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Synthesis, Structure, and Reactivity of Zwitterionic Divalent Rare-Earth Metal Silanides

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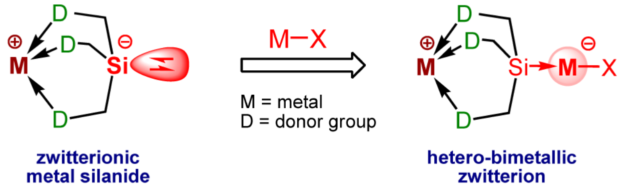
S *Supporting Information*

ABSTRACT: The synthesis and structures of the first zwitterionic divalent rare-earth metal silanides of the formula $[Si(SiMe_2OMe)_3\text{-}\kappa^3]_2M$ (M-**3**), where M = Eu, Yb, and Sm, are reported. M-**3** compounds feature spirocyclic bicyclooctane structures in which the central rare-earth metal ions are being octahedrally coordinated by six methoxy groups. The reaction of Yb-**3** with BPh_3 and $W(CO)_6$ respectively generated the trinuclear zwitterions $[Ph_3BSi(SiMe_2OMe)_3\text{-}\kappa^3]_2Yb$ (Yb-**4**) and $[(CO)_5WSi(SiMe_2OMe)_3\text{-}\kappa^3]_2Yb$ (Yb-**5**) in good yield.

Zwitterionic silanides are an emerging class of donor-substituted silyl anions[1,2] that are potentially useful as ambidentate ligands to support main-group and transition metals.[3−10] Interest in these types of highly reactive zwitterions primarily arises from the "naked" silyl anion that is rigidly locked and insulated from the metal cation by internal donor bridges. Unlike tetracoordinated borate-based zwitterions,[11] zwitterionic silanides are tricoordinated and consequently contain a stereochemically active electron pair localized at the silyl anion, which behaves as a Lewis base that can bind to electrophilic transition and main-group metal centers (Scheme 1).

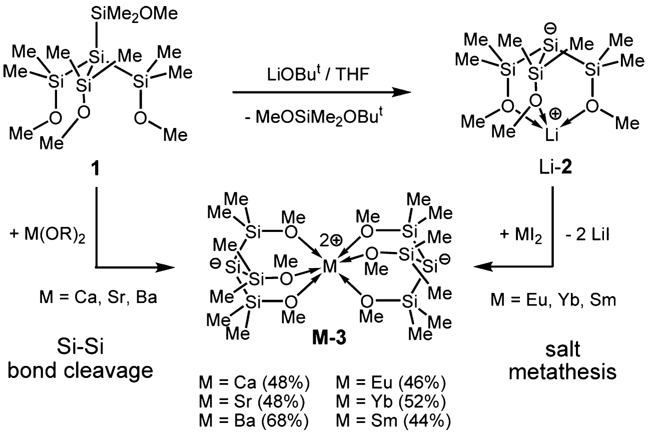
Scheme 1. Design of Heterobimetallic Zwitterions



In this regard, we recently reported the synthesis and discrete structures of zwitterionic alkali-metal silanides of the formula $[Si(SiMe_2OCH_2CH_2OMe)_3\text{-}\kappa^6]M$ (M = Li, Na, K) and demonstrated that the charge-separated "naked" silyl anion is available for additional metal binding, allowing for the synthesis of novel zwitterionic heterobimetallic silanides.[6,8] In addition, we succeeded in synthesizing and structurally characterizing novel zwitterionic alkaline-earth metal silanides of the formula $[Si(SiMe_2OMe)_3\text{-}\kappa^3]_2M$ (M = Mg, Ca, Sr, Ba). These discrete homoleptic complexes represent the first examples of metal-containing zwitterions that are composed of two "naked" silyl anions.[7] On the other hand, zwitterionic silanides of the rare-earth metals regardless of their oxidation state have not been prepared so far. Herein, we report on the synthesis and structures of the first zwitterionic divalent europium, ytterbium, and samarium silanides and the reaction behavior of the divalent ytterbium silanide toward BPh_3 and $W(CO)_6$.

