Divalent Lanthanide Metal Complexes of a Triazacyclononane-Functionalized Tetramethylcyclopentadienyl Ligand: X-ray Crystal Structures of [$C_5Me_4SiMe_2$($^iPr_2$-tacn)]LnI (Ln = Sm, Yb; tacn = 1,4-Diisopropyl-1,4,7-triazacyclononane)

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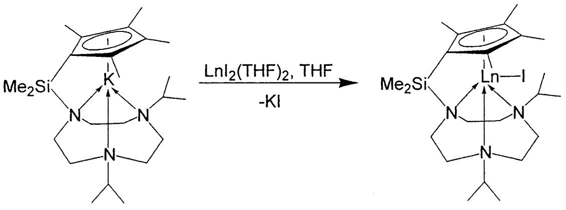
*Summary: The synthesis and characterization of divalent lanthanide complexes of a triazacyclononane-functionalized tetramethylcyclopentadienyl ligand are described. Addition of $LnI_2(THF)_2$ (Ln = Sm, Yb; THF = tetrahydrofuran) to [$C_5Me_4SiMe_2$($^iPr_2$-tacn)]K (tacn = 1,4-diisopropyl-1,4,7-triazacyclononane) in THF yields the monomeric organolanthanides [$C_5Me_4SiMe_2$($^iPr_2$-tacn)]SmI (**1**) and [$C_5Me_4SiMe_2$($^iPr_2$-tacn)]YbI (**2**). The crystal structures of **1** and **2** have been determined.*

Introduction

Over the past decade, there has been increased interest in the coordination chemistry of the lanthanides due to the potential applications of a wide variety of their complexes.[1,2] Pioneering work by Evans et al.[3,4] has shown that divalent organosamarium complexes exhibit a particularly rich reaction chemistry due to the accessibility of the Sm(II)/Sm(III) couple;[5] for example, although bis-Cp* complexes such as Cp^*_2Sm and $Cp^*_2Sm(THF)_2$ do not possess a metal−carbon bond into which ethylene can insert, they nonetheless show high polymerization activity toward ethylene.[6,7] The majority of this chemistry has been done utilizing the combination of two pentamethylcyclopentadienyl ligands; however, complexes incorporating a single Cp* ligand and a second alkyl group, which may allow for further tuning of the reactivity, have received scant attention. This is partially due to difficulties associated with the monoligand starting materials; although the structures of $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$[8] and $[(Me_3Si)_2NSm(\mu\text{-}I)(DME)(THF)]_2$[9] (DME = dimethoxyethane) have been reported, they tend toward ligand redistribution to $SmI_2(THF)_2$ and SmL_2. Recently, amino- and alkoxy-functionalized cyclopentadienyl ligands have been used in divalent organolanthanide chemistry with the rationalization that intramolecular Lewis base coordination reduces coordination of solvent molecules and renders the complexes less sensitive to hydrolysis and oxidation, as well as ligand redistribution.[10−12] We recently reported the synthesis of a monoanionic analogue of the constrained geometry catalysts developed by Bercaw et al.,[13−15] in which the anionic amido linkage was replaced by a neutral, tridentate triazacyclononane moiety.[16] Here we describe the synthesis and characterization of divalent lanthanide complexes utilizing this ligand system.

Results and Discussion

Synthesis of Divalent Samarium and Ytterbium Derivatives. The reaction of [$C_5Me_4SiMe_2$($^iPr_2$-tacn)]K[16] with $LnI_2(THF)_2$ (Ln = Sm, Yb) in THF at room temperature generates the divalent organolanthanides [$C_5Me_4SiMe_2$($^iPr_2$-tacn)]SmI (**1**) and [$C_5Me_4SiMe_2$($^iPr_2$-tacn)]YbI (**2**) in good yield (eq 1). The complexes are isolable as air- and moisture-sensitive solids that are soluble in donor solvents such as THF and pyridine; **1** is nearly insoluble in toluene or benzene while **2** is only sparingly soluble in these solvents. The ^1H NMR



(1)

Ln = Sm **1**
Yb **2**

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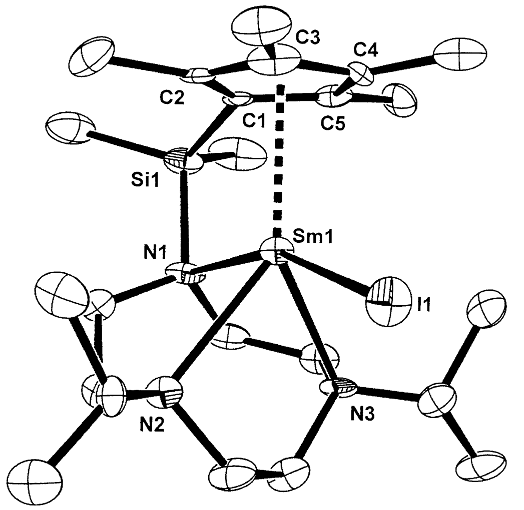

