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Article

Synthesis and Structures of Selected Triazapentadienate of Li, Mn, Fe, Co, Ni, Cu(I), and Cu(II) using 2,4-*N,N′*-Disubstituted 1,3,5-Triazapentadienate Anions as Ancillary Ligands: [N(Ar)C(NMe$_2$)NC(NMe$_2$)N(R)]$^-$ (Ar = Ph, 2,6-^{i}Pr$_2$−C$_6$H$_3$; R = H, SiMe$_3$)

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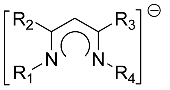
Addition reaction of ArN(SiMe$_3$)M (Ar = Ph or 2,6-^{i}Pr$_2$−C$_6$H$_3$ (Dipp); M = Li or Na) to 2 equivalents of α-hydrogen-free nitrile RCN (R = dimethylamido) gave the dimeric [M{N(Ar)C(NMe$_2$)NC(NMe$_2$)N(SiMe$_3$)}]$_2$ (**1a**, Ar = Ph, M = Li; **1b**, Ar = Ph, M = Na; **1c**, Ar = Dipp, M = Li). **1d** was obtained by hydrolysis of **1c** at ambient temperature. Treatment of a double ratio of **1a** or **1b** with anhydrous MCl$_2$ (M = Mn, Fe, Co) yielded the 1,3,5-triazapentadienato complexes [M{N(Ph)C(NMe$_2$)NC(NMe$_2$)N(SiMe$_3$)}$_2$] (M = Mn, **2**; Fe, **3**; Co, **4**) and with NiCl$_2\cdot$6H$_2$O gave [M{N(Ph)C(NMe$_2$)NC(NMe$_2$)N(H)}$_2$] (M = Ni, **5**). Treatment of an equiv of **1c** with anhydrous CuCl in situ and in air led to complexes [{N(Dipp)C(NMe$_2$)NC(NMe$_2$)N(SiMe$_3$)}CuPPh$_3$] **6** and [Cu{N(Dipp)C(NMe$_2$)NC(NMe$_2$)N(H)}$_2$] **7**, respectively. **1c**, **1d**, and **2**−**7** were characterized by X-ray crystallography and microanalysis. **1c**, **1d**, **5**, and **6** were well characterized by ^{1}H, ^{13}C NMR, **1c** by ^{7}Li, and **6** by ^{31}P NMR as well. The structural features of these complexes were described in detail.

Introduction

1,5-diazapentadienyl (also known as β-diketiminate, **1**) and 1,3,5-triazapentadienato anions are the acyclic analogues of C$_5$H$_5^-$ that contain heteroatoms. The five-membered conjugated π system has attracted increasing attention because of its synthetic utility in organic and organometallic chemistry and theoretical interest in coordination chemistry.[1,2] For 1,5-diazapentadienyl ligands **1**, it has been used in the stabilization of low-valent, low-coordinate main-group and transition-metal adducts,[3,4] and some of their transition-metal complexes are used as catalysts for the polymerization of olefin.[5]



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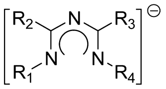

2

The 1,3,5-triazapentadienato ligand **2** is also valuable as a spectator ligand because it is generally firmly bound to the metals by the donor nitrogen atoms; its steric and electronic properties of the ligand can be fine-tuned by variation of the substitutes R^1∼R^4; and three nitrogen atoms in the backbone NCNCN provide the possibility of a variety of bonding modes to metals by adopting W-(κ^1-bonded on the central nitrogen or one of the terminal nitrogen atoms) or U-shaped (κ^2-bonded) conformations.[2,6–9] In many recent

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publications, the motivation to make 1,3,5-triazapentadienes or their metal complexes was governed by highly fluorinated substituents.[10,11] These perfluoroalkyl groups have been used to improve the thermal stability, oxidative resistance, volatility, and fluorocarbon solubility of metal adducts.[12] These fluorinated triazapentadienyl ligands include $[N\{(C_3F_7)C(H)N\}_2]^-$,[13] $[N\{(C_3F_7)C(2,4,6\text{-}Me_3C_6H_2)N\}_2]^-$,[11] $[N\{(C_3F_7)C(Ph)N\}_2]^-$,[8,14] $[N\{(C_3F_7)C(Dipp)N\}_2]^-$,[7,15] $[N\{(C_3F_7)C(C_6F_5)N\}_2]^-$, and $[N\{(C_3F_7)C(2\text{-}F,6\text{-}(CF_3)C_6H_3)N\}_2]^-$.[10] Several neutral nonfluorinated triazapentadienyl ligands and their mononuclear metal complexes, homo- or heterotrinuclear clusters, were isolated.[16–18] Other related reports concerned $[RNC(H)NC(H)NC(H)CHR]^-$ and $[RNC(H)NC(H)NC(H)NR]^-$ ($R = SiMe_3$).[19,20] Recently, we described the synthesis of nonsymmetric guanidinato ligands and their metal complexes via the reaction of $ArN(SiMe_3)Li$ (Ar = Ph or $2,6\text{-}{}^iPr_2{-}C_6H_3$) and α-hydrogen-free nitriles.[21,22] A new system of 2,4-disubstituted 1,3,5-triazapentadienyl ligands $[RNC(NMe_2)NC(NMe_2)NR]^-$ ($R = SiMe_3$) having two guanidinato moieties was developed and used in the isolation of copper(I) complexes.[23] In this article, we report our proceeding studies on addition reaction of $PhN(SiMe_3)M$ (M = Li or Na) or $(Dipp)N(SiMe_3)Li$ with 2 equiv of α-hydrogen-free dimethylcyanamide, which led to in situ synthesis of 1,3,5-triazapentadienato ligands $[N(Ar)C(NMe_2)NC(NMe_2)N(R)]^-$ and further to their derived transition-metal complexes. They are: $[M\{ArNC(NMe_2)NC(NMe_2)N(SiMe_3)\}]_2$ (**1a**, Ar = Ph, M =Li; **1b**, Ar = Ph, M = Na; **1c**, Ar = Dipp, M = Li), $[N(Dipp)C(NMe_2)NC(NMe_2)NH_2]$ **1d**, $M\{N(Ph)C(NMe_2)NC(NMe_2)N(SiMe_3)\}_2$ (M = Mn, **2**; Fe, **3**; Co, **4**); $Ni\{N(Ph)C(NMe_2)NC(NMe_2)N(H)\}_2$ **5**, $\{N(Dipp)C(NMe_2)NC(NMe_2)N(SiMe_3)\}CuPPh_3$ **6**, and $Cu\{N(Dipp)C(NMe_2)NC(NMe_2)N(H)\}_2$ **7**. The NCNCN ligand backbone in **1c** and **1d** adopted a W-shaped configuration, and showed short−long−long−short and short−long−short−long C−N bond distance pattern, respectively; whereas in **2**−**7** the NCNCN backbone adopted a U-shaped configuration. Tetrahedral structures were found for **2**, **3**, **4** and **7**. Square-planar structure was observed for the Ni(II) complex **5**. Three-coordinate Cu(I) atom in **6** featured a trigonal planar environment.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were purchased from commercial sources. Deuterated solvents C_6D_6 and $CDCl_3$ were dried over activated molecular sieves (4 Å) and vacuum transferred before use. Hexane was dried using sodium−potassium alloy. Diethyl ether was dried and distilled from sodium/benzophenone and stored over a sodium mirror under argon. Dichloromethane was distilled from activated molecular sieves (4 Å) or CaH_2. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded on a Bruker DKX-300 instrument, and solvent resonances were used as the internal references for ^1H spectra and ^{13}C spectra. Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were carried out using a Vario EL-III analyzer (Germany).

