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From Lithium Bis(trimethylsilyl)amide with Cyanoamine into Triazine Compounds: Synthesis and Structures of Lithium 6-((Trimethylsilyl)amido)-2,4-bis(dimethylamino)[1,3,5]triazines and Their Manganese and Cobalt Complexes

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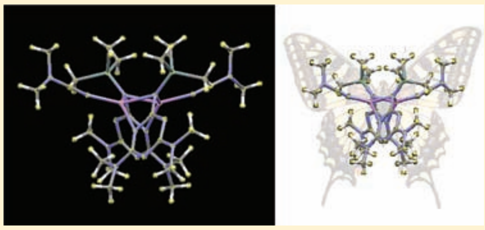
S *Supporting Information*

ABSTRACT: Addition reactions of lithium bis(trimethylsilyl)amide with dimethylcyanamide lead to novel lithium salts of 6-((trimethylsilyl)amido)-2,4-bis(dimethylamino)[1,3,5]triazines [**LLi**(**D**)]$_2$ (**L** = NC(NMe$_2$)NC(NMe$_2$)NC(NSiMe$_3$); **D** = Me$_2$NCN (**1**), Et$_2$O (**2**)) and to the Mn and Co complexes [**LL′M**] (**L′** = N{N(SiMe$_3$)C(NMe$_2$)}$_2$; M = Mn (**3**), Co (**4**)); the structures of crystalline **1**, **3**, and **4** are reported. Their formation involves trimethylsilyl shifts, ring formation, and unusual Me$_2$NSiMe$_3$ elimination.



INTRODUCTION

1,3,5-Triazine heterocyclic π-conjugated systems are attractive and versatile for their structures and applications in medicinal chemistry, materials chemistry, and organic synthesis.[1−3] Accordingly, the 2,4,6-trisubstituted 1,3,5-triazines have attracted much interest.[4−11] 2,4,6-Triphenyl-1,3,5-triazine derivatives have been largely explored,[12] and pyridyl-substituted 1,3,5-triazines such as 2,4,6-tris(2-pyridyl)-1,3,5-triazines have been extensively referenced.[13−16] Recently, lanthanide 2,4,6-tris(2-pyridyl)-1,3,5-triazine complexes with visible light luminescence were reported.[6] 2,4,6-Trimercapto-1,3,5-triazine can be used in wastewater treatment to remove heavy metals[1] and also to prepare polynuclear trithiocyanurato-bridged metal complexes bearing bidentate chelating N and S heterocycles.[17] Triprotic 2,4,6-tris(organoamino)-1,3,5-triazenes are promising potential multisite ligands.[18] Moreover, several 1,2,4-triazines, bi(1,2,4-triazines), or transition-metal complexes with disubstituted triazine-based ligands and bi(1,3,5-triazine)ligands were also prepared.[3,19−21] However, new and effective syntheses of 1,3,5-triazine heterocyclic rings under mild conditions are still of significance in modern organometallic and organic chemistry; moreover, organometallic derivatives of triazine are scarce and the numbers of accessible heterocyclic skeletons are still limited.

In previous publications, the reactions of nitriles free from α-hydrogen with reagents such as LiCH(SiMe$_3$)$_2$ have been shown to yield under mild conditions the corresponding metal 1-azaallyl or β-diketiminate[22] or triazines by the cyclotrimerization of organonitriles.[23,24] These nucleophilic reactions may involve C−C coupling, 1,3-migration of the SiMe$_3$ group from C to N, or elimination of Li[CHR$_2$]. Recently, we described the reactions of N-centered anions with nitriles free from α-hydrogen at a molar ratio of 1:1 or 1:2 which can give guanidinates or 1,3,5-triazapentadienyl ligands e.g. as [Li{N(R)C(R′)NC(R′)N(SiMe$_3$)}]$_2$ (where R = Ph, 2,6-^{i}Pr$_2$C$_6$H$_3$, SiMe$_3$, and R′ = NMe$_2$, 1-piperidino) as their metal complexes. The N-centered nucleophilic reactions involved 1,3-Me$_3$Si migrations from N→N, isomerization, or concomitant N−C bond formation.[25−29] Very recently, alkyl- and arylimidoylamidines were formed via the condensation of nitriles and amides under mild conditions promoted by a coordinatively unsaturated bis[nickel(II) hydroxy] complex.[30]

