magnetic moments of 3.12 μ_B at 26 °C in Me_2SO solutions and 3.06 μ_B at 21 °C in aqueous solutions, which is attributed to the d^8 electronic configuration in octahedral geometry. A possible route for the formation of the complex is proposed in Scheme I. The formation of the macrocyclic ligand containing 1,3-diazacyclopentane ring moieties from a reaction similar to this has been already reported by our laboratory.[25,26]

An ORTEP[27] view of the complex with the atomic numbering scheme is presented in Figure 1. The bond lengths and angles are listed in Table III. The title complex has a distorted octahedral geometry. The hexaaza macrobicyclic ligand serves as a pentadentate ligand by coordinating to the Ni(II) ion with two tertiary [N(1) and N(9)] and three secondary [N(6), N(11), and N(14)] nitrogens. N(4) is clearly uncoordinated to Ni(II) at a distance of 3.349 (5) Å from the metal ion. The bond angles at N(4) indicate that the lone pair of the nitrogen atom is directed away from the Ni(II) ion. The 1,3-diazacyclopentane ring of the ligand assumes an envelope conformation with an N(1)–C(2)–C(3)–N(4) torsion angle of 12.8 (5)°. These four atoms form a plane [maximum deviation 0.090 (6) Å] that is nearly perpendicular to the coordination plane with a dihedral angle of 114°. The Cl^- ligand is located at the axial position toward the same direction as the ethylene portion of the 1,3-diazacyclopentane ring moiety in the macrobicyclic ligand. The complex contains a rarely observed four-membered chelate ring. There are three five-membered chelate rings and one six-membered chelate ring in the complex also. The four-membered chelate ring shows a good planarity with a maximum deviation of 0.035 (9) Å. The bite distance and bite angle are 2.377 (8) Å and 66.7 (2)°, respectively. Each five-membered chelate ring assumes a half-chair conformation with the N–C–C–N torsion angles in the en moiety ranging from 38.8 (5) to 54.5 (5)°. The six-membered chelate ring assumes a near-chair conformation with the intracyclic torsion angles ranging from 24.9 (4) to 87.8 (5)°, and consequently, the seven-membered ring assumes a boat conformation.

The complex is very much distorted from the regular octahedral geometry. The bond lengths involving the Ni(II) ion are not equal, and the bond angles also vary widely, ranging from 66.7 (2) to 101.7 (2)°. The Cl–Ni–N(11) angle deviates from linearity by 22.7°. This severe distortion seems to be caused by the presence of the strained four-membered chelate ring and by the close contact between the ethylene portion of the 1,3-diazacyclopentane ring moiety and the Cl^- ligand. The Cl···C(2) separation of 3.363 (7) Å in this complex is much shorter than the van der Waals contact of 3.50 Å. The coordination plane is distorted such that N(1), N(6), N(9), and N(14) deviate from their best plane by −0.079 (3), 0.079 (3), −0.108 (5), and 0.107 (5) Å, respectively. The Ni(II) ion is out of the plane by 0.146 (1) Å toward the direction of the Cl^- ligand. The average Ni–N bond length is 2.12 ± 0.04 Å. The Ni–N bonds in the four-membered ring are lengthened by up to 0.106 Å compared to the others, presumably to relieve the strain of the ring.

This study presents the first example of a hexaaza macrocycle that serves as a pentadentate ligand.

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Registry No. $[Ni(C_{13}H_{30}N_6O)Cl]ClO_4$, 119769-51-6; triethylenetetramine, 112-24-3; ethylenediamine, 107-15-3; formaldehyde, 50-00-0; methanol, 67-56-1.

Supplementary Material Available: Tables SI–SV, listing a summary of crystal data and data collection parameters, anisotropic thermal parameters, atomic coordinates of the hydrogen atoms, and complete bond lengths and angles involving non-hydrogen and hydrogen atoms (5 pages); tables of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Transition-Metal Silyl Complexes. 29. Formation of Dihydride Complexes from Hydrido(silyl)tetracarbonyliron Derivatives

