Acknowledgment. We thank Dr. Y. Kai of Osaka University for help with the X-ray analysis. This work was supported by Grant-in-Aid of the Ministry of Education, Science and Culture, Japan, for Priority Areas (No. 03233220).

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for **1** (8 pages). Ordering information is given on any current masthead page.

Silaheterocycles. 16.[1] [1,3]-Sigmatropic Migration of an Alkoxy Group: Dichlorosilene to Dimethylsilene Rearrangement

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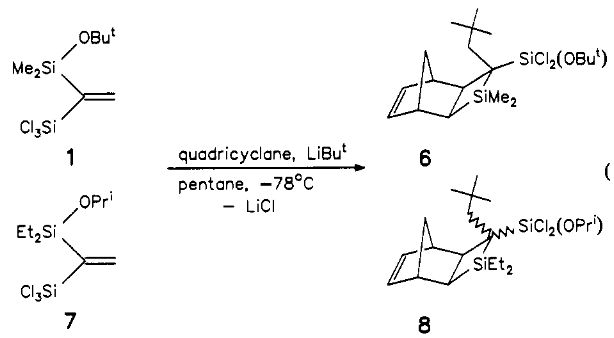
The reactivity of 1,1-dichlorosilenes is different from that of 1,1-diorganosilenes as the studies of 1,1-dichloro-2-neopentylsilene have shown.[2] Previously we described the cycloaddition behavior of 1,1-dichloro-2-neopentyl-2-(trimethylsilyl)silene.[1] In order to alter the properties of the substituent at the silene's carbon atom we synthesized 1-(*tert*-butoxydimethylsilyl)-1-(trichlorosilyl)ethene (**1**).

The reaction of **1** with *tert*-butyllithium yields silene **2**, which isomerizes to **3**, which can be trapped (Scheme I).

2 cannot be trapped, and even the efficient trap methoxytrimethylsilane only gives **4b**. To discriminate **4b** from **4a**, **5** was synthesized, which shows different NMR resonances for the methoxy groups.

An effective trap for electron-deficient dienophiles is quadricyclane.[3] With **3** the exo-$[2_\sigma + 2_\sigma + 2_\pi]$ cycloadduct **6** is formed,[4] although diorganoneopentylsilenes do not react.[5,6]

A cross experiment using a **7**/**1**/LitBu/quadricyclane mixture proves intramolecularity (eq 1). Indicative of the rearrangement **2** → **3** are the ^{29}Si NMR resonances of **6** at −25.37 and 7.36 ppm with relative intensities 1:5. Resonances in ^{13}C and ^{1}H NMR spectroscopy for dimethylsilyl fragment are inequivalent: it is fixed in the ring system. The exo position of the silacyclobutane ring, which is to be expected from theory[7] and experiments,[3] is proved



(1)

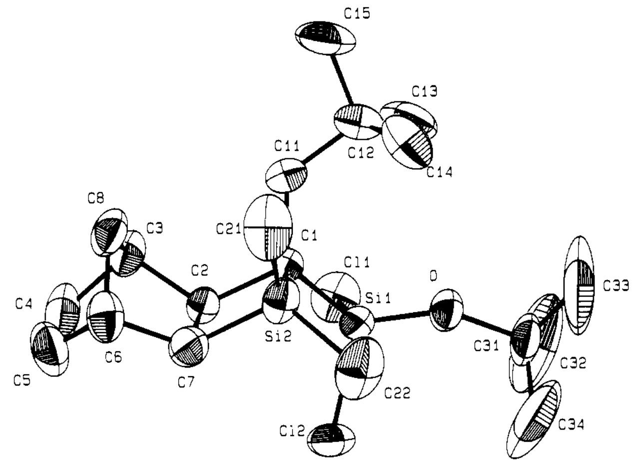
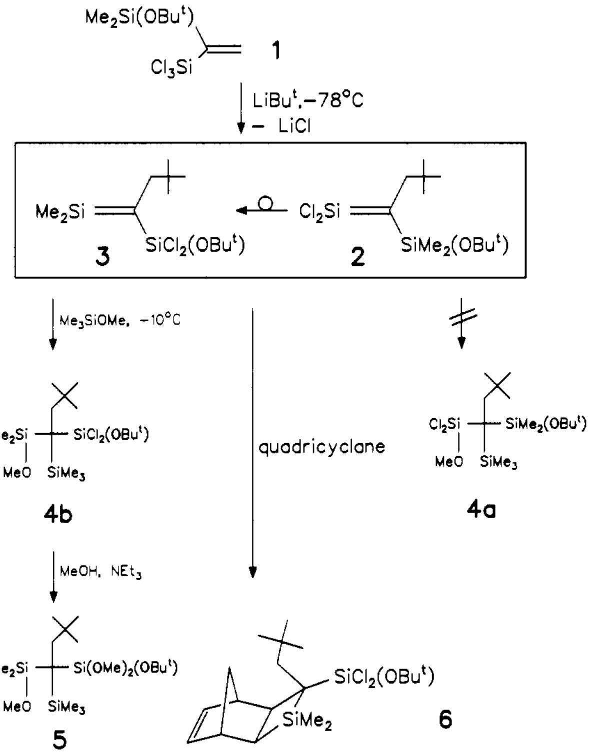
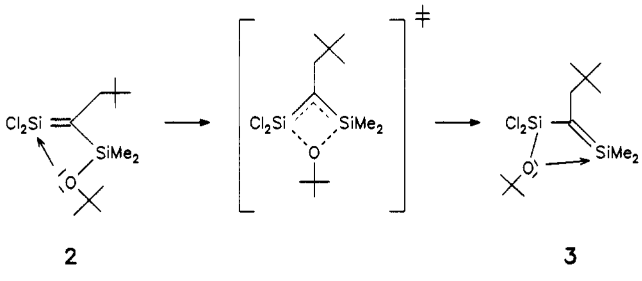


