New Carbide Clusters in the Cobalt Sub-group. Part 15.[1] Synthesis and Crystallographic Characterization of Di-μ_6-carbido-deca-μ-carbonyl-tridecacarbonyl-*polyhedro*-dodecarhodate(4−) as its Tetrapropylammonium Salt, $[N(C_3H_7)_4]_4[Rh_{12}C_2(CO)_{23}]$ ‡

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The compound $[N(C_3H_7)_4]_4[Rh_{12}C_2(CO)_{23}]$ has been prepared by reduction with alkali-metal hydroxide in MeOH of the dianion $[Rh_{12}C_2(CO)_{24}]^{2-}$. Its molecular structure has been determined by single-crystal *X*-ray crystallography: monoclinic, space group $P2_1/c$, $a = 21.132(4)$, $b = 15.334(3)$, $c = 30.093(5)$ Å, $\beta = 103.07(4)°$, and $Z = 4$. The structure has been solved from 7 589 intensities and refined to $R = 0.0738$. The metal-atom polyhedron is almost unchanged from that present in the dianion. It may be described as a three-layer stacking sequence of metal atoms generating two prismatic cavities occupied by two interstitial carbon atoms. The main difference between the two anions is the loss of a CO ligand and the rearrangement of the seven ligands bonded to the equatorial layer with formation of two bridges. The idealized symmetry is C_{2v}. Relevant average distances are: Rh–Rh 2.829, Rh–C(carbide) 2.13 Å; Rh–C and C–O, 1.82, 1.17 and 2.03, 1.20 Å for terminal and bridging CO groups, respectively.

We have recently reported the synthesis and structure of the carbido-carbonyl anion $[Rh_{12}C_2(CO)_{24}]^{2-}$ (**1**) which contains a quite compact metal-atom polyhedron and two interstitial atoms.[2] We have also found that this dianion can be reduced in methanolic solutions of alkali-metal hydroxides to yield $[Rh_{12}C_2(CO)_{23}]^{3-}$ (**2**) and $[Rh_{12}C_2(CO)_{23}]^{4-}$ (**3**). The structures of complexes (**2**) and (**3**) have been determined by single-crystal *X*-ray diffractometry and show that the metal-atom polyhedron of (**1**) is kept almost unaltered. Details of the synthesis and structure of (**2**) were reported in a preliminary communication.[3] In this paper we describe the preparation, chemical characterization, and crystal structure of the tetra-anion $[Rh_{12}C_2(CO)_{23}]^{4-}$ as its tetrapropylammonium salt. A comparison of the structural parameters of complexes (**1**)—(**3**) is also presented.

Results and Discussion

Synthesis and Chemical Characterization.—Anion (**3**) was synthesized by reduction of the alkali-metal salts of (**1**) in MeOH with alkali-metal hydroxides, according to equation (1). A very large excess of hydroxide is required to complete the

$$[Rh_{12}C_2(CO)_{24}]^{2-} + 4\,OH^- \longrightarrow [Rh_{12}C_2(CO)_{23}]^{4-} + CO_3^{2-} + 2\,H_2O \quad (1)$$

reaction (see later). The anion can be isolated as the $[N(C_3H_7)_4]^+$ salt by metathesis with $[N(C_3H_7)_4]Br$; when the metathesis is carried out on the potassium salt, a mixed potassium–tetrapropylammonium salt separates out instead of the pure tetrapropylammonium salt.

Anion (**3**) is also observed among the products of the pyrolysis of $[Rh_6C(CO)_{15}]^{2-}$. When the pyrolysis is performed on the diglyme $[(CH_3OCH_2CH_2)_2O]$-solvated potassium salt of the hexanuclear dianion in refluxing propan-2-ol the corresponding salt of (**3**) separates out from the boiling solution together with other by-products. Purification is achieved by extraction of the potassium salt with methanol containing KOH and metathesis as above. Reactions of anion (**3**) with oxidizing agents such as iodine or with acids have been already reported.[3] We have also found that anion (**3**) slowly reacts with traces of water in MeCN or acetone to give a mixture of (**2**) with other species presently under investigation, therefore it should be handled only in dry solvents, and left in solution for the shortest possible time. (For example, during crystallization by the slow-diffusion technique, partial decomposition is observed, probably due to the long time involved and to the presence of traces of water.) Anion (**3**) is unstable also in MeOH solution, giving mixtures of products similar to those obtained by hydrolysis. Therefore the presence of a large excess of OH^- ions is required not only to complete reaction (1) but also whenever anion (**3**) is handled in this solvent, as for example in the metathesis with $[N(C_3H_7)_4]Br$ after the pyrolytic synthesis.

