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Neutron diffraction study of the highly distorted octahedral complex $FeH_2(CO)_2[P(OPh)_3]_2$

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Abstract

A neutron diffraction analysis was carried out at 20 K on a single crystal of $FeH_2(CO)_2[P(OPh)_3]_2$ in order to accurately locate the hydride ligands. The two hydrides are bonded terminally to the Fe atom, and their small size causes the title complex to assume a highly distorted octahedral geometry. Distances and angles involving the hydride ligands are as follows: Fe–H(1) = 1.521(2) Å, Fe–H(2) = 1.529(2) Å, H(1)···H(2) = 2.011(3) Å, and H(1)–Fe–H(2) = 82.49(13)°. Final agreement factors: $R(F) = 2.8\%$ and $R(wF^2) = 5.4\%$.

Keywords: Neutron diffraction; Iron hydride; *cis*-Dihydride complexes

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1. Introduction

Complexes of the type FeH_2L_4 have had a long history. Although $FeH_2(CO)_4$ has been known since 1931 when it was first synthesized by Hieber and Leutert [1], there were some initial doubts about the locations of the hydride ligands. Some early investigators proposed a tetrahedral structure for $FeH_2(CO)_4$, postulating that the hydrogen atoms might be bonded to the oxygen atoms of the carbonyl ligands [2]. Eventually, an electron diffraction study [3] laid all speculations to rest by demonstrating that $FeH_2(CO)_4$ has a highly distorted *cis*-octahedral geometry, with a stereochemically-active hydride ligand and normal Fe–H bonds of length 1.56(2) Å. However, in that study the precision of the Fe–H distance measurement was rather low because of the inherent limitations of the electron diffraction technique. In this paper, we describe the results of a single-crystal neutron diffraction study on the related compound $FeH_2(CO)_2[P(OPh)_3]_2$, in which the Fe–H distances are measured with much higher precision.

2. Experimental

2.1. Preparation of $FeH_2(CO)_2[P(OPh)_3]_2$

The title compound was prepared according to the method published by Brunet et al. [4]. In a typical experiment, an 80 ml solution of $K[FeH(CO)]_4$ (11 mmol) in THF:H_2O (30:50 ml) is prepared under argon; to this solution, triphenyl phosphite (6.83 g, 22 mmol) is added. An evolution of CO gas is observed, after which (24 h later) evaporation of THF under reduced pressure leads to the formation of an aqueous phase and the concurrent formation of a white precipitate. After water is removed, the microcrystalline product is washed with water previously distilled under argon. Attempts to grow large crystals using a variety of different conditions and solvents were tried, and we found that the best quality crystals could be grown by allowing hexane to diffuse slowly into a THF solution of the title compound at −20 °C.

2.2. Neutron diffraction analysis

A large, transparent, colorless crystal with dimension of 4.3 × 2.4 × 1.0 mm was used in the neutron analysis. The sample was mounted in air onto a 1-mm diameter

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vanadium pin using epoxy resin. Data were collected on instrument D19 at the Institut Laue Langevin equipped with a Displex cryostat and a curved position-sensitive area detector [5], to which was added a new 'square' (192×192 mm) position-sensitive microstrip detector [6]. The crystal was cooled at a rate of 2 K min^{-1} to 20 K while the intensity and peak profile of a strong reflection was monitored, and no change in the mosaicity of that reflection was observed. The space group was confirmed to be $P\bar{1}$ at 20 K. During data collection, three standard reflections were monitored regularly and showed no significant variation in intensity. A total of 15 316 reflections were collected and merged to yield 6402 independent reflections with positive F^2 values [7]. After an analytical absorption correction with the program D19ABS, based on the ILL version of the CCSL program system [8], phasing of the neutron data was carried out using the atomic coordinates of the non-hydrogen atoms obtained from a previous X-ray analysis [9,10]. Least-squares refinement of all atomic coordinates, and anisotropic temperature factors, resulted in final agreement factors of $R(F) = 2.8\%$ and $R(wF^2) = 5.4\%$ for all reflections. Further details of the data collection and refinement are shown in Table 1.