As a continuation of our study of the reactivities of organic nitriles free from α-hydrogen with lithioamides, we now describe our initial findings on the addition reactions of LiN(SiMe$_3$)$_2$ with dimethylcyanamide. The lithium salts of 6-((trimethylsilyl)amido)-2,4-bis(dimethylamino)[1,3,5]triazines [**LLi**(**D**)]$_2$ (**L** = NC(NMe$_2$)NC(NMe$_2$)NC(NSiMe$_3$); **D** = Me$_2$NCN (**1**), Et$_2$O (**2**)) and thereby their Mn and Co complexes [**LL′M**] (**L′** = N{N(SiMe$_3$)C(NMe$_2$)}$_2$; M = Mn (**3**), Co (**4**)) were obtained. Such reactions may implicate a series of silicotropic rearrangements and an unusual elimination of Me$_2$NSiMe$_3$. Considering the rare examples of the monomeric monolithiated (THF)$_3$Li(Ph)$_2$(Bu^{t}Bu^n)C$_3$N$_3$,[24] dimeric dilithiated (THF)$_6$Li$_4$[(RN)$_2$(RNH)C$_3$N$_3$]$_2$,[18] and trilithium tris(trimethylsilylamino) [(Tr^{TMS3})$_2$Li$_6$(THF)$_8$]·2THF and [(Tr^{TMS3})$_2$Li$_6$(DME)$_4$][31] triazinate complexes in the literature, the novel dimeric monolithiated adduct **1** is expected to be a good addition to the family of 1,3,5-triazine ligands. The new heterobicyclic C$_3$N$_6$M ring system also reveals the diversity of addition reactions of LiN(SiMe$_3$)$_2$ with a nitrile and demonstrates its synthetic utility as a ligand transfer reagent.

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EXPERIMENTAL SECTION

General Remarks. . All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvent was purchased from commercial sources. Deuterated solvents C_6D_6 were dried over activated molecular sieves (4 Å) and vacuum-transferred before use. 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. The lithium amide $LiN(SiMe_3)_2$ was easily accessible via the lithiation of 1,1,1,3,3,3-hexamethyldisilazane with $LiBu^n$ in hexane. $LiBu^n$, 1,1,1,3,3,3-hexamethyldisilazane, Me_2NCN, $MnCl_2$, and $CoCl_2$ were used as purchased from Alfa Aesar. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded on a Bruker DRX-300 instrument, and solvent resonances were used as the internal references for ^1H spectra and ^{13}C spectra. IR spectra were recorded on a Shimadzu FTIR8400S instrument. Electron impact mass spectra were taken from solid samples using a GCT-MS Micromass UK instrument. Magnetic susceptibility measurements were carried out on samples with polycrystalline compounds tightly packed and sealed in a capsule at 300 K using a Quantum Design MPMSXL5 SQUID magnetometer. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants.[32] Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were carried out using a Vario EL-III analyzer (Germany).

Preparations. *$[LLi(Me_2NCN)]_2$ (1; L = NC(NMe₂)NC(NMe₂)NC(NSiMe₃)).* Me_2NCN (0.68 mL, 8.40 mmol) was added to a solution of $LiN(SiMe_3)_2$ (0.35 g, 2.10 mmol) in Et_2O (20 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred overnight. The mixture was concentrated in vacuo to ca. 10 cm^3 and left at −25 °C for several days to give colorless crystals of **1** (0.49 g, 71%). Mp: 102−104 °C. Anal. Calcd for $C_{26}H_{54}Li_2N_{16}Si_2$: C, 47.25; H, 8.24; N, 33.91. Found: C, 47.08; H, 8.32; N, 33.96. ^1H NMR (C_6D_6): δ 0.40 (s, 9H, $Si(CH_3)_3$), 2.96 (s, 18H, $N(CH_3)_2$). ^{13}C NMR (C_6D_6): δ 1.98 ($Si(CH_3)_3$), 35.7 ($N(CH_3)_2$), 130.7 ($N{\equiv}CN$), 164.3 (*ipso*-C-NSiMe₃), 170.4 (*ipso*-C-NMe₂). IR (KBr, cm^{-1}): 2945, 2933, 2900, 2864, 2216, 1566, 1525, 1442, 1390, 1240, 1220, 1078, 1054, 879, 842, 813, 748. ^{29}Si NMR (C_6D_6): δ − 10.88 ppm. ^7Li NMR (C_6D_6): δ 2.03 ppm.

