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Differing Coordination Environments in Transition Metal Derivatives of 1,8-Bis(silylamido)naphthalene Ligands

Alexander J. Blake, Nicola L. Gillibrand, Graeme J. Moxey, and Deborah L. Kays*

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom.

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Four low-coordinate transition metal amido complexes featuring sterically demanding 1,8-bis(silylamido)naphthalene ligands are reported. Reaction of one molar equivalent of 1,8-$C_{10}H_6(NLiSiMe_3)_2$ with $ZnCl_2$ yields the structurally authenticated dimer [1,8-$C_{10}H_6(NSiMe_3)_2Zn]_2$ (**1**), where the 1,8-bis(silylamido)naphthalene moiety is acting as both a chelating and bridging ligand. The effect on the resulting transition metal complexes of increasing the steric demands of the ligand was investigated, using the triisopropylsilyl-substituted ligand 1,8-$C_{10}H_6(NSi^iPr_3)_2$. Reaction of one molar equivalent of 1,8-$C_{10}H_6(NLiSi^iPr_3)_2$ with $ZnCl_2$ or $FeCl_2(THF)_{1.5}$ yields 1,8-$C_{10}H_6(NSi^iPr_3)_2M(\mu\text{-Cl})Li(THF)_3$ (M = Zn, **2**; M = Fe, **3**), respectively; the coordination of the $ClLi(THF)_3$ moiety to the metal center in these compounds is a rare structural motif in the coordination chemistry of the d-block elements. Analogous reaction of 1,8-$C_{10}H_6(NLiSi^iPr_3)_2$ with $MnCl_2$ affords the mixed-metal Li−Mn−amido complex 1,8-$C_{10}H_6(NSi^iPr_3)_2Li(THF)MnCl(THF)$ (**4**) which features an unusual $LiMnN_2$ core.

Introduction

The use of sterically demanding amido ligands has allowed the isolation of a number of low-coordinate transition metal species. For example, utilization of $N(SiMe_nPh_{3-n})_2^-$ ($n = 0, 1, 2$), $NRBR'_2$ (R = Ph, R′ = Mes; R = R′ = Mes where Mes = 2,4,6-$Me_3C_6H_2$) and the sterically demanding carbazol-9-yl $NC_{12}H_4Me_2$-3,6-Ph_2-1,8^- has permitted the isolation of complexes featuring a range of two-coordinate open-shell transition metal centers, from Cr(II) through to Ni(II).[1−6] In addition, two-coordinate Fe(II) amido complexes have been formed using the $N(SiMe_3)C(^tBu)CH(C_{10}H_7\text{-}1)^-$, $N(CH_2{}^tBu)(Dipp)^-$ (Dipp = 2,6-$^iPr_2C_6H_3$), and $N^tBu_2^-$ ligands.[7−9]

The utilization of bidentate amido ligands featuring naphthalene frameworks has imparted significant structural rigidity to the resulting complexes, in addition to providing significant steric bulk. Sterically demanding 1,8-bis(silylamido)naphthalene ligands have been utilized in the stabilization of main group compounds, including lithium complexes,[10−13] mixed Tl/Li and Mg/Li systems,[10,11] group 13 complexes,[14−17], and stannylenes.[17,18] Additionally, these bulky 1,8-bis(silylamido)naphthalene systems have also been utilized in the formation of titanium and zirconium complexes which have been shown to act as olefin polymerization catalysts.[15,19−21]

As part of our ongoing investigations into the transition metal chemistry of sterically demanding amido ligands, we have been exploring the utilization of 1,8-bis(silylamido)naphthalene frameworks. In this paper we describe the use of

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*To whom correspondence should be addressed. E-mail: Deborah.Kays@nottingham.ac.uk. Fax: +44 115 9513555.

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1,8-$C_{10}H_6(NLiSiR_3)_2$ (R = Me, ^{i}Pr) ligands in the stabilization and isolation of low-coordinate amido complexes of Mn, Fe, and Zn. The structural rigidity conferred by the naphthalene backbone, together with the ease of modification of the silyl substituents in the 1 and 8 positions of these ligands, allows the design of pockets with varying steric demands. The use of these ligand systems has facilitated the stabilization of complexes featuring unusual coordination modes for the transition metals.

Experimental Section

All manipulations were performed under a nitrogen or argon atmosphere using standard Schlenk line and glovebox techniques. Hexane, THF, and toluene were dried by passing through a column of activated alumina and degassed with a stream of argon prior to use. All solvents were stored over a potassium mirror, with the exception of THF which was stored over activated 4 Å molecular sieves prior to use. Benzene-d_6 (Goss) was dried over potassium and degassed with three freeze−pump−thaw cycles prior to use. $MnCl_2$ (Strem) was used as received. 1,8-$C_{10}H_6(NLiSiMe_3)_2$, 1,8-$C_{10}H_6(NLiSi^iPr_3)_2$, $FeCl_2(THF)_{1.5}$, and anhydrous $ZnCl_2$ were prepared by minor modification of literature methods.[12,13,22,23] Mass spectra were measured by the EPSRC National Mass Spectrometry Service Center, University of Wales, Swansea, UK. Perfluorotributylamine was used as the standard for high-resolution EI mass spectra. Elemental microanalyses were performed by Mr. Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK. ^{1}H, ^{13}C, ^{29}Si, and ^{7}Li NMR for **1** and **2** were collected on Bruker DPX 300 or DPX 400 spectrometers. Chemical shifts are quoted in ppm relative to TMS (^{1}H, ^{13}C, and ^{29}Si) and LiCl/D_2O solution (^{7}Li). NMR data for paramagnetic complexes **3** and **4** were collected (Bruker DPX 300 spectrometer), but were found to be broad and uninformative and are therefore not reported herein. Magnetic moments for **3** and **4** were ascertained using Evans' method at 298 K in benzene-d_6.[24,25] Yields refer to purified products and are not optimized.

