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Preliminary communication

RHODIUM(II) DIMERS: THE PREPARATION AND STRUCTURE OF $[(p\text{-}CH_3C_6H_4NC)_8Rh_2I_2]$-$[PF_6]_2$

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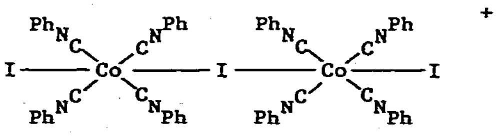
Summary

Oxidation of $[(p\text{-}CH_3C_6H_4NC)_4Rh][PF_6]$ with one half mole of iodine or bromine produces $[(p\text{-}CH_3C_6H_4NC)_8Rh_2X_2][PF_6]_2$. The crystal structure of the iodide complex establishes the existence of a direct Rh-Rh bond (2.785 Å) with pseudooctahedral coordination about each rhodium completed by terminal isocyanide and iodide ligands.

Recently we reported that alkyl isocyanide complexes of Rh(II) are formed by the association of Rh(I) and Rh(III) complexes via equation 1 and, based on spectroscopic evidence, proposed that these Rh(II) cations contain

$$(1)\qquad (RNC)_4Rh^+ + (RNC)_4RhX_2^+ \rightleftarrows (RNC)_8Rh_2X_2^{2+}$$

a direct Rh-Rh bond.[1] Aryl isocyanide complexes $(ArNC)_8Rh_2X_2^{2+}$ have been prepared on several occasions but no spectroscopic or structural data characterizing these species have been reported.[2,3,4] These aryl isocyanide complexes have been formulated as polymers with -Rh-I-Rh-I- chains[3] or as mixed valence Rh(I) - Rh(III) materials.[4] Support for the possibility of a halo bridged structure for $(RNC)_8Rh_2I_2^{2+}$ comes from the analogy with the diamagnetic form of $(PhNC)_4CoI_2$ which has been shown to have the ionic structure $[Co_2I_3(CNPh)_8]I$, 1.[5]



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The Rh(II) complexes $[(p\text{-}CH_3C_6H_4NC)_8Rh_2X_2][PF_6]_2$ (X=I, ν(C≡N) 2194 cm^{-1}; X=Br, ν(C≡N) 2199 cm^{-1}) are readily formed by oxidizing $[(p\text{-}CH_3C_6H_4NC)_4Rh]$-$[PF_6]$ (ν(C≡N) 2160) with one half mole of iodine or bromine in acetonitrile solution. The Rh(II) cations are similar to their alkyl analogs. In solution they dissociate into $(p\text{-}CH_3C_6H_4NC)_4Rh^+$ and $(p\text{-}CH_3C_6H_4NC)_4RhX_2^+$ (X=I, ν(C≡N) 2224 cm^{-1}; X=Br, ν(C≡N) 2229 cm^{-1}) according to the reverse of eq. 1. This equilibrium is established rapidly in both directions but is strongly solvent dependent. Dissociation is essentially complete in solvents of low dielectric (dichloromethane, chloroform) but appreciable amounts of Rh(II) dimer exist in acetone or acetonitrile solution.

In order to determine the precise geometry of one of these Rh(II) dimers the crystal structure of $[(p\text{-}CH_3C_6H_4NC)_8Rh_2I_2][PF_6]_2$ was determined. Air stable brown crystals were obtained by diffusion of diethyl ether into an acetonitrile solution.* Crystal data (150 K): Space group C2/c; a = 28.0475 (24), b = 18.4901 (14), c = 14.9704 (11) Å; β = 120.228 (5); ρ_{exptl}^{298K} 1.612, ρ_{calc}^{150K} = 1.671 g/cm^3; Z = 4; μ_{cu} = 126.8 cm^{-1}. Intensity data were collected at 150 K on a Syntex $P2_1$ automated diffractometer using Cu Kα radiation. A total of 4794 reflections were collected by a variable speed ω scan of the most intense part of the peak. The structure was solved and refined keeping all atoms isotropic by Patterson, Fourier and least squares methods to an R index of 0.11 using 4228 reflections.

The structure consists of discrete $(p\text{-}CH_3C_6H_4NC)_8Rh_2I_2^{2+}$ and PF_6^- ions. The geometry of the cation, which possesses crystal imposed C_2 symmetry, is shown in the figure. There is a direct Rh-Rh bond and the iodide ligands are in terminal positions. The Rh-Rh bond length of 2.785(2) Å is slightly shorter than the other unbridged Rh-Rh bond length which has been determined in bis-(triphenylphosphine)tetrakis (dimethylglyoximato)dirhodium (2.936 Å)[6] but longer than a number of ligand bridged Rh-Rh single bonds.[7-10] It is much shorter than the Rh-Rh distance (3.396) in the bridged Rh(I) complex $Rh_2(Ph_2AsCH_2AsPh_2)_2(CO)_2Cl_2$.[11] In addition to the axial bonds to iodine and rhodium, each rhodium forms bonds to four isocyanide ligands in a square arrangement. The two $(p\text{-}CH_3C_6H_4NC)_4Rh$ units are twisted 26° from an eclipsed configuration. The planes of the phenyl rings lie very nearly in the RhC_4 coordination planes.