Preparations. $\mathbf{[N(Dipp)C(NMe_2)NC(NMe_2)N(SiMe_3)Li]_2}$ **(1c).** $(CH_3)_2NCN$ (0.42 mL, 5.24 mmol) was added to a solution of $(Dipp)N(Li)SiMe_3$ (0.67 g, 2.62 mmol) in Et_2O (30 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for overnight. The mixture was concentrated in vacuo to ca. 10 cm^3 and set aside at room temperature for 2 d to give colorless crystals of **1c** (0.45 g, 60%). Mp: 149∼151 °C. Found: C, 63.70; H, 9.66; N, 16.50. $C_{46}H_{86}Li_2N_{10}Si_2O$ requires C, 63.85; H, 10.02; N, 16.19%. ^1H NMR (C_6D_6): δ 0.55 (s, 18 H, $SiMe_3$), 1.05−1.49 (d, 24 H, $CH(CH_3)_2$), 1.07−1.22, 3.30−3.36 (Et_2O), 2.38−2.81 (m, 24 H, $N(CH_3)_2$), 3.18−3.49 (sep, 4 H, $CH(CH_3)_2$), 7.12∼7.15 (m, 6 H, Ph). ^{13}C NMR (C_6D_6): δ 4.92 ($SiMe_3$), 16.3 (Et_2O), 23.0, 23.6, 24.4, 26.2 ($CH(CH_3)_2$), 28.5, 29.6 ($CH(CH_3)_2$), 39.4 ($N(CH_3)_2$), 66.6 (Et_2O), 123.0 (*p*-CAr), 123.5 (*m*-CAr), 141.0, 141.7 (*o*-CAr), 146.7(C_{ipso}), 161.7, 163.9 (NCN). ^7Li NMR (C_6D_6): δ 2.05, 2.36.

$\mathbf{[N(Dipp)C(NMe_2)NC(NMe_2)NH_2]}$ **(1d).** $(CH_3)_2NCN$ (0.38 mL, 4.74 mmol) was added to a solution of $(Dipp)N(Li)SiMe_3$ (0.61 g, 2.37 mmol) in Et_2O (30 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for overnight. Diethyl ether solution (10 mL) of distilled water (0.09 mL, 4.74 mmol) was added slowly via a syringe at room temperature. After overnight reaction, the pale-yellow mixture was filtered. The filtrate was concentrated in vacuo to ca. 10 cm^3 and left at room temperature for 3 d to give colorless crystals of **1d** (0.45 g, 60%). Found: C, 67.80; H, 10.04; N, 22.09. Anal. Calcd for $C_{18}H_{31}N_5$: C, 68.10; H, 9.84; N, 22.06%. ^1H NMR ($CDCl_3$): δ 1.04∼1.32 (d, 12 H, $CH(CH_3)_2$), 2.66, 2.87 (d, 12 H, NMe), 3.0∼3.3 (sep, 2 H, $CH(CH_3)_2$), 4.04 (s, 2 H, NH_2), 6.8∼7.4 (m, 3 H, *m*- and *p*-Ar). ^{13}C NMR ($CDCl_3$): δ 22.1∼24.0 (m, $CH(CH_3)_2$), 27.3, 28.2 (d, $CH(CH_3)_2$), 36.0, 38.4 (d, $N(CH_3)_2$), 121.6 (*p*-CAr), 122.8, 124.3 (*m*-CAr), 138.6, 139.3 (*o*-CAr), 147.2 (C_{ipso}), 154.9 ($NC(NMe_2)NH_2$) 155.7 ($(Dipp)NC(NMe_2)N$).

$\mathbf{[N(Ph)C(NMe_2)NC(NMe_2)N(SiMe_3)]_2Mn}$ **(2).** $(CH_3)_2NCN$ (0.53 mL, 6.52 mmol) was added to a solution of $PhN(Li)SiMe_3$ (0.56 g, 3.26 mmol) in Et_2O (30 mL) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for overnight. $MnCl_2$ (0.21 g, 1.63 mmol) was added at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for 24 h. The volatiles were removed in vacuo, and the residue was extracted with dichloromethane and filtered. The filtrate was concentrated in vacuo to ca. 15 cm^3 and stored at −25 °C for several days, yielding colorless

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Table 1. Crystal and Refinement Data for **1c**, **1d**, and **2**− **7**

compound	**1c**	**1d**	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_{46}H_{86}Li_2N_{10}OSi_2'$	$C_{18}H_{31}N_5$	$C_{30}H_{52}MnN_{10}\ Si_2$	$C_{30}H_{52}FeN_{10}Si_2$	$C_{30}H_{52}CoN_{10}Si_2$	$C_{24}H_{36}N_{10}Ni$	$C_{40}H_{55}Cl_2CuN_5PSi$	$C_{36}H_{60}CuN_{10}$
M	865.31	317.48	663.94	664.85	667.93	523.34	799.39	696.48
cryst syst	triclinic	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic	tetragonal
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	*P*4(1)2(1)2 (No. 92)
a/Å	13.59(4)	10.1709(17)	11.134(5)	11.130(2)	11.163(2)	6.1011(15)	9.7388(14)	13.633(3)
b/Å	14.56(5)	13.600(2)	12.007(6)	11.964(2)	11.961(3)	9.633(2)	13.984(2)	13.633(3)
c/Å	15.79(4)	13.715(2)	16.169(8)	16.128(3)	16.070(3)	11.585(3)	16.228(2)	21.512(9)
α/°	71.21(19)	90.00	90.45(5)	90.709(2)	90.522(3)	81.911(3)	94.386(2)	90.00
β/°	76.3(2)	92.923(3)	107.54(3)	107.657(2)	107.442(3)	78.156(3)	96.268(2)	90.00
γ/°	73.2(3)	90.00	115.20(3)	115.459(2)	115.851(2)	75.471(3)	102.157(2)	90.00
U/Å^3	2797(14)	1894.6(6)	1841.5(16)	1822.1(6)	1817.6(7)	642.2(3)	2136.2(5)	3998(2)
Z	2	4	2	2	2	1	2	4
absorption coeff. (mm^{-1})	0.103	0.068	0.458	0.514	0.573	0.789	0.735	0.583
unique reflns, R_{int}	9326, 0.0308	3332, 0.0234	6197, 0.028	6291, 0.018	6283, 0.022	2217, 0.024	7382, 0.0196	3534, 0.028
reflections with $I > 2\sigma(I)$	6314	2800	5150	5679	5545	2059	6192	3368
final R indices [$I > 2\sigma(I)$] R_1, wR_2	0.0772, 0.2058	0.0636, 0.1624	0.067, 0.1757	0.044, 0.1043	0.053, 0.1174	0.064, 0.1324	0.0559, 0.1583	0.043, 0.1033
R indices (all data) R_1, wR_2	0.1086, 0.2304	0.0736, 0.1688	0.0813, 0.1899	0.0500, 0.1075	0.062, 0.1222	0.068, 0.1346	0.0651, 0.1666	0.045, 0.1048

