CO Reduction Hot Paper

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Reductive Cleavage of Carbon Monoxide by a Disilenide**

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Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

Abstract: *The complete reductive cleavage of the triple bond in carbon monoxide was achieved using a lithium disilenide at room temperature. The C–C-coupled product can be regarded as a silanone dimer with pending alkyne and silirene moieties and incorporates two equivalents of CO per disilenide unit. A formation mechanism via ketenyl intermediates is proposed on the basis of DFT calculations and elucidated experimentally by employing Group 6 metal carbonyls as both stabilizing entity and source of CO in the reaction with disilenide. The isolation of cyclic silylene complexes with weakly donating ketenyl donor groups further supports the mechanistic scenario.*

The reduction of carbon monoxide (CO) experiences renewed interest in view of the limited availability of fossil hydrocarbons.[1] The Fischer–Tropsch process, a prominent example for the transformation of CO and H_2 to hydrocarbons, proceeds by a C–C coupling step followed by the complete reduction of the carbonyl group.[2] It usually employs heterogeneous transition-metal catalysts at elevated temperatures.[2,3] Considerable efforts have thus been devoted to the cleavage of the extremely strong C≡O bond (1077.1 kJ mol^{-1})[4] under milder, preferably homogeneous conditions.[5] Although d- and f-block elements have been reported to reductively couple CO,[6] much less is known about the subsequent reduction step. Highly reducing early transition-metal complexes, for example, (silox)$_3$Ta or a triply bound ditungsten species, can also cleave the C≡O bond of carbon monoxide.[7]

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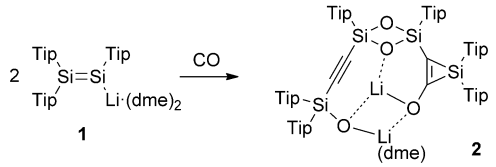
The use of low-valent main-group compounds as alternative for transition-metal catalysts is considered actively,[8] although currently only stoichiometric reactions with CO have been reported: the reduction of CO by potassium results in various C–C coupling products, but stops short of reducing the C≡O bond.[9] Braunschweig et al. recently disclosed the coupling of CO by a species with a B≡B bond stabilized by an N-heterocyclic carbene (NHC), leading to a bis(boralactone).[10] Power et al. have shown that the reaction of a stable diarylgermylene with two equivalents of CO results in the formation of a C–C bond.[11] Conversely, for silylenes, only a transient CO adduct has been studied in the gas phase and in cold matrices.[12] Stable carbenes with a suitable HOMO–LUMO gap readily react with CO to form either oxyallyls or ketenes, but do not seem to result in reductive coupling.[13] In collaboration with the Sekiguchi group, we recently discovered the direct carbonylation of cyclotrisilenes to produce highly functionalized cyclic silenes in the absence of a catalyst,[14] presumably via a highly reactive oxyallyl intermediate.[15] In neither of these cases, the C≡O bond was fully cleaved. A rare case of full CO cleavage has been reported for the frustrated Lewis pair, B(C$_6$F$_5$)$_3$ and P(*t*Bu)$_3$, which reacts with CO/H_2 mixtures under ambient conditions to incorporate a CH_2 group into a B–C$_{aryl}$ bond in the final product.[16] Notably, while organolithium species readily add to CO,[17] to our knowledge there are no reports on analogous reactivity of anionic compounds of the heavier main-group elements.

An anionic low-valent silicon compound could in principle supply the six electrons required for the formation of the C–C bond and the complete reduction of carbon monoxide. We here report the reaction of lithium disilenide **1** (Tip = 2,4,6-triisopropylphenyl) with CO gas, resulting in reductive C–C coupling as well as the complete C≡O bond cleavage of three out of four involved CO equivalents (Scheme 1). We also show that by employing metal-carbonyls as alternative CO sources, stable anionic silylene complexes[18] can be isolated as models for possible intermediates of the reaction with CO gas itself.

