1,3-Dimethylimidazolin-2-ylidene Carbene Donor Ligation in Lanthanide Silylamide Complexes

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Received September 9, 1996⊗

The synthesis and X-ray crystal structures of $Y[N(SiHMe_2)_2]_3(carbene)_x$ (carbene = 1,3-dimethylimidazolin-2-ylidene, $x = 1, 2$) are described. The donor capability of the strongly nucleophilic carbene ligand is expressed in both the displacement of two THF ligands by one carbene ligand in precursor compound $Y[N(SiHMe_2)_2]_3(THF)_2$ and by the addition of a second carbene ligand to yield the preferred (3 + 2) trigonal bipyramidal coordination geometry. In particular, the structural data reveal that the carbene ligands affect the coordination mode of the bis(dimethylsilyl)amide counterligands by forcing them to form close β-Si−H(silylamide)−yttrium agostic contacts. According to Pearson's terminology such carbene ligands have to be classified as hard donor ligands.

Introduction

Lanthanide silylamide complexes are classified as excellent synthetic precursors, particularly in protic exchange reactions known as the "silylamide route".[1] Utilization of the $Ln[N(SiMe_3)_2]$ group as an efficient precatalyst moiety[2] or in alkylation reactions *via* Lewis acid−base derived heterobimetallic species[3] further emphasizes the current interest in this class of compounds. Meanwhile, a variety of differently substituted silylamide ligands appeared in the literature[4,5] optimizing both reactivity[4] and volatility[5b,6] of these complexes. We have been focusing on the former topic and recently presented an extension of the silylamide route utilizing $Ln[N(SiHMe_2)_2]_3(THF)_2$ as tailor-made precursors for otherwise not feasible exchange reactions with bulky alcoholic substrates ($N(SiHMe_2)_2$ = bdsa, *b*is(*d*imethyl*s*ilyl)*a*mide).[4] Our studies on precursor design were further stimulated by recent findings in our Munich laboratories that the type of donor ligand can decisively affect precatalyst behavior of early and late transition metal complexes.[7] Here we wish to report the stepwise exchange of the THF ligands in the versatile precursor $Ln[N(SiHMe_2)_2]_3(THF)_2$ by the strong carbene donor ligand 1,3-dimethylimidazolin-2-ylidene (**1**)[8] and the resulting structural chemistry. During the course of this work the first carbene derivatives of lanthanide(II) cyclopentadienyl and lanthanide(III) β-diketonato complexes appeared in the literature emphasizing the pure "adduct character" of the metal−carbene bonding due to the lack of π-back-donation.[9,10]

Results and Discussion

Ligand Evaluation: Reactivity of Carbene Ligand 1 with $ErCl_3(THF)_{3.25}$ and $Ln[N(SiMe_3)_2]_3$ (Ln = Y, La). The donor capability of 1,3-dimethylimidazolin-2-ylidene (**1**) was initially probed by reaction with a lanthanide chloride. Recently, the structural elucidation of lanthanide halides bonded to various oxygen and nitrogen donating solvents has revealed a structural diversity (*bridging*, *terminal*, *cationic* species), exploitation of which might have a significant implication on reaction chemistry.[11] Displacement of the THF ligands in $ErCl_3(THF)_{3.25}$ by 3 equiv of **1** readily takes place as monitored by IR spectroscopy and elemental analysis (Scheme 1). Especially, IR spectroscopy proved to be a valuable probe for donor ligand exchange reactions for such paramagnetic complexes by indicating the characteristic carbene vibration mode $\nu(C{=}N) = 1573\ cm^{-1}$. Formation of yellow tris(carbene) adduct **2** which is sparingly soluble in THF is in analogy to the isolation of $MCl_4(carbene)_2$ (M = Ti, Zr, Hf).[12]

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⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1997.

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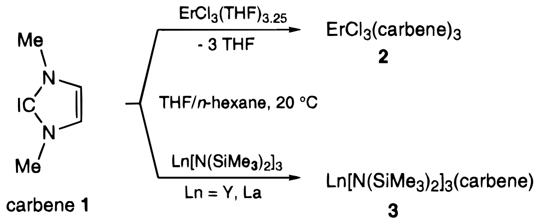
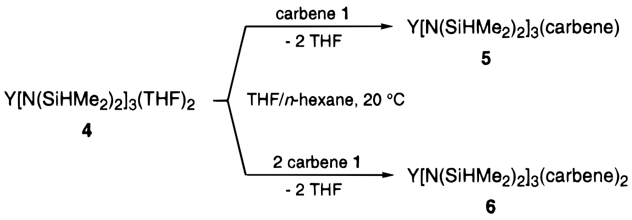
S0276-7333(96)00771-6 CCC: $14.00