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **1c** and **1d**

	1c		
Li(1)—N(1)	1.998(6)	Li(2)—N(3)	2.094(7)
Li(1)—N(3)	2.111(6)	Li(2)—N(5)	2.037(6)
Li(1)—N(6)	2.005(5)	Li(2)—N(8)	2.098(6)
Li(1)—N(8)	2.106(7)	Li(2)—N(10)	2.012(6)
N(1)—C(2)	1314(5)	N(6)—C(3)	1.315(5)
N(2)—C(2)	1.359(3)	N(7)—C(3)	1.362(4)
N(3)—C(2)	1.370(5)	N(8)—C(3)	1.366(4)
N(3)—C(4)	1.374(5)	N(8)—C(9)	1.368(4)
N(4)—C(4)	1.361(4)	N(9)—C(9)	1.373(4)
N(5)— C(4)	1.304(5)	N(10)—C(9)	1.313(4)
N(3)—Li(1)—N(8)	100.1(3)	N(1)—C(2)—N(3)	113.9(2)
N(3)—Li(2)—N(8)	100.9(3)	N(3)—C(4)—N(5)	116.3(3)
Li(1)—N(3)—Li(2)	79.5(3)	N(6)—C(3)—N(8)	114.1(3)
Li(1)—N(8)—Li(2)	79.5(3)	N(8)—C(9)—N(10)	116.3(2)
Li(1)—N(1)—C(2)	92.1(2)	N(1)—Li(1)—N(3)	66.3(2)
Li(1)—N(6)—C(3)	91.7(3)	N(6)—Li(1)—N(8)	66.3(2)
Li(2)—N(5)—C(4)	90.5(3)	N(3)—Li(2)—N(5)	66.1(3)
Li(2)—N(10)—C(9)	90.7(3)	N(8)—Li(2)—N(10)	67.3(2)
1d			
C(1)—N(1)	1.416(2)	N(3)—C(16)	1.311(3)
C(13)—N(1)	1.288(2)	N(4)—C(16)	1.360(3)
C(13)—N(2)	1.388(2)	N(5)—C(16)	1.346(3)
C(13)—N(3)	1.379(3)		
C(1)—N(1)—C(13)	119.01(16)	C(13)—N(3)—C(16)	122.27(17)
N(1)—C(13)—N(2)	118.06(18)	N(3)—C(16)—N(4)	124.38(19)
N(1)—C(13)—N(3)	124.03(17)	N(3)—C(16)—N(5)	118.42(19)
N(2)—C(13)—N(3)	117.84(17)	N(4)—C(16)—N(5)	117.1(2)

crystals of **2** (0.46 g, 42%). Mp: 130∼132 °C. Found: C, 54.72; H, 8.04; N, 20.91. $C_{30}H_{52}N_{10}Si_2Mn$ requires C, 54.27; H, 7.89; N, 21.10%.

[N(Ph)C(NMe$_2$)NC(NMe$_2$)N(SiMe$_3$)]$_2$Fe (3). $(CH_3)_2NCN$ (0.52 mL, 6.48 mmol) was added to a solution of PhN(Na)SiMe$_3$ (0.61 g, 3.24 mmol) in Et$_2$O (30 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for overnight. FeCl$_2$ (0.21 g, 1.62 mmol) was added at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for 24 h, filtered, and the filtrate was concentrated in vacuo to ca. 15 cm^3 and cooled at −25 °C for 3 d, yielding yellow crystals of **3** (0.52 g, 49%). Mp: 98 °C (decomp.). Found: C, 53.99; H, 7.48; N, 21.13. $C_{30}H_{52}N_{10}Si_2Fe$ requires C, 54.20; H, 7.88; N, 21.07%.

[N(Ph)C(NMe$_2$)NC(NMe$_2$)N(SiMe$_3$)]$_2$Co (4). $(CH_3)_2NCN$ (0.41 mL, 5.08 mmol) was added to a solution of PhN(Na)SiMe$_3$ (0.48 g, 2.54 mmol) in Et$_2$O (30 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for overnight. CoCl$_2$ (0.17 g, 1.27 mmol) was added at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for 24 h, filtered, and the filtrate was concentrated in vacuo to ca. 10 cm^3 and left at room temperature for several days, yielding purple crystals of **4** (0.57 g, 67%). Mp: 110∼112 °C. Found: C, 54.07; H, 7.39; N, 21.06. $C_{30}H_{52}N_{10}Si_2Co$ requires C, 53.95; H, 7.85; N, 20.97%.

[N(Ph)C(NMe$_2$)NC(NMe$_2$)N(H)]$_2$Ni (5). $(CH_3)_2NCN$ (0.37 mL, 4.62 mmol) was added to a solution of PhN(Na)SiMe$_3$ (0.43 g, 2.31mmol) in Et$_2$O (30 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for overnight. NiCl$_2$·6H$_2$O (0.28 g, 1.16 mmol) was added at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for 24 h, filtered, and the filtrate was concentrated in vacuo to ca. 10 cm^3 and left at room temperature for several days, yielding red crystals of **5** (0.23 g, 38%) in air. Mp: 161∼163 °C. Found: C, 54.85; H, 6.93; N, 26.11. $C_{24}H_{36}N_{10}Ni$ requires C, 55.08; H, 6.93; N, 26.77%. ^{1}H NMR (CDCl$_3$): δ 2.55∼3.11 (m, 24 H, NMe), 6.4 (s, 2 H, NH), 6.95∼7.35 (m, 10 H, Ph). ^{13}C NMR (CDCl$_3$): δ 39.8, 40.6, 41.9, 42.9 (NMe),

Table 3. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **2**−**5**

	2		
Mn—N(1)	2.096(4)	N(1)—C(7)	1.343(6)
Mn—N(5)	2.076(4)	N(3)—C(7)	1.324(5)
Mn—N(6)	2.074(4)	N(3)—C(10)	1.328(5)
Mn—N(10)	2.103(4)	N(5)—C(10)	1.335 (5)
N(1)—Mn—N(5)	92.85(15)	N(6)—Mn—N(10)	93.02(15)
C(7)—N(3)—C(10)	127.3(4)	Mn—N(1)—C(7)	117.8(3)
N(1)—C(7)—N(3)	125.3(4)	Mn—N(5)—C(10)	114.3(3)
N(3)—C(10)—N(5)	126.8(4)		
3			
Fe—N(1)	2.014(2)	N(1)—C(1)	1.344(3)
Fe—N(5)	2.038(2)	N(3)—C(1)	1.304(3)
Fe—N(6)	2.018(2)	N(3)—C(4)	1.346(3)
Fe—N(10)	2.031(2)	N(5)—C(4)	1.327(3)
N(1)—Fe—N(5)	94.57(8)	N(6)—Fe—N(10)	94.16(8)
C(1)—N(3)—C(4)	127.3(2)	Fe—N(1)—C(1)	116.33(16)
N(1)—C(1)—N(3)	129.3(2)	Fe—N(5)—C(4)	118.20(16)
N(3)—C(4)—N(5)	123.2(2)		
4			
Co—N(1)	1.996(2)	N(1)—C(1)	1.330(4)
Co—N(5)	1.989(2)	N(3)—C(1)	1.338(4)
Co—N(6)	1.990(2)	N(3)—C(4)	1.327(4)
Co—N(10)	1.991(2)	N(5)—C(4)	1.358(4)
N(1)—Co—N(5)	95.94(10)	N(6)—Co—N(10)	96.26(10)
C(1)—N(3)—C(4)	126.8(3)	Co—N(1)—C(1)	113.97(19)
N(1)—C(1)—N(3)	126.3(3)	Co—N(5)—C(4)	118.40(19)
N(3)—C(4)—N(5)	123.8(3)		
5			
Ni—N(1)	1.897(3)	N(3)—C(10)	1.341(5)
Ni—N(5)	1.857(3)	N(5)—C(10)	1.302(5)
N(1)—C(7)	1.368(5)	N(2)—C(7)	1.336(5)
N(3)—C(7)	1.327(5)	N(4)—C(10)	1.355(5)
N(5)— H(5A)	0.8600		
N(1)—Ni—N(5)	87.43(14)	N(3)—C(10)—N(5)	123.9(4)
C(7)—N(3)—C(10)	118.8(3)	Ni—N(1)—C(7)	116.5(3)
N(1)—C(7)—N(3)	126.6(4)	Ni—N(5)—C(10)	125.2(3)

