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Evaluation of a Silylene Divalent Lanthanide Interaction in the Metallocene Complex

$(C_5Me_5)_2Sm[SiN^tBuCHCHN^tBu]$

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*Summary: An $R_2Si{:}\rightarrow Ln(II)$ complex $(C_5Me_5)_2Sm[SiN^tBuCHCHN^tBu]$, **1**, has been synthesized in 90% yield by reaction of $(C_5Me_5)_2Sm$ with 1,3-di-tert-butyl-2,3-dihydro-1H-1,3,2-diazasilol-2-ylidene in toluene. Structural features of the $(C_5Me_5)_2Sm$ part of **1** are similar to those in $(C_5Me_5)_2Sm(THF)$. The silylene ligand is located asymmetrically in the metallocene wedge with one tert-butyl group (Sm−C(Me) = 3.396(4) Å) much closer to the metal than the other (Sm−C(Me) = 4.741(4) Å). The Si−Sm(II) distance is 3.1910(1) Å.*

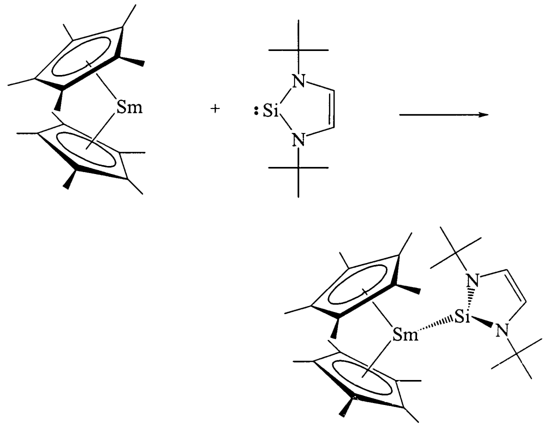
Introduction

Recent developments in the chemistry of carbenes and silylenes have led to synthesis of stabilized R_2C: and R_2Si: species that have the potential to function as two electron donor ligands to metals.[1−5] The utility of these molecules as new ligands has been evaluated with a variety of metals.[6−11] Although several examples of carbene complexes of lanthanides are now known,[12−16] to our knowledge only two silylene lanthanide or yttrium complexes have been reported: trivalent $(\eta^5\text{-}C_5H_5)_3Yb\{Si[(N\{CH_2{}^tBu\})_2C_6H_4\text{-}1,2]\}$[17] and $(\eta^5\text{-}C_5H_5)_3Y\{Si[(N\{CH_2{}^tBu\})_2C_6H_4\text{-}1,2]\}$.[17]

We report here the synthesis and structure of the first silylene complex of a divalent lanthanide using decamethylsamarocene, $(C_5Me_5)_2Sm$.[18] By choosing this system, a direct comparison can be made with a complex of a traditional two-electron donor, $(C_5Me_5)_2Sm(THF)$, **2**,[20] and with the carbene complex $(C_5Me_5)_2Sm[CNMeCMeCMeNMe]_2$, **3**.[12]

Results and Discussion

Dark green solutions of $(C_5Me_5)_2Sm$ in toluene react immediately with $SiN^tBuCHCHN^tBu$ to form dark purple solutions from which $(C_5Me_5)_2Sm[SiN^tBuCHCHN^tBu]$, **1**, can be isolated in 90% yield by removal of the solvent, eq 1. In contrast, no evidence for reaction of solvated $(C_5Me_5)_2Sm(THF)_2$ with $SiN^tBuCHCHN^tBu$ in C_6D_6 was observed over several weeks at 60 °C. This reactivity differs from that of the carbene complex $(C_5Me_5)_2Sm[CNMeCMeCMeNMe]_2$, **3**,[12] which can be



