

Main-Group Clusters

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Isolation and Versatile Derivatization of an Unsaturated Anionic Silicon Cluster (Siliconoid)

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Dedicated to Prof. Armin Berndt on occasion of his 79th birthday

Abstract: The characteristic features of bulk silicon surfaces are echoed in the related partially substituted—and thus unsaturated—neutral silicon clusters (siliconoids). The incorporation of siliconoids into more-extended frameworks is promising owing to their unique electronic features, but further developments in this regard are limited by the notable absence of functionalized siliconoid derivatives until now. Herein we report the isolation and full characterization of the lithium salt of an anionic R_5Si_6 -siliconoid, thus providing the missing link between silicon-based Zintl anions and siliconoid clusters. Proof-of-principle for the high potential of this species for the efficient transfer of the intact unsaturated R_5Si_6 moiety is demonstrated by clean reactions with representative electrophiles of Groups 13, 14, and 15.

The industrial-scale preparation of silicon is one of the most far-reaching scientific developments of the 20th century; the progress in microprocessor performance and thus the information technology-centered society of today would be difficult to imagine without silicon as a readily available key component.^[1] The understanding and the manipulation of silicon surfaces^[2] are key aspects of silicon-based technologies.^[3] Stable siliconoids^[4] are unsaturated neutral silicon clusters^[5] that reproduce the characteristic structural features of silicon nanoparticles and surfaces in the molecular regime, in particular the presence of one or more unsubstituted vertices.^[6] Stable examples were reported by us^[4,7] and the groups of Wiberg,^[8] Breher,^[9] Kyushin,^[10] and Iwamoto.^[11] The pronounced electronic anisotropy of molecular siliconoids—as shown by an unprecedentedly wide distribution of ^{29}Si NMR chemical shifts^[12]—would be an attractive feature

for the construction of structures on the subnano scale. Evidently, functionalized vertices are a prerequisite for the embedding of siliconoids in extended supramolecular assemblies. However, only unfunctionalized siliconoids have been reported so far,^[4,7–11] severely limiting further developments in this regard.

Notably, the structural and NMR spectroscopic properties of siliconoids are reminiscent of Zintl anions of the Group 14 elements.^[13,14] Spurred by novel methods for the extraction from solid-state phases into polar solvents, such as liquid ammonia,^[15] ethylenediamine,^[16] or dimethylformamide,^[17] the potential of Zintl anions as building blocks for extended systems has been recognized in the last few years. Thus, for that Group 14 elements heavier than silicon, rod-like polyanions,^[18] nanoparticles,^[19] or mesostructured elemental allotropes,^[20] are accessible. The multiple negative charges of Zintl anions—which in the widest sense can be considered as nucleophilic functionalities—could in principle be expected to allow for the attachment of substituents and/or functional groups under retention of unsubstituted vertices, thus establishing a conceptual bridge to the partially substituted and neutral siliconoids. In practice, however, the strongly reducing nature conferred by the multiple charges is detrimental to the reaction with electrophiles that would convert a Zintl anion E_x^{n-} into the corresponding neutral siliconoid E_xR_n (E = Group 14 element).^[14a] For germanium^[21] and tin^[22] a few experimental methods exist nonetheless, although low yields and poor selectivity tend to be observed possibly because of the involvement of competing radical mechanisms. In the case of Zintl anions of silicon, the only rational chemical transformations reported so far result in the complexation of the silicide anions to transition-metal centers without any compensation of negative charges.^[23]

Herein we report the synthesis and isolation of an intermediate species containing both an anionic and two neutral unsubstituted vertex atoms, which is accessible by the reverse approach of employing the neutral siliconoid **1** as the starting material rather than a Zintl anion. As demonstrated by reactions with representative electrophiles of Groups 13 to 15, this anionic siliconoid can be efficiently functionalized with various electrophiles, while maintaining the integrity of the unsaturated cluster scaffold.

