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[FeHCl($C_{10}H_{24}P_2$)$_2$]

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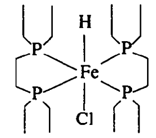
Abstract

trans-Chlorobis[1,2-ethylenebis(diethylphosphine-*P*)]-hydridoiron(II), [FeHCl(depe)$_2$] (depe = $C_{10}H_{24}P_2$), has been prepared from [FeCl$_2$(depe)$_2$] and sodium–naphthalene in tetrahydrofuran solution under nitrogen. The structural characterization of the title compound represents the first of an iron(II) hydride halide complex having a P_4 donor set. The iron centre is surrounded by one hydride ligand, one Cl atom, *trans* to the hydride, and two bis(phosphine) ligands, within a distorted octahedron. The *trans* geometry has also been confirmed in solution by NMR spectroscopy.

Comment

Dinitrogen can be bound and reduced to NH_3 at Mo, V or Fe phosphine-ligated centres, *e.g.* [*M*(diphosphine)$_2$] (*M* = Mo, V or Fe) (Chatt, Dilworth & Richards, 1978; Leigh, 1992; Rehder *et al.*, 1992; Richards, 1991), which serve as model compounds for the biological nitrogen-fixing process in the enzyme nitrogenase (Richards, 1996). The bonding and reduction of dinitrogen within this enzyme is accompanied by the generation of dihydrogen and probably involves a hydridic cofactor species (Lowe & Thorneley, 1984). In the course of an investigation of the bonding of dinitrogen to low-valent transition metal complexes, we tried to prepare the complex [FeN$_2$(depe)$_2$] according to the procedure of Komiya *et al.* (1993) by reacting dichlorobis-(depe)iron(II) with sodium–naphthalene in tetrahydrofuran (THF) solution under nitrogen. From the reaction mixture, we isolated red prisms of [FeHCl(depe)$_2$], (I), suitable for X-ray structural analysis. Hydrogen abstraction from tetrahydrofuran by low-valent transition metal centres has been observed previously (Sacco & Aresta, 1968; Jezowska-Trzebiatowska & Sobota, 1972). The title compound has also been synthesized by reacting either [FeCl$_2$(depe)$_2$] with LiAlH$_4$ (Chatt & Hayter, 1961) or [FeN$_2$(depe)$_2$] with HCl (Komiya *et al.*, 1993). The only other reported structure determination of an iron hydride halide complex having a P_4 donor set is that of [Fe^{III}HBr(depe)$_2$]BPh$_4$ (Evans *et al.*, 1992).



(I)

In the title compound, the iron centre is surrounded by one hydride, one Cl atom and two bis(phosphine) ligands within a distorted octahedron (Fig. 1). The hydride ligand occupies an axial position *trans* to the Cl ligand and the two bis(phosphine) ligands are bound in equatorial positions. The iron centre is located 0.098 (1) Å above the best plane calculated through the four P-atom centres and is shifted in the direction of the Cl ligand. The bis(phosphine) ligand is slightly bent towards the hydride to take advantage of the relatively small steric requirement of this ligand. The Fe—H, Fe—Cl and Fe—P bond lengths (Table 1) are comparable to those reported for [FeCl$_2$(depe)$_2$] [Fe—Cl 2.344 (1) and average Fe—P 2.260 (2) Å; Baker, Field & Hambley, 1988] and [FeH(N$_2$)(depe)$_2$] [Fe—H 1.351 (7) and average Fe—P 2.240 (2) Å; Buys *et al.*, 1993]. However, the Fe—H separation is slightly longer than in the comparable dinitrogen complex due to the stronger σ-donor character of the Cl ligand compared with dinitrogen, but is still shorter than the sum of the covalent radii of Fe and H.

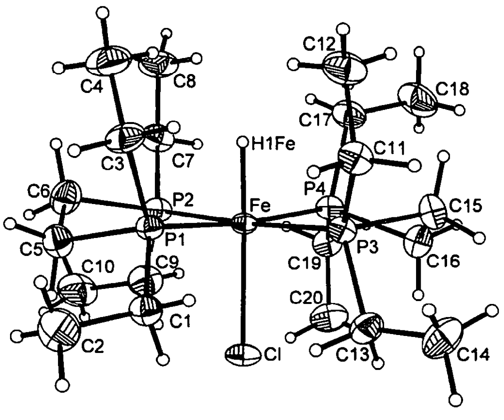


Fig. 1. The molecular structure of [FeHCl(depe)$_2$] with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

In the title complex, the *gauche* P—C—C—P torsion angles in the two bis(phosphine) ligands are of the same sign. Since the dichloro starting complex (Baker, Field & Hambley, 1988) is centrosymmetric and its two bis(phosphine) ligands have opposite conformations, one of the bis(phosphine) ligands has changed the sign of its torsion angle.

