deprotonations of tppm[2b,17] and its sulfides.[18] Perhaps the deprotonation of tppm in I would produce a planar P_3C ligand[19] which could not be accommodated by a single iron atom. Studies of tppm complexes with other metals are in progress to address this point.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, Occidental Research Corp., and Ashland Oil for financial support.

Registry No. I, 95156-04-0; I·CH_2Cl_2, 95156-05-1; III, 95192-55-5; tppm, 28926-65-0; [Fe(*p*-xylene)(Cp)][PF_6], 34978-37-5.

Supplementary Material Available: Listings of positional, thermal, and group parameters (Tables II–V) and experimental and calculated structure factors (Table VI) (31 pages). Ordering information is given on any current masthead page.

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[19] For comparison, the mean P–C distance and P–C–P angles in free [$HC(PSPh_2)_3$],[18e] [NBu_4][$C(PSPh_2)_3$],[18a] and [HgCl{η^3-$C(PSMe_2)_2(PSPh_2)$}],[18d] are 1.883 Å and 115.3°, 1.762 Å and 119.9°, and 1.769 Å and 116.4°, respectively.

Organometallic Compounds of the Lanthanides. 24.[1] Synthesis and X-ray Crystallographic Characterization of the First Organolanthanide Derivative with a Lanthanide–Silicon Bond

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Summary: Bis(cyclopentadienyl)samarium chloride and bis(cyclopentadienyl)lutetium chloride react with (trimethylsilyl)lithium in 1,2-dimethoxyethane (dme) to give complexes of the type [$Li(dme)_3$][$(C_5H_5)_2Ln(Si(CH_3)_3)_2$] (Ln = Sm, Lu). The molecular structure of [$Li(dme)_3$][$(C_5H_5)_2Sm(Si(CH_3)_3)_2$] has been elucidated through complete X-ray analysis. The crystals are monoclinic, space group $P2/n$ (nonstandard setting of $P2/c$, No. 13), with a = 14.460 (4) Å, b = 9.018 (3) Å, c = 14.558 (7) Å, β = 103.96 (3)°, V = 1842.3 Å^3, ρ_{calcd} = 1.269 g/cm^3, and Z = 2. The structure was solved by Patterson and Fourier techniques from 2621 unique reflections ($I \geq 3\sigma(I)$) corrected for Lorentz and polarization effects but not for absorption (μ = 15.89 cm^{-1}). The final R value is 0.062 (R_w = 0.079). Principal dimensions are as follows: Sm–Cp = 2.316 (7) Å, Sm–Si = 2.880 (2) Å, Cp-Sm-Cp′ = 131.6 (2)°, Si-Sm-Si′ = 90.07 (7)°.

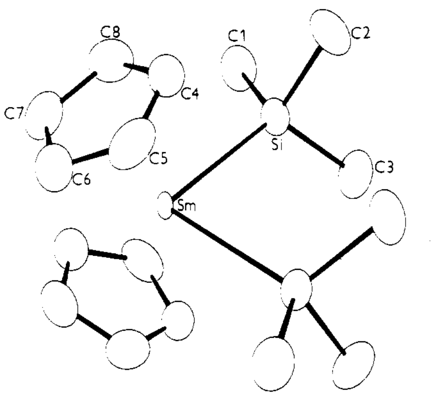
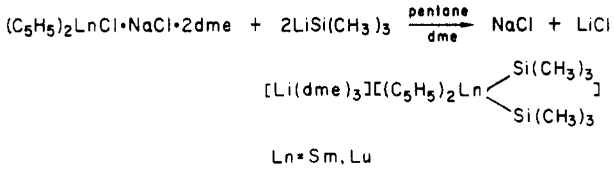


Figure 1. ORTEP plot of the [$(C_5H_5)_2Sm(Si(CH_3)_3)_2$]$^-$ anion.

Lanthanides are generally thought to be hard Lewis acids.[2] Thus the most thermodynamically stable compounds are formed between carbon, halogen, or oxygen donors and lanthanide acceptors.[3] Only few examples of organometallic compounds of the lanthanides with bonds to soft donors such as P,[4-8] As,[9] and S[10] are known. We reported the synthesis of the first bis(cyclopentadienyl)lanthanide triphenylgermyl and triphenylstannyl complexes.[11] Organometallic compounds of the lanthanides with bonds to silicon have not been described as yet. The lanthanide–silicon bond might possess a high degree of "covalency" because of the good donor properties of the trimethylsilyl ligand, although the bonding in organoactinides and organolanthanides is considered to be ionic.[12]

