Mixed-metal Carbido Carbonyl Clusters. Part 1. Synthesis and Structural Characterization of Di-μ_3-acetonitrilecuprio-carbido-ennea-μ-carbonyl-hexacarbonyl-*polyhedro*-hexarhodium, $[Cu_2Rh_6(CO)_{15}(NCMe)_2]\cdot0.5MeOH$

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The title complex has been prepared by direct reaction of the $[Cu(NCMe)_4]^+$ cation with the $[Rh_6C(CO)_{15}]^{2-}$ anion in methanolic solution, and characterized by chemical and crystallographic methods. The species $[Cu_2Rh_6(CO)_{15}(NCMe)_2].0.5MeOH$ crystallizes in the monoclinic space group *C*2/*c* with cell constants a = 18.21(1), b = 10.509(1), c = 20.69(1) Å, β = 126.00(5)°, and Z = 4. 2 175 reflection intensities, collected by counter methods, have been used to solve and refine the structure down to R 0.041. The molecule contains a prism of rhodium atoms capped on the triangular faces by two Cu(NCMe) linear fragments, and the geometry of the CO ligands is the same as in the parent dianion. The idealized molecular symmetry is D_{3h}. The Cu–Rh, Rh–Rh, and Rh–C(carbide) mean distances are 2.660, 2.78, and 2.127 Å, respectively. The Cu–Rh bonds have been described in terms of σ and π dative interactions from the rhodium prism to the copper atoms.

We have already shown that the $[Rh_6C(CO)_{15}]^{2-}$ prismatic anion [1] gives cluster complexes of higher nuclearity upon oxidation with iron(III) ions.[2-4] A similar reaction has been attempted with a milder oxidizing agent, the copper(II) ion. This reaction, which was carried out in methanol with $K_2[Rh_6C(CO)_{15}]$ and $Cu[SO_4]$ under a CO atmosphere, gave, besides soluble unidentified oxidation products, a slow separation of very small amounts of a yellow powder whose analysis indicated the presence of copper. The product was then formulated as the mixed-metal cluster $[Cu_2Rh_6C(CO)_{15}]\cdot n$solvent, formed by the condensation of some copper(I) formed during the oxidation with the hexanuclear dianion. The nature of the product was confirmed by the direct reaction of $K_2[Rh_6C(CO)_{15}]$ in methanol with a preformed copper(I) derivative, $[Cu(NCMe)_4][BF_4]$, which gave the instantaneous separation of a similar yellow crystalline powder in nearly quantitative yield. In this case the product that precipitated contained both acetonitrile and methanol, but while acetonitrile was rather strongly retained the methanol, although not removable *in vacuo*, could be replaced by other solvents on recrystallization. This led to the conclusion that while the acetonitrile was co-ordinated to the copper the other solvents were clathrated, and the product was formulated as $[Cu_2Rh_6C(CO)_{15}(NCMe)_2]\cdot n$solvent.

It was of great interest to structurally characterize this new mixed-metal species in order to gain further insight on the active sites of the prism surface and on the mode of bonding of the entering metal atoms.

EXPERIMENTAL

The solvents were distilled and dried by the usual methods. All operations were carried out in inert atmospheres; $K_2[Rh_6C(CO)_{15}]$ and $[Cu(NCMe)_4][BF_4]$ were prepared as described.[1,5]

Syntheses and Properties of $[Cu_2Rh_6C(CO)_{15}(NCMe)_2]\cdot$0.5*solvent*.—A solution of $K_2[Rh_6C(CO)_{15}]\cdot3$thf (thf = tetrahydrofuran) (0.19 g, 0.14 mmol) in methanol (2 cm³) was treated under nitrogen with a solution of $[Cu(NCMe)_4][BF_4]$ (0.13 g, 0.41 mmol) in methanol (4 cm³). A yellow powder separated immediately, and was filtered off, washed with a little methanol, and dried *in vacuo*. This crude product was purified from the co-precipitated $K[BF_4]$ by extraction with acetone, careful filtration, concentration to *ca.* 4 cm³, and crystallization by slow diffusion of n-hexane (15 cm³) layered on the acetonic solution. The crystals were filtered off, washed with n-hexane, and dried *in vacuo* (yield *ca.* 70%). Gas chromatographic analysis indicated that the product contained *ca.* 0.5 mol of acetone per cluster molecule, which was difficult to remove even after prolonged exposure to vacuum (Found: C, 19.8; H, 0.65; Cu, 9.6; N, 2.15; Rh, 48.6. Calc. for $C_{21.5}H_9Cu_2N_2O_{15.5}Rh_6$: C, 20.05; H, 0.70; Cu, 9.85; N, 2.15; Rh, 48.1%). Recrystallization of the crude product from thf-n-hexane or thf-toluene caused retention of *ca.* 0.5 mol of thf or toluene, respectively.