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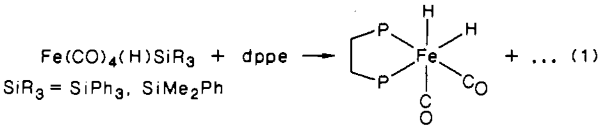
In a series of papers we have recently shown that phosphine- or phosphite-substituted hydrido(silyl)iron derivatives can be prepared by several routes.[1–4] The choice of the most suitable method depends essentially on the nature of the silyl group and the phosphine. Our successful synthesis of $Fe(CO)_2(dppe)(H)SiMeCl_2$ by thermal CO/phosphine exchange starting from $Fe(CO)_4(H)SiMeCl_2$[2] seemingly was in line with the report of Bellachioma and Cardaci,[5] who claimed the synthesis of $Fe(CO)_2(dppe)(H)SiPh_3$ (**1**) by the same method (dppe = $Ph_2PCH_2CH_2PPh_2$). However, when we repeated the latter reaction by the reported procedure, we only isolated the dihydride compound **2** in 40% yield (eq 1) and a small amount (10%) of $Fe(CO)_3(dppe)$. We did not find any evidence for **1**. Interestingly, the melting point and the spectroscopic data for **2** are very similar to those reported[5] for the alleged **1**.



2

The dihydride complex **2** is also obtained from $Fe(CO)_4(H)SiMe_2Ph$ as a precursor (eq 1). Obviously, dppe-substituted derivatives $Fe(CO)_2(dppe)(H)SiR_3$ are only formed from the tetracarbonyl complexes if electron-withdrawing substituents at silicon provide strong Fe–Si bonds (as in the $SiMeCl_2$ derivative).

The real complex **1**, as well as $Fe(CO)_2(dppe)(H)SiMe_2Ph$, can be prepared by silane-exchange reaction from $Fe(CO)_2(dppe)(H)SiMe_3$ and $HSiPh_3$ or $HSiMe_2Ph$, respectively.[2] Spectroscopic data of the hydrido silyl complexes are included in Table I for comparison. They fit into the series of other complexes of the type $Fe(CO)_2(dppe)(H)SiR_3$.[2]

Since **1** is stable toward the conditions employed for reaction 1, it cannot be a precursor for **2**. If reaction 1 is followed ^1H NMR spectroscopically (at 20 °C), no intermediates can be observed. To check the possibility that the second hydride ligand of **2** originates from $HSiPh_3$, which might be formed by decomposition of $Fe(CO)_4(H)SiPh_3$, we reacted a 1:1:1 mixture of $Fe(CO)_4(H)SiPh_3$, dppe, and $DSiPH_3$. ^1H NMR spectroscopically, only **2** and no $Fe(CO)_2(dppe)(H)D$ was observed. Although this experiment eliminates the possibility that $HSiPh_3$ is involved in reaction 1, we cannot rule out that the second hydride ligand in **2** is transferred from another metal moiety by another mechanism. The mechanism of this reaction and particularly the fate of the silyl ligand will be subject to further investigations. The dihydride complex **2** was independently synthesized by photochemical reaction of $Fe(CO)_3(dppe)$ with H_2 (eq 2).

$$\mathrm{Fe(CO)_3(dppe)} + \mathrm{H_2} \xrightarrow{h\nu} \mathbf{2} + \mathrm{CO} \qquad (2)$$

Complex **2** fills the gap between the known dihydride complexes $Fe(CO)_4H_2$[6] and $Fe(dppe)_2H_2$.[7] In **2**, one of the hydride ligands is trans to a CO ligand and the other hydride ligand is trans to

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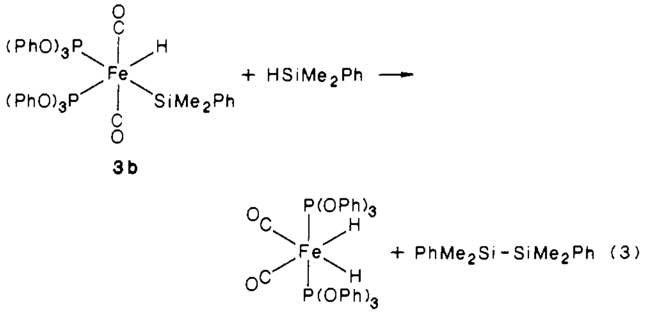
Table I. IR and NMR Data (25 °C)

complex	ν(CO), cm^{-1}	δ(Fe*H*), ppm	*J*(PFeH), Hz	δ(C*H*$_2$), ppm	*J*(PCH), Hz	δ(P), ppm
$Fe(CO)_2(dppe)H_2$ (**2**)	1994 (s), 1947 (s)[a]	−9.6 (t)[b]	31	2.2 (d)	18	92.4 (s)[c,d]
$Fe(CO)_2(dppe)(H)SiMe_2Ph$	1977 (vs), 1934 (s)[e]	−9.7 (t)[b]	38	1.9 (d)	18	88.4 (s)[b]
$Fe(CO)_2(dppe)(H)SiPh_3$ (**1**)	1981 (vs), 1939 (s)[f]	−9.2 (t)[f]	41	2.2 (d)	19	87.1 (s)[b,g]