The i.r. spectrum in MeCN solution (Figure 1) shows bands at 1 970s, 1 795m, 1 770 (sh), and 1 720vw cm^{-1}. Small shifts are observed in other solvents. Crystals suitable for the *X*-ray analysis were obtained by slow diffusion of di-isopropyl ether into MeCN solutions of the tetrapropylammonium salt.

Structural Characterization.—The crystal comprises discrete anions $[Rh_{12}C_2(CO)_{23}]^{4-}$ and cations $[N(C_3H_7)_4]^+$ all lying in general positions. The anion structure is depicted in Figure 2. The Rh_{12} framework shows a stereogeometry almost the same as that of the parent dianion $[Rh_{12}C_2(CO)_{24}]^{2-}$. It can be described, referring to our previous work,[2] either as a square–

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‡ *Supplementary data available* (No. SUP 56210, 4 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

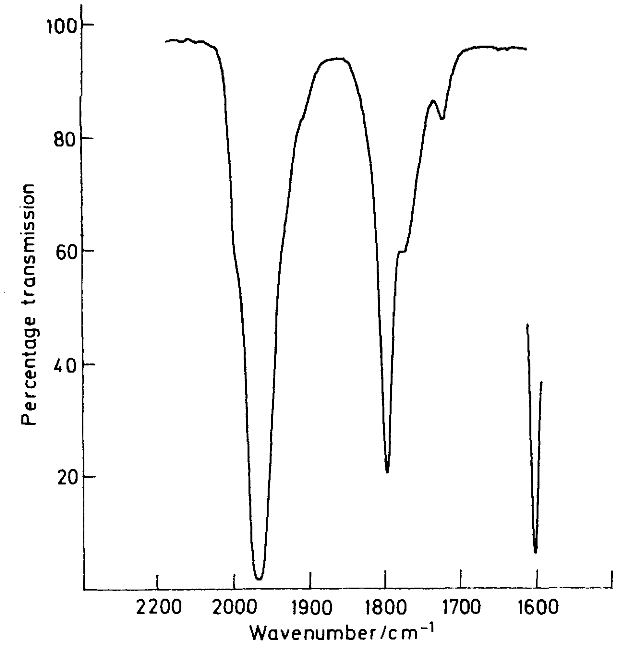

Figure 1. The i.r. spectrum of $[N(C_3H_7)_4]_4[Rh_{12}C_2(CO)_{23}]$ in MeCN solution

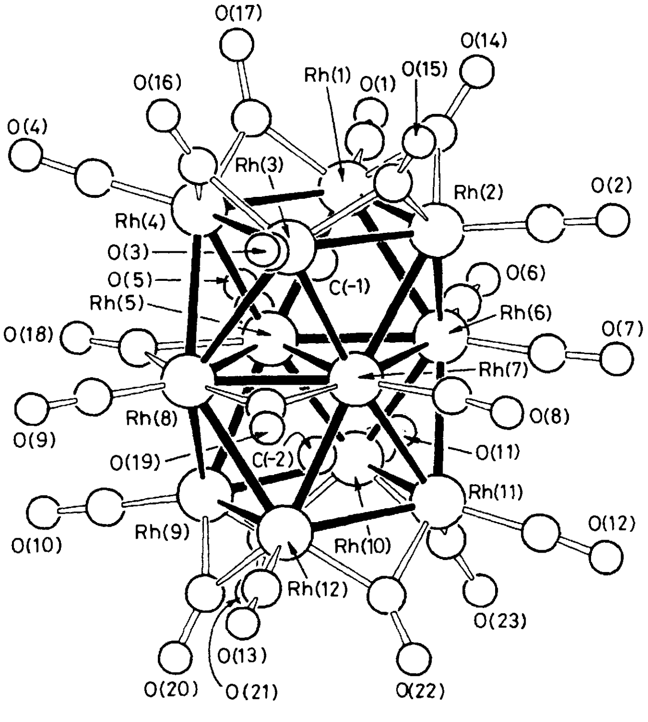

Figure 2. The anion $[Rh_{12}C_2(CO)_{23}]^{4-}$ showing the atom labelling. The carbon atoms of the CO ligands bear the same numbering as the corresponding oxygens

Table 1. Comparison between average bond distances (Å) for the anions $[Rh_{12}C_2(CO)_{23}]^{4-}$ (**3**) and $[Rh_{12}C_2(CO)_{24}]^{2-}$ (**1**)*

