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Molecular Structure of the Penta-coordinate Rh(III) Dihydride $RhCl(H)_2[P(t\text{-}Bu)_3]_2$

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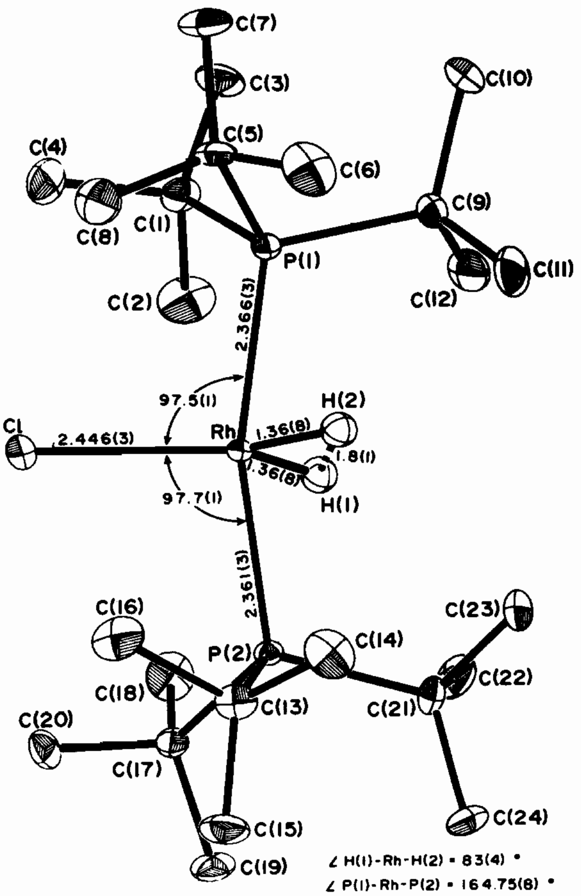
The elusive species $RhCl(H)_2(PPh_3)_2$ or $RhCl(H)_2(PPh_3)_2S$ (S = solvent) [1] is doubtless an important intermediate in catalytic hydrogenation with the versatile $RhCl(PPh_3)_3$ complex. The coordinatively unsaturated compounds $RhCl(H)_2L_2$ stabilized with bulky ligands L such as $PCH_3(t\text{-}Bu)_2$ [2], $P(t\text{-}Bu)_3$ [2], or $P(cyclo\text{-}C_6H_{11})_3$ [3] have been isolated. None of them, however, have received X-ray structural studies. We wish to report here a three-dimensional single crystal X-ray analysis of $RhCl(H)_2[P(t\text{-}Bu)_3]_2$ (I) obtained via a new route.

A mixture of $[Rh(CH_2{=}CH_2)_2Cl]_2$ and an excess of $P(t\text{-}Bu)_3$ in n-hexane was stirred at room temperature for 0.5 hr. The resulting yellow orange solution was filtered and subsequently concentrated *in vacuo* to produce yellow crystals. This is crude $RhCl[P(t\text{-}Bu)_3]_2$ (II) as revealed by the analytical and ^1H nmr data [4]. The solution of II in n-hexane absorbed hydrogen under atmospheric pressure at room temperature. The solid obtained from the concentrated reaction mixture was recrystallized from a toluene/n-hexane mixture to give I [5] in 30% yield (based on $[Rh(CH_2{=}CH_2)_2Cl]_2$) as air-stable, well-developed yellow crystals, dec. 168–72 °C. *Anal.* Calcd for $C_{24}H_{56}ClP_2Rh$: C, 52.87; H, 10.35; Cl, 6.51. Found: C, 52.72; H, 10.50; Cl, 6.48. ^1H nmr (CH_2Cl_2): δ 1.55(t-Bu, t, $^3J_{H-P} + {}^5J_{H-P} = 12.0$ Hz), −23.6 (Rh–H, doublet, $J_{H-P} = 16.2$ Hz, $J_{Rh-H} = 28.7$ Hz). Ir (Nujol mull, cm^{-1}): ν_{Rh-H} (2220 m, 2205 sh), δRh–H (773 s, 760 sh), ν_{Rh-Cl} (260 br). A single crystal of I grown from a toluene/n-hexane mixture was employed for the X-ray analysis.