[a] Et_2O. [b] Benzene-*d*$_6$. [c] Acetone-*d*$_6$. [d] Triplet in the off-resonance spectrum. At −70 °C, δ(P) = 92.0 ppm and *J*(AB) = 17.8 Hz. [e] Benzene. [f] CH_2Cl_2. [f] Doublet in the off-resonance spectrum.

one of the phosphorus atoms: the two ν(CO) bands of approximately equal intensity support a cis arrangement of the carbonyl ligands. A low-temperature $^{31}P\{^1H\}$ NMR spectrum (−70 °C) shows two nonequivalent phosphorus nuclei. At temperatures above −10 °C the AB spin system coalesces to a singlet (triplet in the off-resonance spectrum). Due to the fluxional behavior of **2**, a triplet is observed at room temperature for both the hydride ligands in the ^1H NMR spectrum and the CO ligands in the ^{13}C NMR spectrum (δ(CO) = 216.8 ppm).

We also observed formation of a dihydrido iron derivative from $Fe(CO)_2[P(OPh)_3]_2(H)SiR_3$ with electron-donating SiR_3 ligands (**3a**, SiR_3 = $SiMe_3$; **3b**, SiR_3 = $SiMe_2Ph$).[1] Particularly in the presence of $HSiR_3$, **3a**,**b** decompose to give the known dihydride complex **4**.[8] A 90% yield of **4** is obtained by keeping a benzene solution of **3b** and a 3–4-fold excess of $HSiMe_2Ph$ at room temperature for 2 days. In this reaction (eq 3), which is easily monitored by ^1H NMR spectroscopy, $Si_2Me_4Ph_2$ and small amounts of $Fe(CO)_3[P(OPh)_3]_2$ are also formed.[9] No other Si–CH_3 signals, except that of the disilane, were observed. Dissociative loss of a phosphite or CO ligand followed by oxidative addition of $HSiR_3$ and reductive elimination of disilane would be a possible sequence of events eventually leading to **4**.



3b

4

(3)

The results clearly show that there are at least two different mechanisms leading to a substitution of a silyl ligand by a hydride. Interestingly, both reactions (eq 1 and 2) are restricted to complexes in which the Fe–Si bond of the starting complex is not strengthened by electronegative substituents at silicon.

Experimental Section

All operations were carried out under an atmosphere of dry and oxygen-free nitrogen. All solvents were dried by conventional methods.

$Fe(CO)_2(dppe)H_2$ (2). Method a. To a solution of 0.95 g of $Fe(CO)_4(H)SiPh_3$[10] (2.22 mmol) in 40 mL of benzene is added 0.90 g (2.25 mmol) of dppe at 20 °C within 20 min. Through the solution a weak stream of N_2 is bubbled through a capillary to expel CO. The progress of the reaction is monitored IR and ^1H NMR spectroscopically. After 140 min the starting tetracarbonyl complex is no longer observed. The solution is then filtered and the filtrate concentrated in vacuo, resulting in a colorless solid. Extraction with 65 mL of warm diethyl ether, filtration, concentration to 35 mL, and storage at −25 °C results in precipitation of 0.45 g (40%) of **2** as a pale yellow microcrystalline solid.

Method b. A solution of 1.06 g (2 mmol) of $Fe(CO)_3(dppe)$[11] in 200 mL of toluene, through which a steady stream of dry H_2 is bubbled, is irradiated at −35 °C for 6 h (high-pressure mercury lamp, 180-W, TQ 150 Heraeus). After removal of the solvent in vacuo, the residue is dissolved in a minimum amount of CH_2Cl_2 and the solution chromatographed on SiO_2 at −15 °C with Et_2O/pentane (the ratio is slowly increased from 1:4 to 3:2 during chromatography). Recrystallization of the yellow eluate from hot methylcyclohexane gives 0.21 g (20%) of **2**; mp 139–140 °C dec. Anal. Calcd: C, 65.64; H, 5.12. Found: C, 65.51; H, 5.34.

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