Figure 1. ORTEP representation of **6** (50% probability). Hydrogens are omitted. Bond lengths (Å): Si2–C1 1.92 (2); Si2–C7 1.874 (2); C1–C2 1.609 (3); C2–C7 1.571 (2); Si1–C1 1.851 (1); Si2–C21 1.864 (2); C1–C11 1.567 (3); Si2···C2 2.43 (1); C1···C7 2.47 (3). Bond angles (deg): C1–Si2–C7 81.39 (7); C1–C2–C7 102.2 (1); Si2–C1–C2 86.7 (1); Si2–C7–C2 89.4 (2); Si1–C1–C11 114.6 (2); C1–C11–C12 123.5 (1); O–Si1–C1 113.11 (6).

Scheme I



Scheme II



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(1) Part 15: Ziche, W.; Auner, N.; Behm, J. *Organometallics*, in press.

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(3) Kaupp, G.; Prinzbach, H. *Chem. Ber.* **1971**, *104*, 182.

(4) 8-(*tert*-Butoxydichlorosilyl)-7,7-dimethyl-8-neopentyl-7-silatricyclo-$[4.2.0.1^{2,5}]$non-3-ene (**6**): To **1** and a 3-fold excess of quadricyclane in pentane was added an equimolar amount of LitBu at −78 °C. **6** distills as colorless liquid at 110 °C/10^{-2} mbar and crystallizes from pentane (mp 115 °C): ^{1}H NMR (CDCl$_3$) δ 0.31 (s, 3 H, Si(CH_3)$_3$), 0.52 (s, 3 H, Si(CH_3)$_3$), 1.00 (s, 9 H, C(CH_3)$_3$), 1.21 (d, br, 1 H, J = 8.60 Hz, C9-H-anti), 1.29 (d, br, 1 H, J = 8.55 Hz, SiCH), 1.44 (s, 9 H, C(CH_3)$_3$), 1.55 (d, br, 1 H, J = 8.55 Hz, C1-H), 1.73, 1.91 (AB, 2 H, J = 14.34 Hz, CH_2C(CH$_3$)$_3$), 2.41 (d, 1 H, J = 8.55 Hz, C9-H-syn), 2.76 (s, br, 1 H, C2-H), 2.45 (s, br, 1 H, C5-H), 5.93 (dd, 1 H, J = 5.49, J = 3.06 Hz, C4-H), 6.43 (dd, 1 H, J = 5.49, J = 2.44 Hz, C3-H); ^{13}C NMR (CDCl$_3$) δ 0.44, 2.57 (Si(CH$_3$)$_2$), 23.56 (SiCSi), 29.27 (SiCH), 30.65 (C(CH$_3$)$_3$), 31.32, 31.41 (C(CH$_3$)$_3$), 40.64 (CH$_2$C(CH$_3$)$_3$), 40.94, 42.24, 44.04 (CH), 45.86 (CH$_2$), 79.15 (OC(CH$_3$)$_3$), 134.79, 138.37 (CH=CH); ^{29}Si NMR (CDCl$_3$) δ −25.37 (SiCl$_2$OBu^t), 7.36 (Si(CH$_3$)$_2$); *m/e* (EI) M$^+$ = 404 (0%), 347 (1.03), 256 (1.34), 225 (2.77), 199 (5.74), 57 (100). Anal. Found: C, 56.23; H, 8.39; Cl, 17.52; Si, 14.19. Calcd for $C_{19}H_{34}Cl_2OSi_2$ (405.56): C, 56.27; H, 8.45; Cl, 17.48; Si, 13.85.