∠ H(1)-Rh-H(2) = 83(4) °
∠ P(1)-Rh-P(2) = 164.75(8) °

Figure 1. Stereochemistry of and important bond lengths and angles in $RhCl(H)_2[P(t\text{-}Bu)_3]_2$. Thermal ellipsoids are drawn at the 15% probability level. The H atoms are represented by spheres of an arbitrary radius.

Crystal data: $C_{24}H_{56}ClP_2Rh$, M = 545.02, monoclinic, space-group C2/c, $a = 22.597(3)$, $b = 8.7460(8)$, $c = 29.120(3)$ Å, $\beta = 95.98(2)°$, $Z = 8$, $D_x = 1.266$ g cm^{-3}, μ(Mo–Kα) = 8.62 cm^{-1}. The size of the crystal used was 0.23 × 0.28 × 0.30 mm. Three dimensional data were collected on a computer-controlled Rigaku four-circle diffractometer with a maximum 2θ value of 45° using Zr-filtered Mo–Kα radiation. Absorption corrections with 5000 grids were made; the transmission factors calculated were within the range 0.82 to 0.86. The structure was solved by the heavy atom method. Anisotropic thermal vibrations were assumed for all the non-hydrogen atoms. A difference Fourier map revealed all the hydrogen atoms, and their positions and isotropic thermal factors were refined. Refinement was made by the block diagonal least-squares method to a final R value of 0.055 for 1910 non-zero ($|F_o| > 3\sigma(F_o)$) reflections.

The crystal structure consists of a packing of discrete molecule. The coordination polyhedron around the Rh may be described as a distorted trigonal bipyramid having a bent P(1)–Rh–P(2) (164.87(9)°) axis (Figure 1). Roughly, the plane containing Rh, P(1), and P(2) bisects the H(1)–Rh–H(2) angle (83°). This plane forms an angle of 173° with the Rh–Cl vector. Thus the entire molecule has an approximate C_{2v} symmetry. The nearly eclipsed conformation of the P–C bonds in $P(t\text{-}Bu)_3$ appears to be due to

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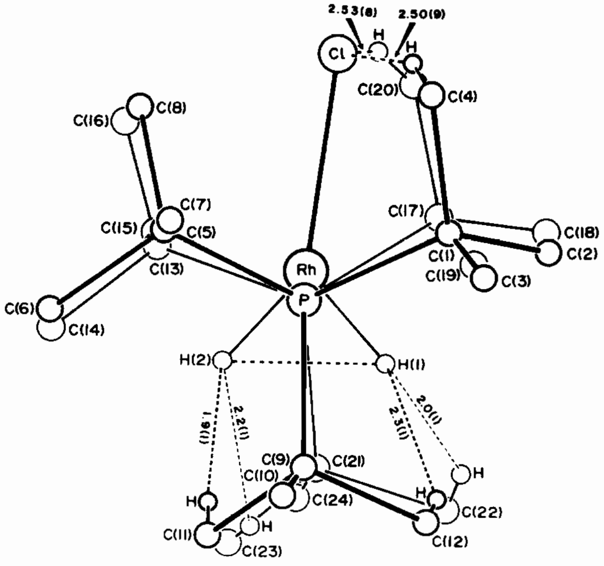

Figure 2. A drawing of $RhCl(H)_2[P(t\text{-}Bu)_3]_2$ viewed along the P(1)–P(2) vector.

steric interaction between the *tert*-butyl groups and the Cl atom (Figure 2). The Rh–P length (av. 2.364(3) Å) is normal for Rh(III) [6–9]. The most remarkable feature of the structure is the very short Rh–H distance (1.36(8) Å), which is considered to be comparable to that (1.41(3) Å) found for $RhH_2(O_2COH)[P(i\text{-}Pr)_3]_2$ [10]. The electron density on the hydride shifts to Rh(III) and the actual Rh–H internuclear distance should be slightly longer than that found. Nevertheless, this is the shortest metal–hydride distance ever found by X-ray studies [9, 11–13]. The short distance of 1.8 Å between H(1) and H(2) and the narrow angle may be compared to those found in *cis*-$Fe(H)_2[PPh(OEt)_2]_4$ [11] (2.11(5) Å and 88.8(23)°) and $Mo(H)_4(PMePh_2)_4$ [12] (av. 1.72(2) Å and 60.7(7)°). The hydride ligand should exert a strong *trans*-influence on the Cl atom. Indeed, the distance of 2.434 Å for the Rh–Cl bond is longer than the values (2.339–2.418 Å) found in Rh(III) complexes, *e.g.*, $RhCl_3[P(n\text{-}Bu)_3]_2P(OMe)_3$ [6] and $Rh(C_6H_7N_2O_2)_2(PPh_3)Cl$ [7].

