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Synthesis and Characterization of Three-Coordinate and Related β -Diketiminate Derivatives of Manganese, Iron, and Cobalt

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Treatment of M{N(SiMe₃)₂} (M = Mn, Fe, Co) with various bulky β -diketimines afforded a variety of new threecoordinate complexes which were characterized by UV-vis, ¹H NMR and IR spectroscopy, magnetic measurements, and X-ray crystallography. Reaction of the β -diketimine H(Dipp)NC(Me)CHC(Me)N(Dipp) (Dipp₂N^NH; Dipp = C₆H₃-2,6-Pr¹₂) with M{N(SiMe₃)₂} (M = Mn or Co) gave Dipp₂N^NMN(SiMe₃)₂ (M = Mn, 1; Co, 3) while the reaction of Fe{N(SiMe₃)₂} with Ar₂N^NH (Ar = Dipp, C₆F₅, Mes, C₆H₃-2,6-Me₂, or C₆H₃-2,6-Cl₂) afforded the series of iron complexes $Ar_2N^NFe\{N(SiMe_3)_2\}$ (Ar = Dipp, 2a; C_6F_5 , 2b; Mes, 2c; C_6H_3 -2,6-Me₂, 2d; C_6H_3 -2,6-Cl₂, 2e). This represents a new synthetic route to β -diketiminate complexes of these metals. The four-coordinate bis- β -diketiminate complex Fe{ $N^{(C_{6}F_{5})}$, 4, was also isolated as a byproduct from the synthesis of 2b. Direct reaction of the Dipp₂N[^]NLi with CoCl₂ gave the "ate" salt Dipp₂N[^]NCoCl₂Li(THF)₂, 5, in which the lithium chloride has formed a complex with Dipp₂N^ANCoCl through chloride bridging. The Fe(III) species Dipp₂N^ANFeCl₂, 6, was obtained cleanly from the reaction of FeCl₃ with Dipp₂N[^]NLi. Magnetic measurements showed that all the complexes have a high spin configuration. The different substituents in the series of iron complexes 2a-e allowed assignment of their paramagnetically shifted ¹H NMR spectra. The X-ray crystal structures 1-2d and 3 showed that they have a distorted three-coordinate planar configuration at the metals whereas complexes 4-6 have highly distorted fourcoordinate geometries.

Introduction

The divalent transition metal silvlamides $M{N(SiMe_3)_2}_2$ $(M = Mn, {}^{1}Fe, {}^{2} or Co^{3})$ are useful hydrocarbon soluble sources of M²⁺ that have semipolar and reactive M–N bonds. They possess two-coordinate monomeric structures in the vapor phase² but exist as amide bridged dimers in the crystalline state.⁴⁻⁶ In solution, at room temperature, they are essentially dissociated to monomers but are weakly associated at low temperatures in an entropy driven equi-

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librium.^{6,7} Their monomeric, coordinatively unsaturated structures confer high reactivity, and their chemistry has been dominated by reactions with Lewis bases such as THF,^{6,8} pyridine, or phosphines, or with protic reagents such as alcohols, phenols, thiols, selenols, tellurols,⁹ calixarenes,¹⁰ boronous acids,¹¹ secondary phosphines,¹² or silanols.¹³ Transamination reactions involving treatment of M{N- $(SiMe_3)_2$ with primary or secondary amines have not been extensively studied. Rare examples include the reaction of H_2NDipp (Dipp = C₆H₃-2,6-Prⁱ₂) with Mn{N(SiMe_3)₂}₂ to

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give $Mn_3\{\mu$ -N(H)Dipp $\}_4\{N(SiMe_3)_2\}_2^{14}$ and the reaction of $Mn\{N(SiMe_3)_2\}_2$ with the 1,2-diamine H(Dipp)NCH₂CH₂N-(Dipp)H to afford $Mn\{N(Dipp)CH_2CH_2N(Dipp)H\}_2$.¹⁵ The steric properties of the diprotic bidentate ligand H(Dipp)-NCH₂CH₂N(Dipp)H bear a resemblance to those of the monoprotic bidentate ligand H(Dipp)NC(Me)CHC(Me)N-(Dipp) which may be abbreviated as Dipp₂N^NH.¹⁶ This ligand and closely related ones have enjoyed considerable recent use in a variety of transition metal^{16–37} and main group complexes^{38–62} which have displayed a variety of stoichi-

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ometries, low-coordination numbers, and bonding. In addition, they have been used as model species for the active sites in metalloenzymes^{28,29,31} and as catalysts for olefin polymerization.^{16,19,22-25,32,33,40,44} Very recent work has disclosed the preparation and characterization of the iron salts $(Dipp_2N^N)Fe(\mu-Cl)_2Li(THF)_2$ and $\{(Dipp_2N^N)Fe(Cl)(\mu-Li(Dipp_2N^N)Fe($ Cl)₂Mg(THF)₂ and the neutral species (Dipp₂N^N)'FeCl in which three coordination has been achieved by increasing the steric properties of the β -diketiminate ligand via replacement of the methyl groups on the central C₃N₂ moiety by tert-butyl groups.⁶³ Moreover, reduction of the latter under N₂ has resulted in very interesting N₂ complexes of the type (Dipp₂N^N)'FeNNFe(N^NDipp₂)' and K₂(Dipp₂N^N)'Fe-NNFe(N^N'Dipp₂)'.⁶⁴ It is now shown that reaction of Dipp₂N^{Λ}NH and related β -diketiminate ligands, as represented by the general formula



with the amides $M\{N(SiMe_3)_2\}_2$ (M = Mn, Fe or Co) smoothly affords new β -diketiminates of the type (Ar_2N^N) - $MN(SiMe_3)_2$ where three coordination has been obtained with use of the bulky coligand $N(SiMe_3)_2$. In addition, it is shown that, in contrast to the reaction of LiN^NDipp₂ with FeCl₂ or CoCl₂ which afford "ate" complexes of the type Dipp₂- $N^NMCl_2Li(THF)_2$ (M = Fe⁶³ or Co), reaction of LiN^NDipp₂ with FeCl₃ affords the neutral derivative Dipp₂N^NFeCl₂.

