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Novel Cyclopentadienyl-Free Organolanthanides: The First Examples of Five-Membered Amidolanthanide Heterocycles[†]

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Reactions of LnCl$_3$ (Ln = Nd, Gd, Yb) and [{Me$_2$SiN(R)Li}$_2$] (R = *t*-Bu, Ph) give the chloride-bridged dimers [{{(*t*-Bu)NSiMe$_2$SiMe$_2$N(*t*-Bu)}Ln(μ-Cl)(THF)}$_2$] (**1**, Ln = Nd; **2**, Ln = Gd; **3**, Ln = Yb) and [{{(Ph)NSiMe$_2$SiMe$_2$N(Ph)}Ln(μ-Cl)(THF)$_2$}$_2$] (**4**, Ln = Nd; **5**, Ln = Gd; **6**, Ln = Yb) in good yields. Compounds **2** and **5** were structurally characterized by X-ray crystallography: **2**, triclinic, $P\bar{1}$, $a = 10.321(2)$ Å, $b = 11.116(2)$ Å, $c = 13.434(3)$ Å, $\alpha = 107.57(3)°$, $\beta = 111.31(3)°$, $\gamma = 90.67(3)°$, $V = 1356.1(5)$ Å^3, $Z = 1$, $R = 0.0233$; **5**, monoclinic, $P2_1/n$, $a = 13.913(13)$ Å, $b = 12.914(9)$ Å, $c = 16.434(14)$ Å, $\beta = 105.64(3)°$, $V = 2843(4)$ Å^3, $Z = 2$, $R = 0.0281$. The chloro functions in **1**−**6** remain reactive, demonstrated by the isolation of the trifluoroacetate derivatives of **1** and **2**. Treatment of **1** or **2** with 2 equiv of NaOCOCF$_3$ gives [{{(*t*-Bu)NSiMe$_2$SiMe$_2$N(*t*-Bu)}Ln(μ-OCOCF$_3$)(THF)}$_2$] (**7**, Ln = Nd; **8**, Ln = Gd). The structure of **8** was determined by a single-crystal X-ray diffraction analysis. Crystal data for **8**: triclinic, $P\bar{1}$, $a = 11.045(2)$ Å, $b = 16.120(3)$ Å, $c = 16.949(3)$ Å, $\alpha = 66.17(3)°$, $\beta = 85.51(3)°$, $\gamma = 78.27(3)°$, $V = 2702.9(9)$ Å^3, $Z = 2$, $R = 0.0311$. The structure of **8** shows the trifluoroacetate group adopting a bridging bidentate mode of coordination.

Introduction

Since 1954, when the first well characterized organolanthanide complexes, (C$_5$H$_5$)$_3$Ln, were reported,[1] the organometallic chemistry of the lanthanide metals has been dominated by cyclopentadienyl ligands.[2] In recent years, the use of the pentamethylcyclopentadienyl ligand (C$_5$Me$_5$) has superseded the unsubstituted C$_5$H$_5$ group and resulted in the discovery of many interesting complexes and properties: for instance, unusual bent metallocenes (C$_5$Me$_5$)$_2$Ln (Ln = Sm, Eu, Yb),[3] lanthanide complexes of dinitrogen,[4] alkenes,[5] and alkynes[6] and the use of lanthanide systems in CO insertion reactions and catalytic olefin hydrogenations.[7]

Despite the advantages of the C$_5$Me$_5$ ligand which make it both sterically and electronically ideal for metals the size of the lanthanides, it is important to develop other ancillary ligands which can stabilize highly reactive organolanthanide species.[8]

Much attention has been focused on the bulky heteroallylic ligands, such as the N-silylated benzamidinate anions, to stabilize relatively low coordination numbers around the large 4f ions by forming sterically saturated coordination compounds.[9,10] These homoleptic lanthanide(III) benzamidinates have been called "steric cyclopentadienyl equivalents".[11] However, unlike preparations using the C$_5$Me$_5$ ligand, where the formation of the (C$_5$Me$_5$)$_3$Ln species is relatively difficult,[12] care must be taken to use an exact 1:2 stoichiometry for isolating the lanthanide bis(benzamidinates); otherwise contamination of the products with the tris(benzamidinates) will occur.[13] This is undesirable since the Ln−X unit, where X is the remaining

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[†] Dedicated to Professor John G. Verkade on the occasion of his 60th birthday.