Table 4. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **6** and **7**

	6		
Cu—N(1)	1.984(3)	N(1)—C(13)	1.327(4)
Cu—N(5)	1.984(3)	N(2)—C(13)	1.393(4)
Cu—P	2.164(9)	N(3)—C(13)	1.342(4)
P—C(22)	1.827(4)	N(3)—C(16)	1.325(4)
P—C(28)	1.833(4)	N(4)—C(16)	1.377(4)
P—C(39)	1.830(3)	N(5)—C(16)	1.342(4)
N(1)—C(1)	1.420(4)	N(5)—Si	1.710(3)
N(1)—Cu—N(5)	95.31(11)	C(22)—P—C(28)	102.21(16)
N(1)—Cu—P	136.94(8)	C(28)—P—C(39)	101.20(16)
N(5)—Cu—P	125.45(8)	C(22)—P—C(39)	104.54(16)
C(22)—P—Cu	105.95(11)	C(28)—P—Cu	119.72(11)
C(13)—N(1)—Cu	118.2(2)	C(39)—P—Cu	120.89(12)
C(16)—N(5)—Cu	112.2(2)	C(13)—N(3)—C(16)	126.5(3)
C(13)—N(1)—C(1)	121.5(3)	N(3)—C(16)—N(5)	127.7(3)
N(1)—C(13)—N(3)	125.7(3)	C(16)—N(5)—Si	126.9(2)
	7		
Cu(1)—N(1)	2.008(2)	N(3)—C(4)	1.340(4)
Cu(1)—N(4)	1.914(2)	N(4)—C(4)	1.308(4)
N(1)—C(1)	1.336(3)	N(2)—C(1)	1.414(4)
N(3)—C(1)	1.319(4)	N(5)—C(4)	1.371(4)
N(1)—Cu(1)—N(4)	89.54(10)	N(3)—C(4)—N(4)	125.7(2)
C(1)—N(3)—C(4)	124.2(2)	Cu(1)—N(1)—C(1)	123.4(19)
N(1)—C(1)—N(3)	128.1(3)	Cu(1) —N(4)—C(4)	129.0(2)

123.8 (*p*-*C*Ph), 127.6 (*m*-*C*Ph), 130.0 (*o*-*C*Ph), 141(*C*ipso), 155.0, 158.8 (N*C*N).

[N(Dipp)C(NMe$_2$)NC(NMe$_2$)N(SiMe$_3$)]CuPPh$_3$ (6). $(CH_3)_2NCN$ (0.40 mL, 5.02 mmol) was added to a solution of (Dipp)N(Li)SiMe$_3$ (0.64 g, 2.51 mmol) in Et$_2$O (30 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for overnight. CuCl (0.25 g, 2.51 mmol) and PPh$_3$ (0.66 g, 2.51 mmol) were added at −78 °C. The resulting mixture was allowed to warm to ca. 25 °C and stirred for 10 h. The volatiles were removed in vacuo, and the residue was extracted with dichloromethane and filtered. The filtrate was concentrated in vacuo to ca. 15 cm^3 and cooled at −25 °C for 2 d, yielding colorless crystals of **6** (0.75 g, 42%). Mp: 154∼156 °C. Found: C, 60.34; H, 6.81; N, 9.28. $C_{40}H_{55}Cl_2N_5PSiCu$ (include CH$_2$Cl$_2$) requires C, 60.10; H, 6.93; N, 8.76%. ^{1}H NMR (CDCl$_3$): δ 0.03∼0.51(m, 9 H, SiMe$_3$), 0.97∼1.44 (m, 12 H, CH(C*H*$_3$)$_2$), 2.5∼2.89 (m, 12 H, N(C*H*$_3$)$_2$), 3.03∼3.19 (m, 2 H, C*H*Me$_2$), 5.35 (s, 2 H, C*H*$_2$Cl$_2$), 7.01∼7.47 (m, 18 H, Ph). ^{13}C NMR (CDCl$_3$): δ 1.52 (SiMe$_3$), 24.5 (CH(*C*H$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 39.0 (N(*C*H$_3$)$_2$), 54.4 (*C*H$_2$Cl$_2$), 123.5 (*p*-*C*Ar), 124.1 (*m*-*C*Ar), 133.7 (*o*-CAr), 129.4 (*p*-CPh-P), 130.7 (*m*-CPh-P), 134.9 (*o*-CPh-P), 142.0 (*C*ipso-Ph-P), 145.3 (*C*ipso-Ar), 145.8, 146.7 (N*C*N). ^{31}P NMR (CDCl$_3$): δ −3.90.

[N(Dipp)C(NMe$_2$)NC(NMe$_2$)N(H)]$_2$Cu (7). $(CH_3)_2NCN$ (0.35 mL, 4.30 mmol) was added to a solution of (Dipp)N(Li)SiMe$_3$ (0.55 g, 2.15 mmol) in Et$_2$O (30 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred for overnight. CuCl (0.11 g, 1.07 mmol) was added at −78 °C. The resulting mixture was allowed to warm to ca. 25 °C and stirred for overnight. The volatiles were removed in vacuo, and the residue was extracted with dichloromethane and filtered. The filtrate was concentrated in vacuo to ca. 10 cm^3 and left at room temperature in air for 3 d, yielding black crystals of **7** (0.32 g, 43%). Mp: 152∼154 °C. Found: C, 62.10; H, 8.83; N, 20.19. $C_{36}H_{60}N_{10}Cu$ requires C, 62.08; H, 8.68; N, 20.11%.

X-ray Crystallography. Data collection of **1c**, **1d**, and **2**−**7** was performed with Mo Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD diffractometer at 298(2) or 213(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. A total of *N* reflections were collected by using ω scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption using multiscans (*SADABS*).[24] The structure was solved by direct method (*SHELXS-97*).[25] Then the remaining non-hydrogen atoms were obtained from the successive difference Fourier map. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were constrained to parent sites, using a riding mode (*SHELXTL*).[26] Crystal data and details of data collection and refinements for **1c**, **1d**, and **2**−**7** are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2, Table 3, and Table 4.

