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A New Class of Dinuclear Rhodium Compound: the Crystal Structure of $[Rh(CO)RhCl_2\{(PhO)_2PN(Et)P(OPh)_2\}_2]\cdot CHCl_3$

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Reaction of $(PhO)_2PN(Et)P(OPh)_2$, (etdp), with $[\{Rh(CO)_2Cl\}_2]$ gave a purple solution from which a purple product of stoichiometry $[\{Rh(CO)(etdp)Cl\}_x]$ (I) $\{\nu(CO) = 2002\ cm^{-1}$, nujol mull$\}$ could be isolated by freeze-drying. The same species was also formed by passing CO through a solution of $[\{Rh(etdp)Cl\}_2]$ [1]. Crystallisation of (I) from benzene gave a yellow crystalline product (II) of the same stoichiometry as (I), but which contained bridging as well as terminal carbonyl groups $\{\nu(CO) = 2008$, 1998, 1840, and 1788, nujol mull$\}$. On recrystallisation from $CHCl_3$/petroleum ether, (II) gave an orange crystalline product(III) containing no bridging carbonyl groups $\{\nu(CO) = 2006\ cm^{-1}$, nujol mull$\}$. Dissolution of (III) gave an orange solution which rapidly turned purple on the passage of CO. On long standing, a solution of (III) turned yellow, as a result of reversion to $[\{Rh(etdp)Cl\}_2]$. It was not clear what the structure of (III) was, so its crystal structure was determined.

Crystals of (III) are triclinic, space group $P\bar{1}$, $a = 10.59(1)$, $b = 22.27(2)$, $c = 12.43(1)$ Å, $\alpha = 91.9(1)$, $\beta = 94.5(1)$, $\gamma = 92.2(1)°$, $U = 2921$ Å^3, $Z = 2$. Data were collected on a Philips PW1100 diffractometer (N.P.R.L., Pretoria) with graphite-monochromated Mo-Kα radiation to $\theta = 25°$. 9859 reflexions were measured. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares to R = 0.075 for all data (Rh, P and Cl atoms anisotropic). The crystallographic analysis showed one molecule of $CHCl_3$ solvent per molecule of complex.

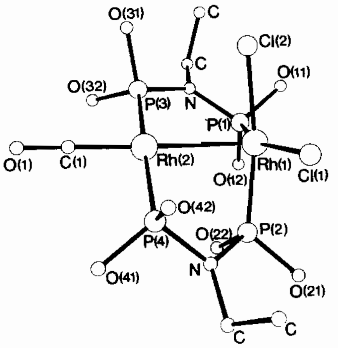

Fig. 1. A projection of the molecule (III) with the phenyl rings omitted. Some bond lengths and angles are: Rh(1)–Rh(2) 2.661; Rh(1)–P(1) 2.184, –P(2) 2.201; Rh(2)–P(3) 2.258, –P(4) 2.258; Rh(1)–Cl(1) 2.377, –Cl(2) 2.374; Rh(2)–C(1) 1.815; mean P–N 1.68 (±0.02), mean P–O 1.61 (±0.01) A; Rh(1)–Rh(2)–P(3) 92, –P(4) 86, –C(1) 172; Rh(2)–Rh(1)–P(1) 87, –P(2) 83, –Cl(1) 113, –Cl(2) 83; P(1)–Rh(1)–P(2) 102, –Cl(1) 159, –Cl(2) 86; P(2)–Rh(1)–Cl(1) 88, –Cl(2) 166; Cl(1)–Rh(1)–Cl(2) 88; P(3)–Rh(2)–P(4) 173. The closest intramolecular contacts involving Cl(1) are: 3.54 A to O(21) and 3.45 A to O(42). The chloroform molecule is beautifully ordered, and appears to be attracted to Cl(1); the distance Cl(1)···C(solvent) is 3.70 A.

The two rhodium atoms are linked by a strong bond of length 2.66 Å, and have different coordination geometries (see Fig. 1). The one is square planar, C.N. = 4, with the CO group bonded to it being colinear with the two Rh atoms, while the two P atoms are coordinated to it *trans*, P(3)–Rh(2)–P(4) = 173°. The other Rh atom has C.N. = 5, and is approximately square pyramidal with the Rh–Rh bond in the apical position. The two Cl atoms are *trans* to the P atoms in the basal plane, *i.e.* the P atoms are *cis* to each other, P(1)–Rh(1)–P(2) = 102°. There are marked distortions from ideality, especially for one Cl atom, Rh(2)–Rh(1)–Cl(1) = 113°. The two diphosphazane ligands (etdp) bridge the metal atoms but the four P atoms are *not* coplanar; the torsion angles, P(1)–Rh(1)–Rh(2)–P(3) and P(2)–Rh(1)–Rh(2)–P(4), are –27 and 45° respectively.

Both Rh atoms have the same electron count and are 16-electron systems if the Rh–Rh interaction is classed as a 2-electron bond. However, their formal oxidation states are different. Rh(1) has oxid. no. = 2, Rh(2) has oxid. no. = 0. This difference in electronic character of the Rh atoms is reflected in the Rh–P bond lengths: mean Rh(1)–P = 2.19 Å, Rh(2)–P = 2.26 Å.

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