Scheme 1



Scheme 2



Simple adduct formation of **1** with lanthanide silylamides could not necessarily be expected. On the one hand, carbene **1** comprises an extremely nucleophilic carbon atom, electron-rich C−N bonds, and an unsaturated C−C bond.[13] On the other hand, the Ln−N(amide) bond is kinetically rather labile and undergoes exchange and insertion reactions readily. For example, the latter feature is responsible for isonitrile insertion into Ln−N bonds[14] and it explains the key steps in the catalytic hydroamination/cyclization of aminoolefins.[2] Very recently, the proximity of silicon- and nitrogen-containing moieties even allowed the unprecedented insertion reaction of a dimethylsilicone into a Ln−N(amide) bond.[15] Readily available and routinely employed compounds $Ln[N(SiMe_3)_2]_3$[16] were chosen to evaluate the reaction of **1**. The availability of additional coordination sites L in monomeric $Ln[N(SiMe_3)_2]_3$ has been structurally proven for several mono(adduct) (L = Ph_3PO,[17] Ph_2CO,[18] $CH_2{=}\overline{CN(Me)C(Me){=}C(Me)N}(Me)$[19]) and bis(adduct) complexes (L = NCPh).[20] However, the yellow materials which are formed by reaction of $Ln[N(SiMe_3)_2]_3$ with **1** in *n*-hexane/THF solution according to Scheme 1 were identified as the mono(carbene) adducts **3** by both IR and NMR spectroscopy and elemental analysis. With these preliminary findings in mind we started exchange reactions of $Y[N(SiHMe_2)_2]_3(THF)_2$ (**4**) with carbene **1**.

Reactivity of Carbene 1 with $Y[N(SiHMe_2)_2]_3(THF)_2$ (4): Synthesis and Spectroscopic Characterization. We have previously described a high-yield synthesis of $Ln[N(SiHMe_2)_2]_3(THF)_2$ (85%; Ln = Y, Nd), producing well-crystallizing complexes.[4a] These compounds have been fully characterized by IR spectroscopy, elemental analysis, mass spectrometry, and multinuclear NMR spectroscopy (e.g. ^{89}Y NMR (C_6D_6, 20 °C) $\delta = 444$). While a mononuclear molecular structure was established by X-ray crystallography for both early (Nd) and late ("Y") elements, the relatively low energetic Si−H stretches at 1939 (Y) and 1957 cm^{-1} (Nd), usually indicating agostic interactions,[21−23] lacked structural evidence. In addition, we found that due to *ate* complexation, the synthesis of $Ln[N(SiHMe_2)_2]_3(THF)_2$ is better performed with educt ratios of approximately 2.9:1.[24] Derivatives of the smaller lanthanide elements which form THF adducts of composition $LnCl_3(THF)_x$ ($x > 2$)[25] are preferably prepared in *n*-hexane solution as exemplified for yttrium (**4**) in eq 1.

$$YCl_3(THF)_{3.5} \xrightarrow[n\text{-hexane, 20 °C, - LiCl}]{2.9\ LiN(SiHMe_2)_2} \underset{\mathbf{4}}{Y[N(SiHMe_2)_2]_3(THF)_2} \quad (1)$$

Treatment of $Y[N(SiHMe_2)_2]_3(THF)_2$ (**4**) with 1 equiv of **1** readily yields mono(carbene) adduct **5**, while addition of a second 1 equiv of **1** generates the corresponding bis(adduct) **6** (Scheme 2). The exchange reactions are carried out in a mixture of *n*-hexane/THF. After evaporation of the solvent, complexes **5** and **6** are obtained in quantitative yield as greenish and light-brown powders, respectively. Like complexes **3**, compounds **5** and **6** are very good soluble in aliphatic solvents. ^1H NMR spectroscopy of **5** shows the presence of some THF which obviously is removed upon crystallization (*vide infra*).

IR spectroscopy provides the first indication of a disturbed Si−H(amide) bond (Table 1). Examination of the Si−H stretching frequencies of complexes **5** and **6** reveals a similar absorption pattern as found in precursor **4**. While ν(Si−H) for the parent tetramethyldisilazane is found at 2118 cm^{-1}, the infrared spectra of the silylamide complexes **4**−**6** exhibit strong bands at 2070−2090 cm^{-1} which fall in the regime of typical noninteracting vibrations (2280−2080 cm^{-1}).[26] However, well-resolved shoulders of medium intensity ranging from 1927 to 2041 cm^{-1} are lower in energy which is indicative of an interaction with the electron-deficient metal center. In $Cp_2Zr(X)[N(tBu)(SiHMe_2)]$ (X = H, F, Cl, Br, I) such a perturbation of the Si−H moiety could be clarified by NMR spectroscopy.[23] However, ^1H and ^{29}Si NMR spectra of **5** and **6** display no distinct upfield shift of the Si−H moiety compared to the parent ligand and precursor **4** (Table 1). The ^{13}C NMR resonances of the carbene carbon at $\delta = 190.3$ ppm (**5**) and 194.0 ppm (**6**), respectively, fit in the scheme proposed recently, where the carbene carbon shifts correlate with the Lewis

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Table 1. Spectroscopic Data for Dimethylsilylamide Complexes

compd	IR[a] ν(SiH)	^{1}H NMR[b] δ(SiH)	^{29}Si NMR[b] δ_{Si} ($^1J_{SiH}$)	ref
$HN(SiHMe_2)_2$	2118	4.40		48
$LiN(SiHMe_2)_2$	1990 s, 1847 m	4.67	28.6	d
$Y[N(SiHMe_2)_2]_3(THF)_2$ (**4**)	2072 s, 1939 m	5.06	−19.6 (171)	d
$Y[N(SiHMe_2)_2]_3$(carbene) (**5**)	2070 s, 1992 m, 1927 m	5.04	−23.1 (164)	d
$Y[N(SiHMe_2)_2]_3$(carbene)$_2$ (**6**)	2088 s, 2041 m	5.10	−22.5 (172)	d
Er[N(*t*Bu)(SiHMe$_2$)]$_3$[c]	1858			5b