Results and Discussion

Synthesis and Characterization. The starting material for the synthesis of the new metal complexes was ArN(SiMe$_3$)Li (Ar = Ph or Dipp).[21,22,27] Treatment with Bu^{t}ONa in hexane yielded the hexane-insoluble ArN(SiMe$_3$)Na.[28] The above lithium and sodium salts were the source of the crystal-

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(24) Sheldrick, G. M. *Correction Software*; University of Göttingen: Göttingen, Germany, 1996.

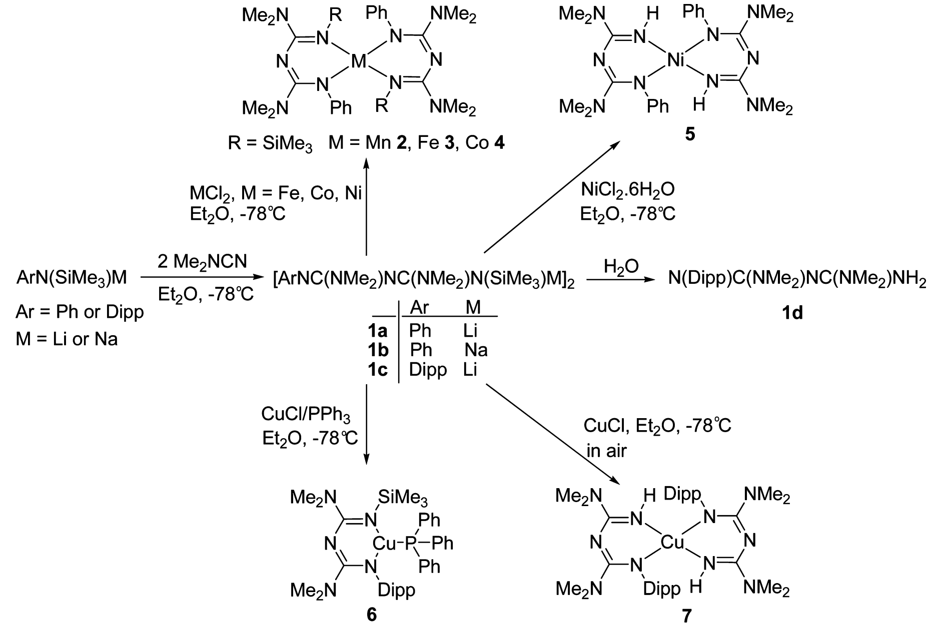
(25) Sheldrick, G. M. *Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(26) *Program for Crystal Structure Refinement*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, USA, 1998.

(27) Bezombes, J.-P.; Hitchcock, P. B.; Lappert, M. F.; Merle, P. G. *J. Chem. Soc., Dalton Trans.* **2001**, 816–821.

(28) Antolini, F.; Hitchcock, P. B.; Lappert, M. F.; Merle, P. G. *Chem. Commun.* **2000**, 1301–1302.

Scheme 1. Synthetic Routes to **1**−**7**



line 1,3,5-triazapentadienate **1a**−**1c** or complexes of manganese **2**, iron **3**, cobalt **4**, nickel **5**, copper(I) **6**, and copper(II) **7**. The synthetic routes to **1**−**7** were illustrated in Scheme 1.

Treatment of (Dipp)N(Li)SiMe$_3$ with 2 equiv of (CH$_3$)$_2$NCN in diethyl ether and recrystallization from Et$_2$O gave **1c** as colorless crystals in 60% yield. **1d** was obtained by careful hydrolysis of **1c** via addition of diluted distilled water in Et$_2$O at ambient temperature. **1a** and **1b** were not isolated but were generated in situ in a similar procedure to that for **1c**.

Treatment of **1a** with anhydrous manganese dichloride in diethyl ether and recrystallization from dichloromethane gave **2** as colorless crystals in 42% yield. **3** and **4** were obtained in good yields via the reaction of **1b** with anhydrous FeCl$_2$ or CoCl$_2$ as brown-yellow and purple crystals, respectively. They were slightly air and moisture sensitive in the solvent

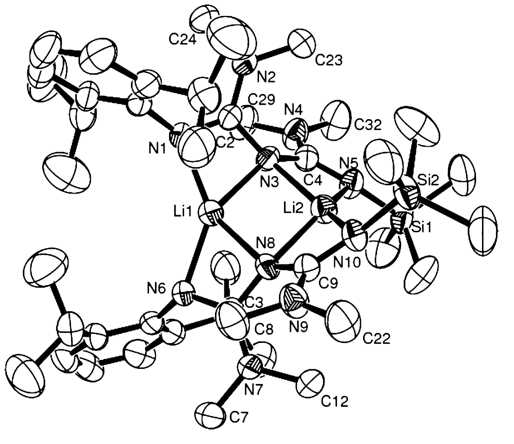


Figure 1. Molecular structure and atom numbering scheme for **1c**.

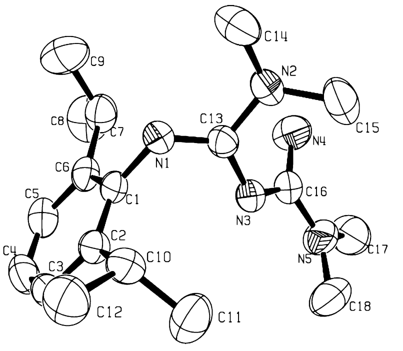


Figure 2. Molecular structure and atom numbering scheme for **1d**.

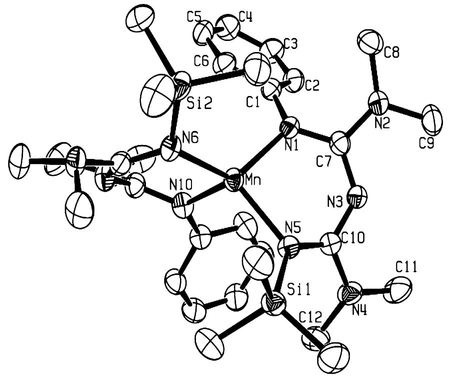


Figure 3. Molecular structure and atom numbering scheme for **2**.

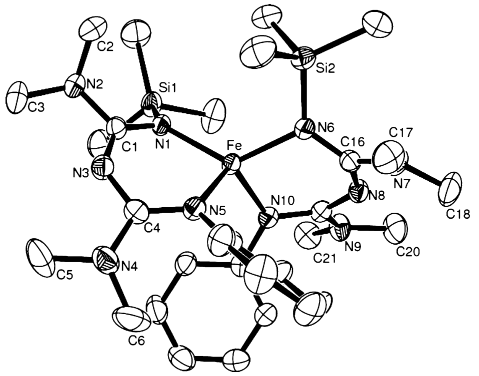


Figure 4. Molecular structure and atom numbering scheme for **3**.