Preparation of [1,8-$C_{10}H_6(NSiMe_3)_2Zn]_2$ (1). Equimolar quantities of $ZnCl_2$ (0.07 g, 0.5 mmol) and 1,8-$C_{10}H_6(NLiSiMe_3)_2$ (0.16 g, 0.5 mmol) were allowed to react in a mixture of toluene (10 mL) and THF (2 mL) at room temperature over a period of 16 h, giving rise to a yellow solution. Volatiles were removed in vacuo and the resultant yellow solid was extracted with hexane (20 mL). Cooling of the saturated hexane solution to −30 °C afforded yellow crystals of **1·C_6H_{14}** suitable for single crystal X-ray diffraction studies. The crystals were dried in vacuo, affording **1** which was used for spectroscopic characterization. Yield 0.11 g, 60%. ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ 0.03 (s, 18H, $Si(CH_3)_3$), 0.64 (s, 18H, $Si(CH_3)_3$), 7.06−7.13 (m, 6H, $C_{10}H_6$), 7.22−7.27 (m, 4H, $C_{10}H_6$), 7.48 (dd, 2H, $C_{10}H_6$, J = 1.6 Hz, 8.0 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 100 MHz): δ 0.5 ($Si(CH_3)_3$), 2.7 ($Si(CH_3)_3$), 115.9 ($C_{10}H_6$), 117.5 ($C_{10}H_6$), 118.6 ($C_{10}H_6$), 121.0 ($C_{10}H_6$), 124.2 ($C_{10}H_6$), 125.3 ($C_{10}H_6$), 126.7 ($C_{10}H_6$), 139.4 ($C_{10}H_6$), 144.7 ($C_{10}H_6$), 152.9 ($C_{10}H_6$). ^{29}Si{^{1}H} NMR (C_6D_6, 298 K, 80 MHz): δ −2.4, 8.5. Elemental analysis: Calcd for $C_{32}H_{48}N_4Si_4Zn_2$: C 52.51, H 6.61, N 7.66; found C 52.51, H 6.63, N 7.79. Mass spec (EI): m/z: 732 ($[C_{32}H_{48}N_4Si_4Zn_2]^+$, 3%), 364 ($[C_{16}H_{24}N_2Si_2Zn]^+$, 95%), 302 ($[C_{16}H_{24}N_2Si_2]^+$, 95%), 290 ($[M - SiMe_3]^+$, 95%), 270 ($[M - NSiMe_3]^+$ 90%), 255 ($[M - NSiMe_3 - Me]^+$, 80%), 225 ($[M - NSiMe_3 - Me_3]^+$, 48%), 215 ($[M - 2SiMe_3]^+$, 50%). Accurate mass (dimer and monomer measured): Calcd for $C_{32}H_{48}N_4Si_4Zn_2$: 728.1533, found 728.1531; calcd for $C_{16}H_{24}N_2Si_2Zn$: 364.0764, found 364.0764. IR (nujol mull) υ/cm^{-1}: 3059 w, 3051 w, 1601 w, 1594 w, 1557 st, 1504 w, 1427 md, 1319 md, 1301 md, 1274 st, 1248 st, 1208 md, 1170 w, 1160 w, 1053 st, 1023 st, 965 w, 903 st, 894 st sh, 858 st sh, 844 st, 831 st sh, 782 md, 761 st, 750 md, 676 w, 655 w, 586 md.

Synthesis of 1,8-$C_{10}H_6(NSi^iPr_3)_2Zn(\mu\text{-}Cl)Li(THF)_3$ (2). Equimolar quantities of $ZnCl_2$ and 1,8-$C_{10}H_6(NLiSi^iPr_3)_2$ (0.06 g, 0.4 mmol and 0.20 g, 0.4 mmol, respectively) were allowed to react in a mixture of toluene (10 mL) and THF (2 mL) at room temperature and the resulting pale yellow solution was stirred for 16 h. Volatiles were removed in vacuo and the resultant yellow oil was extracted with hexane (20 mL). Cooling of the saturated hexane solution to −30 °C afforded orange crystals of **2** suitable for single crystal X-ray diffraction studies. Yield 0.18 g, 56%. ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ 1.25 (m, 12H, THF), 1.37 (d, 36H, $Si(CH(CH_3)_2)_3$, J = 7.5 Hz), 1.81 (sep, 6H, $Si(CH(CH_3)_2)_3$, J = 7.5 Hz), 3.36 (m, 12H, THF), 6.96 (dd, 2H, $C_{10}H_6$, J = 1.2 Hz, 7.5 Hz), 7.20 (m, 2H, $C_{10}H_6$), 7.41 (dd, 2H, $C_{10}H_6$, J = 0.9 Hz, 8.1 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 298 K, 100 MHz): δ 18.6 ($Si(CH(CH_3)_2)_3$), 20.4 ($Si(CH(CH_3)_2)_3$), 24.9 (THF), 69.8 (THF), 118.6 ($C_{10}H_6$), 120.2 ($C_{10}H_6$), 122.8 ($C_{10}H_6$), 126.0 ($C_{10}H_6$), 138.3 ($C_{10}H_6$), 150.4 ($C_{10}H_6$). ^{29}Si{^{1}H} NMR (C_6D_6, 298 K, 80 MHz): δ 2.5. ^{7}Li NMR (C_6D_6, 298 K, 155 MHz) δ 0.35. Elemental analysis: Calcd for $C_{40}H_{72}ClLiN_2O_3Si_2Zn$: C 60.59, H 9.15, N 3.53; found C 60.43, H 9.21, N 3.46. Mass spec (EI): m/z: 1064 ($[\{M - ClLi(THF)_3\}_2]^+$, 5%), 718 ($[M - THF]^+$, 10%), 532 ($[M - ClLi(THF)_3]^+$, 20%), 489 ($[M - ClLi(THF)_3 - {}^iPr]^+$, 40%), 447 ($[M - ClLi(THF)_3 - 2{}^iPr]^+$, 5%). Accurate Mass (EI): Calcd for $C_{28}H_{48}N_2Si_2Zn$ [i.e., $M - ClLi(THF)_3$]: 532.2642; found 532.2644. IR (nujol mull) υ/cm^{-1}: 3043 w, 2696 w, 1587 w, 1570 md, 1430 w, 1302 w sh, 1295 md, 1260 md, 1235 md, 1172 w, 1151 md sh, 1043 s, 1022 s, 967 w, 918 md, 887 st, 832 md, 821 md, 759 md, 729 st, 713 st, 669 md, 642 w, 556 w.

Synthesis of 1,8-$C_{10}H_6(NSi^iPr_3)_2Fe(\mu\text{-}Cl)Li(THF)_3$ (3). Equimolar quantities of $FeCl_2(THF)_{1.5}$ (0.10 g, 0.4 mmol) and 1,8-$C_{10}H_6(NLiSi^iPr_3)_2$ (0.20 g, 0.4 mmol) were allowed to react in a mixture of toluene (10 mL) and THF (2 mL) at room temperature over a period of 16 h giving rise to a dark orange solution. Volatiles were removed in vacuo and remaining dark brown oily solid was extracted into hexane (20 mL); storage of the solution in the freezer at −30 °C gave rise to orange crystals of **3** suitable for single crystal X-ray diffraction studies. Yield 0.17 g, 52%. μ_{eff} = 4.722 μ_B. Elemental analysis: Calcd for $C_{40}H_{72}ClFeLiN_2O_3Si_2$: C 61.32, H 9.26, N 3.58; found C 61.42, H 9.24, N 3.66. Mass spec. (EI) m/z: 1048 ($[\{M - ClLi(THF)_3\}_2]^+$, 5%), 1006 ($[\{M - ClLi(THF)_3\}_2 - {}^iPr]^+$, 5%), 782 ($[M]^+$, 2%), 524 ($[M - ClLi(THF)_3]^+$, 100%), 481 ($[M - ClLi(THF)_3 - {}^iPr]^+$, 3%), 438 ($[M - ClLi(THF)_3 - 2{}^iPr]^+$, 5%). Accurate Mass (EI): Calcd for $C_{28}H_{48}FeN_2Si_2$ [i.e., $M - ClLi(THF)_3$]: 524.2700; found 524.2702. IR (nujol mull) υ/cm^{-1}: 3052 w, 2674 w, 1619 md br, 1553 md, 1402 w, 1348 md, 1312 w, 1299 w, 1260 st, 1228 md sh, 1198 w, 1154 md, 1072 md, 1040 st, 1009 md, 919 md, 886 md, 859 w, 839 md, 824 st, 806 st, 759 md, 730 st, 717 st, 670 md, 666 md, 621 md, 561 w sh, 514 md.

