

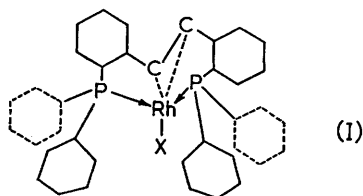
The Reaction of Rhodium Halides with Tri-*o*-tolylphosphine: a Stable Bivalent Rhodium Complex

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ALTHOUGH intermediate rhodium(II) species have been postulated to account for the catalysis of substitution reactions of rhodium(III) complexes by reducing agents,¹ few genuine, paramagnetic rhodium(II) complexes are known. These include $\{\text{Rh}[\text{C}_6\text{Me}_6]_2\}^{2+,2}$ and $[\text{Rh}(\text{MNT})_2]^{2-,3}$ (MNT = maleonitriledithiolate anion). The reduction of rhodium(III) halides by triphenylphosphine to give rhodium(I) complexes of general formula $\text{Rh}(\text{PPh}_3)_3\text{X}$ (X = Cl, Br, or I) has been reported previously.⁴ We now find that, by using tri-*o*-tolylphosphine, $\text{P}(\text{C}_6\text{H}_4\text{Me-}o)_3$, this reduction can be stopped at the rhodium(II) stage.

Ethanollic rhodium(III) chloride reacts with tri-*o*-tolylphosphine(OP) at 25° giving a 30–40% yield of the air-stable, blue-green complex $(\text{OP})_2\text{RhCl}_2$,



X = Cl, Br, or NCS; *ortho*-methyl groups and olefinic hydrogen atoms omitted for clarity.

characterised by full elemental analysis. The magnetic moment μ_{eff} at 20° is $2.3 \pm 0.1 \beta$, indicating one unpaired electron.⁵ The complex is isomorphous with the palladium(II) analogue, and since both show a single strong band due to $\nu(\text{M-Cl})$ at 351 cm^{-1} in their infrared spectra, a

trans-configuration is indicated for $(\text{OP})_2\text{RhCl}_2$ and $(\text{OP})_2\text{PdCl}_2$.⁶ A mauve modification of $(\text{OP})_2\text{RhCl}_2$ (μ_{eff} at 20° = 2.0β) is obtained either by carrying out the original reaction at 0°, or by evaporating *in vacuo* the unstable, purple solutions of the blue-green compound in dichloromethane. The mauve modification, which is not isomorphous with *trans*- $(\text{OP})_2\text{PdCl}_2$, reverts to the blue-green form on treatment with acetone at room temperature. Attempts to prepare the analogous rhodium(II) bromo-complex have so far been unsuccessful.

The e.s.r. spectra of both forms of $(\text{OP})_2\text{RhCl}_2$ have been measured at room temperature. The spectrum of the mauve form (powder) has the characteristic shape for an axial *g*-tensor with small anisotropy; g_{av} (r.m.s.) = 2.03. Under similar conditions, the blue-green form shows a very broad resonance, the range of *g* being from 4 to *ca.* 2; the shape of the resonance absorption at *g* = 4 indicates that this is one of the principal *g*-values. This spectrum resembles that of spin-paired cobalt(II) phthalocyanine,⁷ if allowance is made for the different spin-orbit coupling energies of rhodium and cobalt. Attempts to prepare single crystals of the rhodium(II) complex are in progress.

Prolonged reaction of rhodium(III) halides and tri-*o*-tolylphosphine in high-boiling alcohols or ketones gives yellow, monomeric, diamagnetic complexes of general formula $\text{Rh}(\text{OP})_2\text{X}$ (X = Cl or Br), which show an intense band at *ca.* 920 cm^{-1} in their infrared spectra. Analysis indicates the absence of both M=O and M-OR groups, which give rise to bands in the 900–1100 cm^{-1} region.⁸ The expected⁹ carbonyl complexes $\text{Rh}(\text{OP})_2(\text{CO})\text{X}$ are not formed in the reaction. The 100 Mc./sec.

n.m.r. spectrum of the thiocyanate complex $\text{Rh}(\text{OP})_2\text{NCS}$ [prepared from $\text{Rh}(\text{OP})_2\text{Cl}$ and NaSCN], measured in deuteriochloroform, shows two singlets of equal intensity at τ 7.60 and τ 7.16 (two nonequivalent methyl groups), a doublet of 1:2:1 triplets at τ 6.50 (two protons), and complex aromatic absorption at τ 3.1–2.5. The ratio of aromatic absorption to the other peaks is approximately 2:1, indicating the likely loss of methyl hydrogen atoms in the reaction. The infrared spectrum of the ligand displaced from " $\text{Rh}(\text{OP})_2\text{X}$ " by sodium cyanide shows a strong band at *ca.* 965 cm^{-1} characteristic of the CH deformation mode of a *trans*-disubstituted ethylene,¹⁰ this being shifted from its position at 920 cm^{-1} in the complex. The n.m.r. spectrum of the ligand (in CDCl_3) shows bands at τ 7.63 (singlet, 6 protons, 2CH_3), τ 3.1–2.5 (complex, 12 aromatic protons) and τ 2.36 (singlet, 2 olefinic protons). On this evidence, together with analytical and molecular-weight data, the ligand in " $\text{Rh}(\text{OP})_2\text{X}$ " is identified as *trans*-2,2'-di-(di-*o*-tolylphosphino)stilbene, m.p. 263° (*cf.* m.p. of tri-*o*-tolylphosphine, 125°). The rhodium complexes are assigned the five-co-ordinate trigonal bipyramidal structure(I) with two metal-carbon σ -bonds; other examples of five-co-ordinate rhodium(III) include $\text{RhBr}(\text{1-naphthyl})_2\text{L}_2$ (L = PPr_3^3 or PEt_2Ph)¹¹ and $\text{RhHCl}_2(\text{PPh}_3)_2$ ^{4b}. Alternatively, the complexes can be

regarded as square-planar rhodium(I) derivatives with a conventional metal-olefin μ -bond.

The signal at τ 6.50 in the n.m.r. spectrum of " $\text{Rh}(\text{OP})_2\text{NCS}$ " is assigned to the co-ordinated olefinic protons; it is split into a doublet by ^{103}Rh -H coupling ($J = 1.0$ c./sec.), and each component of the doublet is further split into a 1:2:1 triplet by coupling with two phosphorus atoms ($J = 1.8$ c./sec.). The large upfield shift of the olefinic protons on co-ordination is presumably due at least partly to the formation of the metal-carbon σ -bonds.

Our structural assignment is supported by a study of the reaction of rhodium(III) chloride with diphenyl-*o*-tolylphosphine, $\text{PPh}_2(\text{C}_6\text{H}_4\text{Me-}o)$, in high-boiling alcohols. The main product is the usual carbonyl complex $\text{Rh}(\text{phos})_2(\text{CO})\text{Cl}$, together with a < 1% yield of yellow " $\text{Rh}(\text{phos})_2\text{Cl}$ ". The n.m.r. spectrum of the latter complex shows the characteristic signal at τ 6.50, but there is *no* signal due to methyl protons, indicating that a similar coupling-dehydrogenation reaction has occurred. Solutions of $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ absorb hydrogen at room temperature and pressure,^{4b} and similar rhodium(I) complexes of the *o*-tolylphosphines may be intermediates in the formation of the stilbene derivatives.

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