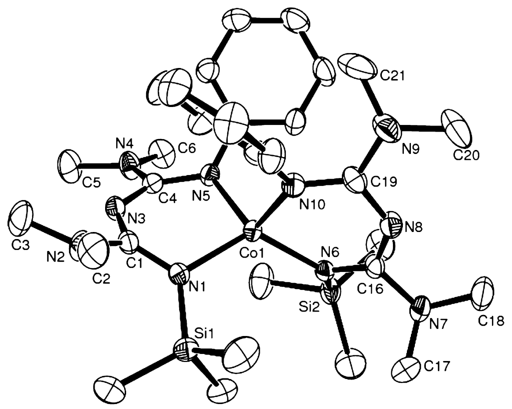


Figure 5. Molecular structure and atom numbering scheme for **4**.

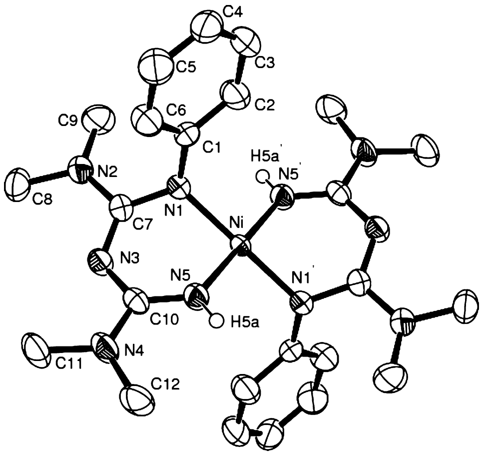


Figure 6. Molecular structure and atom numbering scheme for **5**.

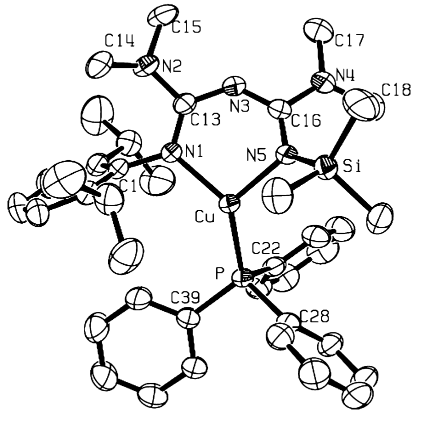


Figure 7. Molecular structure and atom numbering scheme for **6**.

and relatively stable in the solid state for a couple of hours, very soluble in Et_2O. A similar methodology to **3** and **4** was used in the reaction of **1b** and $NiCl_2 \cdot 6H_2O$ gave red crystals of nickel **5**. Because of the d^8 configuration, nickel preferred a planar geometry and trimethylsilyl groups were inevitably hydrolyzed. **6** was obtained via the reaction of **1c** with anhydrous CuCl /PPh_3, and colorless suitable single crystals of **6** for X-ray analysis were obtained by recrystallization in dichloromethane in situ. Black crystals of **7** were obtained via the reaction of **1c** with anhydrous CuCl and recrystallization in dichloromethane in air via oxidation of Cu(I) and hydrolysis of $SiMe_3$.

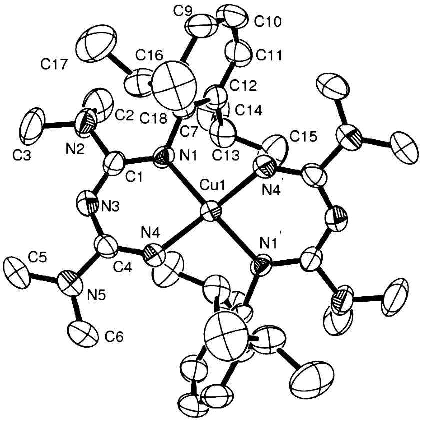
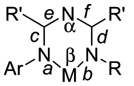


Figure 8. Molecular structure and atom numbering scheme for **7**.

1c, **1d**, and **2**−**7** were characterized by microanalysis and X-ray single-crystal diffraction, and **1c**, **1d**, **5**, **6** by NMR spectra at ambient temperature. **2**, **3**, **4**, and **7** were paramagnetic as demonstrated by broad peaks in their ^1H NMR spectra. The ^1H NMR and ^{13}C NMR spectra of **1c**, **1d**, **5**, and **6** were normal. The ^7Li NMR spectrum of **1c** displayed two signals at δ 2.05 and 2.36 due to two different lithium environments, consistent with the solid-state structure. The ^{31}P NMR spectrum of **6** in $CDCl_3$ showed a broad singlet at δ −3.90 without Cu−P coupling. The microanalysis data of **1c**, **1d**, and **2**−**7** were in agreement with the structures we obtained from the X-ray crystallography.

Crystal Structures. Structure of 1c. The molecular structure of crystalline **1c** is illustrated in Figure 1. **1c** is a head-to-head dimer built around a planar LiNLiN ring; the angles at the nitrogen atoms are narrower [79.5(3), 79.5(3)°] than those at the lithium atoms [100.1(3), 100.9(3)°]. Each lithium atom is coordinated with four nitrogen atoms from two ligands. Each ligand NCNCN backbone adopts a twisted W-shaped conformation. The dihedral angles between the two LiNCN moieties linked by N3 and Li1 are 44.5 and 46.1°, respectively. The molecule **1c** has two fused back-to-back tricyclic boat motifs comprising a central plane N3Li1N8Li2 (mean deviation 0.0043 Å) ring flanked by planes N3Li1N1C2 (mean deviation 0.0633 Å) and N8C9N10Li2 (mean deviation 0.0092 Å), N6Li1N8C3 and N3Li2N5C4, respectively. The dihedral angle between the core N3Li1N8Li2 and the adjacent four-membered rings N1C2N3Li1 or N8C9N10Li2 are 33.5 and 34.2 °. The bond distances N1−C2, C2−N3, N3−C4, and C4−N5 are 1314(5), 1.370(5), 1.374(5), and 1.304(5) Å, respectively, indicating an obvious short−long−long−short pattern of C−N bond lengths in the NCNCN backbone. This is consistent with localized *C*=N and C−N bonding in previously reported monomeric U-shaped lithium 1,3,5-triazapentadienyl adducts of fluorinated ligands $[\{N\{(C_3F_7)C(Dipp)N\}_2\}Li(THF)]$ and $[\{N\{(C_3F_7)C(Mes)N\}_2\}Li(THF)_2]$,[11] also in dimeric W-shaped 1,3,5-triazapentadienyl ligand $[RNC(NMe_2)NC(NMe_2)NR]^-$ (R = $SiMe_3$).[23] The C−N bond distances in NCNCN backbone of **1c** are slightly longer than those in $[RNC(NMe_2)NC(NMe_2)NR]^-$ (R = $SiMe_3$)[23] and comparable to $C(sp^2)$=$N(sp^2)$ [1.28 Å] and $C(sp^2)$−$N(sp^2)$ [1.37 Å] bond distances in tri- and tetraaza-heptatrienyllithium compounds.[20] The delocalized

Table 5. Selected Structural Data for Complexes **2**−**7**[a]

