

Neutral lanthanide silyl complexes via σ -bond metathesis reactions¹

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Received 4 August 1995; in revised form 6 November 1995

Abstract

The alkyl complexes $\text{Cp}_2^* \text{LnCH}(\text{SiMe}_3)_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; Ln = Sm, Nd, Y) and $\text{Cp}_2'' \text{LnCH}(\text{SiMe}_3)_2$ ($\text{Cp}'' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$; Ln = Sm, Nd) react with neat $\text{H}_2\text{Si}(\text{SiMe}_3)_2$ (ca. 5 equivalents) at 85 °C to give the new silyl complexes $\text{Cp}_2^* \text{LnSiH}(\text{SiMe}_3)_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; Ln = Sm (3), Nd (4), Y (5)) and $\text{Cp}_2'' \text{LnSiH}(\text{SiMe}_3)_2$ ($\text{Cp}'' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$; Ln = Sm (6), Nd (7)). These neutral silyl complexes have been completely characterized, and are monomeric in pentane solution at room temperature. The structure of 3 reveals that this compound forms dimers in the solid state via intermolecular Sm \cdots CH₃–Si interactions. The Sm–Si bond length in 3 is 3.052 (8) Å. Initial reactivity studies characterize Ln–Si bonds as being highly reactive.

Keywords: Silicon; Samarium; Neodymium; Yttrium; Cyclopentadienyls; Silyls

1. Introduction

Early transition metal silyl complexes have provided numerous transformations which are not available to late transition metal analogues [1]. In particular, d^0 metal silyl complexes are highly reactive toward insertions [2] and σ -bond metathesis processes [3], which appear to involve participation of the d^0 M–Si σ -bond in four-center, concerted transition states. Observation of stoichiometric σ -bond metathesis reactions involving a d^0 metal center, silicon and hydrogen has led to postulation of a new coordination polymerization mechanism for the dehydrocoupling of silanes (Scheme 1) [3f].

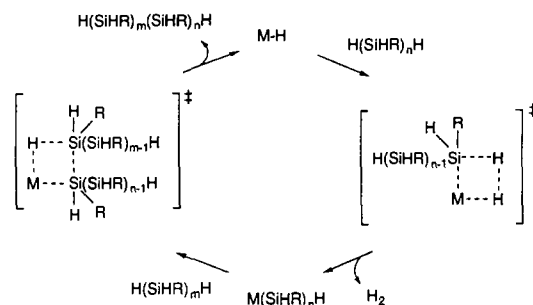
This mechanism strongly suggests that lanthanide and actinide complexes should be active dehydropolymerization catalysts, given their well known participation in related σ -bond metathesis reactions with hydrocarbons [4]. In fact, it has recently been reported that lanthano-cene complexes are catalysts for the dehydrocoupling of primary silanes to polysilanes [5,6]. Our study of the catalytic activity of $[\text{Cp}_2^* \text{LnH}]_2$ [4d] ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; Ln = Sm, Nd) toward dehydropolymer-

ization of phenylsilane revealed low activity toward polysilane chain elongation. These dehydrocoupling polymerizations are slow in comparison with polymerizations catalyzed by mixed-ring zirconium complexes, and produce only small oligomers [6]. This somewhat puzzling observation heightened our interest in the chemistry of lanthanide–silicon bonds, and motivated the investigation described here.

The structure and chemistry of Group 3, lanthanide, and actinide alkyl complexes are well understood [7]. In contrast, very few silyl derivatives of these metals have been prepared and studied, mainly owing to the lack of general synthetic routes to this class of compounds. We recently reported [8] the first scandium silyl complexes $\text{Cp}_2 \text{Sc}(\text{SiR}_3)\text{THF}$ ($\text{SiR}_3 = \text{Si}(\text{SiMe}_3)_3$, $\text{Si}(\text{SiMe}_3)\text{Ph}_2$, Si^tBuPh_2), and Schumann and coworkers [9] have synthesized the only previously reported complexes possessing lanthanide–silicon bonds, $[\text{Li}(\text{DME})_3][\text{Cp}_2 \text{Ln}(\text{SiMe}_3)_2]$ (Ln = Sm, Dy, Ho, Er, Tm, Lu). The first organoactinide silyl complex, $\text{Cp}_3 \text{USiPh}_3$ [10], was recently reported and we have communicated the synthesis of the thorium derivatives $\text{Cp}_2^* \text{Th}(\text{SiR}_3)\text{Cl}$ ($\text{SiR}_3 = \text{SiPh}_3$, Si^tBuPh_2 , $\text{Si}(\text{SiMe}_3)\text{Ph}_2$) [11]. Here we report a new route to stable (but reactive) lanthanide silyl complexes via a σ -bond metathesis process which has produced the first neutral silyl complexes. These synthetic studies, which were previously communicated [12], have

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¹ Dedicated to Professor Herbert Schumann, on the occasion of his 60th birthday.

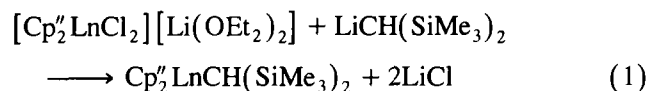


Scheme 1.

involved both Cp^* and Cp'' ($\eta^5-C_5Me_4Et$) derivatives. The latter compounds were utilized in mechanistic studies involving crossover experiments, to be published elsewhere.

2. Synthesis of $(\eta^5-C_5Me_4Et)_2LnCH(SiMe_3)_2$ complexes

The synthesis of $Cp''_2Ln(silyl)$ complexes required starting materials possessing Cp'' ancillary ligands. The alkyl complexes $Cp''_2LnCH(SiMe_3)_2$ ($Cp'' = \eta^5-C_5Me_4Et$; **1**, $Ln = Sm$; **2**, $Ln = Nd$) were synthesized following the procedure previously developed for the analogous Cp^* derivatives (Eq. (1)) [4d].



