

## Molecular-Hydrogen, -Nitrogen and Monohydride Derivatives of the Structurally Characterised Dichloro(*o*-diphenylphosphino-*N,N*-dimethylaniline)[tris(*p*-tolyl)phosphine]ruthenium(II) Complex

D. Chandrika Mudalige, Steven J. Rettig, Brian R. James\* and William R. Cullen\*

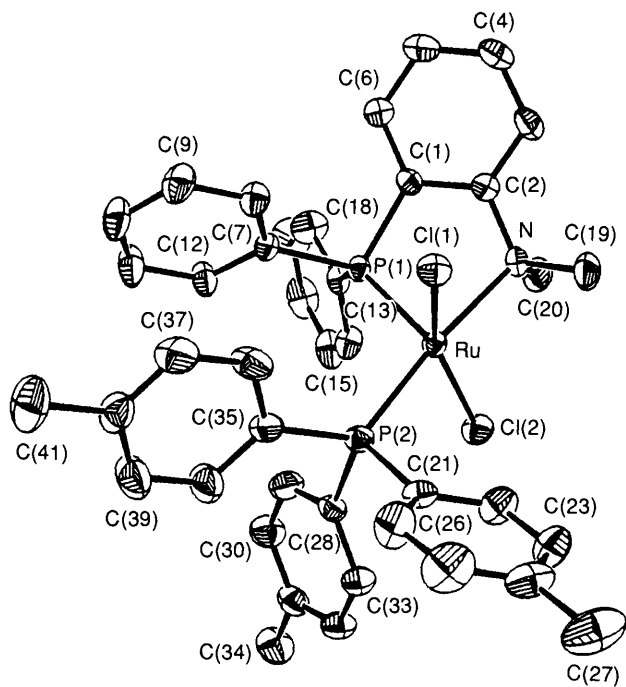
*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, V6T 1Z1, Canada*

The crystallographically characterised, five-coordinate complex [RuCl<sub>2</sub>(*o*-diphenylphosphino-*N,N*-dimethylaniline)-{P(*p*-tolyl)<sub>3</sub>}] reversibly binds H<sub>2</sub> and N<sub>2</sub> to form η<sup>2</sup>-H<sub>2</sub> and σ-N<sub>2</sub> species, respectively; the former reacts with base to generate the chloro(hydrido) derivative.

We recently discovered that replacement of a tertiary phosphine donor group by a corresponding amine donor 'stabilises' a molecular hydrogen (η<sup>2</sup>-H<sub>2</sub>) moiety within dinuclear Ru<sup>II</sup> systems.<sup>1</sup> This prompted a search in to systems containing simple, well-known chelating (P-N) ligands, and we now report that the five-coordinate complex [RuCl<sub>2</sub>(P-N)(PR<sub>3</sub>)<sub>2</sub>] **1a**, where (P-N) is *o*-diphenylphosphino-*N,N*-dimethylaniline

and R = *p*-tolyl, readily forms an η<sup>2</sup>-H<sub>2</sub> complex, which on treatment with base converts to the chlorohydrido species [Ru(H)Cl(P-N)(PR<sub>3</sub>)<sub>2</sub>] **2**.

The green complex **1a** was prepared by stirring RuCl<sub>2</sub>(PR<sub>3</sub>)<sub>3</sub><sup>2</sup> (1.24 g, 1.14 mmol) with 1 equiv. of the amine<sup>3</sup> in CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) for 16 h under Ar at about 20°C; the resulting green solution was concentrated, and hexane added



**Fig. 1** The structure of **1a** (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ru–P(1) 2.170(1), Ru–P(2) 2.290(1), Ru–N 2.238(3), Ru–Cl(1) 2.387(1), Ru–Cl(2) 2.379(1), P(1)–C(1) 1.836(3), N–C(2) 1.464(4); P(1)–Ru–Cl(1) 92.59(4), P(1)–Ru–P(2) 104.74(4), P(1)–Ru–N 81.81(8), P(1)–Ru–Cl(2) 109.75(4), Cl(1)–Ru–N 86.71(8), N–Ru–Cl(2) 89.53(8), Cl(2)–Ru–P(2) 88.16(4), P(2)–Ru–Cl(1) 92.99(4), P(2)–Ru–N 173.45(8), Cl(1)–Ru–Cl(2) 156.58(3).

