	2.746(2)	Rh(1)–C(8)	1.99(2)	Rh(6)–C(18)	2.11(2)	C(7)···C(8)	2.62
Rh(3)–Rh(4)	2.741(2)	Rh(1)–C(9)	2.02(1)	Rh(7)–C(18)	2.13(1)	C(8)···C(9)	2.65
Rh(5)–Rh(6)	2.773(2)	Rh(2)–C(10)	2.11(2)	C(1)–O(1)	1.16(2)	Rh(8)···Rh(8′)	3.27(1)
Rh(5)–Rh(7)	2.783(2)	Rh(3)–C(10)	2.12(1)	C(2)–O(2)	1.13(2)	Rh(8)–C(19)	1.81(2)
Rh(6)–Rh(7)	2.781(1)	Rh(3)–C(11)	2.08(2)	C(3)–O(3)	1.13(2)	Rh(8)–C(20)	1.86(2)
Rh(2)–C(0)	2.14(1)	Rh(4)–C(11)	2.14(1)	C(4)–O(4)	1.15(2)	Rh(8)–N(1)	2.06(2)
Rh(3)–C(0)	2.15(1)	Rh(2)–C(12)	2.12(2)	C(5)–O(5)	1.14(2)	Rh(8)–N(2)	2.05(2)
Rh(4)–C(0)	2.15(1)	Rh(4)–C(12)	2.12(1)	C(6)–O(6)	1.14(2)	C(19)–O(19)	1.15(2)
Rh(5)–C(0)	2.11(1)	Rh(1)···C(10)	3.22	C(7)–O(7)	1.21(3)	C(20)–O(20)	1.11(2)
Rh(6)–C(0)	2.11(1)	Rh(1)···C(11)	3.18	C(8)–O(8)	1.19(3)	N(1)–C(21)	1.11(2)
Rh(7)–C(0)	2.12(1)	Rh(1)···C(12)	3.17	C(9)–O(9)	1.13(2)	N(2)–C(23)	1.16(2)
Rh(2)–C(1)	1.87(1)	Rh(2)–C(13)	2.08(1)	C(10)–O(10)	1.15(2)	C(21)–C(22)	1.48(2)
Rh(1)···C(1)	3.08(1)	Rh(6)–C(13)	1.99(1)	C(11)–O(11)	1.17(2)	C(23)–C(24)	1.43(2)

Rh(2)–C(1)–O(1)	176(1)	Rh(2)–C(10)–O(10)	140(1)	Rh(7)–C(14)–O(14)	140(1)
Rh(3)–C(2)–O(2)	174(1)	Rh(3)–C(10)–O(10)	139(1)	Rh(4)–C(15)–O(15)	133(1)
Rh(4)–C(3)–O(3)	175(1)	Rh(3)–C(11)–O(11)	142(1)	Rh(5)–C(15)–O(15)	139(1)
Rh(5)–C(4)–O(4)	175(1)	Rh(4)–C(11)–O(11)	136(1)	Rh(5)–C(16)–O(16)	136(1)
Rh(6)–C(5)–O(5)	176(1)	Rh(2)–C(12)–O(12)	140(1)	Rh(7)–C(16)–O(16)	142(1)
Rh(7)–C(6)–O(6)	178(2)	Rh(4)–C(12)–O(12)	139(1)	Rh(5)–C(17)–O(17)	140(1)
Rh(1)–C(7)–O(7)	139(1)	Rh(2)–C(13)–O(13)	136(1)	Rh(6)–C(17)–O(17)	138(1)
Rh(1)–C(8)–O(8)	140(1)	Rh(6)–C(13)–O(13)	136(1)	Rh(6)–C(18)–O(18)	139(1)
Rh(1)–C(9)–O(9)	140(1)	Rh(3)–C(14)–O(14)	134(1)	Rh(7)–C(18)–O(18)	138(1)

tropic thermal parameters for the heavy atoms, showed three residual peaks which, on the basis of geometrical and chemical considerations, were assumed to be a CH_2Cl_2 molecule partially occupying the site. Refinement of the occupancy factor converged at 0.29(2). All the light atoms were assigned isotropic thermal parameters. The final agreement indices were $R = 0.042$ and $R' = 0.046$, and a Fourier-difference map computed after refinement showed residual peaks lower than 1.2 e Å^{-3} in the vicinity of the oxygen atoms.

The co-ordinates of all the refined atoms are reported in Table 1, bond distances and relevant angles in Table 2.

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