1, $Ln = Sm$

2, $Ln = Nd$

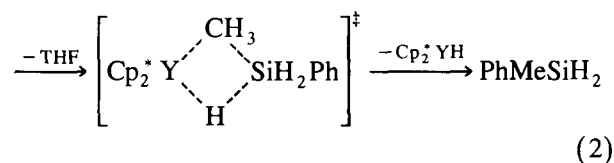
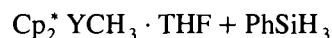
These complexes are air- and moisture-sensitive, thermally stable and extremely soluble in nonpolar solvents. Both **1** and **2** possess equivalent $SiMe_3$ groups, but inequivalent Cp'' ligands (by 1H NMR spectroscopy). For **1**, the Me groups of the Cp'' ligands are well separated in the 1H NMR spectrum, but resonances for the Et groups overlap. The 1H NMR spectrum of **2** at room temperature displays only three resonances for the Cp'' Me groups, in a 6:6:12 ratio (two resonances are overlapping). Also, the inequivalent ethyl groups of **2** give rise to peaks that overlap, but at $40^\circ C$ two sets of distinct resonances are observed. Thus, both **1** and **2** exhibit hindered rotations about their $Ln-C$ bonds, which results in inequivalent Cp'' groups at room temperature and even up to $80^\circ C$. Similar behavior has been reported for the corresponding $Cp^*_2LnCH(SiMe_3)_2$ complexes [4d].

3. Synthesis of silyl complexes

Initially, we attempted to synthesize new lanthanide silyl complexes by salt-elimination procedures (involv-

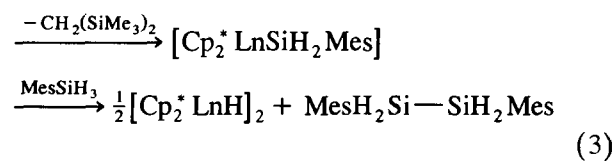
ing silyl anion reagents) which had been successfully employed to prepare silyl derivatives of scandocene [8]. However, reactions of $[Cp^*_2NdCl_2][Li(OEt_2)_2]$ [13] with $(THF)_3LiSi(SiMe_3)_3$, $(THF)_3LiSiPh_3$, and $(THF)_3LiSi^tBuPh_2$ gave only small amounts of the corresponding hydrosilane, along with intractable mixtures of neodymium-containing products. A second approach to the synthesis of $Ln-Si$ bonded compounds was suggested by the successful application of σ -bond metathesis reactions for the preparation of new silyl derivatives of Zr and Hf [14]. We therefore examined this approach, and chose lanthanide alkyl derivatives as the starting materials.

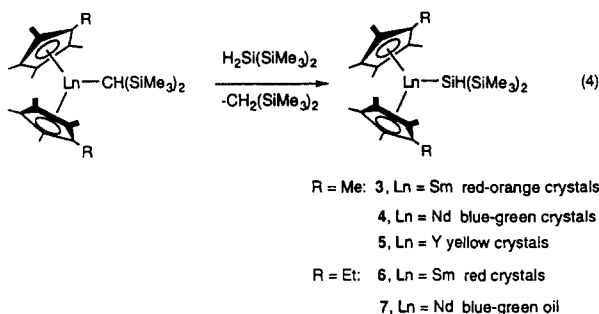
As described below, the σ -bond metathesis route to $Ln-Si$ bonded complexes did prove successful, but, as demonstrated by initial exploratory reaction chemistry, these processes are very sensitive to the steric properties of the starting materials. For example, the yttrium complex $Cp^*_2YMe(THF)$ [15] merely converts $PhSiH_3$ to $PhMeSiH_2$, indicating that the primary σ -bond metathesis process involves a four-center transition state in which the silyl group is transferred to carbon, rather than yttrium (Eq. (2)).



In attempts to sterically direct transfer of the silyl group to the metal, the bulkier alkyl derivatives $Cp^*_2LnCH(SiMe_3)_2$ ($Ln = Sm, Nd$) [4d] were employed. As might be expected, these complexes do not react with sterically hindered silanes. Thus, no reaction is observed between $Cp^*_2NdCH(SiMe_3)_2$ and Ph_3SiH or Ph_2MeSiH (room temperature, 8 days), or between $Cp^*_2YCH(SiMe_3)_2$ and iPr_2SiH_2 (30 h, $85^\circ C$).

Reactions are observed with less hindered silanes. For example, $Cp^*_2YCH(SiMe_3)_2$ [16] reacts rapidly with $PhSiH_3$ and $PhMeSiH_2$ to produce several products (1H NMR spectroscopy). Cleaner reactions were observed to take place between $Cp^*_2LnCH(SiMe_3)_2$ ($Ln = Sm, Nd$) complexes and $MesSiH_3$ ($Mes = mesityl$; 10 min at $70^\circ C$), to quantitatively produce $CH_2(SiMe_3)_2$, the corresponding hydrides $[Cp^*_2LnH]_2$, and $MesH_2Si-SiH_2Mes$ (Eq. (3)).





Similar dehydrocoupling processes were observed upon reaction of $\text{Cp}_2^* \text{NdCH}(\text{SiMe}_3)_2$ with PhMeSiH_2 (12 h, 25 °C), $\text{C}_3\text{H}_6\text{SiH}_2$ (silacyclobutane, 12 h, 25 °C), and $(\text{PhCH}_2)\text{Me}_2\text{SiH}$ (8 h, 75 °C). Such reactions probably involve lanthanide silyl intermediates, which undergo rapid dehydrocoupling reactions to give the observed products [3f]. From the above observations it seemed that a silane of intermediate steric properties was required, since only relatively unhindered silanes react with $\text{Cp}_2^* \text{LnCH}(\text{SiMe}_3)_2$, while steric bulk in the resulting $\text{Cp}_2^* \text{LnSiR}_3$ appeared necessary to provide stabilization toward further σ -bond metathesis reactions [3f].

The alkyl complexes $\text{Cp}_2^* \text{LnCH}(\text{SiMe}_3)_2$ (Ln = Sm, Nd, Y) and $\text{Cp}_2^* \text{LnCH}(\text{SiMe}_3)_2$ (Ln = Sm, Nd) react with neat $\text{H}_2\text{Si}(\text{SiMe}_3)_2$ (ca. 5 equivalents) at 85 °C to give the new silyl complexes $\text{Cp}_2^* \text{LnSiH}(\text{SiMe}_3)_2$ (3, 4, 5) and $\text{Cp}_2^* \text{LnSiH}(\text{SiMe}_3)_2$ (6, 7) (Eq. (4)).

