Metallacyclosilanes of Calcium, Yttrium, and Iron

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ABSTRACT: Utilizing a choice of $\alpha$-$\omega$-oligosilanylene diides, it is possible to synthesize a number of heterocyclosilanes with heteroelements of calcium, yttrium, and iron by metathesis reactions with respective metal halides CaI$_2$, YCl$_3$, and FeBr$_2$. $^{29}$Si NMR spectroscopic analysis of the calcacyclosilanes suggests that these compounds retain a strong oligosilanylene dianion character, which is more pronounced than in the analogous magnesacyclosilanes. As the electronegativity of calcium lies between potassium and magnesium, silyl calcium reagents should be considered as building blocks with an attractive reactivity profile. Reaction of a 1,4-oligosilanylene diide with YCl$_3$ gave the five-membered yttracyclosilane as an ate-complex with two chlorides still attached to the yttrium atom. Reaction of the obtained compound with two equivalents of NaCp led to another five-membered yttracyclosilane ate-complex with an yttracene fragment. When using a dianionic oligosilanylene ligand containing a siloxane unit, the siloxane oxygen acted as an additional coordination site for Ca and Y. When the same ligand was used to prepare a cyclic $^1$-ferra-$^4$-oxatetrasilacyclohexane, an analogous transannular interaction between the iron and oxygen atoms is missing.

INTRODUCTION

For a long time, the synthesis of heterocyclosilanes was either restricted to insertion reactions into strained cyclosilanes or to reactions of $\alpha$-$\omega$-oligosilanylene dihalides with nucleophilic heteroatoms. Preparation of metallacyclosilanes with non-nucleophilic metals, however, was more challenging. The development of a convenient synthetic protocol for $\alpha$-$\omega$-oligosilanylene dianions eventually permitted simple access to this class of compounds, where frequently the interaction between the metal and the neighboring silicon atoms is rather polar or at least weaker than typical silicon main-group bonds.

Silyl Calcium Compounds. One type of compounds with a weak silicon metal interaction are magnesacyclosilanes, which are easily prepared from dipotassium $\alpha$-$\omega$-oligosilanylene diides by reaction with an equimolar amount of MgBr$_2$·Et$_2$O. A major reason for our interest in these compounds was to moderate the reactivity of the associated silanides compared to that of dipotassium compounds. Magnesium silanides can be regarded as sila-Grignard-type reagents. Indeed, we could utilize these compounds in a number of reactions where potassium silanides were either too reducing, too basic, or too reactive in general.

Considering organomagnesium (Grignard) compounds, an obvious question is whether instead of magnesium calcium might be used as an alternative metal. A short answer to this question is, "In principle, yes, but these compounds are neither easily prepared as nor can be handled with the same ease as organomagnesium compounds." Nevertheless, in recent years, the chemistry of organocalcium compounds has been intensively investigated and several synthetically useful methods for their preparation have been developed. The direct (Grignard analogous) synthesis requires activated calcium and preferably organoiodides as starting materials. Other methods include the deprotonation of C–H acidic compounds with calcium amides and transmetallation/metal-exchange reactions.

The synthesis of alkaline-earth derivatives of heavier congeners of carbanions, namely, silanides, is associated with similar problems. Although silyl magnesium compounds have gained wide acceptance over the last few years, they are typically not obtained from direct reactions of silyl halides with elemental magnesium but rather by metathesis of lithium or potassium silanides with magnesium bromide. The same is essentially true for silyl calcium compounds, the number of reported examples still being limited to very few (Chart 1).

Remarkably enough, the very first report of calcium silanides by Mochida and Manishi is the only approach that utilizes the direct Grignard-type reaction of insertion of elemental calcium into a Si–Cl bond. For this purpose, calcium metal vapor was used. Four different silyl calcium compounds (I) (Chart 1) were prepared by this method, and based on derivatization reactions with a number of different electrophiles the yields of formation were rather moderate. All other approaches to calcium silanides reported so far have employed metathesis reactions of lithium or potassium silanides with CaI$_2$.
Ruhlandt-Senge demonstrated the principal feasibility of this by reaction of $\text{(Me}_3\text{Si)}_3\text{SiK}$ with CaI$_2$ to $[\text{(Me}_3\text{Si)}_3\text{Si]}_2\text{Ca}$ (II) (Chart 1). A report by the Sadow group on the formation of $[\text{(Me}_2\text{HSi)}_3\text{Si]}_2\text{Ca}$ (III) (Chart 1) was along the same lines. Subsequently, Sekiguchi and co-workers showed that reaction of the dipotassium tetrasilacyclobutadiene dianion $\text{K}_2[(\text{tBu}_2\text{MeSi})_4\text{Si}]_4$ with CaI$_2$ led to the formation of an interesting building block calcium tetrakis(di-$\text{t}$-$\text{Bu}$-$\text{t}$-$\text{Me}$-$\text{Si}$)tetrasilabicyclo[1.1.0]butane-2,4-diide (IV) (Chart 1).

More recently, Okuda and co-workers prepared $\text{(Ph}_3\text{Si)}_2\text{Ca}$ (V) from $\text{Ph}_3\text{SiK}$, and Mills and Liddle reported the synthesis of THF adducts of $[\text{(Me}_3\text{Si)}_3\text{Si]}_2\text{Ca}$ and $[\text{(tBu}_2\text{MeSi)}_2\text{Ca}$ (VI) from the respective sodium silanides (Chart 1).

