

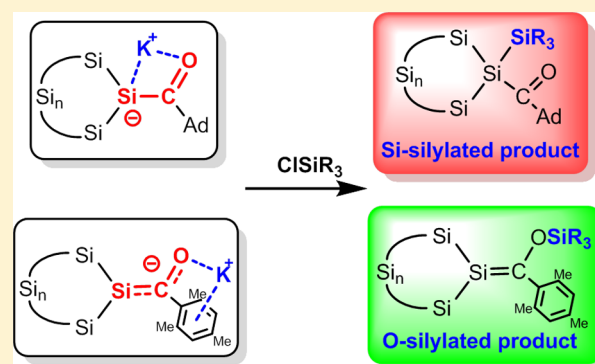
Stable Silenolates and Brook-Type Silenes with Exocyclic Structures

Michael Haas,[†] Roland Fischer,[†] Michaela Flock,[†] Stefan Mueller,[†] Martin Rausch,[†] Robert Saf,[‡] Ana Torvisco,[†] and Harald Stueger^{*†}

[†]Institute of Inorganic Chemistry and [‡]Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, A-8010 Graz, Austria

S Supporting Information

ABSTRACT: The first silenolates with exocyclic structures $[(\text{Me}_3\text{Si})_2\text{Si}(\text{Si}_2\text{Me}_4)_2\text{SiC}(\text{R})\text{O}]^-\text{K}^+$ (**2a**: R = 1-adamantyl; **2b**: mesityl; **2c**: *o*-tolyl) were synthesized by the reaction of the corresponding acylcyclohexasilanes **1a–c** with KO t Bu. NMR spectroscopy and single-crystal X-ray diffraction analysis suggest that the aryl-substituted silenolates **2b,c** exhibit increased character of functionalized silenes as compared to the alkyl-substituted derivative **2a** due to the different coordination of the K⁺ counterion to the SiC(R)O moiety. **2b,c**, thus, reacted with ClSiPr₃ to give the exocyclic silenes $(\text{Me}_3\text{Si})_2\text{Si}(\text{Si}_2\text{Me}_4)_2\text{Si}=\text{C}(\text{OSiPr}_3)\text{R}$ (**3b**: R = Mes; **3c**: *o*-Tol), while **2a** afforded the Si-silylated acylcyclohexasilane **1d**. The thermally remarkably stable compound **3b**, which is the first isolated silene with the sp² silicon atom incorporated into a cyclopolysilane framework, could be fully characterized structurally and spectroscopically.



There is no doubt about the central role of alkenes and metal enolates $[(\text{R}_2\text{CC}(\text{R})\text{O})^-\text{M}^+]$ in organic chemistry, which has led to a thorough understanding of chemical and physical properties and numerous applications of such compounds. In contrast, much less is known about the analogous silenes ($\text{R}_2\text{Si}=\text{CR}_2$) and silenolates $[(\text{R}_2\text{SiC}(\text{R})\text{O})^-\text{M}^+]$, which were long considered unstable and only existent as reactive intermediates.^{1,2} The first stable silene, $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{Ad}$, was isolated by Brook in 1981 after the photolysis of the acylpolysilane $(\text{Me}_3\text{Si})_3\text{SiC}(\text{Ad})=\text{O}$.³ Since then, a relatively large number of stable silenes with various substitution patterns have been synthesized by several alternative preparative approaches.¹ Studies on metal silenolates are less abundant in the literature, and only three isolable species have been prepared and structurally characterized so far by Ottosson et al.²¹ and by the group of Bravo-Zhivotovskii and Apeloig.²¹ Valuable contributions to the field also have been made by Oshita, Ishikawa, and co-workers, who synthesized and characterized Li silenolates $\{(\text{Me}_3\text{Si})_2\text{SiC}(\text{R})\text{O}\}^-\text{Li}^+$ (R = *t*Bu, 1-Ad, *o*-Tol, Mes) by NMR spectroscopy and investigated their reactivity.^{2b–h}