The high concentration of silane is necessary in order to suppress competing thermal decomposition of the

alkyl derivative via an internal metallation which gives $[\text{Cp}_2^* \text{Ln}(\mu\text{-H})(\mu\text{-}\eta^1:\eta^5\text{-CH}_2\text{C}_3\text{Me}_4)\text{LnCp}^*]$ [17]. Attempts to follow the course of this reaction by ^1H NMR spectroscopy revealed that it is characterized by a variable induction time which does not depend on the initial concentrations of starting materials. More thorough mechanistic studies have allowed us to conclude that these reactions do not actually involve direct interactions of Ln–C and Si–H bonds, but instead proceed via a second-order autocatalytic process catalyzed by hydrogen (Scheme 2) [18].

The new silyl complexes are extremely air- and moisture-sensitive, but thermally stable in solution and in the solid state. The presence of impurities (below 5 % by ^1H NMR spectroscopy) is observed to accelerate their decomposition, to $\text{H}_2\text{Si}(\text{SiMe}_3)_2$ and unidentified lanthanide-containing products. The extreme solubility of these complexes in nonpolar solvents complicates their isolation as crystalline solids, and complex 7 was isolated only as a blue-green oil (by concentration and cooling to –78 °C). Attempts to render the latter material crystalline, by concentration and cooling of pentane or hexamethyldisiloxane solutions, failed. Complexes 3 and 4 are monomeric in pentane solution by isothermal distillation (see Experimental section), and we assume that 5 and the more crowded silyls 6 and 7 are also monomeric in solution.

The NMR spectra for the Nd and Sm compounds are paramagnetically shifted and broadened owing to the partially filled f-shell [19]. Figs. 1–3 provide plots of the ^1H NMR chemical shifts for the Cp^* resonances of $\text{Cp}_2^* \text{NdCH}(\text{SiMe}_3)_2$, 4, and 3 as a function of the

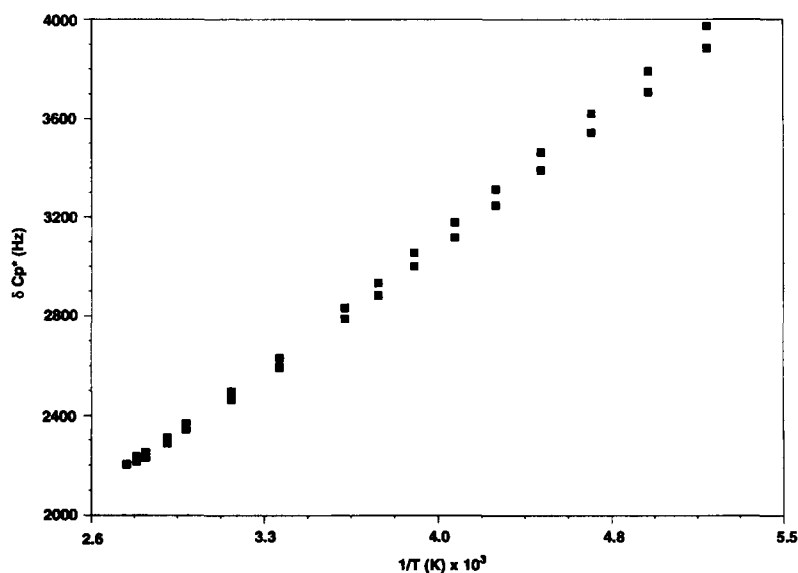


Fig. 1. Plot of δ vs. $1/T$ (K) for the Cp^* protons of $\text{Cp}_2^* \text{NdCH}(\text{SiMe}_3)_2$.

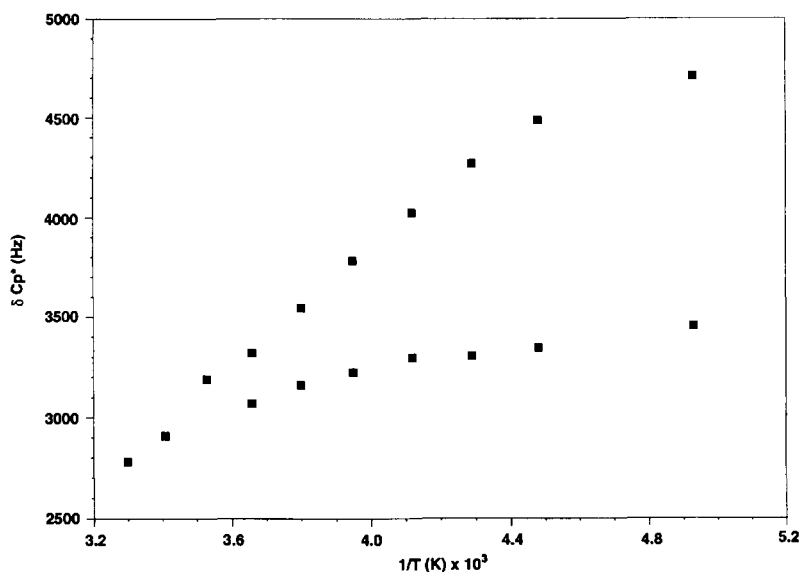


Fig. 2. Plot of δ vs. $1/T$ (K) for the Cp^* protons of $\text{Cp}_2^*\text{NdSiH}(\text{SiMe}_3)$ (**4**).

reciprocal of temperature [20]. Data for $\text{Cp}_2^*\text{NdCH}(\text{SiMe}_3)_2$ displays linear, Curie–Weiss behavior, indicating that this compound does not change its structure down to -80°C . Figs. 2 and 3 show that the temperature dependence of the ^1H NMR chemical shifts for the Cp^* ligands of **3** and **4** deviate considerably from Curie–Weiss behavior (particularly after decoalescence), perhaps because of a temperature-dependent equilibrium involving paramagnetic species [20]. The low temperature (-100°C , toluene- d_8 solution) ^1H NMR spectrum of **4** contains five Cp^* resonances and five resonances in the SiMe_3 region (-3 to -60 ppm, see Experimental section). Therefore, at low temperature several species are resolved. It has not been possible to assign

these peaks, but we assume that the variable-temperature behavior of the spectra reflect monomer–dimer equilibria and/or the presence of agostic $\text{Nd} \cdots \text{CH}_3\text{—Si}$ or $\text{Nd} \cdots \text{H—Si}$ interactions [21] (Eq. (5)). For the samarium silyl **3** and the yttrium silyl **5**, only one species is observed over the temperature range -80 to 25°C , as indicated by ^1H NMR spectra.

