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Inorganic Chemistry
Article

Varied Reactions of $[M(L)]_3$ with $HgCl_2$, $FeBr_2$, $CeCl_3$, AgOTf; Ligand Transfer, Nucleophilic Attack with Recombination and/or Fragmentation [M = Li or Na; L = $N(SiMe_3)\{C(H)N\}_3SiMe_3$]

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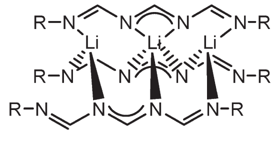
The crystalline compounds $[Hg\{N(R)C(H)NR\}_2]$ (**1**), $[Fe(\mathbf{L})_2]_2$ (**2**), $[Ce(\mathbf{L})_2Cl]_2$ (**3**), $[(AlMe_2)_3\{(N(R)C(H)NC(H)N)_2\text{-}C(H)NC(H)NR\}]$ (**4**), and $[Ag_8Na\{(N(R)C(H)N)_2(C(H)N)_4R\}_3]$ (**5**) were obtained from $[Li(\mathbf{L})]_3$ (**A**) (for **1**) or $[Na(\mathbf{L})]_3$ (**B**) and $HgCl_2$, $FeBr_2$, $CeCl_3$, $Al(Cl)Me_2$, and AgOTf, respectively [$\mathbf{L} = N(R)\{C(H)N\}_3R$; R = $SiMe_3$]. Compounds **1**, **2**, **3**, and **5** were prepared in tetrahydrofuran (THF) at 20 °C; for **4**, it was C_6H_{14} at −78 °C. NMR data for **1** showed only a single $SiMe_3$ environment for **1**, implicating a fast exchange process. Single crystal X-ray data showed dinuclear structures for **2** and **3**. Each ligand $[\mathbf{L}]^-$ in crystalline **2** was bound to each of the two Fe atoms in a κ^1- or κ^2-fashion, respectively, with one $NSiMe_3$ group of the former unattached; this was consistent with VT ^{1}H NMR spectral data indicative of fast exchange (at 313 K) between axial κ^1- and equatorial κ^2-*N,N′*-coordination to Fe. The magnetic moment for **2** in C_6H_6 was appropriate for high-spin octahedral Fe(**II**). The ligands $[\mathbf{L}]^-$ in crystalline **3** are arranged in a helical fashion. The NMR spectra of **4** in $C_6D_5CD_3$ showed that there is an equilibrium between two asymmetric structures; minor co-products were **4′**, assigned as a symmetrical isomer of **4**, and $N(R)C(H)NR_2$. The anion of **5** is proposed to be identical to that of **4′**. Routes to the ligands of **1**, **4**, **4′**, and **5** are suggested; the key feature is that the ligand $[\mathbf{L}]^-$, unless tethered in an appropriate metal-containing matrix (as in **A**, **B**, **2**, or **3**), is labile because of $SiMe_3$ mobility, fragmentation, and/or recombination.

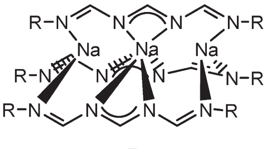
Introduction

Several *N,N′*-chelating ligands are widely used in coordination chemistry. Some of the most prominent are the monoanionic β-diketiminates such as $[\{N(C_6H_3Pr^i_2\text{-}2,6)\text{-}C(Me)\}_2CH]^-$ and benzamidinates $[N(R)C(Ph)NR]^-$ (R = $SiMe_3$).[1] A feature of such species is that they bind strongly to many metal centers and thus play a valuable role as spectator ligands, like cyclopentadienyls. Useful precursors to certain β-diketiminates and amidinates have been cyanoarenes such as PhCN.

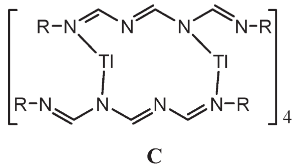
Some time ago we considered generating a β-dialdiminate, for example, $[\{N(R)C(H)\}_2CPh]^-$, or formamidinate, for example, $[N(R)C(H)NR]^-$, by using an HCN-synthon. This led to a study on the behavior of *s*-triazine toward various *N*- and *C*-centered nucleophiles,[2−4] including the reactions, illustrated in Figure 1, which afforded the crystalline metal 1,7-bis(trimethylsilyl)-1,3,5,7-tetraazahepta-1,3,6-trienyls: the lithium (**A**),[2,3] sodium (**B**),[4] and thallium (**C**)[4] salts $[M(\mathbf{L})]_n$; $[\mathbf{L}]^- = [N(R)\{C(H)N\}_3R]^-$ (R = $SiMe_3$).



A



B



C

Related to the present study are 1,3,5-triazapenta-1,3-dienes, which were employed by Würthwein and co-workers[5] as valuable building blocks for further syntheses including the preparation of substituted 1,3,5,7-tetraazahepta-1,3,6-trienes.

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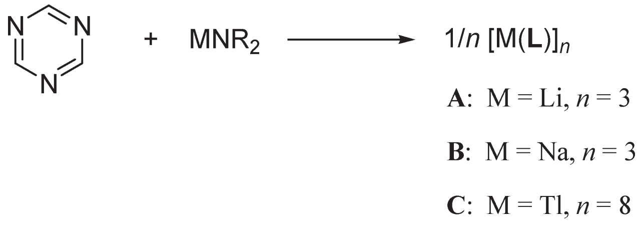


Figure 1. Synthesis of **A**,[2,3] **B**,[3] and **C**;[4] **L** = [N(R){C(H)N}$_3$R], R = SiMe$_3$.

In their deprotonated form, 1,3,5-triazapenta-1,3-dienes were used as monoanionic ligands for several transition and main group metals.[6] In most of such complexes the U-shaped 1,3,5-triazapentadienyl acted as a 1,5-*N,N′*-chelating ligand; however, in Tl,[6c] Ag,[6d] and Hg[6e] complexes the ligand adopted a zigzag shape and a κ^1-coordination mode via the central nitrogen atom.

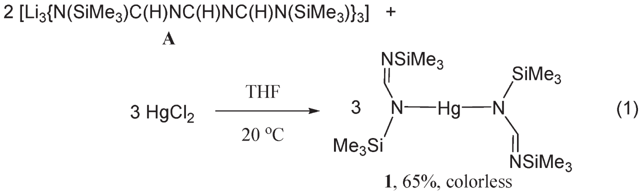
The objective of the present work was to explore the use of **A** or **B** as precursor to a wider range of metal complexes, using a metal halide or triflate as substrate.