Silyl Yttrium Compounds. The origin of the organic chemistry of rare-earth metals dates back to the seminal work of Wilkinson and co-workers on metallocenes in the 1950s. Though with a slow start, this area is nowadays an intensively investigated and flourishing field. Despite a large number of known organic rare-earth metal compounds (containing metal–carbon bonds), examples of silylated rare-earth complexes are still scarce. Cases of silylated yttrium compounds are limited to only seven reported examples (Chart 2). These include the neutral compounds $\text{R}_2\text{YLi}·\text{(THF)}_3$ (R = SiMe$_3$, Et) (VII) by Sgro and Piers and Tilley’s $\text{Cp}^*\text{YSiH(SiMe}_3\text{)}_2$ (VIII) obtained by metathesis of $\text{Cp}^*\text{YCH(SiMe}_3\text{)}_2$ with $\text{H}_2\text{Si(SiMe}_3\text{)}_2$. Sadow and co-workers obtained the dianionic $\text{K}_2[(\text{Et}_2\text{O})_2[Y\text{(Si(SiHMe}_2\text{)}_5]_2\text{Cl}_2(\text{Et}_2\text{O})]]$ (IX) from the reaction of $[\text{(HMe}_3\text{Si)}_3\text{SiK}$ with YCl$_3$. Evans’ ate-complex $\text{K}·[\text{Cp}^*\text{YSiHPh}]_3$ (X) ($\text{Cp}^* = \text{C}_{22}\text{H}_{45}$) was formed in the reaction of the Y(II) compound $\text{K}[\text{Cp}^*\text{Y}]$ with PhSiH$_3$. Most recently, our group reported two disilylated yttrium ate-complexes XI and XII by reaction of a siloxane-containing oligosilylalkene dide with YCl$_3$.

Silyl Iron Compounds. While a considerable number of silyl iron complexes is known, examples with two silyl ligands are not so common, and the tris(trimethylsilyl)silyl group is the only oligosilanyl ligand for which disilylated iron complexes are known. Tilley and co-workers reported the reaction of $\text{(Me}_3\text{Si)}_3\text{SiLi}$ with FeCl$_2$ in DME to give the ferrate complex $[\text{Li(DME)}_2]·\text{[(Me}_3\text{Si)}_3\text{Si]}_2\text{FeCl}$ (XIII) (Chart 3). Abstraction of the chloride with $\text{Me}_3\text{SiOTf}$ gave the neutral complex $\text{[Me}_3\text{Si)}_3\text{Si]}_2\text{Fe}$ (XIV), which was obtained as the DME, Et$_2$O, or THF complex (Chart 3). Only recently, Arata and Sunada demonstrated that the THF adduct of $\text{(Me}_3\text{HSi)}_3\text{SiK}$ with YCl$_3$ forms the ate-complex $\text{K}·[\text{YCl}_2(\text{Me}_3\text{Si)}_3\text{Si}]_2\text{FeCl}_3$ (XV) (Chart 3).
{[(Me,Si)₂Si₂Fe] (XIV) can be obtained directly from the reaction of (Me,Si)₂SiK with FeBr₃ in THF, and they further reported its conversion to the dipyrind complex (Chart 3). With the availability of several oligosilanylene diides, we decided to study the possibility of formation of tetracyclosilanes.

**RESULTS AND DISCUSSION**

**Silyl Calcium Compounds.** Dipotassium oligosilanylene-1,4-diide 1³⁵,³⁶ is arguably the compound that we used most frequently for the preparation of five-membered heterocyclosilanes. In particular, the compound was reacted with MgBr₂, Et₂O to obtain the respective magnesatetrasilsilacylpentane, which may be considered as a reference compound for comparison with other metallasilacylpentasilanes with strong silanide character. Here we treated the dianionic compound 1 with CaI₂ to obtain the expected calcatetrasilacylpentane compound 2 with a decent yield of 81% (Scheme 1).

### Scheme 1. Reaction of Oligosilanylene-1,4-diide 1 with Calcium Diiodide to Calcacyclopentasilane 2

![Scheme 1](image)

To assess the reactivity of compound 2, it is convenient to estimate the silanide character by means of ²⁹Si NMR spectroscopic analysis. Typically, the silanide character correlates well with the up-field shift of the anionic silicon atom. The chemical shifts of the attached SiMe₃ groups are also indicative and compared to a neutral compound, typically a down-field shift of the SiMe₃ signal can be observed. The ²⁹Si NMR spectral properties of the dipotassium oligosilanylene-1,4-diide compound 1 are -4.1 (SiMe₃), -26.7 (SiMe₃), and -191.6 (SiK) ppm. The values for the respective magnesacyclopentasilane obtained from 1 and MgBr₂ are -5.4 (SiMe₃), -27.8 (SiMe₃), and -176.6 (SiMg) ppm.³⁴ Formal replacement of Mg with Zn decreases the silanide character further [-6.3 (SiMe₃), -26.6 (SiMe₃), and -152.1 (SiZn) ppm] (Table 1).³⁵ In the context of these numbers, the ²⁹Si NMR spectrum of 2 [-5.1 (SiMe₃), -28.4 (SiMe₃), and -188.0 (SiCa) ppm] suggests the compound to be very ionic with the chemical shift of the metalated silicon atoms being very close to that of the starting material (Table 1). While this value is almost 16 ppm up-field-shifted compared to the bis[tris(trimethylsilyl)silyl]calcium compound 11 reported by Teng and Ruhlmann-Senge (172.3 ppm), a similar but less pronounced behavior was observed for the comparison of the respective magnesacyclopentasilane (-176.6 ppm) and the bis[tris(trimethylsilyl)silyl]magnesium compound (-171.9 ppm).³⁴,³⁶

Single-crystal XRD analysis of 2 (Figure 1) shows the compound to be a regular calcatetrasilacylpentane with the calcium being further coordinated by two dimethoxyethane (DME) molecules. The five-membered ring is almost flat with all ring atoms except for one of the SiMe₃ units being co-

