

high voltage range. In addition, the plateau between 4.3 V and 5.2 V raised from 4.5 V to ~5 V.

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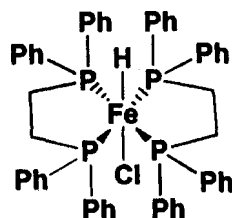
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## Structure of *trans*-Chlorohydrido-bis(diphenylphosphinoethane)iron(II)

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Reductive elimination of hydrogen chloride from chlorohydrido transition metal complexes of the type  $L_nMHCl$  has got continuous interest, because it leads to generation of electron-rich, coordinatively unsaturated complexes with a metal in a low oxidation state.<sup>1</sup> Although the title complex, which is shown below, was prepared a couple of decades ago<sup>2</sup> and its reactions have been extensively studied,<sup>3</sup> its 3-dimensional crystal structure has not been reported yet. Herein we report the molecular structure of *trans*-chlorohydrido-bis(diphenylphosphinoethane)iron(II), *trans*-FeHCl(dppe)<sub>2</sub>, [dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>].



### Experimental

The title compound was prepared by the literature method.<sup>2</sup> This compound was recrystallized from benzene/diethyl ether. X-ray data were collected with use of a Mac Science MXC diffractometer equipped with an Mo X-ray tube and a graphite crystal monochromator. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 20 reflections in the range  $20.0^\circ < 2\theta < 30.0^\circ$ . Two check reflections were measured

**Table 1.** X-ray data collection and structure refinement for *trans*-FeHCl(dppe)<sub>2</sub>

Formula	C <sub>22</sub> H <sub>40</sub> P <sub>4</sub> ClFe
Fw	889.09
Temperature (K)	293
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /n
a, Å	17.209(6)
b, Å	24.425(7)
c, Å	10.696(4)
β, deg	99.98(4)
V, Å <sup>3</sup>	4428(3)
Z	4
d <sub>calc</sub> , g cm <sup>-3</sup>	1.334
μ, mm <sup>-1</sup>	0.581
F(000)	1856
Scan speed	Variable
2θ range (°)	3.4-46.0
Range of hkl	0 ≤ h ≤ 18, 0 ≤ k ≤ 26, -11 ≤ l ≤ -11
No. of reflections measured	5427
No. of reflections with I > 2σ(I)	5266
No. of parameters refined	523
Max. Δ/σ	0.004
Max., min. in Δρ (eÅ <sup>-3</sup> )	0.701, -0.341
S (goodness-of-fit on F <sup>2</sup> )	1.024
R	0.0535
wR <sub>2</sub> <sup>a</sup>	0.1148

$$^a wR_2 = \left( \frac{\sum (w(F_o^2 - F_c^2))^2}{\sum (w(F_o^2))^2} \right)^{1/2}$$

**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for *trans*-FeHCl(dppe)<sub>2</sub>

	x	y	z	U(eq) <sup>a</sup>
Fe	2664(1)	8297(1)	1303(1)	28(1)
Cl	3017(1)	8306(1)	-775(1)	48(1)
P(1)	3590(1)	8917(1)	2031(1)	34(1)
P(2)	3614(1)	7687(1)	2066(1)	31(1)
P(3)	1717(1)	7662(1)	898(1)	32(1)
P(4)	1660(1)	8901(1)	910(1)	32(1)
C(1)	3774(4)	9080(2)	3739(5)	43(2)
C(2)	4507(4)	9282(3)	4327(6)	66(2)
C(3)	4669(5)	9372(3)	5613(8)	93(3)
C(4)	4115(6)	9271(3)	6347(7)	87(3)
C(5)	3399(5)	9074(3)	5807(6)	85(3)
C(6)	3224(4)	8978(3)	4498(6)	61(2)
C(7)	3709(3)	9596(2)	1327(5)	39(1)
C(9)	4023(4)	10131(3)	-406(7)	71(2)
C(10)	3912(4)	10602(3)	207(8)	71(2)
C(11)	3702(4)	10583(3)	1358(7)	68(2)
C(12)	3600(3)	10082(2)	1946(6)	54(2)
C(13)	3988(3)	7133(2)	1147(5)	34(1)
C(14)	3724(3)	7052(2)	-112(5)	43(2)
C(15)	4049(4)	6648(3)	-772(6)	56(2)
C(16)	4640(4)	6318(3)	164(6)	56(2)
C(17)	4912(4)	6390(3)	1110(6)	60(2)
C(18)	4591(3)	6795(2)	1752(6)	55(2)
C(19)	3490(3)	7300(2)	3485(5)	40(1)
C(20)	3233(3)	6761(2)	3391(5)	49(2)
C(21)	3097(4)	6468(3)	4443(7)	73(2)
C(22)	3219(4)	6712(4)	5589(7)	80(2)
C(23)	3453(4)	7242(3)	5727(6)	71(2)
C(24)	3588(4)	7541(3)	4683(6)	55(2)
C(25)	1752(3)	7049(2)	-93(5)	37(1)
C(26)	1745(3)	7109(3)	-1391(5)	49(2)
C(27)	1767(4)	6651(3)	-2147(6)	67(2)
C(28)	1821(4)	6137(3)	-1642(8)	75(2)
C(29)	1830(4)	6069(3)	-366(8)	73(2)
C(30)	1803(4)	6524(2)	410(6)	52(2)
C(31)	1253(3)	7406(2)	2209(5)	39(1)
C(32)	569(4)	7094(2)	1975(6)	55(2)
C(33)	155(4)	6969(3)	2934(8)	71(2)
C(34)	414(5)	7146(3)	4139(8)	81(3)
C(35)	1103(5)	7437(3)	4405(6)	68(2)
C(36)	1517(4)	7567(2)	3455(5)	49(2)
C(37)	1540(3)	9386(2)	2173(5)	35(1)
C(38)	1328(3)	9203(2)	3284(5)	44(2)
C(39)	1283(4)	9566(3)	4281(6)	57(2)
C(40)	1432(4)	10101(3)	4168(7)	66(2)
C(41)	1632(5)	10292(3)	3065(7)	73(2)
C(42)	1687(4)	9938(2)	2066(6)	51(2)
C(43)	1460(3)	9364(2)	-475(5)	38(1)
C(44)	2023(4)	9482(3)	1187(6)	60(2)
C(45)	1900(5)	9871(3)	-2131(7)	75(2)
C(46)	1201(5)	10139(3)	-2400(6)	75(2)
C(47)	625(5)	10021(3)	-1738(7)	78(2)
C(48)	751(4)	9639(3)	-775(6)	68(2)
C(49)	4532(3)	8596(2)	1882(5)	41(1)
C(50)	4557(3)	8056(2)	2595(5)	44(2)
C(51)	844(3)	8001(2)	-22(5)	41(1)
C(52)	720(3)	8520(2)	710(5)	42(1)
Hfe	2400(3)	8278(2)	2382(5)	80(0)

Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. No absorption correction was applied. The systematic absences  $h0l$  ( $h + l = 2n + 1$ ) and  $0k0$  ( $k = 2n + 1$ ) unambiguously indicated  $P2_1/n$  as the space group.

The structure was solved by the heavy atom method and refined by full-matrix least-squares calculations of  $F^2$ 's, initially with isotropic and finally anisotropic temperature factors for all non-hydrogen atoms. The hydride ligand was located in the difference Fourier map and refined with a fixed isotropic temperature factor. The other H atoms were generated in idealized positions and refined using a riding model. All calculations were carried out with use of SHELXS-86<sup>4</sup> and SHELXL-93<sup>5</sup> programs. Final atomic coordinates and bond distances and bond angles are given in Tables 2 and 3.

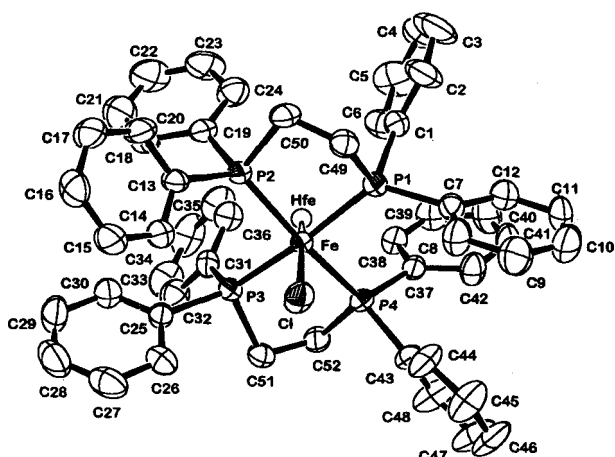
## Results and Discussion

An ORTEP<sup>6</sup> drawing of the title compound is shown below. The coordination sphere of Fe can be described as an octahedron. The chloride and hydride ligands are mutually *trans*. The Fe metal lies 0.194(1) Å above the equatorial plane that is defined by the four phosphorus atoms. Although the hydride ligand (Hfe) could be located in the difference Fourier map and refined with a fixed thermal parameter, the unusually short distance of Fe-Hfe (1.313(3) Å) is not reliable. The other bond distances and bond angles are all normal.

The molecule has a pseudo 4-fold rotation axis that passes through the Fe, Cl, and H (Hfe) atoms and is perpendicular to the equatorial plane, suggesting that the four phosphorus nuclei are equivalent. This crystal structure explains the NMR spectra of the title compound that shows a quintet for the H ligand at  $\delta$  -26.8 ppm in its <sup>1</sup>H NMR and a doublet for the four P atoms at  $\delta$  81.5 ppm ( $^2J_{\text{P-H}} = 49.1$  Hz) in its <sup>31</sup>P NMR.<sup>7</sup> As expected, <sup>31</sup>P{<sup>1</sup>H} NMR spec-