Results and Discussion

A number of experiments involving the interaction of the tetraazaheptatrienyllithium compound **A** with a metal halide [MgBr$_2$, CuI, HgCl$_2$, ZrCl$_4$(THF)$_2$], or KOBu^t under various reaction conditions was investigated using pentane as the reaction medium. **A** failed to react with MgBr$_2$, HgCl$_2$, or ZrCl$_4$ at 20 °C; and unidentified mixtures were obtained with LiN(SiMe$_3$)$_2$, KOBu^t, or CuI under these conditions, or with ZrCl$_4$(THF)$_2$ in refluxing tetrahydrofuran (THF).

B did not react with (i) NaOTf, [RuCl$_2$(COD)], or [RuCl(Cp)(PPh$_3$)$_2$] in THF at 20 °C, (ii) [TiCl$_2$Cp$_2$] in C$_6$H$_{14}$, at 20 °C, or (iii) [NiCp$_2$] in PhMe under reflux. Unidentified products were formed when **B** was treated at 20 °C with (a) [FeCl(Cp)(CO)$_2$], [NiCl$_2$(PPh$_3$)$_2$], [ZrCl$_2$Cp$_2$], or [PdCl$_2$(COD)] in THF, or (b) MgBr$_2$ in C$_5$H$_{12}$, (c) SnCl$_2$ or AgOTf in Et$_2$O, or (d) TiCl$_4$ in C$_6$H$_{14}$.

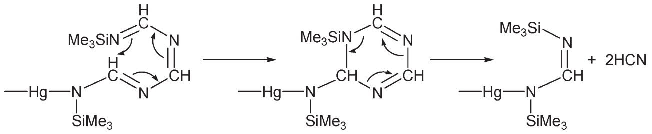
Preparation and Characterization of [Hg{N(R)C(H)-NR}$_2$] (1). Treatment of **A** with mercury(II) chloride in THF yielded the mercury(II) formamidinate **1**; eq 1. The presumed co-products are LiCl and the volatile *s*-triazine.



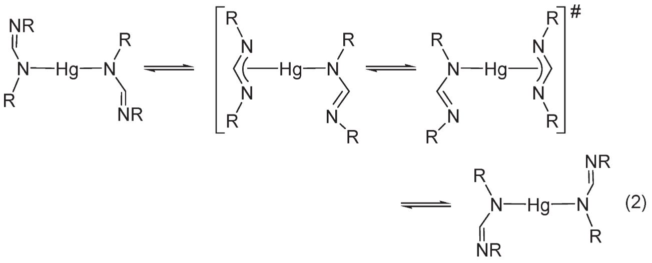
1, 65%, colorless

Compound **1** was characterized by ^{1}H, ^{13}C, and ^{199}Hg-{^{1}H} NMR spectra in C$_6$D$_6$ or C$_6$D$_5$CD$_3$, elemental analysis, and its EI mass spectrum showing the parent molecular peak and appropriate fragment ions. By analogy with the crystalline mercury(II) benzamidinate [Hg{N(SiMe$_3$)C(Ph)=NSiMe$_3$}$_2$][7] and the 1,3-diazaallyl [Hg{N(SiMe$_3$)C(Ph)=NC(Ph)C(SiMe$_3$)$_2$}$_2$],[8] the crystalline compound **1** is assigned the centrosymmetric structure shown in eq 1.

Scheme 1



The ^{1}H NMR spectrum of **1** in C$_6$D$_6$ showed one broad signal at δ 8.72 ppm and a singlet at δ 0.14 ppm, assigned to NC(H)N and the two Si(CH$_3$)$_3$ groups, respectively. Because distinct signals were not observed for each of the trimethylsilyl groups, **1** is presumed to be fluxional in solution, eq 2. Variable temperature NMR spectral measurements failed to provide any supporting evidence, probably because of the very low barrier for the above fluxion. Fluxional behavior was also observed in the 1,3,5-triazapentadienyl compound [Hg(Me){N(C(C$_3$F$_7$)-N(Ph))$_2$}] showing the presence of two κ^1-bound species in solution.[6e] NMR spectral data for Hg{N(SiMe$_3$)-C(Ph)=NSiMe$_3$}$_2$ have not been reported.[7]



The formation of **1** as the product of eq 1, rather than Hg[N(SiMe$_3$)C(H)NC(H)NC(H)NSiMe$_3$]$_2$, is attributed to the facts that (i) Hg(II) favors linear coordination, (ii) the potential additional donor nitrogen atoms in the ligand would not contribute to stability; and (iii) the metal may have activated the C−N bonds facilitating their cleavage, as illustrated in Scheme 1, the monomeric co-product HC≡N finally trimerizing.

The formamidinato ligands in **1** may have originated by the C−N bond formation and fragmentation of the transient ligated tetraazaheptatrienyls with elimination of *s*-triazine. In support, it is noted that Oakley and coworkers found that one of the products of the reaction of *s*-triazine with 2Li[N(SiMe$_3$)$_2$], followed by quenching with Me$_3$SiCl, was N(SiMe$_3$)$_2$C(H)=N(SiMe$_3$).[9] We suggest that the lithium salt **A** was an intermediate, since it is known to be formed from equivalent portions of *s*-triazine and the lithium amide;[2] and that **A** underwent similar fragmentation (as in Scheme 1) when subjected to

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a further equivalent of Li[N(SiMe$_3$)$_2$] and chlorotrimethylsilane.

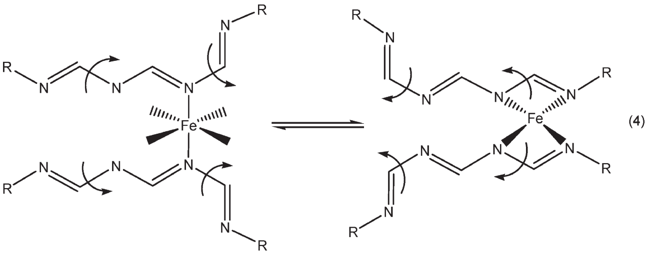
Preparation and Structure of [Fe{N(SiMe$_3$)C(H)NC(H)NC(H)N(SiMe$_3$)}$_2$]$_2$ (2). The reaction of iron(II) bromide with the tetraazaheptatrienyl-sodium salt **B** in THF furnished the dinuclear iron(II) complex **2**, eq 3, isolated as a crystalline red solid in good yield from pentane.

$$\underset{\mathbf{B}}{4/3\ [\mathrm{Na_3\{N(SiMe_3)C(H)NC(H)NC(H)N(SiMe_3)\}_3}]} + 2\ \mathrm{FeBr_2} \xrightarrow[20\,^{\circ}\mathrm{C}]{\mathrm{THF}} \qquad (3)$$

$$\longrightarrow \underset{\mathbf{2},\ 75\%,\ \mathrm{red}}{[\mathrm{Fe\{N(SiMe_3)C(H)NC(H)NC(H)N(SiMe_3)\}_2]_2}}$$

The paramagnetic compound **2** was characterized by its C, H, N microanalysis, VT NMR solution spectra, magnetic moment as a function of temperature, EI mass spectra showing the mononuclear $[M/2]^+$ fragment as the highest m/z peak, and its crystalline molecular structure.