### Table 1. ²⁹Si NMR Data of 1-Metalla-2,2,5,5-tetakis(trimethylsilyl)-3,3,4,4-tetramethylcyclopentasilanes

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| M       | δ ²⁹Si(SiMe₃) | δ ²⁹Si(SiMe₂) | δ ²⁹Si(SiM) | Solvent | Ref |
|---------|--------------|--------------|------------|---------|-----|
| K-(THF)₂ | -4.1         | -26.7        | -191.6     | CdCl₂/THF-ds | ³⁵,³⁶ |
| Mg(THF)₂ | -5.4         | -27.1        | -176.6     | CdCl₂   | ³⁴   |
| Ca(DME)₂ | -5.4         | -27.1        | -176.6     | CdCl₂   | ³⁴   |
| ZnCl₂   | -6.3         | -28.4        | -188.0     | THF-ds  | this work |
| Yb(THF)₄ | -3.5         | -30.5        | -154.0     | CdCl₂   | ³⁹   |
| Yb(DME)₂ | -2.9         | -29.8        | -158.4     | CdCl₂   | ³⁹   |
| YCl₃(DME) | -5.9         | -29.4        | -154.7     | THF-ds  | this work |
| YCp₂(8)  | -4.1         | -26.9        | -152.8     | THF-ds  | this work |
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³⁴The DME content of 2 in this case was determined by ¹H NMR spectroscopy as 1.5. This is different from the number of 2 DME molecules observed in the XRD analysis.
planar. Endo- and exocyclic Si–Si bonds of the ring are fairly short [2.334(2) to 2.365(2) Å] indicating not much steric strain. Accordingly, the Si–Ca distances of 2 [3.0356(13) and 3.0534(15) Å] are also shorter than those of [(Me₃Si)₃Si]Ca(THF) (II) [3.0422(9) and 3.0862(9) Å].²⁰ Due to the cyclic nature of 2 and the long Si–Ca distances, the Si–Ca–Si angle of 93.13(4)° is much smaller than the 125.53° found for II.²⁰ Several of the known acyclic disilylated calcium compounds feature a linear Si–Ca–Si coordination motif. It was observed for Sadow’s tetra-pyridine adduct of [(HMe₃Si)₃Si]₂Ca (III) [Si–Ca: 3.147(3)/3.125(3) Å],²¹ and Okuda’s (Ph₃Si)₂Ca(THF)₃(V) [3.1503 Å]²³ and (Ph₃Si)₂Ca(κ²-triglyme)(THF) [3.175(3) and 3.242(3) Å].²³ A non-linear coordination behavior of (Ph₃Si)₂Ca was imposed by the use of the macrocyclic tetramine ligand Me₄TACD [(Ph₃Si)₂Ca(Me₄TACD): 3.1654(15) Å].⁴⁰

The Ca–O distances of 2 between the calcium ion and the two coordinating DME molecules are longer for the cases where the oxygen atoms are located trans to a silicon atom [2.452(4) and 2.413(4) Å versus 2.398(3) and 2.382(4) Å for the O–Ca–O distances].

In order to extend this chemistry, we repeated the reaction of Ca₄₂ with the siloxane-containing oligosilanylene-1,5-diene 3⁴¹ to obtain the disilanyl calcium compound 4 (Scheme 2).

Scheme 2. Formation of 1-Calca-4-oxacyclohexasilane 4 from the Reaction of Siloxane Containing Oligosilanylene-1,5-diide 3 with Calcium Diodide

Initially, we developed dianion 3 to obtain bidentate silyl ligands with an additional Lewis basic site.⁴¹ It was used for the synthesis of a number of disilylated Yb(II), Eu(II), and Sm(II) complexes,⁴² and more recently for a number of Ln(III) complexes.⁴³

NMR spectroscopic analysis of compound 4 shows it to be fairly similar to 2. Again the ²⁹Si NMR shift of the metallated Si atom of 4 (−179.9 ppm) is close to that of the starting material 3 (−185.7 ppm), indicating a strong silanide character (Table 2), which is significantly more pronounced than in the corresponding magnesium compound (Table 2).⁶ A comparison of Tables 1 and 2 seems to suggest that the siloxane-containing 1,5-oligosilanylene ligand (Table 2) is of diminished silanide character as the chemical shifts are typically shifted down-field compared to the all-silicon 1,4-tetrasilanylene ligand (Table 1). This is true for the listed metals: potassium, magnesium, calcium, and ytterbium. However, for yttrium, a reversed trend seems to occur. To understand this, it needs to be pointed out that while the chemical silanide shift is a good approximation for the silanide character, the nature of the ligand and the counterion are not the only variables here. In particular, solvent effects on the shift can be substantial. A strongly coordinating solvent can compete with the silanide ligand for the counter-ion and thus increase the silanide character. Therefore, the nature of the coordinating solvent (THF vs. DME) and also the solvent used for the NMR experiment contribute to the silanide shift.

For instance, Table 1 shows that the Yb complex with DME displays a stronger up-field shift than the related THF complex. The fact that the YCl₂ complex of the siloxane ligand (XI) (δ = −161.6 ppm, Table 2) displays stronger silanide character than 7 (δ = −154.7 ppm, Table 1) is in part caused by the fact that it was measured in DME, whereas 7 was measured in the less coordinating solvent THF-d₆.⁴⁹

Single-crystal XRD analysis of 4 (Figure 2) shows significantly elongated Ca–Si interactions of 3.1160(10) and 3.1492(10) Å compared to 2 [3.0356(13) and 3.0534(15) Å] and [(Me₃Si)₃Si]₂Ca(THF)₃ (III) [3.0422(9) and 3.0862(9) Å].²⁰ While the Si–Si distances of 4 are even shorter than those in 2 [ranging from 2.314(1) to 2.341(1) Å], the elongated Si–Ca distances are likely caused by a change from hexa- to hepta-coordination of the calcium ion. This occurs by the additional coordination of the siloxane oxygen atom. The phenomenon of elongated Ca–O bonds in trans-position to Si–Ca, which was mentioned above for 2, is even more pronounced in 4, where the Ca–O distances without a trans-Si atom amount to values between 2.39 and 2.44 Å, whereas the respective distances in trans-position to a silanide were found to be between 2.519(2) and 2.580(2) Å. The transannular Ca–O interactions of 2.459(2) and 2.481(2) Å are in between these two extremes.

