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Preliminary communication

$[\{Rh(CO)(MeO)_2PNEtP(OMe)_2Cl\}_2]$: A MOLECULE WITH A SYMMETRICAL FORMULA AND AN ASYMMETRIC STRUCTURE

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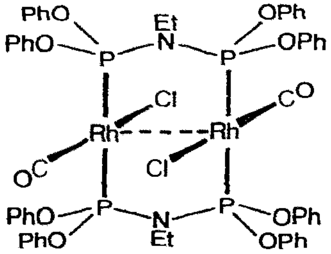
Summary

$[\{Rh(CO)(MeO)_2PNEtP(OMe)_2Cl\}_2]$, synthesised by reaction of $[\{Rh(CO)_2Cl\}_2]$ with $(MeO)_2PNEtP(OMe)_2$, has an unusual asymmetric structure in which one carbonyl group adopts a terminal position while the other is bridging; the two chlorines are both terminal.

Treatment of $[\{Rh(CO)_2Cl\}_2]$ with $Ph_2PCH_2PPh_2$ is known to lead to the formation of $[\{Rh(CO)Ph_2PCH_2PPh_2Cl\}_2]$ (I) [1], a widely employed precursor in the synthesis of dinuclear compounds of rhodium [2]. It was thus not surprising that the corresponding reaction involving the phenoxydiphosphazane



(II)

$(PhO)_2PNEtP(OPh)_2$ was found to afford in solution $[\{Rh(CO)(PhO)_2PNEtP(OPh)_2Cl\}_2]$ (II) of a structure analogous to that of I [1,3]. The reaction of $[\{Rh(CO)_2Cl\}_2]$ with $(MeO)_2PNEtP(OMe)_2$ was found to give $[\{Rh(CO)(MeO)_2PNEtP(OMe)_2Cl\}_2]$ (III), a product of similar stoichiometry, but whose solid state and solution infrared spectra revealed the presence of a bridging as well as a terminal carbonyl group {ν(C—O): 1995s, 1975(sh), and 1805m cm^{-1}, in CH_2Cl_2; 1995(ip). 1985s, 1960w, 1945w, and 1810s cm^{-1}, as a Nujol mull}. This spectroscopic evidence suggested that the compound has an unusual asymmetric structure and its crystal structure was thus determined.

Crystal data. Crystals of III are monoclinic, space group $P2_1/a$, a = 17.89(1), b = 15.77(1), c = 10.693(5) Å, β = 103.2(1)°, V = 2938 Å^3, Z = 4. Data were collected on a Philips PW1100 diffractometer (NPRL, CSIR, Pretoria) with graphite-monochromated Mo-K_α radiation to θ = 27°. Of the 6644 reflexions measured, 4658 were classed as observed {$I > 2.0\sigma(I)$}. The structure was solved by standard Patterson and Fourier methods, and refined by block-diagonal least squares to R = 0.055 for 4658 data, all non-hydrogen atoms anisotropic*.

The molecular structure is illustrated in Fig. 1. The two rhodium atoms are not only bridged by the two diphosphazane ligands but are also symmetrically bridged by one of the carbonyl groups (Rh(1)—C(2) = 1.95, Rh(2)—C(2) = 2.06 Å); the rhodium—rhodium distance is 2.687 Å which corresponds to a formal bond. The atoms of the [Rh_2P_4] system are essentially coplanar, as are those of the [$Rh_2Cl_2(CO)_2$] system with the angle between these two planes

