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Chemistry of silylated rare earths and heavier f-elements: ready to enter the next stage

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The last few years have witnessed exciting development in the chemistry of silylated rare earths and heavier f-elements. First examples of silylated lanthanum (La) and praseodymium (Pr) complexes have been reported so that currently out of all lanthanides only for the radioactive promethium (Pm) silylated complexes are unknown. Previously unknown U(III) silyl complexes have also been described. Spectacular examples of the elusive trisilylated complexes of lanthanides and actinides have been presented. These show unusual magnetic properties, making them susceptible to facile ^{29}Si NMR spectroscopic characterization, which could be rather difficult for compounds with diminished silylation degree. Novel silylene complexes were shown to catalyze hydrosilylation reactions. The novel compound class of silole coordinated f-element complexes was introduced by La and erbium (Er) complexes with the latter exhibiting single molecule magnetic properties.

Introduction

Despite the first compound containing a transition metal-silicon σ -bond being reported by Wilkinson and co-workers as early as in 1956,¹ systematic investigations of transition metal-silyls started only in the 1980s.² In a similar way, first compounds containing silicon-lanthanide bonds were reported by Schumann and co-workers in the 1980s,^{3–5} followed by a first silyl uranium compound described by Porchia *et al.* shortly thereafter.⁶

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Christoph Marschner studied chemistry at TU Graz, Austria, and obtained his PhD in synthetic organic chemistry. After post-doctoral studies with Barry M. Trost at Stanford University, he started his independent research in the field of organosilicon chemistry at TU Graz, where he was promoted to tenured associate professor in 2001. His research interests include main group (especially group 14) and transition metal

organometallic chemistry. The main emphasis of his research over the last 30 years was put on metalated silanes, polysilanes and low-valent group 14 compounds.

An excellent and detailed compilation of the chemistry of silylated f-element compounds until 2020 was published recently by Réant, Liddle, and Mills.⁷ Following their summary, it is possible to come to a number of conclusions. For instance, at 2020, of the 15 lanthanides, there were no known examples for silylated complexes of La, Pr, and Pm and only one or two examples for Ce, Nd, Tb, Dy, Er, and Lu, each. At that time, the by far best studied element was Yb with 15 silylated examples followed by Sm with 11 examples and Eu and Tm with 5 examples, each. All reported silylated Eu and most of the Yb complexes featured the metal in the oxidation state +2. While most of the divalent complexes were disilylated, much less disilylated trivalent complexes had been prepared, left alone examples of trisilylated complexes. In 2020, the number of silylated actinide complexes amounted to 3 Th and 5 U complexes, all of them monosilylated.⁷ All of the uranium complexes featured U(IV).

A reason for the long-lasting neglect of silyl f-element chemistry may be that many of these compounds are paramagnetic. Typically, strong paramagnetism causes problems with NMR spectroscopic characterization. Even if meaningful spectra can be obtained, their diagnostic value is often hard to assess. This is especially true for hetero-nuclei with diminished receptivity such as ^{29}Si .

The present account attempts to provide an overview over the work on silylated rare earths and heavier f-elements, since the mentioned review by Réant, Liddle, and Mills.⁷

The solvent dissociation problem

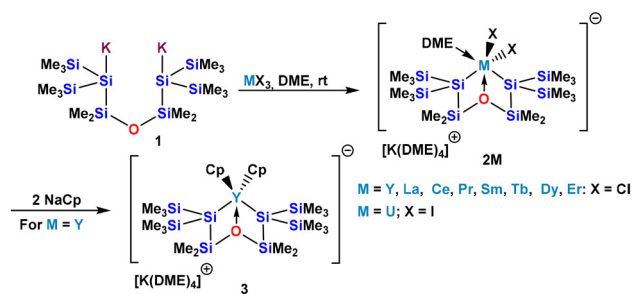
A common issue of f-element chemistry, associated not only with silylated but also with alkylated complexes, is that of

facile dissociation of solvent molecules. Owing to the rather large ionic radii of the f-elements, coordination numbers of six and higher are rather common. As the number of covalently bound (X-type) ligands, is typically two or three for these complexes, at least three or more coordinating entities, frequently Lewis basic solvent molecules, can be expected. The extent of attractive interaction between f-element ions and coordinated Lewis bases is not very high and thus dissociation can be a facile process. Complexes with diminished coordination number are, however, prone to decomposition or aggregation processes.⁸ Therefore, the stability of isolated solvent adducts toward conditions facilitating dissociation is not very high. Information about bond strengths between silicon (or heavy group 14 elements in general) and f-element atoms is scarce. An early contribution by Marks and King reports a bond dissociation energy of 37 kcal mol⁻¹ for the U–Si bond of Cp₃USi(SiMe₃)₃.⁹