[a] IR spectra recorded as Nujol mulls (cm^{-1}). [b] NMR spectra recorded in benzene-d_6 solution at 20 °C (in ppm and $^1J_{SiH}$ in Hz). [c] IR spectra recorded in benzene solution. [d] This work.

acidity of the metal center.[27] For comparison, carbene derivatives of the less Lewis-acidic Yb(II) cyclopentadienyl complexes display carbene carbon resonances in the range 198.1−205.0 ppm.[9] In formally 4-coordinate **5** the carbene carbon resonance appears as a doublet due to coupling with ^{89}Y. $^1J_{YC}$ of 49.6 Hz is significantly higher than the 33 Hz previously reported for 7-coordinate Y(thd)$_3$(carbene) (thd = 2,2,6,6-tetramethylheptane-3,5-dionato; carbene = 1,3,4,5-tetramethylimidazolin-2-ylidene) indicating a strong interaction between yttrium and carbon in solution.[10] Indeed, the coupling is comparable to those found for C$_{ipso}$ resonances in yttrium aryl compounds.[28] To get further insight into the yttrium carbene bonding and the appearance of close (Si−H)−metal contacts we conducted an X-ray structure analysis.

Molecular Structures of Y(bdsa)$_3$(carbene) (5) and Y(bdsa)$_3$(carbene)$_2$ (6). Single crystals of **5** and **6** suitable for structure determination were grown at −35 °C from *n*-hexane solutions. Compound **5** crystallizes with two crystallographically independent molecules in the asymmetric unit. Molecule 1 and 2 of complex **5** differ slightly in the arrangement of the silylamide ligands. Crystallographic data and bond lengths and angles are collected in Tables 2−4. The overall molecular structure of **5** is illustrated in Figure 1 (molecule 1). The distortion of the tetrahedral coordination geometry follows clearly the different interactions of the three amide ligands of the Ψ-C_3 symmetric Y(bdsa)$_3$ fragment with the C_{2v} symmetric carbene ligand, as reflected in the torsion angles ∠N$_{carbene}$, C,Y,N$_{amide}$ and ∠C,Y,N,Si and the C−Y−N angles. The similar Y−C−N angles (128.1(9), 126.5(10)°) do not indicate any *in-plane* bending of the carbene ligand in **5** (Figure 2). However, *out-of-plane* bending is observed: The best plane through the carbene ligand shows an angle of 8.7° against the Y−C bond. Such tilting angles are usually reported in the range of 0−7°.[29]

Bis(adduct) **6** features a less distorted trigonal bipyramidal coordination geometry compared to precursor **4** (Figure 3, Table 3). For example, the C1−C−C11 angle of 177.6(3)° is almost linear, while the corresponding O(THF)−Y−O(THF) is 163.1(1)°. The smallest torsion angles between the planar carbene ligands and the amide ligands are ∠N1,C1,Y,N21 (20.8°) and ∠N12,C11,Y,N31 (28.1°). Sterically more encumbered **6** displays *in-plane* bending of the carbene ligand (Figure 2). The angles Y−C1−N1 and Y−C11−N12 of

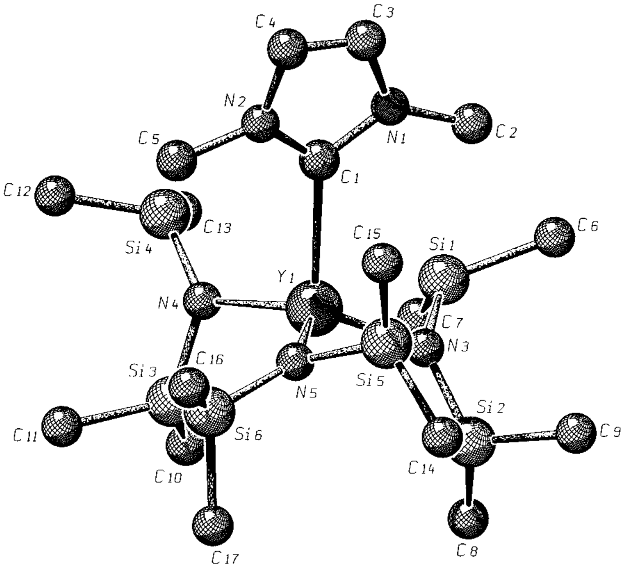

Figure 1. SCHAKAL[49] plot of the molecular structure of Y[N(SiHMe$_2$)$_2$]$_3$(carbene) (**5**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Y[N(SiHMe$_2$)$_2$]$_3$(carbene) (5)