Synthesis of 1,8-$C_{10}H_6(NSi^iPr_3)_2Li(THF)MnCl(THF)$ (4). Equimolar quantities of $MnCl_2$ (0.05 g, 0.4 mmol) and 1,8-$C_{10}H_6(NLiSi^iPr_3)_2$ (0.20 g, 0.4 mmol, respectively) were allowed to react in a mixture of toluene (10 mL) and THF (2 mL) at room temperature for 16 h, giving rise to an orange solution. Volatiles

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were removed in vacuo and the remaining orange solid was extracted into hexane (20 cm^3). Storage of the hexane solution at −30 °C afforded orange crystals of **4** suitable for single crystal X-ray diffraction studies. Yield 0.12 g, 40%. $\mu_{eff} = 5.828\ \mu_B$. Elemental analysis: Calcd for $C_{36}H_{64}ClLiMnN_2O_2Si_2$: C 60.86, H 9.08, N 3.94; found C 60.90, H 9.21, N, 3.87. Mass spec (EI): 523 ([M − THF − Cl − Li(THF)]$^+$, 15%). IR (nujol mull) υ/cm^{-1}: 2827 st, 2708 w, 1555 md, 1462 md, 1369 md, 1339 w sh, 1263 md, 1246 w, 1200 w, 1077 br, 1049 md, 1031 md, 1001 md, 892 md, 881 md, 859 md, 821 md, 754 md, 731 md.

Crystallographic Method

Crystals of **1**−**4** were mounted on a dual-stage glass fiber using YR-1800 perfluoropolyether oil (Lancaster) and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems low-temperature device. Data for compounds **1**, **2**, and **4** were collected on a Bruker SMART APEX and for **3** on a Bruker SMART1000 diffractometer, both equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). Absorption corrections were applied using a multiscan method (SADABS).[26] All non-H atoms were located using direct methods[27] and difference Fourier syntheses. All fully occupied non-H atoms were refined[27] with anisotropic displacement parameters. In the case of **2**, disorder was identified in the two THF molecules coordinated to Li(1) via O(2) and O(3), and affected the C_4H_8 region of each. Distance restraints [C−O 1.42 Å; C−C 1.52 Å] were applied to all three THF molecules, and the angles at C(38) and C(39) were restrained to be tetrahedral. Restraints were also applied to the displacement parameters. The major and minor occupancies for the O(2) ring were refined competitively to values of 0.653(8) and 0.347(8), respectively. For the O(3) ring the corresponding values were 0.540(11) and 0.460(11), respectively. In the case of **3**, the displacement ellipsoid for atom C(32) in a THF molecule is somewhat elongated, but we were unable to develop a credible static disorder model that was superior to the dynamic disorder model adopted here. Crystal data for **1**−**4** can be found in Table 1.

Results and Discussion

Treatment of 1,8-$C_{10}H_6(NLiSiMe_3)_2$ with one equivalent of $ZnCl_2$ in a mixture of toluene and THF at room temperature affords the complex [1,8-$C_{10}H_6(NSiMe_3)_2Zn]_2$ (**1**) (Scheme 1) in good yield. Complex **1** is highly sensitive to air and moisture, although this compound can be stored as a solid at −35 °C under an inert atmosphere for an indefinite period. Complex **1** has been characterized by multinuclear NMR spectroscopy, elemental analysis, mass spectrometry, and IR spectroscopy. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **1** in benzene-d_6 solution each exhibit two resonances for the $SiMe_3$ groups in this molecule, indicating that **1** is likely dimeric in solution, although the formation of higher oligomers cannot be ruled out. This has also been observed in the ^{1}H NMR spectrum of [Zn{$(CH_2)_3$(NDipp)$_2$-1,3}]$_2$.[28] Variable concentration NMR experiments on benzene-d_6 solutions of **1** (2, 10, and 30 mg of complex/mL of solvent) show that only the oligomeric species is present in solution. As has been observed in the mass spectrum of [Zn{$(CH_2)_3$(NDipp)$_2$-1,3}]$_2$,[28] the molecular ion peaks for both the dimeric and monomeric forms of **1** are observed in the EI mass spectrum; *m*/*z* = 732 [[1,8-$C_{10}H_6(NSiMe_3)_2Zn]_2]^+$ and 364 [1,8-$C_{10}H_6(NSiMe_3)_2Zn]^+$, the signals for these ions being at 3% and 95% relative intensity, respectively. Accurate mass measurements for both dimer and monomer have been obtained by EI mass spectrometry.

The dimeric nature of **1** in the solid state has been established by single crystal X-ray diffraction analysis (Figure 1; relevant bond distances and angles can be found in Table 2). Single crystals of suitable quality for X-ray diffraction were obtained by the storage of a saturated hexane solution of **1** at −30 °C, from which this complex is crystallized as the hexane solvate. Complex **1** features the 1,8-bis(trimethylsilylamido)naphthalene moiety acting as both a chelating and bridging ligand, in a manner akin to that observed in the solid state structures of [M{$(CH_2)_3$(NDipp)$_2$-1,3}]$_2$ (M = Mn, Fe, Zn).[28] Complex **1** lies across a crystallographic inversion center, which requires the 1,8-bis(trimethylsilylamido)naphthalene ligands to be parallel. The monomer units dimerize via the formation of amido bridges, leading to one of the nitrogen atoms being three-coordinate and the other being four-coordinate. The solid state structure of **1** features a planar Zn(1)−N(3_2)−Zn(1_2)−N(3) unit [Σ internal angles = 360° by symmetry; symmetry operation _2 = (1 − *x*, 1 − *y*, −*z*)]. The distance between the zinc centers in **1** [Zn(1)···Zn(1_2) = 2.7019(4) Å] is significantly longer than the sum of the single bond covalent radii for this element (2.36 Å);[29] any direct interaction between the two metal centers is therefore likely to be very weak. For **1**, the coordination geometry around Zn is distorted trigonal pyramidal, with the metal atom lying 0.20 Å out of the plane of the three equatorial nitrogen atoms, and is 0.06 Å more shallow than that for [Zn{$(CH_2)_3$(NDipp)$_2$-1,3}]$_2$.[28]

