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Article

Reduction of Carbodiimides by Samarium(II) Bis(trimethylsilyl)amides—Formation of Oxalamidinates and Amidinates through C–C Coupling or C–H Activation

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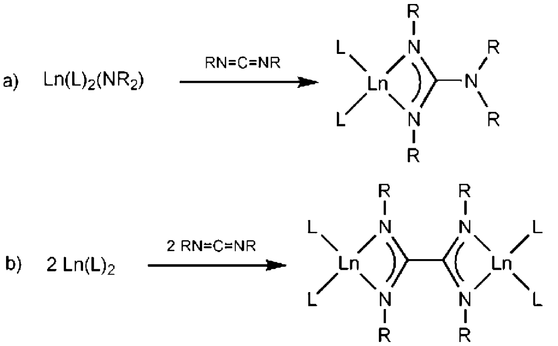
The reaction of [Sm{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (THF = tetrahydrofuran) with carbodiimides RN═C═NR (R = Cy, C$_6$H$_3$-2,6-^{i}Pr$_2$) led to the formation of dinuclear Sm^{III} complexes via differing C–C coupling processes. For R = Cy, the product [{(Me$_3$Si)$_2$N}$_2$Sm(μ-C$_2$N$_4$Cy$_4$)Sm{N(SiMe$_3$)$_2$}$_2$] (**1**) has an oxalamidinate [C$_2$N$_4$Cy$_4$]$^{2-}$ ligand resulting from coupling at the central C atoms of two CyNCNCy moieties. In contrast, for R = C$_6$H$_3$-2,6-^{i}Pr$_2$, H transfer and an unusual coupling of two ^{i}Pr methine C atoms resulted in a linked formamidinate complex, [{(Me$_3$Si)$_2$N}$_2$Sm{μ-(RNC(H)N(Ar–Ar)NC(H)NR)}Sm{N(SiMe$_3$)$_2$}$_2$] (**2**) (Ar–Ar = C$_6$H$_3$-2-^{i}Pr-6-C(CH$_3$)$_2$C(CH$_3$)$_2$-6′-C$_6$H$_3$-2′-^{i}Pr). Analogous reactions of RN═C═NR (R = Cy, C$_6$H$_3$-2,6-^{i}Pr$_2$) with the Sm^{II} "ate" complex [Sm{N(SiMe$_2$)$_3$Na] gave **1** for R = Cy, but a novel C-substituted amidinate complex, [(THF)Na{N(R)C(NR)CH$_2$Si(Me$_2$)N(SiMe$_3$)}Sm{N(SiMe$_3$)$_2$}$_2$] (**3**), for R = C$_6$H$_3$-2,6-^{i}Pr$_2$, via γ C–H activation of a N(SiMe$_3$)$_2$ ligand.

Introduction

Carbodiimides, RN═C═NR, from the heterocumulene family (which includes isoelectronic CO$_2$), are important substrates for metal-based reactivity studies. For example, insertion reactions of carbodiimides into main-group and early-transition-metal M−N bonds have been known for many years.[1] For lanthanoid metals, analogous insertion reactions have been employed for the synthesis of lanthanoid(III) complexes with bulky guanidinate RNC(NR′$_2$)NR$^-$ ligands (Scheme 1a),[2−7] where such ligands are attractive supports for low-coordinate, highly reactive alkyl species.[8,9]

Scheme 1. Reactions of Carbodiimides RN═C═NR with Lanthanoid Complexes: (a) Insertion/Guanidinate Formation; (b) Reductive Coupling/Oxalamidinate Formation



Recently, reductive coupling of carbodiimides has realized an exciting alternative reaction leading to novel M(NCN) metallocycles. With low-valent metallocene complexes [(C$_5$H$_5$)$_2$Ti(CO)$_2$][10,11] or [(MeC$_5$H$_4$)$_2$Sm(THF)][12] (THF = tetrahydrofuran) or metallic lithium[13] as the reducing agent,

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10.1021/ic701497c CCC: $37.00

Scheme 2. Synthesis of Complex **1** (L = $N(SiMe_3)_2$, R = Cy)

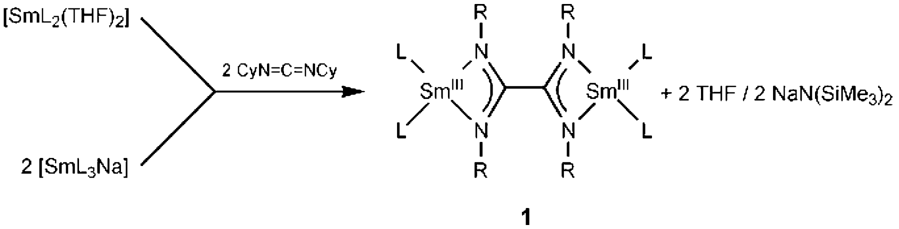

Table 1. A Summary of Crystal Data and Refinement Details for Complexes **1**−**3**

	1	**2**	**3**
formula	$C_{50}H_{116}N_8Si_8Sm_2$	$C_{74}H_{140}N_8Si_8Sm_2$	$C_{47}H_{95}N_5NaOSi_6Sm$
fw	1354.95	1667.36	1088.16
cryst sys	monoclinic	monoclinic	orthorhombic
space group	*C*2/*c*	*P*21/*n*	*Pbca*
a, Å	22.7524(2)	10.8127(2)	19.4815(7)
b, Å	17.3941(2)	18.2560(3)	23.6653(8)
c, Å	20.5878(2)	22.5778(4)	25.3705(9)
β, deg	120.867(1)	101.49501)	90
V, Å^3	6993.73(13)	4367.39(13)	11696.7(7)
Z	4	2	8
ρ_{calc}, g cm^{-3}	1.287	1.268	1.236
F(000)	2832	1752	4616
μ, mm^{-1}	1.835	1.483	1.170
cryst size, mm	0.25 × 0.15 × 0.04	0.15 × 0.08 × 0.05	0.30 × 0.15 × 0.05
θ range, deg	3.47−27.50	1.96−27.50	1.57−27.50
reflns (R_{int})	36 345 (0.046)	48 919 (0.054)	68 565 (0.041)
data/restraints/params	8019/0/322	10017/0/435	13440/0/574
GOF	1.038	1.355	1.115
R1 [$I > 2\sigma(I)$]	0.0274	0.0578	0.0379
wR2 (all data)	0.0549	0.0950	0.0809
residual density, e Å^{-3}	0.607 and −0.493	0.463 and −1.335	0.838 and −0.828

carbodiimides are reduced to oxalamidinate, $[C_2N_4R_4]^{2-}$ (R = Cy, ^{i}Pr, C_6H_4-*p*-Me), ligands (Scheme 1b) via C−C coupling at the central C atoms of two carbodiimides. This transformation parallels CO_2 reduction by $[Sm(C_5Me_5)_2(THF)_2]$ to yield an analogous oxalate complex $[(C_5Me_5)_2Sm(\mu\text{-}O_2CCO_2)Sm(C_5Me_5)_2]$.[14] Our interest in lanthanoid complexes with bulky aryl−formamidinate ligands, $RNC(H)NR^-$, e.g., R = C_6H_3-2,6-^{i}Pr$_2$),[15−17] (for reviews of amidinate complexes, see ref 18) prompted us to investigate the redox reactions of low-valent, non-metallocene lanthanoid complexes with bulky carbodiimides as potential sources of sterically hindered lanthanoid(III) metallocyclic (LnNCN) frameworks.

