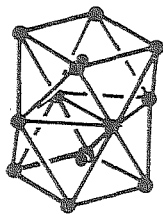


09.3-13 THE CARBIDO-CARBONYL CLUSTER ANION OF RHODIUM

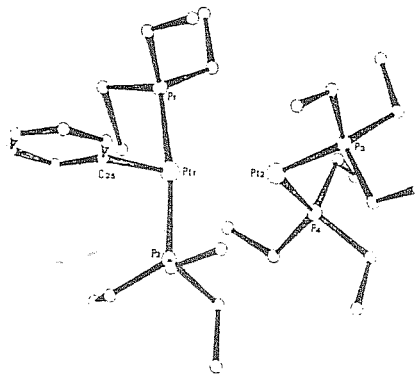
$[\text{Rh}_{12}\text{C}_2(\text{CO})_{24}]^{2-}$ CHARACTERIZED BY CRYSTALLOGRAPHIC METHODS. By V.G. Albano and D. Braga, Faculty of Sciences, University of Bologna. S. Martinengo and D. Strumolo, CNR Centre and Faculty of Sciences, University of Milan, Italy.

The prismatic dianion $[\text{Rh}_6\text{C}(\text{CO})_{15}]^{2-}$ reacts with H_2SO_4 in isopropanol at 80°C under nitrogen affording the new species $[\text{Rh}_{12}\text{C}_2(\text{CO})_{24}]^{2-}$ which has been crystallized as a $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt. The nature of this species has been elucidated by single crystal X-ray methods. $\text{C}_{98}\text{H}_{60}\text{N}_2\text{O}_{24}\text{P}_4\text{Rh}_{12}$ $M = 3008.3$, triclinic, $a = 17.19(2)$, $b = 13.05(1)$, $c = 11.58(1)$ Å, $\alpha = 103.24(3)^\circ$, $\beta = 88.69(2)^\circ$, $\gamma = 102.24(3)^\circ$, $U = 2470$ Å³, $D_m = 2.05$, $Z = 1$, $D_c = 2.02$ gcm⁻³, space group $P\bar{1}$, Mo- K_α radiation, 8600 reflections were collected by counter methods, 3420 of which were used for the structure solution. The final R value is 0.049.

The dianion has precise C_i and idealized D_{2h} symmetry and contains a Rh_{12}C_2 cluster shown in the figure. The metal atom polyhedron can be described as a three-layer system of two outer rectangles (almost squares) and a central rhombus packed in such a way as to form two prismatic cavities, to which two interstitial carbon atoms are allocated. The carbonyl ligands are bonded 8 edge-bridging on the outer rectangles and 16 terminal, two to each atom in the central rhombus and one to each atom in the outer rectangles. The structure clearly shows that this anion originates from the condensation of two Rh_6C moieties of the parent dianion. The Rh-Rh bond lengths are in the range 2.75-2.92, average 2.81. Other mean values are Rh-C (carbide) 2.09, Rh-C-O (terminal) 1.90, 1.10 and Rh-C-O (bridging) 2.04, 1.17 Å respectively. Products obtained by reduction of the present species are being investigated.



chechi, P. Mura and L. Zambonelli, *Angew. Chem. Int. Ed. Engl.* (1978) **17**, 778), and related complexes.



Pt(1)-Pt(2)	2.819(1) Å	P(1)-Pt(1)-Pt(2)	93.2(1)°
Pt(1)-P(1)	2.297(5)	P(1)-Pt(1)-P(2)	171.5(2)
Pt(1)-P(2)	2.293(4)	P(1)-Pt(1)-C(25)	87.5(4)
Pt(1)-C(25)	2.070(15)	P(2)-Pt(1)-Pt(2)	93.8(1)
Pt(2)-P(3)	2.257(4)	P(2)-Pt(1)-C(25)	87.9(4)
Pt(2)-P(4)	2.314(5)	C(25)-Pt(1)-Pt(2)	158.3(4)
		Pt(1)-Pt(2)-P(3)	132.9(1)
		Pt(1)-Pt(2)-P(4)	124.5(1)
		P(3)-Pt(2)-P(4)	102.5(1)

09.3-14 CRYSTAL AND MOLECULAR STRUCTURE OF

A BINUCLEAR PLATINUM DIHYDRIDO BRIDGED COMPLEX. $[\text{Pt}_2\text{H}_2(\text{C}_6\text{H}_5)\{\text{P}(\text{C}_2\text{H}_5)_3\}_4][\text{B}(\text{C}_6\text{H}_5)_4]$. F. Bachechi and L. Zambonelli. Istituto di Strutturistica Chimica "G. Giacomello" CNR CP-10 - 00016 Monterotondo Stazione (Roma), Italy. G. Bracher, D.M. Grove, L.M. Venanzi. Laboratorium für Anorganische Chemie Eidgenössische Technische Hochschule Universitätstrasse 6/8 CH-8006-Zürich, Switzerland.

Recently a new cationic binuclear trihydrido complex containing one four- and one five-coordinate platinum atom was prepared and its molecular structure deduced from ^1H -, ^{31}P - and ^{195}Pt -NMR spectroscopic data (G. Bracher, D.M. Grove, P.S. Pregosin and L.M. Venanzi, *Angew. Chem. Int. Ed. Engl.* (1979) **18**, 155). The complex contains both a dihydrido bridge and a terminal hydride ligand.

An analogous complex with a phenyl group replacing the terminal hydride ligand has been prepared, and its molecular structure will be reported.

No attempts to locate the hydride ligands have been performed at the present, however the heavy donor atom arrangement and the Pt...Pt distance are consistent with two hydrido bridges.

Relevant structural features will be compared with those of its dihydrido monobridged isomer (G. Bracher, D.M. Grove, L.M. Venanzi, F. Ba-

09.3-15 THE CRYSTAL STRUCTURE OF (2,2',2"-

TERPYRIDYL)-AQUATRIPHENYL CHLORO TIN (IV) (1:1). By L. Prasad, F.L. Lee and Y. Le Page, Chemistry Division, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada and F.E. Smith, Chemistry Department, Kenyatta University College, P.O. Box 43844, Nairobi, Kenya.

White needle like crystals of $\text{C}_{33}\text{H}_{28}\text{N}_3\text{ClO}_8\text{Sn}$ were obtained by mixing ethanolic solutions of triphenyl tin chloride and 2,2',2"-terpyridyl. The crystals are monoclinic, space group $P2_1/n$, $a = 10.6644(6)$, $b = 9.4819(4)$, $c = 28.338(2)$ Å, $\beta = 95.922(5)$ at 115 K, $Z = 4$, $D_{\text{calc}} = 1.45$ Mg.m⁻³. Intensities were first measured at room temperature with a four circle Picker diffractometer using graphite monochromatized MoK_α radiation. The crystals deteriorated on exposure to x-rays and the intensities were re-measured at 155 K. The structure was solved using MULTAN (Germain, Main & Woolfson, *Acta Cryst.* (1971) **A27**, 368) and was refined by block diagonal least squares and the final R_F and R_{F_w} are 0.020 and .021 respectively (at 115 K) and .027 and .039 respectively at room temperature.

There is no large structural change between the room temperature and 115 K. The Sn atom was expected to be seven coordinated, similar to the dimethyl diisothiocyanato terpyridyl tin (IV) (Naik and Scheidt, *Inorg. Chem.* (1973) **12**, 272). However, the molecule is a five-coordinated complex, with the Sn atom coordinated to the 3 phenyl groups, the Cl atom and the water molecule oxygen atom. The terpyridyl group is held in the crystal