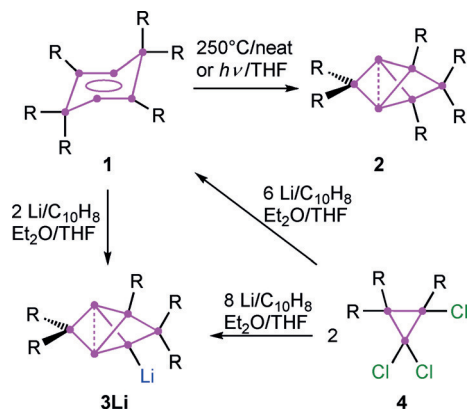
As the reductive cleavage of aryl^[24] and silyl^[25] substituents in silicon compounds is known to generate anionic species (most notably a tetrasilatetrahedranide, a silicon cluster anion without any additional unsubstituted vertex^[25a]),

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we investigated the reduction of the dismutational isomer **1**. Treatment of **1** with two equivalents of lithium/naphthalene in a mixture of diethylether and tetrahydrofuran led to a color change from green to dark orange.^[26] Complete and uniform conversion into a new Si₆-species was detected by ²⁹Si NMR spectroscopy. Six resonance signals with a large dispersion of ²⁹Si chemical shifts, similar to those observed for the global-minimum hexasilabenzene isomer **2** (Tip = 2,4,6-triisopropylphenyl, Scheme 1),^[7c] were assigned on the basis of a two-



Scheme 1. Synthesis of **3Li** from either dismutational hexasilabenzene isomer **1** or 1,1,2-trichlorocyclotrisilane **4** (magenta dots = Si; R = 2,4,6-triisopropylphenyl).

dimensional ¹H–²⁹Si correlation experiment. The ²⁹Si signal of one SiTip₂ moiety appears a long way downfield at $\delta = 159.6$ ppm, while resonances for another SiTip₂ and a mono-substituted SiTip unit appear in the usual region at $\delta = 12.8$ and 27.6 ppm, respectively (in **2**: $\delta = 174.6$, 14.8, and 27.6 ppm). Remarkably, the unsubstituted vertices in the product are apparently not compromised by the reduction as witnessed by two upfield signals at $\delta = -237.3$ and -238.2 ppm (in **2**: $\delta = -274.2$ ppm). A resonance at $\delta = 66.8$ ppm is assigned to a lithium-bonded silicon atom on grounds of the apparent broadening through the coupling to the quadrupolar ⁷Li nucleus. These data are consistent with the reductive elimination of one of the Tip substituents and the formation of the lithiated Si₆ siliconoid **3Li** (Scheme 1).

The lithium salt of the anionic siliconoid crystallizes as **3Li**·(THF)₂ in 62 % yield from *n*-hexane, albeit with variable amounts of co-crystallized THF and residual naphthalene. Under argon, **3Li**·(THF)₂ is stable in solution and in the solid state, but readily decomposes in the presence of air and moisture. Single crystals of **3Li**·(THF)₂ were analyzed by X-ray diffraction and the constitution as a contact ion pair unambiguously confirmed despite the low quality of the data set which is due to pronounced disorder. To obtain higher quality X-ray data, cation-sequestering agents were employed. **3**[Li(DME)₃] (70 % yield) and **3**[Li(12-crown-4)₂] (72 % yield) were isolated as solvent-separated ion pairs. The ²⁹Si NMR spectra of **3**[Li(DME)₃] and **3**[Li(12-crown-4)₂] are very similar to that of **3Li**·(THF)₂, except for the significantly sharpened ²⁹Si signal of the anionic silicon atom (**3**[Li(DME)₃]: $\delta = -73.8$, **3**[Li(12-crown-4)₂]: -72.0 ppm). How-