Complexes **3**, **4** and **5** exhibit equivalent SiMe_3 and Cp^* resonances in their room-temperature ^1H NMR spectra, indicating fast rotation about the Ln—Si bonds. The Cp^* resonances decoalesce into two singlets at low temperature (e.g. -30°C for **3**, -10°C for **4**, and 0°C for **5**). Use of the two site exchange approximation [22] gives activation barriers for rotation about the Ln—Si

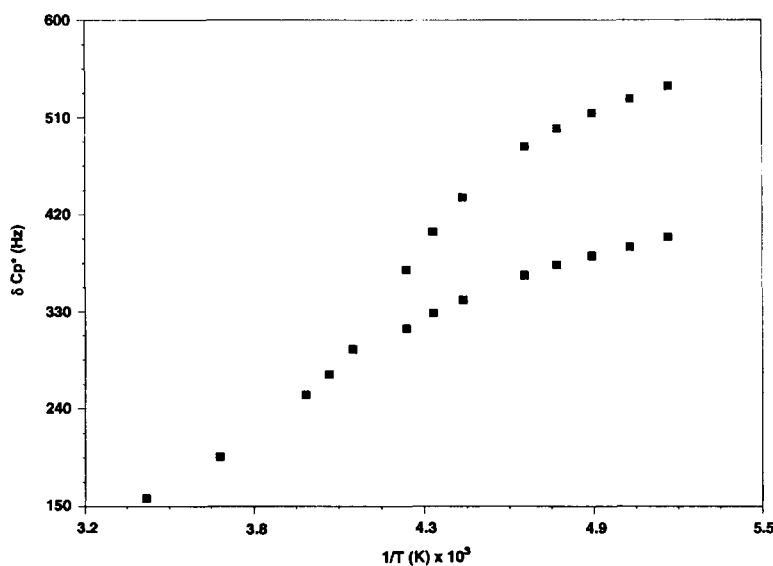
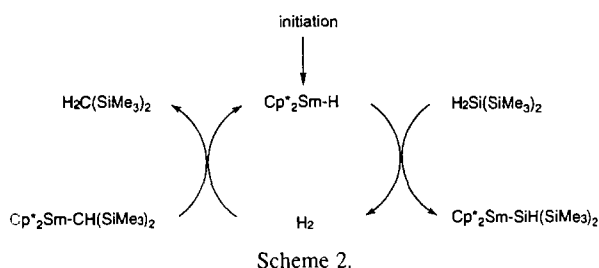
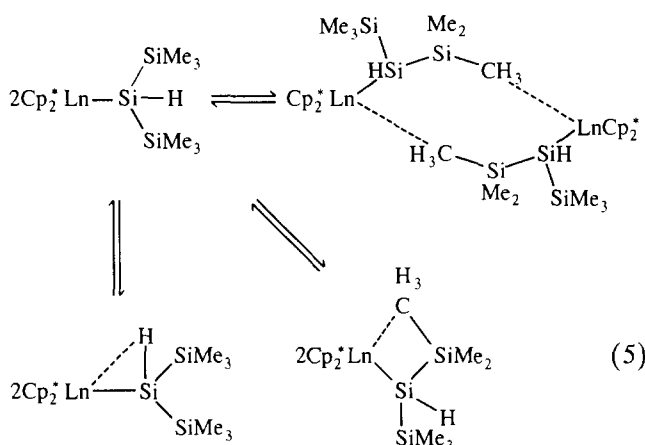


Fig. 3. Plot of δ vs. $1/T$ (K) for the Cp^* protons of $\text{Cp}_2^*\text{SmSiH}(\text{SiMe}_3)_2$ (**3**).



($L_{11} = \text{Sm, Nd, Y}$) bonds of $12.5(1) \text{ kcal mol}^{-1}$, $13.3(1) \text{ kcal mol}^{-1}$, and $15.6(1) \text{ kcal mol}^{-1}$ respectively. Interestingly, the $\text{C}_5\text{Me}_4\text{Et}$ ligands of $\text{Cp}_2^*\text{SmSiH}(\text{SiMe}_3)_2$ (**6**) are inequivalent at room temperature but coalesce at $+40^\circ\text{C}$. The activation barrier for rotation about the $\text{Sm}-\text{Si}$ bond in **7** is $15.5(1) \text{ kcal mol}^{-1}$. As expected, the rotation barrier for the analogous $\text{Nd}-\text{C}$ bond in $\text{Cp}_2^*\text{NdCH}(\text{SiMe}_3)_2$ is considerably higher, at $19.9(1) \text{ kcal mol}^{-1}$.

The ^{29}Si NMR spectrum of **4** shows only one resonance ($\delta -23.51$), which we attribute to the SiMe_3 groups. We were not able to observe any ^{29}Si NMR signals for the neodymium analogue **3** over a $+200$ to -200 ppm spectral window. However, the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum for the yttrium silyl **5** contains two sharp doublets. The higher field resonance ($\delta -120.00$) is assigned to the yttrium-bound silicon atom, which displays a coupling constant to ^{89}Y ($^1J_{\text{Ysi}}$) of 92 Hz . The second resonance (at $\delta -7.33$), which is attributed to the SiMe_3 groups, is also split into a doublet by coupling to yttrium ($^2J_{\text{Ysi}} = 3.6 \text{ Hz}$). We are unaware of any reported $\text{Y}-\text{Si}$ coupling constants that can be compared with the values given here. Infrared spectra for these complexes display $\nu(\text{SiH})$ stretching frequencies (1960 cm^{-1} for **3, 4**, and **5**; 1979 cm^{-1} and 1948 cm^{-1} for **6** and **7** respectively) which are significantly lower than the corresponding value for $\text{H}_2\text{Si}(\text{SiMe}_3)_2$



(2085 cm^{-1}). This reflects bonding of the silyl group to an electropositive element.