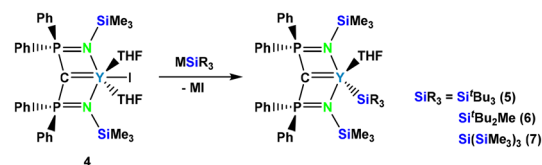
To address problems arising from ligand-dissociation induced decomposition, our research group has sought to suppress such processes by use of multidentate ligands such as oligosilanylene diides and dimethoxyethane (DME) as solvent. In addition, the attachment of additional Lewis basic sites to the ligand, which was successfully applied to trialkyl complexes such as Ln(CH₂C₆H₄-o-NMe₂)₃,¹⁰ was attempted.⁸ Utilizing the 1,5-oligosilanylene diide **1** containing a disiloxane unit, it was possible to isolate first examples of silylated La and Pr complexes as well as a first example of a structurally characterized Si–Dy complex along with complexes of Y, Ce, Sm, Tb, and Er (**2M**) (Scheme 1).¹¹

Although a fair number of silylated rare earths and f-element complexes have been synthesized, the reactivity of these complexes has been barely addressed. In particular, reactions under the preservation of the silyl–metal bond are rare. The reaction of the yttrium complex **2Y** with NaCp is thus extremely promising as it highlights clean replacement of chlorides for cyclopentadienyl ligands to give **3** (Scheme 1).

Similarly, Liddle, Mills and co-workers used a substituted methane diide ligand system, which also features additional donor sites. Reaction of yttrium iodide complex **4** with alkali silanides gave the Y complexes **5**, **6**, and **7** with attached Si^tBu₃, Si^tBu₂Me, and Si(SiMe₃)₃ groups, respectively (Scheme 2).¹²



Scheme 1 Synthetic access to a number of disilylated rare earths and U(III) ate-complexes.



Scheme 2 Silylated Y complexes **5**, **6**, and **7** with a methane diide ligand system.

Uranium(III) and Th(IV) complexes

The same group reported synthesis of Cp₂Th(Cl)Si(SiMe₃)₃ (**8Th**) (Cp⁺ = C₅H₃(SiMe₃)₂-1,3)¹³ and the first example of a U(III)–silyl complex: Cp₂USi(SiMe₃)₃ (**9U**).¹⁴ The compounds were prepared by reaction of Cp₂ThCl₂ and (Cp₂U)₂ with KSi(SiMe₃)₃ or alternatively, reaction of Cp₂UCl₂ with 2 equiv. KSi(SiMe₃)₃, resembling reaction of Cp₂TiCl₂ with 2 equiv. KSi(SiMe₃)₃, where the elimination of a (Me₃Si)₂Si dimer caused formal reduction to Ti(III).¹⁵ La, Ce, and Nd complexes (**9Ln**) isostructural to **9U** were also reported in this work.¹⁴

Shortly after this, Bart and co-workers demonstrated that the mentioned 1,5-oligosilanylene diide ligand **1** can also be used in actinide chemistry. They were able to prepare the first disilylated uranium(III) complex (**2U**) by reacting **1** with UI₃ (Scheme 1).¹⁶ Later, they reported on the reactivity of **2U** with aryl diazenes, which results in the formal insertion of aryl imido units into the Si–U bonds.¹⁷

