A New Family of Nitrido Carbonyl Clusters. Synthesis and Structural Characterization of the Anions $[Rh_6MN(CO)_{15}]^{2-}$ (M=Co, Rh, or Ir), and Evidence for Metal Atom Migration in the Cluster

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The anions $[Rh_6MN(CO)_{15}]^{2-}$ (M=Co, Rh, or Ir), obtained by condensation of $[Rh_6N(CO)_{15}]^-$ and $[M(CO)_4]^-$, contain a metallic array consisting of a trigonal prism capped on a square face, with the nitride inside the prismatic hole; the mixed-metal species show an unexpected migration of the entering metal from the capping position to the vertices of the prism.

Few carbonyl cluster compounds containing fully encapsulated nitrogen atoms are presently known.[1—4] We have previously reported the first example of these species, the trigonal prismatic compounds $[M_6N(CO)_{15}]^-$ (M=Co[1] or Rh[2]), and we are currently studying their reactivity. Condensation of $[M(CO)_4]^-$ with $[Rh_6N(CO)_{15}]^-$ under N_2 in refluxing tetrahydrofuran (THF) gives the new anions $[Rh_6MN(CO)_{15}]^{2-}$ [M=Co, (**1**); Rh, (**2**); Ir, (**3**)]† which contain a novel square face-capped trigonal prismatic array (see Figure 1).

These heptanuclear anions are decomposed by CO by the reverse of the condensation process with regeneration of the starting compounds. The structures of the $[PPh_4]^+$ salts of the anions $[Rh_6MN(CO)_{15}]^{2-}$ have been determined by single crystal *X*-ray analysis.‡

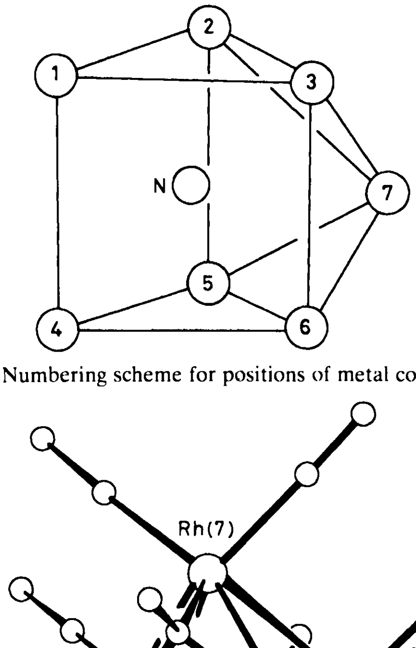

Figure 1. Numbering scheme for positions of metal core atoms.

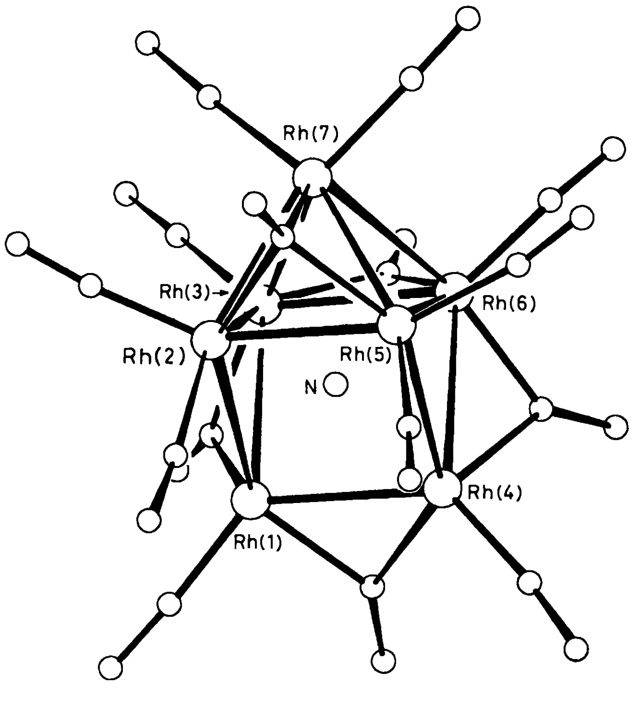

Figure 2. A view of the anion $[Rh_7N(CO)_{15}]^{2-}$. The individual Rh–Rh bond lengths (Å) are: (1)–(2), 2.875; (1)–(3), 2.774; (1)–(4), 2.698; (2)–(3), 2.832; (2)–(5), 2.673; (2)–(7), 2.665; (3)–(6), 2.747; (3)–(7), 2.911; (4)–(5), 2.875; (4)–(6), 2.787; (5)–(6), 2.803; (5)–(7), 2.682; (6)–(7), 2.872: e.s.d.s 0.002 Å.