Several close non-bonding contacts are worth noting. The non-bonded distances Cl···HC(4) (2.50(9) Å) and Cl···HC(20) (2.53(8) Å) are substantially shorter than the sum of the corresponding van der Waals radii (3.0 Å) [14]. A comparable intramolecular contact of Cl and hydrogen atom has been found in $PdCl_2(PhN{=}NPh)_2$ [15]. The deviation of the Cl atom from the idealized trigonal bipyramidal plane may be due to these short Cl···H contacts. One of the most salient feature is the remarkably short non-bonded distances between the *tert*-butyl hydrogen atom and the hydride ligand; *i.e.*, 1.9 (H(2)···HC(11)) and 2.0 Å (H(1)···HC(22)). The repulsive van der Waals force between H(2) and HC(11) is estimated by Hill's equation [16] to be 0.35 Kcal mol^{-1}.

The short Rh–H distance reflects on ν_{Rh-H} (2220, 2205 cm^{-1}); compare with ν_{Rh-H} of $RhCl(H)_2L_2$; 2165, 2120 cm^{-1} for L = $P(c\text{-}C_6H_{11})_3$ [3] and 2066, 2051 cm^{-1} for L = PPh_3 [1]. These ν_{Rh-H} values parallel the increase in cone angle of the phosphines [17] ($P(t\text{-}Bu)_3$, 182°; $P(c\text{-}C_6H_{11})_3$, 170°; PPh_3, 145°). The order of their electron donating properties is $P(t\text{-}Bu)_3 \gtrsim P(c\text{-}C_6H_{11})_3 > PPh_3$ [17]. Thus in this case, the trend in ν_{M-H} is just opposite to that generally observed for phosphine hydride complexes where the more the electron-donating property of the phosphine ligand, the lower is the ν_{M-H} [18]. Consistent with the spectral data, I does not dissociate hydrogen in high vacuum (20 °C) in solid state or under N_2 in solution, a remarkable feature which contrasts the reversibility of $RhCl(H)_2(PPh_3)_2$.

The strong Rh–H bonding and the steric crowding around the metal center are reflected by the reduced catalytic activity of I for hydrogenation. Thus, the rate of hydrogenation of cyclohexene catalyzed by I was found to be 1/16 that found for $RhCl(H)_2(PPh_3)_2$ prepared from $RhCl(PPh_3)_3$ *in situ* [19]. Apparently a kinetic effect induced by the ligand bulk is operating.

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4 Further purification of I1 through recrystallization from n-hexane or n-pentane to obtain an analytically pure sample was unsuccessful due to the extreme solubility and instability. *Anal.* Calcd for $C_{24}H_{54}P_2RhCl$: C, 53.01; H, 10.00. Found: C, 52.15; H, 1018. The ^{1}H nmr (toluene-d_8) showed the main t-Bu proton signal as a doublet (J_{H-P} = 10.0 Hz) at δ 1.31.

5 This dihydride appears to be different in color and some physical properties from the dark red compound of the same stoichiometry reported by Shaw *et al.* [2]. Compare with the reported spectroscopic data: ^{1}H nmr (CH_2Cl_2) δ –25.5 (Rh–H, J_{H-P} = 14.9 Hz, J_{Rh-H} = 26.2 Hz). Ir (nujol mull) ν_{Rh-H} 2240, 2227 cm^{-1} (in Discussion [2]) or 2220, 2200 cm^{-1} (in Table [2]).

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19 1.2 *M* cyclohexene in 10 ml benzene, 25 °C, 1 atm H_2, [Rh] = 1.0×10^{-3} *M*.