The analysis of the NMR spectra was severely hindered by the paramagnetism of **2**, which caused considerable line-broadening; only the trimethylsilyl protons were definitively assigned, showing temperature dependent chemical shifts at δ −7.52 and −9.98 ppm at 293 K, coalescing at δ −7.30 ppm at 313 K. This behavior is rationalized by the "riding" of the ligands on the iron atoms in the dinuclear complex **2**, as shown in eq 4 (R = SiMe$_3$) (for clarity only one-half of the dimer is shown, the axial metal coordination changing to equatorial).



(4)

The magnetic moment of complex **2** was determined at 293−343 K in benzene by the Evans method[10] (see the Supporting Information). The dinuclear complex **2** was thus found to have an effective magnetic moment μ_{eff} of 8.2 ± 0.2 μ_{B} at 293 K, corresponding to 5.8 ± 0.2 μ_{B} for each iron atom, which is slightly higher than the typical value for a high-spin octahedral iron(II) complex of μ_{eff} = 5.0 to 5.5 μ_{B}

The X-ray molecular structure of the crystalline dinuclear compound **2** (Figure 2) shows that the molecule lies on a site of $\bar{4}$ crystallographic symmetry. Selected geometric data are in Tables 1 and 2; the latter shows comparative N−C bond lengths not only for **2** but also for the related Li,[2,3] Na,[4] and Tl[4] tetraazaheptatrienyls. Whereas in each of **A**, **B**, and **C**, the ligand is symmetric (within the e.s.d.'s; Table 2), in **2** the N3−C3 bond is considerably longer than the C1−N2, and the C3−N4 bond is significantly shorter than the N1−C1. The structure of **2** is strikingly similar to that of the dinuclear bis(pentaazadienyl)iron(II) complex [Fe{N(C$_6$H$_4$Me-4)-N$_3$N(C$_6$H$_4$Me-4)}$_2$] (**D**),[11] as illustrated in Figure 3, showing the distorted octahedral environment in each. Another dinuclear iron complex is [{Fe(tim)}$_2$] (tim = **E**), which has an unsupported Fe−Fe bond of length 2.6891(6) Å (cf. the Fe···Fe distance in **2** of ca. 3.49 Å); it is paramagnetic, μ_{eff} = 2.9 μ_{B}, and was formulated as [{Fe$^{2.5}$(tim)$^{-2.5}$}$_2$].[12]

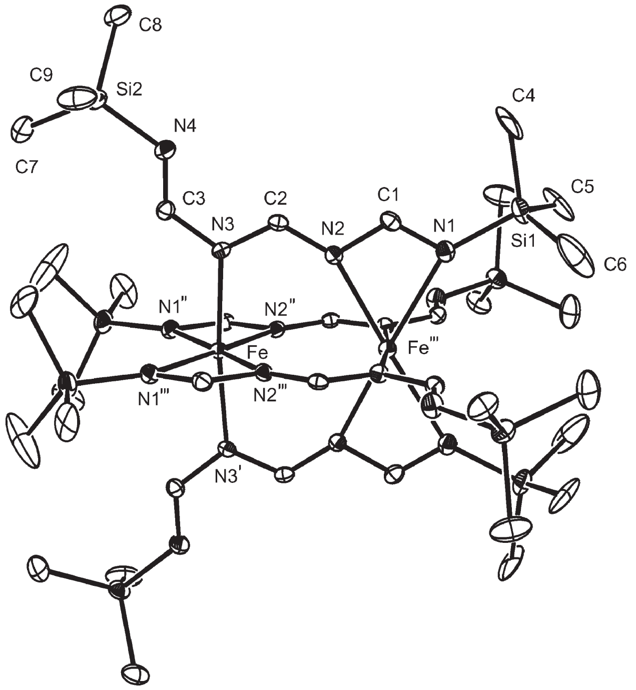
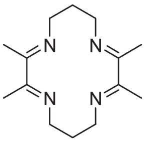


Figure 2. Molecular structure of [Fe{N(SiMe$_3$)C(H)NC(H)NC(H)-N(SiMe$_3$)}$_2$]$_2$ (**2**).

Table 1. Selected Bond Distances and Angles (see also Table 2 and Figure 3) for **2**[a]

	Bond Distances (Å)		
Si1−N1	1.747(3)	Si2−N4	1.733(3)
	Bond Angles (deg)		
N3′−Fe−N3	173.89(3)	N4−C3−N3	125.9(3)
N2″−Fe−N2‴	123.27(12)	C3−N3−C2	116.9(3)
N2″−Fe−N1‴	177.61(9)	N3−C2−N2	122.8(3)
N2‴−Fe−N1	177.61(9)	C2−N2−C1	117.7(3)
Si2−N4−C3	127.3(2)	N2−C1−N1	119.5(3)
Si1−N1−C1	120.0(2)		

[a] Symmetry transformations to generate equivalent atoms: ′ $-x+1, -y+3/2, z$; ″ $-y+5/4, x+1/4, -z+1/4$; ‴ $y-1/4, -x+5/4, -z+1/4$.



E

Preparation and Structure of [Ce{N(SiMe$_3$)C(H)NC(H)NC(H)N(SiMe$_3$)}$_2$Cl]$_2$ (3). From cerium(III) chloride and the sodium salt **B** in THF, after removal of volatiles

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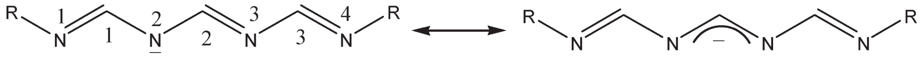
Table 2. N−C Distances (Å) in $[M_k\{N(SiMe_3)C(H)NC(H)NC(H)N(SiMe_3)\}_n]$ [M = Li (**A**)[3] or Na (**B**),[4] with $k = 3 = n$; Tl (**C**),[4] with $k = 8 = n$; Fe (**2**), with $k = 2, n = 4$]

bond[a]	**A**[2]	**B**[3]	**C**[3]	**2**
N1−C1	1.280(4)	1.275(7)	1.24(2)	1.279(4)
C1−N2	1.358(4)	1.380(7)	1.38(2)	1.359(4)
N2−C2	1.328(4)	1.316(7)	1.332(19)	1.320(4)
C2−N3	1.317(4)	1.311(7)	1.335(19)	1.301(4)
N3−C3	1.365(4)	1.360(7)	1.38(2)	1.401(4)
C3−N4	1.281(4)	1.269(7)	1.253(19)	1.256(4)

[a] Labeling of atoms:



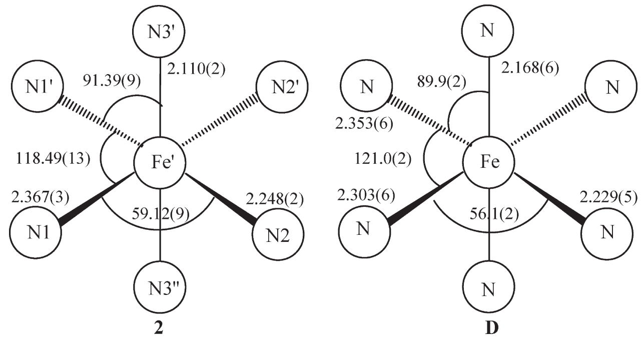


Figure 3. Iron environment in **2** and in $[Fe\{N(C_6H_4Me\text{-}4)N_3N\text{-}(C_6H_4Me\text{-}4)\}_2]$ (**D**).[11]

and crystallization from hexane, there were obtained yellow crystals of the dinuclear complex **3** in good yield, eq 5.

$$\underset{\mathbf{B}}{4/3\,[Na_3\{N(SiMe_3)C(H)NC(H)NC(H)N(SiMe_3)\}_3]} + 2\,CeCl_3 \xrightarrow[20\ ^\circ C]{THF} \quad (5)$$

$$\longrightarrow \underset{\mathbf{3},\ 86\%,\ \text{yellow}}{[Ce\{N(SiMe_3)C(H)NC(H)NC(H)N(SiMe_3)\}_2Cl]_2}$$

The EI mass spectrum of compound **3** revealed its molecular parent ion as the peak of highest mass; its first fragment was of the dechlorinated cation. The ^1H NMR spectrum in C_6D_6 at 293 K showed the trimethylsilyl protons at δ about 1.3 ppm and the terminal and central CH protons at δ about 1.0 and 12.3 ppm, respectively.

The core molecular structure of crystalline **3** was established by a single crystal X-ray analysis, the details of which are in the Supporting Information; a schematic representation is in Figure 4. The molecule lies on a crystallographic inversion center. The Ce, Cl, and Si atoms are correctly related. The tetraazaheptatrienyl ligands are arranged in a helical fashion; and are disordered between the two opposite handed helices which share common Si positions. As a consequence, the geometric data are unreliable. An exception is the Ce−Cl bond length of 2.719(3) Å.

Compound **3** is unusual (or even unprecedented) in having terminal, rather than bridging, chlorides in a binuclear Ce(III) complex. Mononuclear cerium chlorides are also rare; examples include $[Ce\{(N(SiMe_3)\text{-}C(Ph))_2CH\}_2Cl]$[13] and the Ce(IV) complex $[CeCl\{N\text{-}(SiMe_3)_2\}_3]$; the Ce−Cl bond length in the latter is 2.597(2) Å.[14]

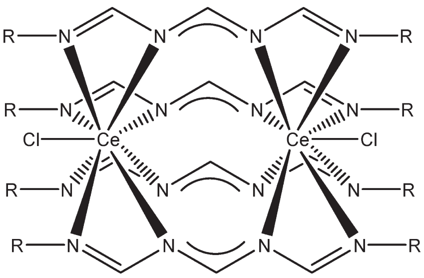


Figure 4. Representation of the molecular structure of **3**.

Preparation and Characterization of a Product Obtained from B and Al(Cl)Me₂. By treating dimethylaluminum chloride with an equivalent portion of **B**, the unexpected crystalline compound **4** was isolated in modest yield, rather than a simple ligand exchange product (as in the synthesis of compounds **2** or **3**). The stoichiometry is 1**B**:3Al(Cl)Me$_2$ and the presumed co-products are $3NaCl + Me_3Si\overline{N\{C(H)N\}_2C}H$ (or its fragmentation products), on the basis of the stoichiometry shown in eq 6. In the mother liquor, small quantities of two other compounds, an isomer of **4** (possibly **4′**) and the formamidine $N(SiMe_3)_2C(H){=}N(SiMe_3)$, in admixture with **4**, were identified by multinuclear NMR spectroscopy.

$$\underset{\mathbf{B}}{[Na_3\{N(SiMe_3)C(H)NC(H)NC(H)N(SiMe_3)\}_3]} + 3\,Al(Cl)Me_2 \xrightarrow[-78\ ^\circ C]{C_6H_{14}} \quad (6)$$

$$\longrightarrow \underset{\mathbf{4},\ 49\%,\ \text{colorless}}{[(AlMe_2)_3\{(N(SiMe_3)C(H)NC(H)N)_2C(H)NC(H)N(SiMe_3)\}]}$$

X-ray quality crystals of **4** were not obtained. However, the structure is assigned on the basis of (i) excellent C, H, and N microanalysis, (ii) the EI-mass spectrum showing as the highest m/z peak the intense signal at 565 corresponding to $[M - CH_3]^+$ and, particularly, (iii) the detailed solution NMR spectral data.

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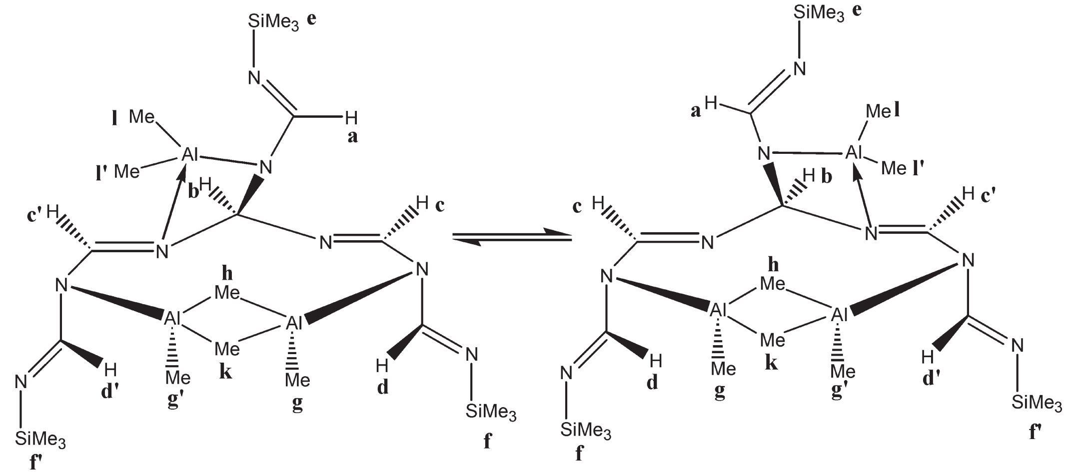

Figure 5. Proposed equilibrium in C_6D_6 for **4**, showing proton and silicon labeling.