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unsubstituted moiety, *e.g.* halide, is lacking and it is generally this group which provides reactivity. To counter this problem, we have utilized a diorganyldisilane to form a cyclic, cyclopentadienyl-free ligand system which provides stability through its bulk and the rigidity of the five-membered ring formed, as well as allowing the retention of the reactive Ln−X species. Herein we describe our findings.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and purified by known procedures and distilled from benzophenone ketyl under nitrogen prior to use. Anhydrous LnCl$_3$ (Ln = Nd, Gd, Yb) and sodium trifluoroacetate were purchased (Strem Chemicals, Inc.) and used without further purification. The preparation of the 1,2-bis(organylamino)-1,1,2,2-tetramethyldisilanes and their subsequent dilithiations were performed according to literature methods.[14] IR spectra were recorded on a Perkin-Elmer Bio-Rad Digilab FTS-7 spectrometer (Nujol mulls between CsI plates or Kel-F mulls between NaCl plates). Melting points (uncorrected) were obtained by using a Büchi 510 and an HWS SG 3000 apparatus. Elemental analyses were carried out in the analytical laboratory of our institute.

[{{(*t*-Bu)NSiMe$_2$SiMe$_2$N(*t*-Bu)}Nd(*μ*-Cl)(THF)}$_2$] (1). To a slurry of NdCl$_3$ (0.60 g, 2.39 mmol) in THF (50 mL) was added a solution of Li(*t*-Bu)NSiMe$_2$SiMe$_2$N(*t*-Bu)Li (2.39 mmol) in THF (20 mL) at 0 °C. The mixture was refluxed for 12 h, and the THF was removed under reduced pressure. Toluene (30 mL) was added to the residue, and the mixture was filtered. A yield of 0.95 g (78%) of blue crystals was obtained (mp 228 °C) after overnight standing at −25 °C. Anal. Calcd for $C_{32}H_{76}Cl_2N_4Nd_2O_2Si_4$: C, 37.66; H, 7.50; N, 5.49. Found: C, 37.6; H, 7.5; N, 5.4. IR (Nujol): 1352 (m), 1248 (m), 1201 (s), 1181 (m), 1045 (s), 981 (s), 887 (m), 838 (s), 818 (s), 782 (s), 752 (s), 695 (s), 658 (m), 520 (s), 486 (m), 422 (m), 283 (m) cm^{-1}.

[{{(*t*-Bu)NSiMe$_2$SiMe$_2$N(*t*-Bu)}Gd(*μ*-Cl)(THF)}$_2$] (2). The reaction was performed by the procedure described for the preparation of **1**. GdCl$_3$ (0.50 g, 1.90 mmol) in THF (40 mL) was treated with a solution of Li(*t*-Bu)NSiMe$_2$SiMe$_2$N(*t*-Bu)Li (1.91 mmol) in THF (20 mL) at 0 °C. After refluxing and extraction with toluene (30 mL), the colorless solution was stored at −25 °C overnight. A yield of 0.72 g (72%) of colorless crystals was obtained (mp >300 °C). Anal. Calcd for $C_{32}H_{76}Cl_2Gd_2N_4O_2Si_4$: C, 36.72; H, 7.32; N, 5.35. Found: C, 36.7; H, 7.3; N, 5.3. IR (Nujol): 1354 (m), 1238 (m), 1192 (s), 1032 (s), 1013 (s), 922 (m), 889 (m), 844 (s), 823 (s), 792 (s), 753 (s), 728 (s), 694 (m), 665 (m), 523 (s), 493 (s), 427 (m), 357 (m) 284 (m) cm^{-1}.

[{{(*t*-Bu)NSiMe$_2$SiMe$_2$N(*t*-Bu)}Yb(*μ*-Cl)(THF)}$_2$] (3). The reaction was performed by the procedure described for the preparation of **1**. YbCl$_3$ (0.50 g, 1.79 mmol) in THF (40 mL) was treated with a solution of Li(*t*-Bu)NSiMe$_2$SiMe$_2$N(*t*-Bu)Li (1.80 mmol) in THF (20 mL) at 0 °C. After refluxing and extraction with toluene (30 mL), the red-brown solution was stored at −25 °C overnight. A yield of 0.78 g (81%) of orange crystals was obtained (mp 244 °C). Anal. Calcd for $C_{32}H_{76}Cl_2N_4O_2Si_4Yb_2$: C, 35.64; H, 7.10; N, 5.20. Found: C, 35.6; H, 7.1; N, 5.2. IR (Nujol): 1353 (m), 1238 (m), 1192 (s), 1032 (s), 1012 (s), 923 (m), 867 (m), 845 (s), 826 (m), 793 (s), 754 (m), 736 (s), 664 (m), 525 (s), 493 (m), 357 (m) 284 (m) cm^{-1}.