	(3)	(1)
Rh–Rh		
Overall	2.829	2.811
Outer square faces	2.787	2.799
Inner rhomb layer	2.752	2.756
Interlayer	2.873	2.821
Short diagonal	2.743	2.758
Rh–C (carbide)	2.13(4)	2.12(2)
Rh–C		
Terminal overall	1.82	1.89
Terminal square faces	1.84(2)	1.89(3)
Terminal rhomb layer	1.80(3)	1.90(3)
Bridge overall	2.03	2.04
Bridge square face	2.01(2)	2.04(3)
Bridge rhomb layer	2.11	—
C–O		
Terminal overall	1.17	1.10
Terminal square faces	1.16(2)	1.12(2)
Terminal rhomb layer	1.18(2)	1.08(2)
Bridge overall	1.20	1.17
Bridge square face	1.20(2)	1.17(3)
Bridge rhomb layer	1.21	—

* Estimated standard deviations (e.s.d.s) are reported only when ideally equivalent sets of distances are averaged.

rhomb–square sequence of layers, stacked in such a way as to generate two prismatic cavities, or as two prismatic Rh_6 units sharing an edge plus two extra rhodium atoms capping simultaneously the facing square faces of the prisms. The two carbide atoms occupy the prismatic cavities. The main difference between the two anions (**1**) and (**3**) results from the loss of one carbonyl ligand formally from one acute apex of the equatorial rhomb [Rh(8)]. The hole left by the outgoing ligand is filled by an in-plane displacement of two terminal ligands bonded to the obtuse apices [Rh(5) and Rh(7)], towards edge-bridging positions. In this way both electronic and steric changes are accommodated.

The distribution of the other 16 carbonyls on the outer square faces is kept unaltered: eight terminal, one on each rhodium apex, and eight bridging every square edge. The overall idealized symmetry decreases from D_{2h} for complex (**1**) to C_{2v} for (**3**), the two-fold axis being coincident with the long diagonal of the central rhomb.

At this point it should be recalled that the tetra-anion (**3**) possesses the same structure as that of the related trianion (**2**).[3] We therefore have a remarkable example of a closely related family of high-nuclearity clusters: two, (**1**) and (**3**), are isoelectronic but not isostructural, while (**2**) and (**3**) are isostructural but not isoelectronic; furthermore the trianion is paramagnetic. Therefore it would be most interesting to compare carefully the three sets of structural parameters. Unfortunately the crystallographic data for (**2**) were rather poor, thus we have to confine the discussion mainly to the dianion (**1**) and the tetra-anion (**3**). A comparison of relevant average parameters for both is reported in Table 1. As expected the increased anionic charge on the cluster causes a small, though appreciable, 'swelling' of the metal polyhedron. The average Rh–Rh distance 2.829(2) Å for complex (**3**) [range 2.714(2)—3.089(2) Å] increases by 0.018 Å with respect to the dianion (**1**). The swelling effect is reduced in the two prismatic sub-units (0.005 Å), showing that an excessive enlargement of the cavities is prevented by the 'inner ligands.' The average Rh–C(carbide) distance is 2.13 Å, with an increase as small as 0.01 Å with respect to the dianion. The actual value is equal to that found in the dianion $[Rh_6C(CO)_{15}]^{2-}$, where the same fractional charge per metal atom is present.[4]

As mentioned above, the reduction causes the loss of a CO group and a rearrangement takes place in the most crowded

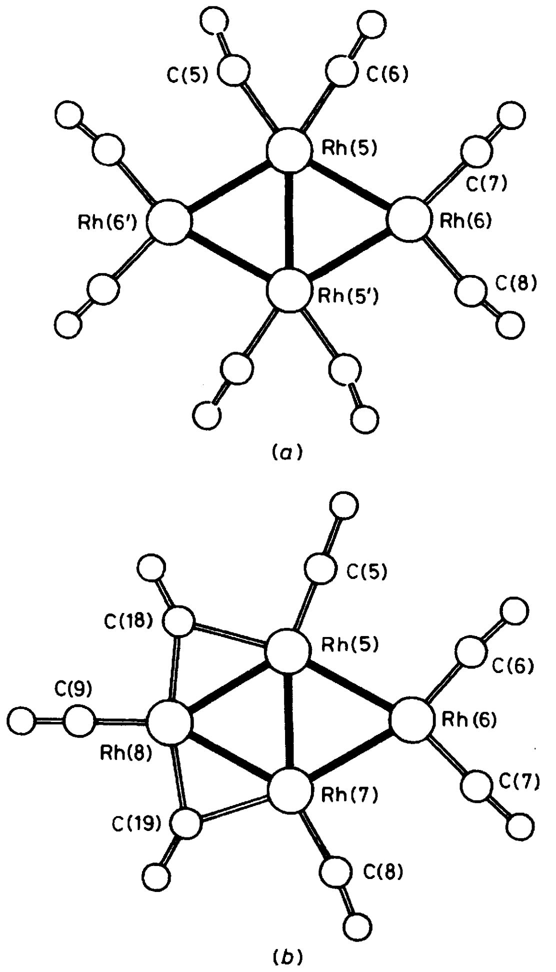

Figure 3. Comparison between the equatorial layers of the dianion $[Rh_{12}C_2(CO)_{24}]^{2-}$ (*a*) and of the tetra-anion $[Rh_{12}C_2(CO)_{23}]^{4-}$ (*b*) showing the different arrangements of the carbonyl ligands. Unlabelled atoms in (*a*) have C_i-$\bar{1}$ crystallographic symmetry