$[LLi(Et_2O)]_2$ (2; L = NC(NMe₂)NC(NMe₂)NC(NSiMe₃)). Me_2NCN (0.50 mL, 6.24 mmol) was added to a solution of $LiN(SiMe_3)_2$ (0.35 g, 2.08 mmol) in Et_2O (20 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred overnight. The mixture was concentrated in vacuo to ca. 10 cm^3 and left at −25 °C for several days to give colorless crystals of **2** (0.45 g, 65%). Anal. Calcd for $C_{28}H_{62}Li_2N_{12}O_2Si_2$: C, 50.27; H, 9.34; N, 25.13. Found: C, 50.39; H, 9.38; N, 25.04. ^1H NMR (C_6D_6): δ 0.63 (s, 9H, $Si(CH_3)_3$), 3.03 (s, 18H, $N(CH_3)_2$), 1.12−1.17 (t, Et_2O), 3.28−3.35 (m, Et_2O). ^{13}C NMR (C_6D_6): δ 1.98 ($Si(CH_3)_3$), 35.9 ($N(CH_3)_2$), 15.1, 65.8 (Et_2O), 166.1 (*ipso*-C-NSiMe₃), 174.6 (*ipso*-C-NMe₂). IR (KBr, cm^{-1}): 2958, 1649, 1637, 1604, 1523, 1427, 1411, 1309, 1261, 1056, 1008, 958, 833, 702, 663, 592. ^{29}Si NMR (C_6D_6): δ −12.12 ppm. ^7Li NMR (C_6D_6): δ 1.55 ppm.

[LL′Mn] (3; L′ = N{N(SiMe₃)C(NMe₂)}₂). Me_2NCN (0.40 mL, 5.00 mmol) was added to a solution of $LiN(SiMe_3)_2$ (0.42 g, 2.50 mmol) in Et_2O (20 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred overnight. $MnCl_2$ (0.16 g, 1.25 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, the residue was extracted with dichloromethane, and the extract was concentrated in vacuo to ca. 15 cm^3 and set aside at ambient temperature for several days, yielding colorless crystals of **3** (0.22 g, 37%). Mp: 105−107 °C. Anal. Calcd for $C_{22}H_{51}MnN_{11}Si_3$: C, 43.39; H, 8.44; N, 25.30. Found: C, 43.15; H, 8.52; N, 25.33. $\mu_{eff} = 1.99\ \mu_B$. IR (KBr, cm^{-1}): 2925, 2864, 1529, 1388, 1299, 1213, 1051, 806, 700, 570, 476. UV−vis (THF, nm): λ_{max} 219. MS (EI; *m*/*z* (%, assignment)): 254 (4, $[L + H]^+$), 210 (100, $[LH - NMe_2]^+$), 195 (67, $[LH - NMe_2 - Me]^+$), 44 (18, $[NMe_2]^+$).

[LL′Co] (4; L′ = N{N(SiMe₃)C(NMe₂)}₂). Me_2NCN (0.32 mL, 4.00 mmol) was added to a solution of $LiN(SiMe_3)_2$ (0.33 g, 2.00 mmol) in Et_2O (20 cm^3) at −78 °C. The resulting mixture was warmed to ca. 25 °C and stirred overnight. $CoCl_2$ (0.13 g, 1.00 mmol) was added at −78 °C. The resulting mixture was warmed to ca. 25 °C, stirred for 2 h, and filtered. The filtrate was concentrated in vacuo to ca. 10 cm^3, yielding purple crystals of **4** (0.29 g, 59%). Mp: 109 °C dec. Anal. Calcd for $C_{22}H_{51}CoN_{11}Si_3$: C, 43.11; H, 8.39; N, 25.14. Found: C, 43.13; H, 8.42; N, 25.22. $\mu_{eff} = 2.26\ \mu_B$. IR (KBr, cm^{-1}): 2979, 2945, 2896, 2871, 2864, 2833, 1541, 1473, 1440, 1359, 1288, 1245, 1041, 979, 912, 842. UV−vis (THF, nm): λ_{max} 225. MS (EI; *m*/*z* (%, assignment)): 359 (8, $[L' + Co]^+$), 301 (2, $[L' + H]^+$), 257 (54, $[L'H - NMe_2]^+$), 73 (32, $[SiMe_3]^+$), 44 (15, $[NMe_2]^+$).

X-ray Crystallography. X-ray diffraction data for **1**, **3**, and **4** were collected on an Bruker SMART APEX diffractometer/CCD area detector using monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. The reflections were collected by using the ω scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption using multiscans (SADABS).[33] The structures were solved by direct methods (SHELXS-97).[34] The remaining non-hydrogen atoms were then obtained from the successive difference Fourier map. All non-H atoms were refined with anisotropic displacement parameters, while the H atoms were constrained to parent sites, using riding modes (SHELXTL).[35] Crystal data and details of data collection and refinements for **1**, **3**, and **4** are summarized in Table 1. Compound **1** was refined as a racemic twin. Selected bond distances and bond angles are given in Tables 2, 4, and 5.