Finally, we were interested in converting the ferrocene-based oligosilanylan diion 5²² to the respective [3]-ferrocenophane calcium compound 6 (Scheme 3). The reaction proceeds again smoothly and ²⁹Si NMR analysis of 6 reiterates the trend previously observed for compounds 2 and 4. Again, the strong silanide character of 6 is reflected by a chemical shift (~116.7 ppm), close to that of the starting material 5 (~121.1 ppm) and shifted to a higher field than that of the corresponding

Table 2. ²⁹Si NMR Data of 1-Metalla-2,2,6,6-tetrasil(trimethylsilyl)-3,3,5,5-tetramethyl-4-oxacyclohexasilanes

| M                  | δ²⁹Si₂M₂          | δ²⁹Si₂M₃          | δ²⁹Si₃M       | Solvent | Ref |
|--------------------|-------------------|-------------------|---------------|---------|-----|
| Mg(DME) (3)        | −7.0              | −152.6            | −166.9        | CaD₆    | ⁶    |
| Ca(DME) (4)        | −6.2              | −179.9            | −153.8        | THF-dₑDME | ⁴¹  |
| Yb(THF) (4)        | −5.0              | −25.37            | −161.6        | DME     | ³¹  |
| YCp₂ (THF)         | −5.3              | 23.7              | −153.4        | DME     | ³¹  |
Scheme 3. Synthesis of 2-Calca-1,3-disila[3]ferrocenophane 6

![Scheme 3](https://example.com/scheme3.png)

Figure 2. Molecular structure of 4 (thermal ellipsoid plot drawn at the 30% probability level). Of the two molecules in the asymmetric unit, only one is shown. All hydrogen atoms and a co-crystallized pentane molecule are omitted for clarity (bond lengths in Å and angles in deg). Only the anionic part is shown. Ca(1)−O(5) 2.4393(2), Ca(1)−O(1) 2.4715(19), Ca(1)−Si(5) 3.1160(10), Ca(1)−Si(10) 3.1492(10), Si(5)−Si(6) 2.3265(11), Si(6)−O(1) 1.6954(19), Si(6)−C(5) 1.8673(3), Si(10)−Si(12) 2.3141(11), Si(12)−O(1) 1.7002(2), Si(5)−Ca(1)−Si(10) 127.01(3), Si(5)−Ca(1)−Si(12) 95.68(3), Si(10)−Ca(1)−Si(12) 41.29(2), O(1)−Si(6)−Si(5) 101.01(7), Si(12)−Si(10)−Ca(1) 74.80(3), O(1)−Si(12)−Si(10) 100.72(7), Si(10)−Si(12)−Ca(1) 63.90(3), and Si(6)−O(1)−Si(12) 139.69(12).

The solid state structure of 7 (Figure 4), features Si−Y distances of 2.9589(9) and 2.9704(9) Å, about 0.1 Å shorter than those found for XI [3.064(2) and 3.057(1) Å]. All other distances, such as Y−Cl and Y−O are very similar for both types of complexes.

It therefore seems valid to assume that the additional Y−O interaction, which distinguishes complex XI from complex 7, is responsible for the increased ionic character of the Si−Y bonds of the former.

Reaction of complex 7 with two equivalents of NaCp proceeds under substitution of the chlorides against cyclopentadienyl ligands to give the yttracene complex 8 (Scheme 4). The 29Si NMR spectrum of 8, with a signal at −152.8 ppm (J_{Si−Y} = 57 Hz) for the metalated silicon, is fairly similar to that of 7 both with respect to chemical shift and J_{Si−Y} coupling constant (Table 1), suggesting that the degree of covalency of the Si−Y bonds in both compounds is very similar. This is consistent with the fact that the Cp₂Y at complex XII, features only a small degree of interaction between the Y atom and the siloxane oxygen atom. While the solid state structure of 8 (Figure 5) features longer Si−Y [3.006(3) and 3.016(13) Å] bonds than 7 [2.9589(9) and 2.9704(9) Å], these distances are substantially shortened compared to the 3.1315(9) and 3.1459(9) Å observed for complex XII.

Silyl Iron Compounds. As outlined in the introduction, Fe(II) complexes with two silyl groups are not completely uncommon. They are, however, paramagnetic and NMR characterization is not easily possible. Arata and Sunada showed that 1H NMR spectra of [(Me₃Si)₂Si]Fe(THF)₂ and [(Me₃Si)₂Si]₂Fe(py)₂ (XIV) can be obtained but feature very broad and strongly shifted lines.

Our approach to cyclic disilylated Fe(II) complexes follows the same strategy as outlined above for the reactions with CaI₂ and YCl₃. Reactions of oligosilanylene diides 1 and 3 with FeBr₂ thus proceeded to form compounds 9 and 10, respectively, as purple and ruby-red crystals (Scheme 5).

The 1H NMR spectrum of 9 is similar to that of [(Me₃Si)₂Si]₂Fe(THF)₂ with the OCH₃ signals shifted to ca. + 25 ppm. Unfortunately, the crystals of 9 were not suitable for single-crystal XRD analysis, but those of 10 proved to be acceptable and structure analysis was possible (Figure 6). As outlined above, we are aware of only three examples of structurally characterized bis(oligosilylated) Fe(II) complexes. These are Tilley’s ate-complex Et₄N−[([Me₃Si]₂Si]₂FeCl] (XIII) and Sunada’s [(Me₃Si)₂Si]₂Fe(py)₂ and [(Me₃Si)₂Si]₂Fe(THF)₂ (XIV) Chart 3). These compounds feature Si−Fe bond distances of around 2.50 Å (Table 4) and the structural features of 10 match with those of...
Apart from a smaller Si−Fe−Si angle, which is caused by the cyclic nature of the attached silyl groups, the Si−Fe as well as the Si−Si distances are very similar.

The conformation of 10 is somewhat unusual. It features a typical large Si−O−Si angle of almost 143°, which we have observed for several other 1-metalla-4-oxa-tetrasilacyclohexanes. This large angle renders the Si−O−Si unit almost as one ring side, thus allowing describing its conformational properties as those of a five-membered ring. While most of the 1-metalla-4-oxa-tetrasilacyclohexanes studied by us so far tend to engage in a distorted envelope conformation with the metal unit as flap, the structure of 10 is more accurately described as a half-chair conformer with the Si−Fe−Si unit and the oxygen atom in a plane and the SiMe₂ extending below and above the plane (Figure 6).

