

## Crystal Structure, Mössbauer Spectra, and Thermal Behavior of $\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OPh})_3]_2$

Vladimir Arion,<sup>1</sup> Jean-Jacques Brunet,\* and Denis Neibecker

Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241, liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne, 31077 Toulouse Cedex, France

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### Introduction

Since the initial discovery<sup>2</sup> and characterization<sup>3</sup> of  $\text{H}_2\text{Fe}(\text{CO})_4$ , very few substituted iron carbonyl dihydrides  $\text{H}_2\text{Fe}(\text{CO})_{4-n}\text{P}_n$  (P = phosphane) have been described.<sup>4</sup> A few years ago, we disclosed a convenient, high-yield method for the preparation of derivatives of the series  $\text{H}_2\text{Fe}(\text{CO})_2(\text{P})_2$  (P =  $\text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OEt})_3$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{P}(n\text{-Bu})_3$ , and  $\text{PMe}_2\text{Ph}$ ).<sup>5,6</sup> This procedure involves a one-pot reaction of the phosphane with  $\text{Fe}(\text{CO})_5/2\text{KOH}$  in protic solvents at room temperature.<sup>7</sup> Herein we report the X-ray crystal structure of  $\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OPh})_3]_2$ , the first X-ray characterization of a mononuclear iron carbonyl dihydride.<sup>8</sup> Some properties (Mössbauer, thermogravimetric, differential thermal) of  $\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OPh})_3]$  are also described and compared with those of related complexes.

### Experimental Section

**Materials.** The complexes  $\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OPh})_3]_2$  (**1**),  $\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2$  (**2**), and  $\text{H}_2\text{Fe}(\text{CO})_3[\text{P}(\text{OPh})_3]$  (**3**) were prepared according to published procedures.<sup>5,6</sup> Single crystals of **1** were grown from a THF/pentane mixture (1:2.5) at 253 K.

**General Procedures and Methods.** Mössbauer spectra were recorded on a constant acceleration conventional spectrometer with a 25 mCi source of <sup>57</sup>Co (Rh matrix). Isomer shift values ( $\delta$ ) are quoted relative to room-temperature  $\alpha$ -iron foil. The absorber was a sample (100–130 mg) of a microcrystalline powder at room temperature enclosed in a 18 mm diameter plastic sample holder. Variable temperature spectra were obtained in the 300–80 K range, using a MD 306 Oxford cryostat, the thermal scanning being monitored by an Oxford ITC4 servocontrol device ( $\pm 0.1$  K accuracy). A least-squares computer program<sup>9</sup> was used to fit the Mössbauer spectra and to determine their standard deviations of statistical origin.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) measurements were carried out simultaneously with a SETARAM TGDTA 92 apparatus. The heating rate of the instrument was 10 °C/min, and the sample was contained under a helium

atmosphere throughout. Electrochemical measurements were performed with an ElectroKemat potentiostat<sup>10</sup> using the interrupting method to minimize the uncompensated resistance (IR) drop. A three-electrode cell was employed that comprised a gold working electrode (125  $\mu\text{m}$ ), a 0.5 mm diameter spiral of Pt wire (8 cm long) with an apparent surface area ca. 1  $\text{cm}^2$  as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode, which was separated from the nonaqueous solutions by a bridge compartment. The supporting electrolyte was  $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ . Deaeration of all solutions was accomplished by bubbling high-purity argon through the solution for 10 min prior to the measurements. Ferrocene was used as an internal standard ( $E_{\text{Fc}^+/\text{Fc}} = 0.601$  V vs SCE).