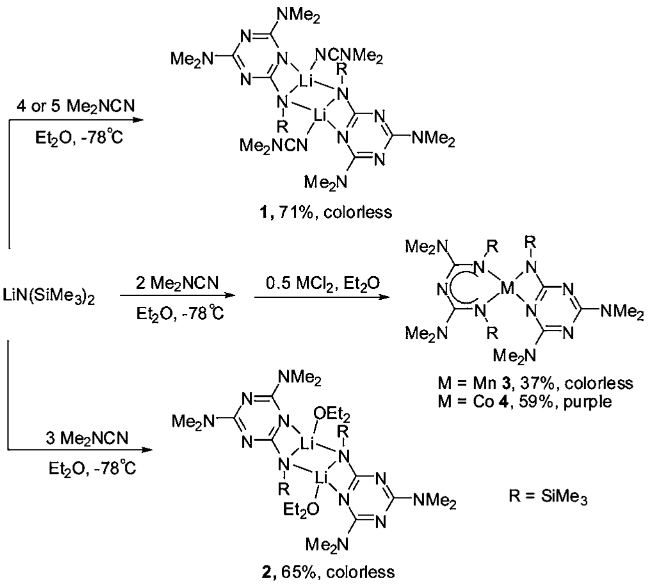
Table 1. Crystal and Refinement Data for 1, 3, and 4

	1	3	4
formula	$C_{26}H_{54}Li_2N_{16}Si_2$	$C_{22}H_{51}MnN_{11}Si_3$	$C_{22}H_{51}CoN_{11}Si_3$
M_r	660.92	608.95	612.94
cryst syst	orthorhombic	triclinic	triclinic
space group	*Fdd*2 (No. 43)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a/Å	19.204(8)	10.603(3)	10.603(3)
b/Å	40.15(2)	12.021(4)	12.021(4)
c/Å	9.900(4)	14.728(4)	14.728(4)
α/deg	90.00	80.444(4)	80.444(4)
β/deg	90.00	80.618(3)	80.618(3)
γ/deg	90.00	72.426(3)	72.426(3)
U/Å^3	7633(6)	1752.0(9)	1752.0(9)
Z	8	2	2
abs coeff (mm^{-1})	0.133	0.508	0.621
no. of unique rflns, R_{int}	2710, 0.0795	5945, 0.0260	5934, 0.0226
no. of rflns with $I > 2\sigma(I)$	2241	4591	4723
final *R* indices ($I > 2\sigma(I)$): R1, wR2	0.0499, 0.1153	0.0834, 0.2256	0.0556, 0.1473
R indices (all data): R1, wR2	0.0650, 0.1201	0.1125, 0.2783	0.0756, 0.1990

RESULTS AND DISCUSSION

Synthesis and Characterization. Treatment of $LiN(SiMe_3)_2$ with 3 equiv of Me_2NCN at low temperature in diethyl ether and crystallization of the product from diethyl ether afforded the dimeric colorless crystalline 1:3 adduct **2** in 65% yield (Scheme 1). Addition of $LiN(SiMe_3)_2$ to Me_2NCN in Et_2O, in a 1:4 or 1:5 ratio, yielded the 1:4 adduct **1** (71%). Similar low-temperature reactions of $LiN(SiMe_3)_2$ and successively Me_2NCN and anhydrous $MnCl_2$ or $CoCl_2$, in a

Scheme 1. Synthesis of Crystalline Complexes $[LLi(Me_2NCN)]_2$ (1), $[LLi(Et_2O)]_2$ (2), [LL′Mn] (3), and [LL′Co] (4) (L = $NC(NMe_2)NC(NMe_2)NC(NSiMe_3)$; L′ = $N\{N(SiMe_3)C(NMe_2)\}_2$)