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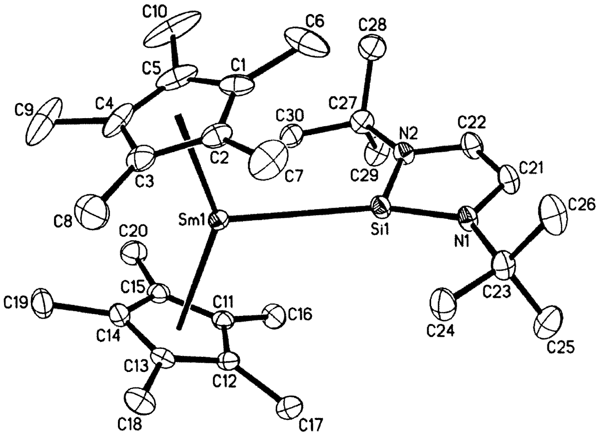
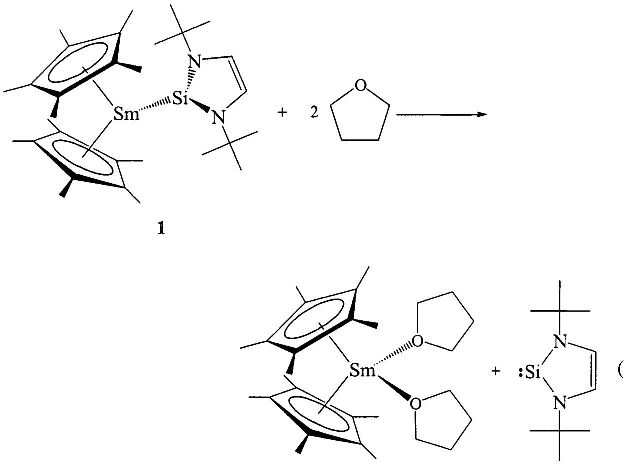


Figure 1. Thermal ellipsoid plot of $(C_5Me_5)_2Sm[Si(N^tBuCHCHN^tBu)]$, **1**, at the 30% probability level.

prepared from the THF solvate $(C_5Me_5)_2Sm(THF)$.[20] Addition of THF to **1** in C_6D_6 formed $(C_5Me_5)_2Sm(THF)_2$ and free $SiN^tBuCHCHN^tBu$ quantitatively, eq 2.



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(2)

The intense purple color of **1** and its NMR spectra are consistent with the presence of Sm(II). The ring methyl carbons in the ^{13}C NMR spectrum are shifted downfield to δ 109.6, while the ring cyclopentadienyl carbon resonances appear much further upfield at δ -92.6 ppm, as is typical for divalent Sm.[18] The chemical shifts of the ^1H NMR resonances are concentration and temperature dependent, as is found for $(C_5Me_5)_2Sm$.[18] No signal attributable to **1** was located in the ^{29}Si NMR spectrum due to the paramagnetism of Sm(II).

Variable high-temperature NMR studies indicate that **1** is more stable than $(\eta^5\text{-}C_5H_5)_3Y\{Si[(N\{CH_2{}^tBu\})_2C_6H_4\text{-}1,2]\}$,[17] **4**, which has a 1:14 ratio of complexed to uncomplexed silylene at room temperature, and $(\eta^5\text{-}C_5H_5)_3Yb\{Si[(N\{CH_2{}^tBu\})_2C_6H_4\text{-}1,2]\}$,[17] **5**, which undergoes dissociation of the silylene at 343 K. The silylene resonances of **1** shift to δ 2.65 $((CH_3)_3C)$ and 6.35 $(-HC{=}CH-)$ ppm at 343 K, but in no case is a signal for the free silylene observed.