Crystals suitable for *X*-ray analysis were obtained directly by slow diffusion of the above reactants in methanolic solution and contained clathrated methanol (*ca.* 0.5 mol). The crystals were stable in air for many months, while the solutions were rapidly oxidized. Prolonged exposure to light caused some darkening of the crystals. The product was soluble in acetone and thf, moderately soluble in methanol, and insoluble in n-hexane; the solutions darkened slowly on standing with separation of some copper metal The i.r. spectrum in thf solution showed bands at 2 070vs and 1 983w(sh) cm⁻¹ in the terminal-carbonyl stretching region, and at 1 882vs and 1 860 m(sh) cm⁻¹ in the bridging-carbonyl region.

A study of the stepwise reaction of the $[Rh_6C(CO)_{15}]^{2-}$ anion with $[Cu(NCMe)_4][BF_4]$ in acetone gave evidence of the intermediate formation of a monocopper derivative. More detailed information on the chemical behaviour of the copper derivatives and on the reaction of $[Rh_6C(CO)_{15}]^{2-}$ with other Group 1B cations will be reported later.[6]

Crystal Data.—$C_{20.5}H_8Cu_2N_2O_{15.5}Rh_6$, M = 1 274.6, Monoclinic, a = 18.21(1), b = 10.509(7), c = 20.69(1) Å, β = 126.00(5)°, U = 3 203.5 Å³, D_m = 2.68 (by flotation), Z = 4, D_c = 2.64 g cm⁻³, $F(000)$ = 2 388, space group *C*2/*c* (no. 15), Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 40.8 cm⁻¹.

Intensity Measurements.—A multifaced crystal with dimensions 0.31 × 0.28 × 0.31 mm was mounted on a Siemens diffractometer. Diffraction intensities in two octants of the reciprocal lattice were collected in the range $3 < \theta < 23°$ by the ω-scan method, with scan width 1.4° and speed 2.5° min^{-1}. The background was measured on each side of the reflections for half of the peak scanning time. 2 258 Reflections were measured, 2 175 of which were used for the structure determination [$F_o > 2\sigma(F_o)$]. One standard reflection was measured periodically and no decay was observed. Integrated intensities were reduced to F_o values by correction for Lorentz, polarization, and absorption effects.

Determination of the Structure.—The structure was solved by direct methods and refined by the least-squares technique using the SHELX package of crystallographic programs.[7] The thermal motion was treated anisotropically for the metal atoms and isotropically for the other atoms. During refinement, weights were applied to the observations according to their estimated standard deviations. A difference-Fourier synthesis, computed when the R index was 0.042 3, showed residual peaks at <1.5 e Å^{-3} in the vicinity of the metal atoms and one peak of 1.2 e Å^{-3} around the inversion centre at $0,\frac{1}{2},\frac{1}{2}$ (special position b). This was the only indication of the presence of methanol as revealed by the chemical analysis. After testing various hypotheses, this peak was treated as a fraction of oxygen and its occupation factor converged at 0.23(2). This result was in very good agreement with the analytical data. No trace was found of the carbon atom bonded to the oxygen. An analysis of the cavity around this special position revealed contacts longer than 3.5 Å, showing that a methanol molecule could well be allocated. Of course only half of the cavities are occupied, with the oxygen in the vicinity of the inversion centre and the methyl group randomly distributed around it.

The final agreement indices of this model of the structure are R 0.040 8 and R' 0.055 4. The co-ordinates of the atoms are reported in Table 1, bond distances and angles in Table 2. Observed and computed structure factors and thermal parameters are given in Supplementary Publication No. SUP 22623 (15 pp.).*

TABLE 1

Final positional parameters (× 10^4) with estimated standard deviations in parentheses

Atom	x	y	z
Rh(1)	6 318(0)	4 239(1)	3 339(0)
Rh(2)	5 561(0)	6 520(1)	3 339(0)
Rh(3)	4 799(0)	4 244(1)	3 339(0)
Cu	6 406(1)	5 001(1)	4 610(1)
C(0)	5 000	4 993(10)	2 500
C(1)	4 482(5)	6 157(8)	3 429(5)
O(1)	3 983(5)	6 703(7)	3 508(5)
C(2)	5 611(5)	2 723(9)	3 436(5)
O(2)	5 683(5)	1 614(8)	3 522(5)
C(3)	6 768(5)	6 142(8)	3 433(5)
O(3)	7 367(5)	6 698(7)	3 513(5)
C(4)	7 473(6)	3 624(8)	4 188(6)
O(4)	8 162(6)	3 179(9)	4 651(6)
C(5)	6 134(6)	7 704(8)	4 183(6)
O(5)	6 488(6)	8 510(9)	4 666(6)
C(6)	4 759(6)	3 683(9)	4 171(6)
O(6)	4 661(7)	3 321(10)	4 656(6)
C(7)	6 475(7)	3 539(9)	2 511(6)
O(7)	7 030(7)	2 973(9)	2 513(5)
C(8)	5 000	7 936(13)	2 500
O(8)	5 000	9 073(12)	2 500
C(9)	8 173(8)	5 011(13)	7 261(7)
C(10)	7 607(6)	4 991(9)	6 412(6)
N	7 163(5)	5 004(8)	5 745(5)
O(9)	0	5 000	5 000

