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Structures of $HRh(PMe_2Ph)_4$ and $HRh(PPh_2Me)_4$ [1]

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Abstract

The mononuclear hydrido complexes $HRh(PMe_2Ph)_4$ (**1**) and $HRh(PPh_2Me)_4$ (**2**) have been prepared and structurally analyzed by X-ray diffraction techniques. The geometry of both compounds consists of a distorted trigonal bipyramidal arrangement of ligands around rhodium. The hydride ligands were not located crystallographically, but were predicted by potential energy calculations to be situated at the axial positions. Crystallographic details: both compounds crystallize in the triclinic space group $P\bar{1}$. For $HRh(PMe_2Ph)_4$ (**1**): $a = 11.058(4)$, $b = 16.332(4)$, $c = 9.530(3)$ Å, $\alpha = 94.07(2)$, $\beta = 99.37(3)$, $\gamma = 102.21(3)°$, $V = 1662.4(9)$ Å^3 for $Z = 2$; $R_F = 0.0463$, $R_{wF} = 0.0496$ for 3550 reflections with $I > 3\sigma(I)$. For $HRh(PPh_2Me)_4$ (**2**): $a = 13.061(6)$, $b = 16.672(7)$, $c = 12.150(6)$ Å, $\alpha = 107.30(3)$, $\beta = 114.19(3)$, $\gamma = 71.45(4)°$, $V = 2245(2)$ Å^3 for $Z = 2$; $R_F = 0.0482$, $R_{wF} = 0.0488$ for 4350 reflections with $I > 3\sigma(I)$. © 1998 Elsevier Science S.A.

Keywords: Crystal structures; Rhodium complexes; Hydrido complexes; Mononuclear complexes

1. Introduction

Our original interest in the geometry of the $HRhL_4$ complexes (L = tertiary phosphine) stemmed from the fact that an early X-ray study [1] on $HRh(PPh_3)_4$ was inconclusive: the four P atoms defined a nearly-tetrahedral coordination about the Rh atom, and it was not obvious where the H atom (which was not found in that study) was located. Subsequently, in a single-crystal neutron study carried out by our group [2], the H atom was located at the axial position of a trigonal bipyramid, but at a distance (Rh–H = 1.31(8) Å) that was extremely short and drastically different from other known terminal Rh–H distances [3]. We thus decided to investigate two more complexes of the $HRhL_4$ type, $HRh(PMe_2Ph)_4$ (**1**) and $HRh(PPh_2Me)_4$ (**2**), in the hope that large crystals could be grown for a neutron study that would confirm or refute the very short distance we found in $HRh(PPh_3)_4$. Unfortunately, however, large crystals could not be grown, and in this paper we report the results of X-ray analyses and HYDEX [4] calculations on complexes **1** and **2**, which place the H ligands in the axial positions of a trigonal bipyramid.

2. Experimental

All operations were carried out under argon. PMe_2Ph, PPh_2Me, $RhCl_3 \cdot xH_2O$ and $Rh(PPh_3)_3Cl$ were purchased from Aldrich or Pressure Chemical Co. and used without further purification. NMR spectra were taken on Bruker AC-250 and AM-360 NMR spectrometers.

2.1. Preparation of $HRh(PMe_2Ph)_4$ (1)

A mixture of 0.13 g (0.62 mmol) $RhCl_3 \cdot xH_2O$, 1.6 ml PMe_2Ph (1.55 g, 11.25 mmol) and 15 ml anhydrous ethanol was refluxed under argon for 25 min. The solution was then allowed to cool to about 60°C, and 0.2 g (5.29 mmol) of solid $NaBH_4$ was added gradually, in about five portions, while the solution was being stirred. After addition of the $NaBH_4$, the color of the solution was found to change from yellow–orange to dark green to brown and finally to bright yellow. After 15 min of stirring, the solution was allowed to cool to room temperature, after which the solvent was removed in vacuo. The rest of the excess PMe_2Ph was later removed by vigorous pumping (4 h in vacuo) at an elevated temperature (60°C). The resulting residue was then extracted with benzene, filtered, pumped dry and extracted with benzene again. Finally, this benzene solution was allowed to evaporate slowly under argon to yield flat orange crystals of **1** after about 5 days. The proton NMR of this compound

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(in toluene-d^8) in the hydridic region showed a sextet at − 12.1 ppm.