region of the molecule, *i.e.* the central layer. Figure 3 shows a comparison between the equatorial plane of the anion (**1**) and those of anions (**2**) and (**3**). The carbonyl ligands bonded to Rh(5) in the dianion (**1**) [C(5) and C(6)] show an exceptionally short C $\cdots$ C contact of 2.23 Å, while the other contacts are more normal [C(6) $\cdots$ C(7) 3.04 and C(7) $\cdots$ C(8) 2.77 Å]. An analogous $M_4(CO)_8$ planar unit was reported in the structure of the anion $[Re_4(CO)_{16}]^{2-}$.[5] Interestingly, very short C $\cdots$ C contacts between adjacent CO groups were not present, because the overcrowding was alleviated by 'puckering' of the CO groups alternatively above and below the plane (deviation range: +0.37 to −0.28 Å). A similar solution is prevented in our case by the layer packing which forces the ligands bonded to the rhomb to adopt planarity (maximum deviation (0.09 Å). Consequently the loss of a carbonyl ligand from this plane alleviates the overcrowding and may account for the facility of the process. The rearrangement of the seven remaining equatorial ligands in complexes (**2**) and (**3**), promoted by steric and electronic requirements, yields two asymmetrically bridging ligands which, moving inwards, become in close contact with the outer-layer rhodium atoms (average Rh $\cdots$ C contact 2.69 Å). These contacts are alleviated by tilting the outer metal-atom layers with respect to the central one. In fact the outer layers are no longer parallel, the mutual angle being 5.87° [0.22° in the dianion (**1**)].

Metal–metal and metal–carbon distances in the equatorial plane conform to C_{2v} idealized symmetry, showing two shorter (mean 2.721 Å) and two longer (mean 2.787 Å) Rh–Rh lengths for bridged and unbridged bonds, respectively. The short diagonal is reduced from 2.758(2) Å in complex (**1**) to 2.743(2) Å in (**3**).

The effect of a doubled anionic charge on the cluster is well evidenced by comparison of Rh–C and C–O distances. A characteristic increase of the carbon–oxygen distances together with a shortening of the rhodium–carbon ones is observed (see Table 1). For the terminal ligands the average C–O distance changes from 1.10 to 1.17 Å, and the average Rh–C from 1.89 to 1.82 Å for (**1**) and (**3**), respectively. The effect is less evident for the bridging ligands (2.04, 2.03; 1.17, 1.20 Å, respectively). These values should also be compared with those observed in the neutral isoelectronic cluster $[Rh_{12}C_2(CO)_{25}]$ (1.87, 2.08; 1.09, 1.15 Å for terminal and bridging Rh–C and C–O distances, respectively).[6] All these values are in keeping with the general trend of an increase in π-back donation with the delocalized anionic charge.

Experimental

General.—All the operations were carried out under an inert atmosphere; solvents were purified by standard methods. The salt $Na_2[Rh_6C(CO)_{15}]$ was prepared as described for the potassium salt[4] by using NaCl in place of KBr in the precipitation. The starting sodium salt of anion (**1**) was prepared as reported for the potassium salt,[2] using the corresponding sodium salts for the synthesis. The diglyme-solvated potassium salt of the $[Rh_6C(CO)_{15}]^{2-}$ anion was prepared from 1 g of the tetrahydrofuran-solvated potassium salt[7] by dissolution in the minimum amount of acetone (about 5 cm^3), addition of diglyme (10 cm^3), and concentration in vacuum until all the acetone was eliminated. The salt separated out as crystals which were filtered off, washed with n-hexane, and vacuum dried; it contains 5—6 mol of solvated diglyme.