The terminal Zn−N distance in **1** [Zn(1)−N(2) = 1.8576(13) Å] is comparable to that found in the monomeric, two-coordinate complex Zn[N(SiMe$_3$)(Si^{t}BuPh$_2$)]$_2$ [1.853(2), 1.858(2) Å][30] and the Zn−N(terminal) distance in dimeric [Zn{$(CH_2)_3$(NDipp)$_2$-1,3}]$_2$ [1.8537(16) Å].[28] In contrast to the relatively short Zn−N(terminal) distance in **1** the bridging distance is significantly longer [Zn(1)−N(3_2) = 2.067(3) Å; symmetry operation _2 = (1 − *x*, 1 − *y*, −*z*)] and is similar to the analogous distance in [Zn{$(CH_2)_3$(NDipp)$_2$-1,3}]$_2$ [2.0798(15) Å]. Reflecting the increased rigidity of the ligand framework in **1**, the N−Zn−N angle within the monomeric unit of **1** [N(2)−Zn(1)−N(3_2) = 99.07(6)°] is ca. 12° smaller than that for the analogous moiety in [Zn{$(CH_2)_3$(NDipp)$_2$-1,3}]$_2$. In **1**, shorter N−Si distances are seen for the three-coordinate nitrogen compared to the four-coordinate nitrogen [Si(2)−N(2) 1.7289(14) Å, Si(3)−N(3) 1.7682(14) Å].

To stabilize the formation of monomeric systems and confer greater stability on the resulting complexes, the 1,8-bis(triisopropylsilylamido)naphthalene ligand was utilized. The reaction of 1,8-$C_{10}H_6$(NLiSi^{i}Pr$_3$)$_2$ with one equivalent of $ZnCl_2$ in a mixture of toluene and THF at room temperature gives rise to 1,8-$C_{10}H_6$(NSi^{i}Pr$_3$)$_2$Zn(μ-Cl)Li(THF)$_3$ (**2**) (Scheme 2) in moderate yield. Complex **2** has been characterized by multinuclear NMR spectroscopy, elemental analysis,

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Table 1. Crystal Data for **1**−**4**

	1	**2**	**3**	**4**
formula	$C_{32}H_{48}N_4Si_4Zn_2 \cdot C_6H_{14}$	$C_{40}H_{72}ClLiN_2O_3Si_2Zn$	$C_{40}H_{72}ClFeLiN_2O_3Si_2$	$C_{36}H_{64}ClLiMnN_2O_2Si_2$
M_w	818.02	792.94	783.42	710.40
crystal system	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/n$
a (Å)	9.1441(7)	12.3345(11)	18.0516(10)	10.799(2)
b (Å)	9.9967(7)	12.7440(12)	15.5805(9)	20.058(3)
c (Å)	12.2605(9)	15.6197(14)	31.812(2)	17.998(3)
α (deg.)	104.502(2)	88.161(2)	90	90
β (deg.)	102.791(2)	70.108(2)	92.097(2)	98.410(3)
γ (deg.)	92.593(2)	70.197(2)	90	90
V (Å^3)	1052.1(2)	2162.6(6)	8941.2(9)	3856.6(11)
T (K)	150(2)	150(2)	150(2)	150(2)
D_{calc} (g cm^{-3})	1.291	1.218	1.164	1.224
F_{000}	434	856	3392	1532
μ (mm^{-1})	1.285	0.722	0.486	0.506
Z	1	2	8	4
reflns measured	9239	25416	28132	35653
independent reflns	4639	9834	10090	8836
R_{int}	0.039	0.074	0.046	0.056
final GooF	1.05	0.92	0.91	0.93
R_1, wR_2	0.0285, 0.0771	0.0615, 0.121	0.0413, 0.0932	0.0442, 0.0667
min. and max. electron densities (e Å^3)	0.81, −0.44	0.77, −0.46	0.39, −0.36	0.65, −0.37

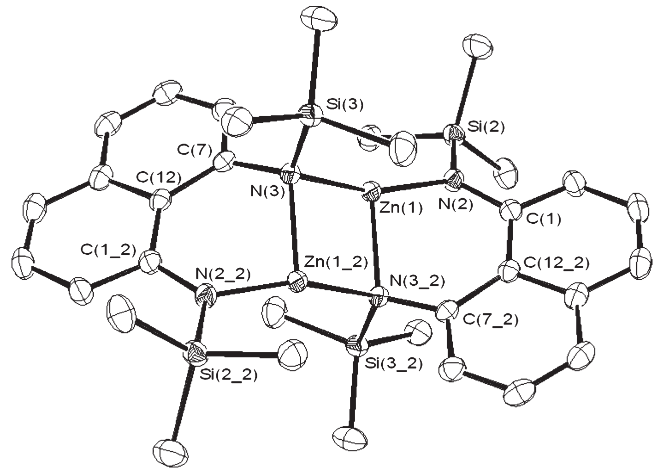
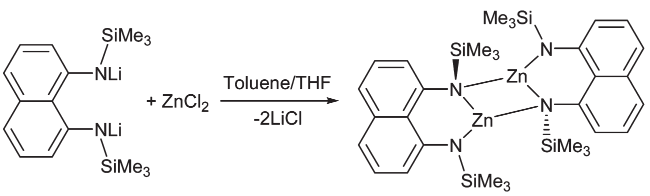


Figure 1. Crystal structure of $[1,8\text{-}C_{10}H_6(NSiMe_3)_2Zn]_2$ (**1**) with displacement ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity. Symmetry operation _2 = (1 − *x*, 1 − *y*, −*z*).

Scheme 1. Synthesis of $[1,8\text{-}C_{10}H_6(NSiMe_3)_2Zn]_2$ (**1**)



mass spectrometry, and IR spectroscopy in addition to a single crystal X-ray diffraction analysis.