Experimental Section

General Procedures. All work was performed by using Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atomspheres HE-43 drybox. All solvents were freshly distilled from Na/K and degassed three times immediately before use.

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β -Diketiminate Derivatives of Mn, Fe, and Co

The compounds $M{N(SiMe_3)_2}_2 {M = Mn, ^1 Fe, ^2 Co^3}$, Dipp₂- N^{NH} ,^{16,61} Mes₂N^NH,²² (2,6-Me₂C₆H₃)₂N^NH,²³ and (2,6-Me₂C₆H₃)₃N^NH,²³ and (2,6-Me₂C₆ Cl₂C₆H₃)₂N[^]NH²³ were synthesized by literature methods. Anhydrous CoCl₂ (Aldrich), FeCl₃ (Aldrich), and 1.6 M n-BuLi in hexanes (Acros) were purchased from the commercial suppliers and were used without further purification. ¹H NMR spectra were recorded in C₆D₆ or CDCl₃ at 300 MHz on a QE-300 spectrometer. Infrared spectra were obtained as Nujol mulls with use of a Perkin-Elmer-1430 spectrometer. Electronic absorption spectra were obtained on a Hitachi U-2000 UV-vis spectrometer. Melting points are uncorrected and were determined for samples in capillaries sealed with grease. For magnetic measurements, the samples were sealed under vacuum in 3.2 \times 2 mm^2 quartz tubing. The sample holder was designed to minimize the background signal. The sample magnetization was measured using a Quantum Design MPMSXL7 superconducting quantum interference device (SQUID) magnetometer. For each measurement, the sample was zero-field cooled to 5 K, and the magnetization was measured as a function of field to 2 T. The field was then reduced to 1 T, and the magnetization of the sample was measured in 5 K increments to 300 K.

 $(C_6F_5)_2N^{\wedge}NH$. A mixture of 2,3,4,5,6-pentafluoroaniline (8.0 g, 43.7 mmol), 2,4-pentanedione (1.9 g, 19.0 mmol), and p-toluenesulfonic acid (3.4 g, 18 mmol) in toluene (150 mL) was refluxed in a Dean-Stark apparatus for 24 h. The slurry was filtered to give a brown solid that was treated with 50 g of Na₂CO₃ in water (300 mL) and 300 mL of diethyl ether. The mixture was stirred for 45 min. The organic layer was isolated, dried with MgSO₄, and filtered. The solvent was removed, and the product was washed with 50 mL of cold methanol. Yield: 4.8 g (59%), mp 66-68 °C. ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 1.95 (s, 6H, CH₃), 5.20 (s, H, g-CH), 12.08 (s, H, NH). ¹³C{¹H} NMR (CDCl₃, 75 MHz, 25 °C): δ 21.0 (CH₃), 99.2 (γ-C), 119.9 (m-C), 136.5 (p-C), 139.5 (o-C), 142.8 (*i*-C), 164.2 (CN). ¹⁹F{¹H} NMR (CDCl₃, 376.12 MHz, 25 °C): δ -146.6 (m, 4F, o-F, ${}^{3}J = 22.9$ Hz, ${}^{4}J = 6.1$ Hz), -158.32 (t, 2F, p-F, ${}^{3}J = 21.3$ Hz), -160.78 (m, 4F, m-F, ${}^{3}J = 21.3$ Hz, ${}^{4}J = 6.1$ Hz).

Dipp₂N^NMnN(SiMe₃)₂ (1). A mixture of Mn{N(SiMe₃)₂}₂ (0.75 g, 2 mmol) and Dipp₂N^NH (0.84 g, 2 mmol) in a Schlenk tube was heated at 110–120 °C under reduced pressure (ca. 0.03 mm) until bubbling had ceased (ca. 5 min). Upon cooling to room temperature, a dark yellow solid was obtained. This was dissolved in hexane (15 mL) and cooled in a ca. -20 °C freezer overnight to afford the product as yellow crystals. Yield: 0.55 g (43%), mp 235–237 °C. IR (Nujol, cm⁻¹): 2950, 2920, 2840, 1520, 1310, 1170, 1095, 1015, 930, 870, 750, 660, 400, and 350. UV–vis (hexane, λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)): 231 (11 000), 376 (11 000), 443 (1040), and 466 (690). μ_{eff} : 5.65(3) μ_{B} .

Dipp₂N^NFeN(SiMe₃)₂ (2a). This was synthesized in a manner similar to the manganese derivative **1** with use of Dipp₂N^NH (0.84 g, 2 mmol) and Fe{N(SiMe₃)₂}₂ (0.75 g, 2 mmol) and recrystallized as orange plates from hexane. Yield: 0.47 g (37%), mp 212–214 °C. IR (Nujol, cm⁻¹): 2920, 2850, 1520, 1315, 1170, 1100, 1020, 980, 875, 760, 670, and 355. UV–vis (hexane, λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)): 318 (12 500), 371 (12 700), 483 (600), and 799 (600). μ_{eff} : 4.94(2) μ_{B} .