Crystallographic characterization of **1** shows a single silylene coordinated to the metal, Figure 1. The ring-centroid−Sm−Si angles of 107.2° and 108.9° in **1** show that the silylene ligand is located midway between the two cyclopentadienyl rings. However, in the plane perpendicular to that of the two cyclopentadienyl ring centroids and samarium, the silicon atom is not positioned symmetrically about the open face of the metallocene, Figure 2. In fact, the silicon atom lies 0.48 Å out of the plane defined by samarium and the two ring centroids. This type of asymmetry was found to a greater extent in the monosolvated $(C_5Me_5)_2Sm(THF)$, **2**, where the oxygen donor atom was located 1.54 Å out of the analogous plane.[20] The Sm−C(ring) ranges are nearly the same for the two complexes: 2.772(3)−2.824(4) Å in **1** and 2.787(5)−2.853(4) Å in **2**. The 143.6° ring-centroid−Sm−ring-centroid of **1** is larger than the 138.5° angle in **2** and is closer to the 140.0° angle found in the mono(tetrahydropyran) solvate $(C_5Me_5)_2Sm(OC_5H_{10})$.[20] These data on **1** are consistent with a normal divalent $(C_5Me_5)_2SmL$ complex in which L is a typical neutral ligand.

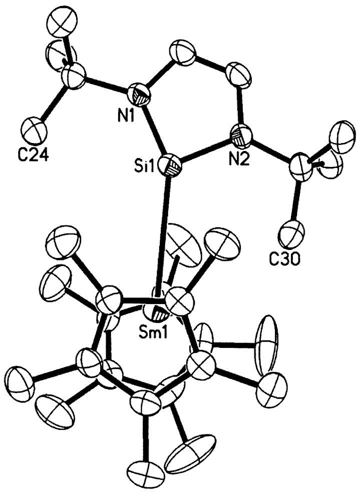

Figure 2. Top view of $(C_5Me_5)_2Sm[Si(N^tBuCHCHN^tBu)]$, **1**, oriented such that the widest part of the bent metallocene wedge is horizontal in the diagram.

The orientation of the silylene ligand in **1** is not symmetrical in the plane perpendicular to that defined by samarium and the two ring centroids. The silylene is bent such that one *tert*-butyl substituent is much closer to the metal center than the other, Figure 2. The closest Sm···C (CMe_3) distance is the 3.396(4) Å Sm(1)···C(30) length. This is much shorter than the corresponding distance on the other side: Sm(1)···C(24) is 4.741(4) Å. Consistent with these disparate bond distances, the Sm(1)−Si(1)−N(2) angle is 118.2(1)° compared to 150.8(1)° for the analogous Sm(1)−Si(1)−N(1) angle. Packing diagrams for the crystal show no obvious intermolecular causes for this asymmetry. No evidence of this solid state asymmetry was observed in solution by ^1H NMR spectroscopy down to −70 °C. Reliable $J(^{13}C-^{1}H)$ coupling constants were not obtainable due to the paramagnetism of the complex.

The asymmetry observed in **1** is unusual for metal complexes of carbenes and silylenes.[6−10] However, long-range metal carbon distances of this type are not unusual with the electrophilic lanthanides. For example, $(C_5Me_5)_2Sm$ has an intermolecular Sm···C distance of

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3.22(1) Å.[23] The divalent Yb(II) complex $[1,3\text{-}(\mathrm{Me_3C})_2\mathrm{C_5H_3}]_2\mathrm{Yb}$[24] contains two close intramolecular Yb···C(CMe$_3$) contacts of 3.09(1) and 3.20(2) Å. Both of these are shorter than the 3.396(4) Å distance in **1**, even considering that the radial size of Yb(II) is 0.13 Å smaller than that of Sm(II) according to Shannon radii.[21] The 3.396(4) Å distance in **1** is approximately equal to the shortest Sm···C(CH$_3$) distance in the trivalent complex $(\mathrm{C_5Me_5})_2\mathrm{Sm[N(SiMe_3)_2]}$,[25] 3.216 Å, considering Sm(II) is 0.19 Å larger than Sm(III).[21]

The 3.1903(10) Å Sm(II)−Si distance in **1** can be evaluated in several ways. It can be compared with the two trivalent lanthanide carbene distances in the literature,[17] with the Sm(II)−carbene distances in $(\mathrm{C_5Me_5})_2\mathrm{Sm}\overline{\mathrm{CNMeCMeCMeN}}\mathrm{Me}$, **3**,[12] and with a traditional two electron donor ligand in $(\mathrm{C_5Me_5})_2\mathrm{Sm(THF)}$, **2**.[20] The comparisons are not direct in any of these cases since differences in metal radius need to be considered and there is ambiguity about which coordination number to choose for Sm in **1**. Using the convention that the $\mathrm{C_5Me_5}$ rings occupy three coordination positions, the Sm in **1** could be 7 or 8 coordinate, depending on how the long-range Sm···C(Me) interaction is considered. Seven coordination will be used here since the Sm···C(Me) distance is long.