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† In a typical synthesis $[PPh_4][Rh_6N(CO)_{15}]$ (0.2 g) was treated under nitrogen in THF (20 ml) with $[PPh_4][M(CO)_4]$ (1.1 equiv.), and the mixture refluxed on an oil bath at 80 °C until the i.r. bands of the initial mixture were replaced by those of the heptanuclear species (2—5 h, depending on M). From the filtered solution crystals were obtained by concentration *in vacuo* to 5—6 ml and slow diffusion of propan-2-ol (20 ml) layered over the solution. Yields 70—80%. The i.r. spectra in THF solution show bands at 2030(sh), 1982vs, 1820m, 1800mw(br), and 1770w(br) cm^{-1} for (**1**), at 2033vw, 1988vs, 1943vw, 1830m, 1803mw(br), and 1778mw(br) cm^{-1} for (**2**), and at 2033vw, 1988vs, 1943vw, 1830m, 1803mw(br), and 1770(sh) cm^{-1} for (**3**).

‡ *Crystal data:* Compound (**1**), $C_{63}H_{40}CoNO_{15}P_2Rh_6$, M = 1789.3, triclinic, space group $P\bar{1}$, a = 14.419(4), b = 19.152(3), c = 11.738(2) Å, α = 101.56(1), β = 93.39(2), γ = 85.19(2)°, U = 3161.6 Å^3, Z = 2.

Compound (**2**), $C_{67}H_{48}NO_{16}P_2Rh_7$, M = 1905.4, triclinic, space group $P\bar{1}$, a = 12.087(6), b = 12.787(7), c = 23.353(7) Å, α = 94.61(4), β = 91.42(3), γ = 105.76(4)°, U = 3458.3 Å^3, Z = 2.

Compound (**3**), $C_{67}H_{48}IrNO_{16}P_2Rh_6$, M = 1994.7, triclinic, space group $P\bar{1}$, isomorphous with (**2**), with a = 12.141(3), b = 12.787(4), c = 23.369(6) Å, α = 94.57(3), β = 91.34(2), γ = 105.62(3)°, U = 3479.1 Å^3, Z = 2.

The intensity data were collected on a Enraf-Nonius CAD4 diffractometer with Mo-K_α radiation (λ = 0.71073 Å), by the ω-scan method, up to a maximum 2θ of 48° for (**1**) and (**2**), and 46° for (**3**). An empirical absorption correction was applied in all cases. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares, on the basis of 3422 for (**1**), 3851 (**2**), and 4491 (**3**) significant $[I>3\sigma(I)]$ reflections. The current values of the conventional R factor are 0.043 for (**1**), 0.054 (**2**), and 0.056 (**3**). In compounds (**2**) and (**3**) one solvated molecule of tetrahydrofuran per asymmetric unit was detected. The mixed-metal species (**1**) and (**3**) exhibit a certain disorder of the Co and Ir atoms. In (**1**) the Co atom partially occupies two vertices of the trigonal prism (positions 5 and 2 with refined occupancies of 0.83 and 0.17, respectively); in (**3**) the Ir atom is disordered between the capping position and one vertex of the prism (positions 7 and 2 with refined occupancies of 0.90 and 0.10, respectively). The disordered metals were refined using appropriately averaged scattering factors. The e.s.d's of the refined occupancy factors are in the range 0.002—0.004, but these values seem to be too optimistic since the parameters are affected by correlations with the thermal parameters of the corresponding atoms.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The structure of the homonuclear anion $[Rh_7N(CO)_{15}]^{2-}$ (**2**) is shown in Figure 2, and its stereochemistry can be considered representative also for the other two anions. The metallic array consists of a somewhat distorted trigonal prism, containing an interstitial N atom, capped on a square face by the seventh metal atom. This type of skeleton is novel although a similar metallic moiety was present in $[Rh_8C(CO)_{18}]$[5] with the eighth metal double bridging a prismatic edge. Other capped trigonal prismatic clusters are known but with the caps on the triangular faces.[6,7,8] Of the 15 CO ligands 10 are terminal, two for each Rh atom of the triangle Rh(2,5,7) and one for each of the other four metals; four carbonyls are almost symmetrically edge-bridging on all edges of the square Rh(1,3,4,6); the remaining CO group is triple bridging on the triangle Rh(2,5,7). The overall idealized anion symmetry is C_s, the mirror plane passing through Rh(7), N, and the middle point of the Rh(1,4), Rh(2,5), and Rh(3,6) edges.

