Organometallics **1998,** *17,* 483−484

[Bis(trimethylsilyl)amido](η^5-pentamethylcyclopentadienyl)iron(II): A Diamagnetic 14-Electron Complex with a “Pogo-Stick” Structure

Ulrich Siemeling,* Udo Vorfeld, Beate Neumann, and Hans-Georg Stammler

Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse 25,
D-33615 Bielefeld, Germany

Received August 19, 1997[⊗]

*Summary: The half-sandwich complex Cp*FeN(SiMe$_3$)$_2$ was synthesized by the reaction of iron(II) chloride in THF with 1 equiv of KN(SiMe$_3$)$_2$ and subsequent addition of Cp*Li and was structurally characterized by X-ray diffraction; its “pogo-stick” structure is unprecedented in the chemistry of open-shell organometallics.*

The great interest in coordinatively and electronically unsaturated iron compounds[1] has been further spurred by the recent finding that six of the seven iron atoms in the FeMo-cofactor of molybdenum nitrogenase from *Azotobacter vinelandii* are essentially three-coordinate with a distorted-trigonal geometry.[2] Ligands that have been utilized to stabilize low-coordinate iron include bulky hydrocarbyl,[3] thiolato,[4] diazenido[5] and, most extensively, amido groups,[6] where a seminal contribution was made as early as 1963 by Bürger and Wannagat.[7] Bis(triorganosilyl)amido ligands, N(SiR$_3$)$_2$,[8] have been the most widely used in this context and have been shown to act predominantly as uninegative two-electron σ-bonding ligands toward transition-metal centers, exhibiting very little or no M−N π-bonding.[6g,9] Low-coordinate iron complexes containing such ligands are, for example, the monomeric compounds Fe(NSiMe$_2$Ph)$_2$[6f] and Fe(NSiMePh$_2$)$_2$[10] as well as Fe[N(SiMe$_3$)$_2$]$_2$,[6g] which is monomeric in the gas phase and in toluene solution but adopts a dimeric amido-bridged structure in the solid state;[6d] the yellow dimer reacts with THF, yielding the green monomeric adduct (THF)Fe[N(SiMe$_3$)$_2$]$_2$, which can be distilled without decomposition at 80 °C/0.2 Torr. All these iron(II) amido complexes are paramagnetic.

We have obtained a novel coordinatively and electronically unsaturated iron(II) bis(trimethylsilyl)amido complex. When iron(II) chloride in THF is allowed to react at 0 °C with 1 equiv of potassium bis(trimethylsilyl)amide and subsequently with 1 equiv of Cp*Li, a dark green solution is formed, from which yellow-orange crystalline Cp*FeN(SiMe$_3$)$_2$ can be isolated in good yield after standard workup. The product is extremely sensitive toward air and moisture. We suppose that the reaction involves an intermediate of the type (THF)$_n$Fe(Cl)N(SiMe$_3$)$_2$; the analogous cobalt species was prepared by Bürger and Wannagat.[7] Solutions of Cp*FeN(SiMe$_3$)$_2$ in C$_6$D$_6$ are yellow and diamagnetic, whereas those in THF-d_8 are green and paramagnetic. We therefore conclude that Cp*FeN(SiMe$_3$)$_2$ forms a solvent adduct in THF solution. However, in contrast to (THF)Fe[N(SiMe$_3$)$_2$]$_2$, the THF is only loosely bound and the adduct is not stable *in vacuo*.

A single-crystal X-ray diffraction study, which was performed for Cp*FeN(SiMe$_3$)$_2$, revealed a “one-legged piano stool” or “pogo-stick” structure (Figure 1).

The iron−carbon distances range from 224.0(2) to 226.9(2) pm (average 225.4 pm), which is *ca.* 20 pm longer than in decamethylferrocene.[11] The distance between the Fe atom and the Cp* ring centroid is 190.3 pm. This is almost identical with the iron−nitrogen bond length of 190.0(2) pm, which falls in the standard range (189.5(3)−193.8(2) pm)[6a] for crystallographically characterized iron(II) terminal amido compounds. These values are indicative of a comparatively high ionic contribution to the bonding of the iron center to its two ligands. The Cp* ring centroid−Fe−N angle is 172.4°. The bond parameters of the amido unit, which contains

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[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1997.

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S0276-7333(97)00743-7 CCC: $15.00
Publication on Web 01/06/1998

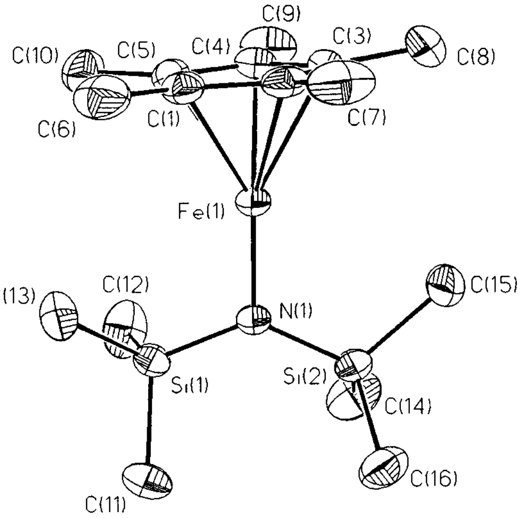

Figure 1. Molecular structure of Cp*FeN$(SiMe_3)_2$. Selected bond lengths (pm) and angles (deg): Si(1)−N(1) = 171.5(2), Si(2)−N(1) = 171.3(2), C(1)−C(2) = 142.7(3), C(1)−C(5) = 142.5(3), C(2)−C(3) = 141.5(3), C(3)−C(4) = 142.0(3), C(4)−C(5) = 141.4(3); Fe(1)−N(1)−Si(1) = 115.37(9), Fe(1)−N(1)−Si(2) = 118.25(9), Si(1)−N(1)−Si(2) = 125.91(10).

a trigonal-planar N atom (sum of angles 359.5°), are unexceptional.