The hydridic sextet at − 12.1 ppm can be rationalized as being generated by the coupling between the hydride atom and the four equivalent phosphorus atoms (generating a quintet), which is further split by rhodium to form a doublet of quintets. The appearance of a sextet can then be explained by assuming that J(P–H) is almost equal to J(Rh–H) (this is true for several other rhodium hydrides [5]). Actually, they are slightly unequal, as evidenced by the fact that shoulders can be discerned on the individual peaks of the sextet. The individual peaks of the sextet integrate to a ratio of 1:5:10:10:5:1, in agreement with this model. From the fine structure of that region, the individual coupling constants can be calculated to be J(Rh–H) = 12.07 and J(P–H) = 15.28 Hz. From the fact that the spectrum is a doublet of quintets, one can also conclude that the four phosphorus atoms are either equivalent with respect to the H ligand, or are fluxional in solution.

2.2. *Preparation of HRh(PMePh$_2$)$_4$ (2)*

Two different methods to make this compound are described here:

2.2.1. *Method A*

The first procedure was modified from a set of related methods found in the literature [6]. A mixture of 0.13 g $RhCl_3 \cdot xH_2O$ (0.62 mmol) and 1.5 ml $PMePh_2$ (1.61 g, 8.06 mmol) in 20 ml EtOH:toluene (1:1) was refluxed for 25 min, during which time an uncharacterized yellow solid was observed to precipitate. The reaction mixture was cooled to about 60°C, and then 0.2 g $NaBH_4$ (5.29 mmol) was added. After the mixture was stirred for 15 min at 60°C, the product (a yellow precipitate) was filtered off and the moist solid dried overnight under vacuum. The residue above, consisting primarily of compound **2** plus excess $NaBH_4$, can be extracted with benzene and the filtrate was used for recrystallization either by slow evaporation or by vapor diffusion.

2.2.2. *Method B*

The second procedure is based on an earlier preparation of compound **2** [7], except that $NaBH_4$ was used in place of hydrazine. A mixture of 0.5 g $RhCl(PPh_3)_3$ (0.54 mmol), 1.5 ml $PMePh_2$ (8.06 mmol) and 20 ml of a toluene:ethanol mixture (1:1) was refluxed for 25 min. The solution was allowed to cool to 60°C and 0.2 g $NaBH_4$ (5.29 mmol) was added. After stirring for an additional 15 min at 60°C, the yellow precipitate was filtered and the moist solid was dried under vacuum overnight. The residue was extracted with benzene and the filtrate used for recrystallization.

The products of both reactions, A and B, gave essentially the same ^{1}H NMR spectrum as that reported in the literature [7]. We have found that, in general, Rh complexes with $PMePh_2$ are more crystalline and easier to purify than complexes with PMe_2Ph. Moreover, $HRh(PPhMe_2)_4$ (**1**) is more reactive than $HRh(PMePh_2)_4$ (**2**), as shown by tests in which both compounds were spotted on a piece of paper and exposed to air. The paper spotted with **1** spontaneously inflamed, while the one with **2** only charred the paper. $HRh(PMePh_2)_4$ (**2**) is insoluble in ethanol, pentane, hexane and soluble in benzene and toluene, while $HRh(PPhMe_2)_4$ (**1**) is soluble in almost all organic solvents. This allowed us to use vapor diffusion (e.g. benzene/hexane, toluene/pentane etc.) for recrystallizing $HRh(PMePh_2)_4$ (**2**).

2.3. *Structure analyses*

The crystal structures for both compounds were determined at room temperature using a Siemens/Nicolet P2$_1$ automated diffractometer. Lattice parameters were determined by a least-squares fit of the setting angles of 15 reflections. Data were collected by the ω-scan technique with graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å) up to a 2θ limit of 45°. Lorentz, polarization and absorption corrections were applied during data processing. The positions of the rhodium atoms were obtained from a Patterson analysis, and the rest of the structure was obtained by standard heavy-atom methods [8].

