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## 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,<sup>1</sup> few genuine, paramagnetic rhodium(II) complexes are known. These include  $\{Rh[C_6Me_6]_2\}^{2+,2}$  and  $[Rh(MNT)_2]^{2-,3}$  (MNT= maleonitriledithiolate anion). The reduction of rhodium(III) halides by triphenylphosphine to give rhodium(I) complexes of general formula  $Rh(PPh_3)_3X$  (X = Cl, Br, or I) has been reported previously.<sup>4</sup> We now find that, by using tri-otolylphosphine,  $P(C_6H_4Me-o)_3$ , this reduction can be stopped at the rhodium(II) stage.

Ethanolic rhodium(III) chloride reacts with tri-otolylphosphine(OP) at  $25^{\circ}$  giving a 30-40% yield of the air-stable, blue-green complex (OP)<sub>2</sub>RhCl<sub>2</sub>,



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

characterised by full elemental analysis. The magnetic moment  $\mu_{\rm eff}$  at  $20^\circ$  is  $2\cdot3\pm0\cdot1~\beta,$  indicating one unpaired electron.<sup>5</sup> The complex is isomorphous with the palladium(II) analogue, and since both show a single strong band due to  $\nu(\rm M-Cl)$  at 351 cm.<sup>-1</sup> in their infrared spectra, a

trans-configuration is indicated for  $(OP)_2 RhCl_2$  and  $(OP)_2 PdCl_2$ .<sup>6</sup> A mauve modification of  $(OP)_2 RhCl_2$  ( $\mu_{eff}$  at 20° = 2.0  $\beta$ ) 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*-(OP)\_2 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  $(OP)_2RhCl_2$ 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 = 4indicates that this is one of the principal g-values. This spectrum resembles that of spin-paired cobalt(II) phthalocyanine,<sup>7</sup> 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  $Rh(OP)_2X$  (X = Cl or Br), which show an intense band at *ca*. 920 cm.<sup>-1</sup> 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.<sup>-1</sup> region.<sup>8</sup> The expected<sup>9</sup> carbonyl complexes  $Rh(OP)_2(CO)X$ are not formed in the reaction. The 100 Mc./sec. n.m.r. spectrum of the thiocyanate complex Rh(OP)<sub>2</sub>NCS [prepared from Rh(OP)<sub>2</sub>Cl and NaSCN], measured in deuterochloroform, shows two singlets of equal intensity at  $\tau$  7.60 and  $\tau$  7.16 (two nonequivalent methyl groups), a doublet of 1:2:1 triplets at  $\tau$  6.50 (two protons), and complex aromatic absorption at  $\tau$  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 "Rh(OP)<sub>2</sub>X" by sodium cyanide shows a strong band at ca. 965 cm.-1 characteristic of the CH deformation mode of a trans-disubstituted ethylene,<sup>10</sup> this being shifted from its position at 920  $cm.^{-1}$  in the complex. The n.m.r. spectrum of the ligand (in CDCl<sub>3</sub>) shows bands at  $\tau$  7.63 (singlet, 6 protons, 2CH<sub>3</sub>),  $\tau$  3·1–2·5 (complex, 12 aromatic protons) and  $\tau 2.36$  (singlet, 2 olefinic protons). On this evidence, together with analytical and molecular-weight data, the ligand in "Rh(OP)<sub>2</sub>X" is identified as trans-2,2'-di-(di-o-tolylphosphino)stilbene, m.p. 263° (cf. m.p. of tri-o-tolylphosphine,  $125^{\circ}$ ). The rhodium complexes are assigned the five-co-ordinate trigonal bipyramidal structure(I) with two metal-carbon  $\sigma$ -bonds; other examples of five-co-ordinate rhodium(III) include RhBr(1 $naphthyl)_{2}L_{2}$  (L =  $PPr_{3}^{n}$  or  $PEt_{2}Ph)^{11}$  and  $RhHCl_{2}$ - $(PPh_3)_2^{4b}$ . Alternatively, the complexes can be regarded as square-planar rhodium(I) derivatives with a conventional metal-olefin  $\mu$ -bond.

The signal at  $\tau$  6.50 in the n.m.r. spectrum of "Rh(OP)2NCS" is assigned to the co-ordinated olefinic protons; it is split into a doublet by <sup>103</sup>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 (I = 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  $\sigma$ -bonds.

Our structural assignment is supported by a study of the reaction of rhodium(III) chloride with diphenyl-o-tolylphosphine, PPh2(C6H4Me-o), in high-boiling alcohols. The main product is the usual carbonyl complex Rh(phos)<sub>2</sub>(CO)Cl, together with a < 1% yield of yellow "Rh(phos)<sub>2</sub>Cl". The n.m.r. spectrum of the latter complex shows the characteristic signal at  $\tau$  6.50, but there is no signal due to methyl protons, indicating that a similar coupling-dehydrogenation reaction has occurred. Solutions of Rh(PPh<sub>3</sub>)<sub>3</sub>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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