Compound	2	3	4	5	6	7
				Ar = Ph or Dipp R = $SiMe_3$ or H R' = NMe_2		
a/Å	2.096(4)	2.038(3)	1.989(2)	1.897(3)	1.984(3)	2.008(2)
b/Å	2.076(4)	2.014(2)	1.996(2)	1.857(3)	1.984(3)	1.914(3)
c/Å	1.343(6)	1.327(3)	1.358(4)	1.368(5)	1.327(4)	1.336(3)
d/Å	1.335(5)	1.344(3)	1.330(4)	1.302(5)	1.342(4)	1.308(4)
e/Å	1.324(5)	1.346(3)	1.327(4)	1.327(5)	1.342(4)	1.319(4)
f/Å	1.328(5)	1.304(3)	1.338(4)	1.341(5)	1.325(4)	1.340(4)
α/°	127.3(4)	127.3(2)	126.8(3)	118.8(3)	126.5(3)	124.2(2)
β/°	92.85(15)	94.57(8)	95.94(10)	87.43(14)	95.31(11)	89.54(10)
γ/°	90.2	88.6	90.1	0	–	38.7
Conformation	U	U	U	U	U	U
Geometry	Tetrahedral	Distorted Tetrahedral	Tetrahedral	Square Planar	Trigonal Planar	Distorted Tetrahedral
Co-ordination number at M	4	4	4	4	3	4

[a] γ: Dihedral angle between two NMN planes of **2**−**7**.

guanidinato system is impaired although the smaller dihedral angles exist between N1C2N3Li1 and C23N2C24 (24.5 °) or N3C4N5Li2 and C29N4C32 (19.8 °). This is also found in the other ligand NCNCN moiety of the molecule.

Structure of 1d. The molecular structure of crystalline **1d** is illustrated in Figure 2. For the NCNCN moiety, a short−long−short−long pattern of C−N bond lengths can be seen: *d*(N(1)−C(13)) and *d*(N(3)−C(16)) are 1.288(2) and 1.311(3) Å, respectively, while *d*(C(13)−N(3)) and *d*(C(16)−N(4)) are 1.379(3) and 1.360(3) Å, respectively. The short bonds correspond to *C*═N fragments and the long bonds to C−N moieties, indicating some *C*═N characteristics of conjugated system in **1d**. However, in the molecule, the N_3C_2 framework is not coplanar. It has instead a distinct helical twist such that the dihedral angle between the N(1)−C(13)−N(3) and N(3)−C(16)−N(4) planes is 56.1°. Therefore, this framework can be described as a somewhat W-shaped or a twisted zigzag (S-shaped) conformation. The bond angles of N1−C13−N3 and N3−C16−N4 are 124.03(17) and 124.38(19)°, respectively. By comparison, a similar C−N bond distance trend is found for the neutral 1,3,5-triazapentadienyl adducts of fluorinated ligands such as W-shaped $[N\{(C_3F_7)C(Dipp)N\}_2]H$,[7] $[N\{(C_3F_7)C(Mes)N\}_2]H$ (where Mes = 2,4,6-trimethylphenyl),[11] and U-shaped $[N\{(C_3F_7)C(Ph)N\}_2]H$.[2] This is also observed in the neutral *β*-diketiminato ligand $[HC\{(C_3F_7)C(Dipp)N\}_2]H$.[29]

For the guanidinato moiety $C13N_3$, although the C−N bond lengths are in the wider range of 1.288(2)∼1.388(2) Å, whereas 1.388 Å was considered to correspond to short single bond; and for the other $(C16N_3)$, the C−N bond lengths are in the range of 1.311(3)∼1.360(3) Å, they are roughly in the range for $C(sp^2)-N(sp^2)$ bonds (ca. 1.36 Å).[30] The dihedral angle between N(1)−C(13)−N(3) and C(14)−N(2)−C(15) planes is 33.7°; and between N(3)−C(16)−N(4) and C(17)−N(5)−C(18) planes is 11.2°. They are much smaller than those guanidinato moieties found in $[\{^iPrNC[N(SiMe_3)_2]N^iPr\}_2ZrCl_2]$ [88.2°], $[\{CyNC[N(SiMe_3)_2]NCy\}_2ZrCl_2]$ [86.3°], or $[\{CyNC[N(SiMe_3)_2]NCy\}_2HfCl_2]$ [85.8°][31] and in $[PhNC(NMe_2)NSiMe_3]_3ZrCl_3$ [40.3°] or $[PhNC(NMe_2)NSiMe_3]_3HfCl_3$ [39.8°],[21,22] indicating the π conjugation to some extent between the NCN and NMe_2 moieties.

The terminal N(1)−C(1) bond distance is 1.416(2) Å, comparable to the 1.402 (2) Å C−N distance in aniline.[32] The phenyl and N1−C13−N3 planes are almost perpendicular with dihedral angle of 86.7°. It is of an arrangement that minimizes steric strain.

Structures of 2, 3, and 4. The crystalline triazapentadienato-manganese **2**, -iron **3**, and -cobalt **4** complexes are monomeric and have a similar geometry.

In the crystal structure of **2** (Figure 3), the central metal manganese is located in a tetrahedral environment defined by the four nitrogen atoms from the two bidentate 1,3,5-triazapentadieno ligands $[PhNC(NMe_2)NC(NMe_2)N(SiMe_3)]^-$, with Mn−N bond distances of 2.096 (4) [Mn−N1], 2.076 (4) [Mn−N5], 2.074 (4) [Mn−N6] and 2.103 (4) Å [Mn−N10], respectively. The bond angles N1−Mn−N5 and N6−Mn−N10 are 92.85 (15) and 93.02 (15) °, respectively. The dihedral angle between N1MnN5 and N6MnN10 is 90.2 °. Within the 1,3,5-triazapentadieno ligand, the N1−C7

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[1.343(6) Å], C7−N3 [1.324 (5) Å], N3−C10 [1.328 (5) Å], C10−N5 [1.335 (5) Å] distances are very similar. Bond angles N1−C7−N3, C7−N3−C10 and N3−C10−N5 are 125.3(4), 127.3(4) and 126.8(4)°, respectively. Each bidentate 1,3,5-triazapentadieno ligand forms a six-membered metallacycle MNCNCN, where the N1C7C10N5 four-membered ring is almost planar with a mean deviation of 0.18 Å. The dihedral angle between the N1C7C10N5 and the N1MnN5 is 7.7°. The dihedral angle between planes N1C7C10N5 and C7N3C10 is 7.7° as well. The dihedral angle formed by the planar NMe_2 function and its adjacent C−N−C plane is 15°.

For both **3** (Figure 4) and **4** (Figure 5), the central metal iron and cobalt are located in a tetrahedral environment defined by the four nitrogen atoms from the two bidentate 1,3,5-triazapentadieno ligands, the dihedral angle between N1MN5 and N6MN10 being 88.6° (**3**) and 90.1° (**4**), respectively. In **3**, the Fe−N bond distances are in the range of 2.014 (2)∼2.038 (2) Å, shorter than the corresponding values found for manganese complex **2** [Mn−N: 2.074-(4)∼2.103(4) Å] and longer than the Co−N bond distances in complex **4** [Co−N: 1.989(2)∼1.996(2) Å]. The bond angles N1−Fe−N5 and N6−Fe−N10 in **3** are 94.57(8) and 94.16(8)°, respectively. They are larger than those in **2** [92.85(15) and 93.02(15)] and smaller than those in **4** [95.94(10) and 96.26(10)]. In the ligand moiety NCNCN, the C−N bond distances are in the range of 1.304(3)∼1.346(3)Å in **3**, and 1.327(4)∼1.358 (4) Å in **4**. The bond angles of N1−C1−N3, C1−N3−C4, and N3−C4−N5 are 129.3(2), 127.3 (2), and 123.2 (2)°, respectively, in **3**, and those in **4** are 126.3(3), 126.8(3), and 123.8(3)°, respectively.