Table 1
Crystal data and structure refinement for $FeH_2(CO)_2[P(OPh)_3]_2$

Empirical formula	$C_{38}H_{32}FeO_8P_2$
Formula weight	732.00
Temperature (K)	20(2)
Wavelength (Å)	1.3150
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.5682(4)
b (Å)	10.3878(4)
c (Å)	18.2514(7)
α (°)	102.323(2)
β (°)	94.527(2)
γ (°)	107.112(2)
V (Å^3)	1674.16(9)
Z	2
D_{calc} (Mg m^{-3})	1.452
Absorption coefficient (cm^{-1})	1.720
Crystal size (mm)	$4.3 \times 2.4 \times 1.0$
θ range for data collection (°)	2.14–61.68
Index ranges	$-12 \le h \le 10$, $-7 \le k \le 13$, $-23 \le l \le 22$
Reflections collected	15316
Independent reflections	6402 [$R_{int} = 0.0217$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6402/0/733
Goodness-of-fit on F^2	1.409
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0264$, $wR_2 = 0.0540$
R indices (all data)	$R_1 = 0.0276$, $wR_2 = 0.0543$
Extinction coefficient	0.00145(6)
Largest difference peak and hole (fm Å^{-3})	0.372 and −0.379

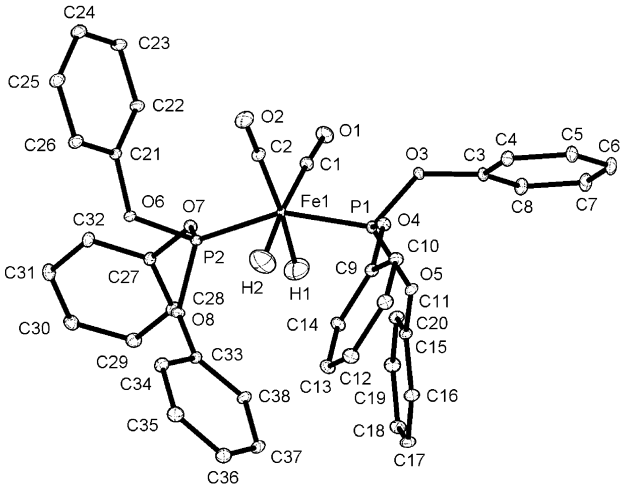


Fig. 1. Molecular structure of $FeH_2(CO)_2[P(OPh)_3]_2$ at 20 K, with hydrogen atoms in the phenyl groups removed for clarity. Ellipsoids are shown at the 50% probability level.

In Fig. 1, the structure of $FeH_2(CO)_2[P(OPh)_3]_2$ is shown with all aryl hydrogen atoms omitted for clarity. Selected distances and angles in the molecule are listed in Table 2. Significantly, this is the most precise structural characterization of a H_2FeL_4-type complex to date, with extremely low esd's for the Fe–H distances (1.521(2) and 1.529(2) Å) and the H···H distance (2.011(3) Å). Part of the motivation for this ultra-high-resolution study was that we wanted to confirm the capabilities of a new square detector recently installed at the D19 beam line [6]. This microstrip detector proved

Table 2
Selected bond distances (Å) and angles (°) in $FeH_2(CO)_2[P(OPh)_3]_2$

Bond lengths (Å)	
Fe(1)–P(2)	2.099(2)
Fe(1)–P(1)	2.119(2)
Fe(1)–C(1)	1.787(1)
Fe(1)–C(2)	1.798(1)
Fe(1)–H(1)	1.520(2)
Fe(1)–H(2)	1.529(2)
H(1)···H(2)	2.011(3)
Bond angles (°)	
C(1)–Fe(1)–C(2)	100.90(6)
H(1)–Fe(1)–H(2)	82.49(13)
P(2)–Fe(1)–P(1)	154.41(5)
C(2)–Fe(1)–P(2)	103.37(6)
C(2)–Fe(1)–P(1)	96.08(6)
C(1)–Fe(1)–P(1)	94.81(7)
C(1)–Fe(1)–P(2)	97.62(7)
C(1)–Fe(1)–H(1)	89.29(10)
C(2)–Fe(1)–H(1)	169.81(10)
C(1)–Fe(1)–H(2)	171.77(10)
C(1)–Fe(1)–H(1)	87.32(10)
P(2)–Fe(1)–H(1)	74.54(10)
P(1)–Fe(1)–H(1)	83.37(10)
P(2)–Fe(1)–H(2)	80.84(11)
P(1)–Fe(1)–H(1)	83.67(10)

to be very reliable and stable, with resolution (3 × 3 mm) well-matched to neutron experiments.

3. Discussion

In this report, we describe an accurate analysis of $FeH_2(CO)_2[P(OC_6H_5)_3]_2$ that confirms a distorted octahedral geometry with the carbonyl ligands in mutually *cis* positions and the phosphite ligands in mutually *trans* positions. In an earlier X-ray analysis of this complex, the following distances and angles involving the hydride ligands were reported: Fe–H = 1.44(2), 1.42(2) Å; H···H = 1.81(1) Å; H–Fe–H = 79.1(13)° [10]. Our more precise neutron diffraction study gives the following molecular parameters: Fe–H = 1.520(2), 1.529(2) Å; H···H = 2.011(3) Å; H–Fe–H = 82.49(13)°. The differences confirm the usual finding [11] that M–H distances derived from X-ray data are generally shorter than their true values, because during least-squares refinement the H position in an X-ray analysis is often drawn in towards the electron density of the heavy atom.