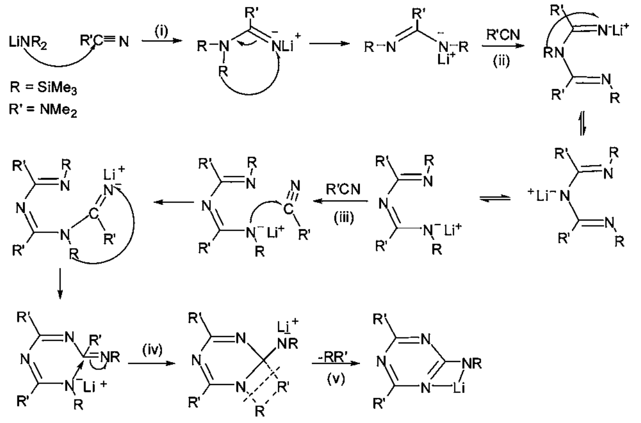


ratio of 1:2:0.5 in Et_2O, gave monomeric **3** or **4** in 36 or 59% yield, respectively. However, attempts to prepare the similar ligand(s)/metal complex with the formula **LL′Fe** were unsuccessful. Compound **1** is highly air and moisture sensitive and very soluble in diethyl ether, whereas **3** was highly air sensitive and quickly became black on contact with air. The highly diethyl ether soluble complex **4** was relatively inert when exposed to air. The colorless crystalline solids **1**−**3** and purple **4** gave satisfactory microanalyses and NMR spectroscopic (**1** and **2**) and X-ray (**1**, **3**, and **4**) data.

The magnetic susceptibilities for complexes **3** and **4** were determined at 300 K using a SQUID magnetometer. The magnetic moment (μ_{eff}) of the manganese(II) complex **3** was found to be 1.99 μ_B, which lies closer to the low-spin d^5 value of 1.73 μ_B and is comparable to the magnetic moment of 2.30 μ_B recorded for the pseudotetrahedral manganese(II) β-diketiminate complex $[Mn(\{N(SiMe_3)C(Ph)\}_2CH)_2]$.[36] However, the magnetic moment of 2.26 μ_B recorded for the cobalt(II) complex **4** is unexpected for a four-coordinated cobalt(II) system in a tetrahedral coordination geometry but is comparable to the μ_{eff} of 2.67 μ_B recorded for the pseudotetrahedral cobalt(II) complex that has the low-spin ground state reported in ref 37, possibly suggesting that there is a spin-state equilibrium, with the low-spin state populated at very low temperature. The spin-state conversion for tetrahedral Co(II) species with N-donor ligands has also been reported by Dong.[38]

The proposed pathway for the formation of **1** and **2**, outlined in Scheme 2, involves successively (i) an attack of the N-centered nucleophile on R′CN, C−N coupling, and 1,3-Me_3Si migration from N→N, (ii, iii) C−N coupling and isomerization, (iv) nucleophilic attack at a terminal alkene, and (v) an unusual elimination of Me_2NSiMe_3 to give the lithium 6-((trimethylsilyl)amido)-2,4-bis(dimethylamino)[1,3,5]triazine complexes **1** and **2**. The formation of **3** and **4**, however, took a different course: reaction of lithium bis(trimethylsilyl)amide with dimethylcyanamide in a ratio of 1:2 gave not only the 1:3 adduct **1** but the 1:2 adduct of the 1,3,5-triazapentadienyl salt, which involves attack of the N-centered nucleophile, 1,3-Me_3Si migration, and N−C bond formation.[27] Therefore, reactions of $LiN(SiMe_3)_2$ and successively Me_2NCN and anhydrous MCl_2 (M = Mn, Co) afforded the Mn and Co complexes **3** and **4**, bearing mixed 1,3,5-triazapentadienato and triazine ligands.

Scheme 2. Proposed Pathway for the Formation of 1 and 2



Crystal Structures. *Structure of 1.* An X-ray crystallographic study of **1** reveals that the dimeric molecule (Figure 1, orthorhombic, *Fdd*2, No. 43) comprises a fused pentacyclic array, having at its core a fused tricyclic boat. The latter has a central N1LiN1′Li′ rhomboid flanked by planar N1LiN6C1 and Li1N1′C1′N6′ rings. The boat is puckered and twisted (Figure 2), with angles between the least-squares plane defined by the two terminal and the central Li_2N_2 components of 66.8° (metallacycle Li−N1−C1−N6) and 113.2° (metallacycle Li′−

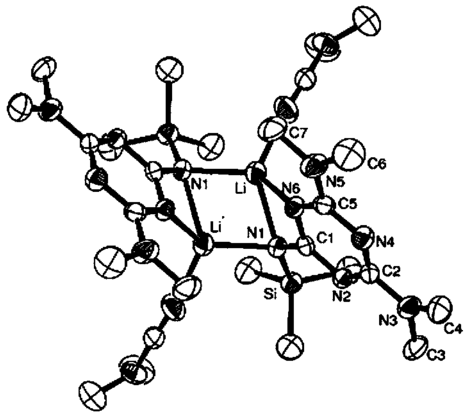


Figure 1. Molecular structure of **1**.