Table 3. ²⁹Si NMR Data of [3]Ferrocenophanes with 2-Metalla-1,3-disila Bridges

| Solvent | Ref |
|---------|-----|
| CaD₆    | ⁴² |
| Mg(THF)₂ | ⁴² |
| Ca(DME)₂ | ⁴² |
| Zn Et₂O | ⁴² |

Figure 3. Molecular structure of 6 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å and angles in deg). Ca(1)−O(1) 2.4078(16), Ca(1)−O(2) 2.4212(17), Ca(1)−Si(2) 3.0765(8), Fe(1)−C(2) 2.024(2), O(1)−C(12) 1.430(3), Si(1)−C(8) 1.878(3), Si(1)−Si(2) 2.3592(10), Si(2)−C(1) 1.915(2), Si(2)−Si(3) 2.3486(10), Si(2)−Ca(1)−Si(2A) 98.26(3), C(1)−Si(2)−Si(3) 105.11(8), Si(3)−Si(2)−Si(1) 102.14(3), C(1)−Si(2)−Ca(1) 108.90(7), Si(3)−Si(2)−Ca(1) 126.72(3), Si(1)−Si(2)−Ca(1) 112.08(3), Si(2)−C(1)−Fe(1) 127.29(11).

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Figure 4. Molecular structure of 7 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å and angles in deg). Only the anionic part is shown. Y(1)−O(1) 2.4215(19), Y(1)−O(2) 2.4455(19), Y(1)−Cl(1) 2.5843(8), Y(1)−Cl(2) 2.5883(8), Y(1)−Si(6) 2.9589(9), Y(1)−Si(1) 2.9704(9), O(1)−C(1) 1.422(4), Si(1)−Si(4) 2.3582(11), Si(2)−C(5) 1.881(3), Si(4)−Si(Si) 2.3537(12), Si(5)−Si(6) 2.3513(12), O(2)−Y(1)−O(1) 68.16(7), Cl(1)−Y(1)−Cl(2) 162.33(3), Si(6)−Y(1)−Si(1) 96.66(2), Si(4)−Si(1)−Y(1) 103.74(3), Si(5)−Si(4)−Si(1) 111.30(4), Si(6)−Si(5)−Si(4) 113.35(4).

CONCLUSIONS

In our ongoing pursuit to develop the chemistry of heterocyclosilanes, we used a choice of oligosilanylene diides to prepare heterocyclic silanes with endocyclic Ca, Y, and Fe atoms. Calcacyclosilanes were obtained by reaction of oligosilanylene dianions with CaI₂. ²⁹Si NMR spectroscopic analysis of the compounds indicates a retained strong silanide character, which is markedly more pronounced than in the analogous magnesium silanes and almost resembles that of the potassium silanides used as starting materials. A degree of reactivity located between potassium and magnesium silanides would render silyl calcium compounds interesting silyl anionic reagents.

The reaction of a dipotassium 1,4-oligosilanylene diide with YCl₃ gave a five-membered yttracyclosilane as an ate-complex with two chlorides still attached to the yttrium atom. Treatment of this compound with two equivalents of NaCp led to a five-membered yttracyclosilane ate-complex containing an yttracene fragment.

NMR spectroscopic analysis of experiments, subjecting the obtained calcacyclosilanes 2 and 4 to reactions with YCl₃ showed the ²⁹Si signatures of 7 and XI, respectively. However, these reactions were less clean than those utilizing the potassium silanides 1 and 3, displaying a small amount of...
products with Si−Si bonds between the previously anionic silicon atoms. In addition, it was not possible to isolate the crystalline material of the ate-complexes, which should contain either Ca$^{2+}$ or CaCl$^+$ counterions. In calcium and yttrium containing six-membered rings featuring a 3-oxa-tetrasilapentylene fragment, the respective siloxane oxygen atom acts as an additional Lewis basic coordination site for transannular interactions with Ca and Y. When the same ligand fragment was used to prepare a 1-ferra-4-oxatetrasilacyclohexane from 1,4-dipotassio-1,1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilane and FeBr$_2$, no transannular interaction between the iron and oxygen atoms could be observed.

### EXPERIMENTAL SECTION

#### General Remarks.
All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glove box. All solvents were dried using a column-based solvent purification system.

44 2,2,5,5-Tetrakis(trimethylsilyl)decamethylhexasilane, 45 1,4-dipotassio-1,1,4,4-tetrakis(trimethylsilyl)tetramethyltetrasilane (1), 36 1,3-bis[potassiobis(trimethylsilyl)silyl]-1,1,3,3-tetramethyldisiloxane (3), 41 Cp$_2$YCl, 46 1,1′-bis[tris(trimethylsilyl)silyl]ferrocene, and 5 42 were prepared following published procedures. All other chemicals were obtained from different suppliers and used without further purification.

$^1$H (300 MHz), $^{13}$C (75.4 MHz), and $^{29}$Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. If not noted otherwise all samples were measured in C$_6$D$_6$. To compensate for the low isotopic abundance of $^{29}$Si, the INEPT pulse sequence was used for the amplification of the signal. $^{47}$$^{49}$ Spectra are calibrated to the deuterium resonance of the solvent (C$_6$D$_6$) and referenced to tetramethysilane (TMS).

Elementary analyses were carried out using a Heraeus VARIO ELEMENTAR.

#### X-ray Structure Determination.
For X-ray structure analyses, crystals were mounted onto the tip of glass fibers, and data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to $F^2$ and corrected for absorption effects with SAINT$^{50}$ and SADABS$^{51}$ respectively. The
structures were solved by direct methods (SHELXT)\(^5\) and refined by the full-matrix least-squares method (SHELXL)\(^6\), and in some cases, OLEX2\(^7\) was used. If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams are drawn with 30% probability thermal ellipsoids and all hydrogen atoms are omitted for clarity.

