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Carbonylation of Cyclotrisilenes**

Michael J. Cowley, Yu Ohmori, Volker Huch, Masaaki Ichinohe, Akira Sekiguchi, and David Scheschkewitz**

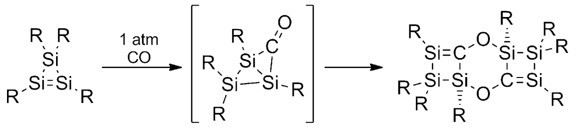
Dedicated to Professor Werner Uhl on the occasion of his 60th birthday

Carbon monoxide (CO) is a common ligand in transition-metal chemistry. In organic chemistry, it is frequently used to introduce a C_1 unit, although carbonylations, such as hydroformylation[1] or the Pauson–Khand reaction,[2] generally require a transition-metal catalyst, even for strained (and thus highly reactive) cyclic compounds.[3] Only a few reports on the reactivity of CO towards compounds of main-group elements other than carbon are available. Although known since the pioneering work by Schlesinger and Burg in the 1930s,[4] borane–CO adducts are usually unstable at room temperature. Only recently, Piers et al. reported a stable adduct between the very Lewis acidic perfluorinated pentaphenylborole and CO.[5] The hydroborating Lewis acid $(F_5C_6)_2BH$ incorporates CO assisted by a alkenyl-functionalized phosphine in a frustrated Lewis pair (FLP) mechanism.[6] A $B(C_6F_5)_3$-based FLP is capable of stoichiometric CO reduction with dihydrogen.[7] A few coordinatively unsaturated and thus Lewis acidic organic species, such as transient triplet carbenes,[8] and Bertrand's cyclic alkyl amino carbenes react with CO in the absence of transition metals, forming ketenes.[9] Despite growing appreciation of the capability of main group species to activate small molecules, such as H_2 and NH_3,[10] reactions of stable low-valent compounds of the heavier elements with CO have not, to our knowledge, been reported. Transient silylene–CO adducts, however, have been observed in the gas phase and in cold matrices.[11]

We have recently shown that reactions of cyclotrisilenes with N-heterocyclic carbenes (NHCs) reversibly afford cyclotrisilene–NHC adducts,[12] which in the case of **1a** can undergo reversible ring-opening to form a highly unsaturated NHC-stabilized disilenylsilylene.[12b] Isonitriles also react with cyclotrisilenes,[13] and, mindful of the isoelectronic relationship to CO, we became interested in the reactivity of the latter. Herein, we report the facile reaction of carbon monoxide with cyclotrisilenes in the absence of a catalyst to form highly functionalized cyclic silenes.

Exposure of a benzene solution of cyclotrisilene **1a** to 1 atm of CO at 25 °C results in precipitation of a yellow powder within a few hours, which owing to its insolubility cannot be characterized spectroscopically.[14] A reaction for several days without stirring under otherwise identical conditions afforded bright yellow single crystals. Elemental analysis confirmed the incorporation of one equivalent of CO per molecule of **1a**. X-ray crystallography revealed the product to be the tricyclic Brook-type[15] bis(silene) **2a**, formally arising from two molecules each of **1a** and CO (Scheme 1, Figure 1).[14]

With a π-donating oxygen atom at carbon, **2a** is reminiscent of donor-stabilized silenes with inverse polarization,[15,16]



1a **Ia** **2a**

Scheme 1. Reaction of **1a** with carbon monoxide yielding the donor-stabilized bis(silene) **2a** (Tip = 2,4,6-$iPr_3C_6H_2$).

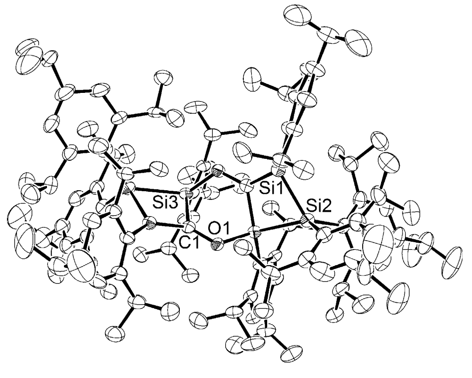


Figure 1. Molecular structure of **2a** in the solid state. Ellipsoids are set to 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C1 1.771(4), Si1–Si2 2.3181(19), Si2–Si3′ 2.4294(17), Si3′–C1 1.906(5); C1-Si1-Si2 94.37(16), Si1-Si2-Si3′ 74.09(6), Si2-Si3′-C1 87.51(14), Si3′-C1-Si1 102.1(2).

