Synthesis and Structural Characterization of Three-Coordinate Mn^{II}, Fe^{II}, and Zn^{II} Complexes Containing a Bulky Diamide Ligand $[DippN(CH_2)_3NDipp]^{2-}$ (Dipp = 2,6-$i$$Pr_2C_6H_3$)

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The reaction of $DippNH(CH_2)_3NHDipp$ (**1**) (Dipp = 2,6-$i$$Pr_2C_6H_3$) with 2 equiv. of MeLi in diethyl ether resulted in the formation of the monomeric dilithium salt $[(Dipp)N(CH_2)_3N(Dipp)][Li(OEt_2)]_2$ (**2**) in high yield. Further reactions of **2** with $MnCl_2$, $FeCl_2$, and $ZnCl_2$, respectively, afforded the complexes $[M_2\{N(Dipp)(CH_2)_3N(Dipp)\}_2]$ [M = Mn (**3**), Fe (**4**), Zn (**5**)] with three-coordinate metal centers. Complexes **2**–**5** were characterized by X-ray structural analysis. The complexes contain a nonplanar MNMN central core. The diamide ligand in complexes **3**–**5** displays a boat conformation and is both chelating and bridging, so that one of the nitrogen atoms is three-coordinate and the other four-coordinate. Complexes **3**–**5** are the first examples with diamide ligands in such a bonding mode. The magnetic investigations of compounds **3** and **4** reveal an antiferromagnetic exchange between the metal atoms.
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Introduction

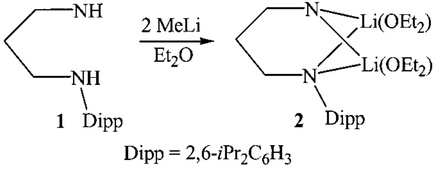
Transition metal complexes with three-coordinate metal centers are rare, since it is difficult to reach the preferred stable configurations with 16 or 18 valence electrons around the metal center using only three donor ligands.[1] Metal amide complexes are of wide interest as they show a broad range of structures and reaction types.[2] Transition metal amides, for instance, are the first examples with unusually low coordinate metal centers due to the strong M−N bonds and flexible steric properties of the amine ligands.[2b] In addition, transition metal amides are a useful hydrocarbon-soluble source of M^{n+} cations and have proved to be good starting materials to prepare other species.[3] However, reports of saturated hydrocarbon-bridged bidentate diamide ligands are rare.[2b] Considering the recent success in the synthesis of complexes of main-group elements, transition metals and lanthanides of unusual properties with the Dippnacnac ligand $[HC(CMeNDipp)_2]^-$ (Dipp = 2,6-$i$$Pr_2C_6H_3$),[4] we were interested in investigating the behavior of the bulky chelating diamide ligand $[DippN(CH_2)_3NDipp]^{2-}$, which has similar steric properties to Dippnacnac and is expected to result in interesting new organometallic chemistry.

The bulky chelating diamide ligand $[DippN(CH_2)_3NDipp]^{2-}$ was previously used by McConville and co-workers as a non-cyclopentadienyl ligand to prepare group 4 complexes that can catalyze olefin polymerization under "living" conditions.[5] Cloke and Roesky et al. have reported lanthanide complexes bearing this ligand.[6] Recently, we obtained the aluminum hydride $[DippN(CH_2)_3NDipp]AlH(NMe_3)$ and its derivatives $\{[DippNH(CH_2)_3NDipp]Al\}_2(\mu\text{-}E)_2$ (E = S, Se and Te) by hydrogen transfer from chalcogen to nitrogen.[7] Herein we describe the synthesis and structural analysis of the dilithium salt $[N(Dipp)(CH_2)_3N(Dipp)][Li(OEt_2)]_2$ (**2**) and the resulting complexes with three-coordinate Mn^{II}, Fe^{II}, and Zn^{II} of composition $[M_2\{N(Dipp)(CH_2)_3N(Dipp)\}_2]$ [M = Mn (**3**), Fe (**4**), Zn (**5**)].