Figure 1. ORTEP view of [$C_5Me_4SiMe_2(^iPr_2$-tacn)]SmI (**1**) drawn with 30% probability ellipsoids; only one of the two independent molecules is shown. An interstitial molecule of THF (half an equivalent) is omitted for clarity. The same general structural features are observed for [$C_5Me_4SiMe_2(^iPr_2$-tacn)]YbI (**2**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for [$C_5Me_4SiMe_2(^iPr_2$-tacn)]SmI (1)

Sm(1)−I(1)	3.2161(12)	Sm(1)−N(1)	2.773(10)
Sm(1)−N(2)	2.663(10)	Sm(1)−N(3)	2.719(10)
Sm(1)−C(1)	2.767(11)	Sm(1)−C(2)	2.857(11)
Sm(1)−C(3)	2.949(11)	Sm(1)−C(4)	2.903(12)
Sm(1)−C(5)	2.794(12)	Sm(1)−Cp	2.583
I(1)−Sm(1)−N(1)	158.7(2)	I(1)−Sm(1)−N(2)	91.7(2)
I(1)−Sm(1)−N(3)	100.6(2)	I(1)−Sm(1)−Cp	110.84
N(1)−Sm(1)−N(2)	68.2(3)	N(1)−Sm(1)−N(3)	65.9(3)
N(1)−Sm(1)−Cp	90.1	N(2)−Sm(1)−N(3)	67.9(3)
N(2)−Sm(1)−Cp	141.2	N(3)−Sm(1)−Cp	132.1

Table 2. Selected Bond Distances (Å) and Angles (deg) for [$C_5Me_4SiMe_2(^iPr_2$-tacn)]YbI (2)

Yb(1)−I(1)	3.0613(6)	Yb(1)−N(1)	2.600(6)
Yb(1)−N(2)	2.584(6)	Yb(1)−N(3)	2.573(6)
Yb(1)−C(1)	2.657(8)	Yb(1)−C(2)	2.714(7)
Yb(1)−C(3)	2.782(7)	Yb(1)−C(4)	2.768(7)
Yb(1)−C(5)	2.695(8)	Yb(1)−Cp	2.443
I(1)−Yb(1)−N(1)	159.7(1)	I(1)−Yb(1)−N(2)	96.0(1)
I(1)−Yb(1)−N(3)	89.6(1)	I(1)−Yb(1)−Cp	106.80
N(1)−Yb(1)−N(2)	70.0(2)	N(1)−Yb(1)−N(3)	72.3(2)
N(1)−Yb(1)−Cp	93.37	N(2)−Yb(1)−N(3)	71.5(2)
N(2)−Yb(1)−Cp	135.81	N(3)−Yb(1)−Cp	143.5

Table 3. Crystallographic Data

compd	**1**·$(THF)_{0.5}$	**2**
formula	$C_{25}H_{48}IN_3O_{0.5}SiSm$	$C_{23}H_{44}N_3SiIYb$
MW	704.03	690.65
temp, K	162	137
cryst system	monoclinic	orthorhombic
space group	$P2_1/c$	*Pbca*
a, Å	17.608(1)	17.8561(9)
b, Å	18.137(1)	16.5768(8)
c, Å	18.090(1)	18.0698(9)
α, deg	90	90
β, deg	90.101(2)	90
γ, deg	90	90
V, $Å^3$	5777.2(6)	5348.6(4)
Z	8	8
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
D_{calc}, g/mL	1.619	1.715
abs coeff, cm^{-1}	31.6	47.11
F(000)	2832	2720
$2\Theta_{max}$, deg	49.4	52.1
total reflns	25541	24078
independent reflns	9392	5064
data/restraints/ parameters	6902/0/569	1927/0/262
GOF	1.606	0.64
final *R* indices [$I > 2\sigma(I)$]	$R = 0.0527$, $wR_2 = 0.0924$	$R = 0.021$, $wR_2 = 0.021$
R indices (all data)	0.0810	0.064
largest diff peak and hole (e $Å^{-3}$)	1.373, −2.152	0.50, −0.50

spectrum of the diamagnetic ytterbium derivative **2** is indicative of a C_s symmetric complex in solution and is otherwise unremarkable; the paramagnetism of the samarium compound **1** did not provide any meaningful characterization by NMR spectroscopy. Both complexes are thermally robust, e.g., **1** decomposes only above 270 °C under nitrogen and its EI-mass spectrum shows a strong [M^+] fragment.