Most known silenes and silenolates are acyclic molecules. Compounds with the coordinatively unsaturated silicon atom incorporated into a cyclopolysilane ring, in particular, have not yet been isolated, although such species are likely to exhibit unusual molecular structures, electronic spectra, and reactivity patterns. Recently we found that moderately stable alkyl-substituted methylenecyclohexasilanes such as **3a** (Scheme 1) can be generated photochemically as mixtures with unreacted starting material and polymeric byproducts and characterized by NMR and UV/vis spectroscopy.⁴

Now we would like to report the synthesis, spectroscopic characterization, and molecular structures of the first cyclic silenolates (**2a–c**) and the selective conversion of **2b** to the silene **3b**, which is the first example of an isolated stable exocyclic silene with the sp² silicon atom incorporated into a cyclopolysilane framework. On the basis of structural and NMR data we further provide striking evidence that the different reactivity observed for alkyl- (**2a**) and aryl-substituted (**2b,c**) silenolates is primarily governed by the different coordination of the K⁺ counterion to the SiC(R)O moiety.

2a–c were obtained with remarkable selectivity by the addition of 1.05 equiv of KO t Bu to the acylcyclohexasilanes **1a–c**⁵ either in THF or in toluene solution in the presence of 1.05 equiv of 18-crown-6 at $-50\text{ }^\circ\text{C}$ (Scheme 1).⁶ The THF solutions, thus obtained, could be used directly for further derivatization. For isolation, **2a–c** were crystallized from toluene/[18]crown-6 at $-30\text{ }^\circ\text{C}$ to give red crystals of the 1:1 [18]crown-6 adducts, which, after filtration, can be stored at $-30\text{ }^\circ\text{C}$ in the absence of air even for prolonged periods of time. The products, however, immediately decomposed to uncharacterized material upon exposure to the atmosphere or the attempted removal of residual solvent and volatile components in vacuo.

2a and **2c** afforded crystals of sufficient quality for single-crystal X-ray crystallography. The molecular structures are depicted in Figures 1 and 2; selected bond lengths and the sum of valence angles around the central Si–C moiety are summarized in Table 1.

Received: September 11, 2014

Published: October 9, 2014

Scheme 1. Synthesis of Cyclic Silenes and Silenolates from Acylcyclohexasilanes

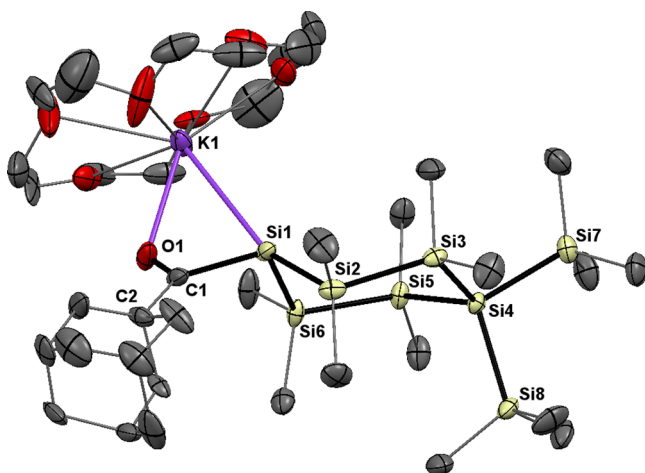
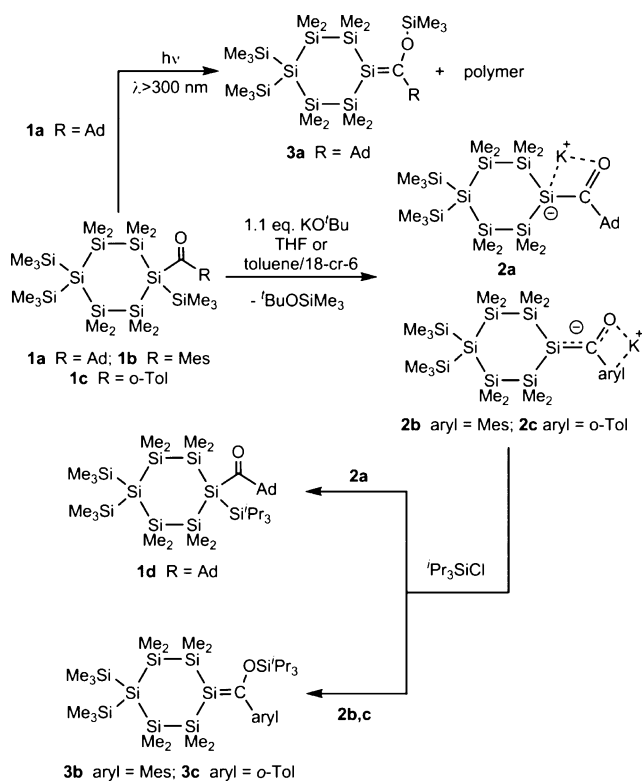