 $(C_6F_5)_2N^{\Lambda}NFeN(SiMe_3)_2$ (2b). The synthesis was accomplished in the same manner with use of $(C_6F_5)_2N^{\Lambda}NH$ (0.81 g, 1.88 mmol) and Fe{N(SiMe_3)_2}_2 (0.75 g, 2 mmol) to afford the product as orange-yellow crystals. Yield: 0.75 g (62%), mp 108–110 °C. IR (Nujol, cm⁻¹): 2920, 2840, 1510, 1500, 1445, 1370, 1310, 1250, 1010, 990, 825, 670, 630, and 350.

 $Mes_2N^{NFe}(SiMe_3)_2$ (2c). This was prepared in the same manner from Mes_2N^{NH} (0.66 g, 2 mmol) and $Fe[N(SiMe_3)_2]_2$ (0.75 g, 2 mmol) to afford the product as orange crystals. Yield: 0.51 g (46%), mp 135–137 °C. IR (Nujol, cm⁻¹): 2920, 2860, 1610, 1460, 1380, 1260, 1100, 800, and 350. UV–vis (hexane, λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 378 (12 400), 406 (11 100), 482 (3400), 779 (130), and 972 (250).

(2,6-Me₂C₆H₃)₂N[^]NFe(SiMe₃)₂ (2d). This was prepared in a manner similar to 2a as orange crystals from $(2,6-Me_2C_6H_3)_2N^{-}$ NH (0.60 g, 2 mmol) and Fe{N(SiMe₃)₂}₂ (0.75 g, 2 mmol). Yield: 0.49 g (47%), mp 88–90 °C. IR (Nujol, cm⁻¹): 2920, 2850, 1520, 1460, 1365, 1260, 1245, 1180, 1095, 1020, 970, 870, 760, 670, 350. UV–vis (hexane; λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)): 376 (12 000), 404 (10 900), 480 (3 200), 776 (130), and 970 (230).

(2,6-Cl₂C₆H₃)₂N[^]NFe(SiMe₃)₂ (2e). This was synthesized in a manner similar to 2a as orange crystals from $(2,6-Cl_2C_6H_3)_2$ N[^]NH (0.78 g, 2 mmol) and Fe{N(SiMe₃)₂}₂ (0.75 g, 2 mmol). Yield: 0.72 g (73%), mp 94–96 °C. IR (Nujol, cm⁻¹): 2920, 2840, 1525, 1435, 1370, 1255, 1195, 1150, 1020, 980, 930, 825, 675, and 365. UV–vis (hexane; λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)): 362 (10 000), 411 (8100), 490 (2100), and 780 (110).

Dipp₂N^NCoN(SiMe₃)₂ (3). This was prepared in a manner similar to the manganese derivative **1** and isolated as red needles from hexane. Yield: 0.35 g (30%), mp 192–194 °C. IR (Nujol, cm⁻¹): 2920, 2840, 1525, 1315, 1175, 1095, 1020, 930, 870, 720, 660, 385, and 360. UV–vis (hexane; λ_{max} (ϵ , M⁻¹ cm⁻¹)): 235 (14 300), 316 (14 300), 437 (1230), 470 (670). μ_{eff} : 4.81(3) μ_{B} .

Fe{**N**^**N**(**C**₆**F**₅)₂}₂ (**4**). This was obtained as red crystals from the mother liquor of **2b**. Yield: 0.70 g (38%), mp 206–208 °C. IR (Nujol, cm⁻¹): 2900(b), 2640, 2440, 1630, 1500, 1360, 1160, 1000, 765, 710, 700, 640, 530, 475, 330, and 300. UV–vis (hexane; λ_{max} (ϵ , M⁻¹ cm⁻¹)): 223 (8400), 338 (12 300), 437 (2900), 868 (230), 976 (140).

Dipp₂N^NCoCl₂Li(THF)₂ (5). *n*-BuLi (6.2 mL of a 1.6 M solution in *n*-hexane) was added dropwise to a stirred solution of Dipp₂NNH (4.0 g, 9.5 mmol) in ca. 30 mL of diethyl ether with cooling in an ice bath. After overnight stirring, the solution of the Dipp₂N^NLi was added dropwise to a suspension of CoCl₂ (1.24 g, 9.5 mmol) in THF (ca. 15 mL) with cooling in an ice bath. After overnight stirring, the color had changed to dark green. The solvents were removed under reduced pressure, and the residue was recrystallized from toluene (30 mL) as red crystals. Yield: 4.4 g (55%) IR (Nujol, cm⁻¹): 1520, 1460, 1315, 1260, 1175, 1100, 1040, 935, 890, 790, 755, 400, and 305. UV–vis (hexane; λ_{max} (ϵ , M⁻¹ cm⁻¹)): 250 (9200), 322 (9300), 432 (1900), 532 (1250), 615 (1100), and 868 (1150).

Dipp₂N^NFeCl₂ (6). The synthesis was accomplished with use of Dipp₂N^NLi (9.5 mmol) and FeCl₃ (1.54 g, 9.5 mmol) in ca. 15 mL of toluene. Filtration and cooling in ca. -20 °C freezer afford green crystals of **6** that were suitable for X-ray crystallography. Yield: 2.75 g (53%), mp 202–204 °C. IR (Nujol, cm⁻¹): 1520, 1460, 1375, 1335, 1315, 1260, 1096, 1020, 930, 795, 755, 400, and 365. UV–vis (hexane; λ_{max} (ϵ , M⁻¹ cm⁻¹)): 319 (8200), 382 (8200), 553 (4600), and 813 (1800).