X-ray Crystal Structure of [$C_5Me_4SiMe_2(^iPr_2$-tacn)]SmI (1) and [$C_5Me_4SiMe_2(^iPr_2$-tacn)]YbI (2). Crystals of compound **1** suitable for X-ray diffraction were grown by cooling a saturated THF solution to −10 °C. The molecular structure of **1** is presented in Figure 1 with a list of partial bond lengths and angles available in Table 1. Complete details of the structural analyses of the samarium and ytterbium derivatives are compiled in Table 3. Compound **1** crystallizes with two independent molecules in the unit cell; since they exhibit similar geometries, only one will be described here. The lattice also contains 0.5 equiv of THF of crystallization. Complex **1** is monomeric in the solid state with the samarium center bound to the cyclopentadienyl group, an iodide, and all three nitrogens of the triazacyclononane moiety. The geometry about the lanthanide center is best described as distorted trigonal bipyramidal, with N(1) of the triazacyclononane ring and the iodide atom occupying the axial positions (N(1)−Sm(1)−I(1) = 158.7(2)°) and N(2), N(3), and the Cp centroid in equatorial positions (N(2)−Sm(1)−N(3) = 67.9(3)°, N(2)−Sm(1)−Cp = 140.15°, N(3)−Sm(1)−Cp = 133.91°). The samarium center is bound to the tetramethylcyclopentadienyl ring in an η^5-manner; the samarium−carbon bond lengths range from 2.767(11) to 2.949(11) Å, resulting in a Sm−Cp(centroid) distance of 2.583 Å. This compares with a related value of 2.534 Å reported for [$(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$.[8] In general, the Sm−Cp(centroid) distances in unsolvated complexes such as $(C_5Me_5)_2Sm$[17] or $(C_5H^iPr_4)_2Sm$[18] are shorter due to the increased electrophilicity of the metal center and/or decreased coordination numbers. The samarium−nitrogen bond lengths are all ~2.7 Å, which is typical for dative bonds between samarium and bulky amine donors, and is similar to the bond lengths observed in (1,4,7-triazacyclononane-1,4,7-triyltris(2-(ethylimino)-propionato))samarium (2.669(4)−2.690(4) Å).[19] The samarium−iodide bond length of 3.2161(12) Å is shorter than the bridging samarium−iodide bonds observed in [$(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ (3.356(2) and 3.459(2) Å)[8] and also shorter than the terminal Sm−I linkages reported for $SmI_2(dme)_3$ (dme = dimethoxyethane; 3.3550(8) and 3.3832(8) Å).[20] By way of comparison, the terminal Sm−I distances in the two crystallographically in-

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dependent molecules in the unit cell of the trivalent species $(C_5Me_5)_2SmI(THF)$ are 3.043(2) and 3.053(2) Å.[21]

Cooling a saturated THF solution of **2** resulted in large red blocks that were amenable to diffraction studies; pertinent bond lengths and angles can be found in Table 2. In contrast to the Sm example above, the ytterbium derivative **2** crystallizes without any solvent molecules in the lattice. The general structural features of **2** are similar to those already discussed for **1**. The smaller ionic radius of ytterbium versus samarium results in smaller Ln−I (3.0613(6) vs 3.2161(12) Å), Ln−N (2.586 (av) vs 2.718 (av) Å), and Ln−C (2.723 (av) vs 2.854 (av) Å) bond lengths in **2**. These observations are in agreement with the difference in ionic radii of Sm(II) and Yb(II), which is generally cited to be 0.18 Å.[22] Compound **2** maintains a Yb−I bond that is shorter than that found in the dimeric species $[(C_5Me_5)Yb(\mu\text{-}I)(THF)_2]_2$ (3.134(1) and 3.175(1) Å)[23] or the monomeric bis-THF adduct $(C_5H_3\text{-}1,2\text{-}(CH_2CH_2NMe_2)_2)YbI(THF)_2$,[24] in which the ytterbium center is also coordinated by two pendant dimethylamine donors (3.2529(8) Å). The closest comparison is with the trispyrazolylborate species, (hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate)YbI(THF), which exhibits a single ytterbium−iodide bond measuring 3.0536(8) Å.[25]

Attempts to alkylate compounds **1** and **2** with a range of typical reagents such as alkyllithiums and potassium species have been unsuccessful to date. Compound **1** showed no tendency to polymerize ethylene upon activation with methylaluminoxane (MAO) in toluene (Al/Sm = 200, 45 °C, 1 atm, 1 h).