For the CN_3 framework in **3**, the three C−N bond distances in the guanidinate ligand are N1−C1 1.344(3) Å, N2−C1 1.424(3) Å, and N3−C1 1.304(3) Å, respectively. All of these bond distances are roughly in the range for $C(sp^2)-N(sp^2)$ bonds. This is also found in **2** and **4** and is an indication of lone pair donation from the nitrogen atom (dimethylamido group) to the central carbon and concomitant electron delocalization involving all three nitrogen atoms of the chelating ligand.

Structure of 5. The centrosymmetric **5** (Figure 6) has a planar geometry different from **2**, **3**, and **4** because of the loss of the two trimethylsilyl groups. The bond distances Ni−N1 and Ni−N5 are 1.897(3) and 1.857(3) Å, respectively. The bond angle N1−Ni−N5 is 87.43(14)°. It is noted that dihedral angle between planes N1C7N5 and N1C10N5 is 10.6°, and thus atoms N1, C7, C10, and N5 can be regarded in a plane (mean deviation 0.06 Å). However, dihedral angles between N1NiN5 or C7N3C10 and N1C7C10N5 are 34.6 and 15.4°, respectively. That means the N3 and nickel atoms actually are out the planes (average vertical distance from nickel and N3 to the plane NC−CN are ca. 0.76 and 0.17 Å, respectively). For the ligand NCNCN moiety, the C−N bond distances are in the range of 1.302(5)∼1.368(5) Å. The bond angles N1−C7−N3, C7−N3−C10, and N3−C10−N5 are 126.6(4), 118.8(3), and 123.9(4)°, respectively. The dihedral angle between N1C7N3 and C8N2C9 is 15.4°. Two reasonably close analogues are the β-diketiminate:

$$[\overline{\mathrm{Ni}\{\mathrm{N(H)C(Bu^t)CHC(1\text{-}piperidino)N}}\mathrm{(H)}\}_2]$$

having Ni−N bond distances of 1.845(3) and 1.855(3) Å,[5] and $[Ni\{NH{=}C(Py)N{=}C(Py)NH\}_2]$ (Py = 4-pyridyl; 3-pyridyl) having the $Ni-N_{sp2}$ distances of 1.847(2), 1.855 (2) Å and 1.876(3) and 1.856(3) Å.[16]

Structure of 6. The X-ray crystal structure of **6** (Figure 7) reveals the presence of a three-coordinate, trigonal-planar copper center. The triazapentadienyl ligand acts as a κ^2-donor. The Cu−N bond distances are both 1.984(3) Å. The four atoms N1, C13, C16, and N5 are essentially planar with a deviation of 0.11 Å, and the dihedral angle between N1C13C16N5 and C13N3C16 is 10.3°. The dihedral angle between N1C13C16N5 and N1CuN5 is 25.2°. The bond angle of N1−Cu−N5 is 95.31(11)°. In the NCNCN moiety, the C−N bond distances are in the range of 1.325(4)∼1.342(4) Å, indicating the NCNCN fragment has π-electron delocalization present as a η^5 anion. The bond angles of N1−C13−N3, C13−N3−C16, and N3−C16−N5 are 125.7(3), 126.5(3), and 127.7(3)°, respectively. The Dipp group is twisted by about 71.9° from the CuN1C13 plane. The Cu−P bond distance in **6** is 2.164(9) Å, similar to 2.166 (8) Å in the three-coordinate Cu(I) β-diketiminate complex containing triphenylphosphine.[33]

Structure of 7. In **7** (Figure 8), the dihedral angle between N1Cu1N4 and N1′Cu1N4′ is 38.7°; both angles of N1−Cu1−N4 and N1′−Cu1−N4′ are 89.54(10) °; N1−Cu1−N1′ and N4−Cu1−N4′ are 154.18(13) and 151.94(16)°, respectively. So the central metal copper is located in a marked distorted tetrahedral geometry environment and bonded by four nitrogen atoms from two ligands. The bond distances Cu1−N1 and Cu1−N4 are 2.008(2) and 1.914(2) Å, respectively. The four atoms N1, C1, C4, and N4 are almost in the same plane (mean deviation 0.0039 Å). The dihedral angle between N1C1C4N4 and N1Cu1N4 is 2.9°, and between N1C1C4N4 and C1N3C4 is 2.2°, respectively. Therefore, each of the six-membered metallacycles is regarded coplanar, giving a π-electron delocalized system.

The dihedral angle [48.9 °] between plane C2N2C3 from guanidinato function NMe_2 and its adjacent plane N1C1N3 suggests the strong π-bonding interaction between the two moieties. For the CN_3 framework in **7**, the three C−N bond distances in the guanidinate part are N1−C1 1.336(3), N2−C1 1.414(4), and N3−C1 1.319(4) Å, respectively. All of these data indicate the lone-pair donation from the nitrogen atom (dimethylamido group) to the central carbon C1 and concomitant electron delocalization involving all three nitrogen atoms of the guanidinato chelating ligand.

Table 5 provides a summary of some important geometric data (bond lengths in Å and angles in degrees) for **2**−**7**. For **2**−**5**, bond lengths M−N(Ar) and M−N(R) decrease in the sequence **2** > **3** > **4** > **5** and for a certain complex of **2**, **3**, **5** and **7**, M−N(Ar) > M−N(R). The mean C−N bond lengths in **2**−**7** are comparable and accord with the $C(sp^2)-N(sp^2)$ bond lengths. Bond angles of N−M−N in **5** [87.43(14)°], **7** [89.54(10)°] and C−N−C in **5** [118.8(3)°]

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are relatively smaller than those in other complexes [from 92.85(15) to 95.94(10)° for **2**−**4** and **6**]. In **2** and **4**, the metal is located in a nearly rigorously tetrahedral coordination environment with 90.2 and 90.1° of dihedral angles between two NMN planes. **5** adopts a square-planar geometry because of the d^8 configuration of nickel atom, **3** and **7** adopt distorted tetrahedral (trigonal planar for **6**) although **3** has a tendency to give a nearly rigorously tetrahedral and **7** toward a square planar configuration.

Conclusions

In this study, we have isolated a series of new 2,4-dimethylamido substituted 1,3,5-triazapentadienato ligands and metal complexes by the reaction of $PhN(SiMe_3)M$ (M = Li or Na) or $(Dipp)N(SiMe_3)Li$ with 2 equiv of α-hydrogen-free dimethylcyanamide, which led to in situ synthesis of functional 1,3,5-triazapentadienato complexes with guanidinato moieties. The NCNCN backbone adopts either W- or U-shaped conformation. Compounds such as **3**, **4**, and **5** may serve as potential catalysts in olefin polymerization[34] and copper complexes **6** and **7** as precursors of atomic layer deposition or magnetic materials in microelectronics.[35] Further studies on the coordination chemistry of this interesting class of triazapentadienato ligands with guanidinato moieties and the application of their metal complexes are presently underway.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of the eight compounds in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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