The NMR spectra in toluene-d$_8$ showed that there is an equilibrium between two asymmetric (chiral) compounds, Figure 5 (with proton labeling: **a** to **l** and **l′**). The time-averaged structure has a plane of symmetry, from the upper $Me_3SiNC(H)NC(H)$ moiety to the two Al-bridged Me groups (protons **h** and **k**). The proposed equilibrium and structure are consistent with NOE and 2D COSY [(^{1}H)(^{13}C{^{1}H}) and (^{1}H)(^{29}Si{^{1}H})] variable temperature experiments.

The ^{29}Si{^{1}H} NMR spectrum at 333 K revealed that the singlet **f** at δ 12.4 ppm split into two at δ 13.0 and 12.9 ppm at 243 K, while the signal corresponding to **e** was found at δ 3.0 (333 K) and δ 3.60 ppm (243 K). The ^{1}H NMR spectrum at 333 K showed a broad signal at δ 6.49 ppm (2H, **c**), singlets at δ 7.02 (1H, **a**), 7.51 (1H, **b**), 0.04 (9H, **e**), 0.00 (18H, **f**), −0.46 (6H, **g**), −0.54 (3H, **h**), −0.62 (3H, **k**), and −0.69 ppm (6H, **l**), as well as a doublet at δ 7.53 ppm (2H, **d**). The ^{1}H NMR spectrum at 223 K disclosed that each of the signals assigned as **c**, **d**, **f**, **g**, and **l** split into two, consistent with the equilibrium of Figure 5 [e.g., the signal at δ 6.49 ppm at 333 K changed at 223 K into two doublets of doublets centered at δ 7.40 and 5.71 ppm with $^4J(\mathbf{c}/\mathbf{d}) = 1.5$ Hz and $^6J(\mathbf{c}/\mathbf{c'}) = 1.6$ Hz].

The two minor components of the product of the reaction of eq 4 were only obtained as a mixture contaminated with **4**, and evidence for their identity, as the formamidine $N(SiMe_3){=}C(H)N(SiMe_3)_2$ (cf. ref 9) and **4′**, rests solely on NMR spectral data. As for the former, this is based on comparison with the literature ^{1}H and ^{13}C{^{1}H} data;[9] the only new contribution was the recording of the ^{29}Si{^{1}H} spectrum; absence of a signal is attributed to a fast exchange process between $SiMe_3$ groups. As for **4′**, our tentative assignment is based on the close resemblance of its multinuclear spectra at 293 K with those for **4** at 223 K, which indicates that **4′** is similar to **4** but asymmetric and a fluxional process such as that of Figure 5 is absent. Additionally, the analogues of protons **c** and **c′** in **4′** (at δ 5.74 and 5.61 ppm) are in a similar environment, in contrast to those in **4** at δ 7.40 and 5.71 ppm.

The key step in the formation of **4** and **4′** from the sodium salt **B** and $Al(Cl)Me_2$ is suggested to be that shown in Figure 6, implicating the coupling of two of the monoanionic fragments of **B**, triggered by the $Al(Cl)Me_2$-assisted elimination of chlorotrimethylsilane (represented as RCl in Figure 6).

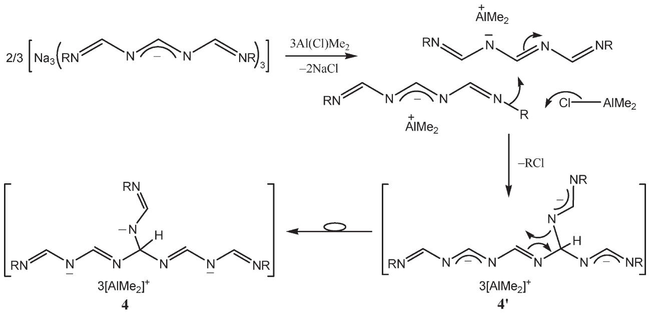

Figure 6. Proposed reaction pathway to **4** and **4′** from **B** and $Al(Cl)Me_2$ ($R = SiMe_3$).

Preparation and Characterization of $[Ag_8Na\{(N(SiMe_3)C(H)N)_2(C(H)N)_4SiMe_3\}_3]$ (5).

The residue obtained from almost equivalent portions of silver triflate and the sodium salt **B** [containing ca. 10% of an impurity, believed on the basis of the ^{1}H NMR spectrum to be sodium bis(trimethylsilyl)formamidinate] in toluene, after removal of volatiles, was crystallized from hexane. Colorless crystals of the cluster complex **5** were thus obtained, albeit in poor yield, eq 7. The presence of this "impurity" was crucial, since repeating the experiment with purified **B** did not produce a characterized material. The presumed co-products of eq 7 are 5NaOTf and 3Me$_3$SiOTf.

$$\underset{\mathbf{B}}{2\,[Na_3\{N(SiMe_3)C(H)NC(H)NC(H)N(SiMe_3)\}_3]} + 8\,AgOTf \xrightarrow[20\,^{\circ}C]{THF} \underset{\mathbf{5},\ 24\%,\ \text{colorless}}{[Ag_8Na\{(N(SiMe_3)C(H)N)_2(C(H)N)_4SiMe_3\}_3]} \quad (7)$$

Compound **5** was characterized by its C, H, and N microanalyses, the EI-mass spectrum showing fragments corresponding to $[Ag\{N(SiMe_3)C(H)NC(H)NC(H)N(SiMe_3)\}_2]^{n+}$ ($n = 1$ or 2), and an X-ray diffraction study. The NMR spectra in toluene-d$_8$ were very complicated [as shown in the Supporting Information for the ^{1}H and ^{29}Si{^{1}H} spectra at 293 K], possibly because of (i) coupling to ^{109}Ag nuclei and (ii) the presence of different conformations. The ^{1}H NMR spectrum bore resemblance to that of the aluminum complex **4** at 223 K, indicative of a highly symmetrical environment; noteworthy are (a) the

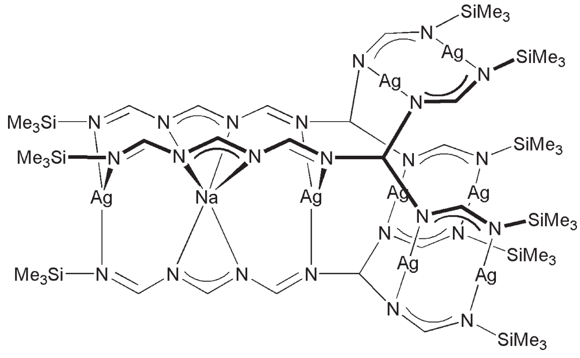

Figure 7. Representation of the molecular structure of **5**.