Molecule 1			
Y1−N3	2.248(6)	Y1−N4	2.237(6)
Y1−N5	2.239(6)	Y1−C1	2.55(1)
Y1−Si1	3.28	Y1−Si2	3.38
Y1−Si3	3.13	Y1−Si4	3.35
Y1−Si5	3.13	Y1−Si6	3.58
N3−Y1−N4	106.9(2)	N3−Y1−N5	120.8(2)
N5−Y1−N4	118.0(2)	C1−Y1−N3	116.9(4)
C1−Y1−N4	102.3(3)	C1−Y1−N5	89.9(3)
Y1−N3−Si1	112.1(3)	Y1−N3−Si2	117.4(4)
Y1−N4−Si3	105.2(3)	Y1−N4−Si4	126.8(3)
Y1−N5−Si5	105.1(3)	Y1−N5−Si6	129.8(4)
Molecule 2			
Y2−N23	2.225(6)	Y2−N24	2.238(6)
Y2−N25	2.228(6)	Y2−C21	2.560(9)
Y2−Si21	3.35	Y2−Si22	3.31
Y2−Si23	3.13	Y2−Si24	3.59
Y2−Si25	3.15	Y2−Si26	3.45
N23−Y2−N24	124.0(2)	N23−Y2−N25	107.2(2)
N25−Y2−N24	114.6(2)	C21−Y2−N23	110.9(3)
C21−Y2−N24	90.3(2)	C21−Y2−N25	107.6(2)
Y2−N23−Si21	116.5(3)	Y2−N23−Si22	114.5(3)
Y2−N24−Si23	105.6(3)	Y2−N24−Si24	129.2(3)
Y2−N25−Si25	106.2(3)	Y2−N25−Si26	129.8(4)

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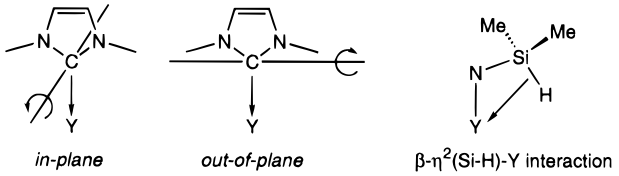

Figure 2. Structural peculiarities in complexes **5** and **6**: different bonding modes of the Y−carbene moieties and agostic β−η^2(Si−H)−Y interactions.

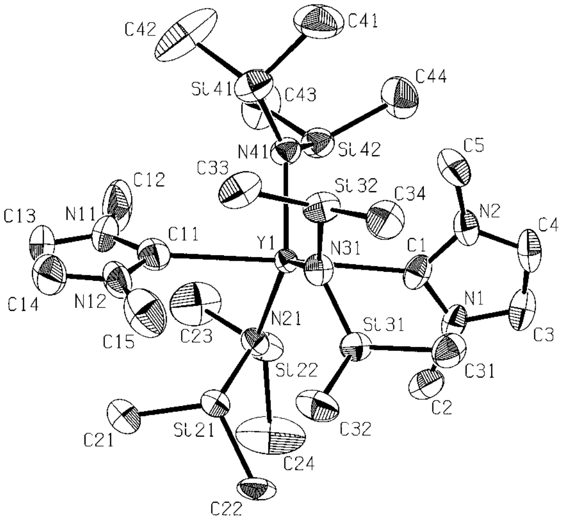

Figure 3. PLATON[50] plot of the molecular structure of Y[N(SiHMe$_2$)$_2$]$_3$(carbene)$_2$ (**6**). Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Y[N(SiHMe$_2$)$_2$]$_3$(carbene)$_2$ (6)

Y−N21	2.322(6)	Y−N31	2.302(6)
Y−N41	2.288(6)	Y−C1	2.648(8)
Y−C11	2.671(9)		
Y−Si21	3.21	Y−Si22	3.71
Y−Si31	3.21	Y−Si32	3.62
Y−Si41	3.52	Y−Si42	3.33
N21−Y−N31	131.9(2)	N21−Y−N41	115.5(2)
N31−Y−N41	112.6(2)	C1−Y−N21	94.0(2)
C1−Y−N31	84.5(2)	C1−Y−N41	91.3(2)
C11−Y−N21	85.3(2)	C11−Y−N31	94.3(3)
C11−Y−N41	91.0(3)	Y−N21−Si21	104.8(3)
Y−N21−Si22	133.0(3)	Y−N31−Si31	105.9(3)
Y−N31−Si32	128.1(3)	Y−N41−Si41	122.7(3)
Y−N41−Si42	112.9(3)	C1−Y−C11	177.6(3)

131.8(6) and 131.5(7)°, respectively, are significantly larger than the corresponding counterparts Y−C1−N2 (125.3(6)°) and Y−C11−N11 (125.3(7)°), respectively. The almost perpendicular arrangement (87.6°) of the mean square planes of the carbene ligands is probably due to increased intramolecular steric interaction, caused by the N(carbene)-bonded methyl groups. π-Donation of the strong carbene donor involving perpendicular metal orbitals is probably a less plausible reason to explain the carbene orientation. For comparison, the THF ligands in precursor **4** are almost coplanar. The (2 + 3) ligand arrangement was earlier found to be a preferred coordination mode as represented by, e.g., Ln(tritox)$_3$(CH$_3$CN)$_2$,[30] Ln[N(SiMe$_3$)$_2$]$_3$(L)$_2$,[20] or Ln[P(SiMe$_3$)$_2$]$_3$(THF)$_2$.[31]

The Y−C distances of 2.55(1) and 2.560(9) Å in **5** and 2.648(8) and 2.671(9) Å in **6**, respectively, compare well with bridging Y−C σ-bonds in methyl-bridged lanthanidocene complexes such as [Cp$_2$Y(μ-Me)]$_2$ (2.553(10), 2.537(9) Å)[32] and [(CpMe$_2$)$_2$Y(μ-Me)]$_2$ (2.60(1), 2.62(2) Å)[33] and with those of previously reported lanthanide carbene complexes considering ionic radii, oxidation state, and coordination number of the metal.[9,10] Nucleophilic isonitriles show a similar complexation tendency and bonding behavior as evidenced in 6-coordinate Ce(OC$_6$H$_3$*t*Bu$_2$-2,6)$_3$(CN*t*Bu)$_2$ (Ce−C, 2.786(12), 2.831(13) Å)[34] and 10-coordinate Cp$_3$Pr(CNC$_6$H$_{11}$) (2.65(1) Å).[35] As expected, the Y−N distances of 2.237(6)−2.248(6) in 4-coordinate **5** are slightly shortened in comparison to 5-coordinate precursor **4** (average 2.260(4) Å). However, in **6** the Y−N bond lengths in the range 2.288(6)−2.322(6) Å are considerably elongated compared to **4**, reflecting the enhanced steric and electronic saturation of the metal center.