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by an X-ray diffraction study (Figure 1).[8] This is the first X-ray crystal structure of an exo-[$2_\sigma + 2_\sigma + 2_\pi$] cycloadduct of quadricyclane with a double-bonded π-partner. There is little distortion in the bicyclo[2.2.1]heptene system while the planar silacyclobutane shows remarkable features. The smallest endocyclic angle, C1–Si2–C7, is 81.39°, and the largest, C1–C2–C7, is 102.2°. Bonds in the ring are elongated; the Si2···C2 distance is shorter than C1···C7. Steric interaction is mirrored by bond angles only.

Intramolecular [1,3] rearrangements in silene chemistry are known.[9] We propose that the rearrangement **2** → **3** occurs by primary nucleophilic attack of the oxygen on the silene silicon atom, thus resembling an intramolecular base stabilized silene, followed by a transition state with a bridging *tert*-butoxy group (Scheme II), and finally full migration to yield **3**.

Acknowledgment. We thank Stiftung Volkswagenwerk, Deutsche Forschungsgemeinschaft, and Fonds der Chemischen Industrie for support.

Registry No. 1, 141248-12-6; **2**, 141248-13-7; **3**, 141248-14-8; **4b**, 141248-15-9; **5**, 141248-16-0; **6**, 141248-17-1; 7, 141248-18-2; **8**, 141248-19-3; $(CH_2{=}CH)ScMe_2(OBu^t)$, 5507-47-1; $Me_2SiCl(CH{=}CH_2)$, 1719-58-0; $(BrCH{=}CBr)SiMe_2(OBu^t)$, 141248-20-6; $(CH_2{=}CBr)SiMe_2(OBu^t)$, 141248-21-7; $Me_2Si(OBu^t)C((OMe)_3Si){=}CH_2$, 141248-22-8; $Et_2SiCl(CH{=}CH_2)$, 15972-93-7; $Et_2Si(OPr^i)(CH{=}CH_2)$, 141248-23-9; $Et_2Si(OPr^i)(CBr{=}CH_2)$, 141248-24-0; Me_3SiOMe, 1825-61-2; quadricyclane, 278-06-8.

Supplementary Material Available: Tables of bond lengths, bond angles, positional parameters, and thermal parameters for **6** and experimental and analytical data (17 pages); listing of observed and calculated structure factors for **6** (18 pages). Ordering information is given on any current masthead page.

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(7) Haselbach, E.; Martin, H.-D. *Helv. Chim. Acta* **1974**, *57*, 472.

(8) **6** ($C_{19}H_{34}Cl_2OSi_2$): space group *P*1 (Int. Tables 2), $a = 8.672$ (3) Å, $b = 9.463$ (3) Å, $c = 14.074$ (5) Å, $\alpha = 89.25$ (2)°, $\beta = 88.50°$, $\gamma = 86.55$ (2)°, $V = 1152$ Å^3, $Z = 2$, μ(Mo Kα) = 3.9 cm^{-1}; Enraf-Nonius CAD-4 diffractometer (graphite monochromator); 3630 unique reflections collected (2° < 2θ < 50°); 2958 reflections considered observed ($I > \sigma(I)$), used to solve (direct methods) and refine (least squares). R and R_w: 0.055 and 0.043.

(9) Eaborn, C.; Happer, D. A. R.; Hitchcock, P. B.; Hopper, S. P.; Safa, K. D.; Washburne, S. S.; Walton, D. R. M. *J. Organomet. Chem.* **1980**, *186*, 309. Wiberg, N.; Köpf, H. *Chem. Ber.* **1987**, *120*, 653. Ishikawa, M.; Nishimura, K.; Ochiai, H.; Kumada, M. *J. Organomet. Chem.* **1982**, *236*, 7. Ando, W.; Sekiguchi, A.; Sato, T. *J. Am. Chem. Soc.* **1981**, *103*, 5573.