Results and Discussion

Synthesis of Compounds 2−5

The lithiation of $DippNH(CH_2)_3NHDipp$ (**1**) with 2 equiv. of MeLi in diethyl ether proceeds smoothly to afford $[(Dipp)N(CH_2)_3N(Dipp)][Li(OEt_2)]_2$ (**2**) as colorless crystals in high yield (Scheme 1). The existence of the coordi-



Scheme 1

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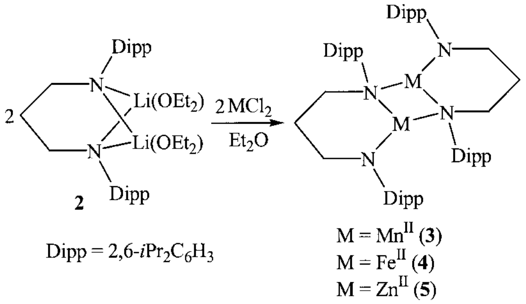
nated diethyl ether molecules was confirmed by ^1H NMR spectroscopy, elemental analysis, and an X-ray solid-state structural analysis. The dilithium salt **2** is soluble in diethyl ether and stable under an inert gas and is a useful reagent for metathesis reactions with metal halides.

The reaction of **2** with 1 equiv. of anhydrous $MnCl_2$, $FeCl_2$, or $ZnCl_2$, respectively, in diethyl ether at low temperature smoothly provided the corresponding dimeric compounds $[M_2\{N(Dipp)(CH_2)_3N(Dipp)\}_2]$ [M = Mn (**3**), Fe (**4**), Zn (**5**)] in good yield (Scheme 2). The same products were obtained even when 2 equiv. of MCl_2 were employed. Complexes **3**−**5** are soluble in CH_2Cl_2 and THF and have a moderate solubility in diethyl ether and toluene.



Scheme 2

Complexes **2**−**5** were characterized by EI-MS, ^1H NMR and IR spectroscopy and X-ray solid-state structural analysis. The molecular ion peaks of **3**−**5** in the EI mass spectra were all observed. However, the most intense peaks of these complexes show different fragments: **3**: m/z = 705 $[M - CH_2NDipp]^+$; **4**: m/z = 504 $[M - N(Dipp)(CH_2)_3N(Dipp)]^+$; **5**: m/z = 456 $[1/2\ M]^+$. In the the monomeric compounds $\{$such as $[N(Dipp)(CH_2)_3N(Dipp)]AlX{\cdot}NMe_3$ (X = H, F)$\}$[7] the four isopropyl methine groups ($CHMe_2$) are not equivalent and give two resonances in the ^1H NMR spectra, whereas compound **5** gives four isopropyl methine resonances, which is consistent with restricted rotation about the $N-C_{ipso}$ bond. The doublets in the range of δ = 0.16−1.36 ppm correspond to the protons of methyl groups ($CHMe_2$).

X-ray Solid-State Structural Analyses

The X-ray solid-state structural analyses for complexes **2**−**5** were undertaken. Crystallographic data for these complexes are given in the Exp. Sect. and selected bond lengths and angles in Tables 1 and 2.

Table 1. Selected bond lengths [Å] and bond angles [°] for **2**

Li(1)−O(1)	1.894(11)	O(1)−Li(1)−N(2)	118.3(5)
Li(1)−N(1)	1.999(10)	N(1)−Li(1)−N(2)	96.8(5)
Li(1)−N(2)	1.971(10)	O(1)−Li(1)−Li(2)	163.6(6)
Li(1)−Li(2)	2.514(13)	N(1)−Li(1)−Li(2)	51.9(3)
Li(2)−N(1)	2.028(10)	N(2)−Li(1)−Li(2)	52.4(3)
Li(2)−N(2)	2.039(10)	O(2)−Li(2)−N(1)	144.0(5)
Li(2)−O(2)	1.949(10)	O(2)−Li(2)−N(2)	114.2(5)
O(1)−Li(1)−N(1)	142.8(6)	N(1)−Li(2)−N(2)	93.7(4)