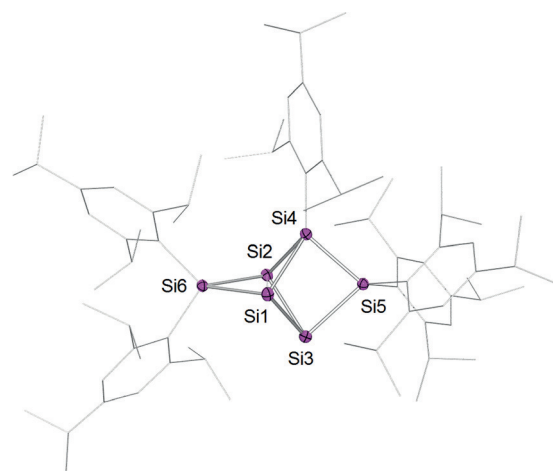


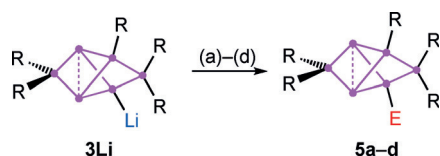
Figure 1. The molecular structure of the anionic moiety in **3**[Li(12-crown-4)₂] in the solid state. Counteranion, hydrogen atoms, and co-crystallized solvent molecules omitted for clarity. Thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.5506(9), Si1–Si3 2.3871(9), Si1–Si4 2.3490(9), Si1–Si6 2.3575(9), Si2–Si3 2.4070(10), Si3–Si5 2.4202(9), Si1–Si6–Si2 65.35(3), Si6–Si1–Si2 57.50(3), Si4–Si1–Si6 98.01(3), Si1–Si3–Si5 83.50(3), Si4–Si5–Si3 85.06(3).

ever, only the structure of **3**[Li(12-crown-4)₂] could be refined without major disorder problems (Figure 1) and will therefore be exclusively referred to in the following: The distance between the unsubstituted bridgehead atoms in **3** (Si1–Si2 2.5506(9) Å) is much shorter than in **2** (2.7076(8) Å)^[7c] or in Breher's pentasilapropellane Si₅Mes₆ (2.636 Å, Mes = 2,4,6-trimethylphenyl),^[9] but longer than in a Si₁₁ siliconoid with a staggered arrangement of the substituent-free vertices.^[4] The release of steric strain by the elimination of one of the Tip groups is reflected in a less-acute angle between the two bridged “propeller blades” in **3** (Si1–Si2–Si3/Si1–Si2–Si4: 107.61°) versus the corresponding angle in **2** (96.7°).

The similarity of reaction conditions during the synthesis of **3Li** and of its precursor, the dismutational isomer **1**, prompted us to also explore the direct reduction of **4** to **3Li** without isolation of the intermediate **1**. Indeed, treatment of a solution of **4** in Et₂O with four equivalents of lithium/naphthalene in THF afforded **3Li** in 51 % yield after crystallization.

With its anionic (and thus nucleophilic) silicon vertex, **3Li** should be a valuable synthon for the further functionalization and transfer of the Si₆R₅-scaffold. Based on the pronounced thermodynamic stability of **2**^[7c] (representing the alleged global minimum on the Si₆H₆ potential-energy surface^[27]), **3Li** can be regarded as the silicon analogue of phenyl lithium in carbon chemistry and might turn out to be equally useful for the transfer of the Si₆R₅ group.

Consequently, we investigated the reactions of **3Li** with representative electrophiles (borane dimethyl sulfide complex BH₃·SMe₂, pivaloyl chloride *t*BuC(O)Cl, silicon tetrachloride SiCl₄, and bis(dimethylamino)chlorophosphane CIP-(NMe₂)₂). Indeed, the corresponding borate-, carbonyl-, silyl-, and phosphanyl-substituted siliconoids **5a–d** (Scheme 2) were obtained by straightforward combination of the reagents in