Samarium(II) bis(trimethylsilyl)amide, $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$, first introduced by Evans,[19] is an attractive reducing agent, as it can be formed conveniently from commercially available reagents and is readily soluble in hydrocarbon solvents.[19,20] Although plausibly milder than lanthanocene reagents (E^0 values for $Ln(C_5R_5)_2$ species[21,22] have been shown to be more negative than for the corresponding $Ln\{N(SiMe_3)_2\}_2$[23]), the reduction of O- and N-containing substrates by $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$ has been explored, mirroring similar reactions using $[Sm(C_5Me_5)_2(THF)_2]$. For example, with fluorenone, both a ketyl radical anion complex $[Sm\{N(SiMe_3)_2\}_2(OC_{13}H_8)(HMPA)]$ (HMPA = hexamethylphosphoric triamide) and the corresponding C−C coupled pinacolate complex $[\{(Me_3Si)_2N\}_2(HMPA)Sm(\mu\text{-}O_2C_{26}H_{16})Sm(HMPA)\{N(SiMe_3)_2\}_2]$ have been characterized.[24] The conversion of nitroaryls ($ArNO_2$) to anilines ($ArNH_2$) can be mediated by $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$ and was shown to proceed via O abstraction and the subsequent reduction of ArN=NAr.[25] Phenyl benzophenone imine (Ph_2C=NPh)

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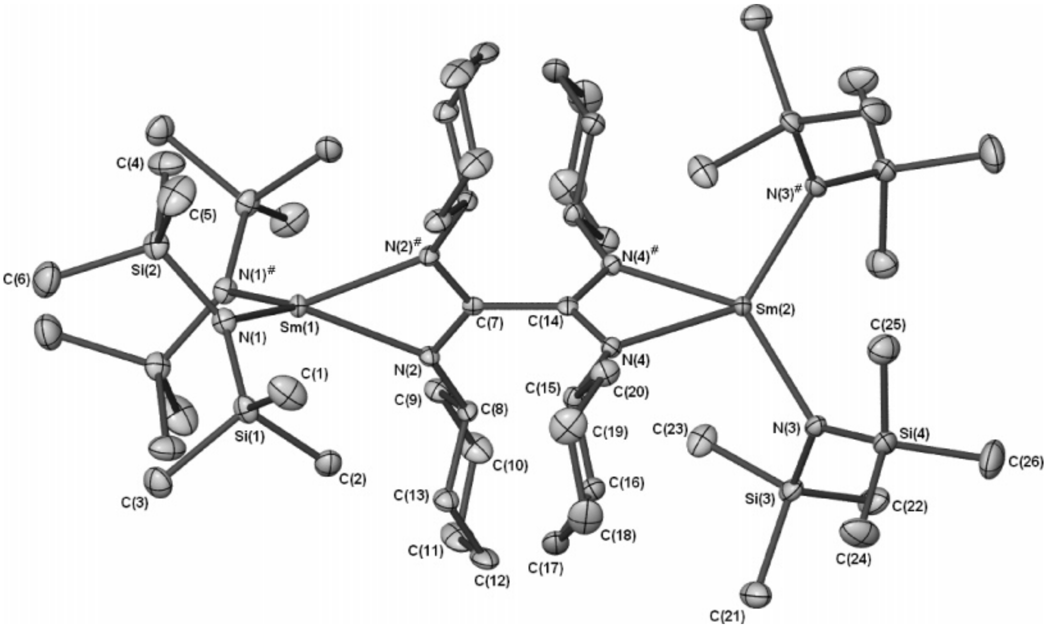


Figure 1. Molecular structure of **1**, viewed approximately down the *c* axis and shown with 50% thermal ellipsoids and H atoms omitted for clarity. Atoms denoted with # are generated by the symmetry operator $-x$, y, $^1/_2 - z$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $\mathbf{1}^a$

Sm(1)−N(1)	2.286(2)	N(1)−Sm(1)−N(1)^a	116.75(9)
Sm(1)−N(2)	2.417(2)	N(1)−Sm(1)−N(2)	134.18(7)
Sm(2)−N(3)	2.293(2)	N(1)−Sm(1)−N(2)^a	103.35(6)
Sm(2)−N(4)	2.418(2)	N(2)−Sm(1)−N(2)^a	55.57(8)
N(2)−C(7)	1.335(2)	N(3)−Sm(2)−N(3)^a	117.17(9)
N(4)−C(14)	1.332(2)	N(3)−Sm(2)−N(4)	102.88(6)
C(7)−C(14)	1.543(4)	N(3)−Sm(2)−N(4)^a	134.38(6)
		N(4)−Sm(2)−N(4)^a	55.54(8)

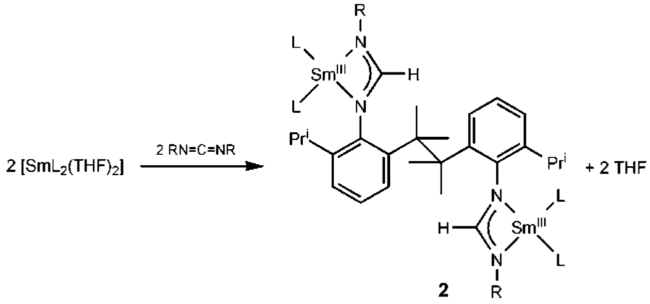
[a] Symmetry transformation: $-x$, y, $^1/_2 - z$.

or phenyl fluorenone imine ($C_{12}H_8C{=}NPh$) also reacts with $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$ to yield Sm^{III} complexes $[Sm\{\eta^2\text{-}(R_2C{-}NPh)\}\{N(SiMe_3)_2\}_2(THF)_3]$ (R_2 = Ph_2 or $C_{12}H_8$), which incorporate three-membered metallocycles (SmCN).[26] We now report the reactions of $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$[19,20] or the "ate" complex, $[Sm\{N(SiMe_3)_2\}_3Na]$,[27] with the bulky carbodiimides RN=C=NR (R = Cy, C_6H_3-2,6-^{i}Pr$_2$) that show formation of both the anticipated Sm^{III} oxalamidinate and some unusual Sm^{III} amidinate complexes that demonstrate the unpredictable and versatile nature of these reduction reactions.

Experimental Section

All manipulations were performed using conventional Schlenk or glovebox techniques under high-purity nitrogen. THF and hexane were dried with sodium/benzophenone while toluene, C_6D_6, and THF-d_8 were dried over sodium. All solvents were distilled and stored under high-purity nitrogen. Infrared spectra (4000−650 cm^{-1}) were recorded as Nujol mulls using sodium chloride plates with a Perkin-Elmer 1600 FTIR spectrophotometer. ^{1}H NMR spectra were recorded using a Bruker DPX 300 or DRX 400 spectrometer at 303 K unless stated otherwise, and chemical shifts are referenced to the residual ^{1}H resonances of the solvent. All assignments were aided by ^{1}H−^{1}H COSY measurements. ^{29}Si NMR spectra were recorded in THF-d_8 using a DRX 400 spectrometer with chemical shifts referenced to an external $SiMe_4$ standard. Electrospray ionization (ESI) mass spectra were determined in positive ion mode using a Micromass Platform II mass spectrometer. Melting points were determined in sealed glass capillaries under nitrogen and are uncalibrated. A magnetic susceptibility measurement for **1** was obtained at 295 K by the Gouy method using an automatic magnetic susceptibility balance (Sherwood Scientific, Cambridge, England). The magnetic moment for **3** was measured at 300 K using a Quantum Design MPMS 5 SQUID magnetometer. Microanalyses were determined by the Campbell Microanalytical Service, University of Otago, New Zealand. Stock solutions of $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$[19] and $[Sm\{N(SiMe_3)_2\}_3Na]$[27] were prepared from 2:1 or 3:1 mole ratio reactions between $Na\{N(SiMe_3)_2\}$ (0.6 M in toluene, Aldrich) and $[SmI_2(THF)_2]$.[28] RN=C=NR (R = C_6H_3-2,6-^{i}Pr$_2$)[29] was prepared according to the literature procedure, and CyN=C=NCy was used as purchased from Aldrich.

