Hexagonal Close Packing of Metal Atoms in the New Polynuclear Anions $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ (n=2 or 3); *X*-Ray Structure of $[(Ph_3P)_2N]_2[Rh_{13}(CO)_{24}H_3]$

By V. G. ALBANO, A. CERIOTTI, P. CHINI,* G. CIANI, S. MARTINENGO, and W. M. ANKER†

(*Istituto di Chimica Generale dell' Università, Via G. Venezian* 21, 20133, *Milano, and* †*Istituto di Chimica delle Macromolecole del C.N.R., Via A. Corti* 12, 20133, *Milano, Italy*)

Summary The $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ (n = 2 or 3) anions have been isolated from the reaction of the $[Rh_{12}(CO)_{30}]^{2-}$ dianion with hydrogen; they are structurally related to a close hexagonal packing of rhodium atoms having mean distances of 2·81 Å.

REACTION of the $[Rh_{12}(CO)_{30}]^{2-}$ dianion[1] with hydrogen in Pr^iOH (50 °C, 1 atm) takes place initially with cleavage of the bond between the two octahedra to give the $[Rh_6(CO)_{15}H]^-$ monoanion, which is probably isostructural with the previously reported $[Rh_6(CO)_{15}X]^-$ (X = Cl, Br, I, CN, SCN, COR, CO_2R or CONHR).[2-4]

With prolonged reaction times (or by heating at 80 °C for 10 h) a further transformation into a mixture of brown anions is observed. Fractional precipitation allows isolation of derivatives of the $[Rh_{13}(CO)_{24}H_3]^{2-}$ anion in 30—50% yield. Reaction with bases gives the $[Rh_{13}(CO)_{24}H_2]^{3-}$ anion; the two anions are easily interconverted (reaction 1).

$$[Rh_{13}(CO)_{24}H_3]^{2-} \underset{H^+}{\overset{OH^-}{\rightleftarrows}} [Rh_{13}(CO)_{24}H_2]^{3-}. \qquad (1)$$

Both these anions have been isolated as salts of bulky cations such as $PPh_3CH_2Ph^+$, both are diamagnetic, and show i.r. absorptions due to terminal and edge bridging CO groups ($n = 2$, ν_{max} 2020 and 1840 in THF; $n = 3$, 1995 and 1810 cm^{-1} in MeCN). The n.m.r. spectra of both anions at 40 °C consist of a complex multiplet ($n = 2$, δ 29·6, 3·7H; $n = 3$, 26·4, 2·5H; in CD_3COCD_3) the integration of which is in fair agreement with the proposed stoicheiometry.

Crystals of $[(Ph_3P)_2N]_2[Rh_{13}(CO)_{24}H_3]$ have been studied by X-ray diffraction.† The structure has been solved by Patterson and Fourier methods and refined by least squares to a final R value of 0·084. All the atoms except the hydrogens have been located.

The geometry of the dianion and some Rh–Rh distances are shown in the Figure (a and b respectively). The 13 rhodium atoms are located in three nearly parallel layers making a cluster of D_{3h} idealised symmetry, and representing a fragment of hexagonal close packing. The central atom is 12-connected, while the surface atoms are all 4-connected with the other metal atoms and 3-connected with the carbonyl ligands. The ligands are bonded 12 linearly, one per surface metal atom, and 12 bridging one half of the polyhedron edges; the idealised symmetry of the dianion is C_s.

The mean values of Rh–C and C–O distances for terminal and edge bridging ligands are 1·78(2), 1·18(3) and 2·01(2), 1·21(3) Å respectively. The overall mean value of the Rh–Rh distances is 2·81 Å; distances from the central atom and distances on the cluster surface are not significantly different. Comparison with rhodium metal (cubic, close packing, 2·69 Å)[5] indicates that the electron density is higher in the cluster.

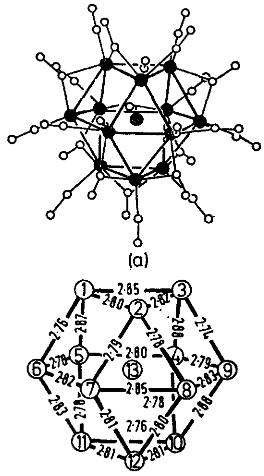

FIGURE. (a) Schematic representation of the molecular structure of the dianion $[Rh_{13}(CO)_{12}(\mu_2\text{-}CO)_{12}H_3]^{2-}$; (b) Atom numbering and bond distances on the surface of the Rh_{13} cluster (oriented as in a). The idealized symmetry plane is defined by Rh(2), Rh(13), and Rh(12). The distances from Rh(13) are: –Rh(1) 2·79, –Rh(2) 2·75, –Rh(3) 2·79, –Rh(4) 2·80, –Rh(5) 2·79, –Rh(6) 2·83, –Rh(7) 2·83, –Rh(8) 2·80, –Rh(9) 2·81, –Rh(10) 2·81, –Rh(11) 2·83, –Rh(12) 2·89; e.s.d. 0·01 Å.

The presence of a central metal atom is comparable with that previously found[6-8] in $[Rh_{15}(CO)_{28}(C)_2]^-$, $[Au_{11}\{P(p\text{-}C_6H_4F)_3\}_7I_3]$ and $[Au_9\{P(p\text{-}C_6H_4Me)_3\}_8]^{3+}$ and in contrast with the structural features of boranes,[9] indicating a less directional type of bonding. The $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$ clusters (170 valence electrons) do not obey the noble gas rule.

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† Crystal data: $C_{96}H_{63}N_2P_4O_{24}Rh_{13}$, M 3092·1, monoclinic, space group $P2_1/c$, a = 15·90(3), b = 26·71(5), c = 25·13(5) Å, β = 92·9(2)°, U = 10658·6 Å^3, D_m = 1·91, D_c = 1·926 g cm^{-3}, Z = 4. 6400 reflections; intensities were collected on an automated four circle diffractometer with Mo-K_α radiation up to sin θ/λ = 0·41. Outside this region the intensities were weak. As the crystal decayed upon X-ray irradiation, data were collected rapidly; during two days of measurements the decay was *ca.* 15%. The intensities were corrected for decay, Lorentz, and polarisation factors, and a set of 2987 reflections, with $I > 3\sigma(I)$, was used.

[1] P. Chini and S. Martinengo, *Inorg. Chim. Acta*, 1969, **3**, 299.
[2] P. Chini, S. Martinengo, and G. Garlaschelli, *J.C.S. Chem. Comm.*, 1972, 709.
[3] P. Chini, S. Martinengo, and G. Giordano, *Gazzetta*, 1972, **102**, 330.
[4] V. G. Albano, P. L. Bellon, and M. Sansoni, *J. Chem. Soc.*, (*A*), 1971, 678.
[5] Tables of Interatomic Distances, Chem. Soc. Special Publication No. 18, 1965.
[6] V. G. Albano, P. Chini, S. Martinengo, M. Sansoni, and D. Strumolo, *J.C.S. Chem. Comm.*, 1974, 299.
[7] P. L. Bellon, M. Manassero, and M. Sansoni, *J.C.S. Dalton*, 1972, 1481.
[8] P. L. Bellon, F. Cariati, M. Manassero, L. Naldini, and M. Sansoni, *Chem. Comm.*, 1971, 1423.
[9] K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1975, **18**.

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