

Neutron Diffraction Analysis of $\text{HRh}[\text{P}(\text{C}_6\text{H}_5)_3]_4$

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Abstract

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We have collected neutron diffraction data on a large single crystal of the title compound. The most surprising result is an extremely short Rh-H distance of 1.31(8) Å, presumably caused by steric interactions involving the bulky triphenyl phosphine ligands. Crystallographic details: $\text{HRh}[\text{P}(\text{C}_6\text{H}_5)_3]_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ crystallizes in the space group Pa3, with $a = b = c = 22.776(3)$ Å, $Z = 8$. Data were collected at the Brookhaven High Flux Beam reactor[1] at a temperature of -23°C , $\lambda = 1.15882(7)$ Å⁻¹. Least-squares refinement (in which the phenyl rings were treated as rigid groups) resulted in an R factor [based on data with $F > 4\sigma(F)$] of 0.12 for 914 reflections and 95 parameters.

Introduction

$\text{HRh}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ has long been an enigmatic molecule in the field of metal hydride complex chemistry. In sharp contrast to virtually all other molecules of this type [e.g., $\text{HCo}(\text{CO})_4$, which has a trigonal bipyramidal geometry], the hydride ligand in $\text{HRh}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ does not seem to occupy a discrete coordination position: i.e., the RhP_4 core is almost tetrahedral, as determined from an early X-ray analysis[2a].

Neutron Diffraction

A transparent, brown crystal with slight desolvation effects noted on the (1 -1 1) face (approximate dimensions 2.5 x 2.8 x 1.5 mm) was mounted in HaloCarbon grease on an aluminum pin oriented along the (1 0 -1) direction and placed in a specially adapted closed cycle refrigerator[3]. Neutron diffraction data were collected at 250 K on an automated four circle diffractometer at Brookhaven High Flux Beam Reactor[1] using a Ge(220)-monochromatized neutron beam wavelength of 1.15882(7) Å[4a]. The relatively high temperature of 250 K was used due to a destructive phase transition observed at 200(1) K on an earlier crystal. One reflection (0 0 -6) was monitored during cooling (298 K to 250 K) and no significant variation in intensity was observed. Unit cell constants,

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determined from the averaged 2θ values of 8 quartets, together with other experimental details are given in Table I.

A thorough investigation of the Laue symmetry was performed and confirmation of the presence of the three-fold and two-fold symmetry relationships were observed. The space group was confirmed to be $Pa\bar{3}$, consistent with the cyclically permutable extinctions $hk0$, $h=2n$ and $h00$, $h=2n$. Intensities of Bragg reflections were measured by the $\theta/2\theta$ step scan, with data being accumulated at each point for a predetermined monitor count of the incident neutron beam. Three reflections [(14 12 0), (12 2 11) and (14 11 4)] were monitored at 200-reflection intervals and no significant variation in the intensity was observed. Difficulties arose during data collection due to the crystal's poor diffracting ability. The crystals were of excellent quality and size. Two reflections, (6 0 0) and (3 3 3), are both seen to diffract amazingly well, but moderate to weak reflections were recorded for the rest of the data set. This was anticipated as a computation of neutron intensities (based on X-ray coordinates) clearly showed[4b]. Rationalization of the problem at the present time is still unresolved.

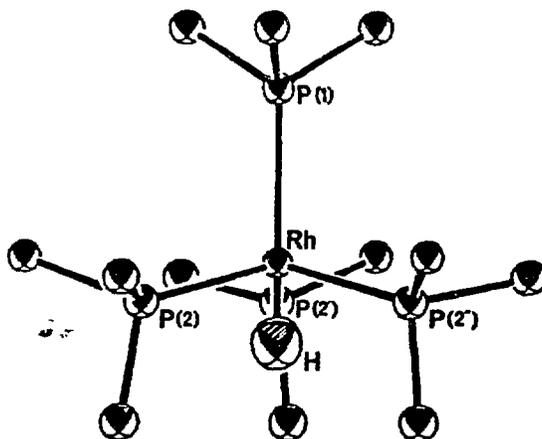
Two refinement models have been carried out in attempts to obtain the most accurate M-H distance, both using the initial coordinates from the X-ray study[2b]. 1) A rigid body refinement model using rigid group parameters for the four phenyl groups, calculated using an idealized geometry (C-H 1.08 Å, C-C 1.395 Å). Individual isotropic thermal parameters were varied. SHELX76 was used for these least-squares refinement calculations[5]. 2) A model in which all the parameters were allowed to vary was applied using full-matrix least-squares refinement[6]. Various sigma cutoff levels and weighting schemes were attempted with R-values ranging from 0.11 to 0.29 depending on which sigma level was applied. The M-H bond distance remained approximately the same at 1.31(8) Å with the e.s.d.'s increasing with increase of sigma level cutoff as expected. A final difference-Fourier map was essentially featureless with both models.

Results and Discussion

It was eventually decided that the results derived from rigid body refinement (method 1 of the previous paragraph) would be considered to represent the most meaningful solution, on the basis of a superior data-to-parameter ratio. Thus, the neutron results given in the ensuing discussion, and in the figure below, are based on a model in which

the phenyl rings are treated as rigid groups. All the distances and angles of the structure are normal, with the singular exception of the extremely short Rh-H distance of 1.31(8) Å. The rhodium atom shows slight distortion in the tetrahedral geometry; 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 = 117.8(9)°, C-P-C = 100.1(9)°.

The geometry of the title compound is shown below, with all phenyl ring atoms except the ipso carbons having been removed for clarity.



Various review articles[7] on metal hydride complexes give a detailed account of the "short" vs. "long" M-H bond length controversy that was actively debated in the literature during the 50's and early 60's. Investigators who favored a "short" (ca. 1.2 Å) M-H distance envisioned a H atom sort of "buried" in the electron cloud of the metal atom, whereas advocates of a "long" (ca. 1.6 Å) M-H distance argued that there was nothing mysterious or special about the M-H bond, and that one could estimate its length in the normal way by simply adding the covalent radii of the metal and the hydrogen atoms. In the mid-sixties, two landmark single crystal neutron diffraction experiments, on K_2ReH_9 [8] and $HMn(CO)_5$ [9] appearing to have settled the controversy in favor of the "long" (or "normal") M-H bond length, and subsequent neutron structure determinations[7e] continued to lend support to this idea.

Hence the dilemma of the Rh-H distance of 1.31(8) Å we find here. A normal terminal Rh-H distance, as measured on $H_2Rh(SiEt_3)_2(C_5Me_5)$, is 1.580(3) Å[10]. Originally we

believed the tremendous steric crowding of the triphenyl phosphine ligands, specifically the ortho H atoms of the phenyl rings [$H(\text{ortho})\dots H(\text{hydride}) = 2.38(4) \text{ \AA}$], and/or the phosphorus atoms themselves [$P\dots H(\text{hydride}) = 2.41(8) \text{ \AA}$], that are "pushing" the H atom into the electron cloud of the Rh atom, although the nonbonding distances do not appear to be anomalously short. Alternatively the M-H bond may actually be "softer" (i.e., more easily elongated or shortened) than originally thought.

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