**Table 3.** Selected bond distances (Å) and bond angles (°) in *trans*-FeHCl(dppe)<sub>2</sub>

Fe-P1	2.238(2)	Fe-P3	2.236(2)	Fe-P2	2.256(2)
Fe-P4	2.255(2)	Fe-Cl	2.404(2)	P1-C49	1.833(5)
P1-C1	1.843(5)	P1-C7	1.848(6)	P2-C19	1.832(5)
P2-C13	1.852(5)	P2-C50	1.858(6)	P3-C31	1.839(6)
P3-C51	1.844(5)	P3-C25	1.842(5)	P4-C37	1.836(5)
P4-C52	1.846(5)	P4-C43	1.848(5)	Fe-Hfe	1.313(3)
P3-Fe-P1	170.88(6)	P3-Fe-P2	94.08(6)	P1-Fe-P2	83.87(6)
P3-Fe-P4	84.73(6)	P1-Fe-P4	95.62(6)	P2-Fe-P4	169.25(6)
P3-Fe-Cl	96.89(6)	P1-Fe-Cl	92.11(6)	P2-Fe-Cl	93.28(6)
P4-Fe-Cl	97.47(6)	C49-P1-C1	100.1(3)	C49-P1-C7	100.7(2)
C1-P1-C7	101.4(3)	C49-P1-Fe	105.5(2)	C1-P1-Fe	118.8(2)
C7-P1-Fe	126.0(2)	C19-P2-C13	99.4(2)	C19-P2-C50	102.6(2)
C13-P2-C50	98.7(2)	C19-P2-Fe	117.3(2)	C13-P2-Fe	125.9(2)
C50-P2-Fe	109.3(2)	C31-P3-C51	98.0(3)	C31-P3-C25	103.0(2)
C51-P3-C25	99.4(2)	C31-P3-Fe	119.1(2)	C51-P3-Fe	106.9(2)
C25-P3-Fe	125.4(2)	C37-P4-C52	101.7(2)	C37-P4-C43	99.5(2)
C52-P4-C43	100.2(3)	C37-P4-Fe	117.8(2)	C52-P4-Fe	108.7(2)
C43-P4-Fe	125.4(2)	Cl-Fe-Hfe	174.26(2)		



**Figure 1.** ORTEP drawing<sup>7</sup> of *trans*-FeHCl(dppe)<sub>2</sub> showing the atom-labeling scheme and 50% probability thermal ellipsoids.

tra of this compound exhibit a singlet at  $\delta$  81.5 ppm. The results of the X-ray crystal structure and NMR spectral data

indicate that the molecule has the same structure both in solution and in the solid state.

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## Reductive Amination of Ketones and Aldehydes with Hydrazine Using Borohydride Exchange Resin (BER)-Nickel Acetate in Methanol

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Reductive amination is an important transformation which allows the direct conversion of carbonyl compounds into the corresponding amines in chemical and biological systems.<sup>1</sup> It is commonly carried out using cyanoborohydrides<sup>2-4</sup> since the hydrides are stable under weakly acidic conditions which is essential for the formation of the imine intermediate. However, borane pyridine (BAP),<sup>5</sup> sodium triacetoxyborohydride,<sup>6</sup> and borohydride exchange resin (BER)<sup>7</sup> were also reported as alternative, less expensive, and less toxic reagents. Using these methods, secondary and tertiary amines are prepared in very good yields; however, primary amines are obtained in poor to moderate yields using cyanoborohydride<sup>2b</sup> and BER.<sup>7</sup> Alternatively primary amines are prepared by the reduction of hydrazones with catecholborane, followed by catalytic hydrogenation of the resulting hydrazines over Raney Ni at 3.5-3.8 bar.<sup>8</sup>

Recently, we have reported that BER-Ni(OAc)<sub>2</sub> in methanol is an excellent reducing system for azides<sup>9</sup> and nitro<sup>10</sup> compounds. In the course of these studies, we found that azobenzene was reduced cleanly to aniline with this reducing system. This suggests that the *N-N* bond could be cleaved readily by this system. Therefore we decided to study the synthesis of primary amines by the reductive amination of aldehydes and ketones via hydrazones using BER-Ni(OAc)<sub>2</sub> in methanol.

The results are summarized in Table 1. As shown in Table 1, yields were relatively good compared with other reported reducing agents. For example, cyclohexylamine was obtained in 88% yield; however only 45% yield was obtained using NaBH<sub>3</sub>CN<sup>2(a)</sup> (entry 1). 2-Heptylamine was obtained in 87% yield, whereas only 25% yield was obtained using BER<sup>7</sup> in the presence of NH<sub>4</sub>OAc (entry 6). In the case of acetophenone, 1-phenethylamine was obtained in 77% yield, comparable yield with NaBH<sub>3</sub>CN (77%).<sup>2(a)</sup> In the reductive amination of aldehydes, benzylamine was obtained in a moderate yield (70%), but hexanal gave only 26% yield. However, 58% yield of hexylamine could be obtained by the reduction of hexanal phenylhydrazone.

The BER-Ni(OAc)<sub>2</sub> system tolerates the presence of ester functional group as shown in the synthesis of methyl 6-amino heptanoate (entry 10); however, the conjugated double bond of benzalacetone was simultaneously reduced to give 3-

### Scheme 1.