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[*] Dr. M. J. Cowley, Dr. V. Huch, Prof. Dr. D. Scheschkewitz
Krupp-Chair of General and Inorganic Chemistry
Saarland University
Dudweiler, Am Markt Zeile 1, 66125 Saarbrücken (Germany)
E-mail: scheschkewitz@mx.uni-saarland.de
Homepage: http://www.uni-saarland.de/fak8/scheschkewitz/
Y. Ohmori, Dr. M. Ichinohe, Prof. Dr. A. Sekiguchi
Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba
Tsukuba, Ibaraki 305-8571 (Japan)
E-mail: sekiguch@chem.tsukuba.ac.jp
Homepage: http://www.chem.tsukuba.ac.jp/sekiguch/

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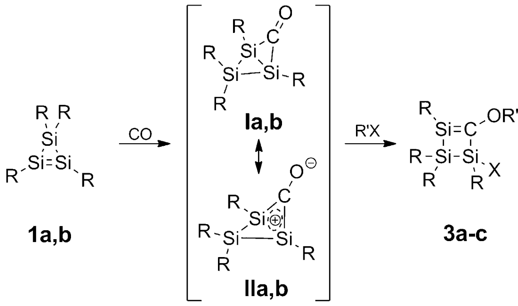
and should thus exhibit a relatively long Si=C bond. Indeed, at 1.771(4) Å the Si1−C1 bond distance is in the expected range. The sum of angles at the Si=C silicon atom, ΣSi1 = 359.9(3)°, however, reveals an almost perfectly planar environment, which suggests that the inversely polarized **2a** is more comparable to that of open-chained silenes with *C*-siloxy goups than to the four-membered cyclic silenes with endocyclic donors previously reported by us.[16c] The geometry around the double bond is nonetheless somewhat distorted, with a twist angle τ about Si1−C1 of 19.05(24)°. The central $Si_2O_2C_2$ ring in **2a** exhibits a boat-type conformation, forcing the Tip substituents of Si3 and Si3′ into axial positions.

Attempts to monitor the reaction of **1a** with CO by NMR or IR spectroscopy were inconclusive, and the insolubility of the isolated product **2a** prevented spectroscopic characterization. We thus sought a route to more tractable CO activation products. In the expectation that the bulkier substituents of cyclotrisilene **1b** ($MetBu_2Si$ vs. Tip for **1a**) would confer greater solubility on the corresponding dimeric silene, we reacted **1b** with CO. Surprisingly, instead of a dimeric product analogous to **2a**, the cyclic silenol **3b** was obtained (see the Supporting Information).[14] The formation of **2a** and **3b** can be explained by the presence of a short-lived intermediate such as bicyclobutanone **I**/oxyallyl species **II** (Scheme 2). In the case of **1a**, "self-trapping" of **I/IIa** forms the dimeric silene **2a**. For comparison: Sorenson et al. reported an analogous all-carbon compound as product of bicyclobutanone dimerization.[17] More recently, the same group also isolated hybrid species between oxyallyl and bicyclobutanone.[18] For the silyl-substituted cyclotrisilene **1b**, it is conceivable that increased steric bulk prevents dimerization of **I/IIb** and results instead in trapping with trace amounts of water, forming **3b**. In further support of the postulated mechanism, the initial products in the reactions of isonitriles with **1a,b** are imino trisilabicyclobutanes, analogous to **Ia,b**.[13,19] Seeking more systematic reactivity, we investigated the reactions of **1a** and **1b** with CO in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and MeOH, respectively.