The 14-valence-electron complex Cp*FeN$(SiMe_3)_2$ is the first example of a half-sandwich compound of the type CpFeX (X = uninegative two-electron ligand). There have been reports of species of the type Cp′FeHal (Cp′ = bulky cyclopentadienyl ligand, Hal = Cl, Br),[12] which can be prepared *in situ* by the metathesis of $FeHal_2$ with Cp′Li in THF, but these are most certainly solvates, which cannot be isolated due to their thermal instability. The half-sandwich metal(II) halide complexes (C_5-*i*-Pr_4H)MHal (M = Fe, Co, Ni), which are thermally stable crystalline compounds, are halogen-bridged dimers,[13] and the closely related complexes $[(C_4H_8N)(CH_2)_2C_5Me_4]FeCl$[14] and $[MeO(CH_2CH_2O)_3(CH_2)_3C_5Me_4]FeCl$,[15] which both contain a donor-functionalized cyclopentadienyl ligand,[16] are intramolecular Lewis base adducts.

The pogo-stick structure of Cp*FeN$(SiMe_3)_2$ is unprecedented in the chemistry of open-shell organometallics.[17,18]

We are currently investigating the chemistry of this compound and will report on our findings in due course.

Experimental Section

General Procedures. All manipulations were performed under 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. NMR spectra were recorded at 300 K with a Bruker DRX 500 spectrometer; TMS was used as external reference. Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld.

Preparation of Cp*FeN$(SiMe_3)_2$. A solution of potassium bis(trimethylsilyl)amide (2.93 g, 14.7 mmol) in THF (30 mL) was added dropwise with stirring to an ice-cold slurry of iron(II) chloride (1.86 g, 14.7 mmol) in THF (30 mL). The mixture was stirred at 0 °C for 14 h. A slurry of Cp*Li (prepared from Cp*H (2.00 g, 14.7 mmol) and *n*-BuLi (9.25 mL of a 1.59 M solution in hexanes, 14.7 mmol) in THF (30 mL)) was added dropwise with stirring, whereupon the color of the reaction mixture changed from brown to dark green. Stirring was continued at 0 °C for 30 min. Volatile components were removed *in vacuo* up to a temperature of 40 °C. The viscous residue, which had gradually turned orange during this procedure, was dissolved in *n*-pentane and filtered to remove insoluble salts. The solvent was removed *in vacuo*, leaving a dark orange oil, which was dissolved in a minimal amount of *n*-hexane. Crystallization at −70 °C afforded crude Cp*FeN$(SiMe_3)_2$ as orange crystals. The product was purified by bulb-to-bulb distillation at 90 °C/0.01 mbar. Recrystallization from a minimal amount of *n*-hexane afforded analytically pure Cp*FeN$(SiMe_3)_2$ as yellow-orange crystals: yield 3.35 g, 65%. ^1H NMR (500.1 MHz, C_6D_6): δ 0.00 (18 H, s, $SiMe_3$), 1.80 (15 H, s, Cp*). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ 2.6 ($SiMe_3$), 9.9 ($C_5\mathit{Me}_5$), 78.2 (C_5Me_5). Anal. Calcd for $C_{16}H_{33}NFeSi_2$: C, 54.68; H, 9.46; N, 3.99. Found: C, 54.33; H, 9.50; N, 4.05.

X-ray Data Collection, Structure Determination, and Refinement of Cp*FeN$(SiMe_3)_2$. Crystal data: triclinic, space group $P\bar{1}$, $a = 8.756(4)$ Å, $b = 9.647(3)$ Å, $c = 13.171(4)$ Å, $\alpha = 103.69(3)°$, $\beta = 99.05(3)°$, $\gamma = 105.12(3)°$, $V = 1014.7(6)$ Å^3, $Z = 2$, $d_{calcd} = 1.150$ g cm^{-3}, $F(000) = 380$, μ(Mo Kα) = 0.854 mm^{-1}, $\lambda = 0.71073$ Å, $T = 173(2)$ K, crystal size 1.10 × 0.60 × 0.50 mm. Of the 6229 total reflections, which were collected with a Siemens P2(1) four-circle diffractometer (ω scans with $1.64 < \theta < 30.07°$), 5877 were unique. The structure was solved by direct methods and developed routinely. Full-matrix least-squares refinement with 192 parameters was based on F^2. Hydrogen atoms were considered in calculated positions. All non-hydrogen atoms were refined anisotropically. The refinement converged at $R_F = 0.0430$ and $R_{wF} = 0.1201$ (for 5030 reflections with $I > 2\sigma(I)$; $w = [\sigma^2(F_o^2) + (0.0728P)^2 + 0.6037P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$); final GOF = 1.030. The final difference map showed no peak greater than 0.4 e Å^{-3} and no hole larger than −0.4 e Å^{-3}. Programs used were Siemens SHELXTL Plus and SHELXL-93.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the University of Bielefeld for financial support.

Supporting Information Available: Complete listings of crystallographic data, atomic coordinates, hydrogen positional parameters, and bond lengths and angles (6 pages). Ordering information is given on any current masthead page.

OM9707432

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