Table 4. Basic Structural Features of Di(oligosilanylated) Iron(II) Complexes

| Compound | \(d_{Si-Si} [\text{Å}]\) | \(d_{Fe-Si} [\text{Å}]\) | \(\angle_{Si-Si-Si} [\text{deg}]\) | Ref. |
|----------|----------------|----------------|----------------|------|
| \(Fe = \text{Fe}(\text{Cl})_2, R = \text{Me}\) | 2.49(5) | 2.30(1) | 136.9(2) | 32 |
| \(Fe = \text{Fe}(\text{py})_2, R = \text{Me}\) | 2.488(5) | 2.37(1) | | |
| \(Fe = \text{Fe}(\text{THF})_2, R = \text{Me}\) | 2.5452(9) | 2.340(1) | 133.60(3) | 34 |
| \(Fe = \text{Fe}(\text{THF})_2, R = \text{O}\) | 2.5318(9) | 2.360(1) | | |
| \(Fe = \text{Fe}(\text{THF})_2, R = \text{O}\) | 2.5445 | 2.350(1) | 135.23 | 34 |
| \(Fe = \text{Fe}(\text{THF})_2, R = \text{O}\) | 2.494 | 2.340(2)-2.369(3) | 110.78 | this work |

By NMR analysis. Orange crystals of \(6\) (90 mg, 95%) were obtained from this solution at \(-50^\circ\text{C}\) mp 206 \(^\circ\text{C}\) (decomp). NMR (\(\delta\) in ppm, \(d_2\)-DME)\(^8\) \(\text{H}: 3.94 (t, J = 1.5 \text{ Hz}, 4\text{H}), 3.55 (t, J = 1.5 \text{ Hz}, 4\text{H}), 0.05\) (s, 36\text{H}). \(\text{C}^1: 78.2, 76.3, 68.0, 3.9, \text{Si}^29: -9.7 \ (\text{SiMe}_3), -116.7 \ (\text{Si}, \text{Si})\).

Potassium-4-DME 1-Ytra-2,2,5,5-tetrakis(trimethylsilyl)tetramethylyclopenta-silane-1-ate DME (7). 2,2,5,5-Tetakis(trimethylsilyl)decamethylhexasilane (150 mg, 0.25 mmol) and KOBu (58 mg, 0.52 mmol) were dissolved in DME (3 mL) and left for reaction at rt for 24 h after which NMR-analysis showed full conversion toward \(1\). Volatiles were removed under reduced pressure and the residue was dissolved in DME (1 mL) and stirred at rt for 4.5 h. The resulting cloudy, slightly yellow reaction mixture was subjected to NMR-analysis, showing full conversion. Precipitates were removed through centrifugation and filtration. Colorless crystals of \(7\) (178 mg, 64%) were obtained from a pentane/DME solution at \(-50^\circ\text{C}\). NMR (\(\delta\) in ppm, \(d_2\)-DME)\(^8\) \(\text{H}: 0.23 \ (\text{s}, 12\text{H}), 0.16 \ (\text{s}, 36\text{H})\). \(\text{C}^1: 6.7, 1.7, \text{Si}^29: -5.9 \ (\text{SiMe}_3), -29.4 \ (\text{SiMe}_2), -154.7 \ (d, J_{\text{Si-C}} = 56 \text{ Hz}, \text{Si})\).

Potassium-4-DME 1,1-Bis(cyclopentadienyl)-1-ytra-2,2,5,5-tetrakis(trimethylsilyl)tetramethylyclopenta-silane-1-ate (8). Method A. A solution of \(1\) (obtained from 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane (156 mg, 0.26 mmol) and KOBu (59 mg, 0.53 mmol)) in DME (1 mL) was added dropwise to a slurry of bis(cyclopentadienyl)yttriumchloride (64 mg, 0.25 mmol) in DME (1 mL) and stirred at rt for 4.5 h. The resulting cloudy, bright yellow reaction mixture was subjected to NMR-analysis, showing full conversion. Precipitates were removed through centrifugation and filtration. Colorless crystals of \(8\) (206 mg, 76%) were obtained from a pentane/DME solution at \(-50^\circ\text{C}\). NMR (\(\delta\) in ppm, \(d_2\)-DME)\(^8\) \(\text{H}: 0.24 \ (d, J_{\text{H-H}} = 0.4 \text{ Hz}, 10\text{H}), 0.21 \ (\text{s}, 36\text{H}), 0.18 \ (\text{s}, 12\text{H})\). \(\text{C}^1: 108.9 \ (\text{pseudo-}t, J_{\text{C-C}} = 3.2 \text{ Hz}), 72.7 \ (\text{pseudo-}t, J_{\text{C-C}} = 2.7 \text{ Hz}), 79.0 \ (d, J_{\text{C-C}} = 2.7 \text{ Hz}), 7.4, 2.1, \text{Si}^29: -3.6 \ (\text{SiMe}_3), -26.4 \ (\text{SiMe}_2), -152.0 \ (d, J_{\text{Si-C}} = 57 \text{ Hz}, \text{Si})\).

Method B. To a solution of \(7\) (using 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane (151 mg, 0.25 mmol), KOBu (57 mg, 0.51 mmol), and YCl\(_3\) (53 mg, 0.27 mmol)) in DME (1 mL), a solution of sodium cyclopentadienyl-DME (91 mg, 0.511 mmol) was added. The reaction mixture was stirred for 80 min at rt. Insoluble parts were removed through centrifugation and filtration, and pentane (9 mL) was added, leading to a biphasic mixture. The lower ionic phase was separated by decantation and was subjected to NMR-analysis, showing pure \(8\) (133 mg, 49%).