Synthesis of $[N(C_3H_7)_4]_4[Rh_{12}C_2(CO)_{23}]$ *from* $Na_2[Rh_{12}C_2(CO)_{24}]$.—The complex $Na_2[Rh_{12}C_2(CO)_{24}]$ (0.85 g) in MeOH (15 cm^3) was treated with a methanolic solution of NaOH (3.65 mol dm^{-3}, 10.5 cm^3) and stirred under nitrogen until the i.r. spectrum of the methanolic solution in the terminal CO-stretching region showed only the band of the tetra-anion at 1 982 cm^{-1} (about 1 h). The dark reddish brown solution was added dropwise while stirring to a solution of $[N(C_3H_7)_4]Br$ (1.5 g) in propan-2-ol (20 cm^3). The precipitate was filtered off, washed first with MeOH (10 cm^3), then twice with propan-2-ol (10 cm^3), and vacuum dried. The product was separated from the mixture with NaBr and Na_2CO_3 by extraction with MeCN (1—2 cm^3 portions) until the extract was nearly colourless (total volume *ca.* 8 cm^3) and the solution was treated dropwise under stirring with toluene (30 cm^3). This caused the initial separation of an oil, which, after stirring for 1 h, partially crystallized; precipitation was completed by two further additions of toluene (10 cm^3), each followed by stirring for 0.5 h. The product was filtered off, washed twice with toluene (5 cm^3), twice with n-hexane (10 cm^3), and vacuum dried. The product so isolated is approximately 94% pure, the remaining part being mostly residual traces of toluene which are difficult to remove; in our experience it is not convenient to try further purification. Yields 65—75% {Found: Rh, 44.0; $[N(C_3H_7)_4]^+$, 26.3%; molar ratio Rh : $[N(C_3H_7)_4]^+$, 3.04:1. $C_{73}H_{112}N_4O_{23}Rh_{12}$ requires Rh, 46.6; $[N(C_3H_7)_4]^+$, 28.1%; Rh:$[N(C_3H_7)_4]^+$, 3:1}.

For the *X*-ray analysis, a layer of di-isopropyl ether was carefully placed over the above mentioned MeCN extract of the crude tetrapropylammonium salt, and the solvents left to diffuse for a few days to give some useful crystals together with