X-ray Crystallographic Studies. Crystals of 1-2d and 3-6 were removed from the Schlenk tube under a stream of N₂ and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and quickly placed in the low-temperature nitrogen stream.⁶⁵ The data were recorded near 90 K (293 K for 6) for a Bruker SMART 1000 (Mo K α radiation and a CCD area detector). The SHELXTL version 5.03 program package was used for the structure solutions and refinements.⁶⁶ Absorption corrections were applied using the SADABS program.⁶⁷ The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-

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Table 1. Data Collection Parameters for Compounds 1, 2a-d, 3-6

	1	2a	2b	2c	2d	3	4	5	6
formula	C35H59Mn-	C35H59Fe-	C ₂₃ H ₂₅ F ₁₀ Fe-	C ₂₉ H ₄₇ Fe-	C ₂₇ H ₄₃ Fe-	C35H59Co-	C ₃₄ H ₁₄ F ₂₀ -	C _{47.5} H _{67.5} Cl ₂ -	C ₂₉ H ₄₁ Cl ₂ -
	N_3S_{12}	N_3S_{12}	N_3S_{12}	N_3S_{12}	N_3S_{12}	N_3S_{12}	FeN ₄	$CoL_1N_2O_2$	FeN ₂
fw	632.97	633.88	645.49	549.73	521.67	636.96	914.34	835.31	544.39
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
a (Å)	9.0944(6)	9.0729(5)	10.1239(5)	17.091(3)	20.321(2)	9.0909(5)	10.1625(4)	16.455(1)	12.5392(6)
b (Å)	20.232(1)	20.186(1)	13.8608(6)	15.102(3)	14.173(1)	20.199(1)	11.3316(4)	17.827(1)	19.5799(9)
<i>c</i> (Å)	20.278(1)	20.215(1)	21.041(1)	12.501(3)	20.577(2)	20.105(1)	15.9244(6)	15.830(1)	13.1323(6)
α (deg)			104.737(1)				100.059(1)		
β (deg)	90.053(2)	90.503(1)	90.050(1)	101.248(9)	96.404(5)	91.090(1)	95.239(1)	91.486(1)	117.136(1)
γ (deg)			100.889(2)				111.038(1)		
$V(Å^3)$	3731.3(4)	3702.1(3)	2800.4(2)	3164.5(11)	5927(1)	3691.4(1)	1673.5(1)	4642.2(5)	2869.3(2)
Ζ	4	4	4	4	8	4	2	4	4
μ (Mo K α) (mm ⁻¹)	0.444	0.498	0.709	0.573	0.608	0.556	0.597	1.195	1.260
<i>T</i> / K	90(2)	90(2)	90(2)	90(2)	91(2)	90(2)	90(2)	90(2)	293(2)
R1	0.0473	0.0349	0.0341	0.0302	0.0493	0.0342	0.0342	0.0394	0.0481
wR2	0.114	0.0933	0.0928	0.0867	0.1463	0.0864	0.0881	0.1047	0.1048

hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions using a riding model included in the SHELXTL program. Some details of the data collection and refinement are given in Table 1. Further details are provided in the Supporting Information.

Results and Discussion

Synthesis. The compounds that have been synthesized and characterized in this paper are indicated by the formulas $Dipp_2N^NMnN(SiMe_3)_2$, 1; $Dipp_2N^NFeN(SiMe_3)_2$, 2a; $(C_6F_5)_2N^NFeN(SiMe_3)_2$, **2b**; Mes₂N^{Λ}NFeN(SiMe₃)₂, **2c**; $(2,6-Me_2C_6H_3)_2N^NFeN(SiMe_3)_2, 2d; (2,6-Cl_2C_6H_3)_2-$ N^NFeN(SiMe₃)₂, 2e; Dipp₂N^NCoN(SiMe₃)₂, 3; Fe{N^N- $(C_6F_5)_2$, **4**; Dipp₂N^ANCoCl₂Li(THF)₂, **5**; Dipp₂N^ANFeCl₂, 6, where the abbreviation N^N has been used to represent the central ring of the β -diketiminate ligand, as illustrated in the Introduction. The series of eight compounds 1-4 were obtained in a facile manner by the direct reaction of the Ar₂N^{Λ}NH ligand with the metal amides M{N(SiMe₃)₂}₂ at ca. 100 °C in the absence of solvent. Purification was accomplished by recrystallization from hexane to give the products as air-sensitive crystals with nonoptimized yields in the range 40-70%. It was found during the preparation of pentafluorphenyl compound **2b** that both $N(SiMe_3)_2$ groups could be displaced from iron to give bis- β -diketiminate species 4. The double substitution probably occurs as a result of the higher acidity of $(C_6F_5)_2N^{\wedge}NH$ and the fact that it is the least sterically crowding of the β -diketiminate ligands used in this work. There was no evidence for a bis-(diketiminate) product in any of the reactions with the bulkier Dipp₂N[^]NH ligand. The lack of a doubly substituted product may be contrasted with the reaction between the sterically related diamine H(Dipp)NCH₂CH₂(Dipp)H and Mn- ${N(SiMe_3)_2}_2$ which afforded the unusual disubstituted species Mn{N(Dipp)CH₂CH₂N(Dipp)H}₂.¹⁵ The reaction of LiN[^]NDipp₂ with CoCl₂ in the hexane/ether/THF solvent mixture afforded the "ate" product 5 as red crystals. This result is similar to the previously reported synthesis of the iron compound Dipp₂N^NFeCl₂Li(THF)₂ which also crystallizes as an "ate" complex.63 Seemingly, the combination of Dipp₂N^AN and a single chloride ligand in the putative species Dipp₂N^{\wedge}NMCl (M = Fe or Co) is insufficiently crowding to prevent association with another chloride. However, it has been shown that when Dipp₂N^{\wedge}N ligand was modified by replacement of the methyls on the ligand backbone with *tert*butyl groups (designated (Dipp₂N^{\wedge}N)') the neutral species (Dipp₂N^{\wedge}N)'-

FeCl was obtained in which lithium chloride was eliminated and the iron is bound only to the β -diketiminate ligand and a chloride to yield a three-coordinate metal environment.⁶³ Direct reaction of Dipp₂N^NLi with FeCl₃ in toluene afforded the neutral Fe³⁺ compound Dipp₂N^NFeCl₂, **6**, as green crystals in ca. 50% yield. No problems were encountered with the separation of LiCl, probably as a result of the more crowded, higher coordinate, character of the iron.