4. Description of the structure of $\text{Cp}_2^*\text{SmSiH}(\text{SiMe}_3)_2$

Orange, X-ray quality crystals of **3** were isolated by cooling a concentrated pentane solution to -40°C . Relevant geometrical parameters are listed in Tables 1 and 2. The ORTEP view of **3**, shown in Fig. 4, reveals that the compound crystallizes with formation of dimers that are held together via intermolecular $\text{Sm} \cdots \text{CH}_3-\text{Si}$ interactions. Each samarium atom is in a pseudotetrahedral environment and bonded to two $\eta^5\text{-Cp}^*$ ligands with an average metal–ring centroid distance of $2.43(1) \text{ \AA}$, which is considerably shorter than those observed for other $\text{Cp}_2^*\text{Sm}(\text{X})(\text{L})$ compounds, $2.68(1)-2.755(2) \text{ \AA}$ [23,24]. The observed (ring centroid)–metal–(ring centroid) angle of $135.7(2)^\circ$ is in the range of values previously observed for trivalent Cp_2^*Sm complexes, $130-138^\circ$ [24].

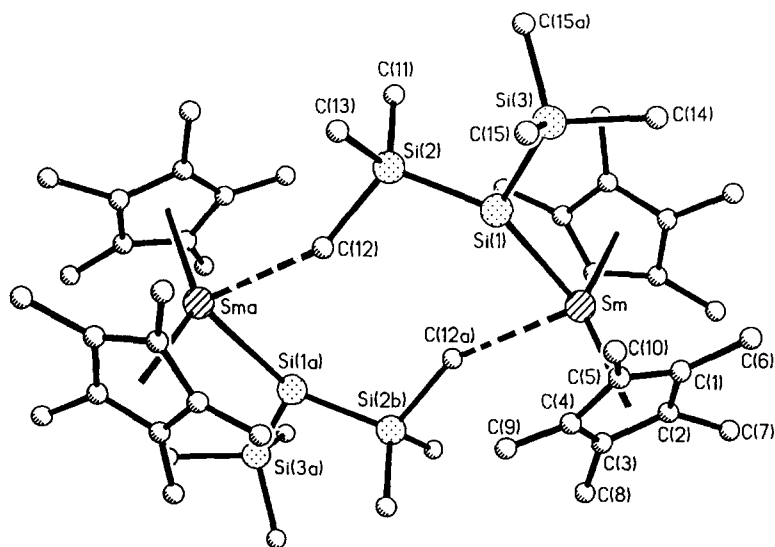


Fig. 4. ORTEP diagram of $\text{Cp}_2^*\text{SmSiH}(\text{SiMe}_3)_2$ (**3**).

The Sm–Si distance of 3.052(8) Å in **3** may be compared with two other lanthanide silyl complexes which have been structurally characterized. The Lu–Si distance in $[\text{Cp}_2\text{Lu}(\text{SiMe}_3)_2]^-$ is 2.888(2) Å [9]. The difference between these two bond lengths (0.16 Å) is larger than can be attributed to the lanthanide contraction (ca. 0.10 Å), and presumably reflects the presence of more intramolecular crowding in **3**. Interestingly, the Yb–Si bond length of 3.158(2) Å in $(\text{Ph}_3\text{Si})_2\text{Yb}(\text{THF})_2$ [25] is slightly long by comparison, since the ionic radius of Sm^{+3} (1.07 Å) is only 0.07 Å less than that for Yb^{+2} (1.14 Å) [26].

The Lewis acidity of the samarium atom leads to an intermolecular 'γ-agostic' interaction between Sm and a methyl group (C12) of the silyl ligand. Many organolanthanides containing an $\text{N}(\text{SiMe}_3)_2$ or $\text{CH}(\text{SiMe}_3)_2$ group have been structurally characterized as containing intramolecular γ-C–H–Ln or β-Si–Me–Ln interactions [7a]. In particular, it is interesting to compare the structure of **3** with those for $\text{Cp}_2^* \text{LnCH}(\text{SiMe}_3)_2$ (Ln = Ce [27], Nd [4d], Y [16]), which are monomeric in the solid state and contain one intramolecular Ln...CH₃–Si interaction. The Sm...C(12) distance of 2.970(22) Å is somewhat longer than the analogous intramolecular distances found in $\text{Cp}_2^* \text{LnCH}(\text{SiMe}_3)_2$ (Ln = Ce 2.853(5) Å [27]; Ln = Nd 2.865(7) Å [4d]; Ln = Y 2.958(7) [16]). The agostic interaction in **3** results in a relatively long Si(2)–C(12) bond distance (1.996(22) Å; compare the Si–C distance in CH_3SiH_3 of 1.867 Å [28]). Intermolecular interactions of this kind are known in a few complexes such as $\text{Cp}^* \text{Be}(\mu\text{-Me})\text{YbCp}_2^*$ [29]. These interactions may be attributed to weak electro-

Table 2

Selected bond distances (Å) and angles (deg) for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{SmSiH}(\text{SiMe}_3)_2$ (**3**)^a

Bond distances			
Sm–CNT(av)	2.43(1)	Si(1)–Si(3)	2.375(28)
Sm–Si(1)	3.052(8)	Si(2)–C(11)	1.881(37)
Sm–C(12)	2.970(22)	Si(2)–C(12)	1.996(22)
Si(1)–Si(2)	2.214(11)	Si(2)–C(13)	1.937(28)
Bond angles			
CNT–Sm–CNT	137.7(2)	Si(1)–Si(2)–C(11)	108.2(12)
Sm–Si(1)–Si(2)	131.0(4)	Si(1)–Si(2)–C(12)	109.4(7)
Sm–Si(1)–Si(3)	124.2(4)	Si(1)–Si(2)–C(13)	114.52(8)
Si(2)–Si(1)–Si(3)	100.9(4)	Si(1)–Sm–C(12a)	88.1(5)

^a CNT is the centroid for the $\eta^5\text{-C}_5\text{Me}_5$ rings.

static attraction between the metal and the methyl carbon atom [30].

5. Reactivity studies

Reactivity studies of the silyl complexes support the expectation that Ln–Si bonds are highly reactive. These complexes react rapidly with hydrogen (1 atm, benzene-*d*₆) to give the corresponding lanthanide hydride complex and $\text{H}_2\text{Si}(\text{SiMe}_3)_2$. Polyethylene is produced (by ¹H NMR spectroscopy) in reactions of **3** and **4** with ethylene (1 atm, benzene-*d*₆). The reaction of **3** with ethylene (less than 5 min) consumes all of the complex, but under comparable conditions only 80% of **4** reacts. Therefore, it appears that these polymerizations probably involve some degree of chain-transfer. Finally, compounds **3** and **4** react rapidly with many hydrosilanes. For example, **3** reacts with MesSiH_3 (3 equivalents) over 10 min at room temperature to produce $[\text{Cp}_2^* \text{SmH}]_2$, $\text{H}_2\text{Si}(\text{SiMe}_3)_2$ and $\text{MesH}_2\text{SiSiH}_2\text{Mes}$ (compare Eq. (3)). Similarly, the reaction of $\text{Cp}_2^* \text{NdSiH}(\text{SiMe}_3)_2$ with PhSiH_3 or PhMeSiH_2 gives the corresponding hydride complex. No reaction was observed between **4** and $\text{Ph}_2\text{HSiSiHPh}_2$ (2 days, room temperature) or $^1\text{Pr}_2\text{SiH}_2$ (18 h, 80 °C), presumably because these silanes are too sterically hindered.