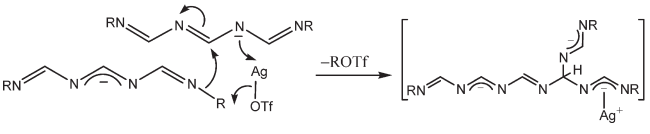

Figure 8. Route to the anions of $[Ag_8Na\{(N(SiMe_3)C(H)N)_2(C(H)N)_4SiMe_3\}_3]$ (**5**).

quartet ^1H signal at δ about 5 ppm and (b) the remarkably sharp $^{23}Na\{^1H\}$ signal at δ 20.8 ($w_{1/2} = 15$ Hz) ppm. The X-ray analysis of **5** showed that the molecule lies on a crystallographic mirror plane but, while consistent with the structure shown in Figure 7, is not definitive, there being extensive disorder problems and unresolved electron density.

As evident from Figure 7, the anion of **5** is suggested to be that shown in **4′**. Thus, the coupling of two anions of **B** is proposed to implicate the sigmatropic transformation shown in Figure 8 or, alternatively, results from successive elimination of ROTf and addition of the resultant metal aldimide to the C=N bond of another **L** moiety.

Concluding Remarks

The molecular structures of five crystalline metal compounds containing the ligand $[N(SiMe_3)C(H)NC(H)NC(H)N(SiMe_3)]^-$ ($\equiv$ $[\mathbf{L}]^-$) are now established: $[Li(\mathbf{L})]_3$ (**A**),[2,3] $[Na(\mathbf{L})]_3$ (**B**),[4] $[Tl(\mathbf{L})]_8$ (**C**),[4] $[Fe(\mathbf{L})_2]_2$ (**2**), and $[Ce(\mathbf{L})_2Cl]_2$ (**3**). However, as experiments leading to the mercury, aluminum, and silver complexes **1**, **4**, and **5**, respectively, have shown this is not inevitably so; nucleophilic attack, fragmentation, and/or recombination of $[\mathbf{L}]^-$ have featured in these cases. It thus appears that the *N*,*N*′-bis(trimethylsilyl)-tetraazaheptatrienyl ligand is only stable if tethered to an appropriate metal template; otherwise, nucleophilic attack, recombination, and/or fragmentation of $[\mathbf{L}]^-$ may feature, as exemplified by the isolation of the complexes **1**, **4**, and **5**. The $SiMe_3$ groups of $[\mathbf{L}]^-$ appear to be mobile and the C(H)=N moieties can be cleaved and recombined in various ways.

Precedents for related nucleophilic recombination processes involving NC(Ph)N fragments are shown in eqs 8,[15] and 9.[16]

$$2N(H){=}(Ph)NH_2 + AlMe_3 \rightarrow [(AlMe_2)\{N(H)C(Ph)NC(Ph)NH\}] + MeH + NH_3 \tag{8}$$

$$2Li\{N(H)C(Ph)NH\} + [PtCl_2(NCPh)_2] \rightarrow [Pt\{N(H)C(Ph)NC(Ph)NH\}_2] + 2LiCl \tag{9}$$

Experimental Section

Materials and Procedures. All manipulations were performed under argon or in a vacuum using standard vacuum line and Schlenk conditions. The solvents were reagent grade or better and were freshly distilled under dry nitrogen gas and freeze−thawed degassed prior to use. Pentane, hexane, and toluene were dried using Na/K alloy. THF was dried and distilled from sodium/benzophenone and stored over a sodium mirror under argon. The following compounds were purchased from Aldrich chemicals and used as received: AgOTf, $Al(Cl)Me_2$ in hexanes, $FeBr_2$, and $HgCl_2$. The compounds $[M\{N(SiMe_3)C(H)NC(H)NC(H)N(SiMe_3)\}]_3$ [M = Li (**A**),[3] or Na (**B**)[4]] were prepared by published procedures. The NMR spectra were recorded in C_6D_6 or $C_6D_5CD_3$ and, except for ^1H and ^{13}C for **1**, were proton-decoupled using a Bruker ACP-250 (^{23}Na, 66.2 MHz), WM-300 (^1H, 300.1; ^{13}C, 75.5 MHz) or AMX-500 (^{27}Al, 131.3; ^{29}Si; 99.4; ^{199}Hg, 89.5 MHz) instrument and were referenced externally with as standard NaCl aq., $AlCl_3 \cdot 6H_2O$, $SiMe_4$, and $HgMe_2$, or internally for ^1H and ^{13}C using residual solvent resonances as standard. EI-mass spectra on solid samples were obtained using a Kratos MS 80 RF instrument. Melting points were determined in sealed capillaries. Elemental analyses were carried out by Medac, Ltd., Brunel University.

Synthesis and Characterization of Bis[*N*,*N*′-bis(trimethylsilyl)formamidinato]mercury(II) (1). Mercury(II) chloride (0.23 g, 0.85 mmol) was added to a stirred solution of the tetraazaheptatrienyllithium compound **A** (0.43 g, 1.7 mmol of the monomer [Li(**L**)]) in THF (ca. 15 mL) at −60 °C. The reaction mixture was allowed to warm to room temperature with stirring for 48 h, then filtered. Volatiles were removed from the filtrate in vacuo to furnish a white solid; crystallization from pentane (ca. 2 mL) at −50 °C afforded colorless crystals of compound **1** (0.32 g, 70%). ^1H NMR: δ 8.72 (br s, 1H), 0.14 (s, 18H, $SiMe_3$) ppm. ^{13}C NMR: δ 158.5 [d, $J(^{13}C{-}^1H)$ 165.9 Hz], 1.0 [q, $J(^{13}C{-}^1H)$ 118.3 Hz] ppm; $^{199}Hg\{^1H\}$ NMR: δ −1388 ppm. EI-MS: *m*/*z* (%): 578 (15) [M^+ (^{204}Hg)], 577 (43), 576 (57) [M^+ (^{202}Hg)], 575 (100) [M^+ (^{201}Hg)], 574 (81) [M^+ (^{200}Hg)], 573 (90) [M^+ (^{199}Hg)], 572 (65) [M^+ (^{198}Hg)], 571 (14), 559 (11), 532 (5), 500 (10). Anal. Calcd for $C_{14}H_{38}HgN_4Si_4$: C, 29.2; H, 6.66; N, 9.74. Found: C, 28.8; H, 6.71; N, 9.86%.