The zwitterionic alkaline-earth metal silanides $[Si(SiMe_2OMe)_3\text{-}\kappa^3]_2M$ (M-**3**; M = Ca, Sr, Ba) can conveniently be synthesized via selective Si−Si bond cleavage of $Si(SiMe_2OMe)_4$ (**1**) with commercially or synthetically readily available metal alkoxides $M(OR)_2$ (M = Ca, Sr, Ba) in tetrahydrofuran (THF) as the solvent (Scheme 2).[7] Owing to their zwitterionic nature, M-**3** compounds proved to be poorly soluble, even in THF, and precipitated from the reaction mixture as crystalline materials, which greatly facilitated their isolation and purification. For synthesis of the zwitterionic divalent rare-earth metal silanides M-**3** (M = Eu, Yb, Sm), assumed to be of low solubility similar to that of their alkaline-earth counterparts, salt metathesis as an alternative route was envisioned because of the lack of commercially available divalent rare-earth alkoxides.

Scheme 2. Synthesis of M-3 (M = Ca, Sr, Ba, Eu, Yb, Sm)



In fact, combining THF solutions of the anhydrous salts MI_2 (M = Eu, Yb, Sm) with $[Si(SiMe_2OMe)_3Li]_\infty$ (Li-**2**), derived from the reaction of **1** with $LiOBu^t$ in THF,[2f] generated upon standing at room temperature for several hours crystalline precipitates of the europium, ytterbium, and samarium silanides M-**3** in acceptable isolated yield (Scheme 2). The use of lithium silanide, Li-**2**, as the nucleophile was crucial to the isolation of

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"salt-free" M-**3** in high purity because the byproduct LiI formed during the course of the reaction is well soluble in THF at room temperature and did not coprecipitate with M-**3**. The isolated compounds M-**3** (M = Eu, Yb, Sm) are extremely air- and moisture-sensitive but appear to be stable at room temperature for extensive periods of time upon storage in a glovebox, while THF solutions of M-**3** very slowly decompose over time at room temperature.

Even though insoluble in hydrocarbons and poorly soluble in THF, Yb-**3** was characterized in solution by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy using THF-d_8 as the solvent. The paramagnetic species Eu-**3** and Sm-**3** were characterized by combustion analysis. In addition, the solid-state structures of M-**3** (M = Eu, Yb, Sm) were determined by X-ray crystallography, and the results for Yb-**3** are exemplary shown in Figure 1 along with selected average bond lengths and angles of all structurally characterized metal silanides (Table 1) and the alkaline-earth metal silanides Mg-**3**, Ca-**3**, Sr-**3**, and Ba-**3**, previously reported.[7] Compounds Eu-**3**, Yb-**3**, and Sm-**3** are isostructural, featuring spirocyclic bicyclooctane structures in which the central metal ions are octahedrally coordinated by six methoxy groups via dative bond interactions. To our knowledge, M-**3** compounds are the first examples of truly zwitterionic silanides that contain rare-earth metal cations regardless of their formal oxidation state.

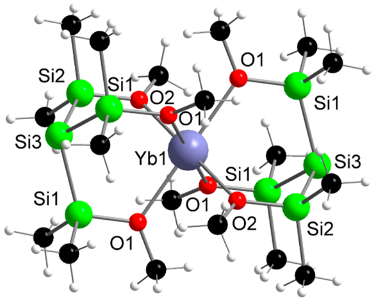


Figure 1. Solid-state structure of Yb-**3** (disorder is not shown for clarity). Color code: black, carbon; white, hydrogen.