2.3.1. *Structure determination of HRh(PMe$_2$Ph)$_4$ (1)*

Compound **1** is air-sensitive and pyrophoric. For crystal mounting, crystals were immersed in a viscous oil (Paratone-N [3]) while still in the glove box. When the samples were subsequently brought out into air, the oil provided a protective coating that allowed crystal mounting to be possible over a period of 1 or 2 h. A single crystal of $HRh(PMe_2Ph)_4$ (**1**) was mounted at the bottom of a glass capillary, and then plugged with a smaller capillary in order to keep the crystal immobile. The crystal lattice was found to be triclinic. Three check reflections, measured periodically during data collection, showed an average decrease in intensity of 3.6%, a decrease probably due to a slow dissolution of the sample in the oil during data collection. The centrosymmetric space group $P\bar{1}$, was tried and was found to lead to a successful structure solution. The structure was then anisotropically refined [8] to final agreement factors of R_F = 0.0463, R_{wF} = 0.0496 for 3550 reflections with $I > 3\sigma(I)$.

The molecular structure of $HRh(PMe_2Ph)_4$ (**1**) consists of four phosphine ligands arranged around the rhodium atom in the form of a distorted tetrahedron. The P–Rh–P angles show some deviation from tetrahedral values: 120.9, 118.2, 111.4, 103.5, 99.9 and 97.3°. This distortion is greater than that found in the analogous complex $HRh(PPh_3)_4$, which has P–Rh–P angles of 111 and 107° (from the X-ray analysis [1]) and angles of 114(1) and 105(1)° (from the neutron analysis [2]). As in the X-ray analyses of $HRh(PPh_3)_4$ [1] and $HRh(PPh_3)_3(AsPh_3)$ [9], the position of the hydride

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[3] Paratone-N, manufactured by the Exxon Chemical Company, P.O. Box 3272, Houston, TX 77001, USA.

ligand in $HRh(PMe_2Ph)_4$ (**1**) is not obvious. One can speculate that it might be situated between atoms P(2), P(3) and P(4) (in other words, *trans* to P(5)), because the P–Rh–P angles associated with those atoms (120.9, 118.2, 111.4°) are larger than the others.

This tentative assignment was tested using the program HYDEX [4], which attempts to predict hydrogen positions using an energy minimization method. This program optimizes hydride positions with specified connectivity. Optimum positions were found for each postulated hydride site by minimization of the potential energy of intramolecular non-bonded interactions involving the hydride atom. The non-hydrogen atomic coordinates of **1** were input and H positions were calculated corresponding to the four possible potential wells (*trans* to each of the four phosphine ligands). Indeed the potential well *trans* to P(5) was calculated to have a substantially lower energy than the other three, and this position can be assumed to be the site of the hydride atom of $HRh(PMe_2Ph)_4$ (**1**). The final structure, including the HYDEX-calculated hydride position, is illustrated in Fig. 1, which shows that the geometry of $HRh(PMe_2Ph)_4$ (**1**) is a highly distorted trigonal bipyramid with three equatorial phosphine ligands distorted towards the small hydride ligand (the three H–Rh–P angles are 79.9, 81.4 and 77.7°). This type of distortion has been observed repeatedly, most recently in an octahedral Rh(III) complex [10]. The calculated Rh–H distance is 1.66 Å, a value which is a little long compared to known terminal Rh–H distances determined by neutron diffraction [3].

2.3.2. *Structure determination of $HRh(PMePh_2)_4$ (2)*

Recrystallization of $HRh(PMePh_2)_4$ (**2**) was carried out either by slow evaporation of a benzene solution (method A) or by vapor diffusion with benzene/hexane (method B). Both methods, A and B, described earlier gave crystals with the same unit cell parameters, as expected. A crystal with dimensions 0.5×0.5×0.2 mm, which extinguished well in polarized light, was chosen for data collection. This crystal was mounted in Paratone-N oil as described earlier, jammed into a glass capillary and sealed. A rotation photograph yielded spots which were centered to give a triclinic unit cell. Three check reflections were measured periodically and showed no significant changes during the data collection. Space group $P\bar{1}$ was tried and was found to lead to a successful structure determination. The structural analysis again involved the use of a Patterson map to locate the rhodium atom, followed by cycles of least-squares refinement and difference-Fourier syntheses to find the remaining non-hydrogen atoms. The final least-squares refinement cycles, with all atoms refined anisotropically, gave agreement factors of $R_F = 0.0482$ and $R_{wF} = 0.0488$ based on a total number of 4350 reflections with $I > 3\sigma(I)$ [8].