Yttrium−η^2(Si−H) Interactions. Sterically unsaturated lanthanide centers tend to increase their inner coordination sphere either by oligomerization, solvent coordination, or agostic interactions.[36] For example, η^2-(Si−Me)−Ln interactions were detected in numerous complexes containing E(SiMe$_3$)$_2$ moieties (E = CH, N).[37] η^2(Si−H) metal interactions were previously reported in amide complexes of electron-deficient zirconium such as [ZrCl(μ-Cl){N(SiHMe$_2$)$_2$}$_2$]$_2$[22] and Cp$_2$Zr(X)[N(*t*Bu)(SiHMe$_2$)].[23] More recently, a tris(agostic) interaction was reported in homoleptic Er[N(*t*Bu)(SiHMe$_2$)]$_3$,[5b] all silicon hydrides forming close metal contacts (Er···H, average 2.37 Å).

Similar close η^2(Si−H)−Ln contacts can also be found in complexes **5** and **6**, the short-end range of the Y···Si distances of 3.13 Å lying far within the sum of van der Waals radii. For comparison, Ln−Si σ-bonds were found at 3.052(8) Å in the neutral species Cp*$_2$Sm[SiH(SiMe$_3$)$_2$][38] and in the range of 2.888(2) Å for anionic species of type [Li(DME)$_3$][Cp$_2$Lu(SiMe$_3$)$_2$].[39] The Y−N−Si angles vary in a wide range, 105−130°, reflecting that several silicon atoms are bent toward the metal center. The Y−N−Si angles associated with the nearby silicon atoms are 105.1(3)−106.2(3)° whereas the others are 112.1(3)−129.8(4)°. Similar distortions are found in Er[N(*t*Bu)(SiHMe$_2$)]$_3$ (Er−N−Si: 99.3(1)−99.7(1), 133.1(2)−133.6(2)°)[5b] and [ZrCl(μ-Cl){N(SiHMe$_2$)$_2$}$_2$]$_2$ (Zr−N−C: 102.8(2), 129.6(2)°).[22] Although, the silicon hydrides could not be located, the geometry of the tetrahedral silicon places the calculated hydrides between the yttrium and the silicon. In the case of an

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interaction the Y···H distances of 2.4 Å agree well with those found in Er[N(tBu)(SiHMe$_2$)]$_3$[56] and in the trimetallic polyhydride complex [(Cp$_2$ErH)$_3$Cl][Li(THF)$_4$] (Er−H, 1.99−2.54 Å).[40] The Ln−H distances in bridging lanthanocene complexes such as [(CpMe)$_2$Y(μ-H)(THF)]$_2$ are considerably shorter (Y-H, average 2.18(8) Å).[41] The almost planar arrangement of the atoms involved in such four-centered interactions, e.g., Y(1), Si(3), N(4), and H(11), show a maximum deviation of <0.03 Å from the mean square plane and support an agostic approach.

The stabilization of 4-coordinate complex **5** by η^2(Si−H)−Y interactions seems to be very reasonable. However, the observation of such close interactions in 5-coordinate **6** is quite remarkable. Compared to the bis(THF) adduct **4**, two contrary effects have to be considered. (a) The stronger donor **1** should render the metal center less electron-deficient and thus discourage close η^2(Si−H)−Y contacts. In addition, and despite the longer Y−C distances compared to Y−O distances, the carbene ligand is sterically larger than THF. (b) The elongated Y−N bond distances (0.045 Å), obviously a result of steric hindrance, should allow better agostic approach of the (Si−H) moiety.[42]

In both **5** and **6** the Si−C(carbene) and C(carbene)−H(Si) distances are significantly shorter than the sum of the van der Waals radii of the corresponding atoms. The dimethylsilyl groups are orientated in such a way that the hydrogen atoms point in the direction of the "empty" p-orbitals of the carbene carbon (e.g. **5**: Si(21)−C(11) 3.41 Å, C(11)−H 2.61 Å). The existence of the electrophilic character of a methylene fragment was pointed out earlier.[43]

