The Structure of Crystalline *trans*-Dichlorobis(triphenylphosphine)rhodium(II), a Square Planar Rhodium(II) Monomer: Isolation of the Proposed Paramagnetic Impurity in Wilkinson's Catalyst

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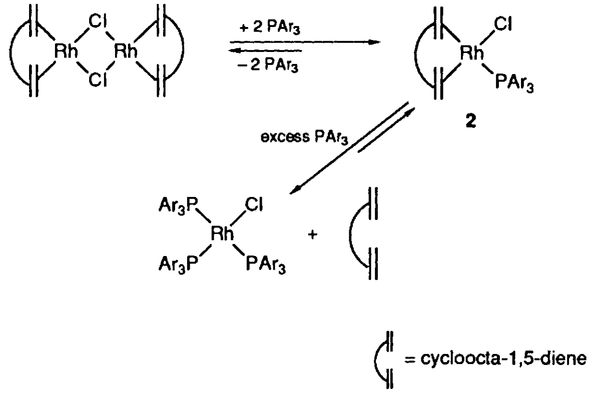
trans-Dichlorobis(triphenylphosphine)rhodium(II), a square planar rhodium(II) monomer, has been isolated and characterized spectroscopically and crystallographically.

Wilkinson's catalyst, $(PPh_3)_3RhCl$, was the first widely applicable homogeneous hydrogenation catalyst effective in a variety of organic solvents at ambient temperatures and pressures. It has triggered many developments in the field of homogeneous catalysis and has been extensively used and studied in the hydrogenation of alkenes and alkynes. Wilkinson's catalyst has been observed to contain a paramagnetic impurity.[1] The identity of this impurity and its contribution to the catalytic cycle are unknown.

We have been studying the reactions of triarylphosphines with $[(cod)_2Rh_2Cl_2]$ (cod = cycloocta-1,5-diene) by rapid injection NMR spectroscopy;[2] $[(cod)_2Rh_2Cl_2]$ reacts very rapidly† with two equivalents of triphenylphosphine and reaches an equilibrium to give predominantly $[(cod)RhClPPh_3]$ **2** in polar solvents such as chloroform. Excess of triphenylphosphine further reacts with **2** to give Wilkinson's catalyst in a much slower reaction (Scheme 1).

We have isolated and characterized several compounds of the type $[(cod)RhClPAr_3]$. Such compounds may be prepared by adding two equivalents of PAr_3 to a chloroform or dichloromethane solution of $[(cod)_2Rh_2Cl_2]$. Single crystals may be obtained by adding light petroleum to the resulting solution and slowly evaporating this solvent mixture under a slow stream of nitrogen. In our attempts to grow crystals of **2** suitable for X-ray diffraction, we have serendipitously isolated† yellow crystals as the dichloromethane solvate of the title compound, *trans*$[(PPh_3)_2RhCl_2]$ **1**, the proposed paramagnetic impurity in Wilkinson's catalyst.[1] The title compound has been characterized by X-ray diffraction, ^1H NMR, far-IR, and EPR spectroscopy, and mass spectrometry.



Scheme 1

A ^1H NMR spectrum of **1** in C_6D_6 revealed only aromatic hydrogen signals, multiplets at δ 7.011 (3H) and 7.955 (2H). The mass spectra (CI and FAB) gave major peaks at 662 *m/z* $[(PPh_3)_2RhCl]^+$, 627 $[(PPh_3)_2Rh]^+$, 262 $[PPh_3]^+$ and 185 $[PPh_2]^+$. The EPR spectrum of **1** at room temperature in degassed dichloromethane is identical to that of Wilkinson's catalyst, two lines at $g = 2.19$ and 2.05.[1] The far-IR (500–100 cm^{-1}) spectrum of **1** shows a band at 310 cm^{-1} (Rh–Cl) and bands at 406, 423, 444 and 454 cm^{-1} (Rh–P) stretching modes.