[{{(Ph)NSiMe$_2$SiMe$_2$N(Ph)}Nd(*μ*-Cl)(THF)$_2$}$_2$] (4). To a slurry of NdCl$_3$ (0.89 g, 3.55 mmol) in THF (50 mL) was added a solution of Li(Ph)NSiMe$_2$SiMe$_2$N(Ph)Li (3.56 mmol) in THF (30 mL) at 0 °C. The mixture was refluxed for 12 h, and the THF was removed under reduced pressure. Toluene (30 mL) was added to the residue, and the mixture was filtered. A yield of 1.38 g (71%) of blue crystals was obtained (mp 148 °C) after overnight standing at −25 °C. Anal. Calcd for $C_{40}H_{76}Cl_2N_4Nd_2O_4Si_4$: C, 46.31; H, 6.15; N, 4.50. Found: C, 46.2; H, 6.1; N, 4.4. IR (Nujol): 1582 (s), 1469 (s), 1256 (m), 1230 (s), 1182 (m), 1032 (s), 993 (s), 913 (s), 888 (m), 846 (m), 822 (m), 792 (s), 774 (s), 763 (s), 700 (s), 599 (s), 511 (m), 468 (m), 337 (m), 297 (m) cm^{-1}.

[{{(Ph)NSiMe$_2$SiMe$_2$N(Ph)}Gd(*μ*-Cl)(THF)$_2$}$_2$] (5). The reaction was performed by the procedure described for the preparation of **4**. GdCl$_3$ (1.03 g, 3.91 mmol) in THF (40 mL) was treated with a solution of Li(Ph)NSiMe$_2$SiMe$_2$N(Ph)Li (3.89 mmol) in THF (20 mL) at 0 °C. After refluxing and extraction with toluene (30 mL), the colorless solution was stored at −25 °C overnight. A yield of 1.66 g (67%) of colorless crystals was obtained (mp 149 °C). Anal. Calcd for $C_{48}H_{76}Cl_2Gd_2N_4O_4Si_4$: C, 45.36; H, 6.03; N, 4.41. Found: C, 45.4; H, 6.0; N, 4.4. IR (Nujol): 1584 (s), 1491 (m), 1467 (s), 1245 (s), 1232 (s), 1183 (m), 1024 (m), 992 (m), 913 (m), 888 (s), 844 (m), 818 (m), 777 (s), 762 (s), 734 (m), 699 (s), 601 (s), 519 (s), 365 (m), 337 (m), 299 (m) cm^{-1}.

[{{(Ph)NSiMe$_2$SiMe$_2$N(Ph)}Yb(*μ*-Cl)(THF)$_2$}$_2$] (6). The reaction was performed by the procedure described for the preparation of **4**. YbCl$_3$ (0.88 g, 3.15 mmol) in THF (40 mL) was treated with a solution of Li(Ph)NSiMe$_2$SiMe$_2$N(Ph)Li (3.16 mmol) in THF (20 mL) at 0 °C. After refluxing and extraction with toluene (30 mL), the red solution was stored at −25 °C overnight. A yield of 1.26 g (61%) of red crystals was obtained (mp 138 °C). Anal. Calcd for $C_{48}H_{76}Cl_2N_4O_4Si_4Yb_2$: C, 44.26; H, 5.88; N, 4.30. Found: C, 44.1; H, 5.8; N, 4.3. IR (Nujol): 1584 (s), 1492 (m), 1475 (s), 1243 (s), 1228 (s), 1169 (m), 1024 (s), 993 (m), 913 (s), 885 (m), 846 (m), 819 (m), 781 (m), 753 (m), 701 (s), 668 (m), 603 (s), 523 (s), 368 (m), 339 (m), 300 (m) cm^{-1}.

[{{(*t*-Bu)NSiMe$_2$SiMe$_2$N(*t*-Bu)}Nd(*μ*-OCOCF$_3$)(THF)}$_2$] (7). To a solution of **1** (1.00 g, 0.98 mmol) in THF (30 mL) was added a solution of NaOCOCF$_3$ (0.27 g, 1.98 mmol) in THF (20 mL) at 0 °C. The mixture was refluxed for 12 h, and the THF was removed under reduced pressure. Toluene (30 mL) was added, and the mixture was filtered. A yield of 0.84 g (73%) of blue crystals was obtained (mp 204 °C) after overnight standing at −25 °C. Anal. Calcd for $C_{36}H_{76}F_6N_4Nd_2O_6Si_4$: C, 36.77; H, 6.51; F, 9.69; N, 4.76. Found: C, 36.6; H, 6.5; F, 9.6; N, 4.7. IR (Kel-F): 1689 (s), 1463 (m) cm^{-1}. IR (Nujol): 1355 (m), 1200 (s), 1155 (m), 1040 (m), 1027 (s), 874 (m), 842 (s), 792 (s), 752 (m), 720 (s), 662 (m), 607 (m), 524 (m), 491 (m), 455 (m), 357 (m) cm^{-1}.