Ordered Oxygen on Mo(112): Modification of Surface Electronic Structure and Control of Reaction Path

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It has been a long-sought goal in chemistry to design an active and selective catalyst for each particular reaction. This requires knowledge of the microscopic principle of surface modification and various means to modify the electronic structure and the steric confinement of the surface. We have studied the oxygen modification of the Mo(112) surface. On the Mo(112)-p(1×1) surface (Figure 1), oxygen atoms are expected to occupy trough sites. We have succeeded in controlling the electronic structure of the first-layer Mo atoms as probed directly by the CO adsorption. We have also succeeded in selectively blocking the second-layer Mo atoms. High-coordination metal sites exhibit high electronic fluctuation and are believed to play a major role in structure-sensitive catalytic reactions.[1] The blocking of the second-layer atoms resulted in a new methanol dehydrogenation path, unlike the oxidative dehydrogenation usually observed on molybdenum oxides.

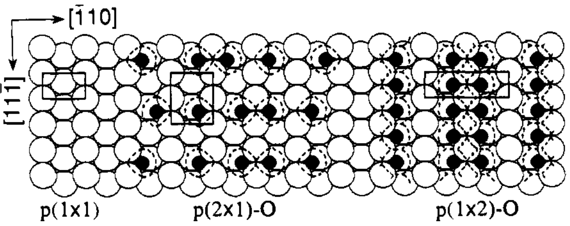

Figure 1. Models for the Mo(112)–p(1×1), Mo(112)–p(2×1)–O, and Mo(112)–p(1×2)–O surfaces. The van der Waals spheres of O atoms are shown by the dotted lines.

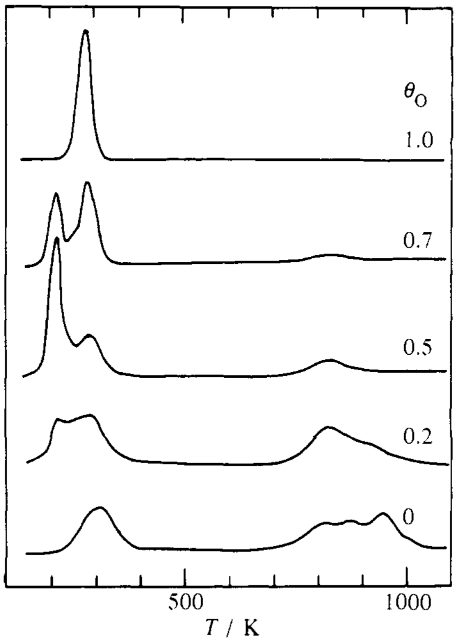

Figure 2. TPD traces of CO from clean and O-precovered Mo(112). Desorption peaks above 800 K are due to dissociatively adsorbed CO.[2]

The low-energy electron diffraction experiments after exposure of clean Mo(112) at 300 K to oxygen followed by annealing to 600 K showed a series of ordered structures, p(2×1)–O at θ_O = 0.5, p(1×2)–O at θ_O = 1.0, and four intermediate phases,[2] where θ_O denotes the oxygen coverage. Figure 2 shows the results of temperature-programmed desorption (TPD) of CO from O-precovered Mo(112). CO adsorbed molecularly on clean Mo(112) gives rise to a desorption peak (α_1) at 310 K. With increasing θ_O, this peak decreases in intensity and shifts to 280 K, while a new peak (α_2) appears at 220 K. The α_1:α_2 ratio reaches 1:2 at θ_O = 0.5 (p(2×1) surface), beyond which α_2 is again suppressed and α_1 regrows. The α_2 peak disappears completely at θ_O = 1.0 (p(1×2) surface).

We suppose that O(a) on Mo(112) occupies a quasi-3-fold hollow site composed of one second-layer and two first-layer Mo atoms on the basis of the result of an ion-scattering study for O/W(112).[3] The models for Mo(112)-p(2×1)–O and Mo(112)-p(1×2)–O are shown in Figure 1. There are two equivalent quasi-3-fold sites in a p(1×1) unit mesh. If all O(a) atoms occupy the sites in the same side, it is difficult to explain the two CO desorption peaks from p(2×1)–O. We, therefore, suppose that each O(a) occupies either of the two equiprobable sites randomly.[4] This causes three types of top-layer Mo atoms to be formed on p(2×1)–O: those coordinated by two O(a) atoms (Mo_{2C}), those

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(4) A model calculation showed that this structure gives rise to a slightly weak but sharp p(2×1) diffraction pattern.

0002-7863/92/1514-4911$03.00/0