The molecular structure of $HRh(PMePh_2)_4$ (**2**) is similar to that of compound **1**. The three P–Rh–P angles around P(1) (96.5, 97.4, 106.7°) are smaller than the others (113.1, 115.3, 122.7°). HYDEX calculations [4] for **2** again support a hydride position in the cone defined by atoms P(2), P(3) and P(4), the ligands that make up the three larger P–Rh–P angles around the central atom. The resulting geometry is depicted in Fig. 2. The calculated Rh–H bond distance in **2** is 1.56 Å, quite close to the known terminal Rh–H distances of 1.581(3) Å in $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2]$ [11] and 1.536(2) Å in $[Rh_2(H)_2(\mu\text{-}H)_2L_2]^{2+}$ [12], determined by neutron diffraction.

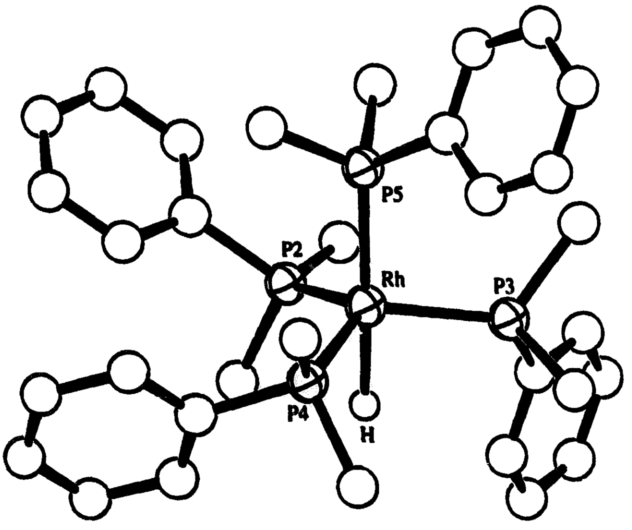

Fig. 1. The molecular structure of $HRh(PMe_2Ph)_4$ (**1**), showing the position of the hydride ligand calculated using the energy-minimization program HYDEX [4]. Selected distances: Rh-P(2) = 2.293(2), Rh-P(3) = 2.279(2), Rh-P(4) = 2.257(2), Rh-P(5) = 2.295(2) Å, respectively.

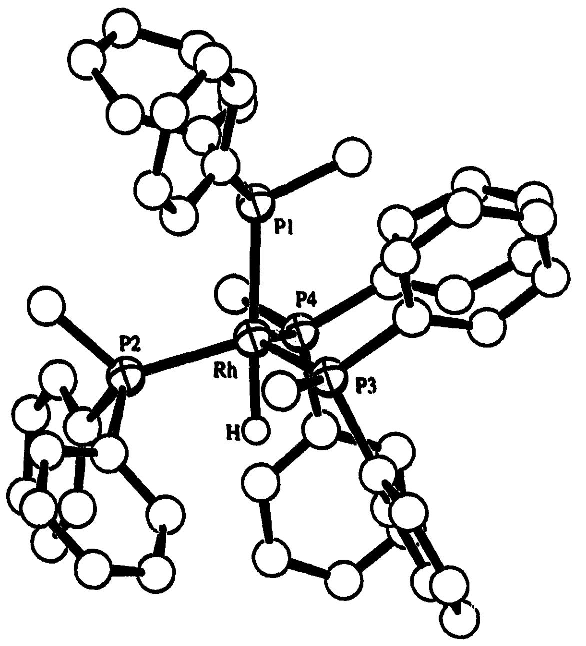

Fig. 2. The molecular structure of $HRh(PPh_2Me)_4$ (**2**), again showing a HYDEX-calculated hydride position. Selected distances: Rh-P(1) = 2.337(2), Rh-P(2) = 2.289(2), Rh-P(3) = 2.318(2), Rh-P(4) = 2.316(2) Å, respectively.