**Crystallographic Structure Determination.** A colorless parallelepiped-shaped single crystal was pasted on a glass fiber (oil-coated shock-cooled crystal)<sup>11</sup> on a STOE imaging plate diffraction system (IPDS). The diffractometer employed graphite monochromated Mo  $K\alpha$  radiation and was equipped with an Oxford Cryostream cooler device. Data were collected at 150 K, and the final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections, selected according to the criterion  $I > 10 \sigma(I)$ . Crystal decay was checked by monitoring 200 reflections by image, and no significant fluctuations of diffracted intensities were observed during the measurement. A total of 16 806 reflections were collected (6202 of which were unique) ( $R_{\text{int}} = 0.0459$ ). The structure was solved by direct methods and refined by least-squares procedures on  $F^2$  by minimizing the function  $\sum w(F_o^2 - F_c^2)^2$ , where  $F_o$  and  $F_c$  are the observed and calculated structure factors, respectively. All hydrogen atoms were located on difference Fourier maps and isotropically refined. The accuracy of localization of H atoms is 0.002–0.003 Å. Non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme  $w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.0246P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ , was used. Computer programs used were the following: structure solution, SHELXS-86;<sup>12a</sup> refinement, SHELXL-97;<sup>12b</sup> molecular diagrams, ZORTEP.<sup>12c</sup> The computer used was a Pentium II. Scattering factors are taken from ref 12d.

### Results and Discussion

**Description of the Structure of 1.**  $\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OPh})_3]_2$  (**1**) crystallizes in the triclinic space group  $P\bar{1}$ . To the best of our knowledge this is the first dihydridoiron(II) complex of the type  $\text{H}_2\text{Fe}(\text{CO})_2(\text{phosphane})_2$  to be crystallographically characterized. A ZORTEP plot of the complex is shown in Figure 1. Crystallographic data for **1** are in Table 1, and selected bond distances and angles for **1** are provided in Table 2.

The complex exhibits a distorted octahedral geometry with the triphenyl phosphite ligands mutually trans and the carbonyl ligands mutually cis. The two other equatorial sites are occupied by two hydrides with Fe–H100 and Fe–H200 bond distances of 1.44(2) and 1.42(2) Å, respectively. These contacts are shorter than Fe–H distances in related complexes; for example, the Fe–H distance is 1.469(1) Å in  $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$ ,<sup>13</sup> 1.56(7) Å in  $[\text{PPN}][\text{cis-HFe}(\text{CO})_3\text{P}(\text{OPh})_3]$ ,<sup>14</sup> and 1.57(12) Å

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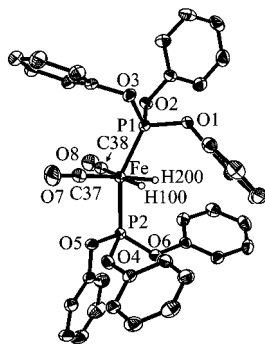
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**Figure 1.** ORTEP representation of the complex  $\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OPh})_3]_2$ , showing 50% probability thermal ellipsoids. Aryl hydrogen atoms were omitted for clarity.

**Table 1.** Crystallographic Data for **1**

chemical formula	$\text{H}_2\text{Fe}(\text{CO})_2[\text{P}(\text{OPh})_3]_2$	fw	734.43
$a$ , Å	9.6397(12)	space group	$P\bar{1}$ (No. 2)
$b$ , Å	10.4410(13)	temp, K	150
$c$ , Å	18.381(2)	$\lambda$ , Å	0.710 73
$\alpha$ , deg	102.148(15)	$\rho_{\text{obsd}}$ , $\text{g cm}^{-3}$	1.431
$\beta$ , deg	94.667(15)	$\mu$ , $\text{cm}^{-1}$	5.90
$\gamma$ , deg	107.402(14)	$R1^a [I > 2\sigma(I)]$	0.0269
$V$ , Å <sup>3</sup>	1705.0(4)	$wR2^b$ [all data]	0.0721
$Z$	2		