Reaction of $(C_5H_5)_2SmCl{\cdot}NaCl{\cdot}2dme$ (dme = 1,2-dimethoxyethane) or $(C_5H_5)_2LuCl{\cdot}NaCl{\cdot}2dme$ with an equimolar amount of $LiSi(CH_3)_3$ in dme at −78 °C does not yield the hoped for bis(cyclopentadienyl)lanthanide trimethylsilyl complexes $(C_5H_5)_2Ln{-}Si(CH_3)_3$ (Ln = Sm, Lu) but instead the cation–anion pairs [$Li(dme)_3$][$(C_5H_5)_2Ln(Si(CH_3)_3)_2$] (Ln = Sm, Lu) (eq 1).[13]



$$(C_5H_5)_2LnCl{\cdot}NaCl{\cdot}2dme + 2LiSi(CH_3)_3 \xrightarrow[dme]{pentane} NaCl + LiCl + [Li(dme)_3][(C_5H_5)_2Ln\left\langle\begin{matrix}Si(CH_3)_3\\ Si(CH_3)_3\end{matrix}\right.] \quad (1)$$

Ln = Sm, Lu

The yellow complexes are extremely sensitive toward moisture and air. They decompose slowly at room tem-

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[13] $Na(C_5H_5)$ (0.84 g, 9.4 mmol) was added to a suspension of $SmCl_3$ (1.2 g, 4.7 mmol) in 70 mL of dme. After 3 h of stirring, the reaction mixture was cooled to −78 °C. Formation of $(C_5H_5)_2SmCl{\cdot}NaCl{\cdot}2dme$ in 80% yield was assumed and an equimolar amount of $LiSi(CH_3)_3$ (3.76 mmol, 18.8 mL of a 0.2 M pentane solution) was added slowly. After the mixture was warmed to room temperature, stirred for an additional 14 h, decanted from the LiCl formed, and concentrated to 20 mL, pentane (20 mL) was added. After the mixture was cooled to −23 °C for 1 week, yellow crystals of [$Li(dme)_3$][$(C_5H_5)_2Sm(Si(CH_3)_3)_2$] were collected in 20% yield, based on $SmCl_3$.

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Table I. Selected Distances (Å) and Angles (Deg) in $[Li(dme)_3][(C_5H_5)_2Sm(Si(CH_3)_3)_2]$ with Standard Deviations in Parentheses

Bond Distances			
Sm-Si	2.880 (2)	Sm-C7	2.582 (7)
Sm-C4	2.637 (8)	Sm-C8	2.604 (8)
Sm-C5	2.636 (7)	Sm-Cp[a]	2.316 (7)
Sm-C6	2.602 (7)		
Bond Angles			
Si-Sm-Si′ [b]	90.07 (7)	Si-Sm-Cp′	107.8 (2)
Si-Sm-Cp	105.9 (2)	Cp-Sm-Cp′	131.6 (2)

[a] Cp denotes the centroid of the cyclopentadienyl ring. [b] Primed atoms represent transformed coordinates of the type $1.5 - x, y, 1.5 - z$.

perature, even when kept in an argon atmosphere. Both derivatives were identified by elemental analyses[14] and NMR spectroscopy.[15] Hydrolysis yields $(CH_3)_3SiH$ identified by its absorption in the IR spectrum[16] at 2123 cm^{-1}.

The molecular structure shows $[Li(dme)_3][(C_5H_5)_2Sm(Si(CH_3)_3)_2]$ as discrete cation and anion pairs. Both the cation and the anion possess crystallographically imposed C_2 symmetry;[17] half of both is unique.

The anion $[(C_5H_5)_2Sm(Si(CH_3)_3)_2]^-$, shown in Figure 1, is composed of two cyclopentadienyl and two trimethylsilyl ligands arranged in a distorted tetrahedral fashion around the samarium atom, providing a formal coordination number of eight for Sm. The length of the five Sm–C(η^5) bonds varies between 2.582 (7) and 2.637 (8) Å with an average of 2.61 (3) Å (Table I). This value appears surprisingly short when compared with the d(Sm–C(η^5)) for octacoordinated compounds reported earlier[19] (2.75 (5),[18] 2.76 (3),[20] 2.72 (3) Å[7]).

It has been shown[12] that the distance M–C(η^5) for bis- and tris(cyclopentadienyl)lanthanide and -actinide complexes varies in direct proportion to the metal ion size, which is a clear indication of predominantly ionic bonding in these compounds. The effective ionic radius for the C_5H_5 ligand was calculated by substracting the metal ion radius[21] from d(M–C(η^5)) and determined to be 1.64 (4) Å for 23 organolanthanide and -actinide derivatives included in the calculations.