Figure 1. ORTEP diagram for compound **2a** (1:1 adduct with [18]crown-6). Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.⁷

Surprisingly the observed molecular structures are strongly influenced by the nature of the R group attached to the carbonyl C atom. **2a** adopts a structure quite close to the one observed for the acyclic silenolate $[(\text{Me}_3\text{Si})_2\text{SiC}(\text{tBu})\text{O}]^-\text{K}^+[\text{18}]\text{crown-6}$ (**5**) by Ottosson et al.²¹ with simultaneous coordination of the K^+ cation to O and Si, a C–Si bond that is even longer than typical Si–C single bonds,⁸ a C–O bond length characteristic of C=O double bonds,⁹ and a markedly pyramidal central Si atom. On the basis of these structural features Ottosson concluded that **5** is best described as an acyl silyl anion, which is certainly also valid for compound **2a** (structure A in Chart 1). In comparison the structure of **2c** is

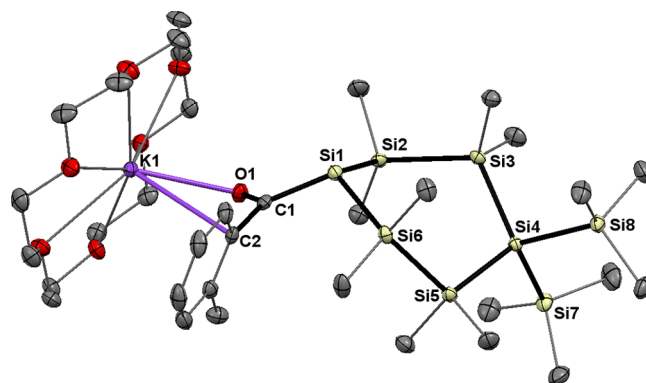
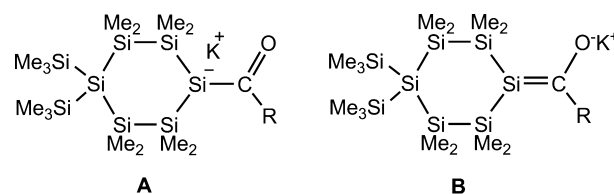


Figure 2. ORTEP diagram for compound **2c** (1:1 adduct with [18]crown-6). Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths d [Å] and Sum of Valence Angles $\sum\alpha(\text{Si1})$ and $\sum\alpha(\text{C1})$ [deg] for K-Silenolates **2a,c**

	2a	2c
d C(1)–Si(1)	1.966(2)	1.874(2)
d C(1)–O(1)	1.244(2)	1.260(2)
d K(1)–O(1)	2.743(1)	2.701(1)
d K(1)–Si(1)	3.603(2)	4.935(1)
d K(1)–C(2)	4.899(2)	3.257(2)
$\sum\alpha(\text{Si1})$	316.7	326.8
$\sum\alpha(\text{C1})$	359.9	359.7