Table 2. Selected bond lengths [Å] and bond angles [°] for **3**−**5**

Compound **3**			
Mn(1)−N(1)	1.932(2)	N(1)−Mn(1)−N(2)	106.79(10)
Mn(1)−N(2)	2.126(3)	N(1)−Mn(1)−N(3)	146.55(9)
Mn(1)−N(3)	2.078(3)	N(2)−Mn(1)−N(3)	96.72(10)
Mn(1)−Mn(2)	2.690(2)	N(1)−Mn(1)−Mn(2)	133.93(8)
Mn(2)−N(2)	2.093(3)	N(2)−Mn(1)−Mn(2)	49.86(8)
Mn(2)−N(3)	2.128(3)	N(3)−Mn(1)−Mn(2)	51.07(8)
Mn(2)−N(4)	1.935(2)	Mn(1)−N(2)−Mn(2)	79.20(9)
Compound **4**			
Fe(1)−N(1)	1.878(3)	N(1)−Fe(1)−N(2A)	146.98(12)
Fe(1)−N(2)	2.085(3)	N(2)−Fe(1)−N(2A)	97.94(12)
Fe(1)−N(2A)	2.022(3)	N(1)−Fe(1)−Fe(1A)	137.06(9)
Fe(1)−Fe(1A)	2.557(2)	N(2)−Fe(1)−Fe(1A)	50.39(9)
Fe(1A)−N(2)	2.022(3)	N(2A)−Fe(1)−Fe(1A)	52.61(9)
N(1)−Fe(1)−N(2)	108.89(12)	Fe(1)−N(2)−Fe(1A)	77.00(11)
Compound **5**			
Zn(1)−N(1)	1.8537(16)	N(1)−Zn(1)−N(2A)	111.45(6)
Zn(1)−N(2)	1.9969(16)	N(2)−Zn(1)−N(2A)	92.92(6)
Zn(1)−N(2A)	2.0798(15)	N(1)−Zn(1)−Zn(1A)	136.14(5)
Zn(1)−Zn(1A)	2.6505(5)	N(2)−Zn(1)−Zn(1A)	50.82(4)
Zn(1A)−N(2)	2.0798(15)	N(2A)−Zn (1)−Zn(1A)	48.10(5)
N(1)−Zn(1)−N(2)	148.69(6)	Zn(1)−N(2)−Zn(1A)	81.08(5)

The X-ray structural analysis of **2** (Figure 1) reveals a monomer with two three-coordinate lithium atoms. Each of the lithium atoms is bonded to two nitrogen atoms of the chelating ligand and one oxygen atom of the coordinated ether ligand. It is better to describe the coordination sphere of the Li atoms as trigonal-planar rather than trigonal-pyramidal. Two C_3N_2Li six-membered rings are formed, one of which displays a boat conformation while the other is in a chair conformation. The interplanar angle between the two central LiN_2 planes is 43.8°. The Li−N distances are in the normal range (1.94−2.15 Å).[2b] In addition, there are some very close contacts between Li(1), Li(2) and various carbon and hydrogen atoms from the chelating ligand [Li(1)−H(26a): 2.29(4) Å; Li(2)−C(2): 2.36(2) Å; Li(2)−H(2a): 2.02(4) Å]. Similar contacts have been observed in $[Li(Dipp)NCH_2CH_2N(Dipp)Li]_2$.[2b]

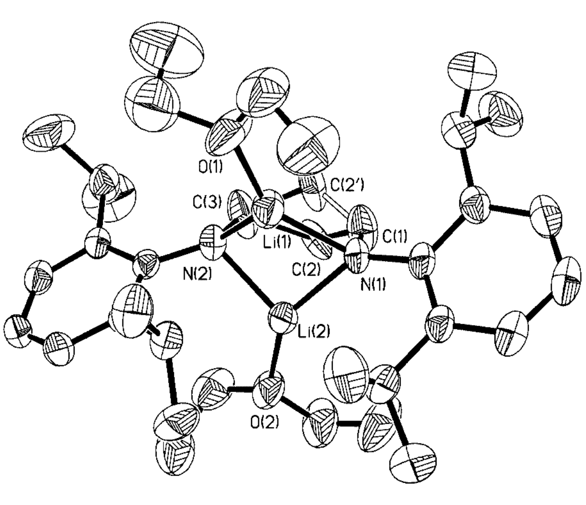


Figure 1. ORTEP drawing for **2** (50% probability ellipsoids)