Conclusion

We have shown that carbene ligands of type **1** form stable compounds with ErCl$_3$ and lanthanide(III) silylamide complexes by simple addition and THF displacement reactions. Under the prevailing conditions the number of electron-donating coligands depends on both basicity and steric bulk of a given coligand as evidenced by the isolation of Ln[N(SiHMe$_2$)$_2$]$_3$(carbene) and the bis(adducts) Ln[N(SiHMe$_2$)$_2$]$_3$(L)$_2$ (L = THF, carbene). The isolation of bis(carbene) adduct **6** is in agreement with the previously reported high steric flexibility of Ln[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ based on a THF dissociation/adduct formation process. Displacement of one THF ligand by the bulkier carbene ligand is due to the increased donor strength ("harder" base according to Pearson) of carbene **1** as already reported in carbene donor complexes of ytterbium(II).[9,10] Approach of carbene **1** forces redistribution of the three bis(dimethylsilyl)amide ligands by loss of their equatorial positions and displacement of the second, less strongly coordinated THF ligand. While 4-coordination in bis(trimethylsilyl)amide complexes is commonly observed with small donor ligands, e.g. Ln[N(SiMe$_3$)$_2$]$_3$(L) (L = NCPh),[20] isolation of formally 4-coordinated **5** is surprising with respect to steric considerations. Formation of **6**, e.g., ligation of another carbene ligand, has to be driven by the enhanced donor capability of the carbene ligand which re-establishes the "original" equatorial position of the silylamide ligands.

On the other hand, the number of coligands also directs the coordination mode of the silylamide counteranions which form intramolecular β-η^2(Si−H) metal interactions and hence prevent steric unsaturation of the metal center. Such intramolecular coordination of Si−H moieties with metal centers are relevant as models for the four-center σ-bond metathesis pathway in the dehydrogenative polymerization of hydrosilanes by electron-deficient metallocene complexes.[44,45] The extent of β-(Si−H) metal interactions is further documented by the flexible behavior in solution at room temperature. Both number and kind of donor ligands and the resulting silylamide coordination should have a significant impact on complex reactivity. For example, strong donor ligands are capable of disrupting dimeric or oligomeric structures.[46] Further reactivity studies will show whether these complexes also undergo THF-analog carbene-dissociation processes.

Experimental Section

General procedures have been previously described.[47] LnCl$_3$(THF)$_x$,[25] LiN(SiHMe$_2$)$_2$,[48] Ln[N(SiMe$_3$)$_2$]$_3$,[16] and carbene **1**[8] were prepared according to the literature. All manipulations were performed in an argon-filled glovebox (MB Braun MB150B-G-II).

ErCl$_3$(carbene)$_3$ (2). A 22.6 mL amount of a 0.14 M THF solution of carbene **1** (3.25 mmol) dissolved in 1 mL of THF was added slowly to a suspension of ErCl$_3$(THF)$_{3.25}$ (0.508 g, 1.0 mmol) in 50 mL of n-hexane. The mixture was stirred for 3 d at ambient temperature and then filtered. The residue was dried under vacuum for several hours yielding yellow **2** (0.392 g, 70%). Anal. Calcd for $C_{15}H_{24}Cl_3ErN_6$ (562.0): C, 32.06; H, 4.30; N, 14.95; Cl, 18.92. Found: C, 31.92; H, 4.15; N, 13.98; Cl, 18.98. IR (Nujol, cm^{-1}): 3153 s, 3101 s, 1573 s, 1397 vs, 1313 s, 1221 vs, 1174 s, 1113 s, 1076 m, 1018 m, 1003 m, 972 m, 938 m, 917 m, 894 w, 740 vs, 648 w, 622 m, 609 w, 450 m. MS (EI): m/e 96 (100) [carbene$^+$], 81 (4) [carbene$^+$ − Me].

Y[N(SiMe$_3$)$_2$]$_3$(carbene) (3a). A 0.024 g (0.25 mmol) amount of carbene **1** dissolved in 1 mL of THF was added slowly to a solution of Y[N(SiMe$_3$)$_2$]$_3$ (0.143 g, 0.25 mmol) in 4 mL of n-hexane. The solution was stirred for 24 h at ambient temperature. The solvent was removed *in vacuo* yielding quantitatively yellow **3a** (0.158 g). Anal. Calcd for $C_{23}H_{62}Si_6N_5Y$ (666.2): C, 41.47; H, 9.38; N, 10.51. Found: C, 40.75; H, 9.35; N, 9.72. IR (Nujol, cm^{-1}): 1366 (sh) s, 1258 (sh) s, 1247 s, 1219 m, 1169 w, 1155 w, 1111 w, 981 m, 946 vs, 844 vs, 831 vs, 774 s, 754 m, 695 m, 667 m, 610 m, 448 w, 419 w. ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C): δ 0.37 (s, 54 H), 3.38 (s, 6 H), 5.77 (s, 2 H). ^{13}C{^{1}H} NMR (100.5 MHz, C$_6$D$_6$, 20 °C): δ 6.4 (SiCH_3), 38.8 (NCH_3), 121.6 (CH). ^{29}Si NMR (79.5 MHz, C$_6$D$_6$, 20 °C): δ −9.9. ^{15}N NMR (40.5 MHz, C$_6$D$_6$, 20 °C): δ −208.5 (d, $^2J_{NH} = 4$ Hz).