Table 2. Final positional parameters (× 10^4) for $[N(C_3H_7)_4]_4[Rh_{12}C_2(CO)_{23}]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	8 095(1)	2 338(1)	4 950(1)	O(22)	9 278(8)	3 826(10)	3 044(6)
Rh(2)	7 292(1)	3 750(1)	4 695(1)	C(23)	7 536(11)	3 809(15)	2 682(8)
Rh(3)	6 247(1)	2 611(1)	4 323(1)	O(23)	7 551(8)	4 131(11)	2 323(6)
Rh(4)	7 034(1)	1 218(1)	4 951(1)	N(1)	5 511(10)	365(13)	1 439(10)
Rh(5)	7 854(1)	1 811(1)	4 034(1)	C(24)	5 414(16)	1 210(20)	1 704(14)
Rh(6)	8 370(1)	3 458(1)	4 267(1)	C(25)	4 806(15)	1 112(18)	1 896(13)
Rh(7)	7 084(1)	3 249(1)	3 783(1)	C(26)	4 696(16)	1 948(17)	2 182(12)
Rh(8)	6 598(1)	1 628(1)	3 562(1)	C(27)	4 957(13)	268(15)	999(10)
Rh(9)	7 698(1)	1 380(1)	3 111(1)	C(28)	4 917(13)	1 092(16)	713(11)
Rh(10)	8 764(1)	2 437(1)	3 568(1)	C(29)	4 394(11)	893(14)	254(10)
Rh(11)	8 015(1)	3 903(1)	3 332(1)	C(30)	6 183(12)	453(13)	1 309(10)
Rh(12)	6 982(1)	2 844(1)	2 861(1)	C(31)	6 337(10)	−356(13)	1 062(11)
C(−1)	7 734(9)	2 610(12)	3 422(6)	C(32)	7 049(11)	−170(15)	997(13)
C(−2)	7 274(7)	2 516(10)	4 423(6)	C(33)	5 499(12)	−478(13)	1 723(10)
C(1)	8 910(10)	2 186(13)	4 329(7)	C(34)	6 073(12)	−459(14)	2 134(11)
O(1)	9 421(8)	2 087(11)	5 560(6)	C(35)	5 998(13)	−1 300(15)	2 428(12)
C(2)	7 293(12)	4 911(17)	4 820(8)	N(2)	1 522(11)	3 092(16)	421(8)
O(2)	7 263(9)	5 660(12)	4 868(6)	C(36)	1 094(16)	3 074(18)	779(12)
C(3)	5 369(10)	2 755(13)	4 148(7)	C(37)	1 198(17)	3 828(20)	1 118(13)
O(3)	4 797(9)	2 834(12)	4 053(6)	C(38)	782(18)	3 676(21)	1 492(14)
C(4)	6 920(10)	21(14)	4 686(7)	C(39)	2 258(15)	3 048(16)	654(12)
O(4)	6 875(8)	—689(12)	4 773(6)	C(40)	2 394(14)	2 283(16)	984(11)
C(5)	8 632(9)	1 285(12)	4 310(6)	C(41)	3 146(15)	2 373(17)	1 221(13)
O(5)	9 098(7)	871(9)	4 446(5)	C(42)	1 355(13)	2 290(15)	98(11)
C(6)	9 224(10)	3 241(13)	4 530(7)	C(43)	1 694(13)	2 272(15)	−300(12)
O(6)	9 770(8)	3 141(11)	4 720(6)	C(44)	1 419(12)	1 436(15)	−593(11)
C(7)	8 429(10)	4 605(1)	4 334(3)	C(45)	1 444(12)	3 940(15)	130(10)
O(7)	8 522(9)	5 359(13)	4 409(7)	C(46)	745(12)	4 076(15)	−136(10)
C(8)	6 875(10)	4 373(14)	3 730(7)	C(47)	761(12)	4 810(14)	−507(11)
O(8)	6 705(8)	5 124(12)	3 689(6)	N(3)	6 145(13)	5 068(17)	1 148(11)
C(9)	5 920(13)	971(17)	3 293(9)	C(48)	6 590(11)	5 295(14)	1 620(11)
O(9)	6 496(11)	542(15)	3 115(8)	C(49)	6 317(12)	6 092(15)	1 809(12)
C(10)	7 674(11)	236(13)	2 923(8)	C(50)	6 828(13)	6 312(16)	2 270(12)
O(10)	7 631(10)	−478(13)	2 795(7)	C(51)	5 465(12)	4 763(16)	1 201(11)
C(11)	9 626(11)	2 186(14)	3 749(8)	C(52)	5 116(13)	4 365(15)	748(12)
O(11)	10 188(9)	2 093(12)	3 833(6)	C(53)	4 544(12)	3 901(15)	917(13)
C(12)	8 125(12)	5 074(16)	3 292(9)	C(54)	6 513(13)	4 312(15)	973(12)
O(12)	8 245(9)	5 833(12)	3 321(6)	C(55)	6 557(11)	3 509(14)	1 277(11)
C(13)	6 248(14)	3 215(16)	2 451(10)	C(56)	6 829(12)	2 747(14)	1 017(12)
O(13)	5 790(10)	3 464(13)	2 206(7)	C(57)	6 072(11)	5 853(14)	813(11)
C(14)	7 851(9)	3 347(13)	5 300(7)	C(58)	6 727(11)	6 292(14)	848(11)
O(14)	7 996(8)	3 631(10)	5 686(6)	C(59)	6 429(11)	7 039(14)	494(11)
C(15)	6 403(12)	3 492(13)	4 808(9)	N(4)	−402(12)	1 092(16)	1 798(11)
O(15)	6 114(8)	3 764(10)	5 099(6)	C(60)	329(12)	1 169(14)	2 039(11)
C(16)	6 149(9)	1 543(13)	4 689(7)	C(61)	399(11)	1 397(15)	2 539(12)
O(16)	5 766(7)	1 267(9)	4 880(5)	C(62)	1 167(12)	1 407(14)	2 722(12)
C(17)	7 667(10)	1 328(13)	5 205(7)	C(63)	−550(11)	179(16)	1 972(12)
O(17)	7 768(7)	930(10)	5 546(5)	C(64)	−1 237(11)	−87(14)	1 746(11)
C(18)	7 263(11)	689(15)	3 791(8)	C(65)	−1 361(12)	−987(14)	1 974(10)
O(18)	7 332(6)	−105(9)	3 800(5)	C(66)	−941(13)	1 732(15)	1 873(12)
C(19)	6 113(9)	2 758(13)	3 420(7)	C(67)	−658(10)	2 606(14)	1 785(12)
O(19)	5 624(7)	3 130(10)	3 238(5)	C(68)	−1 233(11)	3 286(15)	1 789(11)
C(20)	7 234(10)	1 861(14)	2 503(8)	C(69)	−389(11)	1 037(14)	1 284(11)
O(20)	7 168(9)	1 661(13)	2 113(7)	C(70)	−127(13)	219(15)	1 109(12)
C(21)	8 618(10)	1 488(13)	3 079(7)	C(71)	−143(12)	413(15)	588(12)
O(21)	8 986(8)	1 139(11)	2 883(6)				
C(22)	8 903(10)	3 520(13)	3 243(7)				

an amorphous material containing anion (**3**) and some decomposition products.

Synthesis of $[Rh_{12}C_2(CO)_{23}]^{4-}$ *from* $K_2[Rh_6C(CO)_{15}]$·*n*-diglyme.—The diglyme-solvated potassium salt (33.2% Rh; 1 g, 0.54 mmol) in propan-2-ol (30 cm^3) was refluxed on an oil-bath at 110 °C until the solution was only slightly coloured, and a finely crystalline dark brown precipitate was formed (8—10 h). The precipitate was filtered off, washed with propan-2-ol, and extracted from the septum with a 1 mol dm^{-3} solution of KOH in MeOH in 3—4 cm^3 portions until the extract was no longer red-brown (total volume *ca.* 18 cm^3), leaving some insoluble black by-product. The alkaline methanolic solution was treated as described above using a solution of $[N(C_3H_7)_4]Br$ (1 g) in propan-2-ol (15 cm^3); in this case, however, a mixed salt containing approximately one potassium and three tetrapropylammonium cations separated out, which was crystallized in the same way. Yields 50—60% (Found: C, 29.0; H, 3.65; K, 1.65; N, 1.85; Rh, 49.0. $C_{61}H_{84}KN_3O_{23}Rh_{12}$ requires C, 29.3; H, 3.40; K, 1.55; N, 1.70; Rh, 49.4%).