The 13 Rh–Rh bond lengths are rather scattered [range 2.665(2)—2.911(2) Å] but follow the ideal C_s anionic symmetry. Within the prism the edges of the triangles [range 2.875(2)—2.774(2) Å, the shorter being the CO bridged ones] are significantly longer than the three interlayer edges (mean 2.706 Å). The capping Rh(7) atom shows two quite different types of metal–metal interactions: two bonds are short [with Rh(2) and Rh(5), mean 2.673 Å], and two long [with Rh(3) and Rh(6), mean 2.891 Å]. These distortions suggest an alternative description of the cluster as derived by the overlap of a triangular $Rh_3(\mu_3\text{-}CO)(CO)_6$ unit [Rh(2,5,7), mean Rh–Rh 2.673 Å] and a square $Rh_4(\mu\text{-}CO)_4(CO)_4$ unit [Rh(1,3,4,6), mean Rh–Rh 2.751 Å], joined only through Rh–N interactions and six longer metal–metal bonds (mean Rh–Rh 2.861 Å).

The interstitial nitrogen atom is closer to the four atoms of the square Rh(1,3,4,6) (mean Rh–N 2.06 Å) than to the other two metals of the cage [Rh(2)–N 2.17(1), Rh(5)–N 2.30(1) Å].

The mean values of the Rh–C and C–O bond lengths for the terminal and double bridging CO groups are 1.86 and 1.15, and 2.02 and 1.15 Å, respectively. The triple bridging carbonyl has a shorter Rh(7)–C bond [2.09(2) Å] than the Rh(2,5)–C bonds (mean 2.21 Å).

The mixed-metal anion $[Rh_6CoN(CO)_{15}]^{2-}$ shows the unexpected feature that the Co atom does not occupy the capping position 7 but is disordered on two stereochemically equivalent vertices of the trigonal prism (positions 2 and 5, with occupancies of 17% and 83%, respectively). The anion geometry is the same as that found in the homonuclear Rh_7 species but the bond distances for the Co atom (in position 5) show the expected shortenings owing to its smaller covalent radius. The Co–Rh bonds are 0.06—0.08 Å shorter than the corresponding Rh–Rh interactions. Other typical shortenings are: Co–N, 2.087(9) Å; Co–C for terminal CO groups, 1.69 Å (mean); and Co–C (triple bridge) 1.97(1) Å.

In the anion $[Rh_6IrN(CO)_{15}]^{2-}$ the Ir atom is mainly localized in the capping position (occupancy 90%) but 10% occupies one vertex of the prism (position 2). Owing to the similarity of the covalent radii of Ir and Rh the bond parameters of the anion are very similar to those found in the homonuclear species.

The migration of the entering metal in the two mixed-metal anions from the cap to the prism can be rationalised by assuming that the $M_3(\mu_3\text{-}CO)(CO)_6$ moiety can rotate about its idealized three-fold axis. This rotation, however, does not lead in the resulting molecule, at least in the solid state, to a statistical distribution of the entering metal atom over the three possible positions, but Co and Ir show some preference for particular sites; the factors responsible for these preferences are difficult to understand, one possibility being the attainment of an M–N interaction.

Finally these anions possess 100 valence electrons, corresponding to 50 cluster valence molecular orbitals (c.v.m.o.s), exactly those expected from the noble gas rule, at variance with previous suggestions on capped polyhedra, requiring 51 c.v.m.o.s,[9] but in accord with more recent counting schemes based on condensed polyhedra.[10,11]

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