Experimental Section

General Methods. Standard Schlenk-line and glovebox techniques were used. Tetrahydrofuran was purified by passage through a column of activated alumina and degassed with argon prior to use. C_5D_5N was vacuum transferred from sodium. $[C_5Me_4SiMe_2(^iPr_2\text{-tacn})]K$,[16] $SmI_2(THF)_2$,[26] and $YbI_2(THF)_2$[26] were prepared by literature methods. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected. ^1H NMR spectra were recorded at ambient temperature on a Bruker AMX-300 spectrometer. ^1H NMR chemical shifts are given relative to C_5D_4HN (8.71 ppm). IR samples were prepared as Nujol mulls and taken between KBr plates. Elemental analyses were determined at the College of Chemistry, University of California, Berkeley. (For both complexes, carbon analyses were lower than expected despite numerous recrystallization attempts and extended combustion in the analyzer. The cause is still not clear, but would seem to be due to either the presence of undetected impurities or incomplete combustion.) Single-crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley.

$[C_5Me_4SiMe_2(^iPr_2\text{-tacn})]SmI$ (1). $[C_5Me_4SiMe_2(^iPr_2\text{-tacn})]K$ (0.43 g, 1.0 mmol) and $SmI_2(THF)_2$ (0.55 g, 1.0 mmol) were combined in a Schlenk tube and THF (20 mL) was added. This caused the immediate formation of a red blue solution. The slurry was stirred overnight, and was then filtered to remove insoluble KI. The solution was concentrated and then stored at −30 °C overnight, resulting in the formation of dark red crystals of **1** (0.57 g, 85% yield). Mp: 270 °C dec. EI-MS: 669 (M^+, correct isotope pattern observed). Anal. Calcd for $C_{25}H_{48}N_3O_{0.5}ISiSm$: C, 42.65; H, 6.87; N, 5.97. Found: C, 41.87; H, 6.81; N, 6.23.

$[C_5Me_4SiMe_2(^iPr_2\text{-tacn})]YbI$ (2). The ytterbium derivative **2** was prepared in a similar manner from $[C_5Me_4SiMe_2(^iPr_2\text{-tacn})]K$ and $YbI_2(THF)_2$ as red blocks (0.55 g, 80% yield). ^1H NMR (C_5D_5N): δ 2.91 and 2.61 (mult, 8H, ring CH_2), 2.72 (sept, 2H, $CHMe_2$, $^3J_{H-H} = 6.5$ Hz), 2.36 (s, 4H, ring CH_2), 1.99 and 1.85 (s, 12H, C_5Me_4), 0.92 (d, 12H, $CHMe_2$, $^3J_{H-H} = 6.5$ Hz), 0.11 (s, 6H, $SiMe_2$). EI-MS: 691 (M^+, correct isotope pattern observed). Anal. Calcd for $C_{23}H_{44}N_3ISiYb$: C, 40.00; H, 6.42; N, 6.08. Found: C, 39.4; H, 6.19; N, 6.50.

General Procedures for X-ray Crystallography. A crystal of appropriate size was mounted on a glass capillary with Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART diffractometer/CCD area detector,[27] centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrix and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected and the raw data were then integrated (XY spot spread = 1.60°; Z spot spread = 0.60°) with SAINT.[28] Cell dimensions were calculated from the reflections with $I > 10\sigma$. Data analysis and absorption correction were performed with Siemens XPREP.[29] The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on comparison of redundant and equivalent reflections was applied with SADABS.[30] The measured reflections were averaged. The structures were solved and refined with the teXsan software package[31] using direct methods[32] and expanded using Fourier techniques.[33] All non-hydrogen atoms were refined anisotropically, unless stated otherwise. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations, but were not refined, unless stated otherwise. The final residuals were refined against the data for which $F^2 > 3\sigma(F^2)$. The quantity minimized by the least-squares program was $\sum_w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

The initial solution of the structure of $[C_5Me_4SiMe_2(^iPr_2\text{-tacn})]SmI$ (**1**) was executed in teXsan, but exhibited a number of anomalously large peaks in its Fourier map, and upon

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refinement of the smaller atoms anisotropically, numerous atoms were found to be nonpositive definite. Twinning in the crystals was determined, and a 2-fold rotation twin law (on *a*) was applied to the structure in SHELXTL.[34] The structure was then refined in SHELXTL.[35] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included but not refined.

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Supporting Information Available: Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ [fax +44-1223-336033 or e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk]. This material is available free of charge via the Internet at http://pubs.acs.org.

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