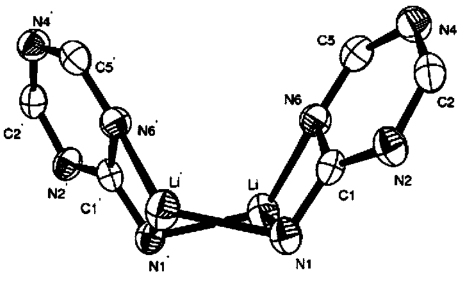


Figure 2. Core of **1** highlighting the twisted-boat structure.

N1′–C1′–N6′). The Li–N bonds are in the range 2.064(7)–2.180(6) Å (Table 2). The four atoms N1, Li, N1′, and Li′ are alternating above and below the mean plane by ca. 0.21 Å, as shown in Figure 2. The two lithium atoms Li and Li′, separated by 2.453(11) Å, are bridged by $NSiMe_3$ groups, and each is in a four-coordinate environment. The endocyclic angles at the nitrogen atoms (69.8(3)°) are narrower than those at the Li atoms (105.3(3)°). These features are similar to those of several other known dimeric N_{exo},N_{endo}-chelating ligand systems such as the dilithiated triprotic 2,4,6-tris(organoamino)-1,3,5-triazene **II** (Li–N–Li: = 77.2(7)°, N–Li–N = 102.8(7)°)[18] and silylaminopyridinate **III** (Li–N–Li = 75.5(3)°, N–Li–N = 104.5(3)°)[39] with an eight-membered $[Li-N_{exo}-C-N_{endo}-]_2$ ring core (Figure 3).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

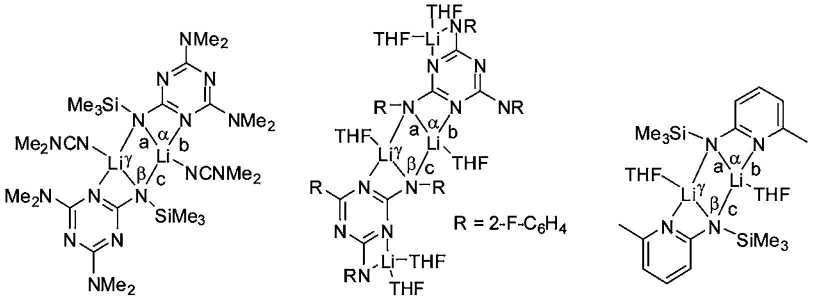
C1–N1	.1.333(4)	N1–Li′	2.105(6)
C1–N2	1.359(4)	C2–N2	1.329(5)
C1–N6	1.376(4)	C2–N4	1.341(4)
N1–Li	2.180(6)	N4–C5	1.341(4)
N6–Li	2.064(7)	N6–C5	1.344(4)
Li–Li′	2.453(11)		
N1–Li–N6	65.04(19)	Li–N6–C1	90.3(3)
N1–C1–N6	114.9(3)	Li–N1–Li′	69.8(3)
Li–N1–C1	86.5(3)	N1–Li–N1′	105.3(3)

A comparison of some key bond lengths and angles for complex **1** with those of **II** and **III** is presented in Table 3. The $Li-N_{exo}$ bond lengths in **1**, **II**, and **III** are obviously longer than those of $Li-N_{endo}$. The fact that both $Li-N_{exo}$ (except for **II**) and $Li-N_{endo}$ lengths in **1** are slightly longer than those in **II** and **III** may be due to the essential boat arrangement (rather than centrosymmetric ladder-shaped backbone in **II** and **III**) of the $[Li-N_{exo}-C-N_{endo}-]_2$ ring core in **1**, where both the trimethylsilyl groups at N_{exo} atoms and the fragments attached to lithium atoms are oriented in a cis fashion, resembling that in the amide complexes *cis*-$[Li\{\mu\text{-}N(SiMe_3)(SiMe_2Ph)\}]_2$ and $[Li\{\mu\text{-}N(SiMe_3)Ph\}\text{-}cis]_2[\mu\text{-}\{N(SiMe_3)Ph\}Li\text{-}cis]_2$.[40] The bridging Li–N distances in **1**, **II**, and **III** are almost identical and comparable to the reported Li–N(amido) bonds in the dimeric lithium salts of *β*-diketiminate $[Li\{N(SiMe_3)_2C(Ph)\}_2CH]_2$ (2.095(9) Å),[41] guanidinate $[(Et_2O)LiN(SiMe_3)C(NMe_2)N(Ph)]_2$ (2.057(3) Å),[25] and amidinate $[Li\{\mu{:}\kappa^2\text{-}N(R)C(C_6H_4Me\text{-}4)NPh\}(OEt)_2]_2$ (2.058(5) Å).[42] The bond angle $N_{exo}-Li-N_{endo}$ (N1–Li–N6) in **1** is wider than that in **II** but narrower than that in **III**.