Single crystals of suitable quality for X-ray diffraction studies were obtained by storing a saturated hexane solution of **2** at −30 °C; the crystal structure of **2** can be seen in Figure 2 and relevant bond lengths and angles can be found in Table 3. The Zn center is surrounded by two amido groups and a $ClLi(THF)_3$ moiety in a distorted trigonal planar environment [sum of angles around Zn(1) = 360.0(2)°]. The coordination of an $XLiL_n$ (X = halide, L = donor ligand) unit represents a rare structural motif in the coordination chemistry of the d-block elements, and complex **2** is, to the best of our knowledge, the first structurally authenticated example of a three-coordinate zinc center adopting this particular coordination mode. More commonly, zinc adopts a dibridging $Zn(\mu\text{-}Cl)_2LiL_n$ bonding motif.[31]

Table 2. Selected Distances (Å) and Angles (deg) for **1**[a]

Zn(1)···Zn(1_2)	2.7019(4)	N(2)−Zn(1)−N(3_2)	99.07(6)
Zn(1)−N(2)	1.8576(13)	N(2)−Zn(1)−N(3)	160.28(6)
Zn(1)−N(3)	1.9461(13)	N(3_2)−Zn(1)−N(3)	95.42(5)
Zn(1)−N(3_2)	2.0673(13)	Zn(1)−N(3)−Zn(1_2)	84.58(5)
Si(2)−N(2)	1.7289(14)	C(1)−N(2)−Zn(1)	115.69(11)
Si(3)−N(3)	1.7682(14)	C(7)−N(3)−Zn(1)	119.33(10)
N(2)−C(1)	1.398(2)	C(7)−C(12)−(C1_2)	127.17(14)
N(3)−C(7)	1.448(2)	Zn(1)···N(2),N(3),N(3_2) mean plane	0.20

[a] Symmetry operation _2 = (1 − *x*, 1 − *y*, −*z*).

There are significant differences in the positions of the Zn centers relative to the 1,8-bis(silylamido)naphthalene ligand systems between **1** and **2**, reflecting the differing coordination modes and steric environments within these two complexes. In **1**, the Zn center sits 0.85 Å out of the least-squares mean plane of the naphthalenyl moiety (Figure 3), with some twisting of the amido groups out of the naphthalenyl plane [N(2)···naphthalenyl mean plane = 0.13 Å; N(3_2)···naphthalenyl mean plane = 0.14 Å; symmetry operation _2 = (1 − *x*, 1 − *y*, −*z*)]. In contrast, for **2** the Zn center sits 0.09 Å out of the plane of the naphthalenyl moiety and there is significant twisting of the ligand framework with the amido-bonded carbon atoms sitting 0.19 and 0.21 Å above and below the naphthalenyl best mean plane, respectively; concomitant with this the N atoms are also significantly distorted from the naphthalenyl plane [N···naphthalenyl plane distances are 0.70 and 0.63 Å for N(1) and N(2), respectively] (Figure 3).

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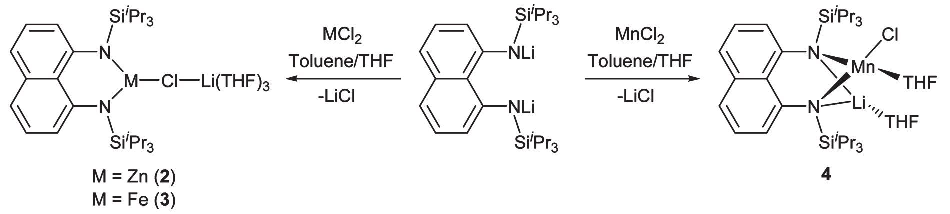
[31] See, for example: (a) Prust, J.; Hohmeister, H.; Stasch, A.; Roesky, H. W.; Magull, J.; Alexopoulos, E.; Usón, I.; Schmidt, H. −G.; Noltemeyer, M. *Eur. J. Inorg. Chem.* **2002**, 2156. (b) Varonka, M. S.; Warren, T. H. *Inorg. Chim. Acta* **2007**, *360*, 317. (c) Eisenmann, T.; Khanderi, J.; Schulz, S.; Florke, U. *Z. Anorg. Allg. Chem.* **2008**, *634*, 507. (d) Prust, J.; Most, K.; Müller, I.; Stasch, A.; Roesky, H. W.; Usón, I. *Eur. J. Inorg. Chem.* **2001**, 1613.

Scheme 2. Synthesis of 1,8-$C_{10}H_6(NSi^iPr_3)_2M(\mu\text{-}Cl)Li(THF)_3$ [M = Zn, **2**, MCl_2 = $ZnCl_2$; M = Fe, **3**, MCl_2 = $FeCl_2(THF)_{1.5}$] and 1,8-$C_{10}H_6(NSi^iPr_3)_2Li(THF)MnCl(THF)$ (**4**)



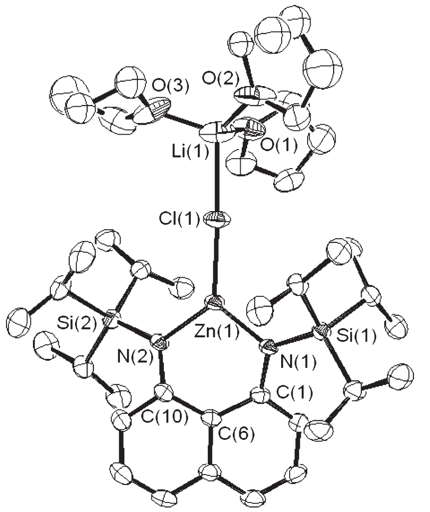


Figure 2. Crystal structure of 1,8-$C_{10}H_6(NSi^iPr_3)_2Zn(\mu\text{-}Cl)Li(THF)_3$ (**2**) with displacement ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity.

The two Zn−N distances in **2** are identical within experimental error [Zn(1)−N(1) = 1.898(3), Zn(1)−N(2) = 1.900(3) Å], and are longer than that found for the terminal Zn−N distance in **1** [1.8576(13) Å]. The chlorine atom bridges the Zn and Li centers [Zn(1)−Cl(1)−Li(1) = 165.0(2) Å]. The Zn−Cl distance in **2** [2.2218(10) Å] reflects the coordination of the $Li(THF)_3$ moiety with the Cl; it is longer than that found in $\{ClZn[\mu\text{-}(Me_3Si)NP(Ph)_2]_2C\}_2Zn$, which features a three-coordinate zinc center surrounded by two amido ligands and a terminal chloride [Zn−Cl = 2.1857(9) and 2.2066(10) Å].[32] The Zn−Cl distance in **2** is somewhat shorter than the analogous distance in $\{HC[(DippN)C(Me)]_2\}Zn(Cl)(\mu\text{-}Cl)Li(THF)_3$ [Zn−Cl = 2.312(1) and 2.238(1) Å for the Zn−(μ-Cl)$Li(THF)_3$ and Zn−Cl(terminal) moieties, respectively],[31b] which features a four-coordinate zinc center. In **2**, the Li center is coordinated to the Cl and three THF moieties in a distorted tetrahedral geometry. The Li−Cl distance of 2.406(8) Å in **2** is somewhat longer than that found in $\{HC[(DippN)C(Me)]_2\}Zn(Cl)(\mu\text{-}Cl)Li(THF)_3$ [2.372(8) Å], the latter complex displaying an additional interaction of the $Li(THF)_3$ moiety with a terminal chloride.

