$(THF)_3LiCl$ as a Ligand for Low-Coordinate Fe(II): Crystal Structure of $[(Me_3Si)_2N]_2Fe(\mu\text{-}Cl)Li(THF)_3$

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Introduction

Complexes containing three-coordinate non-d^{10}-configurated transition metal centers are of great current interest.[1] In the chemistry of iron, this has been further spurred by the finding that six of the seven iron atoms in the FeMo cofactor of molybdenum nitrogenase[2] from *Azotobacter vinelandii*[3] are essentially three-coordinate with a distorted-trigonal geometry. The earliest well-characterized example of a compound containing three-coordinate iron is $Fe[N(SiMe_3)_2]_3$, which was published by Wannagat and Bürger in 1963.[4] This paper also describes the synthesis of the two-coordinated $Co[N(SiMe_3)_2]_2$. Since then, bulky amido ligands have been utilized more extensively than any other type of ligand for the stabilization of coordinatively and electronically unsaturated transition metal complexes.[5] The common view that bis(triorganosilyl)amido ligands act predominantly as uninegative two-electron σ-bonding ligands toward low-coordinate transition metal centers, exhibiting almost negligible M−N π-bonding,[5b,6] is currently under revision.[7] In any case, the extent of M−N π-bonding is expected to be next to nothing for borylamido complexes, since the nitrogen lone pair engages in strong B−N π-bonding.[8]

The iron(II) analogue of $Fe[N(SiMe_3)_2]_3$ is $Fe[N(SiMe_3)_2]_2$, which was prepared by metathesis of $FeBr_2(THF)_2$ with lithium bis(trimethylsilyl)amide in diethyl ether.[6] It is monomeric in the gas phase but adopts a dimeric amido-bridged structure with three-coordinate iron in the solid state.[9] The yellow dimer reacts with the Lewis base THF, yielding the pale-green monomeric adduct $(THF)Fe[N(SiMe_3)_2]_2$.[9] In contrast to this, bis(trimethylsilylamido)cobalt(II), which is also an amido-bridged dimer in the solid state,[10] does not react with THF,[4] but it does form adducts with stronger donors, an example being $(Ph_3P)Co[N(SiMe_3)_2]_2$.[11] The three-coordinated anionic complexes $\{M[N(SiMe_3)_2]_3\}^-$ are known for both iron and cobalt and may be rationalized as adducts of $M[N(SiMe_3)_2]_2$ with the very strong base $[N(SiMe_3)_2]^-$.[12]

To date, only four examples of structurally characterized monomeric complexes containing three-coordinate iron are known,[13] viz. $\{Fe[N(SiMe_3)_2]_3\}^{n-}$ ($n = 0$,[14] 1 [12]), $(THF)Fe[N(SiMe_3)_2]_2$,[9] and $\{ClFe[Si(SiMe_3)_3]_2\}^-$.[15] Here we report on an unusual fifth example.

Results and Discussion

We recently described the synthesis and structure of $Cp^*FeN(SiMe_3)_2$.[16] This complex was prepared by the reaction of iron(II) chloride in THF with 1 equiv of $KN(SiMe_3)_2$ and subsequent addition of Cp*Li. Our attempt to obtain the unmethylated $CpFeN(SiMe_3)_2$ by an analogous procedure using CpLi instead of Cp*Li led to the formation of the title compound $[(Me_3Si)_2N]_2Fe(\mu\text{-}Cl)Li(THF)_3$, which was isolated as very pale-green, extremely air-sensitive crystals after removal of the second product, ferrocene, by crystallization from *n*-hexane.

