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Location of the Elusive Hydride Ligand in $HRh[P(C_6H_5)_3]_4$ Via a Neutron Diffraction Analysis

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Hydride complexes of the transition metals have been known since the isolation of the two thermally unstable hydridocarbonyls $H_2Fe(CO)_4$ and $HCo(CO)_4$ in the early 1930s [1]. Many hundreds of transition metal hydride complexes have been synthesized and characterized since that time; in fact there now exists probably at least one hydride complex for every transition metal. The early X-ray and neutron diffraction structural data on transition metal hydride complexes established some concepts about the nature of the M–H bond, which have been reinforced with the passage of time. With the exception of only a few compounds (*vide infra*), the hydride ligand occupies a definite coordination position, or at least significantly affects the stereochemistry of the complex. In the early days of metal hydride chemistry, assertions were made that hydride ligands did not occupy distinct coordination positions but rather were buried in the metal's outer shell orbitals (for a detailed account of this early controversy, see refs. 2 and 3). The earlier investigators who held this point of view proposed an anomalously short (approximately 1.2 Å) M–H bond, a suggestion which was essentially disproven in 1964 when Abrahams *et al.* [4] performed their now classic neutron diffraction study on K_2ReH_9, revealing an average M–H bond distance of 1.68(1) Å, consistent with the sum of the covalent radii of Re and H. This study was followed, 5 years later, by a neutron diffraction analysis on the metal carbonyl hydride $HMn(CO)_5$ by La Placa *et al.* [5]. This gave an Mn–H distance of 1.60(2) Å, again, a figure which is consistent with a normal sum of covalent radii. The above two landmark structural determinations effectively ended the controversy surrounding the nature of the M–H bond. Many additional definitive structural studies followed [6, 7], from both X-ray and neutron diffraction data, and these have reinforced the conclusion that there is nothing extraordinary about the terminal M–H bond; i.e. (a) it occupies a discrete coordination position about the metal atom; and (b) M–H bond distances are 'normal'.

However, as previously mentioned, there are a few notable exceptions to at least one of the above rules. The complexes $HCo(PF_3)_4$, $HRh[P(C_6H_5)_3]_4\cdot\frac{1}{2}C_6H_6$ and $HRh[P(C_6H_5)_3]_3(As(C_6H_5)_3)$ have been examined by X-ray diffraction [8–10] and all show a nearly tetrahedral geometry with regard to the P or As atoms, with no direct stereochemical evidence for the hydride ligands. (Normally one would expect such complexes to exhibit a trigonal-bipyramidal or a square-pyramidal geometry.) These complexes present an intriguing problem: Where do the hydrides lie? Is the stereochemical bulk of the other ligands distorting the geometry to such an extent that the hydrides no longer exert any stereochemical influence but still remain in their expected positions, or are they disordered? Are these complexes truly anomalous, with the hydrides buried in the metal orbitals and therefore not occupying distinct coordination positions? In an attempt to answer the above questions we decided to perform a neutron diffraction structural analysis on $HRh[P(C_6H_5)_3]_4\cdot\frac{1}{2}C_6H_6$.

The previous [9] X-ray structural analysis of the title compound had revealed an essentially tetrahedral geometry, with a crystallographic three-fold axis of symmetry passing through the rhodium atom and one of the phosphorus atoms, and with effectively equal Rh–P distances of 2.34(5) Å to this apical phosphorus and 2.39(3) Å to the other three phosphorus atoms. The P–Rh–P angles were found to be 107(1)° and 111(1)°. The hydride ligand was thought to lie on the three-fold axis, opposite the apical phosphorus. Nevertheless, since the hydride was not detected in this X-ray study, the authors noted that it could 'occupy at random a position more or less in any of the tetrahedral faces, or in fact anywhere' [9].

It was decided to repeat this structural determination of $HRh[P(C_6H_5)_3]_4\cdot\frac{1}{2}C_6H_6$ (because atomic coordinates from the earlier X-ray work were unavailable), and then to proceed with the growth of a large, high-quality crystal of the complex which would be suitable for use in a neutron diffraction study.