Chart 1. (A) Keto and (B) Enol Form of **2a–c**



quite different: K^+ now is coordinated to O and the aromatic ring, the Si–C distance is significantly smaller, the C–O bond is slightly longer, and the sum of valence angles $\sum\alpha(\text{Si1})$ is larger by 10° . These findings are perfectly in line with the results of a recent computational study on the effects of counterion coordination on the structures of silenolates.¹⁰ There it has been pointed out that metal ion coordination to the O atom results in shorter Si–C bonds and a smaller degree of pyramidalization around Si(1) as compared to the naked silenolate due to the increasing influence of the enol structure (structure B in Chart 1) to the overall molecular geometry. Thus, aryl-substituted silenolates such as **2b,c** apparently exhibit increased character of functionalized silenes and link the properties of Ottosson's keto-form silenolate **5** with the enol-form silenolates $(\text{R}_3\text{Si})_2\text{Si}=\text{C}(\text{Ad})\text{OLi}$ recently published by Apeloig and Bravo-Zhivotovskii.²¹ This study also relates the relative contribution of the keto and the enol form to the structure of silenolates mainly to solvation effects.

This picture is supported further by the NMR data obtained for **2a–c**.⁶ Again in close agreement with the corresponding data of **5** ^{29}Si and ^{13}C NMR chemical shifts of the Si and C atoms of the Si–C bond of $\delta = -92.0$ and 272.2 ppm, respectively, were measured for **2a**·[18]crown-6. For the [18]crown-6 adducts of **2b,c** the ^{29}Si signals of the central Si atoms are significantly low field shifted to $\delta = -67.1$ (R = o-

Tol) and $\delta = -73.1$ ppm ($R = \text{Mes}$), while only minor shift differences were found for the ^{13}C resonances. Similar trends were observed earlier by Ishikawa and Oshita for Li-silenolates $(\text{Me}_3\text{Si})_2\text{SiC}(\text{OLi})\text{R}$ ($R = t\text{Bu}, \text{Ad}, o\text{-Tol}, \text{Mes}$) and rationalized in terms of increased double-bond character of the central Si–C bond in the aryl-substituted derivatives,^{2b} although the measured ^{29}Si NMR shifts are still in the range typical for silyl anions.¹¹ In line with this interpretation three SiMe_2 resonances, at 0.6, 0.5, and -0.45 ppm, are clearly resolved in the ^{13}C spectrum of the Mes derivative **2b**, while in the ^1H and ^{29}Si spectra the signals at 0.6 and -35.1 ppm, respectively, arising from the SiMe_2 groups adjacent to the central silicon atom are significantly broadened. This finding clearly indicates hindered rotation around the central Si–C bond in compound **2b**, which suggests enhanced sp^2 character.

The reactivity of **2a–c** with chlorosilanes also reflects the different coordination of the central silicon atom in the alkyl and aryl derivatives (compare Scheme 1). While **2a**, with an alkyl group attached to the carbonyl C atom, smoothly reacted with an equimolar amount of $i\text{Pr}_3\text{SiCl}$ at 0°C in THF to give the Si-silylated product **1d** in nearly quantitative yields,⁶ the aryl-substituted compounds **2b,c** under the same conditions exclusively afforded the O-silylated silenes **3b,c**. This result parallels the chemical behavior of Oshita's and Ishikawa's Li-silenolates and easily can be explained by the structural and NMR spectroscopic data discussed above. Apparently the coordination of K^+ to O (1) and the aromatic ring in **2b,c** effectively withdraws negative charge from Si(1), which makes O(1) the preferred reaction site for R_3Si^+ , while **2a**, with the K^+ cation coordinated simultaneously to O(1) and Si(1), behaves more or less like a typical silyl anion.

3b turned out to be thermally remarkably stable and could be isolated as yellow crystals in 60% yield by crystallization from diethyl ether and fully characterized structurally and spectroscopically.⁶ **3c**, in contrast, was formed already along with considerable amounts of several unidentified byproducts and could not be purified by crystallization because it decomposed further even at -70°C possibly due to incomplete steric protection of the Si=C double bond.