Scheme 2. Syntheses of functionalized siliconoids **5a–d**. Reagents: a) $\text{BH}_3\cdot\text{SMe}_2$, b) $t\text{BuC}(\text{O})\text{Cl}$, c) SiCl_4 , d) $\text{ClP}(\text{NMe}_2)_2$. **5a**: $\text{E} = \text{BH}_3^-$; **5b**: $\text{E} = \text{C}(\text{O})t\text{Bu}$; **5c**: $\text{E} = \text{SiCl}_3$; **5d**: $\text{E} = \text{P}(\text{NMe}_2)_2$.

toluene.^[26] All the reactions proceeded quantitatively according to NMR spectroscopy. The presence of intact Si_6 cluster motifs akin to **2** was unequivocally confirmed by the ^{29}Si NMR spectra of **5a–d** through the characteristic dispersions of chemical shifts (Table 1). Note that the two unsubstituted

Table 1: Selected analytical data of functionalized siliconoids **3Li** and **5a–d** (data for homoleptic siliconoid **2**^[7c] for comparison).

Compound	Functional group E	^{29}Si Si1, Si2 [ppm]	^{29}Si Si6 [ppm]	Si1–Si2 [Å]
3 [Li(12-crown-4)] ₂	Li	–230.9, –232.6	152.2	2.5506(9)
5a	BH_3^-	–257.3, –265.0	161.2	2.620(1)
5b	$\text{C}(\text{O})t\text{Bu}$	–264.7, –271.1	171.8	2.6430(6)
5c	SiCl_3	–252.3, –264.2	175.4	2.635(1)
5d	$\text{P}(\text{NMe}_2)_2$	–256.0, –261.4	168.7	2.6231(5)
2 ^[7c]	Tip ^[a]	–274.2 ^[a]	174.6 ^[a]	2.7076(8) ^[a]

[a] Atom numbering differs in Ref. [7c].

vertices, Si1 and Si2, give rise to two different signals in ^{29}Si NMR spectra in all cases, despite an apparent chemical equivalence. We tentatively attributed this to hindered rotation of the functional groups. For **5a** and **5c**, broadened signals at room temperature suggested that coalescence was within reach. This assumption was verified by VT-NMR in case of **5c**: cooling to 223 K resulted in significantly sharpened ^{29}Si NMR signals at $\delta = -255.8$ and -266.2 ppm. Coalescence is observed at 315 K, finally leading to a still somewhat broadened signal at $\delta = -256.7$ ppm at 343 K. By application of the Eyring equation, the barrier of rotation for the SiCl_3 group is estimated to $\Delta G^\ddagger = 58 \text{ kJ mol}^{-1}$ (see Supporting Information). In **5a**, additionally, a broadening of the signal for Si3 ($\delta = -4.8$ ppm) is observed as a result of the coupling with the quadrupolar ^{11}B nucleus. In the ^{11}B NMR spectrum of **5a**, the resonance at $\delta = -41.3$ ppm is split into a quartet by coupling with the three chemically equivalent hydrogen atoms of the BH_3 moiety ($^1J_{\text{B-H}} = 75 \text{ Hz}$). The ^{13}C shift of the carbonyl carbon of **5b** is observed at $\delta = 239.0$ ppm in the typical range for silyl-substituted ketones.^[28] In line with reported CO stretching frequencies,^[29] the two characteristic absorptions in the infrared spectrum of **5b** at $\nu = 1637$ and 1602 cm^{-1} are assigned to the asymmetric and symmetric $\text{C}=\text{O}$ stretches of the carbonyl moiety.