Comparison with the trivalent compounds will be done using the 1.22 Å seven-coordinate Shannon radius of Sm(II) and assuming 1.131 and 1.099 Å radii for 10-coordinate Y and Yb. Extrapolation with these numbers suggests that the Ln−Si distances equivalent to the Sm−Si distance in **1** would be 3.10 and 3.07 Å in $(\eta^5\text{-}\mathrm{C_5H_5})_3\mathrm{Y\{Si[(N\{CH_2{}^tBu\})_2C_6H_4\text{-}1,2]\}}$,[17] **4**, and $(\eta^5\text{-}\mathrm{C_5H_5})_3\mathrm{Yb\{Si[(N\{CH_2{}^tBu\})_2C_6H_4\text{-}1,2]\}}$,[17] **5**, respectively. The actual Ln−Si distances in **4** and **5** are 3.038(2) and 2.984(2) Å, respectively. Hence, although these trivalent silylenes are less stable than **1** in solution (vide supra), the trivalent ions appear to pull the silylenes in somewhat closer. However, this comparison does not account for the difference in the steric bulk of the different silylenes.

To evaluate the distances in **1** versus **3**, an estimate of Ln−Si versus Ln−C bond distances is needed. Comparison of $[(\mathrm{C_5H_5})_2\mathrm{Lu(SiMe_3)_2}]^-$ (Lu−Si = 2.880(2) Å)[26,27] with $[(\mathrm{C_5H_5})_2\mathrm{Y(CH_2SiMe_3)_2}]^-$[28] (Y−C = 2.402(6) and 2.445(6) Å; eight-coordinate Lu is 0.042 Å shorter than eight-coordinate Y) and $(\mathrm{C_5H_5})_2\mathrm{Lu(CMe_3)(THF)}$ (Lu−C = 2.47(2) Å)[29] suggests that silicon binds to a lanthanide at a distance 0.41−0.52 Å greater than carbon. Comparison of $(\mathrm{C_5Me_5})_2\mathrm{Sm[SiH(SiMe_3)_2]}$[30] (Sm−Si, 3.052(8) Å) with $(\mathrm{C_5Me_5})_2\mathrm{Nd[CH(SiMe_3)_2]}$[31] (Nd−C, 2.517(7) Å; Nd is 0.03 Å larger than Sm) suggests a 0.56 Å difference. For comparison, the difference in atomic radii of carbon and silicon is 0.40 Å.[32]

Using these silicon versus carbon numbers and the fact that seven-coordinate Sm(II) is 0.05 Å shorter than eight-coordinate Sm(II), a Sm(II)−carbene distance of 2.68−2.84 Å in **3** would be expected to be equivalent to the 3.1903(10) Å Sm−Si distance in **1**. The actual distances in **3** are 2.837(7) and 2.845(7) Å. Within the limits of these estimates, this suggests that the silylene is at least as good a ligand as the carbene for Sm(II).

A comparison of the Sm−Si distance can also be made with the Sm−O distances in $(\mathrm{C_5Me_5})_2\mathrm{Sm(THF)}$ and $(\mathrm{C_5Me_5})_2\mathrm{Sm(OC_5H_{10})}$, although one would expect the hard oxygen donor ligands to bind better to the samarium ion. Using a 0.51 Å difference in atomic radii of oxygen and silicon,[32] the Sm−O distance equivalent to the 3.190(1) Å distance in **1** would be 2.68 Å. The actual Sm−O distances in $(\mathrm{C_5Me_5})_2\mathrm{Sm(THF)}$ and $(\mathrm{C_5Me_5})_2\mathrm{Sm(OC_5H_{10})}$ are 2.569(3) and 2.630(6) Å, respectively.[20] This suggests that the oxygen donor atom ligands are held closer to Sm(II) than the silylene. This is consistent with the solution reactivity, which shows THF to be preferred over the silylene. Again these bond distance comparisons do not take into account the different steric bulk of the ligands.