A single-crystal X-ray diffraction study was performed for the novel iron complex (Figure 1). The iron atom is surrounded by three ligands in a distorted trigonal planar arrangement (sum of angles is 359.9°). The nitrogen atoms of the two $N(SiMe_3)_2$ groups are also trigonal planar (sum of angles is 360.0/359.9°). The two NSi_2 planes are almost orthogonal (dihedral angle is 84.2°). The two Fe−N bond lengths [Fe(1)−N(1), 194.5(5) pm; Fe(1)−N(2), 195.4(5) pm] are identical within experimental error. The corresponding Fe−N(terminal amido) distances are 191.6(5) and 192.3(3)/192.7(3) pm, respectively, for the neutral $(THF)Fe[N(SiMe_3)_2]_2$ [9] and $\{Fe[\mu\text{-}N(SiMe_3)_2][N(SiMe_3)_2]\}_2$ [9] and range from 197.3(5) to 199.4(4) pm for the anionic $\{Fe[N(SiMe_3)_2]_3\}^-$.[12] A $ClLi(THF)_3$ moiety acts as the third ligand in the title complex. The chlorine atom brigdes the two metal atoms [Fe(1)−Cl(1)−Li(1), 124.4(3) °]. The Fe−Cl bond length [231.8(2) pm] is slightly, but significantly, longer than that in $[NEt_4]^+\{ClFe[Si(SiMe_3)_3]_2\}^-$ [228.4(6) pm], which contains a terminal chloro ligand.[15] The lithium atom resides in a distorted tetrahedral environment. The Li−O distances range from 190.6(13) to 194.1(14) pm (average, 192.0 pm), as is typical for tetracoordinate Li^+.[17] The Li−Cl distance is 234.5(13) pm. These values are very similar to those found for the contact ion pairs $LiCl(H_2O)(C_5H_5N)_2$[18] and $LiI(THF)_3$[19] (after ionic radius correction). Finally, we note that intermolecular distances are well above 400 pm.

The structure of the title compound closely resembles that of the di(borylamido)cobalt(II) complex $[Ph(Mes_2B)N]_2Co(\mu\text{-}Cl)Li(THF)(OEt_2)_2$, which was obtained from the reaction of

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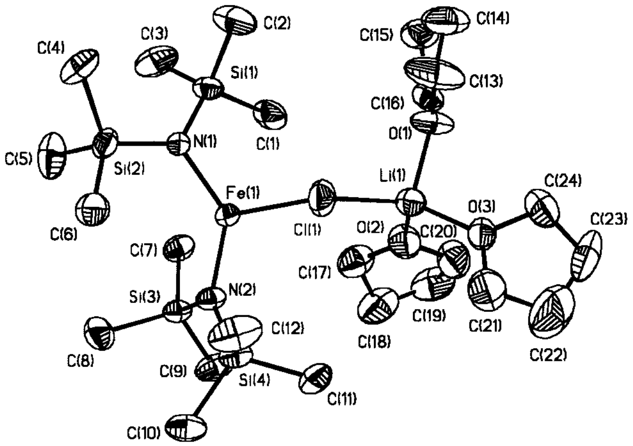

Figure 1. Molecular structure of $[(Me_3Si)_2N]_2Fe(\mu\text{-}Cl)Li(THF)_3$ in the crystal. Selected interatomic distances (Å) and angles (deg) not discussed in the text are the following: Si(1)−N(1) 172.8(5), Si(2)−N(1) 170.6(5), Si(3)−N(2) 172.9(5), Si(4)−N(2) 171.4(5), O(1)−Li(1) 191.2(13), O(2)−Li(1) 194.1(14), O(3)−Li(1) 190.6(13); N(1)−Fe(1)−N(2) 130.8(2), N(1)−Fe(1)−Cl(1) 114.67(16), N(2)−Fe(1)−Cl(1) 114.43(17), Si(1)−N(1)−Si(2) 123.9(3), Si(1)−N(1)−Fe(1) 118.8(3), Si(2)−N(1)−Fe(1) 117.3(3), Si(3)−N(2)−Si(4) 123.1(3), Si(3)−N(2)−Fe(1) 118.5(3), Si(4)−N(2)−Fe(1) 118.3(3), O(1)−Li(1)−Cl(1) 107.3(6), O(2)−Li(1)−Cl(1) 117.4(6), O(3)−Li(1)−Cl(1) 114.9(6), O(1)−Li(1)−O(2) 106.1(7), O(1)−Li(1)−O(3) 103.7(6), O(2)−Li(1)−O(3) 106.4(7).

cobalt(II) chloride with 2 equiv of $(Et_2O)_2Li[N(BMes_2)Ph]$ in THF.[8] The M−Cl distances in this complex are 230.0(2) (M = Co) and 235.3(11) pm (M = Li). The Co−Cl−Li angle has a value of 160.0°.[20] The two nitrogen atoms are trigonal planar (sum of angles is 358.2/357.3°; dihedral angle is 17.0°). Only three related crystallographically characterized transition metal complexes have been published, namely, $(t\text{-}Bu_2C_5H_3)_3Nd(\mu\text{-}Br)Li(THF)_3$ [Nd−Br−Li, 136.4(6)°],[21] $(t\text{-}Bu_2C_5H_3)_3Pr(\mu\text{-}Br)Li(THF)_3$ [Pr−Br−Li, 137.3(3)°],[22] and $Cl_4(THF)Zr(\mu\text{-}Cl)Li(THF)_3$ [Zr−Cl−Li, 117.16(14)°].[23] An $XLi(THF)_3$ unit (X = Cl, Br) acts as a ligand for a very Lewis acidic metal center in these three cases. This represents a very rare structural motif in coordination chemistry, a much more common one being the simultaneous coordination of both atoms of LiX by a suitable metal−ligand unit.[24] In fact, this behavior causes the tenacity of LiX in many transition metal complexes, which is most notorious for the rare-earth elements (Ln), where, for example, $Cp^*_2Ln(\mu\text{-}X)_2LiL_2$ (L = Et_2O, THF) is a well-known structure type.[25]