Experimental

Two equivalents of sodium–naphthalene in THF were added to a THF suspension of dichlorobis(depe)iron(II) at 233 K. The mixture was then stirred for 3 h at room temperature to give a deep-red solution. After evaporation of all volatile matter *in vacuo*, the residual red–brown solid was recrystallized from pentane to afford red prisms of [FeHCl(depe)$_2$]. The complex, which is thermally stable but air sensitive, was characterized by NMR, IR and Raman spectroscopy. The ^{1}H NMR spectra were recorded at 500 MHz with a Bruker DRX 500 spectrometer. The IR spectra were recorded with a Mattson Instruments 2030 Galaxy FTIR spectrometer. The Raman spectrum was recorded with an argon laser at 514.5 nm on a Model Spectra Physics 2020 with a double monochromator Spex 1404. The characteristic IR frequency due to ν(Fe—H) at 1856 cm^{-1} (room temperature) (Chatt & Hayter, 1961) occurs in the Raman spectrum at 1841 cm^{-1} (30 K). NMR studies on [FeHCl(depe)$_2$] confirm the *trans* nature of the product in solution, even at room temperature, because the proton resonance of the unique H atom consists of five sharp equally spaced bands with intensities in the approximate ratios 1:4:6:4:1, consistent with coupling between the proton and four equivalent P nuclei of spin $\frac{1}{2}$. ^{1}H NMR (C_6D_6, 500 MHz, Bruker DRX 500, δ p.p.m.): −31.95 (*q*, $^2J_{PH}$ = 48 Hz, Fe—H), 0.85 (*m*, 4 × $-CH_3$), 1.14 [*m*, 4 × $-CH_3$ and one of the two $-CH_2-$ protons from four $-CH_2CH_3$ arms (*A*)], 1.40 (*m*, $\frac{1}{2}$ $-CH_2-CH_2-$), 1.72 [*m*, $\frac{1}{2}$ $-CH_2-CH_2-$ and one of the two $-CH_2-$ protons from four $-CH_2CH_3$ arms (*A*) and the other $-CH_2-$ protons from four $-CH_2CH_3$ arms (*B*)], 2.61 [*m*, one of the two $-CH_2-$ protons from four $-CH_2CH_3$ arms (*B*)]. This assignment was confirmed by temperature-dependent measurements and H,H-COSY (correlated spectroscopy) spectra. The bridging ethylene protons and the protons of the ethyl arms are not equal (neither in the solid state nor in solution) due to their different environments (either Cl or hydride neighbours) and appear to be rigid because there are four different $-CH_2-$ signals for the protons of the ethyl arms. The title compound is stable in benzene under a nitrogen atmosphere for days.

Crystal data

[FeHCl($C_{10}H_{24}P_2$)$_2$]
M_r = 504.77
Orthorhombic
Pbcn
a = 10.747 (2) Å
b = 27.457 (4) Å
c = 17.837 (3) Å
V = 5263.3 (15) Å^3
Z = 8
D_x = 1.274 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 106 reflections
θ = 17.5–20.0°
μ = 0.922 mm^{-1}
T = 180 (2) K
Prism
0.68 × 0.56 × 0.28 mm
Red

Data collection

Stoe AED-II diffractometer
ω–θ scan
Absorption correction: face indexed
T_{min} = 0.562, T_{max} = 0.774
5148 measured reflections
4616 independent reflections
3296 reflections with $I > 2\sigma(I)$

R_{int} = 0.021
θ_{max} = 24.98°
$h = -12 \rightarrow 0$
$k = -32 \rightarrow 1$
$l = -21 \rightarrow 1$
4 standard reflections
frequency: every 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.157
S = 1.073
4600 reflections
246 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0808P)^2 + 11.4418P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.811 e Å^{-3}
$\Delta\rho_{min}$ = −0.728 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Fe—P2	2.1970 (13)	Fe—P3	2.2231 (12)
Fe—P4	2.2053 (13)	Fe—Cl	2.4044 (12)
Fe—P1	2.2093 (12)	Fe—H1	1.45 (5)
P2—Fe—P4	94.22 (5)	P1—Fe—P3	93.76 (5)
P2—Fe—P1	86.57 (5)	P2—Fe—Cl	92.87 (5)
P4—Fe—P1	173.59 (5)	P4—Fe—Cl	94.92 (4)
P2—Fe—P3	176.10 (5)	P1—Fe—Cl	91.39 (4)
P4—Fe—P3	85.03 (5)	P3—Fe—Cl	91.01 (4)

All Fe, Cl, P and C atoms were refined with anisotropic displacement parameters. The hydride H atom was located in a difference electron density map and its position was refined while its isotropic displacement parameter was held fixed. All other H atoms were positioned with ideal geometry and refined with fixed individual isotropic displacement parameters [U_{iso} = 1.2U_{eq}($C_{methylene}$) or 1.5U_{eq}(C_{methyl})] using a riding model with C—H distances of 0.99 (methylene) or 0.98 Å (methyl).

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1021). Services for accessing these data are described at the back of the journal.