Table 3. Selected distances (Å) and angles (°) for $[N(C_3H_7)_4]_4[Rh_{12}C_2(CO)_{23}]$ with e.s.d.s in parentheses

Rh(1)–Rh(2)	2.750(1)	C(–1)–Rh(5)	2.18(2)	C(13)–Rh(12)	1.84(2)	C(1)–O(1)	1.15(2)
Rh(1)–Rh(4)	2.836(2)	C(–1)–Rh(7)	2.17(2)	C(14)–Rh(1)	2.00(2)	C(2)–O(2)	1.16(2)
Rh(1)–Rh(5)	2.807(2)	C(–1)–Rh(9)	2.10(2)	C(14)–Rh(2)	2.03(2)	C(3)–O(3)	1.18(3)
Rh(1)–Rh(6)	2.837(1)	C(–1)–Rh(10)	2.14(2)	C(15)–Rh(2)	2.02(2)	C(4)–O(4)	1.13(3)
Rh(2)–Rh(3)	2.839(2)	C(–1)–Rh(11)	2.11(1)	C(16)–Rh(3)	2.01(2)	C(5)–O(5)	1.17(2)
Rh(2)–Rh(6)	2.893(2)	C(–1)–Rh(12)	2.07(2)	C(16)–Rh(4)	2.02(2)	C(6)–O(6)	1.18(2)
Rh(2)–Rh(7)	2.787(2)	C(–2)–Rh(1)	2.09(1)	C(17)–Rh(1)	2.03(2)	C(7)–O(7)	1.19(2)
Rh(3)–Rh(4)	2.716(2)	C(–2)–Rh(2)	2.06(1)	C(17)–Rh(4)	2.03(2)	C(8)–O(8)	1.20(3)
Rh(3)–Rh(7)	2.834(2)	C(–2)–Rh(3)	2.13(2)	C(18)–Rh(5)	2.16(2)	C(9)–O(9)	1.14(2)
Rh(3)–Rh(8)	2.973(2)	C(–2)–Rh(4)	2.14(2)	C(18)–Rh(8)	2.02(2)	C(10)–O(10)	1.16(2)
Rh(4)–Rh(5)	2.823(2)	C(–2)–Rh(5)	2.17(1)	C(19)–Rh(7)	2.26(2)	C(11)–O(11)	1.17(2)
Rh(4)–Rh(8)	3.089(2)	C(–2)–Rh(7)	2.19(2)	C(19)–Rh(8)	2.01(2)	C(12)–O(12)	1.19(3)
Rh(5)–Rh(6)	2.777(2)	C(–1) ··· Rh(6)	2.90	C(20)–Rh(9)	2.01(2)	C(13)–O(13)	1.14(2)
Rh(5)–Rh(7)	2.743(2)	C(–1) ··· Rh(8)	2.94	C(20)–Rh(12)	1.99(2)	C(14)–O(14)	1.21(3)
Rh(5)–Rh(8)	2.727(2)	C(–2) ··· Rh(8)	2.99	C(21)–Rh(9)	1.98(2)	C(15)–O(15)	1.25(3)
Rh(5)–Rh(9)	2.799(2)	C(–2) ··· Rh(6)	2.86	C(21)–Rh(10)	2.04(2)	C(16)–O(16)	1.17(3)
Rh(5)–Rh(10)	2.792(2)			C(22)–Rh(10)	1.98(2)	C(17)–O(17)	1.17(3)
Rh(6)–Rh(7)	2.797(2)	C(1)–Rh(1)	1.85(2)	C(22)–Rh(11)	2.04(2)	C(18)–O(18)	1.23(3)
Rh(6)–Rh(10)	2.890(2)	C(2)–Rh(2)	1.82(2)	C(23)–Rh(11)	1.99(2)	C(19)–O(19)	1.20(3)
Rh(6)–Rh(11)	2.828(2)	C(3)–Rh(3)	1.82(2)	C(23)–Rh(12)	2.03(2)	C(20)–O(20)	1.19(2)
Rh(7)–Rh(8)	2.714(2)	C(4)–Rh(4)	1.88(2)	C(18) ··· Rh(4)	2.69(3)	C(21)–O(21)	1.20(3)
Rh(7)–Rh(11)	2.817(2)	C(5)–Rh(5)	1.85(2)	C(18) ··· Rh(9)	2.65(3)	C(22)–O(22)	1.19(2)
Rh(7)–Rh(12)	2.802(2)	C(6)–Rh(6)	1.83(2)	C(19) ··· Rh(3)	2.68(3)	C(23)–O(23)	1.20(3)
Rh(8)–Rh(9)	2.969(2)	C(7)–Rh(6)	1.77(2)	C(19) ··· Rh(12)	2.76(3)		
Rh(8)–Rh(12)	3.059(2)	C(8)–Rh(7)	1.78(2)				
Rh(9)–Rh(10)	2.862(2)	C(9)–Rh(8)	1.79(2)				
Rh(9)–Rh(12)	2.716(2)	C(10)–Rh(9)	1.84(2)				
Rh(10)–Rh(11)	2.748(2)	C(11)–Rh(10)	1.82(2)				
Rh(11)–Rh(12)	2.830(2)	C(12)–Rh(11)	1.82(2)				