3. Discussion

It is noted that the geometry obtained from the X-ray structural analysis of $HRh(PMePh_2)_4$ (**2**) is different from that assigned earlier based on NMR data [7]. The ^1H NMR spectrum at $-60°C$ showed a ten-line pattern interpreted as being a doublet of quintets. This was taken as evidence that the four phosphine ligands are chemically identical with respect to the hydride ligand. Thus, a static square-pyramidal structure, with an axial hydride ligand, was proposed for $HRh(PMePh_2)_4$ [7]. But the X-ray structural determination of compound **2** indicated a distorted trigonal bipyramid (Fig. 2). The ^1H NMR data can be rationalized by either a static square-pyramidal structure or by rapidly equilibrating trigonal bipyramidal structures. Our structural results clearly suggest the latter as the species existing in solution.

Comparison of the Rh–P distances in compounds **1** and **2** shows a significant difference between axial and equatorial bond lengths. The Rh–P bond distances in $HRh(PMe_2Ph)_4$ (**1**) are 2.295 Å for the Rh–P bond *trans* to H^-, and an average of 2.276 Å for the other three. In the case of **2**, the Rh–P bond distances are 2.337 Å (axial), and an average of 2.308 Å (equatorial). In both cases, the longer axial Rh–P bond distances might be due to the well-known *trans* influence of the hydride ligand [13,14].

By now it is clear that the distorted trigonal bipyramid, with an axial H ligand, is the dominant geometry for HMP_4-type complexes. It has been found not only in $HRh(PPh_3)_3(PF_3)$ [14], $HRh(diop)_2$ [15] and $HRh(PHCy_2)[(t\text{-}Bu)P(C_3H_6PPh_2)_2]$ [16], but also in several closely-related $HCoP_4$ [17] and $HIrP_4$ [18] complexes. Other examples include $CoH(PF_3)_4$ [19], $RuHCl(PPh_3)_3$ [20], $RhH(CO)(PPh_3)_3$ [21], $CoH(N_2)(PPh_3)_3$ [22], $[IrH(NO)(PPh_3)_3]ClO_4$ [23] and $RhHCl(SiCl_3)(PPh_3)_2$ [24]. There is, however, at least one exception: an iron complex, $FeH(SiCl_3)_2(CO)(\pi\text{-}C_5H_5)$ [25] is believed to have a square pyramidal geometry from X-ray crystallographic evidence.

The HYDEX-calculated Rh–H distances of 1.66 Å in **1** and 1.56 Å in **2** fall within the range 1.5–1.7 Å normally observed for terminal second-row transition-metal hydrides [3]. Of the two, the value of 1.56 Å calculated for **2** agrees much better with the 'neutron-derived' values of 1.581(3) Å in $[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2]$ [11] and 1.536(2) Å in $[Rh_2(H)_2(\mu\text{-}H)_2L_2]^{2+}$ [12]. Other reported values include Rh–H distances of 1.6 Å found in $HRh(PPh_3)_3(PF_3)$ [14] and $HRh(diop)_2$ [15], X-ray structure determinations in which the hydride ligands were located but not refined. Overall, it can be concluded that HYDEX [4] gives reliable predictions for the hydride positions, although the actual distances calculated may be off by as much as ±0.1 Å.

The status of the extra-short distance of 1.31(8) Å found in the neutron analysis of $HRh(PPh_3)_4$ [2] remains unresolved. Whether it is real, or an artifact of the high crystallographic symmetry of the sample used in the neutron study, has yet to be determined in a future crystallographic investigation.

4. Supplementary material

Crystallographic details for the structure analyses of compounds **1** and **2** are available from author R.B. Fractional atomic coordinates are listed in Tables 1 and 7; and relevant thermal parameters, bond distances and angles are collected in Tables 2–6 (for **1**) and 8–12 (for **2**).

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