In reactions of **3** with some hydrosilanes, redistribution at silicon [31] is observed [32]. In one example, the reaction of $\text{Cp}_2^* \text{SmCH}(\text{SiMe}_3)_2$ with neat $\text{HSi}(\text{SiMe}_3)_3$ (12 h, 85 °C) was observed to give complex **4** (24% yield), rather than the expected silyl complex $\text{Cp}_2^* \text{SmSi}(\text{SiMe}_3)_3$, and trace amounts of $\text{Me}_3\text{SiSiMe}_3$ (Eq. (6)).

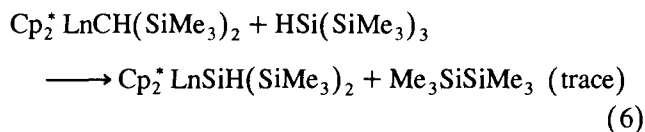


Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{SmSiH}(\text{SiMe}_3)_2$ (**3**)

	x	y	z	U_{eq}^a
Sm	5000	823(1)	6463(1)	50(1)
Si(1)	5000	1870(5)	5416(3)	95(4)
Si(2)	5492(6)	1635(5)	4560(3)	64(3)
Si(3)	5000	3293(5)	5428(4)	100(4)
C(1)	3720(8)	1438(13)	7114(7)	129(13)
C(2)	3832	630	7287	155(17)
C(3)	3529	126	6849	130(12)
C(4)	3229	22	6406	83(7)
C(5)	3347	1433	6570	90(8)
C(6)	3757(18)	2118(21)	7453(15)	323(31)
C(7)	3998(13)	455(28)	7885(10)	377(40)
C(8)	3447(17)	–740(17)	6909(18)	362(36)
C(9)	2767(12)	414(16)	5901(10)	169(15)
C(10)	3003(12)	2122(12)	6293(12)	169(15)
C(11)	6718(24)	1722(26)	4571(15)	112(19)
C(12)	5000	601(13)	4282(10)	107(13)
C(13)	5000	2323(19)	3988(11)	192(26)
C(14)	5000	3776(21)	6150(15)	196(27)
C(15)	4042(13)	3797(13)	5082(12)	176(15)

^a Equivalent isotropic U defined as one third of the trace of the orthogonal U_{ij} tensor.

6. Experimental section

All manipulations were performed under an inert atmosphere of nitrogen or argon using either standard Schlenk techniques or a Vacuum Atmospheres glove box. Dry, oxygen-free solvents were employed throughout. To remove olefin impurities, pentane and benzene were pretreated successively with concentrated H_2SO_4 , 0.5 N KMnO_4 in 3 M H_2SO_4 , NaHCO_3 , and finally MgSO_4 . All solvents were distilled from sodium benzophenone ketyl. Benzene- d_6 was purified by vacuum distillation from Na–K alloy. Ethylene (Linde Specialty Gases) was used as-received. The compounds $\text{Cp}_2^*\text{Ln-CH}(\text{SiMe}_3)_2$ (Ln = Nd, Sm) [4d] and $\text{H}_2\text{Si}(\text{SiMe}_3)_2$ [33] were prepared by literature procedures. Commercial silanes were distilled prior to use. The silanes PhSiH_3 and ${}^i\text{Pr}_2\text{SiH}_2$ were obtained from reduction of the corresponding chlorosilane with LiAlH_4 . Elemental analyses were performed by Desert Analytics or the UCB Microanalytical Laboratory. NMR spectra were recorded on a GE QE-300, a Bruker AMX (300 MHz), a Bruker AMX (400 MHz), or a Varian UN-500 spectrometer. IR spectra were recorded on Perkin–Elmer 1330 and Mattson Galaxy Series FTIR 3000 spectrometers. Molecular weights were determined using the Signer method [34].

6.1. $\text{Cp}_2^*\text{SmCH}(\text{SiMe}_3)_2$ (1)

A synthetic procedure analogous to that used for $\text{Cp}_2^*\text{SmCH}(\text{SiMe}_3)_2$ was employed [4d]. Cp^*Li (0.88 g, 5.6 mmol), SmCl_3 (0.73 g, 2.84 mmol) and $(\text{OEt}_2)_{0.4} \cdot \text{LiCH}(\text{SiMe}_3)_2$ (0.58 g, 2.97 mmol) gave the product as red crystals (m.p. 168–170 °C) that were isolated by concentration and cooling of a pentane solution, in an isolated yield of 27% (0.47 g). Anal. Found C, 56.7; H, 8.83. $\text{C}_{29}\text{H}_{53}\text{Si}_2\text{Sm}$. Calc.: C, 57.3; H, 8.78%. ${}^1\text{H}$ NMR (benzene- d_6 , 22 °C, 500 MHz) δ –4.62 (s, 18 H, SiMe_3), 0.69 (s, 6 H, $\text{C}_5\text{Me}_4\text{Et}$), 0.79 (s, 6 H, $\text{C}_5\text{Me}_4\text{Et}$), 0.88 (s, 6 H, $\text{C}_5\text{Me}_4\text{Et}$), 0.99 (s, 6 H, $\text{C}_5\text{Me}_4\text{Et}$), 1.52 (q, 4 H, $\text{C}_5\text{Me}_4\text{Et}$), 1.75 (t, 6 H, $\text{C}_5\text{Me}_4\text{Et}$), 20.40 (s, 1 H, CH); ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR (benzene- d_6 , 22 °C, 125.7 MHz) δ –2.80 (SiMe_3), 9.85 ($\text{C}_5\text{Me}_4\text{Et}$), 9.99 ($\text{C}_5\text{Me}_4\text{Et}$), 19.20 ($\text{C}_5\text{Me}_4\text{Et}$), 19.22 ($\text{C}_5\text{Me}_4\text{Et}$), 19.70 ($\text{C}_5\text{Me}_4(\text{CH}_2\text{CH}_3)$), 19.77 ($\text{C}_5\text{Me}_4(\text{CH}_2\text{CH}_3)$), 27.63 ($\text{C}_5\text{Me}_4(\text{CH}_2\text{CH}_3)$), 28.00 ($\text{C}_5\text{Me}_4(\text{CH}_2\text{CH}_3)$), 119.25 ($\text{C}_5\text{Me}_4\text{Et}$), 119.39 ($\text{C}_5\text{Me}_4\text{Et}$), 119.59 ($\text{C}_5\text{Me}_4\text{Et}$), 119.69 ($\text{C}_5\text{Me}_4\text{Et}$), 126.11 ($\text{C}_5\text{Me}_4\text{Et}$), 126.39 ($\text{C}_5\text{Me}_4\text{Et}$); IR (Nujol, CsI, cm^{-1}): 1250 s, 1240 s, 1170 w, 1150 w, 1020 m, 855 vs, 825 s, 755 m, 720 m, 650 br w, 570 m, 430 br w, 370 m, 315 m.