Table 3. Selected Distances (Å) and Angles (deg) for **2** and **3**

	2	**3**
M(1)−N(1)	1.898(3)	1.9168(18)
M(1)−N(2)	1.900(3)	1.9307(18)
M(1)−Cl(1)	2.2218(10)	2.2624(7)
Cl(1)−Li(1)	2.406(8)	2.373(4)
N(1)−Si(1)	1.736(3)	1.7322(18)
N(2)−Si(2)	1.738(3)	1.7471(18)
N(1)−C(1)	1.410(4)	1.408(3)
N(2)−C(10)	1.401(4)	1.408(3)
Li(1)−O(1)	1.898(9)	1.935(5)
Li(1)−O(2)	1.896(10)	1.903(5)
Li(1)−O(3)	1.870(10)	1.923(5)
N(1)−M(1)−N(2)	106.97(12)	100.20(7)
M(1)−Cl(1)−Li(1)	165.0(2)	110.77(11)

It is also possible to synthesize the Fe analogue of **2**; the reaction of 1,8-$C_{10}H_6(NLiSi^iPr_3)_2$ with one equivalent of $FeCl_2(THF)_{1.5}$ in a mixture of toluene and THF at room temperature gives rise to 1,8-$C_{10}H_6(NSi^iPr_3)_2Fe(\mu\text{-}Cl)Li(THF)_3$ (**3**) (Scheme 2) in moderate yield. Complex **3** has been characterized by elemental analysis, mass spectrometry, IR spectroscopy, and magnetic measurements. The magnetic moment for **3** (4.722 μ_B) indicates the presence of a high-spin Fe(II) center in this complex. The formulation of **3** was further confirmed by X-ray diffraction analysis (Figure 4, Table 3). The Fe center is coordinated by two amido groups and a $ClLi(THF)_3$ moiety in a pyramidal environment [Fe sits 0.14 Å out of the mean plane defined by N(1), N(2), and Cl(1)]. The Li center is coordinated to the Cl and three THF groups in a distorted tetrahedral geometry. The two amidonaphthalene nitrogen atoms are in distorted trigonal planar environments [sums of angles around N(1) and N(2) are 359.9(2) and 359.4(2)°, respectively]. The two Fe−N distances in **3** are different from each other [Fe(1)−N(1) = 1.9168(18), Fe(1)−N(2) = 1.9307(18) Å] and are shorter than those found in the related complex $[(Me_3Si)_2N]_2Fe(\mu\text{-}Cl)Li(THF)_3$ [1.945(5) and 1.954(5) Å],[33] the longer distance in **3** [Fe(1)−N(2)] being comparable to that found in $\{HC[(DippN)C(^tBu)]_2\}Fe(\mu\text{-}Cl)K(18\text{-crown-}6)$ [1.934(6) Å].[34] Such differences between Fe−N distances in three-coordinate iron complexes featuring bidentate amido ligands is not without precedent.[35] The Fe(1)−N(1) distance in **3** is similar to that found in the three-coordinate Fe(II) complex $Fe[N(SiMe_3)_2]_2(THF)$ [1.916(5) Å].[36] The Fe−Cl bond in **3** [2.2624(7) Å] is somewhat shorter than that in $[(Me_3Si)_2N]_2Fe(\mu\text{-}Cl)Li(THF)_3$ [2.318(2) Å],[33] and longer than that in the related complex $\{HC[(DippN)C(^tBu)]_2\}Fe(\mu\text{-}Cl)K(18\text{-crown-}6)$ [2.235(3) Å].[34]

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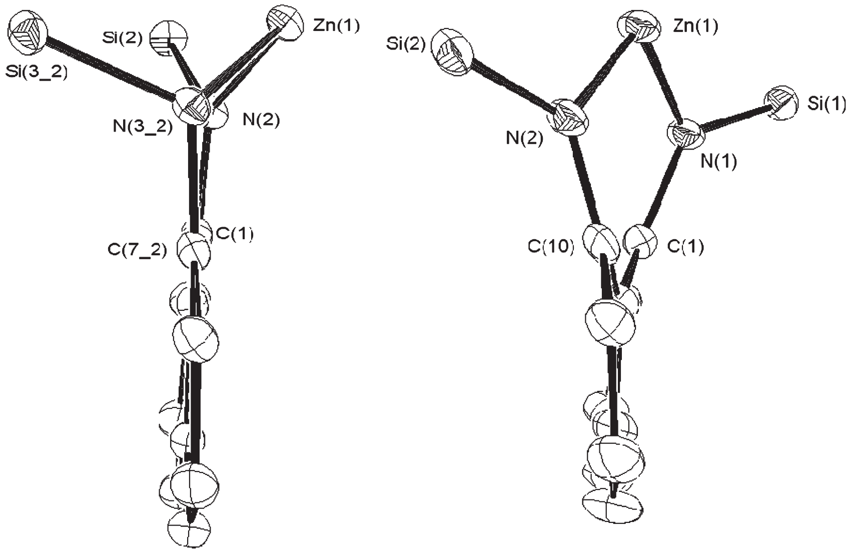

Figure 3. Side view of the Zn-naphthalenyl moieties in **1** (left) and **2** (right). H atoms, methyl groups in the case of **1**, and isopropyl groups in the case of **2**, are omitted for clarity.

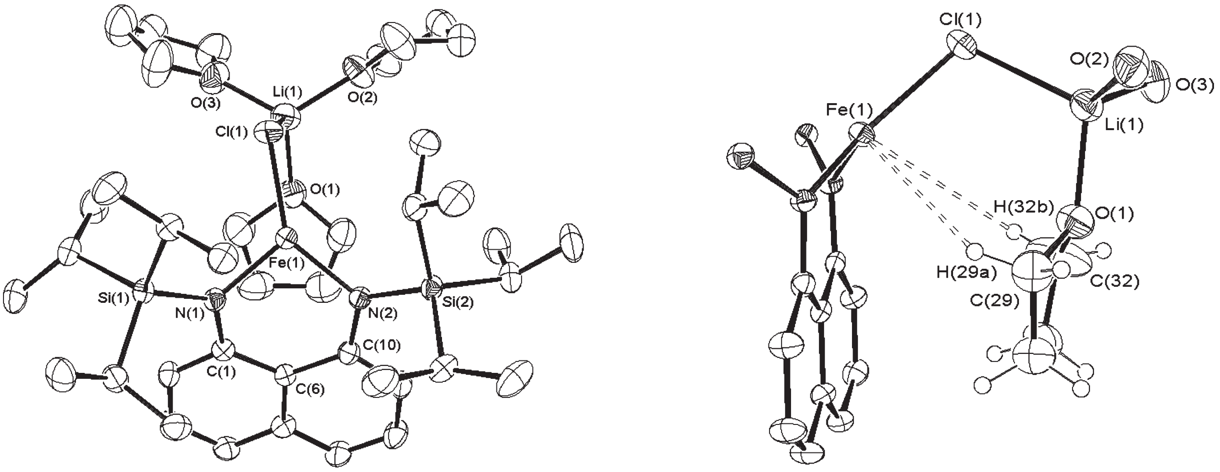

Figure 4. Left: crystal structure of $1,8\text{-}C_{10}H_6(NSi^iPr_3)_2Fe(\mu\text{-}Cl)Li(THF)_3$ (**3**) with displacement ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity. Right: side view of **3** highlighting the short contacts between Fe(1) and the H atoms of the THF molecule.