Figure 3 shows the molecular structure of **3b** as determined by single-crystal X-ray crystallography. The geometry of the central Si–C moiety closely resembles the one observed for

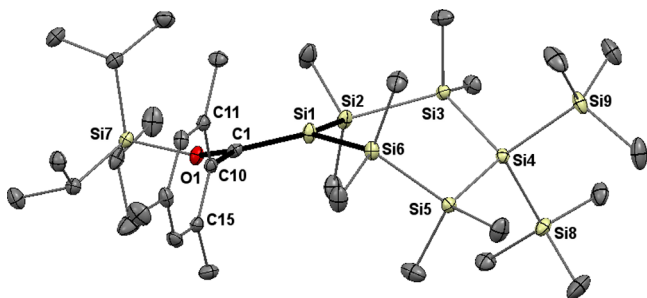
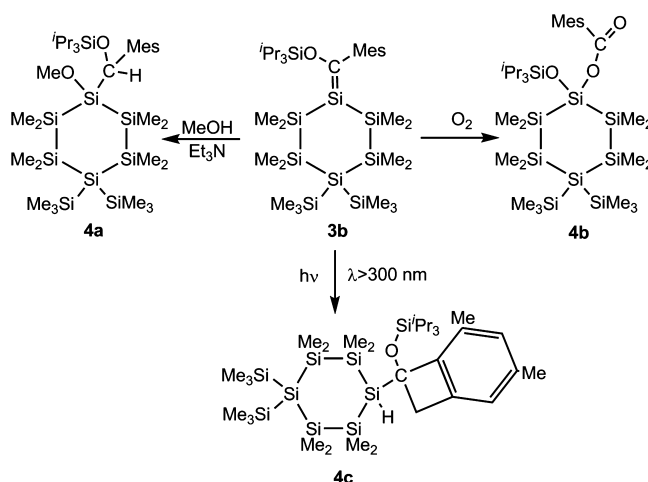


Figure 3. ORTEP diagram for compound **3b**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond and torsional angles [deg] with estimated standard deviations: Si(1)–C(1) 1.767(2), C(1)–O(1) 1.386(2), Si–Si (mean) 2.345, Si–Si–Si (endo, mean) 110.9, $\sum\alpha\text{Si}(1)$ 357.8, $\sum\alpha\text{C}(1)$ 359.8, Si(6)–Si(1)–C(1)–C(10) 10.6(2), Si(2)–Si(1)–C(1)–O(1) -0.8 , C(11)–C(10)–C(1)–Si(1) 113.1, Si(1)–C(1)–C(10)–C(11) 71.9, Si(1)–C(1)–C(10)–C(11) -105.9 .

Brook's acyclic silene $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{Ad}$ (**6**)^{3,12} with nearly identical Si=C bond lengths (1.767 vs 1.762 Å) and an essentially planar C(1) atom ($\sum\alpha\text{C}(1) = 359.8^\circ$). As compared to **6**, Si(1) in **3b** is slightly more pyramidalized by 2° , while the twist angle around the Si=C bond in **3b** is significantly smaller, as shown by the torsion angles Si(6)–Si(1)–C(1)–C(10) and Si(2)–Si(1)–C(1)–O(1), likely as a result of the incorporation of Si(1) into the cyclohexasilane cycle. Otherwise the Si_6 ring in **3b** adopts a twisted conformation with unexceptional endocyclic Si–Si bond distances and Si–Si–Si bond angles. For steric reasons, finally, the mesityl ring is arranged roughly perpendicular to the adjacent Si=C double bond with a torsion angle Si(1)–C(1)–C(10)–C(11) of 71.9° .

NMR spectral data and the reactivity of **3b** (compare Scheme 2) are also typical of a Brook-type silene. ^{13}C and ^{29}Si signals

Scheme 2. Reactivity of Compound **3b**



characteristic of Si=C were observed at $\delta(^{29}\text{Si}) = 31.2$ ppm and $\delta(^{13}\text{C}) = 200.3$ ppm. The ^1H , ^{13}C , and ^{29}Si NMR spectra, furthermore, display sharp, distinct absorptions for each of the four endocyclic SiMe_2 groups present, which are magnetically nonequivalent due to the lack of freedom of rotation about the silicon–carbon double bond. Methanol readily adds across the Si=C bond to give the expected product **4a**. When **3b** was treated with dry air for 2 h, the ester **4b** was formed just as observed earlier for acyclic Brook-type silenes.¹³ On photolysis of **3b**, finally, the C–H bond of the ortho methyl group of the mesityl substituent added to the silicon–carbon double bond to form the benzocyclobutene **4c**. Older studies reported similar reactions for acyclic mesityl-substituted Brook-type silenes.¹⁴ While **4a,c** could be isolated and completely characterized, only slightly impure samples of **4b** were obtained due to the lack of crystallization.¹⁵