Scheme 3. Synthesis of Complex **2** (L = $N(SiMe_3)_2$, R = C_6H_3-2,6-^{i}Pr$_2$)



Synthesis of $[\{(Me_3Si)_2N\}_2Sm(\mu\text{-}C_2N_4Cy_4)Sm\{N(SiMe_3)_2\}_2]$ (1). (a) A solution of *N*,*N*′-dicyclohexylcarbodiimide (0.41 g, 2.00 mmol) in THF (20 mL) was added at ambient temperature with stirring to a purple solution of $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$ (0.10 M,

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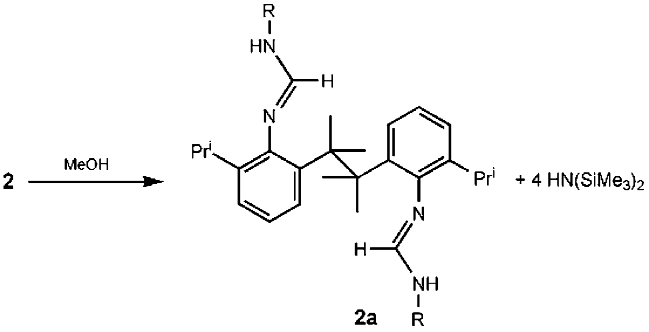
Scheme 4. Hydrolysis of **2** Yielding **2a** (R = C_6H_3-2,6-^{i}Pr_2)



20 mL, 2.00 mmol) in hexane. The color gradually turned light yellow, and the mixture was stirred continuously for 0.5 h. The volume of solvent was reduced to 20 mL and stored at −30 °C for 1 week, after which time light-yellow crystals of **1** were collected (1.00 g, 74%). Mp: 340−344 °C. IR (Nujol): ν 1364 m, 1346 w, 1245 m, 1175 w, 1121 w, 1075 w, 1012 s, 860 w, 829 m, 759 w, 674 w, 656 w cm^{-1}. ^{1}H NMR (THF-d_8, 300 MHz): δ 8.09 (br s, 4H, CyNCNCy), 3.99 (br s, 8H, CyNCNCy), 1.75 (br s, 8H, CyNCNCy), 1.46 (br d, ^3J = 12.4 Hz, 8H, CyNCNCy), 1.37 (br d, ^3J = 12.8 Hz, 4H, CyNCNCy), 0.40 (m, 4H, CyNCNCy), −0.53 (br s, 8H, CyNCNCy), −2.50 (br s, 72H, $SiCH_3$). μ_{eff} (295 K): 1.35 μ_B. Found: C, 44.45; H, 8.72; N, 8.07. Anal. Calcd for $C_{50}H_{116}N_8Si_8Sm_2$: 44.32; H, 8.63; N, 8.27. Crystallization from THF provided crystals suitable for X-ray crystallography. (b) Using a similar procedure to that above, *N*,*N*′-dicyclohexylcarbodiimide (0.41 g, 2.00 mmol) in THF (20 mL) was treated with a solution of [Sm{N(SiMe$_3$)$_2$}$_3$Na] (0.10 M, 20 mL, 2.00 mmol) in hexane. After workup, **1** was obtained as light-yellow crystals (0.93 g, 68%). The product had IR and ^{1}H NMR spectra in agreement with those obtained for the product of (a) above.

Synthesis of [{(Me$_3$Si)$_2$N}$_2$Sm{*μ*-(RNC(H)N(Ar−Ar)NC(H)-NR)}Sm{N(SiMe$_3$)$_2$}$_2$] (2) (R = C_6H_3-2,6-^{i}Pr_2; Ar−Ar = C_6H_3-2-^{i}Pr-6-C(CH_3)$_2$C(CH_3)$_2$-6′-C_6H_3-2′-^{i}Pr). A solution of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (0.73 g, 2.00 mmol) in hexane (20 mL) was added at ambient temperature with stirring to a purple solution of [Sm{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (0.10 M, 20 mL, 2.00 mmol) in hexane. The color gradually turned light-green/yellow, and the mixture was stirred continuously for 1 h. The volume of solvent was reduced to 20 mL and stored at ambient temperature for 2 weeks, after which time light-yellow crystals of **2** were collected (0.77 g, 46%). Mp: 224−228 °C. IR (Nujol): ν 1511 s, 1422 m, 1334 w, 1308 w, 1283 s, 1247 s, 1200 w, 1178 w, 1098 w, 1076 w, 1052 w, 1022 w, 955 s, 878 w, 832 s, 768 m, 756 m, 661 m, 608 m, cm^{-1}. ^{1}H NMR (THF-d_8, 400 MHz, 323 K): δ 18.13 (s, 1H, NC(H)N), 17.78 (s, 1H, NC(H)N), 9.93 (s, 1H, CH, ^{i}Pr), 8.20−5.70 (m, 15H, C_6H_3 + CH, ^{i}Pr), 3.16 (s, 6H, CH_3), 2.84 (s, 6H, CH_3), 2.22 (s, 6H, CH_3), 1.92 (s, 6H, CH_3), 1.23 (s, 6H, CH_3), 0.66 (s, 6H, CH_3), −0.73 (s, 6H, CH_3), −1.28 (s, 6H, CH_3), −2.20 (s, 36 H, $SiCH_3$), −2.46 (s, 36H, $SiCH_3$), −3.47 (br s, 1H, CH, ^{i}Pr), −4.01 (br s, 1H, CH, ^{i}Pr); at 233 K, 18.69 (s, 1H, NC(H)N), 17.81 (s, 1H, NC(H)N), 11.08 (s, 1H, CH, ^{i}Pr), 8.79 (s, 1H, CH, ^{i}Pr), 7.87−5.54 (m, 14H, C_6H_3 + CH, ^{i}Pr), 3.77 (s, 3H, CH_3), 3.15 (s, 3H, CH_3), 3.07 (s, 3H, CH_3), 2.87 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 0.67 (s, 3H, CH_3), 0.40 (s, 3H, CH_3), −0.66 (s, 3H, CH_3), −0.96 (s, 3H, CH_3), −1.44 (s, 3H, CH_3), −2.46 (s, br, 72H, $SiCH_3$), −4.04 (s, br, 1H, CH, ^{i}Pr), −5.13 (s, br, 1H, CH, ^{i}Pr). Found: C, 53.49; H, 8.43; N, 6.43. Anal. Calcd for $C_{74}H_{140}N_8Si_8Sm_2$: 53.31; H, 8.46; N, 6.72. Crystals suitable for X-ray crystallography were obtained by crystallization from C_6D_6.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**^{a}

Sm(1)−N(1)	2.433(3)	N(2)−C(14)	1.432(5)
Sm(1)−N(2)	2.482(3)	C(20)−C(20)^a	1.596(8)
Sm(1)−N(3)	2.260(4)	N(1)−Sm(1)−N(2)	55.69(11)
Sm(1)−N(4)	2.276(4)	N(3)−Sm(1)−N(4)	112.07(13)
C(1)−N(1)	1.333(5)	N(1)−Sm(1)−N(4)	118.99(12)
C(1)−N(2)	1.319(5)	N(2)−Sm(1)−N(3)	121.88(13)
N(1)−C(2)	1.433(5)	N(1)−C(1)−N(2)	119.9(4)

^{a} Symmetry transformation: $1 - x, -y, -z$.