The structures of superficially similar **2** and **3** show a number of differences. In **3**, the atoms N(1) and N(2) are essentially coplanar with the carbons of the naphthalenyl moiety; this near-planarity is in contrast to that seen in the Zn analogue **2**. The Fe center in **3** sits 0.77 Å out of the plane of the amidonaphthalene ligand, and the angle between the N(1)Fe(1)N(2) and the N(1)C(1)C(6)C(10)N(2) planes is ca. 141.2°; a similar angle is exhibited in the stannylene $1,8\text{-}C_{10}H_6(NSiMe_3)_2Sn$ (ca. 144.8°).[18] Comparison to "fold angles" in main group and transition metal β-diketiminato complexes place the value exhibited by **3** at the more acute end of this range. This is presumably due to the steric demands around the Fe center in **3**; the degree of folding in β-diketiminato complexes is attributed to the steric requirements of the flanking groups.[37] Interestingly, the N−Si distances for **2** are identical within experimental error [N(1)−Si(1) = 1.736(3) Å, N(2)−Si(2) = 1.738(3) Å], but there is a large variation in the same measurement for **3** [N(1)−Si(1) = 1.7322(18) Å, N(2)−Si(2) = 1.7471(18) Å].

The chlorine atom in **3** bridges the Fe and Li centers [Fe(1)−Cl(1)−Li(1) 110.77(11)°]. The Li−Cl distance for **3** [Li(1)−Cl(1) = 2.373(4) Å] is similar to that found in other $Fe(\mu\text{-}Cl)Li(THF)_3$ systems, for example $[(Me_3Si)_2N]_2Fe(\mu\text{-}Cl)Li(THF)_3$[33] and $\{2,6\text{-}[2,6\text{-}{}^iPr_2C_6H_3NC(=CH_2)]_2C_5H_3N\}Fe(\mu\text{-}Cl)Li(THF)_3$ [2.345(13) and 2.362(13) Å, respectively],[38] and the contact ion pairs $LiCl(H_2O)(C_5H_5N)_2$ [2.329(18) Å] and $LiCl(DME)_2$ [2.386(4) Å; DME = 1,2-dimethoxyethane].[39] The M−Cl−Li angle in **3** is ca. 14° smaller than that in $[(Me_3Si)_2N]_2Fe(\mu\text{-}Cl)Li(THF)_3$ [124.4(3)°]. In addition, this angle in **3** is ca. 64° more acute than that in **2** [165.0(2) Å]; it appears that small changes within these

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[37] See, for example: (a) Stender, M.; Eichler, B. E.; Hardman, N. J.; Power, P. P.; Prust, J.; Noltemeyer, M.; Roesky, H. W. *Inorg. Chem.* **2001**, *40*, 2794. (b) Panda, A.; Stender, M.; Wright, R. J.; Olmstead, M. M.; Klavins, P.; Power, P. P. *Inorg. Chem.* **2002**, *41*, 3909.

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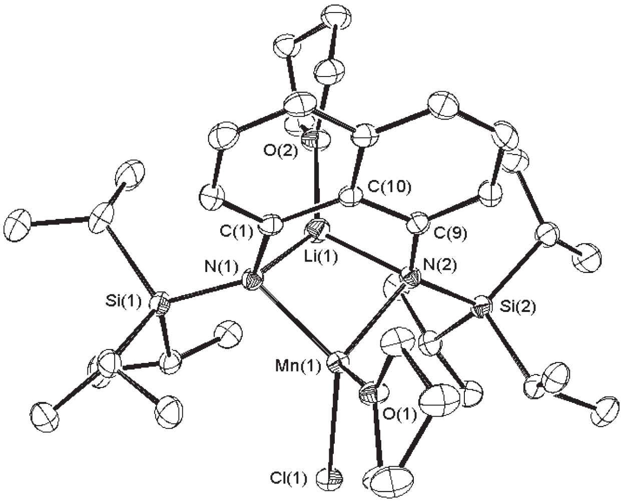

Figure 5. Crystal structure of 1,8-$C_{10}H_6(NSi^iPr_3)_2Li(THF)MnCl(THF)$ (**4**) with displacement ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity.

complexes can give rise to large structural differences in the solid state. Indeed, in the crystal structure of $\{[CH_2SiMe_2C(SiMe_3)_2]_2\}Mn(\mu\text{-}Cl)Li(THF)_3$ there are three molecules in the asymmetric unit which featured Mn−Cl−Li angles in the range 157.7(2)−176.0(3)° (a fourth molecule in the asymmetric unit featured two coordinated THF molecules and one Et_2O).[40] A likely explanation for the degree of bending in **3** comes from close examination of the solid state structure of this complex. The Fe(1)−Cl(1)−Li(1) angle of 110.77(11)° brings one of the lithium-coordinated THF molecules into close proximity to the electrophilic metal center. The closest approaches of the H atoms in the THF moiety toward the Fe center are 3.0868(4) Å [Fe(1)···H(29a)] and 3.3410(3) Å [Fe(1)···H(32b)], the former being significantly shorter than the sum of the van der Waals interactions for these two atoms (3.25 Å).[41]

The high steric demands of the 1,8-$C_{10}H_6(NSi^iPr_3)_2$ ligand are presumably why **2** and **3** form monomeric $ClLi(THF)_3$ adduct-type systems, whereas **1** exists as an amide-bridged dimer. That the metal centers in **2** and **3** should coordinate $ClLi(THF)_3$ is somewhat unexpected, but the coordination of this moiety to transition metal centers, although rare, is not without precedent. It has also been tentatively suggested that under certain circumstances $ClLi(THF)_3$ might be a better donor ligand than THF.[33]

The analogous reaction of 1,8-$C_{10}H_6(NLiSi^iPr_3)_2$ with $MnCl_2$ yields 1,8-$C_{10}H_6(NSi^iPr_3)_2Li(THF)MnCl(THF)$ (**4**, Scheme 2), the harder Mn^{2+} ion forming a complex similar to that of 1,8-$C_{10}H_6(NSiMe_3)_2Li(THF)MgBr(THF)$, reported by Gade and co-workers.[11] Complex **4** has been characterized by elemental analysis, mass spectrometry, IR spectroscopy, and magnetic measurements. The magnetic moment for **4** is 5.828 μ_B indicating the presence of a high-spin Mn(II) center. The molecular structure of **4** is shown in Figure 5 and the relevant bond distances and angles can be found in Table 4. The molecule displays a $LiMnN_2$ ring, the geometry of which is enforced by the rigidity of the naphthalenyl framework, leading to nonplanarity in the $LiMnN_2$ moiety; the sum of the inner angles in the ring is 347.7(2)° and the angle between the Mn(1)−N(1)−Li(1) and Mn(1)−N(2)−Li(1) planes is 36.9(2)°.