Silene **3b** showed an intense absorption band at 364 nm ($\epsilon = 16\,500$), which is the longest wavelength absorption maximum measured for a Brook-type silene so far. It is considerably red-shifted relative to the corresponding bands in the spectra of the acyclic silene **6** ($\lambda_{\text{max}} = 340$ nm, $\epsilon = 7400$)³ and the endocyclic silene $[-\text{Tip}_2\text{Si}-\text{TipSi}=\text{C}(\text{Ad})-\text{O}-]$ ($\lambda_{\text{max}} = 354$ nm).¹⁶ According to time-dependent DFT calculations at the mPW1PW91/6-31+G** level performed for **3b** and **6**,¹⁷ these longest wavelength absorption bands are unequivocally assigned to the HOMO–LUMO transition with a smaller excitation energy for **3b** due to slight destabilization of the HOMO and stabilization of the LUMO. Both compounds possess nearly

identical HOMOs dominated by the $\pi(\text{Si}-\text{C})$ bond with some admixture of the oxygen lone pair of proper symmetry. The LUMO of **6**, however, primarily is $\pi^*(\text{Si}-\text{C})$ in nature, while the LUMO of **3b** is localized mainly on the aromatic ring (compare Figure 4). As a result **3b** shows a HOMO–LUMO transition of different origin ($\pi_{\text{Si}=\text{C}} \rightarrow \pi^*_{\text{Si}=\text{C}}$ for **6** vs $\pi_{\text{Si}=\text{C}} \rightarrow \pi^*_{\text{aryl}}$ for **3b**).

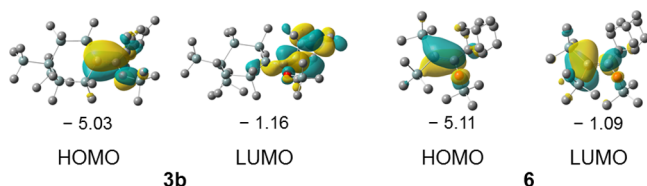


Figure 4. Frontier orbitals and orbital energies in eV for model compound of **3b** and **6**.

In conclusion, we were able to demonstrate that the stable silenolates **2a–c** and the silene **3b** with the coordinatively unsaturated silicon atom incorporated into cyclohexasilane frameworks are synthetically accessible and can be isolated and structurally characterized spectroscopically and by X-ray crystallography. Furthermore, the disagreeing reactivities of silenolates with alkyl or aryl substituents attached to the carbonyl C atom toward chlorosilanes ClSiR_3 could be related to the different coordination of the K^+ counterion to the $\text{SiC}(\text{R})\text{O}$ moiety and to the resulting increased enol character of the aryl-substituted derivatives. UV absorption spectroscopy and DFT calculations, finally, provide evidence for considerable contributions of the aromatic π system to the UV/vis absorption characteristics of **3b**.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental and computational details, analytical data, figures of NMR spectra, the UV absorption spectrum of **3b**, a figure giving the crystal structure of **4c**, tables and CIF files giving crystal, collection, and refinement data for the structures of compounds **2a**, **2c**, **3b**, and **4c**, tables of DFT mPW1PW91/6-31+G** calculated structures (Cartesian coordinates) and absolute ZPVE-corrected energies of **3b** and **6**, a table of selected TDDFT mPW1PW91/6-31+G** calculated excitation wavelengths and oscillator strengths of **3b** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: harald.stueger@tugraz.at.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the FWF (Wien, Austria) for financial support (project number P21271-N19). The authors gratefully acknowledge support from NAWI Graz. This work is dedicated to Prof. G. Roewer on the occasion of his 75th birthday.