For **5c**, an additional ^{29}Si NMR resonance was observed at $\delta = -38.3$ ppm for the SiCl_3 substituent. In the phosphanyl-substituted siliconoid **5d**, the ^{31}P NMR resonance ($\delta = 148.0$ ppm) is strongly deshielded for a silicon-substituted dialkylamino phosphane^[30] which we tentatively attribute to

the cluster current in the Si_6 core, also responsible for the unusual deshielding of one of the SiTip_2 bridges.^[7c] The silicon–phosphorus coupling constant of $^1J_{\text{Si-P}} = 187 \text{ Hz}$ in **5d** is fairly large for Si–P single-bond coupling indicating high s character in this exohedral bond.^[31]

Single crystals of **5a–d** were obtained in moderate to excellent yields (**5a**: 60 %, **5b**: 38 %, **5c**: 68 %, and **5d**: 91 %) and X-ray diffraction studies confirmed the formation of the corresponding functionalized Si_6 siliconoids (Figure 2). The

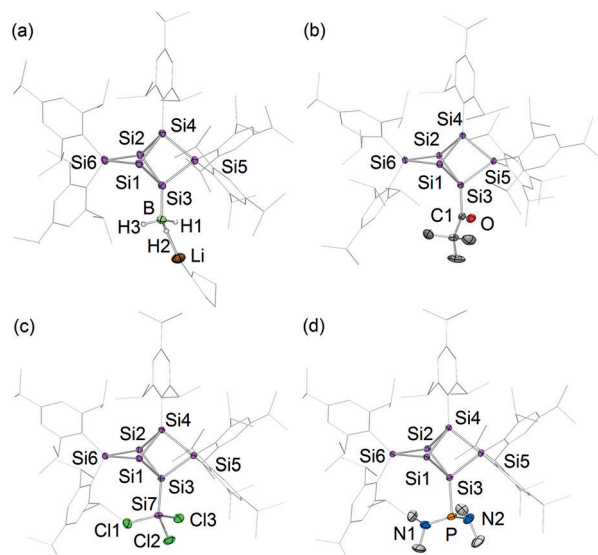


Figure 2. Molecular structures of functionalized Si_6 -siliconoids in the solid state: a) borate **5a**; b) ketone **5b**; c) trichlorosilane **5c**; d) bis(dimethylamino)phosphane **5d**. Hydrogen atoms, disordered Tip-*i*Pr groups, and co-crystallized solvent omitted for clarity. Thermal ellipsoids set at 50% probability.

distances between the unsubstituted bridgehead atoms in **5a–d** are considerably shorter than in the all Tip-substituted species **2**, but longer than in **3Li** (Table 1). The longest wavelength absorptions in the UV/Vis spectra of **5a–d** (**5a,b,d**: $\lambda_{\text{max}} = 475 \text{ nm}$, **5c**: $\lambda_{\text{max}} = 460 \text{ nm}$) are in good agreement with that observed for **2** ($\lambda_{\text{max}} = 473 \text{ nm}$) and are thus assigned to the HOMO–LUMO vertical singlet excitation.^[7c] The intensity of the absorptions varies with the type of substituent linked to the Si_6 backbone ($\epsilon = 220$ (**5a**); 545 (**5b**); 834 (**5c**), $1212 \text{ M}^{-1} \text{ cm}^{-1}$ (**5d**)).

In summary, by reduction of dismutational hexasilabenzenes isomer **1**, we obtained the first example of an anionic unsaturated silicon cluster **3**, which closes the conceptual gap between siliconoids and Zintl anions of silicon. As the previously reported neutral Si_6 -siliconoid **2**^[7c] represents the likely global minimum on the Si_6H_6 potential-energy surface,^[27] the structurally related anionic siliconoid **3** could be seen as a silicon analogue of phenyl lithium, if only in terms of thermodynamic stability. Indeed, it turned out to be a powerful synthon for the transfer of the intact Si_6 cluster motif (with both unsubstituted vertices untouched) to Group 13, 14, and 15 electrophiles as shown by the preparation of the representative set of functionalized Si_6 -siliconoids **5a–d**.