Scheme 2. Reactions of **1a**,**b** with CO in the presence of H_2O, Me_3SiOTf or MeOH, yielding silenes **3a** (R = Tip = 2,4,6-$iPr_3C_6H_2$, R′ = TMS = $(CH_3)_3Si$, X = OTf = OSO_2CF_3) and **3b**,**c** (R = SiMe*t*Bu_2, **3b**: R′ = H, X = OH; **3c**: R′ = H, X = OMe) via the intermediates **I/II.**

The reaction of **1a** with CO in the presence of TMSOTf results in clean formation of monomeric **3a** with a trimethylsiloxy substituent at the carbon center of the Si=C bond (Scheme 2).[14] The cyclic silene **3a** displays four ^{29}Si NMR signals at $\delta = 89.19, 17.24, 9.44$, and −40.19 ppm. According to a ^1H–^{29}Si correlation, the downfield resonance arises from the SiTip moiety. On this basis and owing to the chemical shift in the expected region for silenes,[20] the signal is assigned to the Si=C bond. The remaining resonances arise from the $SiMe_3$, Si(OTf)Tip, and $SiTip_2$ moieties, respectively. The Si=C ^{13}C NMR signal is observed at $\delta = 178.06$ ppm.

The NMR chemical shifts of the Si=C moiety suggest that there is little pyramidalization at silicon, in contrast to silenes bearing strong nitrogen-based donor substituents at the carbon center,[21] or in cyclic silenes with endocyclic donor atoms.[16c] The strong pyramidalization in the latter case was attributed to the increased p-character of the endocyclic bonds that is due to ring strain. Corresponding increased s-character for the residual electron density at silicon thus favors increased negative charge (and pyramidalization) at silicon. The Si=C silicon atom in **3a**, does not experience the same ring-strain (formal replacement of oxygen by a third silicon atom), and thus pyramidalization at the silicon center is not favored.

An X-ray diffraction study on single crystals of **3a** (Figure 2)[14] indeed reveals the geometry around the silicon and carbon centers in the Si=C bond to be relatively undistorted. Only slight pyramidalization at silicon is observed (ΣSi(1) = 357.63 (19)°), while C1 is almost perfectly planar (ΣC(1) = 359.54(32)°). The Si1−C1 bond distance (1.761(3) Å) is identical (within experimental error) to that in **2a** at 1.771(4) Å. Nevertheless, the geometry around the Si=C bond shows some deviation from planarity with *trans*-bent angles of $\theta_{C1} = 5.83(18)°$ and $\theta_{Si1} = 16.78(14)°$ and a twist angle of $\tau = 18.38(12)°$.

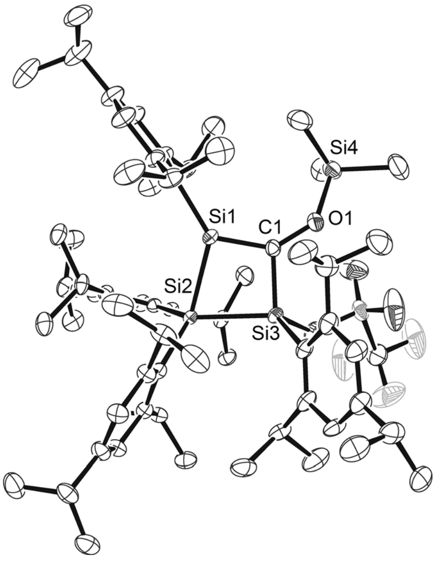


Figure 2. Molecular structure of **3a**·$(C_5H_{12})_{0.5}$ in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms and disorder of OTf group are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C1 1.761(3), C1–Si3 1.850(3), Si3–Si2 2.3894(11), Si2–Si1 2.3579(11), C1–O1 1.376(3), O1–Si4 1.656(2); Si2-Si1-C1 92.52(10), Si1-C1-Si3 101.84(15), C1-Si3-Si2 89.31(9), Si3-Si2-Si1 72.40(4).