The structure found agrees with our former predictions and is in accord with results obtained from the oxidation of ligand bridged rhodium(I) dimers $Rh_2(Ph_2PCH_2PPh_2)_2(CNR)_4^{2+}$ [12] and $Rh_2[CN(CH_2)_3NC]_4^{2+}$.[13] In all of these cases the bridging geometry facilitates transannular oxidative addition of a

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*Although the addition of ether will alter the position of equilibrium 1 in solution, the component which crystallizes is determined by solubility considerations. The Rh(II) dimer must be the least soluble compound of the mixture.

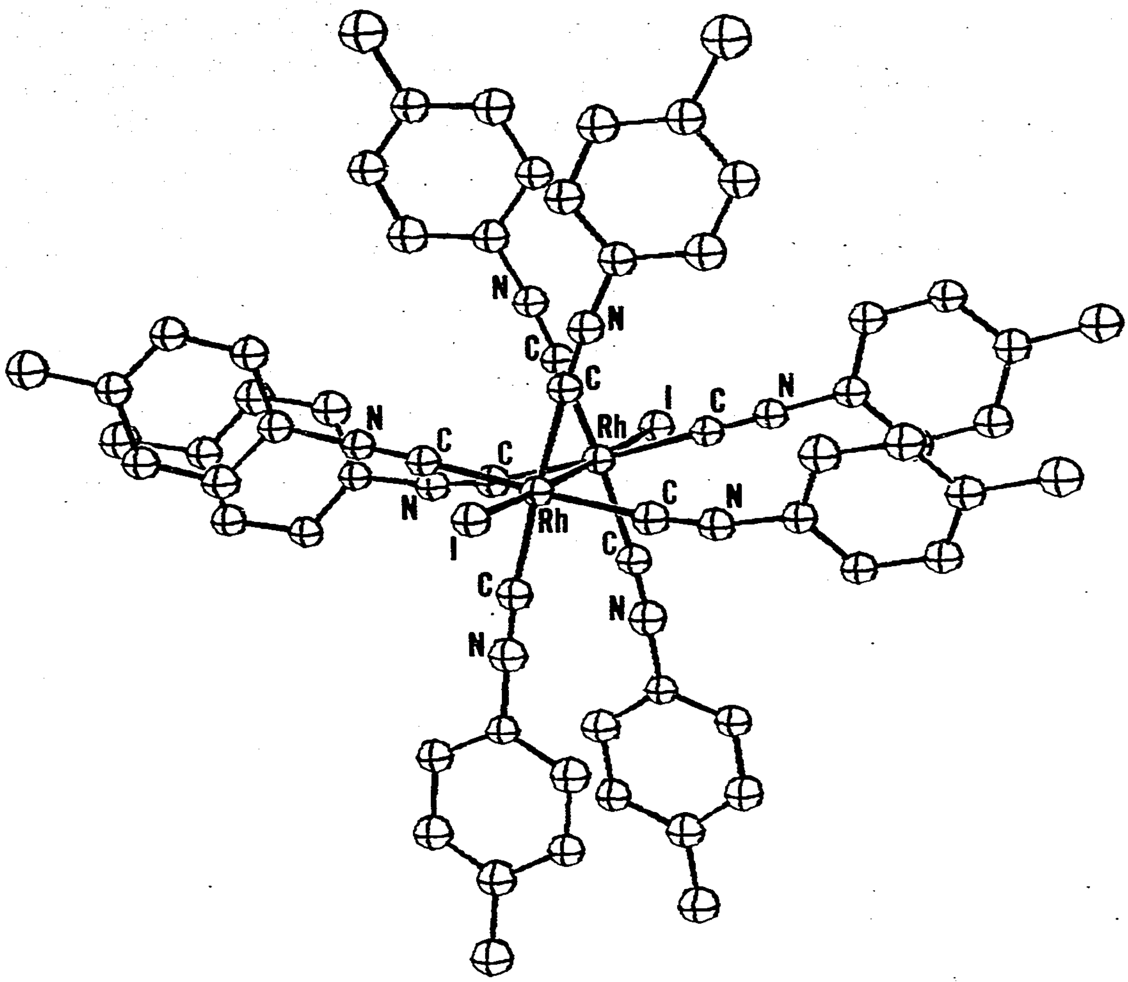

Figure 1. An ORTEP drawing of $(p\text{-}CH_3C_6H_4NC)_8Rh_2I_2^{2+}$ showing 50% thermal ellipsoids. Bond lengths are: Rh-Rh, 2.785(2), Rh-I, 2.735(1); Rh-C, range 1.97 to 1.99; C≡N, range 1.12-1.16 Å. Bond angles are Rh-Rh-I, 178.4 (2); I-Rh-C, range 90.7-87.0; C-Rh-C, range 85.5-91.8°.

halogen to two rhodium centers while restricting the insertion of a halide between the metals.

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