The X-ray solid-state structural analysis reveals that complexes **3**−**5** are isostructural and dimeric. The dimers are formed through two bridging nitrogen atoms. Compound $[Mn_2\{N(Dipp)(CH_2)_3N(Dipp)\}_2]$ (**3**; Figure 2) crystallizes in the triclinic space group $P\bar{1}$, while compounds $[Fe_2\{N(Dipp)(CH_2)_3N(Dipp)\}_2]$ (**4**; Figure 3) and $[Zn_2\{N(Dipp)(CH_2)_3N(Dipp)\}_2]$ (**5**; Figure 4) crystallize in the monoclinic space group *C*2/*c*. The central core of these compounds contains a nonplanar MNMN four-membered ring, which is in a butterfly configuration, with dihedral angles of 28.6° in **3**, 30.9° in **4**, and 35.0° in **5**. This arrangement is caused by the strain of the bulky aryl groups. Each metal atom is surrounded by three nitrogen atoms and always lies out of the plane formed by these nitrogen atoms (0.33 Å in **3**, 0.26 Å in **4**, and 0.26 Å in **5**), so that all the metal atoms are in a trigonal-pyramidal geometry. The two ligands chelate two metal atoms to fuse two six-membered MN_2C_3 rings, which display a boat conformation with the two metal atoms at the stern and the corresponding opposite carbon atoms at the bow. The metal atoms are about 0.20 Å (av. 0.17 Å in **3**, 0.22 Å in **4**, and 0.18 Å in **5**) out of the plane formed by the two carbon and two nitrogen atoms. The opposite carbon atoms are about 0.70 Å (av. 0.72 Å in **3**, 0.71 Å in **4**, and 0.73 Å in **5**) out of the plane.

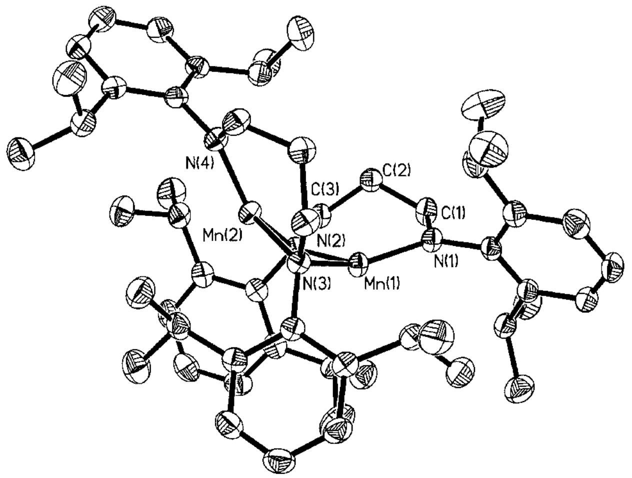


Figure 2. ORTEP drawing for **3** (50% probability ellipsoids)

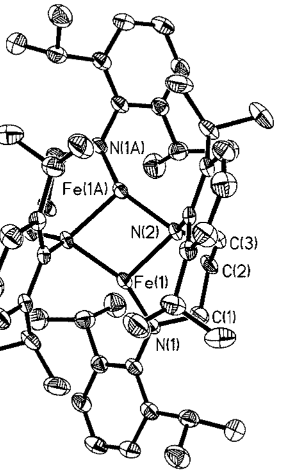


Figure 3. ORTEP drawing for **4** (50% probability ellipsoids)