[{{(*t*-Bu)NSiMe$_2$SiMe$_2$N(*t*-Bu)}Gd(*μ*-OCOCF$_3$)(THF)}$_2$] (8). The reaction was performed by the procedure described for the preparation of **7**. A solution of **2** (1.00 g, 0.96 mmol) in THF (30 mL) was treated with a solution of NaOCOCF$_3$ (0.28 g, 2.06 mmol) in THF (20 mL) at 0 °C. After refluxing and extraction with toluene (30 mL), the colorless solution was stored at −25 °C overnight. A yield of 0.87 g (75%) of colorless crystals was obtained (mp 210 °C). Anal. Calcd for $C_{36}H_{76}F_6Gd_2N_4O_6Si_4$: C, 35.98; H, 6.37; F, 9.48; N, 4.66. Found: C, 35.9; H, 6.3; F, 9.4; N, 4.6. IR (Kel-F): 1697 (s), 1469 (m) cm^{-1}. IR (Nujol): 1355 (m), 1202 (s), 1157 (m), 1039 (s), 1019 (s), 873 (m), 842 (s), 822 (m), 791 (s), 750 (m), 720 (m), 661 (m), 524 (m), 492 (m), 460 (m) cm^{-1}.

Crystal Structure Solution and Refinement. Diffraction data for compound **2** were collected on a Siemens-Stoe AED four-circle diffractometer at 120 K with Mo Kα radiation ($\lambda = 0.710\,73$ Å). Diffraction data for compounds **5** and **8** were collected at 193 K on a Siemens-Stoe Huber four-circle diffractometer equipped with a SMART CCD area detector and using Mo Kα radiation ($\lambda = 0.710\,73$ Å). The sample to detector distance was set to be 6 cm. Reflections were collected by means of φ-scan (for **5**) and φ- and ω-scan (for **8**) rotations (step width 0.3°), with an exposure time of 15 s/frame. Absorption corrections were applied using a semiempirical method.

All three structures were solved by direct methods using SHELXS-90[15] and refined versus F^2 by full-matrix least-squares procedures using SHELXL-93.[16] For all three compounds, all non-hydrogen atoms could be refined anisotropically. The hydrogen atoms were inserted in calculated positions and refined "riding" on their respective carbon

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Table 1. Crystallographic Data for **2**, **5**, and **8**

	2·C_7H_8	**5**	**8**
empirical formula	$C_{32}H_{76}Cl_2Gd_2N_4O_2Si_4 \cdot C_7H_8$	$C_{48}H_{76}Cl_2Gd_2N_4O_4Si_4$	$C_{36}H_{78}F_6Gd_2N_4O_6Si_4$
mol wt	1138.86	1270.88	1203.88
crystal size (mm)	0.22 × 0.18 × 0.10	0.60 × 0.50 × 0.40	0.80 × 0.40 × 0.40
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	10.321(2)	13.913(13)	11.045(2)
b (Å)	11.116(2)	12.914(9)	16.120(3)
c (Å)	13.434(3)	16.434(14)	16.949(3)
α (deg)	107.57(3)	90	66.17(3)
β (deg)	111.31(3)	105.64(3)	85.51(3)
γ (deg)	90.67(3)	90	78.27(3)
V (Å^3)	1356(5)	2843(4)	2703(9)
Z	1	2	2
D_{calcd} (g cm^{-3})	1.395	1.484	1.479
μ (mm^{-1})	2.643	2.532	2.581
2*θ* range (deg)	3.5−25	2−25	2.5−25
no. of reflns collected	6013	26361	29288
no. of indep reflns	4767	4836	9394
no. of restraints/parameters	169/310	0/294	412/609
R_F[a]	0.0233	0.0281	0.0311
R_{wF}[b]	0.0634	0.0720	0.0853
largest diff peak and hole (electrons Å^{-3})	1.016 and −1.741	0.821 and −1.362	0.986 and −1.230

[a] $R_F = \sum|F_o - F_c|/\sum F_o$ ($F > 4\sigma(F)$). [b] $R_{wF} = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ (all data).