La[N(SiMe$_3$)$_2$]$_3$(carbene) (3b). A 0.024 g (0.25 mmol) amount of carbene **1** dissolved in 1 mL of THF was added

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slowly to a solution of La[N(SiMe$_3$)$_2$]$_3$ (0.155 g, 0.25 mmol) in 3 mL of *n*-hexane. The solution was stirred for 24 h at ambient temperature. The solvent was removed *in vacuo* yielding quantitatively yellow **3b** (0.177 g). Anal. Calcd for $C_{23}H_{62}Si_6N_5La$ (716.2): C, 38.57; H, 8.73; N, 9.78. Found: C, 38.75; H, 8.82; N, 8.91. IR (Nujol, cm^{-1}): 1399 m, 1246 vs, 1219 m, 1169 w, 1152 w, 1107 w, 1084 w, 1009 w, 974 vs, 955 vs, 887(sh) s, 862 vs, 829 vs, 766 s, 753 (sh) s, 730 s, 665 s, 609 m, 596 w, 445 w. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 0.38 (s, 54 H), 3.34 (s, 6 H), 5.79 (s, 2 H). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 20 °C): δ 5.4 (Si*C*H$_3$), 38.1 (N*C*H$_3$), 121.4 (*C*H).

Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (4). A 2.576 g (18.5 mmol) amount of LiN(SiHMe$_2$)$_2$ was added slowly to a suspension of 2.910 g (6.5 mmol) of YCl$_3$(THF)$_{3.5}$ in 50 mL of *n*-hexane. Upon being stirred for 12 h at room temperature, the reaction mixture was filtered and the white residue washed with 30 mL of *n*-hexane. The *n*-hexane phases were combined, and the solvent was removed *in vacuo*. The thus obtained white powder was crystallized from *n*-pentane yielding 3.70 g of **4** (85%). Anal. Calcd for $C_{20}H_{58}N_3Si_6O_2Y$ (630.1): C, 38.12; H, 9.28; N, 6.67. Found: C, 37.98; H, 8.99; N, 6.27. IR (Nujol, cm^{-1}): 2072 s, 1939 (sh) m, 1296 w, 1243 vs, 1072 (br) vs, 936 vs, 896 s, 835 s, 787 m, 761 m, 675 m, 619 m, 606 m, 404 m. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 0.19 (d, 36H, SiCH$_3$), 1.18 (m, 8H, THF), 3.98 (m, 8H, THF), 5.06 (sept, 6H, SiH; $^1J_{\mathrm{SiH}} = 171$ Hz). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 20 °C): δ 3.5 (Si*C*H$_3$), 25.4 (THF), 71.1 (THF). ^{29}Si (79.5 MHz, C_6D_6, 20 °C): δ −19.6. ^{89}Y (19.45 MHz, C_6D_6, 30 °C): 444 ppm.

Y[N(SiHMe$_2$)$_2$]$_3$(carbene) (5). A 4.2 mL amount of a 0.3 M THF solution of carbene **1** (1.2 mmol) was added slowly to a solution of **4** (0.756 g, 1.2 mmol) in 35 mL of THF. After the reaction was stirred for 24 h at ambient temperature, the solvent was removed *in vacuo*. The residue was redissolved in *n*-hexane, the mixture centrifuged, and the solvent removed. Greenish **5** was obtained in quantitative yield (0.695 g). Anal. Calcd for $C_{17}H_{50}N_5Si_6Y$ (582.0): C, 38.56; H, 8.94; N, 10.71. Found: C, 38.17; H, 8.61; N, 10.56. IR (Nujol, cm^{-1}): 3169 (sh) w, 3135 w, 2070 vs, 1992 (sh) m, 1927 (sh) m, 1773 w, 1540 w, 1401 m, 1316 m, 1243 vs, 1220 m, 1169 w, 1154 w, 1112 m, 1048 vs, 970 vs, 941 vs, 898 vs, 836 vs, 788 vs, 763 vs, 682 m, 624 w, 609 w, 446 w, 409 w. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 0.35 (s, 36 H, SiCH$_3$), 1.41 (d, THF), 3.38 (s, 6 H, NCH$_3$), 3.56 (d, THF), 5.04 (sept, 3 H, SiH; $^1J_{\mathrm{SiH}} = 164$ Hz), 5.79 (s, 2 H, CH). ^{13}C NMR (100.5 MHz, C_6D_6, 20 °C): δ 3.2 (q, Si*C*H$_3$), 25.7 (t, THF), 37.5 (q, N*C*H$_3$), 67.9 (t, THF), 121.1 (d, *C*H), 190.3 (d, $^1J_{\mathrm{YC}} = 49.6$ Hz, N*C*N). ^{29}Si NMR (79.5 MHz, C_6D_6, 20 °C): δ −23.1. ^{15}N NMR (40.5 MHz, C_6D_6, 20 °C): δ −208.8 (d, $^2J_{\mathrm{NH}} = 5$ Hz).