References

Baker, M. V., Field, L. D. & Hambley, T. W. (1988). *Inorg. Chem.* **27**, 2872–2876.
Buys, I. E., Field, L. D., Hambley, T. W. & McQueen, A. E. D. (1993). *Acta Cryst.* C**49**, 1056–1059.
Chatt, J., Dilworth, J. R. & Richards, R. L. (1978). *Chem. Rev.* **78**, 589–625.
Chatt, J. & Hayter, R. G. (1961). *J. Chem. Soc.* pp. 5507–5511.
Evans, D. J., Henderson, R. A., Hills, A., Hughes, D. L. & Oglieve, K. E. (1992). *J. Chem. Soc. Dalton Trans.* pp. 1259–1265.

Jezowska-Trzebiatowska, B. & Sobota, P. (1972). *J. Organomet. Chem.* **46**, 339–343.
Komiya, S., Akita, M., Yoza, A., Kasuga, N., Fukuoka, A. & Kai, Y. (1993). *J. Chem. Soc. Chem. Commun.* pp. 787–788.
Leigh, G. J. (1992). *Acc. Chem. Res.* **25**, 177–181.
Lowe, D. J. & Thorneley, R. N. F. (1984). *Biochem. J.* **224**, 877–886.
Rehder, D., Woitha, C., Priebsch, W. & Gailus, H. (1992). *J. Chem. Soc. Chem. Commun.* pp. 364–365.
Richards, R. L. (1991). *Biology and Biochemistry of Nitrogen Fixation*, edited by M. J. Dilworth & A. R. Glenn, p. 58. Oxford: Elsevier.
Richards, R. L. (1996). *Coord. Chem. Rev.* **154**, 83–97.
Sacco, A. & Aresta, M. (1968). *J. Chem. Soc. Chem. Commun.* pp. 1223–1224.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1990). *SHELXTL/PC.* Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Stoe & Cie, Darmstadt, Germany.

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trans-Bis(acetylacetonato-*O*,*O*′)(3-methylpyridine-*N*)nitrocobalt(III)

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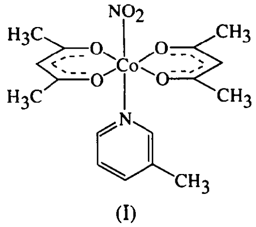
Abstract

The crystal structure determination of the title compound, [$Co(C_5H_7O_2)_2(NO_2)(C_6H_7N)$], shows that the coordination geometry around the Co^{III} atom is slightly distorted octahedral, with a Co—NO_2 bond distance of 1.905 (3) Å. The crystal is photostable, which may be due to the narrow cavity around the nitro group.

Comment

Solid-state photochemical nitro–nitrito linkage isomerization has been investigated in single crystals of [$Co(NH_3)_5(NO_2)$]Cl_2 (Kubota & Ohba, 1992) and in [$Co(NH_3)_5(NO_2)$]Br_2 powder (Masciocchi *et al.*, 1994). Johnson & Martin (1969) reported the solid-state photochemical reaction of [$Co(acac)_2(py)(NO_2)$], based on IR spectra (acac is the acetylacetonate ion and py is pyridine). Recrystallization of the pyridine complex failed in the present study. When the pyridine ligand was replaced by 2-, 3- or 4-methylpyridine, only the 3-methylpyridine complex, (I), gave good crystals. However, the IR spectra showed no change before and after irradiation of the KBr disk with Xe light.



(I)

The Co atom and the 3-methylpyridine ligand lie on the mirror plane which bisects the nitro O—N—O bond angle. The dimensions of the reaction cavity of NO_2 were calculated (Kubota & Ohba, 1992), from which it was ascertained that there is no room in the crystal to allow isomerization from the nitro (Co—NO_2) to the nitrito (Co—ONO) form. The intermolecular contacts with the nitro O atom near the NO_2 plane are 2.405 (2) Å for O4···H11*A*—C11 $(\frac{3}{2}-x, y+\frac{1}{2}, z+\frac{1}{2})$ and 2.687 (2) Å for O4···H16—C16 $(x+\frac{1}{2}, \frac{1}{2}-y, \frac{3}{2}-z)$.

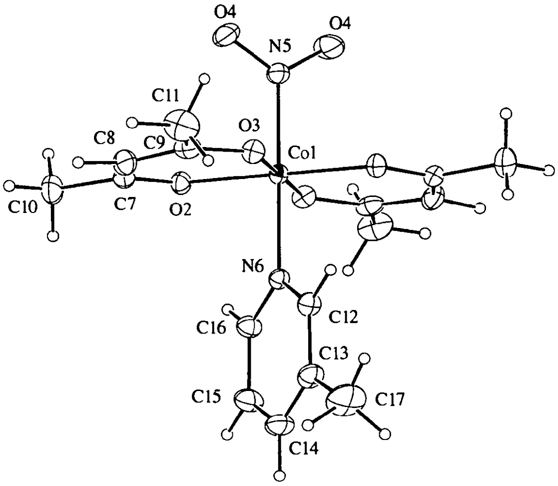


Fig. 1. The molecular structure of (I) with displacement ellipsoids at the 20% probability level. H atoms are represented by circles of radius 0.1 Å.

Experimental

The compound was prepared according to the method of Boucher & Bailar (1965) from Na[$Co(acac)_2(NO_2)_2$] and 3-methylpyridine. Crystals were grown from an acetonitrile solution.