The far bulkier substituents of cyclotrisilene **1b** (R = $t\mathrm{Bu_2MeSi}$), which apparently prevent formation of the dimeric product upon reaction with CO, render it considerably more stable towards nucleophilic attack than the aryl-substituted cyclotrisilene **1a**. Thus, carbonylation of **1b** in the presence of methanol results in formation of the surprisingly stable 2-hydroxy silene **3c** (Scheme 2). The ^{29}Si NMR spectrum of **3c** contains resonances for the ring silicon atoms at $\delta = 90.2$, 21.4, and -95.3 ppm. The low field resonance is assigned to the Si=C functionality,[20b] the one at 21.4 ppm to the methoxy-substituted silicon atom and the upfield resonance to the $\mathrm{Si(SiR_3)_2}$ group. The ^{13}C resonance at $\delta = 207.1$ ppm is due to the Si=C group.

Single crystals of silenol **3c** were obtained from pentane, and the molecular structure was determined by X-ray crystallography (Figure 3).[14] The Si1–C1 bond of **3c** (1.7638(16) Å) is short relative to the Si3–C1 bond (1.8754(16) Å), showing its double-bond character. This length is also very close to that of Brook's silene (1.764(3) Å).[15] Furthermore, the C1–O1 bond (1.3876(19) Å), which is a typical $\mathrm{C_{sp^2}}$–O single-bond length,[22] and the almost planar geometry of Si1 and C1 atoms (Σ(Si1) = 360.0°, Σ(C1) = 359.6°) also support the sp^2 character of the Si=C moiety.

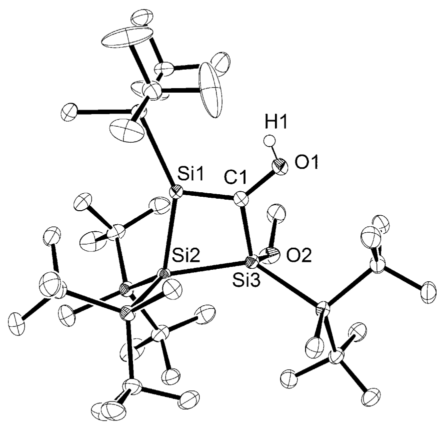


Figure 3. Molecular structure of **3c** in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms except for H1 are omitted for clarity. Selected bond distances [Å] and angles [°]: Si1–C1 1.7638(16), Si1–Si2 2.3666(6), Si2–Si3 2.4481(6), Si3–C1 1.8754(16), O1–C1 1.3876(19); C1-Si1-Si2 92.80(5), Si1-C1-Si3 104.90(8), Si1-Si2-Si3 73.637(18), C1-Si3-Si2 87.56(5).

It is surprising that the enol form of **3c** was obtained instead of the keto form. Therefore, the relative energy of the optimized model structures **III** and **IV** were calculated at B3LYP/6-31G(d) level by using $\mathrm{SiMe_3}$ group instead of $\mathrm{SiMe}t\mathrm{Bu_2}$ (Figure 4). The result shows that both *cis*- and *trans*-**IV** have much lower energy than enol form **III**, as expected, which indicates that **3c** might be produced under kinetic control (formed through the intermediate **I/IIb**). Surprisingly however, silenol **3c** is stable up to 100 °C, only decomposing above 120 °C, without any evidence of tautomerization to the *keto* form. This suggests that the relative stability of the keto/enol forms is controlled by the size of substituents at silicon, which may well reverse the order of relative stabilities.[23]

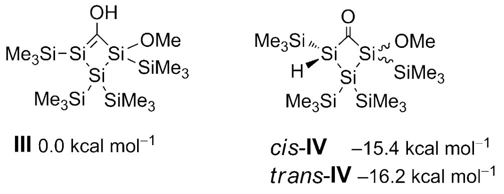


Figure 4. Relative energy of enol form **III** and *cis*- or *trans*-keto form **IV** (B3LYP/6-31G(d)).

In conclusion, cyclotrisilenes undergo direct carbonylation with CO at atmospheric pressure and room temperature. The initial $\mathrm{C_1}$-expanded products are not stable but may either dimerize or be trapped by suitable electrophiles ($\mathrm{H_2O}$, MeOH, $\mathrm{Me_3SiOTf}$) to yield the corresponding functionalized silenes with a newly generated Si=C unit. The scope and generality of this reaction is currently being investigated in our laboratories.

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