6.2. $\text{Cp}_2^*\text{NdCH}(\text{SiMe}_3)_2$ (2)

The synthetic procedure used for the synthesis of $\text{Cp}_2^*\text{NdCH}(\text{SiMe}_3)_2$ was employed [4d].

$[\text{Cp}_2^*\text{NdCl}_2][\text{Li}(\text{OEt}_2)_2]$ (1.88 g, 2.81 mmol) and $\text{LiCH}(\text{SiMe}_3)_2$ (0.514 g, 3.09 mmol) afforded green crystals (m.p. 164–165 °C) of **2** in 34% yield (0.58 g). Anal. Found: C, 55.8; H, 8.15. $\text{C}_{29}\text{H}_{53}\text{NdSi}_2$. Calc.: C, 57.8; H, 8.87%. ${}^1\text{H}$ NMR (benzene- d_6 , 22 °C, 500 MHz) δ –16.11 (s, 18 H, SiMe_3), 3.65 (brs, 2 H, $\text{C}_5\text{Me}_4\text{Et}$), 3.84 (brs, 2 H, $\text{C}_5\text{Me}_4\text{Et}$), 7.07 (s, 6 H, $\text{C}_5\text{Me}_4\text{Et}$), 7.71 (s, 6 H, $\text{C}_5\text{Me}_4\text{Et}$), 7.93 (s, 6 H, $\text{C}_5\text{Me}_4\text{Et}$), 9.00 (s, 12 H, $\text{C}_5\text{Me}_4\text{Et}$), 58.18 (brs, 1 H, CH); IR (Nujol, CsI, cm^{-1}): 1248 s, 1238 s, 1170 w, 1150 w, 1048 m, 950 br w, 840 vs, 820 s, 755 m, 720 m, 685 br w, 650 br w, 565 m, 430 br w, 370 m, 315 m.

6.3. $\text{Cp}_2^*\text{SmSiH}(\text{SiMe}_3)_2$ (3)

A 150 ml thick-walled reaction flask, equipped with a Teflon stopcock, was charged with $\text{Cp}_2^*\text{SmCH}(\text{SiMe}_3)_2$ (1.00 g, 1.7 mmol) and $\text{H}_2\text{Si}(\text{SiMe}_3)_2$ (1.44 g, 8.16 mmol) in the dry box. The resulting red oil was heated at 85 °C for 30 min. The volatile materials were removed in vacuo, and the red residue was extracted into pentane (20 ml). Filtration, concentration and cooling (–35 °C) of the pentane solution afforded red crystals (m.p. 173–175 °C) of **3** in 48% yield (0.50 g). Anal. Found: C, 52.14; H, 8.21; MW, 578 (cryoscopy in pentane). $\text{C}_{26}\text{H}_{49}\text{SmSi}_3$. Calc.: C, 52.37; H, 8.28%; MW, 596 (monomer). ${}^1\text{H}$ NMR (benzene- d_6 , 22 °C, 500 MHz) δ –2.47 (s, 18 H, SiMe_3), 0.50 (s, 30 H, C_5Me_5), 10.10 (s, 1 H, SiH); ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR (benzene- d_6 , 22 °C, 125.7 MHz) δ –0.39 (SiMe_3), 20.39 (C_5Me_5), 120.89 (C_5Me_5); ${}^{29}\text{Si}\{{}^1\text{H}\}$ NMR (benzene- d_6 , 22 °C, 99.3 MHz) δ –23.51 (SiMe_3); IR (Nujol, CsI, cm^{-1}): 2720 w, 1960 s, 1246 s, 1238 s, 1180 m, 1060 br w, 1020 m, 890 s, 777 m, 750 m, 680 m, 660 m, 612 s, 599 s, 396 m, 305 s.

6.4. $\text{Cp}_2^*\text{NdSiH}(\text{SiMe}_3)_2$ (4)

The above procedure was followed using 0.44 g (0.77 mmol) of $\text{Cp}_2^*\text{NdCH}(\text{SiMe}_3)_2$ and 0.68 (3.8 mmol) of $\text{H}_2\text{Si}(\text{SiMe}_3)_2$, to afford blue-green crystals (179–180 °C) of **4** (0.23 g, 49%). Anal. Found: C, 50.4; H, 7.22; MW, 534 (cryoscopy in pentane). $\text{C}_{26}\text{H}_{49}\text{NdSi}_3$. Calc.: C, 52.9; H, 8.37%; MW, 590 (monomer). ${}^1\text{H}$ NMR (benzene- d_6 , 22 °C, 500 MHz) δ –24.46 (s, 1 H, SiH), –16.52 (s, 18 H, SiMe_3), 9.47 (s, 30 H, C_5Me_5); ${}^1\text{H}$ NMR (toluene- d_8 , –100 °C, 300 MHz) δ –50.06 (s, 1.5 H), –36.93 (s, 1.8 H), –33.92 (s, 7.3 H), –18.95 (s, 1.8 H), –10.10 (s, 1.1 H), 9.68 (s, 4.7 H), 13.08 (s, 14 H), 17.95 (s, 15 H), 20.08 (s, 5.1 H), 23.03 (s, 1.8 H); IR (Nujol, CsI, cm^{-1}): 2720 w, 1960 s, 1246 s, 1238 s, 1180 m, 1060 br w, 1020 m, 890 s, 777 m, 750 m, 680 m, 660 m, 612 s, 599 s, 396 m, 305 s.