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

Gd(1)−N(1)	2.203(3)	N(1)−Si(1)	1.723(3)
Gd(1)−N(2)	2.211(2)	N(2)−Si(2)	1.719(3)
Gd(1)−O(1)	2.400(2)	Si(1)−Si(2)	2.3881(13)
Gd(1)−Cl(1)	2.7849(17)	N(1)−C(1)	1.479(4)
Gd(1)−Cl(1a)	2.7550(10)	N(2)−C(9)	1.473(4)
N(1)−Gd(1)−N(2)	102.97(10)	N(1)−Gd(1)−O(1)	92.70(9)
N(1)−Gd(1)−Cl(1)	130.72(7)	N(2)−Gd(1)−O(1)	95.19(9)
N(2)−Gd(1)−Cl(1)	126.13(7)	N(1)−Si(1)−Si(2)	107.05(10)
N(1)−Gd(1)−Cl(1a)	99.26(7)	N(2)−Si(2)−Si(1)	107.96(9)
N(2)−Gd(1)−Cl(1a)	100.10(7)	C(1)−N(1)−Gd(1)	124.14(19)
O(1)−Gd(1)−Cl(1)	80.14(6)	C(1)−N(1)−Si(1)	126.6(2)
O(1)−Gd(1)−Cl(1a)	157.90(5)	C(9)−N(2)−Gd(1)	123.15(19)
Gd(1)−N(1)−Si(1)	108.71(13)	C(9)−N(2)−Si(2)	127.1(2)
Gd(1)−N(2)−Si(2)	109.52(13)	Cl(1)−Gd(1)−Cl(1a)	77.96(3)
		Gd(1a)−Cl(1)−Gd(1)	102.04(3)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **5**

Gd(1)−N(1)	2.240(3)	N(1)−Si(1)	1.725(3)
Gd(1)−N(2)	2.314(3)	N(2)−Si(2)	1.735(3)
Gd(1)−O(1)	2.407(3)	Si(1)−Si(2)	2.379(2)
Gd(1)−O(2)	2.476(3)	N(1)−C(1)	1.418(5)
Gd(1)−Cl(1)	2.731(3)	N(2)−C(11)	1.396(5)
Gd(1)−Cl(1a)	2.8113(17)		
N(1)−Gd(1)−N(2)	100.33(11)	N(1)−Gd(1)−O(1)	98.90(10)
O(1)−Gd(1)−O(2)	74.80(9)	N(1)−Gd(1)−O(2)	82.82(10)
N(1)−Gd(1)−Cl(1)	93.20(8)	N(2)−Gd(1)−O(1)	85.91(10)
N(2)−Gd(1)−Cl(1)	96.29(8)	N(2)−Gd(1)−O(2)	160.71(10)
N(1)−Gd(1)−Cl(1a)	155.63(7)	N(1)−Si(1)−Si(2)	109.28(11)
N(2)−Gd(1)−Cl(1a)	103.46(10)	N(2)−Si(2)−Si(1)	108.35(12)
O(1)−Gd(1)−Cl(1)	167.13(6)	C(1)−N(1)−Gd(1)	130.1(2)
O(1)−Gd(1)−Cl(1a)	88.07(7)	C(1)−N(1)−Si(1)	117.3(2)
O(2)−Gd(1)−Cl(1)	102.56(7)	C(11)−N(2)−Gd(1)	128.6(2)
O(2)−Gd(1)−Cl(1a)	76.49(8)	C(11)−N(2)−Si(2)	122.2(2)
Gd(1)−N(1)−Si(1)	110.67(14)	Cl(1)−Gd(1)−Cl(1a)	79.08(4)
Gd(1)−N(2)−Si(2)	109.04(15)	Gd(1a)−Cl(1)−Gd(1)	100.92(4)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **8**

Gd(1)−N(1)	2.190(3)	N(1)−Si(1)	1.710(4)
Gd(1)−N(2)	2.194(4)	N(2)−Si(2)	1.701(4)
Gd(1)−O(1)	2.322(3)	Si(1)−Si(2)	2.381(2)
Gd(1)−O(2)	2.367(3)	C(17)−O(2)	1.221(5)
Gd(1)−O(3)	2.424(3)	C(17)−O(1a)	1.220(5)
N(1)−C(1)	1.469(6)	C(17a)−O(2a)	1.199(5)
N(2)−C(9)	1.448(7)	C(17a)−O(1)	1.220(5)
N(1)−Gd(1)−N(2)	104.24(13)	N(2)−Gd(1)−O(1)	97.89(14)
N(1)−Si(1)−Si(2)	108.09(14)	O(1)−Gd(1)−O(2)	83.51(11)
N(2)−Si(2)−Si(1)	108.80(14)	Gd(1)−O(2)−C(17)	145.5(3)
Si(1)−N(1)−Gd(1)	109.48(18)	Gd(1a)−O(1a)−C(17)	174.5(3)
Si(2)−N(2)−Gd(1)	109.19(19)	Gd(1)−O(1)−C(17a)	162.3(4)
N(1)−Gd(1)−O(1)	100.35(15)	Gd(1a)−O(2a)−C(17a)	143.0(3)
N(2)−Gd(1)−O(2)	127.32(14)	O(2)−C(17)−O(1a)	128.9(4)
N(1)−Gd(1)−O(2)	127.47(13)	O(1)−C(17a)−O(2a)	128.3(4)

atom. Crystals of **2** and **5** possess one half-molecule in the asymmetric unit whereas crystals of **8** show two half-molecules per asymmetric unit (root-mean-square of the fit of the two half-molecules in the asymmetric unit is 0.22(5) Å, without taking into account the THF molecules). In addition, one toluene molecule was found per molecular unit of **2**.