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

**Table 2.** Selected Bond Distances and Angles for **1**

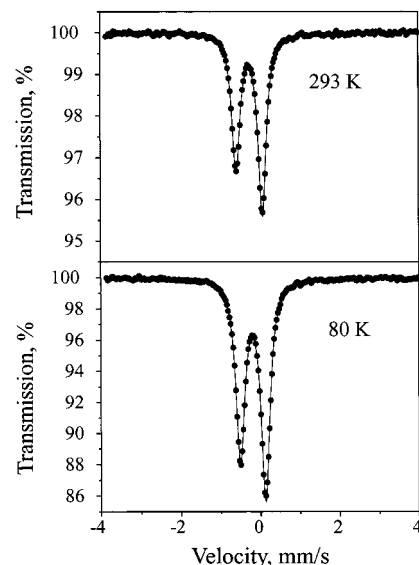
atoms	bond distances (Å)	atoms	bond distances (Å)
Fe–H100	1.44(2)	Fe–H200	1.42(2)
Fe–C37	1.789(2)	Fe–C38	1.776(2)
Fe–P1	2.1004(7)	Fe–P2	1.1180(7)
O7–C37	1.141(2)	O8–C38	1.149(2)
P1–O1	1.6020(12)	P1–O2	1.6139(14)
P1–O3	1.6246(12)	P2–O4	1.6053(13)
P2–O5	1.6004(12)	P2–O6	1.6044(12)

atoms	bond angles (deg)	atoms	bond angles (deg)
H100–Fe–H200	79.1(13)	H100–Fe–C37	87.5(9)
H100–Fe–C38	171.7(9)	H200–Fe–C37	166.6(9)
H200–Fe–C38	92.6(9)	C37–Fe–P1	103.46(6)
C38–Fe–P1	97.53(6)	C37–Fe–P2	95.99(6)
C38–Fe–P2	95.04(6)	P1–Fe–P2	154.35(2)
C37–Fe–C38	100.77(9)	Fe–C37–O7	177.7(2)
Fe–C38–O8	177.25(17)		

in  $[\text{PPN}][\text{HFe}(\text{CO})_4]$ .<sup>15</sup> The most significant structural deviation from an octahedral coordination environment at Fe is the bending of the  $\text{P}(\text{OPh})_3$  and CO ligands toward the hydride sites. For example, the  $\text{P1–Fe–P2}$  angle is  $154.35(2)^\circ$  and the angle subtended at Fe by the CO ligands ( $\text{C37–Fe–C38}$ ) is  $100.77(9)^\circ$ . It is also important to note that the  $\text{H100–Fe–H200}$  angle is only  $79.1(13)^\circ$ , the distance  $\text{H100–H200}$  being  $1.82(1)$  Å, which is very large compared with the interatomic distance in dihydrogen ( $0.7414$  Å).

Comparison of pertinent distances and bond angles of six-coordinate **1** (Table 2) with those of the distorted trigonal-pyramidal complex  $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$  reveals that the Fe–P distances in **1** are longer than those in  $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2]$  ( $\text{Fe–P}_{\text{ax}} = 2.083(1)$  Å and  $\text{Fe–P}_{\text{eq}} = 2.076(1)$  Å).<sup>13</sup> Similarly, the Fe–C distances in **1** are longer than those of related complexes such as  $[\text{Et}_4\text{N}][\text{HFe}(\text{CO})_2-$



**Figure 2.** Mössbauer spectra of **1** at 293 and 80 K.

**Table 3.** Mössbauer Spectra Parameters<sup>a</sup> for **1–3**,  $\text{H}_2\text{Fe}(\text{CO})_4$ , and  $\text{H}_2\text{Fe}(\text{depb})_2$

complex	$T$ (K)	$\delta$ ( $\text{mm s}^{-1}$ )	$\Delta E_Q$ ( $\text{mm s}^{-1}$ )	$\Gamma$ ( $\text{mm s}^{-1}$ )
<b>1</b>	293	−0.267	0.633	0.241
	80	−0.194	0.607	0.268
<b>2</b>	250	−0.257	0.463	0.226
	80	−0.199	0.439	0.256
<b>3</b>	80	−0.187	0.517	0.300
<i>cis</i> - $\text{H}_2\text{Fe}(\text{CO})_4^b$	80	−0.18	0.55	not reported
<i>trans</i> - $\text{H}_2\text{Fe}(\text{depb})_2^b$	295	−0.05	1.84	not reported
	80	−0.03	1.68	not reported

<sup>a</sup> Accuracy of parameters is  $\pm 0.005$  for **1–3** and  $\pm 0.01$   $\text{mm s}^{-1}$  for  $[\text{H}_2\text{Fe}(\text{CO})_4]$  and  $[\text{H}_2\text{Fe}(\text{depb})_2]$ . <sup>b</sup> From ref 19.