Hydrolysis of 2 and Synthesis of RN(H)C(H)N(Ar−Ar)NC-(H)N(H)R (2a) (R = C_6H_3-2,6-^{i}Pr_2; Ar−Ar = C_6H_3-2-^{i}Pr-6-C(CH_3)$_2$C(CH_3)$_2$-6′-C_6H_3-2′-^{i}Pr). Absolute methanol (0.5 mL) was added to a test tube containing **2** (0.33 g, 0.20 mmol) under nitrogen. The mixture was stirred continuously for 0.5 h. The volatile components were removed under vacuum, the residue was extracted with ether (3.0 mL × 2), and the ethereal solution was dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to leave a colorless crystalline compound **2a** (0.13 g, 90%). Mp: 228−232 °C. IR (Nujol): ν 3190 w, 3137 w, 1934 w, 1916 w, 1862 w, 1800 w, 1658 s, 1582 m, 1362 m, 1329 m, 1289 s, 1198 w, 1183 m, 1164 w, 1138 w, 1088 m, 1013 m, 923 w, 822 m, 805 m, 753 s, 717 w cm^{-1}. ^{1}H NMR (C_6D_6, 300 MHz): δ 9.73 (br s, 2H, NC-(H)=N), 7.08 (s, 12H, C_6H_3), 4.25 (br s, 2H, NH), 3.43 (m, 6H, CH, ^{i}Pr), 1.20−1.70 (m, 48H, CH_3, ^{i}Pr). MS-ESI: 727 ([MH]$^+$, 100%). Found: C, 82.49; H, 9.85; N, 7.85. Anal. Calcd for $C_{50}H_{70}N_4$: C, 82.59; H, 9.70; N, 7.71. Crystals suitable for X-ray crystallography were obtained from toluene (see the Supporting Information for the X-ray structure of **2a**).

Synthesis of [(THF)Na{N(R)C(NR)CH$_2$Si(Me$_2$)N(SiMe$_3$)}Sm-{N(SiMe$_3$)$_2$}$_2$] (3) (R = C_6H_3-2,6-^{i}Pr_2). A solution of *N*,*N*′-bis-(2,6-diisopropylphenyl)carbodiimide (0.73 g, 2.00 mmol) in hexane (20 mL) was added at ambient temperature with stirring to a purple solution of [Sm{N(SiMe$_3$)$_3$}$_3$Na] (0.10 M, 20 mL, 2.00 mmol) in hexane. The solution turned colorless within 5 min. The mixture was heated to 60 °C and stirred continuously at this temperature for 1 h. The volume of solvent was reduced to 20 mL and stored at −30 °C overnight, after which time colorless crystals of **3** were collected (0.75 g, 35%). Mp: 213 °C (dec). IR (Nujol): ν 1428 m, 1342 m, 1308 m, 1246 s, 1191 m, 1159 w, 1112 w, 1091 w, 1042 m, 969 s, 955 s, 886 w, 860 w, 830 s, 775 w, 754 m, 743 m, 666 m, 630 s, cm^{-1}. ^{1}H NMR (THF-d_8, 400 MHz): δ 12.71 (br s, 1H, CH, ^{i}Pr), 7.39−7.00 (m, 3H, C_6H_3), 5.67 (d, ^3J = 7.41 Hz, 1H, C_6H_3), 5.34 (t, ^3J = 7.59 Hz, 1H, C_6H_3), 5.23 (m, 1H, CH, ^{i}Pr), 5.00 (m, 1H, CH, ^{i}Pr), 4.79 (d, ^3J = 7.53 Hz, 1H, C_6H_3), 3.45 (s, 2H, CH_2), 2.54 (d, ^3J = 5.82 Hz, 3H, CH_3, ^{i}Pr), 1.89 (d, ^3J = 7.14 Hz, 3H, CH_3, ^{i}Pr), 1.86 (d, ^3J = 6.84 Hz, 3H, CH_3, ^{i}Pr), 1.45 (d, ^3J = 4.74 Hz, 3H, CH_3, ^{i}Pr), 1.39 (d, ^3J = 6.45 Hz, 3H, CH_3, ^{i}Pr), 1.09 (s, 9H, $SiCH_3$), 0.92 (m, 1H, CH, ^{i}Pr), 0.72 (d, ^3J = 6.54 Hz, 3H, CH_3, ^{i}Pr), 0.68 (d, ^3J = 6.03 Hz, 3H, CH_3, ^{i}Pr), 0.30 (s, 18H, $SiCH_3$), −0.81 (d, ^3J = 6.27 Hz, 3H, CH_3, ^{i}Pr), −1.48 (s, 6H, $SiCH_3$), −3.27 (s, 18H, $SiCH_3$). Resonances of THF were observed at 3.54 and 1.67 ppm, partially overlapping residual solvent THF signals, and could not be reliably integrated. ^{29}Si NMR (THF-d_8, 79.495 MHz): δ 0.23, −1.43, −10.68, −11.96. μ_{eff} (300 K): 1.69 μ_B. Found: C, 51.63; H, 8.59; N, 6.38. Anal. Calcd for $C_{47}H_{95}N_5NaOSi_6Sm$: C, 51.88; H, 8.80; N, 6.44. Crystallization from toluene provided crystals of **3** suitable for X-ray crystallography.

Synthesis of [(THF)$_2$NaN(R)C(NR)CH$_2$Si(Me$_2$)N(SiMe$_3$)Sm-{N(SiMe$_3$)$_2$}$_2$]·$^1/_2$(C$_7$H$_8$) (3a) (R = C_6H_3-2,6-^{i}Pr_2). Crystallization of **3** (0.22 g, 0.20 mmol) from a minimum amount of THF/toluene (v/v 1:1) gave colorless crystals of **3a** (0.21 g, 87%). Mp: 207 °C

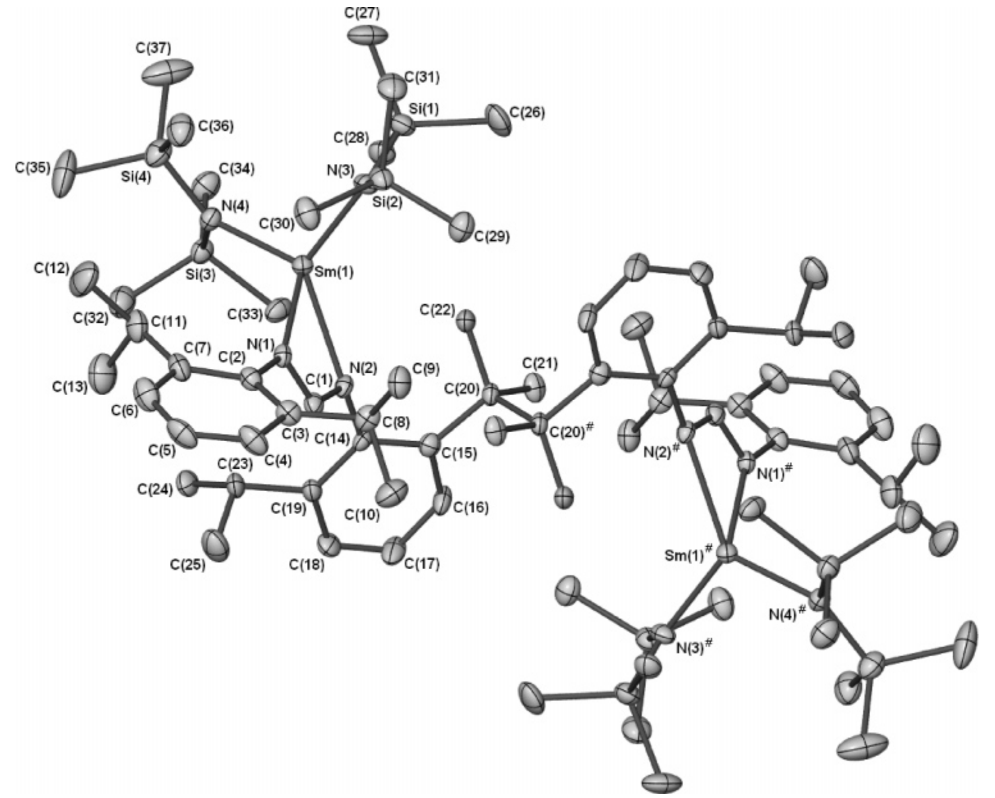


Figure 2. Molecular structure of **2**, viewed approximately down the *a* axis and shown with 50% thermal ellipsoids and H atoms omitted for clarity. Atoms denoted with # are generated by the symmetry operator $1 - x, -y, -z$.