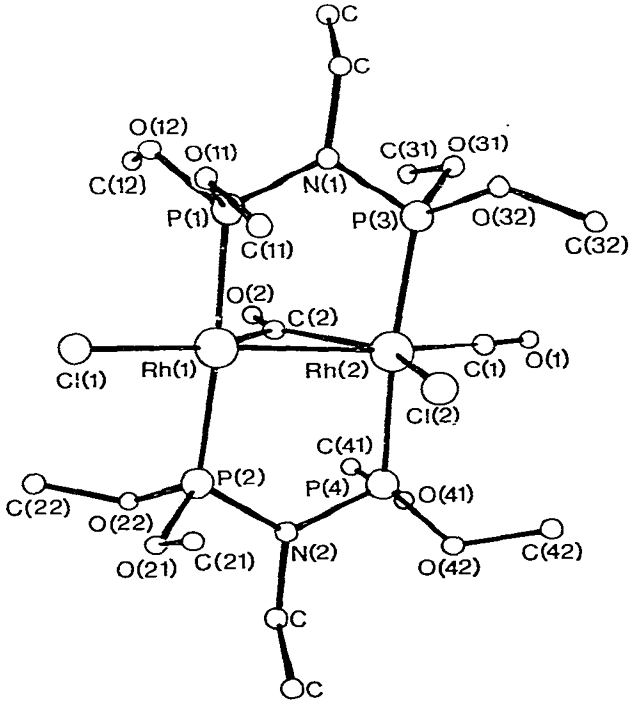


Fig. 1. The molecular stereochemistry of [{$Rh(CO)(MeO)_2PNEtP(OMe)_2Cl$}$_2$]. Bond lengths and angles: Rh(1)—P(1), 2.28; Rh(1)—P(2), 2.29; Rh(2)—P(3), 2.30; Rh(2)—P(4), 2.30; Rh(1)—Cl(1), 2.36; Rh(2)—Cl(2), 2.52; Rh(2)—C(1), 1.86; mean P—N, 1.67 (± 0.02); mean P—O, 1.59 (± 0.01) Å. Rh(1)—Rh(2)—Cl(2), 86; Rh(1)—Rh(2)—P(3), 93; Rh(1)—Rh(2)—P(4), 93; Rh(1)—Rh(2)—C(1), 157; Rh(2)—Rh(1)—Cl(1), 163; Rh(2)—Rh(1)—P(1), 93; Rh(2)—Rh(1)—P(2), 92; Rh(1)—C(2)—Rh(2), 84°.

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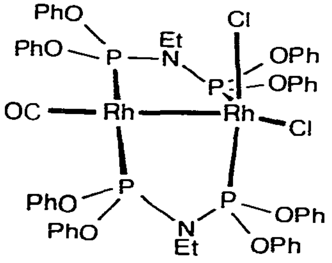
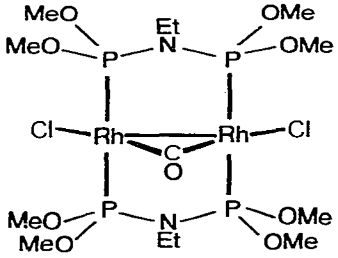
*Supplementary material is available from the authors.

being 89°. While one of the chlorine ligands is essentially colinear with the Rh—Rh vector (Rh(2)—Rh(1)—Cl(1) = 163°) the other is almost orthogonal to it (Rh(1)—Rh(2)—Cl(2) = 86°).

The coordination numbers of the two rhodium atoms are different, that for Rh(1) being 5 while that for Rh(2) is 6; the Rh(1)—Cl(2) distance of 3.558 Å is too long to be considered as bonding. Both rhodium atoms have the same formal oxidation number of 2, but have different electron counts; Rh(1) is a 16-electron system, while Rh(2) is an 18-electron system.



(IV)



(V)

It was previously established that II readily decarbonylates in chloroform solution to give a monocarbonyl derivative $[Rh_2(CO)\{(PhO)_2PNEtP(OPh)_2\}_2Cl]$ (IV) of unusual structure illustrated [4]. Compound III also decarbonylates readily in chloroform solution but the monocarbonyl product, $[\{Rh(MeO)_2PNEtP(OMe)_2Cl\}_2(\mu\text{-}CO)]$ (V) exhibits a single bridging carbonyl stretching mode in both its solution and solid state infrared spectrum $\{\nu(C—O)$: 1795 cm^{-1}, in CH_2Cl_2; 1785 cm^{-1}, as a Nujol mull$\}$ indicating that it has the symmetrical structure shown. This structure is analogous to that very recently established X-ray crystallographically for $[\{RhPh_2PCH_2PPh_2Br\}_2(\mu\text{-}CO)]$ [5]. It is thus apparent that fairly small differences in the diphosphazane ligands can lead to significant structural changes in the types of dirhodium compounds under consideration.

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