$\{\text{P}(\text{OPh})_3\}_2$  ( $1.756(3)$  and  $1.756(2)$  Å),<sup>13</sup>  $[\text{PPN}][\text{HFe}(\text{CO})_4]$  ( $\text{Fe–C}_{\text{ax}} = 1.72(2)$  Å,  $\text{Fe–C}_{\text{eq}} = 1.75(3)$  Å),<sup>15</sup>  $[\text{Et}_4\text{N}][\text{trans-HFe}(\text{CO})_3\text{PPh}_3]$  ( $\text{Fe–C}_{\text{eq}} = 1.719(9)$  Å),<sup>16</sup> and  $[\text{PPN}][\text{cis-HFe}(\text{CO})_3\text{P}(\text{OPh})_3]$  ( $\text{Fe–C}_{\text{eq}} = 1.732(9)$  Å and  $\text{Fe–C}_{\text{ax}} = 1.728(10)$  Å).<sup>14</sup> The longer Fe–C distances in **1** can be attributed to the trans influence of the hydride, which is a powerful  $\sigma$  donor. The carbonyl ligands exhibit typical bonding parameters and will not be discussed further.

It is worth noting that the overall coordination geometry of iron(II) in **1** resembles those determined for  $\text{H}_2\text{Fe}(\text{CO})_4$  by gas-phase electron diffraction ( $\text{Fe–H}$  distance is  $1.556(21)$  Å)<sup>3</sup> and for  $\text{H}_2\text{Fe}[\text{PhP}(\text{OEt})_2]_4$  ( $\text{Fe–H}$  distance is  $1.51(4)$  Å), by X-ray crystallography.<sup>15,17</sup> More recent neutron diffraction studies of  $\text{H}_2\text{Fe}(\eta^2\text{-H}_2)(\text{PEtPh}_2)_3$  afford the following Fe–H distances for the hydride ligands:  $1.538(7)$  Å (trans to  $\text{H}_2$ ) and  $1.514(6)$  Å (trans to  $\text{PEtPh}_2$ ).<sup>18</sup>

The Mössbauer spectra of diamagnetic **1** (293 and 80 K), **2** (250 and 80 K), and **3** (80 K) consist of single quadrupole split doublets (Figure 2, Table 3). The isomer shift ( $\delta$ ) and quadrupole splitting ( $\Delta E_Q$ ) parameters were obtained by least-squares fits of the data to Lorentzian line shapes. The slight asymmetry observed for **1** and **2** is more pronounced at room temperature.

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The relative left and right peak intensity for **1** (Figure 2) is 0.823 and 0.756 at 293 and 80 K, respectively. The asymmetry of the spectra is probably due to the influence of texture in the absorber. Note, however, that a number of spectra of *trans*-FeCl<sub>2</sub>(ArCN)<sub>4</sub> measured at different angles to the  $\gamma$  beam show no changes in the line area ratios.<sup>19</sup> Asymmetric Mössbauer spectra have been documented for a large number of both *cis* and *trans* iron(II) six-coordinate complexes.<sup>19</sup>

Typical isomer shift values for low-spin six-coordinate iron(II) complexes lie in the broad range from  $-0.2$  to  $+0.4$  mm s<sup>-1</sup>.<sup>19,20-23</sup> It is instructive to compare the parameters of the spectra of complexes **1–3** to those for *cis*-H<sub>2</sub>Fe(CO)<sub>4</sub> (Table 3). *cis*-H<sub>2</sub>Fe(CO)<sub>4</sub> displays the most negative isomer shift reported for a low-spin iron(II) compound.<sup>19</sup> This is perhaps unsurprising considering that H<sup>-</sup> is a powerful  $\sigma$  donor, CO a strong  $\pi$  acceptor, and P(OPh)<sub>3</sub> and P(OMe)<sub>3</sub> good  $\sigma$  and  $\pi$  ligands. Increase in *s* electron density at the iron nucleus results from the  $\sigma$ -bonding of H<sup>-</sup> and P(OR)<sub>3</sub> ligands with d<sup>2</sup>sp<sup>3</sup> hybrid iron orbitals and from  $\pi$ -back-bonding from the filled iron d<sub>xy</sub>, d<sub>xz</sub>, and d<sub>yz</sub> to the vacant low-energy  $\pi^*$  orbitals of CO. Similar to *cis*-H<sub>2</sub>Fe(CO)<sub>4</sub>, complexes **1–3** show small quadrupole splitting values indicative of *cis* structures for these compounds, a conclusion supported by <sup>1</sup>H NMR and X-ray diffraction studies. Interestingly, a quadrupole splitting value has been employed successfully in distinguishing between *trans* and *cis* structures in low-spin octahedral iron(II) complexes.<sup>19</sup> A *trans* isomer shows approximately twice the quadrupole splitting value of the *cis* isomer. Note that *trans*-H<sub>2</sub>Fe(depb)<sub>2</sub>, where depb = 1,2-bis(diethylphosphino)benzene, has a large quadrupole splitting value (1.84 mm s<sup>-1</sup>) at 295 K.<sup>19</sup>