Spectroscopic and Magnetic Studies

The magnetic moments of the compounds were measured in C₆D₆ solution by the Evans' method. These measurements afforded $\mu_{eff}(C_6D_6)$ values that were consistent with high spin d⁵ (1, $\mu_B = 5.9(1)$; **6**, $\mu_B = 5.9(1)$), d⁶ (**2a**-**e** and **4**, $\mu_B =$ 4.9-5.1(1)), and d⁷ (**3**, $\mu_B = 4.9(1)$; **5**, $\mu_B = 5.0(1)$) configurations that have five, four, and three unpaired electrons, respectively. Magnetic studies of crystalline samples of **1**, **2a**, and **3** were also undertaken. Plots of $1/\chi$ versus temperature in the range 5-300 K afforded linear or near linear relationships. The compounds displayed the expected Curie–Weiss behavior and afforded μ_{eff} values of 5.65(3) μ_B (**1**), 4.94(2) μ_B (**2a**), and 4.81(3) μ_B (**3**). These values are slightly lower than the solution values in the case of **1** and **3**. The reasons for these differences are unclear.

The presence of unpaired electrons in all the compounds gives rise to paramagnetically shifted ¹H NMR spectra. The spectra of the iron compounds $2\mathbf{a}-\mathbf{e}$ (Table 2), which differ only in their nitrogen substituents, can be assigned as a result of the effects of the differences in substitution on the signals. The simplest ¹H NMR spectrum arises from C₆F₅ substituted species **2b** which has only three types of magnetically inequivalent hydrogens. In C₆D₆ at 25 °C, three major broadened signals were observed at δ –9.58, 50.84, and 93.45. In addition, a minor signal at –66.50 ppm was observed. The three major signals can be assigned to β -Me (δ –9.58), N(SiMe₃)₂ (δ 50.84), and γ -H (δ 93.45). Their

⁽⁶⁵⁾ Hope, H. Prog. Inorg. Chem. 1995, 41, 1.



Figure 1. ¹H NMR spectrum of (2,6-Me₂H₃C₆)₂N[^]NFeN(SiMe₃)₂ (2d) in C₆D₆ at 25 °C. Solvent and free ligand peaks are marked x.

Table 2. ¹H NMR Shifts (ppm) of the Iron Compounds $Ar_2N^NFeN(SiMe_3)_2$, **2a**-e in C₆D₆ at ca. 298 K

	Ar	γ-Н	β -Me	N(SiMe ₃) ₂	o-R	<i>m</i> -H	p-H(R)
2a	C ₆ H ₃ -2,6-Pr ⁱ ₂	83.2	-9.2	13.6	3.2, -44.1	51.6	-52.8
2b 2c 2d 2e	$\begin{array}{c} C_6F_5\\ C_6H_22,4,6Me_3\\ C_6H_32,6Me_2\\ C_6H_32,6Cl_2 \end{array}$	93.45 93.73	-9.58 -12.41 -12.51 -9.46	50.84 19.44 20.35 30.34	-55.41 -55.91	48.01 46.24 9.13	27.2 (Me) -65.92 -67.99

integration corresponded to the ratio of β -Me (6), N(SiMe₃)₂ (18), and γ -H (1) hydrogens present in the complex. The minor signal at δ –66.50 may be due to a small amount of bis- β -diketiminate complex 4 which is a byproduct of the reaction. The assignment of the δ 50.84 signal to the N(SiMe₃)₂ hydrogens is also supported by the similarity of the shift value to the δ 63.5 signal observed for monomeric $Fe{N(SiMe_3)_2}_2^7$ and the methyl signals in the related monomeric complexes $Fe\{N(SiMe_2Ph)_2\}_2$ (δ 49.9) and Fe{N(SiMePh₂)₂}₂ (δ 57.6).⁶⁸ A change in the aryl substituents at nitrogen from C_6F_5 (2b) to C_6H_3 -2.6-Cl₂ (2e) should result in two new hydrogen signals (i.e., of the meta and para hydrogens), and this is what is observed. The signals in the spectrum of **2e** due to N(SiMe₃)₂ (δ 30.34), β -Me (δ -9.46), and γ -H (δ 93.73) are readily assignable. The new signals appear at δ 9.13 and δ -67.99. These are assignable to the meta and para hydrogens. They integrate in a 2:1 ratio and in the correct intensity relative to the $N(SiMe_3)_2$ and β -Me signals. Replacement of the chlorines in **2e** with methyl groups affords 2d whose ¹H NMR spectrum is shown in Figure 1. The β -Me (δ -12.51) and N(SiMe₃)₂ (δ 20.35) signals of 2d are shifted slightly upfield in comparison with