The question arises as to why the title compound is isolated instead of a mixture of the known $(THF)Fe[N(SiMe_3)_2]_2$ [9] and a THF solvate of lithium chloride such as $[(THF)LiCl]_n$ [26] and $[(THF)_2LiCl]_2$.[27] We remind ourselves of the fact that bis(trimethylsilylamido)cobalt(II) does not form a THF adduct (vide supra). However, the adduct $[(Me_3Si)_2N]_2Co(\mu\text{-}Cl)Li(THF)_3$ obviously exists, since it is briefly mentioned in ref 8 as unpublished work. It is therefore tempting to conclude that in the present system $ClLi(THF)_3$ is a better donor ligand than THF. As a caveat, we note that $[Li(THF)_4][ZrCl_5(THF)]$ and $(THF)ZrCl_4(\mu\text{-}Cl)Li(THF)_3$ were obtained under very similar conditions,[23] underlining the intricacies caused by differences in experimental parameters.

Table 1. Crystallographic Data for $[(Me_3Si)_2N]_2Fe(\mu\text{-}Cl)Li(THF)_3$

chemical formula	$C_{24}H_{60}ClFeLiN_2O_3Si_4$	fw	635.34
a, Å	12.122(6)	space group	$P\bar{1}$ (No. 2)
b, Å	12.627(5)	temp, °C	173
c, Å	14.352(6)	λ, Å	0.710 73
α, deg	82.75(3)	ρ_{calcd}, g/cm^3	1.101
β, deg	85.38(4)	μ, mm^{-1}	0.612
γ, deg	61.57(3)	$R(F_o)^a$	0.0987
V, Å^3	1915.9(15)	$R_w(F_o2)^b$	0.2481
Z	2		

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

Experimental Section

All manipulations were performed in an inert atmosphere (purified argon or dinitrogen) by using standard Schlenk and cannula techniques or a conventional glovebox. Solvents and reagents were appropriately dried and purified by using standard procedures. Elemental analyses were performed by Mikroanalytisches Labor Beller, Göttingen, Germany.

Synthesis of $[(Me_3Si)_2N]_2Fe(\mu\text{-}Cl)Li(THF)_3$. A solution of $KN(SiMe_3)_2$ (3.46 g, 17.4 mmol) in THF (30 mL) was added dropwise to a stirred suspension of $FeCl_2$ (2.20 g, 17.4 mmol) in THF (30 mL) cooled to 0 °C. After stirring of the mixture at 0 °C for 10 h, CpLi (1.25 g, 17.4 mmol) in THF (60 mL) was added and the mixture allowed to warm to room temperature. After 1 h at room temperature volatile components were removed in vacuo until a viscous greenish-brown oil was left. *n*-Hexane (70 mL) was added and insoluble material removed by filtration. The volume of the filtrate was reduced to ca. 30 mL. Storing of the solution at 0 °C for 2 days afforded the product as a very pale-green crystalline solid. Small amounts of ferrocene (orange crystals) were removed manually. Yield, 3.20 g (58%). Anal. Calcd for $C_{24}H_{60}ClFeLiN_2O_3Si_4$: C, 45.37; H, 9.52; N, 4.41. Found: C, 44.40; H, 8.71; N, 4.10.

X-ray Crystallography. A suitable single crystal was mounted in inert oil and transferred to the cold gas stream of a Siemens $P2_1$ four-circle diffractometer. The structure was solved using direct methods and developed routinely. Programs used were Siemens SHELXTL plus and SHELXL-97. Crystal parameters and details of the data collection and refinement are given in Table 1 (for full details see Supporting Information).

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of $[(Me_3Si)_2N]_2Fe(\mu\text{-}Cl)Li(THF)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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