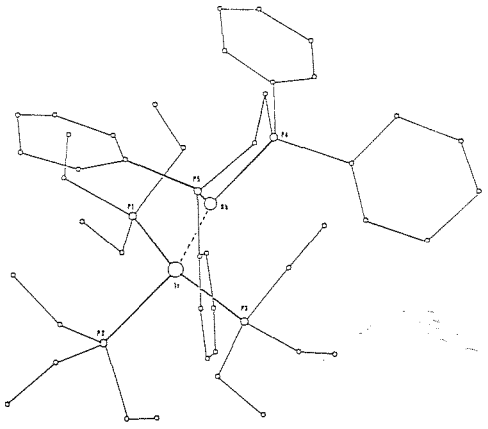


Molecular structure of cation (I) (diphosph = $Ph_2PCH_2CH_2PPh_2$).

The $[Rh_2(TMB)_4Cl_2](PF_6)_2$ crystals are orthorhombic, space group Pbcn (No. 60), a=13.846, b=24.773, c=17.068 Å, Z=4. The structure was solved by a combination of Patterson and direct methods. Convergence was obtained in a full-matrix least-squares refinement (anisotropic Rh, Cl, C, N, P, F, constrained isotropic H, R=0.12, R_w=0.078, 1903 reflections with $F > 1.5\sigma(F)$) with a partially disordered ligand molecule. The bonded Rh atoms are related by a twofold axis, and the Rh-Rh vector is closely aligned with the c axis. Thus the orientation of the molecule is suitable for a single-crystal spectroscopic study of the formal Rh-Rh single bond (Rh-Rh, 2.77 Å, compared to 3.26 Å in the corresponding Rh (I) complex.)

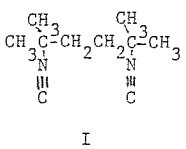
$[Ir_2(TMB)_4I_2](BPh_4)_2$ crystallizes in the orthorhombic space group Pccn (No. 56), a=15.141, b=28.104, c=23.877 Å, Z=4. Although 9019 unique reflections were measured many of the intensities were low, and the quality of fit is not as good as in the Rh structure. The Ir and I atoms occupy special positions (1/4 1/4 z). Serious questions remain concerning possible disorder within the molecule,but the bonding arrangement, and the Ir-Ir distance of 2.82 Å, are confirmed.

We are indebted to the U.S. and Swiss National Science Foundations for support of this work, and to Jack D. Dunitz, K.N. Trueblood, Paul Seiler, Richard E. Marsh, Harry B. Gray, and Carolyn Knobler for assistance and advice.

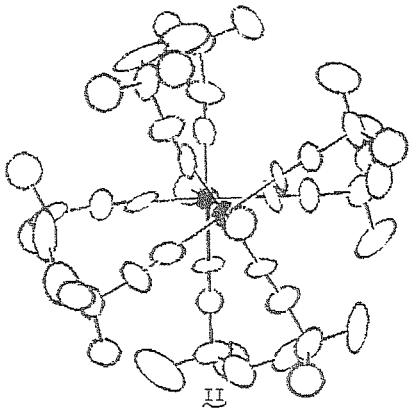
09.4-44 CRYSTAL STRUCTURE ANALYSES OF BINUCLEAR RHODIUM (II) AND IRIDIUM (II) ISOCYANIDE COMPLEXES.

By A.W.Maverick and T.P.Smith, California Institute of Technology, and E.Maverick, University of California, Los Angeles.

We have determined the crystal structures of $[Rh_2(TMB)_4Cl_2](PF_6)_2$ and $[Ir_2(TMB)_4I_2](BPh_4)_2$ (TMB= 2,5-diisocyano-2,5-dimethylhexane, I), both of which involve a propeller-like arrangement of the bridging diisocyanoalkane ligands about the central X-M-M-X unit. The two approximately planar $M(CNR)_4$ moieties are partially staggered, with average C-M-M-C torsion angles of 32° (M=Rh) and 30° (M=Ir). These angles are identical (within experimental error) to those found in the corresponding Rh (I) complex (Mann, K.R., Thich, J.A., Bell, R.A., Coyle, C.L., and Gray, H.B., Inorg. Chem. (1980) 19, 2462-2468). An Ortep drawing of the cation (II) appears below.



I



II

09.4-45 MIXED VALENCE COMPLEXES OF PLATINUM. THE CRYSTAL STRUCTURES OF $[Pt(Meen)_2][PtBr_2(Meen)_2](ClO_4)_4$ AND $[Pt(tn)_2][PtI_2(tn)_2](ClO_4)_4$.

Bernd Keppler and Barbara Müller, Anorganisch-Chemisches Institut der Universität, 69 Heidelberg 1, BRD. Mario Cannas and Giaime Marongiu, Istituto Chimico dell'Università, 09100 Cagliari, Italy.

We have performed single crystal diffraction studies of the title compounds mainly to determine the geometry of the linear chains showing alternating Pt(II) and Pt(IV) atoms. Both compounds occur as coloured, lustrous metallic, fine needles. $[Pt(Meen)_2][PtBr_2(Meen)_2](ClO_4)_4$ (Meen = 1,2-diaminopropane) is orthorhombic (Pc2a) with a = 7.74(1), b = 11.14(2), c = 17.42(3) Å and Z = 2; a total of 1800 data were collected to 2θ = 52°. $[Pt(tn)_2][PtI_2(tn)_2](ClO_4)_4$ (tn = 1,3-diaminopropane) is monoclinic (P2) with a = 10.29(2), b = 11.33(2), c = 8.62 (1) Å, β = 125.7°, Z = 1. A total of 1700 data were collected. Most crystals are twinned along [010] simulating a pseudo-orthorhombic symmetry with a centered cell very close to that reported for Br and Cl derivatives.

$Pt(Meen)_2$ and $Pt(tn)_2$ groups in the crystals of the two compounds stack with the molecular plane perpendicular to the b axis, which results in a linear Pt(II) ···X-Pt(IV) -X··· chain. At this stage of refinement (R ≈ .10) the Pt(II)-Pt(IV) spacings in each structure are equal ($\frac{1}{2}$ b) although not required crystallographically. The difference in metal-metal separation between the two compounds is due to corresponding differences in the direct M-X bonds (Pt-Br=2.52 Å; Pt-I = 2.66 Å); the lengths of the charge-transfer Pt···X are rather unaffected.