Stepwise displacement of CO ligands in *cis*-H<sub>2</sub>Fe(CO)<sub>4</sub> by P(OPh)<sub>3</sub> results in a weak tendency of  $\delta$  values to decrease (Table 3). The weaker  $\pi$ -accepting properties of triphenyl phosphite compared to those of carbon monoxide are compensated by its stronger donor ability. The slight decrease of  $\delta$  values on going from *cis*-H<sub>2</sub>Fe(CO)<sub>4</sub> to H<sub>2</sub>Fe(CO)<sub>2</sub>[P(OPh)<sub>3</sub>]<sub>2</sub> is due to the prevalence in  $\sigma$ -donor abilities of CO and P(OPh)<sub>3</sub> over the difference in their  $\pi$ -accepting abilities.

The weak temperature dependence of the quadrupole splitting for **1**, **2**, and **3** indicates a relatively large energy separation between the ground state and the higher orbital states, which

rules out significant thermal population of the higher orbital states at room temperature. It is worth noting that the magnitude of the quadrupole splitting for compounds **1** and **2** decreases somewhat upon cooling (Table 3). This indicates that for these compounds the  $\Delta E_Q$  is presumably negative, as is the case for one site in Fe<sub>3</sub>(CO)<sub>12</sub>.<sup>24</sup>

**Thermal Behavior.** The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of **1** that were obtained simultaneously show the complex to be stable up to 473 K. A relatively strong endothermic effect on the DTA curve that is not accompanied by weight loss on the TG curve at  $\sim 365$  K is indicative of sample melting. We also recall that *cis*-H<sub>2</sub>Fe(CO)<sub>4</sub> may be vacuum-distilled at 250 K without significant decomposition (less than 3%),<sup>19</sup> but the complex is known to decompose at room temperature with hydrogen evolution to give Fe<sub>3</sub>(CO)<sub>12</sub>.<sup>25,26</sup>

**Electrochemical Studies.** Complex **1** in dichloromethane proved to be electrochemically silent at a gold electrode at a scan rate of 0.1 V s<sup>-1</sup> in the  $-2.0$  to  $+2.0$  V range. Complex **2** shows one anodic peak at  $+0.99$  V vs Fc<sup>+</sup>/Fc, which corresponds to an irreversible electron-transfer process. The cyclic voltammogram of **3** reveals two anodic oxidations at 0.96 and 1.15 V vs Fc<sup>+</sup>/Fc, which lead to deposition of decomposition products on the electrode. After the electrode was cleaned, the cyclic voltammogram became reproducible. Note that electrolytic oxidation of [HFe(CO)<sub>4</sub>]<sup>-</sup> has been shown to produce Fe(CO)<sub>5</sub>.<sup>27</sup> Fe(CO)<sub>5</sub> has also been observed as a decomposition product of H<sub>2</sub>Fe(CO)<sub>4</sub>.<sup>28</sup>

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**Supporting Information Available:** X-ray crystallographic file that includes the structural data for H<sub>2</sub>Fe(CO)<sub>2</sub>[P(OPh)<sub>3</sub>]<sub>2</sub> (**1**) in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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