■ REFERENCES

(1) For general reviews about silenes, see e.g.: (a) Ottosson, H.; Ohshita, J. In *Science of Synthesis: Knowledge Updates 2011/3*; Oestreich, M., Ed.; Thieme: Stuttgart, 2011; pp 47–55. (b) Ottosson, H.; Eklöf, A. M. *Coord. Chem. Rev.* **2008**, *252*, 1287. (c) Ottosson, H.;

Steel, P. G. *Chem.—Eur. J.* **2006**, *12*, 1576. (d) Gusel'nikov, L. E. *Coord. Chem. Rev.* **2003**, *244*, 149. (e) West, R. J. *Organomet. Chem.* **2001**, *21*, 467. (f) Morkin, T. L.; Leigh, W. J. *Acc. Chem. Res.* **2001**, *34*, 129. (g) Müller, T.; Ziche, W.; Auner, N. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z.; Apeloig, Y., Eds.; John Wiley & Sons Ltd.: New York, 1998; pp 1233–1310. (h) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71.

(2) For example: (a) Biltueva, I. S.; Bravo-Zhivotovskii, D. A.; Kalikhman, I. D.; Vitovskii, V. Yu.; Shevchenko, S. G.; Vyazankin, N. S.; Voronkov, M. G. *J. Organomet. Chem.* **1989**, *368*, 163. (b) Ohshita, J.; Masaoka, Y.; Masaoka, S.; Hasebe, M.; Ishikawa, M.; Tachibana, A.; Yano, T.; Yamabe, T. *Organometallics* **1996**, *15*, 3136. (c) Guliashevili, T.; El-Sayed, I.; Fischer, A.; Ottosson, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 1640. (d) Dobrovetsky, R.; Zborovsky, L.; Sheberla, D.; Botoshansky, M.; Bravo Zhivotovskii, D.; Apeloig, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, 4084.

(3) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K.; Poon, Y. C.; Chang, Y. M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

(4) Stueger, H.; Hasken, B.; Haas, M.; Rausch, M.; Fischer, R.; Torvisco, A. *Organometallics* **2014**, *33*, 231.

(5) **1b,c** were easily synthesized using a slightly modified procedure that previously had been applied for the preparation of **1a**: ref 3. Experimental details and analytical and structural data are included in the Supporting Information.

(6) Experimental details and analytical data for **2a–c**, **1d**, and **3b** are given in the Supporting Information.

(7) Only the major contributions for the disordered adamantyl group and crown ether are shown. For details see the Supporting Information.

(8) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z.; Apeloig, Y., Eds.; Wiley: Chichester, 1998; p 181.

(9) Berthier, G.; Serre, J. In *The Chemistry of the Carbonyl Group*, Vol. 1; Patai, S., Ed.; Wiley: London, 1966; p 1.

(10) Eklöf, A. M.; Ottosson, H. *Tetrahedron* **2009**, *65*, 5521.

(11) Tamao, K.; Kawashi, A. *Adv. Organomet. Chem.* **1995**, *38*, 1.

(12) Nyburg, S. C.; Brook, A. G.; Abdesaken, F.; Gutekunst, G.; Wong-Ng, W. *Acta Crystallogr.* **1985**, *41*, 1632.

(13) Brook, A. G.; Baumegeger, A.; Lough, A. J. *Organometallics* **1992**, *11*, 3088.

(14) (a) Baines, K. M.; Brook, A. G.; Ford, R. R.; Lickiss, P. D.; Saxena, A. K.; Chatterton, W. J.; Sawyer, J. F.; Behnam, B. A. *Organometallics* **1989**, *8*, 693. (b) Brook, A. G.; Wessely, H.-J. *Organometallics* **1985**, *4*, 1487.

(15) Experimental details and analytical data including the molecular structure of **4c** are given in the Supporting Information.

(16) Bejan, I.; Güclü, D.; Inoue, S.; Ichinohe, M.; Sekiguchi, A.; Scheschkevitcz, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 3349.

(17) For simplification **3b** was modeled by substituting the OSiPr_3 group by OSiMe_3 . Detailed computational results are given in the Supporting Information.