(dec). IR (Nujol): ν 1621 w, 1585 w, 1523 w, 1342 m, 1308 m, 1247 s, 1191 w, 1159 w, 1113 w, 1091 w, 1042 w, 970 m, 955 s, 868 w, 840 m, 831 m, 767 w, 754 w, 723 w, 666 w cm^{-1}. ^{1}H NMR (THF-d_8, 300 MHz): δ 12.68 (br s, 1H, CH, ^{i}Pr), 7.36−6.94 (m, 5.5H, C_6H_3 and PhMe), 5.64 (d, $^3J = 7.11$ Hz, 1H, C_6H_3), 5.31 (t, $^3J = 7.56$ Hz, 1H, C_6H_3), 5.19 (m, 1H, CH, ^{i}Pr), 4.97 (m, 1H, CH, ^{i}Pr), 4.76 (d, $^3J = 8.07$ Hz, 1H, C_6H_3), 3.41 (s, 2H, CH_2), 2.51 (d, $^3J = 5.40$ Hz, 3H, CH_3, ^{i}Pr), 2.27 (s, 1.5H, PhMe), 1.86 (d, $^3J = 7.14$ Hz, 3H, CH_3, ^{i}Pr), 1.83 (d, $^3J = 6.60$ Hz, 3H, CH_3, ^{i}Pr), 1.42 (d, $^3J = 4.74$ Hz, 3H, CH_3, ^{i}Pr), 1.36 (d, $^3J = 6.48$ Hz, 3H, CH_3, ^{i}Pr), 1.09 (s, 9H, $SiCH_3$), 0.89 (m, 1H, CH, ^{i}Pr), 0.69 (d, $^3J = 6.42$ Hz, 3H, CH_3, ^{i}Pr), 0.65 (d, $^3J = 6.45$ Hz, 3H, CH_3, ^{i}Pr), 0.26 (s, 18H, $SiCH_3$), −0.84 (d, $^3J = 6.00$ Hz, 3H, CH_3, ^{i}Pr), −1.51 (s, 6H, $SiCH_3$), −3.31 (s, 18H, $SiCH_3$). Resonances of THF were observed at 3.60 and 1.74 ppm, overlapping residual solvent THF signals, and could not be integrated reliably. Found: C, 54.00; H, 8.74; N, 5.77. Anal. Calcd for $C_{54.5}H_{107}N_5NaO_2Si_6Sm$: C, 54.26; H, 8.94; N, 5.81. Crystallization of **3a** (0.24 g) from toluene gave **3** (0.18 g, 85%) as colorless prismatic crystals (as identified by unit cell measurements).

X-ray Crystallography. A summary of crystal data and refinement parameters is given in Table 1. Crystalline samples of compounds **1**−**3** were mounted on glass fibers in viscous paraffin oil at −150 °C (123 K). Reflection data were obtained using an Enraf−Nonius Kappa CCD or Bruker X8 APEX CCD diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å). Each data set was empirically corrected for absorption (*SORTAV*;[30] *SADABS*[31]), then merged (R_{int} as quoted) to *N* unique reflections. The structures were solved by conventional methods and refined by full-matrix least squares on all F^2 data using *SHELX 97*.[32] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 655689−655693. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, int. code + 44(1223)336-033; e-mail, deposit@ccdc.cam.ac.uk).

Results and Discussion

The reaction of a deep-purple solution of $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$ in hexane with an equivalent amount of *N*,*N*′-dicyclohexylcarbodiimide in THF resulted in a rapid color change to light yellow, indicative of the oxidation of Sm^{II}. From the resulting solution, crystals of the yellow Sm^{III} oxalamidinate complex **1** could be isolated in good yield. The same product was also obtained, in a similar yield, from the carbodiimide and the Sm^{II} "ate" complex $[Sm\{N(SiMe_3)_2\}_3Na]$ (Scheme 2).

Complex **1** is thermally stable up to its melting point (340−344 °C) and gave satisfactory elemental analyses, while the IR and NMR spectra were consistent with the proposed formulation. The ^{1}H NMR spectrum was shifted from the normal diamagnetic region due to the paramagnetic Sm^{III} center ($\mu_{eff} = 1.7\ \mu_B$),[33] but a broad singlet for the SiMe$_3$ protons was clearly evident at −2.50 ppm, (cf. $[Sm\{N(SiMe_3)_2\}_2(THF)(\mu\text{-}PhNNPh)Sm\{N(SiMe_3)_2\}_2]$, $\delta = -1.97$ ppm[25]). The cyclohexyl protons appear as seven individual

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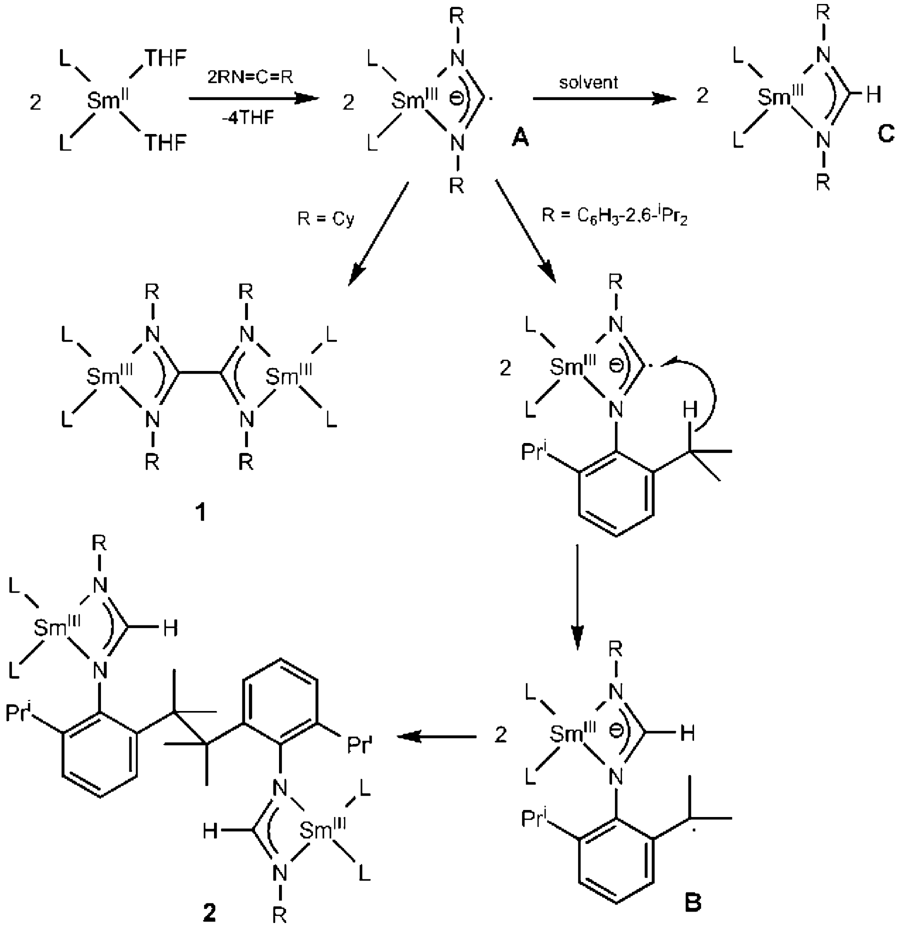
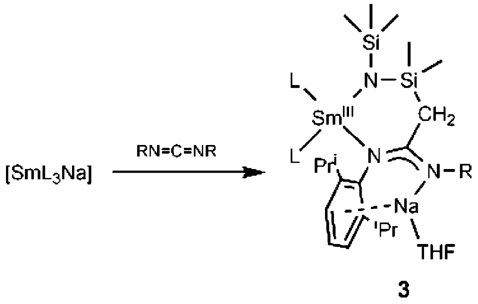
Scheme 5. Proposed Reaction Pathway Leading to the Formation of Oxalamidinate and Formamidinate Complexes from the Reduction of Carbodiimides by [Sm{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (L = N(SiMe$_3$)$_2$)