For the three accurately described bis(cyclopentadienyl)samarium derivatives[7,18,20] effective ionic radii between 1.68 and 1.64 Å are obtained for the C_5H_5 ligand (r_{Sm} = 1.08 Å for octacoordinated compounds[21]). In contrast to this, the Sm–C(η^5) distance for the anion $[(C_5H_5)_2Sm(Si(CH_3)_3)_2]^-$ would lead to an effective ionic radius of only 1.53 Å for the cyclopentadienyl group. We take this as an indication for a considerably degree of "covalency" in the Sm–C bonds of this anion which was not yet observed this clearly. This trend persists, when the Sm–Si bonds are considered. For the predominantly ionic bonding in $(C_5H_5)_2Zr(Cl)(Si(C_6H_5)_3)$,[22] the Zr–Si separation is 2.813 (2) Å. The ionic radius of Sm is 0.239 Å greater;[21] however, the Sm–Si bond is only 0.067 Å longer (d(Sm–Si) = 2.880 (2) Å) than the Zr–Si bond. Again a covalent shortening of the bonds to samarium may be taking place.

Since all bonds to samarium are shorter than expected for a typical ionic complex, we propose that there is a transfer of electronic charge from the ligands to the metal atom. This behavior can introduce partially covalent bonding into the bonds to samarium and thus cause the observed shortening of the bonds. To examine this possibility, we are presently investigating the f–f transitions of the complex. The bonding parameters associated with the $[Li(dme)_3]^+$ cation are normal.

Acknowledgment. We thank the Fonds der Chemischen Industrie for a "Doktoranden-Stipendium" (E.H.) as well as for generous support of this work, which was also supported by the Deutsche Forschungsgemeinschaft and by special grants of the TU Berlin within the exchange program TU Berlin/University of Oklahoma and the research project "Materialien für neue Technologien".

Registry No. Dme, 110-71-4; $Na(C_5H_5)$, 4984-82-1; $SmCl_3$, 10361-82-7; $(C_5H_5)_2SmCl$, 56200-25-0; $LiSi(CH_3)_3$, 18000-27-6; $[Li(dme)_3][(C_5H_5)_2Sm(Si(CH_3)_3)_2]$, 95156-25-5; $[Li(dme)_3][(C_5H_5)_2Lu(Si(CH_3)_3)_2]$, 95156-27-7; $(C_5H_5)_2LuCl$, 76207-13-1.

Supplementary Material Available: Tables of data collection details, final fractional coordinates, thermal parameters, bond distances and angles, calculated hydrogen positions, least-squares planes, and structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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(14) Anal. Calcd for $C_{28}H_{58}LiO_6Si_2Sm$: C, 47.75; H, 8.31; Sm, 21.35. Found: C, 46.55; H, 7.25; Sm, 22.12; decomp pt, 136 °C. Anal. Calcd for $C_{28}H_{58}LiLuO_6Si_2$: C, 46.14; H, 8.03; Lu, 24.00. Found: C, 45.51; H, 7.73; Lu, 24.04; decomp pt, 86 °C. Satisfactory microanalytical data were difficult to obtain since the crystalline products lose coordinatively bonded dme when dried in vacuo.

(15) ^1H NMR (C_6D_6): Sm derivative, δ 0.18 (s, $(CH_3)_3Si$, half width 14.5 Hz), 3.15 (s, CH_3O), 3.26 (s, CH_2O), 12.09 (s, C_5H_5, half width 37.8 Hz); Lu derivative, δ 0.515 (s, $(CH_3)_3Si$), 3.07 (s, CH_3O), 3.15 (s, CH_2O), 6.13 (s, C_5H_5).

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(17) Crystal data: space group $P2/n$, monoclinic (nonstandard setting of $P2/c$, No. 13), a = 14.460 (4) Å, b = 9.018 (3) Å, c = 14.558 (7) Å, β = 103.96 (3)°, ρ_{calcd} = 1.269 g·cm^{-3}, Z = 2 cation–anion units. Raw data corrected for Lorentz and polarization effects, but because of the low absorption coefficient (μ = 15.89 cm^{-1}) not for absorption. Full-matrix least-squares refinement based on 2621 observed reflections ($I \geq 3\sigma(I)$) led to a final $R = \sum(|F_o| - |F_c|/\sum|F_o| = 0.062$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Sm and Li lie on a special position on the twofold axis (Wyckoff notations e and f). The twofold axis bisects one of the three dme ligands of the cation.

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ESR Study of Paramagnetic Intermediates in the Low-Temperature Photochemistry of Olefins and $Fe(CO)_5$

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Summary: The low-temperature UV irradiation of dilute pentane solutions of $Fe(CO)_5$ and tetramethylethylene produces intense ESR spectra of (1,1,2-trimethylallyl)$Fe(CO)_3$· radicals (I). Similar irradiation of 2,3-dimethyl-1-butene yields the isomeric (2-isopropylallyl)$Fe(CO)_3$· radical II at −130 °C but only I at −80 °C. The mechanism for the formation and isomerization of these and homologous radicals is discussed.

The thermal and photochemical isomerization of olefins in the presence of simple iron carbonyls has been exten-

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