Synthesis and Characterization of Bis[1,7-bis(trimethylsilyl)-1,3,5,7-tetraazaheptatrienyl]iron(II) (2). Iron(II) bromide (0.24 g, 1.1 mmol) was added to a stirred solution of the tetraazaheptatrienylsodium compound **B** (0.58 g, 2.2 mmol of the monomer [Na(**L**)]) in THF (10 mL) at −78 °C. The mixture containing a red suspension was brought to room temperature and was stirred for 15 h. Volatiles were removed in vacuo. The residue was extracted with pentane; concentration of the extract yielded compound **2** (0.44 g, 82%) as a red solid. Crystallization, by cooling the solution to 5 °C, furnished **2** as red-block and needle-shaped crystals (0.24 g, 45%), mp 91 °C. The ^1H NMR spectra of the paramagnetic **2** in benzene-d_6 in the range 293−343 K showed extensive line-broadening; only the $SiMe_3$ groups were assigned at δ −7.52 and δ−9.98 ppm at 293 K corresponding to δ −7.30 ppm at 313 K. The magnetic moment of **2** of $\mu_{eff} = 8.2 \pm 0.2\,\mu_B$ in C_6D_6 at 293 K was derived using Evans' method.[10] EI-MS: *m*/*z* (%) (the three highest signals): 538 (20) [$M/2^+$], 511 (5.5) [$M/2 - HCN]^+$, 428 (1) [$M/2 - Fe]^+$. Anal. Calcd for $C_{36}H_{84}Fe_2N_{16}Si_8$: C, 40.1; H, 7.86; N, 20.8. Found: C, 40.0; H, 7.82; N, 20.5%.

Synthesis and Characterization of Chlorobis[1,7-bis(trimethylsilyl)-1,3,5,7-tetraazaheptatrienyl]cerium(III) (3). Compound **B** (0.22 g, 0.83 mmol of the monomer [Na(**L**)]) was added to a

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[15] Aris, D. R.; Barker, J.; Phillips, P. R.; Alcock, N. W.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1997**, 909.

[16] Barker, J.; Kilner, M.; Mahmoud, M. M.; Wallwork, S. C. *J. Chem. Soc., Dalton Trans.* **1989**, 837.

stirred suspension of cerium(III) chloride (0.103 g, 0.42 mmol) in THF (50 mL) at room temperature and stirring was continued for 24 h .Volatiles were removed in vacuo. The residue was extracted with hexane. The extract was concentrated in vacuo to about 15 mL, then set aside for about 12 h, whereafter yellow crystals of the paramagnetic compound **3** (0.25 g, 86%), mp 195−198 °C (decomp) were deposited. ^{1}H NMR (C_6D_6, 293 K); δ 12.32 (br s, 1H), 1.27 (s, 18H), 0.98 (br s, 2H) ppm; ^{1}H MNR (C_6D_6, 323 K); δ 11.99 (br s, 1H), 2.39 (br s, 2H), 1.07 (s, 18H) ppm. EI-MS: m/z (%): 1316 (19) ($[M]^+$), 1281 (3) ($[M - {}^{35}Cl]^+$), 1075 (58) ($[M - Ce]^+$) .

Synthesis and Characterization of [{**6-(3′-trimethylsilyl-1′,3′-diazapropenyl)**}**-(1,3,5,7,9,11-hexaaza-undecatetraenyl)trialuminumhexamethyl**] **(4).** Dimethylaluminum chloride (5.3 mL of a 1.0 *M* solution in hexanes, 5.3 mmol) was added by syringe to a stirred solution of compound **B** (1.40 g, 5.3 mmol of the monomer [Na(**L**)]) in hexane (40 mL) at −78 °C. A white suspension was rapidly formed. The mixture was brought to room temperature and was stirred for 12 h, then filtered. Volatiles were removed from the filtrate in vacuo. The colorless residue (0.96 g) was recrystallized three times from pentane yielding the crystalline compound **4** (0.50 g, 49% based on $AlClMe_2$), mp 122−124 °C, which was filtered off (for the nature of the filtrate, vide infra). Multinuclear variable temperature NMR spectra in $C_6D_5CD_3$ were recorded, using the symbols **a**, **b**, **c** and **c′**, **d** and **d′**, **e**, **f** and **f′**, **g** and **g′**, **h**, **k**, **l** and **l′** in the assignments (Figure 5). ^{1}H NMR ($C_6D_5CD_3$, 333 K): δ 7.53 (d, ^4J = 1.5 Hz, 2 h, **d**), 7.51 (s, 1H, **b**), 7.02 (s, 1H, **a**), 6.49 (br, 2H, **c**), 0.04 (s, 9H, $SiMe_3$, **e**), 0.00 (s, 18H, $2SiMe_3$, **f**), −0.46 (s, 6H, 2AlMe, **g**), −0.54 (s, 3H, AlMe, **h**) −0.62 (s, 3H, AlMe, **k**), −0.69 (s, 6H, 2AlMe, **l**) ppm; ^{29}Si{^{1}H} NMR ($C_6D_5CD_3$, 333 K): δ 12.6 (s, $2SiMe_3$, **f**), 3.0 (s, $SiMe_3$, **e**) ppm; ^{27}Al{^{1}H} ($C_6D_5CD_3$, 333 K): δ 157 (br, $w_{1/2}$ = 5 kHz) ppm. ^{13}C NMR ($C_6D_5CD_3$, 293 K): δ 164.7 (d, ^1J = 178.5 Hz, **d**), 153.1 (d, ^1J = 192.5 Hz, **b**), 148.4 (d, ^1J = 182.4 Hz, **a**), 0.2 (q, ^1J = 128.6 Hz, $2SiMe_3$, **f**), −1.0 (q, ^1J = 130 Hz, $SiMe_3$, **e**), −7.8 (q, ^1J = 110.8 Hz, 2AlMe), −8.5 (q, *J* unresolved, AlMe), −9.8 (q, ^1J = 112.6 Hz, 2AlMe), −10.5 (q, *J* unresolved, AlMe) ppm. ^{29}Si{^{1}H} NMR ($C_6D_5CD_3$, 243 K): δ 13.0 (s, $SiMe_3$), 12.9 (s, $SiMe_3$), 3.6 (s, $SiMe_3$, **e**) ppm. ^{1}H NMR ($C_6D_5CD_3$, 203 K): δ 7.60 (d, ^4J = 1.4 Hz, **d**), 7.46 (d, ^4J = 1.5 Hz, 1H, **d′**), 7.40 (dd, ^6J = 1.6 Hz, 1H, **c′**), 7.18 (s, 1H, **b**), 6.71 (s, 1H, **a**), 5.71 (dd, 1H, **c**), 0.06 (s, 9H, $SiMe_3$, **e**), 0.01 (s, 9H, $SiMe_3$, **f′**), −0.15 (s, 3H, AlMe, **g′**), −0.17 (s, 9H, **f**), −0.26 (s, 3H, AlMe, **g**), −0.28 (s, 3H, AlMe, **h**), −0.38 (s, 3H, AlMe, **k**), −0.54 (s, 3H, AlMe, **l**), −0.58 (s, 3H, AlMe, **l′**) ppm. EI-MS: m/z (%): 1206 (1), 1131 (1.6), 1073 (1.6), 811 (2.2), 737 (9.5), 713 (7), 565 (100), $[M - Me]^+$. Anal. Calcd for $C_{21}H_{51}Al_3N_8Si_3$: C, 43.4; H, 8.85; N, 19.3. Found: C, 43.2; H, 8.73; N, 19.2%.