TABLE 2

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

Rh(1)–Rh(2)	2.765(1)	Cu · · · C(5)	2.93(2)
Rh(1)–Rh(3)	2.765(1)	Cu · · · C(6)	2.92(2)
Rh(2)–Rh(3)	2.765(1)	C(1)–O(1)	1.17(1)
Rh(2)–Rh(2′)	2.811(1)	C(2)–O(2)	1.17(1)
Rh(1)–Rh(3′)	2.810(1)	C(3)–O(4)	1.16(1)
Rh(1)–Cu	2.662(1)	C(4)–O(4)	1.14(1)
Rh(2)–Cu	2.659(1)	C(5)–O(5)	1.17(1)
Rh(5)–Cu	2.658(1)	C(6)–O(6)	1.18(1)
Rh(1)–C(0)	2.123(4)	C(7)–O(7)	1.17(1)
Rh(2)–C(0)	2.133(4)	C(8)–O(8)	1.19(2)
Rh(3)–C(0)	2.125(4)	Rh(1)–C(4)–O(4)	174(1)
Rh(1)–C(4)	1.89(1)	Rh(2)–C(5)–O(5)	174(1)
Rh(1)–C(2)	2.13(1)	Rh(3)–C(6)–O(6)	175(1)
Rh(1)–C(3)	2.13(1)	Rh(1)–C(7)–O(7)	138(1)
Rh(1)–C(7)	2.03(1)	Rh(3′)–C(7)–O(7)	135(1)
Rh(2)–C(5)	1.88(1)	Rh(2)–C(1)–O(1)	140(1)
Rh(2)–C(1)	2.11(1)	Rh(3)–C(1)–O(1)	139(1)
Rh(2)–C(3)	2.13(1)	Rh(1)–C(2)–O(2)	137(1)
Rh(2)–C(8)	2.05(1)	Rh(3)–C(2)–O(2)	141(1)
Rh(3)–C(6)	1.86(1)	Rh(1)–C(3)–O(3)	140(1)
Rh(3)–C(1)	2.13(1)	Rh(2)–C(3)–O(3)	139(1)
Rh(3)–C(2)	2.11(1)	Rh(2)–C(8)–O(8)	137(1)
Ph(3)–C(7′)	2.06(1)	Cu–N–C(10)	178(1)
Cu–N	1.90(1)	N–C(10)–C(9)	179(1)
N–C(10)	1.12(1)	N–Cu–Rh(1)	143.2(1)
C(9)–C(10)	1.42(2)	N–Cu–Rh(2)	143.0(1)
Cu · · · C(1)	3.11(2)	N–Cu–Rh(3)	143.2(1)
Cu · · · C(2)	3.10(2)	Rh(1)–Cu–Rh(2)	62.6(1)
Cu · · · C(3)	3.11(2)	Rh(1)–Cu–Rh(3)	62.6(1)
Cu · · · C(4)	2.94(2)	Rh(2)–Cu–Rh(3)	62.7(1)

DISCUSSION

The molecule [$Cu_2Rh_6C(CO)_{15}(NCMe)_2$] contains a prism of rhodium atoms capped on both triangular faces by copper atoms, each bearing a linearly bonded acetonitrile ligand. The carbonyl ligands have the geometry found[1] in the parent dianion [$Rh_6C(CO)_{15}$]$^{2-}$ and the bond parameters of the Rh–Rh and Rh–C–O interactions show only minor changes after addition of the two [Cu(NCMe)]$^+$ cations. The idealized molecular symmetry is D_{3h} within experimental error, but only the two-fold axis passing through C(0), C(8), and O(8) is retained in the crystal (see Figure).

The carbide atom occupying the prismatic cavity has an average C–Rh distance of 2.127(3) Å, which is slightly shorter than the value in the dianion [2.134(4) Å]. The basal and inter-basal Rh–Rh distances have mean values of 2.765 and 2.810(1) Å, respectively, which, compared with the corresponding values in the dianion [2.776 and 2.817(1) Å], show tiny but significant shortenings indicating a contraction of the cluster orbitals upon disappearance of the anionic charge.