those of **2e**. The *p*-H signal (δ -65.92) is very close to that in **2e** but the *m*-H signal is observed at δ 46.24. The new signal at δ -55.91 is attributable to the *o*-Me hydrogens. No signal readily assignable to γ -H could be observed. The mesityl substituted 2c differs from 2d at the para positions only. Thus, the chemical shifts of β -Me, N(SiMe₃)₂, *o*-Me, and *m*-H of 2c are very similar to those observed in 2d. The *p*-H signal seen at δ -65.92 in **2d** is not observed in **2c**. Instead, a new, more intense, narrow signal at δ 27.2, attributable to the *p*-Me of the mesityl groups, is observed. Finally, in 2a, the resonances at δ -9.2 and δ 13.6 are assignable to the β -Me hydrogens and N(SiMe₃)₂ groups, and the signal at δ 51.6 is due to the *m*-Hs. These values are similar to those observed in 2c and 2d. Assignments of further peaks at δ -52.8 and δ 83.2 to the *p*-H and γ -H signals seem reasonable in view of their similarity to the corresponding signals in 2b, 2d, and 2e. The assignment of the signals associated with the Prⁱ substituents is more complicated because the methyl groups are diastereotopic, and two equally intense resonances which integrate in the ratio 12H each (when their intensity is compared to the N(SiMe₃)₂ and β -Me signals) were observed at δ 3.2 and -44.1.

The electronic spectra of 1-6 are characterized by intense absorptions (ϵ values as high as 14 000) at wavelengths generally shorter than 380 nm that are attributable to $\pi - \pi^*$ transitions of the β -diketiminate and aryl substituents or metal- β -diketiminate charge transfer transitions. These intense peaks tail into the visible region, and this feature is probably responsible for the prevalence of the yellow to red color of the majority of the complexes. Less intense absorptions are observed at longer wavelengths, and those that occur at ca. <500 nm are usually shoulder features on the more intense $\pi - \pi^*$ absorption at shorter wavelengths. The spectra of the iron complexes $2\mathbf{a} - \mathbf{e}$ feature two

⁽⁶⁶⁾ SHELXL, version 5.1; Bruker AXS: Madison, WI.

⁽⁶⁷⁾ SADABS an empirical absorption correction program, part of the SAINTPlus NT version 5.0 package; Bruker AXS: Madison, WI, 1998.

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Figure 2. Illustrations (30% thermal ellipsoids) of the structures of Dipp₂N^{Λ}NMnN(SiMe₃)₂ (1), (C₆F₅)₂N^{Λ}NFeN(SiMe₃)₂ (2b), Dipp₂N^{Λ}NCoN(SiMe₃)₂ (3), Fe{N^{Λ}N(C₆F₅)₂} (4), Dipp₂N^{Λ}NCoCl₂Li(THF)₂ (5), and Dipp₂N^{Λ}NFeCl₂ (6). H atoms are not shown. Selected bond distances and angles are in Table 3.

prominent absorptions in the ranges 480–490 nm and 775– 790 nm with a shoulder feature at ca. 400 nm visible for **2c**, **2d**, and **2e**. A weak band at ca. 970 nm in **2c** and **2d** is also apparent. The ground state of the free ion Fe²⁺(d⁶) term is ⁵D, and this is expected to split into ⁵A' + ⁵E' + ⁵E'' terms in a trigonal planar (D_{3h}) field so that at least two d–d transitions are expected. However, the geometric distortions due to the β -diketiminate ligand lower the local symmetry at the metal further to $C_{2\nu}$. Thus, the E bands could be further split which, if great enough, could give rise to further absorptions. However, the spectra of **2a** suggest that this splitting is not large.

Structures

All compounds except **2e** were characterized by X-ray crystallography. Six of these nine structures, that is, **1**, **2a**–**d**, and **3**, are related in that they feature the metal bound to one β -diketiminate and one N(SiMe₃)₂ ligand. Representative structures are shown in Figure 2. Selected bond lengths and angles are given in Table 3. They display an essentially planar, three-coordinate^{69–72} geometry at the metals. How-

ever, there are very marked deviations of the interligand angles from 120°. The narrowest angle in each complex is associated with the β -diketiminate ligand where the N(1)-M-N(2) angles are in the range 92.57(6)-96.60(4)°. The remaining interligand angles are wider and span the range 126.98(5)-139.76(5)°. Another notable structural distortion concerns the MN₂C₃ ring geometries which display folding along the $N(1)\cdots N(2)$ line in the case of 1, 2a, and 3 (fold angles = ca. 165°) but are much closer to planarity for 2b, 2c, and 2d. It is noteworthy that the greatest folding is observed in the derivatives of the bulkiest Dipp2N^N ligand (i.e., complexes 1, 2a, and 3) and this finding is consistent with previous structural studies of other metal complexes of this ligand where folding was attributed to the steric requirements of the Dipp substituents.⁶² Within the β -diketiminate rings, the N₂C₃ moiety is planar, and the N-C and C-C distances lie in the narrow ranges 1.328(2)-1.347(2)Å and 1.396(3) - 1.416(2) Å consistent with the multiple character of these bonds. The internal angles within the rings display little variation across the series. In each complex, the widest angle is observed at C(2) which has an average value of 129.3(4)°. The angle in each complex is within ca. 0.6° of this value. The M–N bonds to the β -diketiminate ligands are ca. 0.05-0.10 Å longer than those to the N(SiMe₃)₂ groups. This is consistent with their semidative character. The compounds 1, 2a, and 3 have the same ligand

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Table 3. Selected Bond Distances (Å) and Angles (deg) for 1-5