Conclusion

The silylene ligand $\overline{\mathrm{SiN^tBuCHCHN}}{}^t\mathrm{Bu}$ forms a base adduct complex with $(\mathrm{C_5Me_5})_2\mathrm{Sm}$ like other stable two electron donor ligands. In contrast to the carbene ligand, $\overline{\mathrm{CNMeCMeCMeN}}\mathrm{Me}$, a 1:1 rather than a 2:1 complex is formed, but the silylene attaches in an asymmetrical way to orient one *tert*-butyl group toward the metal to fill up the coordination sphere. Bond distance arguments can be made to suggest that the silylene is as good a ligand for Sm(II) as a carbene. However, it may be possible that the silicon donor atom is more flexible and can more readily allow asymmetric orientations of the overall ligand.

Experimental Section

The complexes described below are extremely air and moisture sensitive. Syntheses and manipulations of these compounds were conducted under nitrogen or argon with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. The argon glovebox used in these experiments was free of coordinating solvents. Toluene was dried over Q-5 and activated 4 Å molecular sieves. Benzene-d_6 was distilled over NaK alloy and benzophenone. $(\mathrm{C_5Me_5})_2\mathrm{Sm}$[18] and $\overline{\mathrm{SiN^tBuCHCHN}}{}^t\mathrm{Bu}$[4] were prepared as previously described.

NMR spectra were measured using a Bruker 400 MHz spectrometer. IR samples were prepared as thin films, and spectra were obtained using an ASI ReactIR 1000 spectrometer. Complexometric analyses were performed as previously described.[19]

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$(C_5Me_5)_2Sm[\overline{SiN^tBuCHCHN}{}^tBu]$, 1. A dark green solution of $(C_5Me_5)_2Sm$ (20 mg, 0.048 mmol) in 5 mL of toluene was reacted with white $\overline{SiN^tBuCHCHN}{}^tBu$ (9.3 mg, 0.048 mmol). The color immediately changed to dark purple. The reaction was stirred for 4 h at 25 °C. Removal of the solvent under vacuum gave **1** as a microcrystalline purple solid (26 mg, 90%). Crystals suitable for X-ray diffraction were grown from toluene at −37 °C. ^1H NMR (0.05 M, C_6D_6, 25 °C): δ 2.85 (s, 30H) $C_5(CH_3)_5$, 5.52 (s, 2H) $-HC{=}CH-$, 7.80 (s, 18H) $(CH_3)_3C$. ^{13}C NMR (0.07 M, C_6D_6, 25 °C): δ −92.6 $C_5(CH_3)_5$, 46.3 $(CH_3)_3C$, 57.6 $(CH_3)_3C$, 104.5 $-HC{=}CH-$, 109.6 $C_5(CH_3)_5$. IR (thin film): 3640w, 3096w, 2960s, 2910s, 2864s, 2725w, 2173m,br, 1613w, 1444m, 1390m, 1363s, 1266s, 1227s, 1116s, 1004s, 837s, 702m. Anal. Calcd for $C_{30}H_{50}N_2SiSm$: Sm, 24.36. Found: Sm, 23.8. Mp: 220 °C.

X-ray Data Collection, Structure Solution, and Refinement for 1. A purple crystal of approximate dimensions 0.10 × 0.15 × 0.28 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[1s] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[2s] and SADABS[3s] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4s] program. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group *Pbcn*, which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5s] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0675 and Goof = 1.098 for 307 variables refined against 6620 data (0.80 Å resolution). As a comparison for refinement on F, R1 = 0.0298 for those 4885 data with $I > 2.0\sigma(I)$.

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Supporting Information Available: Atomic coordinates, thermal parameters, and complete bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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