1-Fe**ra-2,2,5,5-tetra**-kis(trimethylsilyl)tetramethylyclopenta-silane-1-ate (THF)\(_2\) (9). A solution of 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane (151 mg, 0.25 mmol) and potassium tert-butoxide (58 mg, 0.52 mmol) in THF (3 mL) was added dropwise to a slurry of iron dibromide (59 mg, 0.274 mmol) in THF (1 mL) and stirred for 3 h. During the addition, the solution first turned deep purple and then brown. Volatiles were removed under vacuum and the residue was dissolved in DME (1 mL) at rt for 4.5 h. The resulting cloudy, bright yellow reaction mixture was subjected to NMR-analysis, showing full conversion. Precipitates were removed through centrifugation and filtration. Colorless crystals of \(9\) (178 mg, 64%) were obtained from a pentane/DME solution at \(-50^\circ\text{C}\). NMR (\(\delta\) in ppm, \(d_2\)-DME)\(^8\) \(\text{H}: 0.24 \ (d, J_{\text{H-H}} = 0.4 \text{ Hz}, 10\text{H}), 0.18 \ (\text{s}, 36\text{H}), 0.18 \ (\text{s}, 12\text{H})\). \(\text{C}^1: 108.9 \ (\text{pseudo-}t, J_{\text{C-C}} = 3.2 \text{ Hz}), 72.7 \ (\text{pseudo-}t, J_{\text{C-C}} = 2.7 \text{ Hz}), 79.0 \ (d, J_{\text{C-C}} = 2.7 \text{ Hz}), 7.4, 2.1, \text{Si}^29: -3.6 \ (\text{SiMe}_3), -26.4 \ (\text{SiMe}_2), -152.0 \ (d, J_{\text{Si-C}} = 57 \text{ Hz}, \text{Si})\).
reduced pressure, and pentane (3 mL) was added. Precipitated salts were removed through centrifugation and filtration, and purple crystals of (130 mg, 79%) were obtained from the remaining solution at −50 °C. mp 104–106 °C. NMR (δ in ppm, d4-THF) 1H: 24.90 (s, 8H), 1.26 (s, 8H), 0.94 (s, 12H), 0.26 (s, 36H). Neither 13C nor 29Si NMR spectra could be obtained due to the paramagnetism of 9. Anal. Calcd. for C24H24Fe3O3Si6 (665.30): C, 43.33; H, 9.70. Found: C, 42.71; H, 10.01.

1-Ferra-4-oxa-2,6-tetramethylcyclohexasilane-2-THF (10). The compound was prepared following the same procedure as for 9 but using 1,3-bis(2-trimethylsilyl)yl)-1,1,3,3-tetramethylcyclohexane (150 mg, 0.24 mmol), potassium tert-butoxide (55 mg, 0.49 mmol), and iron dibromide (56 mg, 0.26 mmol) in THF (1 mL). Upon addition, the solution turned bright pink and then dark brown. Volatiles were removed under reduced pressure and pentane (2 × 2 mL) was added. Precipitates were removed through centrifugation and filtration and red crystalline 10 (120 mg, 74%) was obtained from this solution at −50 °C. mp 118 °C (decomp). NMR (δ in ppm) 1H: 3.64 (br s, 48H). Neither 13C nor 29Si NMR spectra could be obtained from paramagnetic 10. Anal. Calcd. for C64H64Fe6O6Si6 (681.30): C, 42.31; H, 9.47. Found: C, 41.69; H, 9.62.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c02508.

Crystallographic data of all structurally characterized compounds; 1H, 13C, and 29Si NMR spectra for compounds 2, 4, 6, 7, and 8; and 1H NMR spectra of 9 and 10 (PDF).

Accession Codes

CCDC 2071455–2071456, 2071458, 2071461, and 2071463–2071464 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Dedicated to Prof. Thomas Müller (Universität Oldenburg), on the occasion of his 60th birthday.

■ REFERENCES

(1) Marschner, C. Preparation and Reactions of Polysilyl Anions and Dianions. Organometallics 2006, 25, 2110–2125.

(2) Fischer, R.; Konopka, T.; Ully, S.; Baumgartner, J.; Marschner, C. Route Si6 revisited. J. Organomet. Chem. 2003, 685, 79–92.

(3) Fischer, R.; Konopka, T.; Baumgartner, J.; Marschner, C. Small Cyclolanes: Syntheses and Reactions toward Mono- and Dianions. Organometallics 2004, 23, 1899–1907.

(4) Gaderbauer, W.; Zirngast, M.; Baumgartner, J.; Marschner, C.; Tilley, T. D. Synthesis of Polysilylalkynylmagnesium Compounds. Organometallics 2006, 25, 2599–2606.

(5) Luo, J.; Yan, E.-H.; Zhao, H.; Xiao, X.-Q.; Li, Z. Synthesis, structure and reactivity of sterically demanding oligosilylamagnesium compounds. Polyhedron 2015, 102, 233–238.

(6) Zita, R.; Baumgartner, J.; Marschner, C. Chemistry of a 1,5-Oligosilylalene Dianion Containing a Disiloxane Unit. Organometallics 2019, 38, 1159–1167.

(7) Kayser, C.; Frank, D.; Baumgartner, J.; Marschner, C. Reactions of Oligosilyl Potassium Compounds with Group 4 Metallocene Dichlorides. J. Organomet. Chem. 2003, 667, 149–153.

(8) Westerhausen, M.; Koch, A.; Görts, H.; Krieck, S. Heavy Grignard Reagents: Synthesis, Physical and Structural Properties, Chemical Behavior, and Reactivity. Chem.—Eur. J. 2017, 23, 1456–1483.

(9) Hatano, M. Product Class 7: Calcium Compounds. In Knowledge Updates 2013/1; Yamamoto, H., Ed.; Georg Thieme Verlag: Stuttgart, 2013—b:003125699.

(10) Alexander, J. S.; Ruhlrandt-Senge, K. Not Just Heavy “Grignards”: Recent Advances in the Organometallic Chemistry of the Alkaline Earth Metals Calcium, Strontium and Barium. Eur. J. Inorg. Chem. 2002, 2761–2774.

(11) Westerhausen, M. 100 Years after Grignard: Where Does the Organometallic Chemistry of the Heavy Alkaline Earth Metals Stand Today? Angew. Chem., Int. Ed. 2001, 40, 2975–2977.

(12) Goddard, R.; Krüger, C.; Ramadan, N. A.; Ritter, A. Silicon Analogues of Grignard Compounds: Synthesis and Structure of Amine-Stabilized Trimethylsilylmagnesium Halides. Angew. Chem., Int. Ed. 1995, 34, 1030–1032.

(13) Tamao, K.; Kawachi, A. Silyl Anions. Adv. Organomet. Chem. 1995, 38, 1–58.

(14) Lickiss, P. D.; Smith, C. M. Silicon Derivatives of the Metals of Groups I and 2. Coord. Chem. Rev. 1995, 145, 75–124.

(15) Belzner, J.; Dehner, U. Alkaline and Alkaline Earth Silyl Compounds—Preparation and Structure. In The Chemistry of Organic Silicon Compounds; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons, Ltd: Chichester UK, 2003; pp 779–825.

(16) Lerner, H.-W. Silicon Derivatives of Group 1, 2, 11 and 12 Elements. Coord. Chem. Rev. 2005, 249, 781–798.