6.5. $Cp_2^* YSiH(SiMe_3)_2$ (**5**)

The above procedure was followed using 0.42 g (0.81 mmol) of $Cp_2^* YCH(SiMe_3)_2$ and 0.56 g (5.7 mmol) of $H_2Si(SiMe_3)_2$, to afford yellow crystals (117–120 °C) of **5** (0.10 g, 23%). HRMS calc. for $C_{26}H_{49}YSi_3 = 534.220$, found 534.217. 1H NMR (benzene- d_6 , 22 °C, 500 MHz) δ 0.54 (s, 18 H, $SiMe_3$), 1.90 (s, 30 H, C_5Me_5); $^{13}C\{^1H\}$ NMR (benzene- d_6 , 22 °C, 100.6 MHz) δ 5.32 ($SiMe_3$), 11.65 (C_5Me_5), 120.85 (C_5Me_5); $^{29}Si\{^1H\}$ NMR (benzene- d_6 , 22 °C, 59.6 MHz, INEPT): δ -120.00 (d, SiH , $^1J_{YSi} = 92$ Hz), -7.33 (d, $SiMe_3$, $^2J_{YSi} = 3.6$ Hz); IR (Nujol, cm^{-1}): 2720 w, 1960 s, 1246 s, 1238 s, 1180 m, 1060 br w, 1020 m, 890 s, 777 m, 750 m, 680 m, 660 m, 612 s, 599 s, 396 m, 305 s.

6.6. $(C_5Me_4Et)_2SmSiH(SiMe_3)_2$ (**6**)

The procedure used for **3** was employed with $Cp_2^* SmCH(SiMe_3)_2$ (0.27 g, 0.44 mmol) and $H_2Si(SiMe_3)_2$ (0.14 g, 0.80 mmol). The product was isolated as dark red crystals (m.p. 88–89 °C) in 35% yield (0.10 g). 1H NMR (benzene- d_6 , 60 °C, 500 MHz) δ -5.13 (s, 4 H, $lw = 231$ Hz, C_5Me_4Et), -1.20 (s, 18 H, $SiMe_3$), -0.19 (s, 6 H, C_5Me_4Et), 1.25 (s, 6 H, $lw = 72$ Hz, C_5Me_4Et), 1.57 (s, 6 H, $lw = 45$ Hz, C_5Me_4Et), 10.49 (s, 1 H, $lw = 18$ Hz, SiH); $^{13}C\{^1H\}$ NMR (cyclohexane- d_{12} , 60 °C, 125.7 MHz) δ 0.57 ($SiMe_3$), 3.68 ($C_5Me_4(CH_2CH_3)$), 20.31 (C_5Me_4Et), 22.10 (C_5Me_4Et), 27.98 ($C_5Me_4(CH_2CH_3)$), 120.62 (C_5Me_4Et), 121.95 (C_5Me_4Et), 127.81 (C_5Me_4Et); IR (Nujol, cm^{-1}): 2720 w, 1979 s, 1948 s, 1236 s, 1177 m, 1045 br w, 1021 m, 826 s, 745 m, 724 m, 678 m, 625 s, 611 s, 590 m, 320 s.

6.7. $(C_5Me_4Et)_2NdSiH(SiMe_3)_2$ (**7**)

The procedure used for **3** was employed with $Cp_2^* NdCH(SiMe_3)_2$ (0.33 g, 0.55 mmol) and $H_2Si(SiMe_3)_2$ (0.73 g, 4.14 mmol). The product was isolated as a blue-green oil in 20% yield (0.07 g). 1H NMR (benzene- d_6 , 80 °C, 300 MHz) δ -9.57 (s, 18 H, $SiMe_3$), 5.04 (s, 6 H, $lw = 60$ Hz, C_5Me_4Et), 6.08 (s, 12 H, C_5Me_4Et), 9.93 (s, 12 H, C_5Me_4Et); IR (Nujol, cm^{-1}): 2720 w, 1979 s, 1948 s, 1235 s, 1177 m, 1045 br w, 1020 m, 826 s, 745 m, 720 m, 675 m, 610 s, 590 m, 320 s.

6.8. Crystallographic structural determination

Crystallographic data are condensed in Table 3. Photographic evidence revealed *mmm* Laue symmetry and systematic absences in the diffraction data suggested either *Cmca* (centric) or *C2cb* (acentric, non-standard *Aba2*). All indicators pointed toward the centric alterna-

Table 3
Crystallographic data for compound **3**

Chemical formula	$C_{54}H_{94}Si_6Sm_2$
<i>a</i> (Å)	15.301(4)
<i>b</i> (Å)	16.690(5)
<i>c</i> (Å)	23.895(5)
<i>V</i> (Å ³)	6102(2)
<i>Z</i>	4
ρ_{calc} (g cm ⁻³)	1.294
μ (MoK α) (cm ⁻¹)	20.53
Formula weight	297.1
Space group	<i>Cmca</i>
Diffractometer	Siemens P4
Radiation	MoK α
λ (Å)	0.71073
<i>T</i> (K)	299
2θ range (deg)	4–48
Reflections collected	4242
Independent reflections	2489
Observed reflections	1595 ($5\sigma F$)
<i>R</i> (<i>F</i>), <i>R</i> (<i>wF</i>) (%)	6.83, 7.89
GOF	1.53
Δ/s (max)	0.028
N_o/N_v	10.9
$\Delta\rho$ (e Å ⁻³)	0.97

tive. Si(2) is disordered and occurs in two crystallographically equivalent positions. Although this disorder disappears in the acentric space group, the Cp^* rings are significantly distorted. Correlation was examined in 42 Friedel pairs; no systematic pattern was apparent. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were treated as idealized contributions. Computations used the SHELXTL (4.2) program library (G. Sheldrick, Siemens, Madison, WI).

Acknowledgment

We thank the Divisions of Chemistry and Materials Research at the National Science Foundation and the Petroleum Research Foundation for support of this work. We also thank Professor R.A. Andersen for valuable discussions.

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Note added in proof

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