

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

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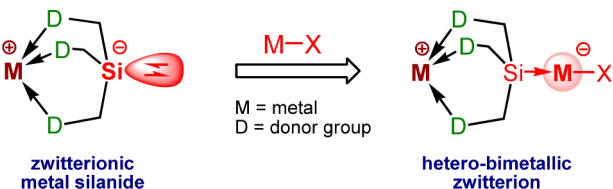
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## Supporting Information

**ABSTRACT:** The synthesis and structures of the first zwitterionic divalent rare-earth metal silanides of the formula  $[\text{Si}(\text{SiMe}_2\text{OMe})_3\text{-}\kappa^3]_2\text{M}$  (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. The reaction of Yb-3 with  $\text{BPh}_3$  and  $\text{W}(\text{CO})_6$  respectively generated the trinuclear zwitterions  $[\text{Ph}_3\text{BSi}(\text{SiMe}_2\text{OMe})_3\text{-}\kappa^3]_2\text{Yb}$  (Yb-4) and  $[(\text{CO})_5\text{WSi}(\text{SiMe}_2\text{OMe})_3\text{-}\kappa^3]_2\text{Yb}$  (Yb-5) in good yield.

Zwitterionic silanides are an emerging class of donor-substituted silyl anions<sup>1,2</sup> that are potentially useful as ambidentate ligands to support main-group and transition metals.<sup>3–10</sup> 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,<sup>11</sup> 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

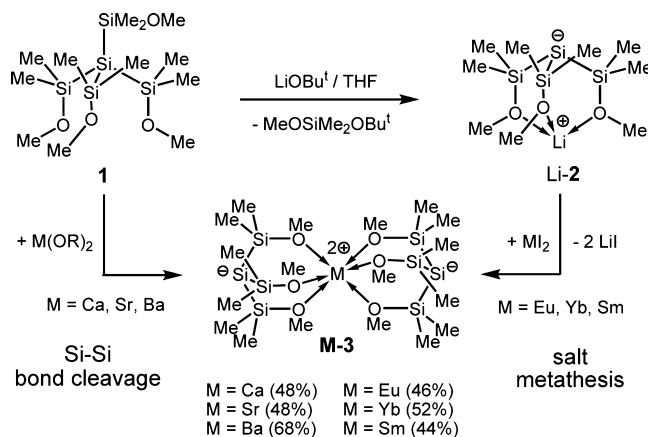


In this regard, we recently reported the synthesis and discrete structures of zwitterionic alkali-metal silanides of the formula  $[\text{Si}(\text{SiMe}_2\text{OCH}_2\text{CH}_2\text{OMe})_3\text{-}\kappa^6]\text{M}$  (M = Li, Na, K) and demonstrated that the charge-separated “naked” silyl anion is available for additional metal binding, allowing for the synthesis of novel zwitterionic heterobimetallic silanides.<sup>6,8</sup> In addition, we succeeded in synthesizing and structurally characterizing novel zwitterionic alkaline-earth metal silanides of the formula  $[\text{Si}(\text{SiMe}_2\text{OMe})_3\text{-}\kappa^3]_2\text{M}$  (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.<sup>7</sup> 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  $\text{BPh}_3$  and  $\text{W}(\text{CO})_6$ .

The zwitterionic alkaline-earth metal silanides  $[\text{Si}(\text{SiMe}_2\text{OMe})_3\text{-}\kappa^3]_2\text{M}$  (M-3; M = Ca, Sr, Ba) can conveniently be synthesized via selective Si–Si bond cleavage of  $[\text{Si}(\text{SiMe}_2\text{OMe})_4]$  (1) with commercially or synthetically readily available metal alkoxides  $\text{M}(\text{OR})_2$  (M = Ca, Sr, Ba) in tetrahydrofuran (THF) as the solvent (Scheme 2).<sup>7</sup> Owing to

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



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.

In fact, combining THF solutions of the anhydrous salts  $\text{MI}_2$  (M = Eu, Yb, Sm) with  $[\text{Si}(\text{SiMe}_2\text{OMe})_3\text{Li}]_\infty$  (Li-2), derived from the reaction of 1 with  $\text{LiOBu}^t$  in THF,<sup>2f</sup> 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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