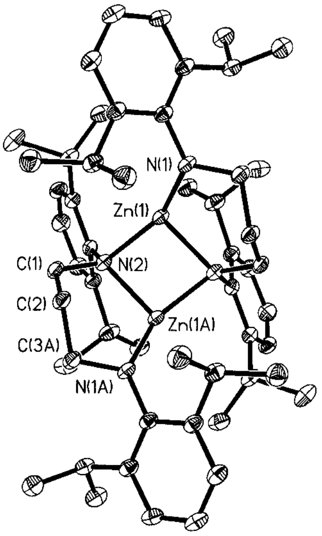


Figure 4. ORTEP drawing for **5** (50% probability ellipsoids)

The ligand in complexes **3**−**5** is both chelating and bridging, so that one of the nitrogen atoms is three-coordinate and the other four-coordinate. To the best of our knowledge, complexes **3**−**5** are the first examples with the diamide ligands in such a bonding mode. The terminal M−N distances in these complexes (Mn−N: 1.93 Å; Fe−N: 1.88 Å; Zn−N: 1.85 Å) are significantly shorter than those of the corresponding bridging ones (Mn−N: 2.10 Å; Fe−N: 2.05 Å; Zn−N: 2.04 Å). The M−N distances decrease in the order Mn−N > Fe−N > Zn−N, while the N−M−N angles increase in the order N−Mn−N < N−Fe−N < N−Zn−N, which is consistent with the relative sizes of the cations: $Mn^{2+} > Fe^{2+} > Zn^{2+}$.[8] The terminal and bridging M−N distances in **3** and **4** are about 0.06 Å shorter than the corresponding distances in the dimeric silylamides $Mn_2[N(SiMe_3)_2]_4$ [9] and $Fe_2[N(SiMe_3)_2]_4$.[10] The terminal M−N bond lengths in complexes **3** and **4** are even shorter than those found in amides with two coordinate metal centers $[Mn\{N(SiMePh_2)_2\}_2]$ (Mn−N 1.99 Å) and $[Fe\{N(SiMe_2Ph)_2\}_2]$ (Fe−N 1.92 Å).[11] This possibly results from the strong N→Si interaction in the silylamide.[10]

The M−M distances and the M−N−M angles in complexes **3** and **4** are 2.69 Å and 79.2°, and 2.56 Å and 77.0°, respectively, which indicates that there is some contact between the metal centers. The M−M distances are significantly shorter than those in the commonly planar MNMN four-membered rings.[9,10]

Magnetic Susceptibility Measurements

The temperature dependence of the molar magnetic susceptibility, χ_m and $\chi_m T$, for compounds **3** and **4** are displayed in Figures 5 and 6, respectively. The plots of $\chi_m T(T) - T$ for the two compounds indicate a magnetic behavior with an antiferromagnetic exchange interaction between the nearest neighboring spins. The value of $\chi_m T$ at 300 K is estimated to 6.82 emu·K·mol^{-1} for **3** and 5.16 emu·K·mol^{-1} for **4**. These values are lower than those of the spin-only value ($S = 5/2$ for Mn^{II} dimer and $S = 2$ for Fe^{II} dimer). This reveals that there is an antiferromagnetic exchange interaction between the two metal atoms in both compounds.

