Carbonylation of Cyclotrisilenes**

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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 C₁ 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 penta-phenylborole and CO.[5] The hydroborating Lewis acid F₅C₆BH incorporates CO assisted by a alkenyl-functionalized phosphine in a frustrated Lewis pair (FLP) mechanism.[6] A B(C₅F₅)₂-based FLP is capable of stoichiometric CO reduction with dihydrogen.[7] A few coordinately 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 H₂ and NH₃,[10] reactions of stable low-valent compounds of 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 disilylensilylene.[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]

Scheme 1. Reaction of 1a with carbon monoxide yielding the donor-stabilized bis(silene) 2a (Tip = 2,4,6-iPr₃C₆H₂).

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–Cl₁ 1.771(4), Si₁–Si₂ 2.581(19), Si₂–Si₃ 2.4294(17), Si₃–Cl₁ 1.906(5); C₁–Si₁–Si₂ 94.37(16), Si₁–Si₂–Si₃ 87.51(14), Si₁–C₁–Si₁ 102.1(2).
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.[10] The geometry around the double bond is nonetheless somewhat distorted, with a twist angle r about Si1–C1 of 19.05(24)°. The central Si1–O–C 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 (MeBu2Si 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 bicyclobutane I/oxallyl 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 bicyclobutane dimerization.[17] More recently, the same group also isolated hybrid species between oxallyl and bicyclobutane.[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 isonitrides with 1a,b are imino trisilabicyclobutanes, analogous to 1a,b.[11,19] Seeking more systematic reactivity, we investigated the reactions of 1a and 1b with CO in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and MeOH, respectively.

The reaction of 1a with CO in the presence of TMSOTf results in clean formation of monomeric 3a with a trimethylsilyloxy substituent at the carbon center of the Si=C bond (Scheme 2).[14] The cyclic silene 3a displays four 29Si NMR signals at δ = 89.19, 17.24, 9.44, and –40.19 ppm. According to a 1H–29Si 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 SiMe3, Si(OTf)Tip, and SiTip2 moieties, respectively. The Si=C 13C NMR signal is observed at δ = 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.[19] 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 atoms.

**Figure 2.** Molecular structure of 3a (C18H24) 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 2.3594(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), O1–Si4–Si2 18.38(12), while C1 is almost perfectly planar. Selected bond lengths and angles: Si1–C1, 1.761(3); C1–Si3, 1.850(3); Si3–Si2, 2.3594(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); O1–Si4–Si2, 18.38(12).
The far bulkier substituents of cyclotrisilene 1b (R = tBu,MeSi), 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 29Si NMR spectrum of 3c contains resonances for the ring silicon atoms at δ = 90.2, 21.4, and −95.3 ppm. The low field resonance is assigned to the Si=C functionality, which is one at 21.4 ppm to the methoxy-substituted silicon atom and the upfield resonance to the Si(SiH3)3 group. The 13C resonance at δ = 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–Cl bond of 3c (1.7638(16) Å) is short relative to the Si3–Cl 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 Cl–O1 bond (1.3876(19) Å), which is a typical C sp2=O single-bond length, [23] and the almost planar geometry of Si1 and Cl atoms (Σ(Si1) = 360.0°, Σ(Cl1) = 359.6°) also support the sp2 character of the Si=C moiety.

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 SiMe3 group instead of SiMe2Bu3. (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/1b). 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]

In conclusion, cyclotrisilenes undergo direct carbonylation with CO at atmospheric pressure and room temperature. The initial C1-expanded products are not stable but may either dimerize or be trapped by suitable electrophiles (H2O, MeOH, Me2SiOTf) 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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Experimental details are supplied in the Supporting Information. CCDC 964781 (2a), 964782 (3a), and 964783 (3c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] DFT calculations of the real systems to back the mechanism would be extensive and are beyond the scope of this Communication.