The inter-base bridging ligands have Rh–C and C–O mean lengths [2.05(1) and 1.18(1) Å] which are not significantly different from the values in the dianion [2.04(1) and 1.17(1) Å, respectively]. The base-bridging groups have mean bond lengths [2.13(1) and 1.17(1) Å] comparable with those [2.12(1) and 1.14(1) Å] in the dianion, and a similar situation applies for the terminal ligands [mean lengths 1.88(1) and 1.18(1), *cf.* 1.89(1) and 1.13(1) Å in the dianion]. From these figures one can infer that the only measurable effect of the copper

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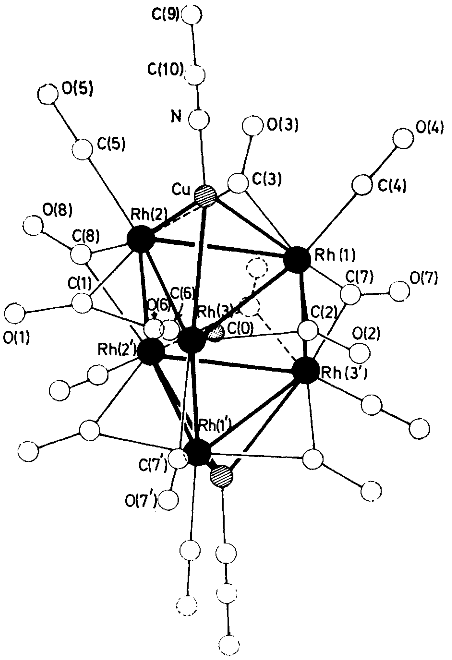
* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

insertion is a 0.03—0.05 Å lengthening of the C–O distances for base-bridging and terminal groups. This effect is not easy to explain because it contradicts the evidence from the C–O stretching frequencies which, as expected, lie some 50 cm^{-1} to higher wavenumbers than in the spectrum of the dianion. A slight bending of the terminal ligands [Rh–C–O 174(1), *cf.* 178(2)° in the dianion] is another effect attributable to the copper insertion. In fact, although the copper atoms do not establish definite bonds with the carbonyl ligands, some degree of long-range interaction can be postulated on the basis of the Cu–C contacts (2.93 Å).

The mean Rh–Cu distance [2.660(1) Å] has the value expected on the basis of the covalent radii of rhodium and copper[8] in cluster compounds, 1.39 and 1.27 Å respectively. This value indicates that the strength of the Cu–Rh interactions is in the range of normal metal–metal bonds in cluster complexes. The copper atoms are actually four-co-ordinate but their bond geometry is far from tetrahedral, the bond angles Rh–Cu–Rh and Rh–Cu–N being 62.6(1) and 143.1(1)°, respectively. The copper bonds can be described in terms of σ and π interactions of two *sp* linearly hybridized orbitals and the remaining *p*-type orbitals, respectively. The σ bonds are with the acetonitrile ligand and, in local C_{3v} symmetry, the A_1 combination of the prism orbitals on the triangular face. The π bonds are essentially with the *E* combination of the cluster orbitals. This description of the copper–rhodium interactions is very similar to that previously used by Chini[9] for face-bridging carbonyls. In order for the copper to attain the closed electronic configuration the bonds must have dative character, from rhodium to copper. The most remarkable feature of the Cu–Rh interactions is that the implied prism orbitals have non-bonding character with respect to the Rh–Rh bonds, as shown by the very limited effects on the Rh–Rh distances.



The acetonitrile ligands are linear within experimental error and the Cu–N and N–C distances [1.90(1) and 1.12(1) Å] are normal.

It is noteworthy that the two triangular faces are selectively capped in the additions of the two copper atoms to the prism surface. This fact is even more significant when compared to the other addition products from $[M_6C(CO)_{15}]^{2-}$ anions, namely $[Rh_8C(CO)_{19}]$ and $[Co_8C(CO)_{18}]^{2-}$.[2,10] In these complexes only the rectangular faces or the basal edges are the addition sites. An analysis of the sizes and shapes of the holes on the surface of $[Rh_6C(CO)_{15}]^{2-}$ has shown that neither kind of faces is sterically hindered;[2] therefore, the essentially acidic character of the $[Cu(NCMe)]^+$ cation indicates that the triangular faces are the most basic sites on the prism surface.

Finally, we note that $[Cu_2Rh_6C(CO)_{15}(NCMe)_2]$, $[Rh_8C(CO)_{19}]$, and $[Co_8C(CO)_{18}]^{2-}$ are isoelectronic species but do not contain the same metal-atom polyhedron.[2,10] It is interesting that Lauher[11] has recently predicted the same total of valence electrons (114) for the bicapped trigonal prism C_{2v} and the square antiprism. The characterization of this copper mixed cluster gives a strong indication that a similar capping of a triangular unit takes place also in the reported $[AgNi_9(CO)_{18}]^-$ anion.[12]

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