New complexes of La and Ce

Fang and co-workers reported a number of silylated La and also Ce ate-complexes of the type M[Cp₃LnSiR₃] (M = Li, Na, K; Ln = La, Ce; R₃Si = Si(H)Me₂ (**10Ln**), SiMePh₂ (**11Ln**), SiPh₃ (**12Ln**) and SiPh₂SiPh₃ (**13Ln**)).¹⁸ This was followed by the synthesis of related monosilylated ate-complexes of other trivalent lanthanides (Ln = Sm, Tb, Dy, Yb) of the type [Li(DME)₃][Cp₃LnSiPh₃] (**12Ln**) and an example of a disilylated Lu ate-complex: [Li(DME)₃][Cp₂Lu(SiPh₃)₂] (**14Lu**).¹⁹ Fang and co-workers showed also that their synthetic strategy can be extended to triphenylgermyl and triphenylstannyl groups, yielding the respective La and Ce complexes: [Li(DME)₃][Cp₃LnEPh₃] (Ln = La, Ce; E = Ge, Sn).²⁰

Di- and trisilylated f-element complexes

Extending the series of disilylated Yb, Eu and Sm complexes Kaltsoyannis, Mills, Liddle and co-workers prepared Yb, Eu and Sm complexes with Si^tBu₃ and Si^tBu₂Me ligands: (Si^tBu₃)₂Ln(THF)₂ (**15**) and (Si^tBu₂Me)₂Ln(THF)₃ (**16**) (Ln = Yb, Eu, Sm).²¹

Reviewing the organometallic chemistry of the lanthanides, it becomes evident that the number of homoleptic neutral trialkylated complexes is rather small.²² Although examples of Ln{CH(SiMe₃)₂}₃^{23–25} and Ln(CH₂Ph)₃(THF)₃^{26,27} are known, also these can suffer from ligand-dissociation caused instability. For this reason, it seemed not surprising that there were also no examples of homoleptic neutral trisilylated complexes known. However, recently Réant *et al.* were able to present first examples of this previously elusive class of compounds.



Already in 2014 Sgro and Piers had reported the reactions of the THF adducts of YI_3 and GdI_3 with $(\text{Me}_3\text{Si})_3\text{SiK}$ to proceed to $(\text{Me}_3\text{Si})_3\text{SiYI}_2(\text{THF})_3$ and $(\text{Me}_3\text{Si})_3\text{SiGdI}_2(\text{THF})_3$, respectively.²⁸ Attempts to obtain di- or even trisilylated complexes were not mentioned in the study. Nevertheless, utilizing a similar approach, formation of the trisilylated complexes of La, Ce, Pr, Nd, and U (**17M**) by reacting three equivalents of $(\text{Me}_3\text{Si})_3\text{SiK}$ with the respective triiodides was reported (Scheme 3).²⁹

These compounds are quite unique. They constitute the first ever known examples of trisilylated f-element complexes and show most unusual properties with respect to their receptivity to NMR spectroscopic characterization. As mentioned, the detection of NMR signals of silylated f-element complexes is frequently hampered by their paramagnetism. However, for compounds **17M** ^{29}Si NMR chemical shift values for the metal bound silicon atoms could be detected for all (*i.e.* also the paramagnetic Ce, Pr, Nd, and U) complexes. An alignment of the most magnetic axis along the three-fold rotation axis occupied by the coordinated THF molecules seems responsible for this unexpected behavior. The metal-bound silicon atoms and also the trimethylsilyl groups are thus not much affected (see Fig. 1 for calculated magnetic axes of complex **17Ce**). The chemical shift value of diamagnetic $[(\text{Me}_3\text{Si})_3\text{Si}]_3\text{La}(\text{THF})_3$ (**17La**) in solution ($\text{C}_6\text{D}_6/\text{C}_4\text{D}_8\text{O}$: 9/1) was found to be -82.3 ppm. The fact that the respective values of paramagnetic $[(\text{Me}_3\text{Si})_3\text{Si}]_3\text{M}(\text{THF})_2$ ($\text{M} = \text{Ce}, \text{Pr}, \text{Nd}, \text{and U}$) were all observed within a small spectral window between -65.5 and -79.4 ppm, indicates how effective the suppression of the paramagnetic influence for this particular geometry is. CASSCF-SO-calculations were used to obtain a suitable model of the magnetic susceptibility tensor and to model the pNMR shifts of the