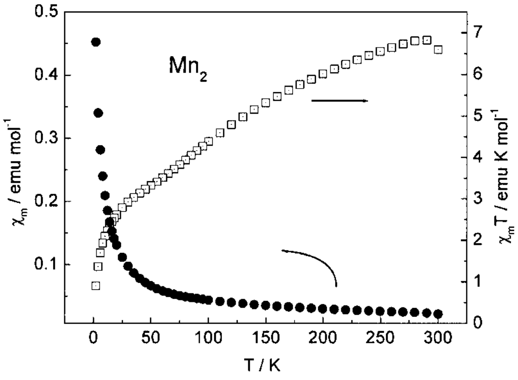


Figure 5. Plots of $\chi_m(T) - T$ and $\chi_mT(T) - T$ for compound **3**

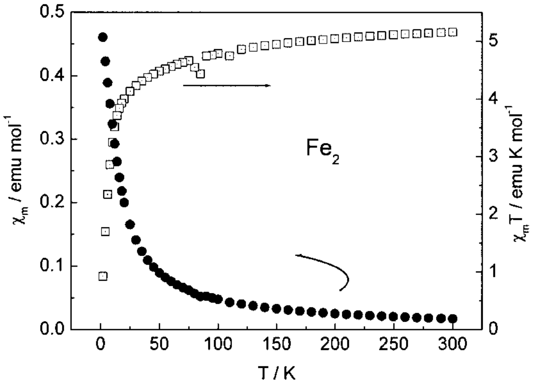


Figure 6. Plots of $\chi_m(T) - T$ and $\chi_mT(T) - T$ for compound **4**

In summary, we have successfully synthesized and characterized novel dimeric Mn^{II}, Fe^{II}, and Zn^{II} complexes, which contain three-coordinate metal centers by using the bulky diamide ligand $DippNH(CH_2)_3NHDipp$. In complexes **3**−**5** the ligand is both chelating and bridging, so that one of the nitrogen atoms is three-coordinate and the other four-coordinate. Complexes **3**−**5** are the first examples with diamide ligands in such a bonding mode.

Experimental Section

General: All reactions were performed using standard Schlenk and dry-box techniques. Solvents were appropriately dried and distilled under dinitrogen prior to use. ^1H and ^7Li NMR spectra were recorded with Bruker AM-250, AM-300 and AM-500 instruments. The chemical shifts are reported in ppm with reference to external standards: $SiMe_4$ for ^1H and $LiCl/D_2O$ for ^7Li. The magnetic susceptibility measurements were carried out with a Quantum-Design-MPMS-5S SQUID magnetometer in the range from 300 K to 2 K. The powdered samples were placed in a gel bucket and fixed in a nonmagnetic sample holder. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Mass spectra were recorded with a Finnigan Mat 8230. IR spectra were measured with a Bio-Rad Digilab FTS-7 spectrometer as Nujol mulls between KBr plates. $[DippNH(CH_2)_3NH(Dipp)]$ (**1**) was prepared according to a literature method.[5c]

$[N(Dipp)(CH_2)_3N(Dipp)][Li(OEt_2)]_2$ (2): MeLi (5.5 mL, 1.6 M in diethyl ether, 8.8 mmol) was added at −78 °C to a diethyl ether (35 mL) solution of **1** (1.58 g, 4 mmol). The mixture was warmed to room temperature and stirred for an additional 14 h. The precipitate was removed by filtration. The filtrate was concentrated to about 10 mL and kept at −26 °C for 24 h to give colorless crystals. The crystals were collected by filtration and the mother liquor was concentrated to about 4 mL and kept at −26 °C for 24 h to give colorless crystals. Total yield: 2.04 g (92%). M.p. 110 °C (dec). ^1H NMR (250 MHz, C_6D_6): $\delta = 0.95$ (t, 12 H, $J = 7.1$ Hz, $MeCH_2O$), 1.23 (d, 12 H, $J = 6.8$ Hz, Me_2CH), 1.34 (d, 12 H, Me_2CH), 1.79 (br., 2 H, NCH_2CH_2), 3.00−3.25 (m, 4 H, $J = 7.2$ Hz, NCH_2CH_2), 3.12 (t, 8 H, $J = 7.0$ Hz, $MeCH_2O$), 3.38 (sept, 4 H, $J = 6.9$ Hz, $CHMe_2$), 6.91−7.22 (m, C_6H_3, 6 H) ppm. ^7Li NMR (300 MHz, C_6D_6): $\delta = 1.90$ ppm. $C_{35}H_{60}Li_2N_2O_2$ (554.75): calcd. C 75.78, H 10.90, N 5.05; found C 75.92, H 11.02, N 4.85.