The results of the X-ray structure determination for **1**‡ are shown in Fig. 1. The Rh–Cl and Rh–P bond lengths are 2.428(4) and 2.323(2) Å, respectively. The metal centre sits on a crystallographic inversion centre, requiring that the P–Rh–P and Cl–Rh–Cl angles be 180°. These bond lengths are comparable to the bond lengths found for the square pyramidal, $[Rh^{II}(PPh_3)_2Cl(s\text{-}bqdi)]$, Rh–Cl, 2.410 Å and Rh–P, 2.277 Å.[3] The analogous palladium compound, *trans*-$[(PPh_3)_2PdCl_2]$, has a much shorter metal–chlorine bond [2.290(1) Å] and a comparable metal–phosphorus bond length [2.337(1) Å].[4]

Rh^{II} compounds with bulky phosphine ligands have been prepared by the controlled chlorination of $[(PAr_3)_4Rh_2Cl_2]$[5]

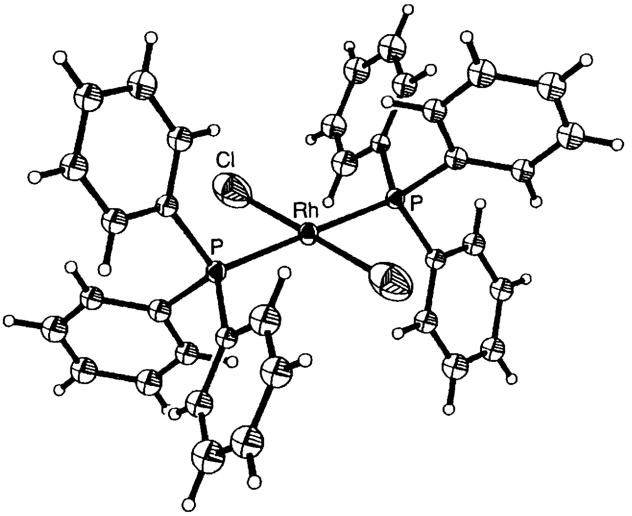


Fig. 1 ORTEP perspective of $C_{36}H_{30}Cl_2P_2Rh$, selected bond lengths (Å) and angles (°): Rh–Cl 2.428(4), Rh–P 2.323(2); Cl–Rh–Cl 180.0, P–Rh–P 180.0, Cl–Rh–P 93.5(1)

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† $t_{\frac{1}{2}}$ for $[(cod)_2Rh_2Cl_2]$ is <200 ms at room temperature, $[(cod)_2Rh_2Cl_2]_i = 15$ $[PPh_3]_i = 25$ mmol dm^{-3}. Although **1** is certainly present as an impurity, we were only once fortunate to have suitable conditions for the fractional crystallisation of **1** (≈30 mg) from solution. Crystalline **1** is fairly air stable surviving several months in air in a capped vial, losing solvate slowly. In solution in the presence of air **1** decomposed to undetermined products.

‡ *Crystal data*: $C_{36}H_{30}Cl_2P_2Rh(CH_2Cl_2)$, $M = 783.34$, orthorhombic, space group *Pcab*, $a = 8.0565(16)$, $b = 20.546(6)$, $c = 23.348(7)$ Å, $U = 3865(2)$ Å^3 $Z = 4$, $D_c = 1.346$ g cm^{-3}, crystal size = 0.12 × 0.12 × 0.38 mm, Mo-Kα (λ = 0.71073 Å), $T = 294$ K, $F(000) = 1588$, $\mu = 0.818$ mm^{-1}, $R = 0.063$, $R_w = 0.056$ for 1558 observed reflections with $I > 3\sigma(I)$. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.

and by treatment of $[RhCl_3(H_2O)_x]$ with the phosphine in ethanol.[6]§ Various Rh^{II} species have been observed as short-lived intermediates in flash photolysis studies[7] and as intermediates in the stepwise reduction of Rh^{III} compounds in cyclic voltammetry experiments.[8] It is interesting to note the similarity in the preparation of *trans*$[(o\text{-tolyl}_3P)_2RhCl_2]$,[6] Wilkinson's catalyst[1] and $[(cod)_2Rh_2Cl_2]$[9] implying that perhaps a Rh^{II} intermediate is involved in each of those cases in which a Rh^{II} compound is not the isolated product.

Although there are numerous examples of Rh^{II} dimers with Rh–Rh bonds,[10] the title compound represents one of the few examples of a fully characterized Rh^{II} monomer.

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§ Thus far, we have been unable to prepare **1** independently by either the controlled chlorination of $[(PPh_3)_4Rh_2Cl_2]$ or ligand exchange of PPh_3 with *trans*$[(o\text{-tolyl}_3P)_2RhCl_2]$.

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