Rh(1)–C(1)–O(1)	179(2)	Rh(9)–C(10)–O(10)	177(2)	Rh(3)–C(16)–O(16)	137(2)	Rh(9)–C(20)–O(20)	137(2)
Rh(2)–C(2)–O(2)	175(2)	Rh(10)–C(11)–O(11)	173(2)	Rh(4)–C(16)–O(16)	138(2)	Rh(12)–C(20)–O(20)	138(2)
Rh(3)–C(3)–O(3)	177(2)	Rh(11)–C(12)–O(12)	172(2)	Rh(1)–C(17)–O(17)	136(2)	Rh(9)–C(21)–O(21)	138(2)
Rh(4)–C(4)–O(4)	175(2)	Rh(12)–C(13)–O(13)	178(2)	Rh(4)–C(17)–O(17)	135(2)	Rh(10)–C(21)–O(21)	131(2)
Rh(5)–C(5)–O(5)	172(2)	Rh(1)–C(14)–O(14)	138(2)	Rh(5)–C(18)–O(18)	137(2)	Rh(10)–C(22)–O(22)	140(2)
Rh(6)–C(6)–O(6)	176(2)	Rh(2)–C(14)–O(14)	136(2)	Rh(8)–C(18)–O(18)	142(2)	Rh(11)–C(22)–O(22)	134(2)
Rh(6)–C(7)–O(7)	174(2)	Rh(2)–C(15)–O(15)	132(2)	Rh(7)–C(19)–O(19)	132(2)	Rh(11)–C(23)–O(23)	138(2)
C(6)–Rh(6)–C(7)	95(2)	Rh(3)–C(15)–O(15)	137(2)	Rh(8)–C(19)–O(19)	148(2)	Rh(12)–C(23)–O(23)	133(2)
Rh(7)–C(8)–O(8)	177(2)						
Rh(8)–C(8)–O(9)	178(2)						

Crystallography.—Crystal data. $C_{73}H_{112}N_4O_{23}Rh_{12}$, M = 2 648.6, monoclinic, a = 21.132(4), b = 15.334(3), c = 30.093(5) Å, β = 103.07(4)°, U = 9 498.7 Å^3, D_m = 2.0, Z = 4, D_c = 1.85 g cm^{-3}, F(000) = 5 208, space group $P2_1/c$ (no. 14), Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 19.0 cm^{-1}.

Intensity measurements. A suitable crystal with dimensions 0.3 × 0.4 × 0.55 mm was mounted on a Philips PW1100 diffractometer. Diffraction intensities were measured in the range $1.5 < \theta < 23°$ by the ω-scan method, with scan interval 1.2° and speed 1.8° min^{-1}. The background was measured on both sides of the reflections for a total time equal to the peak scanning time. 14 192 Diffraction intensities were collected, 7 589 of which having $F_o > 5\sigma(F_o)$ 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 computations the SHELX[8] package of crystallographic programs was used. The structure was solved by direct methods. Although the rationalization of the geometry presented some difficulties because of multiple images in the Fourier map, our previous knowledge of the Rh_{12} polyhedron helped in working out the solution. After location of the heavy atoms, all light atoms were found by subsequent Fourier difference maps. Only the metal atoms were allowed to vibrate anisotropically. The final agreement indices were R = 0.0738 and R' = 0.0876. The weighting scheme employed was $w = k[\sigma^2(F) + |g|F^2]$, where k = 1.0 and g = 0.0042. Residual peaks lower than 1e Å^{-3} were observed in the vicinity of the metal atoms in the final Fourier difference map. Atomic co-ordinates are reported in Table 2, bond distances and relevant angles in Table 3.

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