Y[N(SiHMe$_2$)$_2$]$_3$(carbene)$_2$ (6). A 8.7 mL amount of a 0.3 M THF solution of carbene **1** (2.4 mmol) was added to a solution of **4** (0.756 g, 1.2 mmol) in 35 mL of THF. After the reaction was stirred for 24 h at ambient temperature, the solvent was removed *in vacuo*. The residue was redissolved in *n*-hexane, the mixture centrifuged, and the solvent removed. Light brown **6** was obtained in quantitative yield (0.805 g). Anal. Calcd for $C_{22}H_{58}Si_6N_5Y$ (678.2): C, 38.96; H, 8.62; N, 14.46. Found: C, 39.88; H, 7.86; N, 13.92. IR (Nujol, cm^{-1}): 3163 w, 3130 w, 2088 m, 2041 (sh) m, 1532 w, 1400 m, 1312 w, 1247 s, 1240 s, 1216 m, 1169 w, 1155 w, 1104 w, 1032 s, 969 (sh) m, 936 s, 893 vs, 834 s, 781 s, 760 s, 728 s, 693 w, 675 w, 615 w, 602 w, 445 w, 433 w. MS (CI): *m*/*e* 677 (4) [M$^+$], 662 (10) [M$^+$ − Me], 648 (100) [M$^+$ − 2Me + H], 633 (5) [M$^+$ − 3Me + H], 581 (67) [M$^+$ − carbene], 449 (9) [M$^+$ − bdsa − carbene]. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 0.26 (s, 36 H, SiCH$_3$), 3.70 (s, 12 H, NCH$_3$), 5.10 (sept, 3 H, SiH; $^1J_{\mathrm{SiH}} = 172$ Hz), 6.03 (s, 4 H, CH). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6, 20 °C): δ 3.5 (Si*C*H$_3$), 38.6 (N*C*H$_3$), 120.7 (*C*H), 194.0 (N*C*N). ^{29}Si NMR (79.5 MHz, C_6D_6, 20 °C): δ −22.5.

X-ray Structure Determination of Y[N(SiHMe$_2$)$_2$]$_3$(carbene) (5). A colorless to pale yellow crystal of approximate dimensions 0.28 × 0.26 × 0.33 mm^3 was transferred into a glass capillary under inert gas atmosphere and mounted on an image plate diffraction system (STOE) with graphite monochromator. The compound crystallizes as monoclinic, space group $P2_1/c$ (No. 14). Details of data collection and refinement are presented in Table 4. The data were collected at 27(±3) °C and a distance from crystal to image plate of 100 mm (5.7° < 2θ < 42.0°), with 360 images (0° < φ < 360°, $\Delta\varphi$ = 1°) and an exposure time of 15 min. The data were corrected for Lorentz and polarization effects. A total of 46 896 data were measured with 8864 overlaps, 1568 reflections systematically absent, 45 328 data merged ($R = 0.083$), 7295 independent reflections, 869 with negative intensity, and 4154 reflections with $I > 1.0\sigma(I)$ used for refinement. The structure was solved by direct methods[51] and refined with standard difference Fourier techniques.[52] All hydrogens were calculated in ideal geometry. A total of 523 parameters (7.9 data/parameter) were refined, using polynomial weights,[53] and leaving shift/error < 0.0001 and a residual electron density of +0.43 e Å^{-3} (1.71 Å near Si(24)) and −0.30 e Å^{-3} in the last cycle of refinement. Values of R and R_w are given by $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.052$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.053$.

Table 4. Crystallographic Data for Y[N(SiHMe$_2$)$_2$]$_3$(carbene) (5) and Y[N(SiHMe$_2$)$_2$]$_3$(carbene)$_2$ (6)

formula	$C_{17}H_{50}N_5Si_6Y$	$C_{22}H_{58}N_7Si_6Y$
fw	582.0	678.2
space group	$P2_1/c$	$P\bar{1}$
a, Å	18.568(4)	11.138(4)
b, Å	11.094(3)	11.551(4)
c, Å	35.072(8)	17.143(6)
α, deg		79.75(3)
β, deg	100.70(2)	86.10(3)
γ, deg		62.26(3)
V, Å^3	7099	1921
Z	8	2
T, K	300	223
λ, Å	Mo Kα, 0.710 73	Mo Kα, 0.710 73
ρ_{calcd}, g cm^{-3}	1.09	1.17
μ, mm^{-1}	1.86	1.73
no. of obsd rflns	4154 ($I > 1.0\sigma(I)$)	3522 ($I > 2.0\sigma(I)$)
$R(F_o)$	5.2	6.8
$R_w(F_o)$	5.3	6.4

X-ray Structure Determination of Y[N(SiHMe$_2$)$_2$]$_3$(carbene)$_2$ (6). A colorless to pale yellow crystal of approximate size 0.23 × 0.21 × 0.21 mm^3 was transferred into a glass capillary under inert gas atmosphere and mounted on an Enraf-Nonius CAD4 diffractometer. The compound crystallizes as triclinic, space group $P\bar{1}$ (No. 2). Details of data collection and refinement are presented in Table 4. The data were collected at −50(±3) °C in the θ-range 2° < 2θ < 50° with graphite-monochromatized Mo Kα (λ = 0.710 73 Å) radiation using the ω-scan mode with maximum scan time of 90 s and scan width 1.5 + 0.2 tan θ. A total of 6997 data were measured, 1746 with negative intensity ($I/\sigma(I) < 0.01$), 233 data merged, 5085 independent reflections, and 3522 reflections with $I > 2.0\sigma(I)$ used for refinement. All data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[51] and refined with standard difference Fourier techniques.[52] All hydrogen atoms were calculated at their idealized positions. A total of 325 param-

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eters (10.8 data/parameter) were refined, using polynomial weights,[53] and leaving shift/error < 0.0001 and residual electron density +0.83 e $Å^{-3}$ (1.03 Å near Si(22)) and −0.66 e $Å^{-3}$ in the last cycle of refinement. Values of R and R_w are given by $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.068$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.064$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for generous support for this research and the award of a fellowship to R.A.

Supporting Information Available: A fully labeled molecular structure diagram of **5** and tables of atomic coordinates, atomic displacement parameters, and bond distances and angles for **5** and **6** (18 pages). Ordering information is given on any current masthead page.

OM9607715