Crystallographic data are listed in Table 1, and selected bond lengths and angles are given in Tables 2−4.

Results and Discussion

Anhydrous lanthanide trichlorides, $LnCl_3$ (Ln = Nd, Gd, Yb), react in tetrahydrofuran with 1 equiv of the dilithium salt of 1,2-bis(*tert*-butylamino)-1,1,2,2-tetramethyldisilane with the formation of dimeric $[\{\{(t\text{-Bu})\overline{\text{NSiMe}_2\text{SiMe}_2\text{N}(t\text{-Bu})\}\text{Ln}}(\mu\text{-Cl})(\text{THF})\}_2]$ (**1**, Ln = Nd; **2**, Ln = Gd; **3**, Ln = Yb; Scheme 1). Compounds **1**−**3** were isolated in good yields upon crystallization from toluene. The IR spectra of all the compounds are identical, inferring identical structural configurations.

Similarly, reaction of $LnCl_3$ (Ln = Nd, Gd, Yb) with 1 equiv of the dilithium salt of 1,2-bis(phenylamino)-1,1,2,2-tetramethyldisilane gave dimeric $[\{\{(\text{Ph})\overline{\text{NSiMe}_2\text{SiMe}_2\text{N}(\text{Ph})\}\text{Ln}}(\mu\text{-Cl})(\text{THF})_2\}_2]$ (**4**, Ln = Nd; **5**, Ln = Gd; **6**, Ln = Yb; Scheme 1). The IR spectra of **4**−**6** are also identical. The neodymium complexes (**1** and **4**) are blue and the gadolinium complexes (**2** and **5**) are colorless, while the ytterbium complexes (**3** and **6**) are orange and red, respectively.

From microanalytical analyses, it was observed that complexes **1**−**3** have one molecule of THF coordinated to each metal atom, while **4**−**6** have two coordinated THF molecules per metal atom. This was confirmed by the elucidation of the structures of **2** and **5** by single-crystal X-ray analysis. Complexes **2** and **5** are dimeric with bridging chlorine atoms (Figures 1 and 2). Selected bond lengths and angles are listed in Tables 2 and 3.

In **2**, each gadolinium atom has a distorted square pyramidal geometry, while the extra coordinated THF molecule causes the gadolinium atoms in **5** to have a distorted octahedral geometry. The THF molecules in **5** are in mutual *cis* positions around the gadolinium atom with the O(1)−Gd(1)−O(2) angle

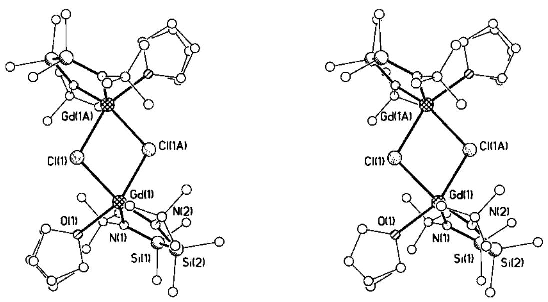


Figure 1. Stereoview of compound **2**. Hydrogen atoms are omitted for clarity. All bonds involving carbon are drawn with thin lines.

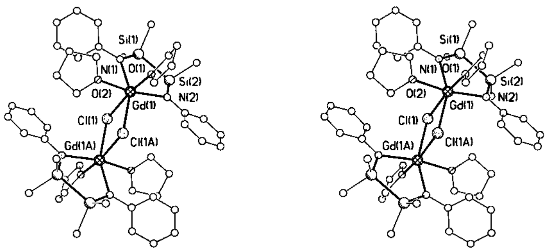
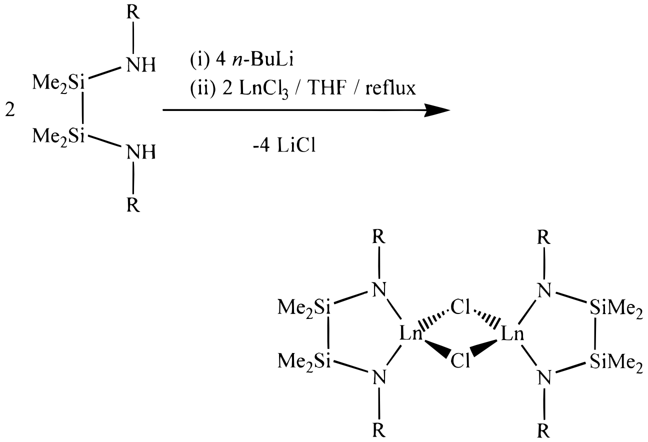


Figure 2. Stereoview of compound **5**. Hydrogen atoms are omitted for clarity. All bonds involving carbon are drawn with thin lines.