	1	2a	3
M-N(1)	2.050(1)	2.027(1)	1.982(1)
M-N(2)	2.096(1)	1.988(1)	1.947(1)
M-N(3)	1.992(1)	1.928(1)	1.903(1)
N(1)-M-N(2)	92.57(5)	94.33(4)	96.60(4)
N(1)-M-N(3)	135.81(6)	131.07(4)	129.03(4)
N(2)-M-N(3)	131.54(6)	134.39(4)	132.83(4)
M - N(1) - C(6)	118.98(10)	116.96(7)	118.20(8)
M - N(2) - C(18)	116.66(10)	118.95(7)	119.39(8)
N(1) - C(1)	1.342(2)	1.328(2)	1.330(2)
N(2) - C(3)	1.325(2)	1.340(2)	1.339(2)
C(1) = C(2) C(2) = C(3)	1.396(2)	1.410(2) 1.400(2)	1.411(2) 1.206(2)
V(2) = V(3) V(3) = Si(1)	1.410(2) 1.707(2)	1.400(2) 1.716(1)	1.390(2) 1.713(1)
N(3) - Si(2)	1.707(2) 1.709(2)	1.710(1) 1.718(1)	1.713(1) 1.721(1)
M = N(3) = Si(1)	109.95(8)	111.77(5)	114.72(6)
M - N(3) - Si(2)	121.88(8)	121.58(6)	125.49(6)
Si(2) - N(3) - Si(3)	127.12(8)	125.50(6)	125.49(6)
fold angle/metal	164.2/0.394	164.8/0.365	165.3/0.340
distance from			
N ₂ C ₃ plane			
	2b	2c	2d
M-N(1)	2.008(1)	1.9969(9)	1.999(2)
M-N(2)	1.993(1)		1.990(2)
M-N(3)	1.908(1)	1.915(1)	1.917(2)
N(1) - M - N(2)	93.20(5)	95.73(5)	94.23(8)
N(1) - M - N(3)	126.98(5)	132.13(3)	129.79(8)
N(2) = M = N(3) M N(1) C(2)	139.76(5)	119 00(7)	135.88(8)
M = N(1) = C(2) M = N(1) = C(2)	110.20(10) 116.28(10)	118.90(7)	110.3(2) 121.2(2)
N(1) = C(2)	1341(2)	1 338(1)	121.2(2) 1 331(3)
N(2) - C(2)	1.347(2)	1.550(1)	1.331(3) 1.346(3)
C(1) - C(2)	1.399(2)	1.404(1)	1.408(3)
C(2) - C(3)	1.401(2)		1.396(3)
N(3) - Si(1)	1.718(1)	1.7221(7)	1.726(2)
N(3)-Si(2)	1.716(1)	. ,	1.714(2)
M - N(3) - Si(1)	114.81(7)	118.51(4)	114.5(1)
M-N(3)-Si(2)	115.52(7)		120.2(1)
Si(2)-N(3)-Si(3)	129.31(8)	122.98(8)	124.7(1)
fold angle/metal	178.6/0.028	178.4/0.031	157.3/0.556
distance from			177.8/0.039
N_2C_3 plane			
	4	5	6
M(1)-N(1)	2.038(1)	1.963(2)	1.978(2)
M(1) - N(2)	2.013(1)	1.957(2)	1.951(2)
M(1)-N(3)	2.016(1)		
M(1) - N(4)	1.999(1)		
M(1)-Cl(1)		2.2933(6)	2.1852(6)
M(2) - Cl(2)	1.005(0)	2.2955(6)	2.2106(6)
N(1) - C(1) N(2) - C(2)	1.337(2)	1.336(3)	1.331(3)
N(2) = C(3) N(2) = C(19)	1.343(2) 1.224(2)	1.55493)	1.545(3)
N(3) = C(18) N(4) = C(20)	1.334(2) 1.250(2)		
C(1) = C(20)	1.330(2)	1 /05(3)	1 /15(3)
C(1) = C(2) C(2) = C(3)		1.402(5)	1.413(3) 1 401(3)
N(1) - Fe(1) - N(2)	89,52(5)	98,23(8)	95,57(7)
N(3) - Fe(1) - N(4)	92.67(5)	20.23(0)	20.01(1)
N(1) - Fe(1) - N(4)	121.00(5)		
N(2) - Fe(1) - N3)	118.54(5)		
Fe(1) - N(1) - C(6)	119.72(9)	119.03(14)	121.51(1)
Fe(1) - N(2) - C(12)	120.68(9)	118.601(4)	~ /
Fe(1) - N(2) - C(18)			124.9(1)
Cl(1)-Fe(1)-Cl(2)		100.18(2)	117.15(3)
fold angle/metal	144.0/0.305	166.0/0.317	143.5/0.797
distance from	168.3/0.098		
N_2C_3 plane			

set (isoleptic), and the M–N bond lengths are in the sequence Mn-N > Fe-N > Co-N which is consistent with the decreasing size of the M^{2+} ions.⁷⁴ The M–N(SiMe₃)₂ distances are very similar to the terminal M–N bond lengths

in the neutral M(II) dimers $[M{N(SiMe_3)_2}_2]_2^{4-6}$ which also feature three-coordinate metals. However, they are up to ca. 0.08 Å longer than the M–N distances in the threecoordinate, M(II) anions $[M{N(SiMe_3)_2}_3]^{-.73}$ The longer M–N distances in the latter are probably a result of increased interelectronic repulsion due to the presence of negative charge from the "extra" electron. The terminal MNSi₂ moieties in **1**, **2**, and **3** have planar geometries (as they have in all the structures), and they are oriented at angles of ca. 74° with respect to the MN₃ coordination planes.