Table 1. Average Distances (Å) and Angles (deg) of $[Si(SiMe_2OMe)_3\text{-}\kappa^3]_2M$ (M-3; M = Mg, Ca, Sr, Ba, Eu, Yb, Sm)

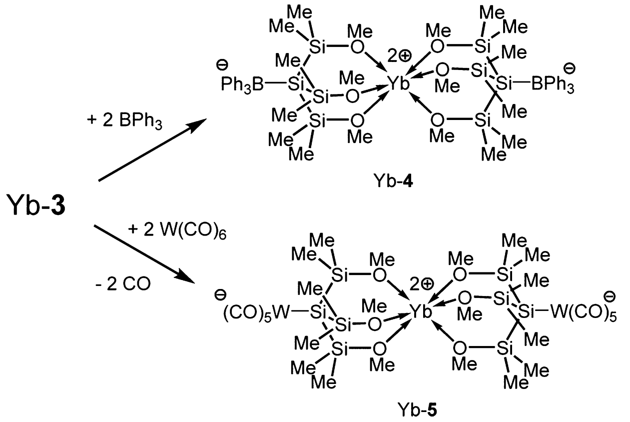
	Mg-**3**^{a}	Ca-**3**^{a}	Yb-**3**^{b}	Sr-**3**^{a}	Eu-**3**^{b}	Sm-**3**^{b}	Ba-**3**^{a}
$r(M^{2+})^c$	0.72	1.00	1.02	1.16	1.17	1.22	1.36
Si−Si	2.30	2.30	2.30	2.30	2.30	2.31	2.31
Si−O	1.72	1.70	1.70	1.69	1.70	1.70	1.70
M−O	2.15	2.38	2.43	2.51	2.52	2.54	2.66
M···Si	3.98	3.79	3.72	3.72	3.68	3.69	3.70
Si−O−M	128	120	117	116	115	115	114
Si−Si−Si	95	105	106	108	108	108	109

^{a}Reference 7. ^{b}This work. ^{c}The ionic radius of M^{2+}.

The structural parameters of M-**3** (M = Eu, Yb, Sm) are fairly similar, except the M−O distances, which increase as the size of the metal ion becomes larger. Note that the M···Si distances in M-**3** (3.68−3.72 Å) are longer than those in the very few reported nonzwitterionic divalent rare-earth metal silanides $(Me_3Si)_3SiYbCp^*(THF)_2$ (3.03 Å),[12] $(Me_3Si)_3SiYb[N(SiMe_3)_2]_2K$ (3.04 Å),[13] $(Ph_3Si)_2Yb(THF)_4$ (3.16 Å),[14] and $[Cp^*_2Eu(THF)SiH_3K(THF)]$ (3.24 Å)[15] and the silylene complex $[Cp^*_2SmSi[N(Bu^t)CH]_2]_3$ (3.19 Å),[16] indicating only weak electrostatic interactions between the silyl anion and metal cation in M-**3**. A structural comparison of the rare-earth derivatives with the alkaline-earth derivatives M-**3** reveals striking similarities (Table 1). For example, the Si−Si distances (ca. 2.30−2.31 Å) and, except for Mg-**3**, the Si−O (1.69−1.70 Å) and Si···M (3.68−3.79 Å) distances as well as the Si−Si−Si (105−109°) and Si−O−M (114−120°) angles are very close to each other. The M−O distances, on the other hand, appear to be a function of the metal cation radius; e.g., the larger the radius of M^{2+}, the larger the M−O distance.

To elucidate the donor ability of the "naked" silyl anions, Yb-**3** was reacted with BPh_3, a medium Lewis acid,[17] and $W(CO)_6$, known to undergo substitution reactions with loss of CO.[18−20] In fact, the reaction with 2 equiv of BPh_3 in THF resulted in the formation of a microcrystalline precipitate identified by multinuclei NMR spectroscopy and elemental analysis as $[Ph_3BSi(SiMe_2OMe)_3\text{-}\kappa^3]_2Yb$ (Yb-**4**). The ^{29}Si NMR data are most instructive because the signal of the central silicon anion drastically shifted to higher field, from −202.9 ppm in zwitterion Yb-**3** to −132.0 ppm upon the addition of BPh_3. The ^{11}B NMR spectrum displays a broad signal at ca. −8.0 ppm indicative of a boron atom in a tetrahedral coordination environment. The reaction of Yb-**3** with $W(CO)_6$ proceeded similarly, giving rise to the formation of a trimetallic zwitterion of the formula $[(CO)_5WSi(SiMe_2OMe)_3\text{-}\kappa^3]_2Yb$ (Yb-**5**), as confirmed by NMR spectroscopy and the results of elemental analysis (Scheme 3). Again, in the ^{29}Si NMR spectrum, the signal of the central anionic silicon shifted to higher field, from −202.9 ppm in zwitterion Yb-**3** to −152.0 ppm upon the addition of $W(CO)_6$. The IR spectrum (THF) of the carbonyl region of Yb-**5** displays four bands at 2042 (m), 1957 (m), 1907 (vs), and 1878 (s) cm^{-1}. These values are characteristic of $M[W(CO)_5X]$ species, which do not have rigorous C_{4v} geometry,[21] and are similar to the values of the tungsten silyl complexes reported previously.[2i,18−20]