Scheme 6. Synthesis of Complex **3** (L = N(SiMe$_3$)$_2$, R = C$_6$H$_3$-2,6-^{i}Pr$_2$)



resonances over a range from 8.09 to −0.53 ppm. The identity of compound **1** was unequivocally established by an X-ray structure determination. The molecular diagram is shown in Figure 1, with selected bond distances and angles listed in Table 2. The complex crystallizes in monoclinic *C*2/*c* with the two Sm atoms and the two central amidinate C atoms, C(7) and C(14), lying on a crystallographic two-fold axis (thus, only half the molecule is unique). Each Sm atom is bound in an amidinate fashion (rather than as a diamide, e.g., in [{Li(py)$_2$}$_2$(μ-C$_2$N$_4$R$_4$)] (R = *p*-tolyl)[13]) to either side of a tetracyclohexyloxalamidinate(2−) ligand with two N(SiMe$_3$)$_2^-$ ligands completing each coordination sphere. Both samarium centers are four-coordinate, and each adopts a pseudo-trigonal-planar geometry if the oxalamidinate ligands are considered to be point donors located at the central carbon atoms. Both trigonal planes are approximately orthogonal (dihedral angle 82.46(8)°) as are also the two amidinate Sm(NCN) planes (dihedral angle 83.3(1)°), which results in a favorable staggered arrangement of the two N(SiMe$_3$)$_2$ ligands and the Cy rings, as well as the two pairs of Cy groups attached to the oxalamidinate ligand. The Sm−N(SiMe$_3$)$_2$ distances (Table 2) are comparable with those in related complexes (e.g., five-coordinate [Sm{N(SiMe$_3$)$_2$}$_2$-(THF)(μ-PhNNPh)Sm{N(SiMe$_3$)$_2$}$_2$] average = 2.28(2) Å),[25] while the bond distances to the μ-C$_2$N$_4$Cy$_4$ ligand (Table 2) are shorter than those (2.560(5) and 2.447(5) Å) in nine-coordinate [{Sm(MeC$_5$H$_4$)$_2$(HMPA)}$_2$(μ-C$_2$N$_4$Cy$_4$)],[12] consistent with the difference in ionic radii (ca. 0.18 Å)[34] due to the change in coordination number. The central C−C distance (Table 2) is typical of a single bond, whereas the C−N distances (Table 2) in the C$_2$N$_4$ unit are shorter and equal, indicating a typically delocalized amidinate fragment.

Replacement of the *N*,*N*′-dicyclohexylcarbodiimide with the bulkier *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (RN=C=NR, R = C$_6$H$_3$-2,6-^{i}Pr$_2$), in the reaction with [Sm{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] also gave a color change from purple to yellow, signifying oxidation of the samarium center to Sm^{III}. However, crystallization of the product from solution did not give the corresponding oxalamidinate complex but instead a binuclear Sm^{III} C−C coupled formamidinate

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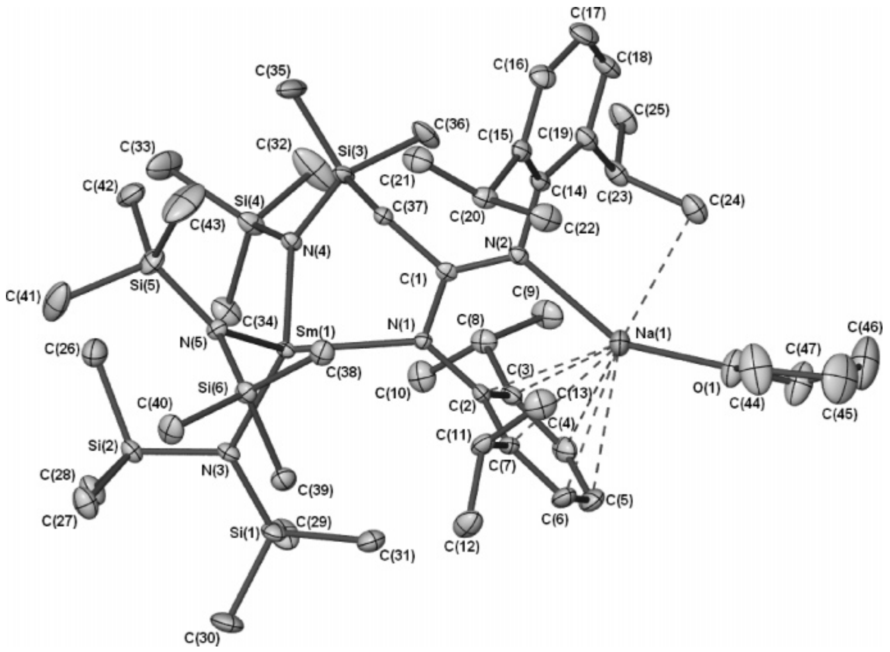

Figure 3. Molecular structure of **3**, shown with 50% thermal ellipsoids and H atoms omitted for clarity.

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

Sm(1)−N(1)	2.501(2)	Na(1)−O(1)	2.265(2)
Sm(1)−N(3)	2.330(2)	Na(1)−C(24)	2.967(3)
Sm(1)−N(4)	2.324(2)	N(1)−C(1)	1.363(3)
Sm(1)−N(5)	2.320(2)	N(2)−C(1)	1.320(3)
Na(1)−N(2)	2.396(2)	C(1)−C(37)	1.510(3)
Na(1)−C(2)	2.678(3)	N(1)−Sm(1)−N(3)	124.82(7)
Na(1)−C(3)	2.858(3)	N(1)−Sm(1)−N(4)	91.57(7)
Na(1)−C(4)	3.087(3)	N(1)−Sm(1)−N(5)	108.41(7)
Na(1)−C(5)	3.121(3)	N(3)−Sm(1)−N(4)	114.85(7)
Na(1)−C(6)	2.918(3)	N(3)−Sm(1)−N(5)	105.52(8)
Na(1)−C(7)	2.703(3)	N(4)−Sm(1)−N(5)	111.05(8)

complex **2**. This unusual product results from H transfer to the central C atom of the carbodiimide and coupling at the methine C atoms on one of the ^{i}Pr groups (Scheme 3).