$[Mn_2\{N(Dipp)(CH_2)_3N(Dipp)\}_2]$ (3): A solution of **2** (1.1 g, 2 mmol) in diethyl ether (10 mL) was added to a suspension of $MnCl_2$ (0.25 g, 2 mmol) in diethyl ether (30 mL) at −78 °C. The mixture was warmed to room temperature and stirred for additional 14 h. The precipitate was removed by filtration and extracted with dichloromethane (10 mL). A yellow-green solid was obtained by removing the solvent in vacuo. The mother liquor was concentrated to about 10 mL and yellow-green crystals were obtained at room temperature after 5 d. Total yield: 0.64 g (72%). M.p. 220 °C (dec). EI-MS: *m*/*z* (%) = 894 (49) $[M]^+$, 705 (100) $[M - CH_2NDipp]^+$, 447 (68) $[1/2\ M]^+$. $C_{54}H_{80}Mn_2N_4$ (895.10): calcd. C 72.39, H 8.94, N 6.26; found C 72.15, H 8.94, N 6.17. IR (KBr, nujol mull): $\tilde{\nu}$ = 1426 (w), 1308 (w), 1260 (w), 1243 (w), 1169 (w), 1092 (w), 1073 (w), 1041(w), 1019 (w), 857 (w), 800 (w), 786 (w), 722 (w) cm^{-1}.

$[Fe_2\{N(Dipp)(CH_2)_3N(Dipp)\}_2]$ (4): A solution of **2** (1.1 g, 2 mmol) in diethyl ether (10 mL) was added to a suspension of $FeCl_2$ (0.25 g, 2 mmol) in diethyl ether (30 mL) at −78 °C. The mixture was warmed to room temperature and stirred for additional 14 h. The precipitate was removed by filtration. The dark-blue filtrate was concentrated to about 10 mL and crystals of **4** were obtained at room temperature after 5 d. Yield: 0.67 g (75%). M.p. 228 °C (dec). EI-MS: *m*/*z* (%) = 896 (68) $[M]^+$, 504 (100) $[M - N(Dipp)(CH_2)_3N(Dipp)]^+$, 448 (13) $[1/2\ M]^+$. $C_{54}H_{80}Fe_2N_4$ (896.92): calcd. C 72.25, H 8.92, N 6.24; found C 72.08, H 8.63, N 6.13. IR (KBr, nujol mull): $\tilde{\nu}$ = 1403 (w), 1308 (w), 1262 (w), 1201 (w), 1155 (w), 1094 (m), 1030 (m), 973 (w), 933 (w), 918 (w), 890 (w), 801 (m), 750 (w), 722 (m), 658 (w), 597 (w), 564 (w), 540 (w), 465 (w) cm^{-1}.

$[Zn_2\{N(Dipp)(CH_2)_3N(Dipp)\}_2]$ (5): The procedure is the same like that described for **3**. Yield: 0.72 g (79%). M.p. 223 °C (dec). EI-MS: *m*/*z* (%) = 916 (7) $[M]^+$, 456 (100) $[1/2\ M]^+$. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.16$ (d, 6 H, $J = 6.8$ Hz, Me_2CH), 0.43 (d, 6 H, Me_2CH), 0.99 (d, 6 H, Me_2CH), 1.21−1.28 (m, 24 H, Me_2CH), 1.36 (d, 6 H, Me_2CH), 2.20−2.34 (m, 4 H, $J = 9.7$ Hz, NCH_2CH_2), 2.71(t, 2 H, $J = 7.1$ Hz, NCH_2CH_2), 2.81 (m, 2 H, $J = 6.9$ Hz, $CHMe_2$), 3.02 (t, 2 H, NCH_2CH_2), 3.12 (m, 4 H, NCH_2CH_2), 3.27 (m, 2 H, $CHMe_2$), 3.72 (m, 2 H, NCH_2CH_2), 3.97 (t, 2 H, NCH_2CH_2), 4.04 (m, 2 H, $CHMe_2$), 3.72 (m, 2 H, $CHMe_2$), 6.78−7.45 (m, 12 H, C_6H_3) ppm. $C_{54}H_{80}N_4Zn_2$ (915.96): calcd. C 70.75, H 8.73, N 6.11; found C 70.34, H 8.68, N 5.85. IR