*Structures of **3** and **4**.* Crystalline **3** (Figure 4) and **4** (Supporting Information) are the first structurally characterized examples of manganese and cobalt complexes having 1,3,5-triazapentadienato and triazine ligands. Compound **4** is essentially isostructural with **3**, and therefore their structures are described together as follows. Both **3** and **4** contain one η^2-chelating triazapentadienato and one η^2-triazine ligand around the distorted-tetrahedral Mn or Co center, with dihedral angle between planes N1MN5 and N6MN10 of 111.3 and 112.4°, respectively. The core units of **3** and **4** comprise a C_3N_3M system with a four-membered $M-N_{exo}-C-N_{endo}$ ring and a six-membered M–N–C–N–C–N metallacycle with similar M–N6 and M–N7 bond lengths and identical M–N1 and M–N5 bond lengths.

The four-membered ring $MN_{exo}CN_{endo}$ is essentially planar with a mean deviation of 0.0290 Å in **3** and 0.0266 Å in **4**, respectively. The dihedral angles between N6–M–N7 and N7–C22–N11 planes in **3** and **4** are 6.5 and 6.7°, respectively, indicating that the $MN_{exo}CN_{endo}$ ring is almost coplanar with the C_3N_3 ring of the triazine. The *π* electrons of the exocylic N center allow delocalization of negative charge across the entire C_3N_6 core of the triazine. The M–N6 and M–N7 bond lengths in **3** (Mn–N = 2.098(4), 2.206(4) Å) and in **4** (Co–N = 2.026(3), 2.131(3) Å) are comparable to those in the corresponding Mn and Co amidinate complexes $[\{M[PhC(NSiMe_3)(NAr)]_2\}_2\cdot(TMEDA)]$ (M = Mn, Co; Ar = 2,6-$Me_2C_6H_3$) (Mn–N = 2.177(3)–2.223(2) Å; Co–N = 2.016(2)–2.246(2) Å) (Tables 4 and 5).[43] The bond angles of N6–M–N7 in **3** (62.60(16)°) and **4** (65.54(11)°) are somewhat larger than those in $[\{M[PhC(NSiMe_3)(NAr)]_2\}_2\cdot(TMEDA)]$ (M = Mn, Co; Ar = 2,6-$Me_2C_6H_3$) (N–Mn–N = 61.58(9), 61.97(9)°; N–Co–N = 62.96(7), 63.66(7)°).[43]

The six-membered MNCNCN ring in both **3** and **4** is planar (with a mean deviation of 0.1357 Å in **3** and 0.1336 in **4**), with almost identical C–N bond lengths, indicative of *π* delocalization in the ligand backbone. When the M–N bond lengths are compared among the different six-membered *π* delocalized systems, the M–N lengths in **3** (Mn–N1 = 2.071(4); Mn–N5 = 2.083(4) Å) and in **4** (Co–N1 = 2.004(3); Co–N5 = 1.981(3) Å) are comparable to those in the asymmetric 1,3,5-triazapentadienyl compounds $[M\{N(Ph)C(NMe_2)NC(NMe_2)N(SiMe_3)\}_2]$ (M = Mn, Co; Mn–N = 2.074(4)–2.103(4) Å; Co–N = 1.989(2)–1.996(2) Å).[28] The Co–N bond lengths in **4** are also similar to those in the 1,5-diazapentadienyl species $[Co[\{N(SiMe_3)C(Ph)\}_2CH]_2]$ (1.994(7), 2.007(6) Å).[41] The bond angle N1–Mn–N5 in **3**



1 **II** **III**

Figure 3. Complex **1** and its analogues **II** and **III** with a $[Li-N_{exo}-C-N_{endo}-]_2$ ring core.