Acknowledgements

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- [1] a) L. Venema, *Nature* **2011**, 479, 309; b) B. K. Teo, X. H. Sun, *Chem. Rev.* **2007**, 107, 1454–1532.
- [2] J. M. Buriak, *Chem. Rev.* **2002**, 102, 1271–1308.
- [3] W. Lu, C. M. Lieber, *Nat. Mater.* **2007**, 6, 841–850.
- [4] K. Abersfelder, A. Russel, H. S. Rzepa, A. J. P. White, P. R. Haycock, D. Scheschkewitz, *J. Am. Chem. Soc.* **2012**, 134, 16008–16016.
- [5] Review on heavier Group 14 metalloids: A. Schnepf, *Chem. Soc. Rev.* **2007**, 36, 745–758.
- [6] H. Neergaard Waltenburg, J. T. Yates, Jr., *Chem. Rev.* **1995**, 95, 1589–1673.
- [7] a) D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2005**, 44, 2954–2956; *Angew. Chem.* **2005**, 117, 3014–3016; b) K. Abersfelder, A. J. P. White, H. S. Rzepa, D. Scheschkewitz, *Science* **2010**, 327, 564–566; c) K. Abersfelder, A. J. P. White, R. J. F. Berger, H. S. Rzepa, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2011**, 50, 7936–7939; *Angew. Chem.* **2011**, 123, 8082–8086.
- [8] G. Fischer, V. Huch, P. Mayer, S. K. Vasisht, M. Veith, N. Wiberg, *Angew. Chem. Int. Ed.* **2005**, 44, 7884–7887; *Angew. Chem.* **2005**, 117, 8096–8099.
- [9] D. Nied, R. Köppe, W. Kloppe, H. Schnöckel, F. Breher, *J. Am. Chem. Soc.* **2010**, 132, 10264–10265.
- [10] Although seemingly constituting electron-precise species, a polycyclic Dewar-benzene as well as a bicyclic cyclotrisilene exhibit the siliconoid hallmark of hemispheroidal coordination of selected vertices: a) A. Tsurusaki, C. Iizuka, K. Otsuka, S. Kyushin, *J. Am. Chem. Soc.* **2013**, 135, 16340–16343; b) A. Tsurusaki, J. Kamiyama, S. Kyushin, *J. Am. Chem. Soc.* **2014**, 136, 12896–12898.
- [11] T. Iwamoto, N. Akasaka, S. Ishida, *Nat. Commun.* **2014**, 5, 5353.
- [12] R. J. F. Berger, H. S. Rzepa, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2010**, 49, 10006–10009; *Angew. Chem.* **2010**, 122, 10203–10206.
- [13] E. Zintl, A. Harder, *Z. Phys. Chem. Abt. A* **1931**, 154, 47–92.
- [14] a) T. F. Fässler, *Struct. Bonding (Berlin)* **2011**, 140, 91–131; b) S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. F. Fässler, *Angew. Chem. Int. Ed.* **2011**, 50, 3630–3670; *Angew. Chem.* **2011**, 123, 3712–3754.
- [15] a) J. M. Goicoechea, S. C. Sevov, *J. Am. Chem. Soc.* **2004**, 126, 6860–6861; b) S. Joseph, C. Suchentrunk, F. Kraus, N. Korber, *Eur. J. Inorg. Chem.* **2009**, 4641–4647; c) M. Neumeier, F. Fendt, S. Gärtner, C. Koch, T. Gärtner, N. Korber, R. M. Gschwind, *Angew. Chem. Int. Ed.* **2013**, 52, 4483–4486; *Angew. Chem.* **2013**, 125, 4579–4582.
- [16] a) D. Kummer, L. Diehl, *Angew. Chem. Int. Ed. Engl.* **1970**, 9, 895; *Angew. Chem.* **1970**, 82, 881–882; b) T. F. Fässler, U. Schütz, *Inorg. Chem.* **1999**, 38, 1866–1870.