Experimental

All reactions were performed in Schlenk ware under argon or in a Vacuum Atmospheres Company inert atmosphere dry-box, capable of maintaining a dry, oxygen-free (<1 ppm) nitrogen atmosphere. The synthetic procedure is a modification of the published method [11]. A thorough NMR analysis of the title compound had been previously described

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by Strauss and Shriver [12]. An X-ray analysis was completed on a smaller crystal and the results confirmed the earlier findings of Baker and Pauling [9].

Neutron Diffraction

Neutron diffraction data were collected at 250 K on a transparent, dark orange crystal, at the Brookhaven High Flux Beam Reactor.* The relatively high temperature of 250 K was employed in order to avoid a destructive phase transition observed to occur at 225(1) K in a previously-examined crystal. Difficulties arose during data collection due to the crystal's poor diffracting ability, in spite of the fact that the crystals were of optimal size. Two reflections, (6 0 0) and (3 3 3), were observed to diffract exceedingly strongly, but moderate to weak intensities were recorded for the rest of the data set. This unusual intensity distribution was confirmed to be in accord with that calculated based on the X-ray structure model.

Structure refinement based on the neutron data was initiated, with coordinates of atoms taken from the X-ray study, and using a rigid-body procedure in which each phenyl ring was assigned an idealized geometry (C–H = 1.08 Å, C–C = 1.395 Å, C–C–C = C–C–H = 120°). Individual isotropic thermal parameters were varied. The hydride ligand was located from a difference-Fourier map and found to lie on the three-fold axis. SHELX-76 was used for the least-squares refinement calculations [13]. The structure refinement converged to an R factor of 0.126 for 914 reflections ($F > 4\sigma(F)$) with 95 variable parameters. A final difference-Fourier map was essentially featureless.

All distances and angles are normal, with the single exception of the apparently very short Rh–H distance of 1.31(8) Å. The RhP_4 arrangement shows a geometry intermediate between tetrahedral and trigonal bipyramidal; neutron-determined values are P(1)–Rh–P(2) = 104.6(9)°, P(2)–Rh–P(2′) = 113.9(9)°, Rh–P(1) = 2.57(4) and Rh–P(2) = 2.38(4) Å. Angles involving the hydrogen atom are P(1)–Rh–H = 180.0° and P(2)–Rh–H = 75.4(9)°. Other average bond distances and angles follow: P–C = 1.86(2) Å, Rh–P–C = 117.7(9)°, C–P–C = 99.9(9)°.

Discussion

A neutron diffraction analysis of the hydride complex $HRh[P(C_6H_5)_3]_4 \cdot \frac{1}{2}C_6H_6$ has revealed the structure shown in Fig. 1. The hydride ligand has been definitively located in a coordination position on the crystallographic three-fold axis passing through Rh–P(1), above the center of the P(2)–P(2′)–P(2″) face of the RhP_4 tetrahedron. The RhP_4 arrangment shows, as mentioned earlier, a greater distortion from a tetrahedral geometry than previously reported, with enlargement of the P(2)–P(2′)–P(2″) face; the P–Rh–P angles are about 5° removed from the tetrahedral value (the corresponding figure from the earlier X-ray analysis [9] is 3°).

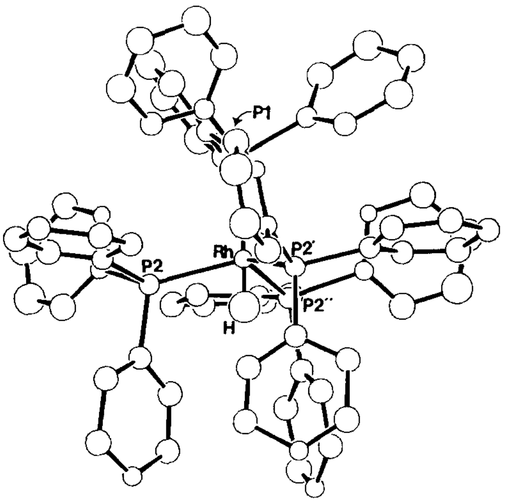

Fig. 1. A partial ORTEP [15] plot, showing the non-hydrogen core of the title compound, from the neutron diffraction study at 250 K. Probability ellipsoids are at 50%.