paramagnetic **17M** complexes for 0, 1, and 2 coordinated THF molecules.²⁹

New silylene complexes of di- and trivalent rare earth metals

Continuing work on silylene coordinated divalent f-elements,³⁰ P. Roesky and co-workers have introduced new ligand systems.³¹ A ferrocene based bis(silylene) ligand provided thermally stable complexes **18Ln** ($\text{Ln} = \text{Eu}, \text{Yb}$) of Eu and Yb (Scheme 4). The other ligand is a silylene with an attached 2-pyridine unit which gave the respective complexes of divalent Eu and Yb (**19Ln**) ($\text{M} = \text{Eu}, \text{Yb}$) as well as trivalent Y, La, and Lu complexes (**20RE**) ($\text{M} = \text{Y}, \text{La}, \text{Lu}$) (Scheme 4). Complexes **18Yb**, **20Y**, **20La**, and **20Lu** were shown to be effective catalysts for the hydrosilylation of terminal alkenes with PhSiH_3 .³¹

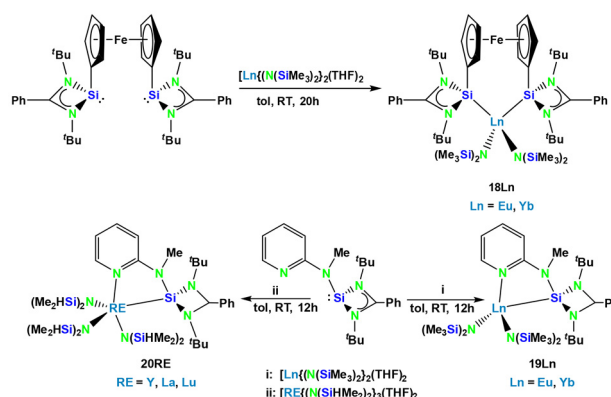
Silole complexes

P. Roesky and co-workers also reported the first example of a rare earths silole complex.³² Reaction of the cyclooctatetra-dienyl (COT) lanthanum iodide complex $[\text{La}(\eta^8\text{-COT})\text{I}(\text{THF})_3]$ ³³ with a 2,5-bis(trimethylsilyl)silole dianion³⁴ gave the anionic silole COT La complex (**21La**) which in the solid state was found to exist as a dimer, with a silole-Si lanthanum (La-Si') interaction providing the attractive force for the dimerization (Scheme 5).³²

Layfield and co-workers reported the first erbium COT silole and stannole complexes.³⁵ Reacting a COT $[\text{BH}_4]$ $[\text{THF}]_2$



Scheme 3 Synthetic access to a number of trisilylated ate-complexes **17M**.



Scheme 4 Synthesis of new divalent lanthanide bis(silylene) complexes (top trace), new Eu(II) and Yb(II) mono-silylene complexes (bottom trace right) and also trivalent mono-silylene complexes with the same ligand of Y, La and Lu (bottom trace left).

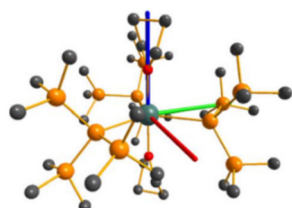
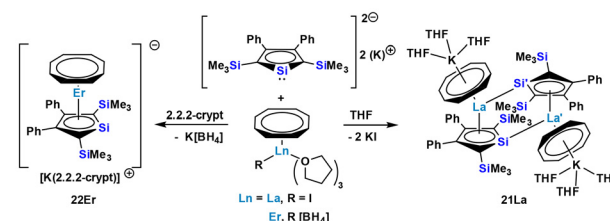


Fig. 1 CASSCF-SO-calculated magnetic axes for **17Ce** (blue: g_1 , most magnetic; green: g_2 , intermediate; red: g_3 , least magnetic) for complexes. Metal, silicon, carbon, and hydrogen atoms shown as metallic green, orange, gray, and light gray, respectively (figure reproduced from ref. 29).



Scheme 5 First examples of silole coordinated La and Er complexes **21La** and **22Er**.