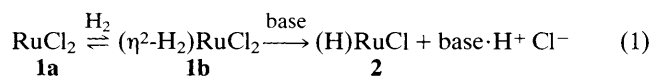
to precipitate **1a** which was purified by washing with hexane and drying *in vacuo* (80% yield). X-Ray analysis of a crystal of **1a** grown by a layering technique reveals (Fig. 1)<sup>†</sup> an approximately square-pyramidal geometry with *trans*-chlorides, the monodentate phosphine and the  $\text{-NMe}_2$  in the equatorial positions, and the P atom of the chelate ligand in the apical position. The Ru atom is about 0.42 Å above the mean plane of the equatorial atoms towards the apical phosphorus. The structure is analogous to those of  $[\text{RuCl}_2(\text{PPh}_3)_3]^4$  and  $[\text{RuCl}_2(\text{P-P})(\text{PPh}_3)]$ , where (P–P) is a chelating ditertiary phosphine of the type  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 3$  or 4) or chiral analogues.<sup>5</sup> However, unlike these 'all phosphine' complexes, which in solution partially dissociate  $\text{PPh}_3$  with generation of  $[\text{RuCl}(\text{P-P})]_2(\mu\text{-Cl})_2$ ,<sup>5a</sup> **1a** in solution retains a monomeric five-coordinate structure as shown by  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR, and shows versatile reactivity toward small gas molecules. [The  $^{31}\text{P}\{^1\text{H}\}$  NMR data for **1a** (121.42 MHz,  $\text{CD}_2\text{Cl}_2$ , 20 °C) show just an AX pattern ( $\delta_{\text{A}}$  81.42,  $\delta_{\text{B}}$  45.24 relative to 85%  $\text{H}_3\text{PO}_4$ ) with a  $^2J$  coupling of 36 Hz,

<sup>†</sup> *Crystal data*:  $\text{C}_{47}\text{H}_{47}\text{Cl}_2\text{NP}_2\text{Ru}$ ,  $M = 859.82$ , monoclinic, space group  $P2_1/c$  (no. 14),  $a = 12.874(3)$ ,  $b = 11.088(4)$ ,  $c = 30.198(6)$  Å,  $\beta = 96.35(2)^\circ$ ,  $V = 4284(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.333$  g cm<sup>-3</sup>. Data were collected on a Rigaku AFC6S diffractometer at 294 K. The final unit-cell parameters were obtained by least-squares analysis on the setting angles for 25 reflections with  $2\theta = 20.45$ – $26.80$ . The intensities of three standard reflections, measured every 200 reflections throughout the data collection, decayed uniformly by 18.00%, and a linear correction factor was applied. The structure was solved by conventional heavy atom methods, the coordinate of the Ru atom being determined from the Patterson function and those of the remaining non-hydrogen atoms from a subsequent Fourier synthesis. Calculations were performed using a TEXSAN/TEXRAY structure analysis package (Molecular Structure Corporation, 1985). The final  $R$  and  $R_w$  values were 0.036 and 0.031, respectively, for 5637 reflections with  $I \geq 3.0\sigma(I)$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

consistent with *cis*-phosphines;<sup>5a</sup> the solution structure could be that of the solid, or the complex could be fluxional, in equilibrium with a species containing *cis*-chlorides.]

Solutions of **1a** react rapidly and reversibly at 20 °C with 1 atm of  $\text{H}_2$  to give *in situ* formation (85% conversion) of the  $\eta^2\text{-H}_2$  adduct  $[\text{RuCl}_2(\text{H}_2)(\text{P-N})(\text{PR}_3)]$  **1b** as evidenced by  $^1\text{H}$  NMR data [300 MHz,  $\text{CDCl}_3$ , 20 °C,  $\delta$  (all singlets):  $-11.02$  (2 H, br,  $\text{H}_2$ ), 2.13 (9 H, Me of *p*-tolyl), 3.03 (3 H, N-Me), 3.57 (3 H, N-Me); the resonance of the  $\eta^2\text{-H}_2$  has a typically short  $T_1$  relaxation time<sup>6</sup> of 22 ms (300 MHz, 20 °C,  $w_{1/2}$  17 Hz)]. The  $^{31}\text{P}\{^1\text{H}\}$  spectrum shows doublets at  $\delta$  48.04, 42.14 ( $J$  27 Hz). The temperature dependence of  $T_1$  over the range 202–293 K gives a sharp V-shaped plot, as predicted by theory,<sup>6</sup> and the minimum  $T_1$  value of  $13.4 \pm 0.2$  ms at 232 K yields an intermolecular H–H distance of  $0.87 \pm 0.03$  Å, comparable with that determined for other  $\text{Ru}^{\text{II}}\text{-H}_2$  species;<sup>1,6a,7</sup> the calculations follow the method of Hamilton and Crabtree, using the correction factor of 0.79 suggested by Morris *et al.* for systems where the  $\eta^2\text{-H}_2$  rotation is relatively rapid. Treatment of a  $\text{CD}_2\text{Cl}_2$  solution of **1a** with 1 atm of  $\text{D}_2$  generates the  $\eta^2\text{-HD}$  isotopomer, the  $^1\text{H}$  NMR of the HD ligand being a 1 : 1 : 1 triplet ( $J_{\text{HD}}$  30 Hz) of 1 : 2 : 1 triplets (*cis*,  $^2J_{\text{HP}}$  8.5 Hz) centred at  $\delta$   $-10.96$ ; the data are very similar to those found for  $[(\eta^2\text{-H}_2)(\text{dppb})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{Cl})(\text{dppb})]$ , where  $\text{dppb} = \text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ .<sup>7</sup>