Table 3. Crystallographic data for compounds **2**−**5**

	2	**3**	**4**	1/2 **5**
Empirical formula	$C_{35}H_{60}Li_2N_2O_2$	$C_{54}H_{80}Mn_2N_4$	$C_{54}H_{80}Fe_2N_4$	$C_{27}H_{40}N_2Zn$
Formula mass	554.73	895.10	896.92	457.98
Temperature [K]	200(2)	203(2)	203(2)	133(2)
Wavelength [Å]	0.71073	0.71073	0.71073	1.54178
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$C2/c$
Unit cell dimensions [Å]	a = 11.224(2)	a = 11.545(9)	a = 25.14(2)	a = 25.057(2)
	b = 9.6466(19)	b = 13.642(10)	b = 11.472(12)	b = 11.447(2)
	c = 32.070(6)	c = 18.014(15)	c = 18.121(9)	c = 17.881(2)
	α = 90°	α = 105.26(8)°	α = 90°	α = 90°
	β = 92.19(3)°	β = 94.01(3)°	β = 108.12(6)°	β = 108.00(2)°
	γ = 90°	γ = 111.954(18)°	γ = 90°	γ = 90°
Volume [$Å^3$]	3469.7(12)	2490(1)	4970(1)	4877.7(11)
Crystal size [mm]	1.00 × 0.70 × 0.60	1.00 × 0.50 × 0.30	1.30 × 0.40 × 0.40	0.10 × 0.10 × 0.10
Z	4	2	4	8
Absorption coefficient [mm^{-1}]	0.063	0.545	0.623	1.491
θ range for data collection	3.60 to 22.53°	3.54 to 25.04°	3.55 to 22.51°	3.71 to 60.69°
F(000)	1224	964	1936	1968
Reflections collected	7629	11007	3256	11348
Independent reflections	4515 (R_{int} = 0.0710)	8774 (R_{int} = 0.0616)	3219 (R_{int} = 0.0799)	3661 (R_{int} = 0.0383)
Data/restraints/parameters	4515/0/393	8774/0/557	3219/0/279	3661/0/279
Goodness-of-fit on F^2	1.115	1.023	1.044	1.032
Final R indices [$I > 2\sigma(I)$]	0.0979, 0.2922	0.0461, 0.1150	0.0591, 0.1561	0.0295, 0.0736
R (all data)	0.1357, 0.3219	0.0601, 0.1258	0.0661, 0.1665	0.0328, 0.0754
Largest difference peak/hole [$e{\cdot}Å^{-3}$]	0.527/−0.427	0.533/−0.638	0.491/−1.112	0.032/−0.460

(KBr, nujol mull): $\tilde{\nu}$ = 1587 (w), 1320 (w), 1309 (m), 1273 (w), 1262 (w), 1245 (w), 1167 (m), 1100 (m), 1073 (w), 1043 (w), 967 (w), 931 (w), 888 (w), 861 (w), 801 (w), 788 (m), 759 (w), 746 (w), 722 (m), 610 (w), 556 (w), 479 (w) cm^{-1}.

X-ray Crystallography: Crystallographic data for **2**−**4** (Table 3) were collected with a Stoe−Siemens−Huber four-circle diffractometer coupled to a Siemens CCD area-detector with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and for **5** with a Bruker three-circle diffractometer equipped with a SMART 6000 CCD area-detector using Cu-K_α radiation (λ = 1.54178 Å). All structures were solved by direct methods (SHELXS-97)[12] and refined against F^2 using SHELXL-97.[13] All non-hydrogen atoms were refined anisotropically. The central carbon atom C(2) in **2** is disordered over two positions C(2) and C(2′), which were isotropically refined with site-occupation factors of 0.34 and 0.66, respectively. CCDC-233452 (**2**), -233453 (**3**), -233454 (**4**), and -233455 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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