- [17] a) J. M. Goicoechea, S. C. Sevov, *Inorg. Chem.* **2005**, 44, 2654–2658; b) A. Nienhaus, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2006**, 632, 1752–1758.
- [18] M. S. Denning, J. M. Goicoechea, *Dalton Trans.* **2008**, 5882–5885.
- [19] S. M. Kauzlarich, Q. Liu, S. C. Yin, H. W. H. Lee, B. Taylor, *Mater. Res. Soc. Symp. Proc.* **2001**, 638, 6.5.1–6.5.6.
- [20] a) M. G. Kanatzidis, S. Armatas, *Science* **2006**, 313, 817–820; b) D. Sun, A. E. Riley, A. J. Cadby, E. K. Richman, S. D. Korlann, S. H. Tolbert, *Nature* **2006**, 441, 1126–1130.
- [21] a) M. W. Hull, S. C. Sevov, *J. Am. Chem. Soc.* **2009**, 131, 9026–9037; b) F. Li, A. Muñoz-Castro, S. C. Sevov, *Angew. Chem. Int. Ed.* **2012**, 51, 8581–8584; *Angew. Chem.* **2012**, 124, 8709–8712; c) F. Li, S. C. Sevov, *J. Am. Chem. Soc.* **2014**, 136, 12056–12063.
- [22] a) D. J. Chapman, S. C. Sevov, *Inorg. Chem.* **2008**, 47, 6009–6013; b) F. S. Kocak, P. Y. Zavalij, Y. F. Lam, B. W. Eichhorn, *Chem. Commun.* **2009**, 4197–4199.
- [23] a) S. Joseph, M. Hamberger, F. Mutzbauer, O. Härtl, M. Meier, N. Korber, *Angew. Chem. Int. Ed.* **2009**, 48, 8770–8772; *Angew. Chem.* **2009**, 121, 8926–8929; b) M. Waibel, F. Kraus, S. Scharfe, B. Wahl, T. F. Fässler, *Angew. Chem. Int. Ed.* **2010**, 49, 6611–6615; *Angew. Chem.* **2010**, 122, 6761–6765.
- [24] a) D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2004**, 43, 2965–2967; *Angew. Chem.* **2004**, 116, 3025–3028; b) C. Strohmman, D. Schildbach, D. Auer, *J. Am. Chem. Soc.* **2005**, 127, 7968–7971.
- [25] a) M. Ichinohe, M. Toyoshima, R. Kinjo, A. Sekiguchi, *J. Am. Chem. Soc.* **2003**, 125, 13328–13329; b) C. Strohmman, J. Hörnig, D. Auer, *Chem. Commun.* **2002**, 766–767.
- [26] Experimental details including those on the X-ray diffraction studies of **3Li**·(THF)₂, **3**[Li(DME)₃], **3**[Li(12-crown-4)₂] and **5a–d** are supplied in the Supporting Information. CCDC 1410252 (**5c**), 1410253 (**5d**), 1410254 (**3Li**·(THF)₂), 1410255 (**5a**), 1410256 (**3**[Li(DME)₃]), 1410257 (**5b**), 1410258 (**3**[Li(12-crown-4)₂]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
- [27] M. Moteki, S. Maeda, K. Ohno, *Organometallics* **2009**, 28, 2218–2224.
- [28] H. Stueger, B. Hasken, M. Haas, M. Rausch, R. Fischer, A. Torvisco, *Organometallics* **2014**, 33, 231–239.
- [29] T. P. Robinson, M. J. Cowley, D. Scheschkewitz, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2015**, 54, 683–686; *Angew. Chem.* **2015**, 127, 693–696.
- [30] E. E. Nifantiev, N. S. Vyazankin, S. F. Sorokina, L. A. Vorobieva, O. A. Vyazankina, D. A. Bravo-Zhivotovskiy, A. R. Bekker, *J. Organomet. Chem.* **1984**, 277, 211–225.
- [31] V. Y. Lee, M. Kawai, A. Sekiguchi, H. Ranaivonjatovo, J. Escudie, *Organometallics* **2009**, 28, 4262–4265.

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