Scheme 1



1·nTHF; Ln = Nd, R = *t*Bu, n = 2

2·nTHF; Ln = Gd, R = *t*Bu, n = 2

3·nTHF; Ln = Yb, R = *t*Bu, n = 2

4·nTHF; Ln = Nd, R = Ph, n = 4

5·nTHF; Ln = Gd, R = Ph, n = 4

6·nTHF; Ln = Yb, R = Ph, n = 4

being relatively small (74.80(9)°). Both **2** and **5** basically consist of two five-membered gadolinium heterocycles linked by two bridging chlorine atoms, thus forming a third four-membered ring, which is exactly planar, as the molecules lie on an inversion center (Figures 1 and 2). The gadolinium heterocycles in **2** and **5** are themselves almost planar with root-mean-square deviations from the plane (Gd(1)−N(1)−Si(1)−Si(2)−N(2)) being 0.112 Å for **2** and 0.092 Å for **5**. To the best of our knowledge, compounds **2** and **5** represent the first structurally characterized five-membered organolanthanide amido heterocyclic systems.

In the five-membered rings of **2** and **5**, the silicon atoms are in an almost perfect tetrahedral environment. However, the geometry around the nitrogen atoms deviates from the expected trigonal planar configuration of a sp^3-hybridized amide nitrogen atom.

The Gd−N bond distances in **2** are shorter than those in **5** (2.203(3) and 2.211(3) Å in **2** compared with 2.240(3) and 2.314(3) Å in **5**). In the latter case, these compare well with values for the known compound $[\{\{(Me_3Si)_2N\}_2GdCl(THF)\}_2]$[17] (Gd−N(1) 2.239(5) Å and Gd−N(2) 2.264(5) Å). $[\{\{(Me_3Si)_2N\}_2GdCl(THF)\}_2]$ also has two gadolinium bis(amido) moieties bridged by two chlorine atoms, and the average Gd−Cl bond distance (2.752(4) Å)[17] closely approximates those for **2** (2.770(2) Å) and **5** (2.771(3) Å). The angles within the four-membered gadolinium−chlorine ring are also similar for the three compounds (Cl−Gd−Cl = 77.96(3), 79.08(4), and 74.3(2)°, while Gd−Cl−Gd = 102.04(3), 100.92(4), and 105.7(2)° for **2**, **5**, and $[\{\{(Me_3Si)_2N\}_2GdCl(THF)\}_2]$, respectively).

The dimeric natures of **2** and **5** are in agreement with the structures of other disubstituted organolanthanide chlorides such as $[\{(C_5H_5)_2LnCl\}_2]$[2,18] and cyclopentadienyl-free complexes.[8] The use of bulky amido groups has allowed the isolation of similar halide-bridged dimers.[17,19] Introduction of a trimethylsilyl moiety, bonded to the nitrogen atom of the amido group, provides the steric bulk necessary to stabilize relatively low coordination numbers around the lanthanide metal center. In fact, all the lanthanide benzamidinates reported by Edelmann and co-workers have a trimethylsilyl group attached to the nitrogen atoms bonded to the lanthanide center and not a C-substituted bulky group.[9,13] It may be possible that the stabilities of these amidinato systems are enhanced by the inclusion of the silicon atom. Up to now, only the steric effect of the trimethylsilyl group, and not any electronic contribution to the stabilization by the N−Si system, has been considered. Therefore, we assume that an “electronic silicon effect” has a predominant influence on benzamidinates rather than just the steric effect. Complexes **1**−**6** may be considered to be inversions of these traditional bulky amido complexes. Instead of a trimethylsilyl group allowed to rotate freely around the nitrogen atom, two dimethylsilyl units form the backbone of a five-membered ring. The bis(dimethylsilyl) backbone does not provide steric bulk around the metal atom, and this function is left to the organyl groups bonded to the nitrogen atoms.

By use of these bis(organylamino)disilane ligands stable lanthanide complexes, whose structures mimic those of the well-known bis(cyclopentadienyl) halide-bridged dimers, are formed. Due to the steric similarity between these two systems, it was decided to also compare their reactivities by forming derivatives of **1**−**6** through simple metathetical reactions.