Treatment of **1a** with  $\text{H}_2$  in the presence of a base generates  $[\text{Ru}(\text{H})\text{Cl}(\text{P-N})(\text{PR}_3)]$  **2** which almost certainly has a structure analogous to that of **1a** with a chloride replaced by hydride. Complex **2** is isolated following reaction of a solution of **1a** (0.04 g, 0.05 mmol) and 4 equiv. of 'proton sponge' (PS = 1,8-dimethylaminonaphthalene) in benzene (2 cm<sup>3</sup>) with 1 atm of  $\text{H}_2$  at 20 °C. The initially dark-green solution becomes red after a few minutes with concomitant precipitation of  $\text{PSH}^+\text{Cl}^-$ ; the orange solid **2** is isolated analytically pure in 80% yield following addition of hexane to the filtrate obtained after removal of  $\text{PSH}^+\text{Cl}^-$  using Celite. [NMR data,  $\text{CD}_2\text{Cl}_2$ , 20 °C:  $\delta_{\text{P}}$  83.44 (d), 64.58 (d) ( $J$  34 Hz).  $\delta_{\text{H}}$  (all singlets)  $-27.6$  (Ru-H), 2.25 (Me of *p*-tolyl), 2.90 (N-Me), 3.50 (N-Me); the broad  $-27.6$  peak resolved into a pseudo-triplet at  $-80$  °C ( $^2J_{\text{HP}}$  28 Hz)]. Use of 1 or 2 equiv. of PS rather than 4 led to *in situ* formation of a mixture of **1b** and **2**, and it is clear that production of **2** follows the sequence (phosphine ligands omitted) shown in eqn. (1).



Such an overall net heterolytic cleavage of  $\text{H}_2$  *via* a molecular hydrogen species has been discussed in some detail,<sup>6a,8</sup> but the sequence within well characterised, mononuclear, neutral species starting from a five-coordinate complex seems to be unprecedented. The  $\text{H}_2$ -reaction in the presence of base with the closely related  $\text{RuCl}_2(\text{PPh}_3)_3$  species does yield  $\text{Ru}(\text{H})\text{Cl}(\text{PPh}_3)_3$ , the well-known hydrogenation catalyst, but the system is more complex because of an initial phosphine dissociation and formation of dinuclear species.<sup>1,9</sup> A sequence akin to **1a**  $\rightarrow$  **2** starting from five-coordinate, cationic monochlororuthenium(II) phosphine-containing species has been reported.<sup>10</sup>

Complex **1a** reversibly binds  $\text{N}_2$  in the vacant coordination site and, in  $\text{CDCl}_3$  at 20 °C and 1 atm, the equilibrium conversion is about 40%; the *in situ* product is characterised by NMR [ $\delta_{\text{P}}$  47.94 (d), 36.44 (d) ( $J$  27.2 Hz)] and IR [ $\nu/\text{cm}^{-1}$  2161 ( $\text{N}_2$ )]. The  $\nu_{\text{N}_2}$  frequency is at the upper limit of the range expected for analogues of stable dihydrogen complexes.<sup>6a</sup> Complex **1a** also coordinates a range of other small molecules including,  $\text{O}_2$ , CO,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and MeOH; in some cases, the initially formed adduct transforms to other species, chemistry which is currently being elucidated.

The chemistry outlined above can be entered also *via* the  $\text{Ru}^{\text{III}}$  complex  $[\text{RuCl}_3(\text{P-N})(\text{PR}_3)]$ , which is formed on

refluxing a suspension in hexane containing equimolar amounts of the (P-N) ligand and precursor  $[\text{RuCl}_3(\text{PR}_3)_2\text{-}(N,N'\text{-dimethylacetamide})]$  complex;<sup>5a</sup> the red solid product, which is obtained analytically pure after washing well with hexane, is rapidly reduced by  $\text{H}_2$  in toluene-MeOH at 20 °C, and a simple work-up procedure yields **1a**.

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