Table 3. Comparison of Selected Bond Lengths (Å) and Angles (deg) of 1 and Its Analogues II and III

compd	a/Å	b/Å	c/Å	α/deg	β/deg	γ/deg	ref
1	2.180(6)	2.064(7)	2.105(6)	65.04(19)	69.8(3)	105.3(3)	this work
II	2.32(2)	2.03(2)	2.07(2)	61.2(5)	77.2(7)	102.8(7)	18
III	2.097(7)	2.042(7)	2.063(7)	67.4(2)	75.5(3)	104.5(3)	39

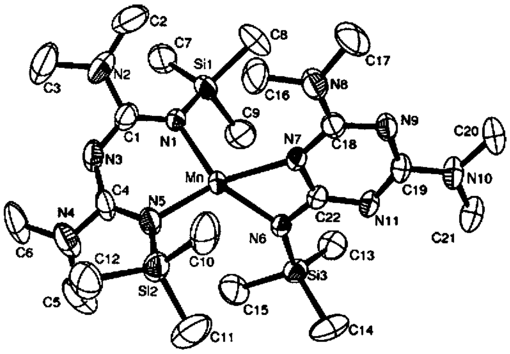


Figure 4. Molecular structure of **3**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3

Mn–N1	2.071(4)	C22–N6	1.319(6)
Mn–N5	2.083(4)	C22–N7	1.376(7)
Mn–N6	2.098(4)	C18–N7	1.340(7)
Mn–N7	2.206(4)	C18–N9	1.336(7)
C1–N1	1.345(7)	C19–N9	1.337(7)
C1–N3	1.326(7)	C19–N11	1.324(7)
C4–N3	1.313(8)	C22–N11	1.360(6)
C4–N5	1.335(7)		
N1–Mn–N5	94.43(17)	N1–C1–N3	127.5(5)
N6–Mn–N7	62.60(16)	N5–C4–N3	125.9(5)
Mn–N1–C1	114.0(4)	N6–C22–N7	112.3(4)
Mn–N5–C4	114.0(3)	Mn–N7–C22	89.2(3)
Mn–N6–C22	95.6(3)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 4

Co–N1	2.004(3)	C22–N6	1.314(4)
Co–N5	1.981(3)	C22–N7	1.381(4)
Co–N6	2.026(3)	C18–N7	1.345(4)
Co–N7	2.131(3)	C18–N9	1.371(4)
C1–N1	1.337(5)	C19–N9	1.339(5)
C1–N3	1.335(5)	C19–N11	1.344(5)
C4–N3	1.338(5)	C22–N11	1.378(4)
C4–N5	1.336(5)		
N1–Co–N5	96.48(12)	N1–C1–N3	126.1(4)
N6–Co–N7	65.54(11)	N5–C4–N3	125.8(4)
Co–N1–C1	115.7(2)	N6–C22–N7	113.3(3)
Co–N5–C4	114.7(2)	Co–N7–C22	87.2(2)
Co–N6–C22	93.6(2)		

(94.43(17)°) is comparable to those in [Mn{N(Ph)C(NMe$_2$)-NC(NMe$_2$)N(SiMe$_3$)}$_2$] (92.85(15) and 93.02(15)°),[28] whereas N1–Co–N5 in **4** (96.48(12)°) is narrower than in the analogous [Co[{N(SiMe$_3$)C(Ph)}$_2$CH]$_2$] (102.7(2) and 103.2(2)°)[41] but very similar to those in [Co{N(Ph)C(NMe$_2$)-NC(NMe$_2$)N(SiMe$_3$)}$_2$] (95.94(10), 96.26(10)°).[28]

In summary, we have prepared the first structurally characterized dimeric lithium 6-((trimethylsilyl)amido)-2,4-bis(dimethylamino)[1,3,5]triazenes **1** and **2** having a novel triazine scaffold and, further, the monomeric Mn (**3**) and Co (**4**) complexes [LL′M] (**L** = NC(NMe$_2$)NC(NMe$_2$)NC(NSiMe$_3$), **L′** = N{N(SiMe$_3$)C(NMe$_2$)}$_2$). A proposed pathway involves a series of nucleophilic attacks, trimethylsilyl shifts, ring formation, and unusual Me$_2$NSiMe$_3$ elimination , for the formation of **1** and **2**. Particularly, complexes **1** and **2** are of interest as potential precursors in the synthesis of a wide range of metal compounds. Furthermore, compounds **3** and **4** are rare examples of Mn and Co complexes bearing mixed 1,3,5-triazapentadienato and triazine ligands.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving X-ray crystallographic data for **1**, **3** and **4** and figures giving the structure of **4** and 1/χ vs T plots for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystal data are also available from the CCDC (reference numbers 808013, 808015 and 808014).

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Notes

The authors declare no competing financial interest.

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