(17) Prässang, C.; Scheschkwetz, D. Silyl Anions. In Functional Molecular Silicon Compounds II; Scheschkwetz, D., Ed.; Springer: Heidelberg, 2013; pp 1–47.

(18) Marschner, C. Organosilicon Compounds: Theory and Experiment (Synthesis). Volume 1. In Silicon-Centered Anions; Lee, V. Y., Ed.; Academic Press: London, 2017; Vol. I, pp 295–360.

(19) Mochida, K.; Manishi, M. Insertion Reactions of Calcium Atom into Si–Cl and Ge–Cl Bonds. Chem. Lett. 1984, 13, 1077–1080.
(20) Teng, W.; Ruhlandt-Senge, K. Syntheses and Structures of the First Heavy Alkaline Earth Metal Bis(tris(trimethylsilyl))silanides. *Organometallics* 2004, 23, 2694–2700.

(21) Lampland, N. L.; Pindwal, A.; Yan, K.; Ellern, A.; Sadow, A. D. Rare Earth and Main Group Metal Poly(hydrosilyl) Compounds. *Organometallics* 2017, 36, 4546–4557.

(22) Takashani, K.; Lee, V. Ya.; Yokoyama, T.; Sekiguchi, A. Base-Free Molybdenum and Tungsten Bicyclic Silylene Complexes Stabilized by a Homoaromatic Contribution. *J. Am. Chem. Soc.* 2009, 131, 916–917.

(23) Okuda, J.; Spaniol, T. P.; Leich, V.; Maron, L. Hydrosilylation Catalysis by Earth Alkaline Metal Silyl: Synthesis, Characterization, and Reactivity of Bis(triphenylsilyl)calium. *Chem. Commun.* 2014, 50, 2311–2314.

(24) Réant, B. L. L.; Berryman, V. E. J.; Basford, A. R.; Hodakari, L. E.; Wooler, A. J.; Tuna, F.; Kaltsoyannis, N.; Mills, D. D.; Liddle, S. T. 28Si NMR Spectroscopy as a Probe of s- and f-Block Metal(II)−Silanide Bond Covalency. *J. Am. Chem. Soc.* 2021, 143, 9813–9824.

(25) Wilkinson, G.; Birmingham, J. M. Cyclopentadienylium Compounds of Sc, Y, La, Ce and Some Lanthanide Elements. *J. Am. Chem. Soc.* 1954, 76, 6210.

(26) For a really comprehensive survey of organolanthanide chemistry, see the annual reviews by Frank Edelmann and coworkers, the latest of which is: Edelmann, F. T.; Farnaby, J. H.; Soc. Acta 2014, 50, 916–930.

(27) Réant, B. L. L.; Liddle, S. T.; Mills, D. P. f-Element Silicon and Reactivity of Bis(triphenylsilyl)calcium. *Organometallics* 2004, 23, 2891–2895.

(28) Mitzel, N. W. Methylene-bridged, Intramolecular Donor-Acceptor Complexes of Rare Earth and Main Group Poly(hydrosilyl) Compounds. *Coord. Chem. Rev.* 2016, 315, 1518–1520.

(29) Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. NMR Nomenclature. Nuclear Spin Properties and Conventions for Chemical Shifts (IUPAC Recommendations 2001). *Pure Appl. Chem.* 2001, 73, 1795–1818.

(30) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercau, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* 2010, 29, 2176–2179.

(31) Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. NMR Nomenclature. Nuclear Spin Properties and Conventions for Chemical Shifts (IUPAC Recommendations 2001). *Pure Appl. Chem.* 2001, 73, 1795–1818.

(32) Roddick, D. M.; Tilley, T. D.; Tung, F. E.; Wooles, A. J.; Tuna, F.; Kaltsoyannis, N.; Mills, D. D.; Liddle, S. T. 50Catalysis by Earth Alkaline Metal Silyl: Synthesis, Characterization, and Reactivity of Bis(triphenylsilyl)calium. *Chem. Commun.* 2018, 55, 5328–5341.

(33) Tietze, R.; Hlina, J.; Gatterer, K.; Marschner, C.; Szilvási, T.; Baumgartner, J. Using Functionalized Silyl Ligands To Suppress Solvent Coordination to Silyl Lanthanide-II Complexes. *Inorg. Chem.* 2017, 56, 8762–8770.

(34) Wagner, H.; Baumgartner, J.; Marschner, C. 1,1′-Oligosilylferrocene Compounds. *Organometallics* 2007, 26, 1762–1770.

(35) Zitz, R.; Pöcheim, A.; Baumgartner, J.; Marschner, C. A 1,5-Oligosilylanilene Dianion as Building Block for Oligosiloxane Containing Cages, Ferrocenophanes, and Cyclic Germylenes and Stannylene. *Molecules* 2020, 25, 1322.

(36) Réant, B. L. L.; Liddle, S. T.; Mills, D. P.; Farnaby, J. H.; Soc. Acta 2014, 50, 2311–2314.

(37) For a really comprehensive survey of organolanthane chemistry, see the annual reviews by Frank Edelmann and coworkers, the latest of which is: Edelmann, F. T.; Farnaby, J. H.; Soc. Acta 2014, 50, 916–930.

(38) Lampland, N. L.; Pindwal, A.; Yan, K.; Ellern, A.; Sadow, A. D.; Hodakari, L. E.; Wooler, A. J.; Tuna, F.; Kaltsoyannis, N.; Mills, D. D.; Liddle, S. T. 28Si NMR Spectroscopy as a Probe of s- and f-Block Metal(II)−Silanide Bond Covalency. *J. Am. Chem. Soc.* 2021, 143, 9813–9824.

(39) Wilkinson, G.; Birmingham, J. M. Cyclopentadienylium Compounds of Sc, Y, La, Ce and Some Lanthanide Elements. *J. Am. Chem. Soc.* 1954, 76, 6210.

(40) For a really comprehensive survey of organolanthane chemistry, see the annual reviews by Frank Edelmann and coworkers, the latest of which is: Edelmann, F. T.; Farnaby, J. H.; Soc. Acta 2014, 50, 916–930.