Various bond distances and angles in selected *cis*-dihydride iron complexes are summarized in Table 3. Perhaps the most striking feature in this table is the highly distorted value of the *trans*-LFeL angle, which ranges from 136.70(6)° in $FeH_2[PPh(OEt)_2]_4$ [12] to 154.41(5)° in the title complex, far less than the 180° expected for an ideal octahedral structure. Curiously, the extent of this distortion appears to be independent of the steric bulk of the L ligand, which varies from small (CO) to large ($P(OPh)_3$). In other words, the FeL_4 portion of the FeH_2L_4 skeleton in virtually all cases seems to be midway between octahedral and tetrahedral. This observation is rather puzzling because other six-coordinate hydrido complexes that have been analyzed by neutron diffraction, such as $MnH(CO)_5$ [13] and *fac*-$IrH_3(PMePh_2)_3$ [14], do not show anywhere near that amount of distortion from octahedral symmetry.

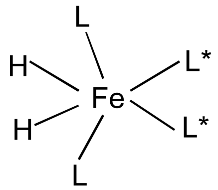
The H atoms in $FeH_2(CO)_2[P(OPh)_3]_2$ make a slightly acute H–Fe–H angle of 82.5(1)°, and hence can be considered very slightly 'compressed' as compared to that in an ideal octahedral complex. Nevertheless, the corresponding H···H distance of 2.011(3) Å is definitely in the non-bonding range, very far from the 1.5–1.6 Å distance that marks the beginning of incipient H–H bond formation [11b,15,16]. Originally, we were speculating that the large steric bulk of the triphenylphosphite ligands might force the hydride ligands to assume an unusually close H···H distance, such as the 1.357(7) Å found in $ReH_7[P(tolyl)_3]_2$ [15] and 1.49(4) Å in $[OsH_5(PMePh_2)_3]^+$ [16]. However, that turned out not to be the case.

Finally, as far as the Fe–H distance itself is concerned, the values of 1.521(2) and 1.529(2) Å we find in $FeH_2(CO)_2[P(OPh)_3]_2$ agree very well with other terminal Fe–H bond lengths measured via neutron diffraction: 1.514(6) and 1.538(7) Å in $FeH_2(\eta^2\text{-}H_2)(PPh_2Et)_3$ [17] and 1.535(12) Å in $[Fe(H)(\eta^2\text{-}H_2)(dppe)]^+[BPh_4]^-$ [18]. From all of these results, we can estimate an average value of 1.53 Å for a covalent Fe–H single bond, a number which fits very well along the following trend for first-row transition metals: Mn–H = 1.59 Å, Fe–H = 1.53 Å, Co–H = 1.52 Å, and Ni–H = 1.45 Å [11a]. We also note that this distance is slightly but significantly shorter than Fe–H distances involving non-classical dihydrogen ligands, $\eta^2\text{-}H_2$, which have been measured to be in the 1.58–1.61 Å range [17,18].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Table 3
Bond distances and angles in selected iron *cis*-dihydride complexes



	L	L*	Fe–H (Å)	H–Fe–H (°)	H···H (Å)	L–Fe–L (°)	L*–Fe–L* (°)	Method [a]	References
$FeH_2(CO)_4$	CO	CO	1.56(2)	100(10)	2.39(2)	148.5(15)	96.0(6)	E	[3]
$FeH_2(CO)_2[P(OPh)_3]_2$	$P(OR)_3$	CO	1.525(2) (avg.)	82.5(1)	2.011(3)	154.41(5)	100.90(6)	N	This work
$FeH_2[PPh(OEt)_2]_4$	$PR(OR')_2$	$PR(OR')_2$	1.51(4) (avg.)	89(2)	2.12(5)	136.70(6)	102.28(6)	X	[12]
$FeH_2(\eta^2\text{-}H_2)(PPh_2Et)_3$	PR_3	PR_3, H_2	1.526(7) (avg.)	88.2(3)	2.124(7)	149.8(2)		N	[17]
$FeH_2(N_2)(PPh_2Et)_3$	PR_3	PR_3, N_2	1.43(4) (avg.)	79(2)	1.82(4)	148.9(1)	97.2(2)	X	[18]
$FeH_2(CO)_3(AsPh_3)$	CO	$AsPh_3$, CO	1.35 (avg.)	84	1.81	151.6(3)	100.3(3)	X	[19]

[a] *Experimental technique:* E, electron diffraction; N, neutron diffraction; X, X-ray diffraction.

Data Center, CCDC no. 208347 for compound $FeH_2(CO)_2[P(OC_6H_5)_3]_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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