The Rh–H bond distance has been found to have the apparently very short value of 1.31(8) Å. This is the shortest value of an M–H bond distance yet obtained. A normal terminal Rh–H distance, as measured in $H_2Rh(SiEt_3)_2(C_5Me_5)$, is 1.580(3) Å [14]. However, the difference in these values is just barely above 3σ, given the relatively low precision of the present analysis, so that definite conclusions about the significance of this short bond distance cannot be drawn.

Future work will concentrate on altering the crystal lattice in some way. Alternatives include changing the molecule of solvation (currently benzene), deuteration (of the hydride ligand and/or the phenyl protons) or altering the organic substituents (i.e., through substitution of the phenyl rings). In this manner it is hoped to obtain a crystal with a more uniform distribution of neutron intensities, and hopefully a more accurate Rh–H bond length. Regardless of what the Rh–H distance actually is, we have, in this paper, unambiguously located the H atom to lie on the three-fold rotation axis of the title compound and have resolved the ambiguity arising from the earlier work.

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*Crystal data for $HRh[P(C_6H_5)_3]_4 \cdot \frac{1}{2}C_6H_6$: space group $Pa3$; a = 22.776(3) Å, V = 11815(3) Å^3; crystal dimensions 2.8 × 2.5 × 1.5 mm. Final refinement yielded $R(F)$ = 0.126 and $R(F)_w$ = 0.142 for 95 variable parameters and 914 unique observations with $I > 4\sigma(I)$. The neutron wavelength is 1.15882(7) Å.

Supplementary Material

Atomic positional and thermal parameters (Table S1), bond distances (Å) and angles (°) (Table S2) and observed and calculated structure factors (Table S4) (8 pages) are available from the authors.

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References

1 H. D. Kaesz and R B. Saillant, *Chem. Rev., 72* (1972) 231 (1972) and refs. therein.

2 B. A. Frenz and J. A. Ibers, in E. L. Muetterties (ed.), *Transition Metal Hydrides,* Marcel Dekker, New York, 1971, p. 33.

3 A. P. Ginsberg, *Trans. Metal. Chem., 1* (1965) 112.

4 S. C. Abrahams, A. P. Ginsberg and K. Knox, *Inorg. Chem., 3* (1964) 558.

5 S. J. La Placa, W. C. Hamilton, J. A. Ibers and A. Davison, *Inorg. Chem., 8* (1969) 1928.

6 R. Bau, R. G. Teller, S. W. Kirtley and T. F. Koetzle, *Acc. Chem. Res., 12* (1979) 176.

7 R. G Teller and R. Bau, *Struct. Bonding (Berlin), 44* (1981) 1.

8 B. A. Frenz and J. A. Ibers, *Inorg. Chem., 9* (1970) 2403.

9 R. W. Baker and P. Pauling, *Chem. Commun.,* (1969) 1495.

10 R. W. Baker, B. Ilmaier, P. J. Pauling and R. S. Nyholm, *Chem. Commun.,* (1970) 1077.

11 K. C. Dewhirst, W. Keim and C. A. Reilly, *Inorg. Chem., 7* (1968) 546.

12 S. H. Strauss and D. F. Shriver, *Inorg. Chem., 17* (1978) 3069.

13 G. M. Sheldrick, *SHELX* programs for crystal structure determination, University of Cambridge, U.K., 1976.

14 M. J. Fernandez, P. M. Bailey, P. O. Bentz, J. S. Ricci, T. F. Koetzle and P. M. Maitlis, *J. Am. Chem. Soc., 106* (1984) 5458.

15 C. K. Johnson, *ORTEP, Report ORNL (U.S.) ORNL-5138,* Oak Ridge National Laboratory, TN, U.S.A., 1976.