The filtrate (vide supra) contained the formamidine $N(SiMe_3){=}C(H)N(SiMe_3)_2$ [^{1}H NMR (C_6D_6, 293 K): δ 8.11 (s, 1H, CH), 0.23 (br s, 27H, $SiMe_3$) ppm; ^{13}C{^{1}H} NMR (C_6D_6, 293 K): δ 158.5, 2.2 (br) ppm; no signal was observed in the ^{29}Si{^{1}H} NMR (C_6D_6, 293 K) spectrum] and compound **4′**. The latter was identified solely by the following spectral details: ^{1}H NMR (C_6D_6, 293 K): δ 7.61 (d, ^4J = 1.6 Hz, 1H), 7.31 (s, 1H), 7.29 (s, 1H), 7.08 (d, ^4J = 1.6 Hz, 1H), 5.74 (dd, ^6J = 1.5 Hz, 1H), 5.61 (dd, ^6J = 1.5 Hz, 1H), 0.15 (s, 9H, $SiMe_3$), 0.11 (s, 9H, $SiMe_3$), 0.07 (s, 9H, $SiMe_3$), −0.28 (s, 6H, 2AlMe), −0.35 (s, 3H, AlMe), −0.52 (s, 3H, AlMe), −0.55 (s, 3H, AlMe) ppm; ^{13}C{^{1}H} NMR (C_6D_6, 293 K): δ 164.2, 161.0, 157.4, 153.0, 72.2, 70.7, −0.4 ($SiMe_3$), −1.0 ($SiMe_3$), −1.3 ($SiMe_3$) ppm; ^{27}Al{^{1}H} NMR (C_6D_6, 333 K): δ 145.9 (br, $w_{1/2}$ = 5.7 kHz) ppm; ^{29}Si{^{1}H} NMR (C_6D_6, 293 K): δ 13.8, 12.45, 3.2 ppm.

Synthesis and Characterization of [$\mathbf{Ag_8Na}$**{(RNCHN)$_2$CH-NCHNCHNCHNR}$_3$**] **(5).** A solution of compound **B** (0.51 g, 1.9 mmol of the monomer [Na(**L**)]) containing about 10% of an impurity [probably Na{$N(SiMe_3)C(H)N(SiMe_3)$}: ^{1}H NMR (C_6D_6, 293 K): δ 0.09 (s, $SiMe_3$) ppm; ^{13}C{^{1}H} (C_6D_6, 293 K): δ 2.6 ppm; ^{29}Si{^{1}H}(C_6D_6, 293 K): δ 2.1 ppm] in toluene (10 mL) was added to a stirred suspension of silver triflate (0.55 g, 2.1 mmol) in toluene (20 mL) at −55 °C. After about 30 min, the mixture was brought to room temperature. Stirring was continued for 12 h, whereafter the mixture was filtered. Volatiles were removed from the filtrate in vacuo. The residue was crystallized from hexane at −40 °C to give colorless crystals of compound **5** (0.30 g, 24%), mp 135 °C (decomp). ^{23}Na{^{1}H} NMR ($C_6D_5CD_3$, 298 K): δ 20.8 ppm ($w_{1/2}$ = 15 Hz); ^{29}Si{^{1}H} NMR ($C_6D_5CD_3$, 298 K): δ 7.05, 6.17 [d, J (^{29}Si-$^{107/109}$Ag) 1.1 Hz], 5.14 [d, J(^{29}Si-$^{107/109}$Ag) 1.1 Hz] ppm. EI-MS: m/z (%): 619 (0.4), 590 (2.0) ($[Ag\{Me_3SiNCHNCHNCHN(SiMe_3)\}_2]^+$), 295 (2.9) ($[Ag\{Me_3SiNCHNCHNCHN(SiMe_3)\}_2]^{2+}$), 171(100). Anal. Calcd for $C_{45}H_{99}Ag_8N_{24}NaSi_9$: C, 25.55; H, 4.72; N, 15.9. Found: C, 25.65; H, 4.75; N, 15.9%.

Table 3. Crystal Data and Refinement Parameters for Compounds **2** and **3**

compounds	**2**	**3**
formula	$C_{36}H_{84}Fe_2N_{16}Si_8$	$C_{36}H_{84}Ce_2Cl_2N_{16}Si_8$
M_r	1077.6	1317.1
crystal system	tetragonal	monoclinic
space group	$I4_1/a$ (No.88)	$P2_1/n$ (No. 14)
a / Å	20.959(5)	10.941(2)
b / Å	20.959(5)	27.269(4)
c / Å	14.360(4)	10.953(2)
β / deg	90	94.78(2)
V / Å^3	6308 (3)	3256.5(10)
Z	4	2
μ/mm^{-1}	0.65	1.65
unique reflections, R_{int}	2767, 0.0501	5700, 0.0407
reflections with $I > 2\sigma(I)$	1972	4259
R_1, wR_2 [$I > 2\sigma(I)$]	0.043, 0.093	0.072, 0.169
R_1, wR_2 (all data)	0.071, 0.103	0.099, 0.218

Crystal Data and Refinement Details for 2 and 3. Diffraction data were collected on an Enraf-Nonius Kappa CCD diffractometer using monochromated Mo Kα radiation, λ 0.71073 Å at 173(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. The dimeric **2** lies on a site of $\bar{4}$ symmetry. The Si(1) methyl groups are disordered over three different orientations in the ratio 0.42:0.32:0.26 and Si−C and C···C distances were constrained (SADI).

The dimeric **3** lies on a crystallgraphic inversion center; the Ce, Cl, and Si atoms are correctly related by the inversion center. However, the $[N(SiMe_3)C(H)NC(H)NC(H)NSiMe_3]$ ligands are arranged in a helical arrangement and are disordered between the two opposite handed helices, but sharing common Si positions. In order for the refinement to converge it was necessary to put loose constraints on the Si−C bonds and the C···C methyl distances; both Si atom sites were included for each ligand. Only Ce and Cl atoms were anisotropic.

The structures were refined on all F^2 using SHELXL-93 (**3**)[17] or SHELXL-97 (**2**, **5**).[18] Further details are in Table 3.

Acknowledgment. We thank that European Community for a Human Capital and Mobility Grant (category 20) for W.M.B., and Drs. Li Gang and A. V. Protchenko for helpful discussions. This paper is dedicated to the memory of Dr. W. Marco Boesveld.

Supporting Information Available: CIF file containing X-ray data for compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] Sheldrick, G. M. *SHELXL-93, Program for refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1993.

[18] Sheldrick, G. M. *SHELXL-97, Program for refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.