The identity of complex **2** was confirmed by an X-ray structure determination (see below), while the bulk product gave satisfactory elemental analyses. However, the ^{1}H NMR spectrum of paramagnetic **2** in THF-d_8 was extremely complex. Two singlet resonances at 18.13 and 17.78 ppm, each integrating as 1H, were assigned to formamidinate backbone CH while two $SiCH_3$ resonances at −2.20 and −2.46 ppm, each integrating as 36H, are clearly identified by comparison with **1** above. At first sight, these data may indicate the presence of more than one product in the bulk material, and indeed, the putative complexes (Sm-$\{N(SiMe_3)_2\}_2)_2(\mu$-$C_2N_4R_4R)$ (**2L**) or Sm$\{N(SiMe_3)_2\}_2$(RNC(H)NR) (**2M**) (R = C_6H_3-2,6-^{i}Pr$_2$) would both give virtually indistinguishable elemental analyses (and are plausible products of a common intermediate radical species; see below). However, in the ^{1}H NMR spectrum of **2**, there are *eight* distinct isopropyl CH_3 resonances, each integrating as 6H, in the range of 3.16 to −1.28 ppm. This observation argues against the possibility that the bulk material is a mixture of **2** and either **2L** or **2M**. The last two complexes would each be expected to show a single CH_3 resonance for all eight isopropyl CH_3 groups (24H in total). Indeed, reported spectra of highly crowded bis(2,6-diisopropylphenyl)formamidinate complexes of Sm^{III}, e.g., [Sm(RNC(H)NR)$_3$] and [Sm(RNC(H)NR)$_2$F(THF)] (R = C_6H_3-2,6-^{i}Pr$_2$), show only one broad singlet each for the isopropyl CH_3 groups at δ 1.45 and 0.89, respectively.[16] Thus, the current data are consistent with the observed structure, apart from observation of two NC(H)N resonances at 323 K, suggesting a less symmetrical structure in solution than in the solid state, though this is not evident from the number of methyl resonances (eight). However, a spectrum at 233 K reveals greater separation of the NC(H)N resonances and 16 equal-intensity methyl resonances consistent with a lower symmetry structure in solution. Further evidence of the presence of the coupled ligand was obtained on hydrolysis of bulk **2** which gave **2a** as the sole nonvolatile organic product in high yield (Scheme 4).

The solid-state structure of **2** is shown in Figure 2, with selected bond distances and angles listed in Table 3. The complexes crystallizes in monoclinic $P2_1/n$ with a crystallographic inversion center located at the midpoint of the (ArMe$_2$)C−C(Me$_2$Ar) bond, relating the two halves of the molecule. The Sm center is four-coordinate and bound to two $N(SiMe_3)_2^-$ ligands and two N atoms of the chelating formamidinate fragment. The coordination geometry is pseudo-pyramidal (assuming the formamidinate to occupy a single coordination site at the central C atom, C(1), of the NCN fragment) rather than planar, as in **1** above. The Sm atom resides out of the C(1)N(3)N(4) plane by 0.292(2) Å. The Sm−$N(SiMe_3)_2$ bond lengths (Table 3) are slightly shorter than those in **1** (Table 2) whereas the Sm−N(formamidinate) bond lengths (Table 3) are marginally longer (Table 2), reflecting the bulkier C_6H_3-2,6-^{i}Pr$_2$ substitution on the amidinate nitrogen donors in the present complex. These bond lengths match those of related complexes, e.g., six-coordinate [Sm(RNC(H)NR)$_3$] (2.448(6)−2.467(6) Å),[16] and are shorter than those (2.529(3) and 2.617(3) Å) of the six-coordinate Sm^{II} complex [Sm(RNC(H)NR)$_2$(THF)$_2$] (R

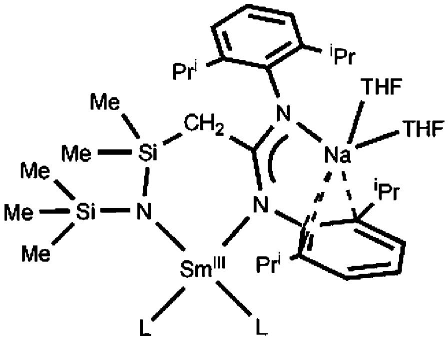

Figure 4. Schematic representation of the molecular structure of **3a**.

= C_6H_3-2,6-^{i}Pr$_2$),[16] consistent with the relative sizes of $Sm^{2+/3+}$.[34] The C(20)−C(20)′ bond length formed by C−C coupling is 1.596(8) Å, which is slightly longer than the corresponding C−C bond in **1** (Table 2), plausibly attributable to the bulk of the C_6H_3-2,6-^{i}Pr$_2$ substituents.

The formation of both complexes **1** and **2** is considered to proceed via radical intermediates (Scheme 5). Thus, the one-electron reduction of a carbodiimide RN═C═NR by a Sm^{II} center presumably generates radical anions bound to Sm^{III} (e.g., **A** in Scheme 5). The subsequent fate of species **A** then appears to depend upon the substituents at the carbodiimide N atoms, although other factors such as solvent or the ancilliary ligands on the Sm may also be significant. Thus, direct coupling of **A** will give the oxalamidinate complex as in **1** and $[\{(MeC_5H_4)_2(HMPA)Sm\}_2(\mu\text{-}C_2N_4R_4)]$ (R = Cy, ^{i}Pr).[12] For the more bulky, C_6H_3-2,6-^{i}Pr$_2$ substituents, this process may be kinetically hindered, allowing intervention of other events. The formation of **2** could be envisaged to occur by H abstraction from a proximal ^{i}Pr group, forming the formamidinate radical fragment **B** (Scheme 5), which subsequently C−C couples at the methine C atoms. Proton abstraction, typically thought to be derived from solvents such as THF by radical species, has been proposed previously in lanthanoid systems,[35] and thus, the formation of **C** by this route is plausible, but is not formed as a major product. The coupling in **2** is unusual, as in reported lanthanoid systems (e.g., ref 24), C−C coupling usually occurs on C atoms proximal to a (coordinated) N or O atom (as is the case for **1**). However, species **B** should have significant stability as a bulky tertiary radical.

The reaction of the Sm^{II} "ate" complex $[Sm\{N(SiMe_3)_2\}_3Na]$ with RN═C═NR (R = C_6H_3-2,6-^{i}Pr$_2$) also gives an unusual product. In this reaction, the purple color of the divalent Sm complex rapidly changes to colorless, indicative of oxidation to Sm^{III}, but different from the formation of yellow **1** and **2** above. After workup and crystallization from toluene, colorless crystals of the substituted acetamidinate complex **3** were isolated (Scheme 6).

The THF coordinated to the Na atom presumably originates from the $[SmI_2(THF)_2]$ starting material used for the in situ preparation of $[Sm\{N(SiMe_3)_2\}_3Na]$. The identity of complex **3** was confirmed by an X-ray structure determination (see below), and the bulk material gave satisfactory elemental analyses. As with **2** above, the ^1H NMR spectrum of paramagnetic **3** was extremely complex. The N−$SiMe_3$ protons appear as four singlets ranging from 1.09 to −3.27 ppm in a ratio of 9:18:6:18. Consistent with this observation, there are four distinct ^{29}Si NMR resonances in the range of 0.23 to −11.96 ppm (relative to $SiMe_4$). Two different aromatic environments are observed with two sets of CH resonances at 7.39−7.00 ppm, and at 5.67−4.79 ppm, consistent with the unsymmetrical binding of the amidinate to both Sm and Na (see below). Furthermore, each isopropyl group shows distinct CH and CH_3 resonances, over a wide chemical shift range.