Scheme 3. Synthesis of Yb-4 and Yb-5



The solid-state structure of Yb-**4** was confirmed by single-crystal X-ray crystallography; suitable crystals were grown from THF at room temperature (Figure 2). Yb-**4** contains two molecules of noncoordinating THF; crystalline samples, which had been exposed to vacuum for ca. 2 h, lost approximately one molecule of THF. Similar to Yb-**3**, silyl borate Yb-**4** features a central spirocyclic bicyclooctane structure, with the central ytterbium ion being octahedrally coordinated by six methoxy

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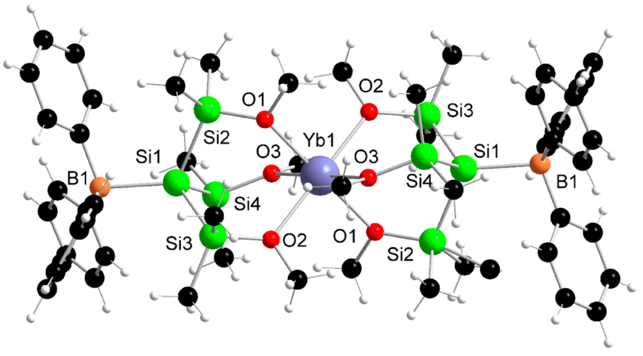

Figure 2. Structure of Yb-**4** (THF molecules are omitted for clarity). Color code: black, carbon; white, hydrogen. Average distances (Å) and angles (deg): Yb−O 2.43, Si1−B1 2.17, Si−Si 2.34, Si−O 1.72, C−B 1.63; Si−Si−Si 102.6, Si−O−Yb 127.2.

groups. The triphenylborane units are bound to the central silicon atoms, generating two tetracoordinated silyl borate units. The Si−B distances (2.17 Å) are in agreement with those of the structurally related silyl borate complexes [$(C_6F_5)_3$BSi($SiMe_2OCH_2CH_2OMe)_3$-κ^6-K] (2.17 Å) and [$(C_6F_5)_3$BSi($SiMe_2OCH_2CH_2OMe)_3$-κ^6-Zn][MeB$(C_6F_5)_3$] (2.14 Å).[8] Notably, upon coordination with BPh_3, the average Si−Si distance significantly increases from 2.30 Å in Yb-**3** to 2.34 Å in Yb-**4**. Also, the Si−O distances slightly increase (from 1.70 to 1.72 Å), while the M−O distances remain unchanged (both 2.43 Å).

In conclusion, the synthesis and structures of the first zwitterionic divalent rare-earth metal silanides of the formula [Si$(SiMe_2OMe)_3$-κ^3]$_2$M (M-**3**), where M = Eu, Yb, and Sm, are reported. M-**3** compounds feature spirocyclic bicyclooctane structures in which the central rare-earth metal ions are being octahedrally coordinated by six methoxy groups similar to that seen in the alkaline-earth zwitterions M-**3** (M = Ca, Sr, Ba). Yb-**3** reacts with BPh_3 and $W(CO)_6$ respectively to produce the zwitterions Yb-**4** and Yb-**5** in good yield.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data for all compounds and CIF file including Yb-**3** (CCDC 1050382), Eu-**3** (CCDC 1050383), Sm-**3** (CCDC 1050381), and Yb-**4** (CCDC 1050384). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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