Table 4. Selected Distances (Å) and Angles (deg) for **4**

Mn(1)−N(1)	2.1063(17)	N(1)−Si(1)	1.7502(18)
Mn(1)−N(2)	2.1123(17)	N(2)−Si(2)	1.7582(17)
Mn(1)−Cl(1)	2.3237(7)	Mn(1)···Li(1)	2.827(4)
Mn(1)−O(1)	2.1649(14)	N(1)−Mn(1)−N(2)	85.83(7)
Li(1)−N(1)	2.028(4)	N(1)−Li(1)−N(2)	89.87(16)
Li(1)−N(2)	2.039(4)	Li(1)−N(1)−Mn(1)	86.21(12)
Li(1)−O(2)	1.898(4)	Li(1)−N(2)−Mn(1)	85.80(12)
N(1)−C(1)	1.426(3)	O(1)−Mn(1)−Cl(1)	101.38(4)
N(2)−C(9)	1.421(3)		

In the solid state structure of **4** the Mn center is coordinated by two amido groups, one chloride, and a THF molecule in a distorted tetrahedral environment. The Mn−N distances in **4** [2.1063(17) and 2.1123(17) Å] are somewhat shorter than the Mn−N(bridging) distances in $Mn\{N(SiMe_3)_2\}_3Li(THF)$ [2.143(3) Å],[42] presumably due in part to the influence of the rigid naphthalenyl framework on the coordination environment in this compound. The Mn−Cl distance in **4** [2.3237(7) Å] is within the range of distances found for other four-coordinate Mn centers, for example Mn−Cl = 2.287(1) Å and 2.3890(11) Å for $\{HB[1\text{-}^tBu\text{-}3\text{-}^iPrC_3HN_2]_3\}MnCl$ and $[\{C(Me)N(^iPr)\}_2CH]^+[\{HC[(DippN)C(Me)]_2\}MnCl_2]^-$, respectively.[43] The Li center in **4** is coordinated by two amido groups and a THF molecule in a pyramidal geometry [sum of angles around Li = 347.4(3)°; Li lies 0.39 Å out of the plane defined by N(1), N(2), and O(2)]. The Li−N distances in **4** [2.028(4) and 2.039(4) Å] are within the range expected for related complexes[44] and are similar to those found in the lithium-bridged complex 1,8-$C_{10}H_6(NSi^iPr_3)_2\{Li(THF)\}_2$ [2.023(5) and 2.028(5) Å].[13] The N−Si distances [1.7502(18) and 1.7582(17) Å] reflect the four-coordination of the N atom in **4**: they are longer than those in **2** and **3**, but are ca. 0.01 Å shorter than the four-coordinate N−Si distance in **1**.

As has been observed in 1,8-$C_{10}H_6(NSi^iPr_3)_2\{Li(THF)\}_2$, the silyl substituents in **4** are unequally twisted out of the naphthalene plane−both Si atoms are deviated away from the Mn(Cl)THF moiety at 0.23 and 0.08 Å out of the arene plane for Si(1) and Si(2), respectively, presumably due to the steric demands of the Mn(Cl)THF moiety. The closest Cl···H(ligand) distances are 2.938(1) and 2.977(1) Å for Cl(1)···H(26a) and Cl(1)···H(11a), respectively. This twisting also brings the isopropyl substituents into close proximity with the Li atom; the closest Li···H distances are 2.366(4) and 2.383(4) Å for Li(1)···H(27C) and Li(1)···H(13B), concomitant with this are Li···C distances of 3.208(4) and 2.982(5) Å for Li(1)···C(27) and Li(1)···C(13), respectively. These distances in **4** are somewhat longer than those for the weak intramolecular interactions in the related complex $Li[Mn(NSiMe_3)_2](OC^tBu_3)_2$ [Li···H = 2.1(1), 2.1(1), 2.2(1) Å; Li···C = 2.52(3) Å],[45] but are nevertheless smaller than the sum of the van der Waals radii for these elements.[41] In **4** the N−Mn−N angle [85.83(7) Å] is considerably more acute than the N−M−N angles in **2** and **3** [106.97(12) and

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100.20(7)°, respectively], and we ascribe this to the coordination of the Li atom in **4**.

The Mn···Li distance in **4** is 2.827(4) Å, which is somewhat longer than that found in Mn{N(SiMe$_3$)$_2$}$_3$Li(THF) [2.718(6) Å], Li[Mn(NSiMe$_3$)$_2$](OC^{t}Bu$_3$)$_2$ [2.640(7) Å] and Li$_2$[MnBr$_2$(OC^{t}Bu$_3$)$_2$](THF)$_2$,[42,45] and is presumably due to the influences of the differing ligand frameworks and coordination numbers at the manganese centers in these systems.

Conclusions

Sterically demanding 1,8-bis(silylamido)naphthalene ligands can be used to stabilize complexes featuring mid and late d-block metal centers in unusual coordination geometries. [1,8-C$_{10}$H$_6$(NSiMe$_3$)$_2$Zn]$_2$ (**1**) exhibits a dimeric structure, where the amidonaphthalene ligand acts as both a chelating and a bridging ligand. In the case of Zn and Fe, increasing the steric demands of the 1,8-bis(silylamido)naphthalene ligand yields 1,8-C$_{10}$H$_6$(NSi^{i}Pr$_3$)$_2$M(μ-Cl)Li(THF)$_3$ (M = Zn, **2**; M = Fe, **3**). In particular, the coordination of the ClLi(THF)$_3$ moiety to the metal center in **2** and **3** represents a rare structural motif in the coordination chemistry of the d-block elements. Use of the harder Mn^{2+} ion leads to a differing coordination environment for the metal cation, as seen in 1,8-C$_{10}$H$_6$(NSi^{i}Pr$_3$)$_2$Li(THF)MnCl(THF) (**4**), which features a rare example of a four-membered LiMnN$_2$ ring. Reactivity investigations on these complexes are now underway.

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Supporting Information Available: Crystallographic data for complexes **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.