The solid-state structure of **3** is shown in Figure 3, with selected bond distances and angles listed in Table 4. The structure features a binuclear species containing a four-coordinate Sm atom bound to two $N(SiMe_3)_2^-$ ligands and two N atoms, one from the amidinate moiety and one from the $N(SiMe_3)(SiMe_2CH_2)$ lariat attached to the amidinate backbone. The Na atom is bound to the remaining N atom of the amidinate ligand and is supported by an η^6-arene interaction with one of the C_6H_3-2,6-^{i}Pr$_2$ substituents. The coordination environment of the Na atom is completed by a THF molecule and an agostic Na···Me interaction (see below) giving overall six-coordination. The Sm−$N(SiMe_3)_2$ bond distances (Table 4) fall in a narrow range and are marginally longer than those of **1** and **2** above. Similarly, the Sm(1)−N(1) (amidinate) distance (Table 4) is longer than those in **2** (Table 3) despite both complexes being four-coordinate. The coordination geometry around Sm(1) is distorted by the six-membered metallocycle, which has an internal N−Sm−N angle narrower than that of the others (Table 4). The Na atom has a short Na(1)−N(2) distance (Table 4) by comparison with those of analogous formamidinate complexes (e.g., $[Na(RNC(H)NR)(THF)_3]$, Na−N = 2.406(2) and 2.457(2) Å or $[Na(RNC(H)NR)(DME)_2]$, Na−N = 2.411(3) Å, R = C_6H_3-2,6-^{i}Pr$_2$),[36] which have chelating, bidentate formamidinate ligands rather than unidentate ligands (to Na) as in **3**. The η^6-aryl−Na interaction is characterized by Na−C distances in the range of 2.678(3)−3.121(3) Å with the longest distance to the C atom para to the amidinate N atom. The Na−CH_3 interaction involves one of the ^{i}Pr$_2$ groups attached to the remaining (non-η^6-bound) C_6H_3-2,6-^{i}Pr$_2$ substituent and has a Na−C distance near the middle of the above range (Table 4). Alkali metal cation−arene coordination has been increasingly observed, and the current Na−C bond lengths are typical (e.g., Na/C_6H_3-2-6-^{i}Pr$_2$, 2.881(2)−3.084(2) Å;[37,38] see also ref 39 for non-chelation supported Na−arene complexes, e.g., [Ln-$(L)_4$Na(PhMe)], L = C_3HN_2-3,5-^{t}Bu$_2$). A unidentate N/η^6-

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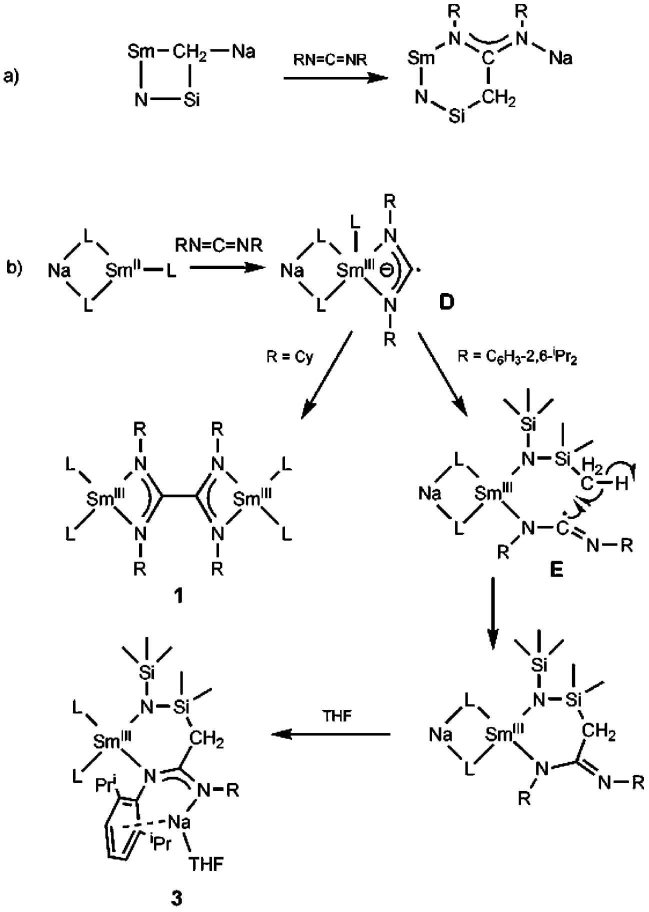
Scheme 7. Possible Reaction Pathways Leading to the Formation of Complex **3** (L = $N(SiMe_3)_2$): (a) Insertion of a Carbodiimide into a Metallocyclic Sm−C Bond and (b) Reductive C−C Coupling Involving the Formation of a Radical Intermediate Having a Unidentate RN(C•)NR⁻ unit



aryl−M arrangement similar to that evident in **3** has been observed in $[K(RNC(H)NR)_2K(THF)_2]_n$ (R = C_6H_3-2,6-^{i}Pr$_2$).[40]

The Na environment in **3** was modified on crystallization from THF/toluene (1:1), which gave the daughter complex **3a**. X-ray crystallography of crystals of **3a** confirmed the atom connectivity (Figure 4) and showed coordination of a second THF molecule to Na replacing the agostic Na···Me interaction, but the poor data quality precluded a detailed structural comparison with **3**. Complex **3a** reverts to **3** when recrystallized from toluene.

The observation of the metallocyclic $SmN(SiMe_3)SiMe_2CH_2C(NR)_2$ fragment in **3** was unexpected, although γ-CH_3 deprotonation of Ln−$N(SiMe_3)_2$ systems has been observed previously. For example, metallocyclic $[Ln\{N(SiMe_3)_2\}_2\{N(SiMe_3)SiMe_2CH_2\}Na(THF)_3]$ has been isolated from homoleptic $[Ln\{N(SiMe_3)_2\}_3]$ (Ln = Sc, Yb, Lu) when treated with $NaN(SiMe_3)_2$.[41] A similar deprotonated $N(SiMe_3)_2$ ligand has also been observed in $[Sm(L)\{N(SiMe_3)(SiMe_2CH_2\}Na(C_7H_8)\}]$ (H_2L = *trans-N,N′*-dimethyl-*meso*-octaethyl-porphyrinogen)[42] while $[Yb\{N(SiMe_3)SiMe_2CH_2BPh_3\}(THF)_2]$, having a chelating amidosilylmethylborate ligand, was isolated as a side product in the synthesis of $[YbN(SiMe_3)_2(thf)BPh_4]$.[43] Although insertion of the carbodiimide into a putative metallocyclic Ln−$CH_2SiMe_2(SiMe_3)N$ moiety (Scheme 7a) would generate the functionalized amidinate ligand observed in **3**, this process does not require an oxidation state change for the Sm center (a magnetic moment measurement confirms the oxidation state of **3**); hence, a radical pathway is likely. It is plausible that the radical intermediate **D** (Scheme 7b, analogous to **A** above) is initially formed from the carbodiimide and $[Sm\{N(SiMe_3)_2\}_3Na]$. For R = Cy, C−C coupling and elimination of $NaN(SiMe_3)_2$ giving **1** occurs, whereas for R = C_6H_3-2,6-^{i}Pr$_2$, the larger R group may induce unidentate binding of the amidinate radical which possibly undergoes intramolecular attack on a proximal CH_3−Si group (e.g., **E**, Scheme 7b), ultimately yielding **3**. Steric modulation of reduction reactions of α,α′-diimines, RN=C(H)C(H)=NR, by ytterbocenes, leading to unusual insertion of C=N moieties into Yb−L bonds (L = fluorenyl), has been observed with the bulky C_6H_3-2,6-^{i}Pr$_2$ substituent on the substrate.[44]

Conclusions

These studies demonstrate that Sm^{III} oxalamidinate complexes, such as **1**, can be prepared by the reduction of carbodiimides using “non-metallocene” lanthanoid reagents, e.g., $[Sm\{N(SiMe_3)_2\}_2(THF)_2]$. Furthermore, there was no evidence of competitive Ln−N insertion reactions. However, the reductive coupling to oxalamidinates is not exclusive, as a different carbodiimide yielded a linked formamidinate complex **2**. Both products are considered to be derived from a common radical intermediate, and the differing outcomes are believed to be a consequence of the size of the R group on the carbodiimide substrate. The larger R group also resulted in the formation of an unusual functionalized amidinate ligand when the “ate” complex $[Sm\{N(SiMe_3)_2\}_3Na]$ was the reducing agent.

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Supporting Information Available: Selected X-ray crystal data information. This material is available free of charge via the Internet at http://pubs.acs.org.

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