Table 1 M–Si distances and ^{29}Si NMR shifts of compounds discussed in this frontier article

Complex	Si–M (Å)	δ_{Si} (Si–M) (ppm)	Complex	Si–M (Å)	δ_{Si} (Si–M) (ppm)
2Y ¹¹	3.064(2)/3.057(1)	–161.6	12Yb ¹⁹	2.9389(13)	n.d.
2Ce ¹¹	3.144(2)/3.159(2)	n.d.	13La ¹⁸	3.1860(15)	–21.1 ^a
2Pr ¹¹	3.119(2)–3.167(2)	n.d.	13Ce ¹⁸	3.1705(9)	n.d.
2Sm ¹¹	3.089(2)/3.099(2)	n.d.	14Lu ¹⁹	2.982(2)/2.9162(17)	n.d.
2Tb ¹¹	3.073(2)/3.081(2)	n.d.	15Yb ²¹	3.060(3)	54.2
2Dy ¹¹	3.077(3)/3.077(3)	n.d.	15Eu ²¹	3.258(4)	n.d.
3Y ¹¹	3.1315(9)/3.1459(9)	–153.4	15Sm ²¹	3.261(3)	n.d.
2U ¹⁶	3.1149(6)–3.1713(14)	n.d.	16Yb ²¹	3.0678(14)	29.2
5Y ¹²	3.062(2)	33.5	16Eu ²¹	3.2075(9)	n.d.
6Y ¹²	3.017(10)	12.9	16Sm ²¹	3.2196(10)	n.d.
7Y ¹²	3.0126(7)	–148.5	17La ²⁹	3.197(3)	–82.3
8Th ¹³	3.1053(13)	–66.3	17Ce ²⁹	3.172(2)	–79.4
9U ¹⁴	3.116(2)	n.d.	17Pr ²⁹	3.161(3)	–65.5
9La ¹⁴	3.178(2)	–130.3 ^b	17Nd ²⁹	3.131(2)	–71.6
9Ce ¹⁴	3.153(2)	n.d.	17U ²⁹	3.114(2)	–70.5
9Nd ¹⁴	3.112(2)	n.d.	18Eu ³¹	3.3276(10)/3.3294(9)	n.d.
10La ¹⁸	3.1897(10)	–36.0 ^a	18Yb ³¹	3.2431(5)/3.1881(6)	64.6
10Ce ¹⁸	3.1446(16)	n.d.	19Eu ³¹	3.2309(6)	n.d.
11La ¹⁸	3.1846(6)	–1.7 ^a	19Yb ³¹	3.0766(7)	14.3
11Ce ¹⁸	3.1446(16)	n.d.	20Y ³¹	3.0134(5)	9.4
12La ¹⁸	3.1733(4)	7.0 ^a	20La ³¹	3.1868(8)	14.7
12Ce ¹⁸	3.1415(6)	n.d.	20Lu ³¹	2.9380(7)	27.9
12Sm ¹⁹	3.0729(7)	n.d.	21La ³²	3.0888(5) Si/3.2908(6) Si'	187.9
12Tb ¹⁹	3.0277(7)	n.d.	22Er ³⁵	2.882(2)	n.d.
12Dy ¹⁹	3.0092(7)	n.d.			

^a Solid state CP/MAS ^{29}Si NMR data. ^b Tentatively assigned.

erbium complex with the same 2,5-bis(trimethylsilyl)silole dianion used by Roesky in 1,4-dioxane gave the anionic complex **22Er**, which is monomeric in the solid state (Scheme 5).³⁵ Investigations of the magnetic properties of the respective silole, stannole³⁵ and germole³⁶ erbium complexes revealed them as single-molecule magnets.

Si–M distances and ^{29}Si NMR shifts of the presented compounds

Table 1 provides a summary of reported metal–Si distances and ^{29}Si NMR shifts of the discussed compounds.

Conclusions

The chemistry of silylated rare earth and heavier f-elements has started as a lab curiosity some 40 years ago. Less than 70 papers dealing with these substances have been published. Approximately half of these derive from the last decade. Within these years, substantial progress has been made filling a number of obvious gaps in the field. The chemistry seems ready to enter the next phase, from exploratory discoveries to systematic studies of reactivity and properties and further on to applications in catalysis and material science.

Data availability

Since this is a review type article, the data used for the composition of the article consist only of the cited references.

Conflicts of interest

There are no conflicts to declare.

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