Treatment of **1** or **2** with 2 molar equiv of sodium trifluoroacetate in tetrahydrofuran leads to $[\{\{(t\text{-Bu})NSiMe_2SiMe_2N(t\text{-Bu})\}Ln(OCOCF_3)(THF)\}_2]$ (**7**, Ln = Nd; **8**, Ln = Gd). In the IR spectra of **7** and **8**, the asymmetric carboxylate vibrations can be found at 1689 and 1697 cm^{-1}, respectively. The symmetric vibrations for **7** and **8** are at 1463 and 1469 cm^{-1}, respectively. The separations between the symmetric and asymmetric stretching frequencies ($\Delta\nu$) are approximately 225 cm^{-1} for both complexes, and this is similar to the $\Delta\nu$ values found for bridging bidentate group 4 fluoro carboxylates.[20] Furthermore, many cyclopentadienyllanthanide carboxylates have been shown to be dimeric with bridging bidentate

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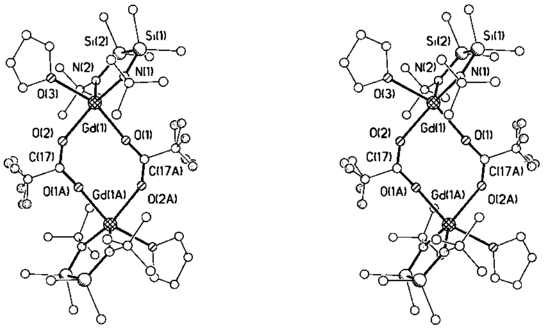

Figure 3. Stereoview of compound **8**. Hydrogen atoms are omitted for clarity. All bonds involving carbon are drawn with thin lines.

carboxylate groups, either by spectral analysis[21] or by X-ray structural determinations.[22] To confirm the bridging bidentate coordination mode of the trifluoroacetate ligand in **7** and **8**, a single-crystal X-ray structure analysis of **8** was carried out.

The molecular structure of **8** is shown in Figure 3, and selected bond lengths and angles are listed in Table 4. The dimeric nature of **8** is maintained by the two trifluoroacetate groups which link two gadolinium atoms in a bridging bidentate manner. Therefore, **8** consists of two five-membered gadolinium heterocycles, as was found for **2** and **5**, and a central eight-membered gadolinium trifluoroacetate ring. The CF_3 groups of the trifluoroacetate ligands show some degree of rotational disorder.

Within the internal ring formed by the trifluoroacetate ligands, the Gd−O bond distances show no significant differences (Gd(1)−O(1) 2.322(3) Å and Gd(1)−O(2) 2.367(3) Å). However, from the Gd−O−C bond angles it is clear that the bonding in the bridging carboxylate groups is not symmetric (Gd(1)−O(2)−C(17) 145.5(3)°, Gd(1a)−O(1a)−C(17) 174.5(3)°, Gd(1)−O(1)−C(17a) 162.3(4)°, and Gd(1a)−O(2a)−C(17a) 143.0(3)°). This phenomenon, where the angle at one carboxylate oxygen is bent while the other is almost straight, was also observed in the ytterbium complex $[\{(C_5H_5)_2Yb(OCOC_6F_5)\}_2]$.[22a] The pentafluorobenzoate ligands coordinate in a bridging bidentate manner with one set of Yb−O−C bond angles being 145(1) and 171(1)° and the other being 164(1) and 150(1)°.

The coordinated THF molecules in **8** cause the gadolinium atoms to adopt a distorted square pyramidal geometry, as in the case of **2**. Once again, the five-membered gadolinium heterocycles (Gd(1)−N(1)−Si(1)−Si(2)−N(2)) are almost planar (root-mean-square deviation from the plane being 0.08(5) Å for one molecule in the asymmetric unit and 0.05(2) Å for the other). The angles and bond lengths of the five-membered rings of **8** are similar to those found in **2** (Table 4).

Conclusion

For the first time, five-membered organolanthanide amido heterocyclic systems have been prepared. These cyclopentadienyl-free complexes are structurally similar to well-known cyclopentadienyllanthanide halides in that they are dimeric with halide bridges. The stability of complexes **1**−**6** can be considered to be due to the formation of the five-membered heterocycle. One factor that may also influence their stabilities is the possible electronic effect of the N−Si system on the metal atom. Investigations into whether silicon attached to an amido nitrogen atom plays a part in any such stabilization (a so-called "electronic silicon effect") are necessary before any firm conclusions may be drawn.

The remaining chloro function in **1**−**6** allows further reaction, shown by the isolation of the bis(μ-trifluoroacetato) complexes (**7** and **8**). Thus, it may be possible to generate a range of derivatives containing unusual ligand environments, and investigations in this respect are currently under way.

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Supporting Information Available: Listings of crystal data, atomic coordinates, hydrogen positional and thermal parameters, anisotropic displacement parameters, and bond distances and angles and figures showing alternative ORTEP views for complexes **2**, **5**, and **8** (25 pages). Ordering information is given on any current masthead page.

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