The structures of the series of four iron derivatives 2a-dalso display interesting trends. The Fe–N (β -diketiminate) bond lengths are all within 0.01 Å of each other and have an average value of 2.000(9) Å. This is significantly longer than the 1.948(2) Å reported for (Dipp₂N^N)'FeCl (in which the Me groups on the core ring are replaced by Bu^t groups).⁶³ Seemingly, the electronegative chloride ligand in the latter complex decreases the effective ionic radius of iron. This, together with the relatively small size of Cl, which relieves steric crowding, results in shorter Fe-N bonds. The trend for the $Fe-N(SiMe_3)_2$ bond lengths in 2a-d lends support to the importance of steric effects. The longest distance, 1.928(1) Å, is observed for the bulkiest $Dipp_2N^N$ derivative, **2a**, whereas the shortest distance, 1.908(1) Å, is seen with the least bulky $(C_6F_5)_2N^N$ complex, **2b**. The essentially equal intermediate distances of 1.915(1) and 1.917(2) Å are observed with the Mes₂N^N and 2,6-Me₂C₆H₃N^N derivatives 2c and 2d which have almost identical steric properties near the iron and sizes between the extremes of **2a** and **2d**. In essence, the observed trend suggests that the bond length variations in these complexes are mainly a result of steric effects. However, electronic effects may also play a role because the widest Si-N-Si angle (129.31(3)°) corresponds to the shortest Fe–NSi₂ bond in the least crowded **2b**, which suggests that greater charge separation occurs across the Fe-NSi₂ bond. In addition, the torsion angles between FeNSi₂ and FeN₃ do not display a regular pattern. Thus, 2b, the least sterically crowded molecule in the series, has an average torsion angle of 71.8° whereas the bulkier mesityl substituted 2c has a torsion angle of 52.3° and the sterically very similar 2d has a torsion angle of 85.0°.

The three compounds 4, 5, and 6 are also illustrated in Figure 2. The structure of 4 shows that iron is bound to two β -diketiminate ligands to afford an FeN₄ array that approximates D_{2d} symmetry with an average Fe–N distance of 2.017(11) Å. However, this averaged distance obscures the fact that for each β -diketiminate ligand one of the Fe–N distances is ca. 0.02 Å longer than the other, for example, Fe–N(1),N(2) = 2.038(1), 2.013(1) Å. The origin of this difference is uncertain, and it could be due to several factors among which are the unequal occupancy of $d_{x^2-y^2}$ and d_{z^2} orbitals of a d⁶ electron configuration in an approximately tetrahedral crystal field and crystal packing effects. The Fe–N distances in 4 are on average longer than the Fe–N(β -diketiminate) distances in 2b, 2c, and 2d but are

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similar to those in **2a**. The lengthening in **4** is consistent with the higher coordination number of iron in this complex. The greater steric crowding in **2a** apparently eliminates the difference so that very similar distances are observed. Both β -diketiminate rings display folding, but the amount of folding in each ring is quite different. For the ring associated with N(1) and N(2), the fold angle is 154.0°, and the iron is 0.305 Å out of the N₂C₃ plane. For the N(3) and N(4) ring, the angle is 168.3°, and the deviation is 0.098 Å.

Cobalt species **5** crystallizes with 1.5 toluene molecules per asymmetric unit. The cobalt is bound to two β -diketiminate nitrogens and also to two chlorides which act as bridges to lithium. The lithium is further complexed by two THF oxygens. Thus, both metals have distorted tetrahedral coordination. The structure is similar to that of recently reported iron complex Dipp₂N^NFeCl₂Li(THF)₂.⁶³ The Co–N and Co–Cl bonds, av 1.960(3) and 2.294(1) Å, are shorter by ca. 0.04 Å than the corresponding Fe–N and Fe–Cl distances in the iron species which is in keeping with the smaller effective ionic radius of Co²⁺ relative to Fe²⁺.⁷⁴ As in the iron complex, the narrowest interligand angle in the Co²⁺ coordination sphere involves the β -diketiminate ligand (98.23(8)°). The Li–Cl and Li–O distances 2.340(4) and 1.90(1) Å are also similar to those seen in the iron complex.

Iron(III) complex **6** is monomeric and features the metal in distorted tetrahedral coordination with Fe–N distances that are ca. 0.03 Å shorter than those in compounds $2\mathbf{a}-\mathbf{d}$. This is unexpected on the basis of the higher iron coordination number but is in agreement with the higher oxidation state of iron in **6**. In contrast, the average Fe–Cl distance, ca. 2.20 Å, in 6 is longer than the 2.172(7) Å observed in $(Dipp_2N^N)$ 'FeCl which is in agreement with the higher iron coordination number but not its higher oxidation state.⁶³ The structure of 6 may be compared with those recently reported for Dipp₂N[^]NVCl₂²² and the group 13 derivatives Dipp₂N[^]- $NMCl_2$ (M = Al, Ga, or In).⁶² The structural parameters for 6 and Dipp₂N^ANGaCl₂ are particularly close although the compounds are not isomorphous. However, the distortions in 6 are greater than those in the DippN^N group 13 metal halide derivatives; the iron lies 0.797 Å out of the averaged core N_2C_3 plane, and there is an angle of 143.5° between the FeN₂ and N₂C₃ planes. In sharp contrast to the monomeric formulas of **6** and its vanadium analogue,²² the recently reported chromium derivative {Dipp₂N^{Λ}NCr(Cl)(μ -Cl)}₂ is dimeric.³³ The reasons for the differences in association for the complexes are not obvious. The structure of 6 also resembles those of the more crowded (Dipp₂N^N)'ScCl₂³² and (Dipp₂N^N)'TiCl₂²² complexes in which the methyl substituents on the β -diketiminate ring are replaced by tertiary butyl groups.

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