Exposure of a solution of lithium disilenide **1**[19] in benzene to 1 atm of CO for one hour at room temperature results in a color change from orange-red to yellow-brown. The formal addition product **2** of four equivalents of CO to two molecules of **1** was isolated as a pale yellow solid by crystallization from hexane at room temperature in 82% yield (Scheme 1).[20] The ^{29}Si NMR spectrum of **2** shows four resonances at $\delta = -9.14$, -29.50, -45.63, and -98.33 ppm, in line with the four chemically inequivalent Si atoms in compound **2** (Scheme 1). The signal at the highest field is in



Scheme 1. Reductive coupling of CO by disilenide **1** (Tip = 2,4,6-iPr$_3$C$_6$H$_3$).

the typical region for 1-silacyclopropenes (silirenes).[21] The ^{13}C NMR spectrum is complicated by the broadening of several signals. Nonetheless, a characteristic resonance at 201.23 ppm provides further support for the presence of a silirene ring in **2**. Furthermore, two ^{13}C signals at 96.44 and 114.76 ppm are indicative of an alkynyl moiety. The ^{7}Li NMR spectrum shows one signal at 1.18 ppm with a low-field shoulder at room temperature, which splits into two distinct resonances at lower temperature (coalescence at $T_c = 253$ K).

Although X-ray diffraction on a single crystal unambiguously established the connectivity of **2** (Figure 1), we refrain from a discussion of bonding parameters because of the low quality of the data.[20] In agreement with NMR data, the molecular structure of **2** comprises a silanolato[22]-substituted

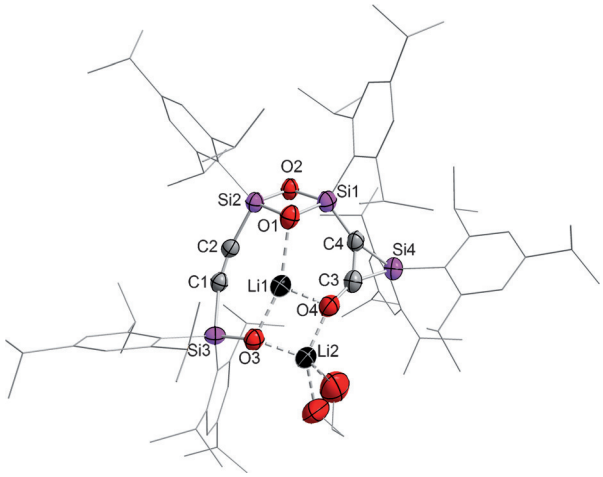
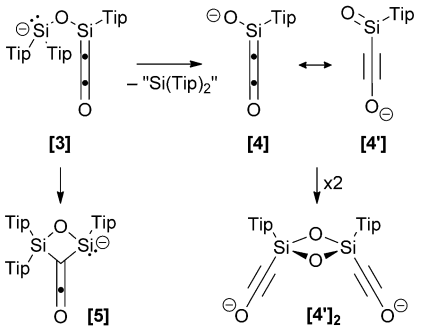


Figure 1. Molecular structure of **2** in the solid state (thermal ellipsoids at 50%). Hydrogen atoms and uncoordinated solvent molecules omitted for clarity.

unsymmetrical alkynyl group (C1, C2) and a three-membered silirene ring (C3, C4, Si4), which are bridged by a four-membered 1,3-dioxadisiletane unit[23] (Si1, Si2, O1, O2). The silirene-bound O4 is the only oxygen atom still attached to a carbon atom; three out of four carbon–oxygen bonds of the incorporated CO molecules have thus been cleaved. In contrast, the only reported reaction of CO with a carbon-based vinyl lithium gives a cyclopropanone by [2+1] cycloaddition of CO without C–O bond cleavage.[24] In **2**, Li1 is coordinated to one dioxadisiletane oxygen atom (O1) and to both alcoholato oxygen atoms (O3, O4), thus residing in a trigonal coordination environment.

In view of the excellent yield, the formation of unsymmetrical **2** almost certainly involves a symmetrical dimerization step. Both CC moieties attached to the 1,3-disiladioxetane ring can formally be derived from ethynolato functionalities. We therefore propose the intermediacy of silylenoid **[3]** generated by the twofold addition of CO to disilenide **1**.[25,26] Although it can be anticipated to be strongly endergonic, silylene extrusion (Tip_2Si:) from anionic **[3]** is plausible in the presence of donor solvents (Figure S45; see the Supporting Information) and would generate a silaketenylidene **[4]** (equally well described as ethynolato-substituted **[4′]**). Silanone **[4′]** should readily dimerize head-to-tail through the strongly polar Si=O bond to the 1,3-disiladioxetane **[4′]$_2$** (Scheme 2). The *cis* selectivity could be explained

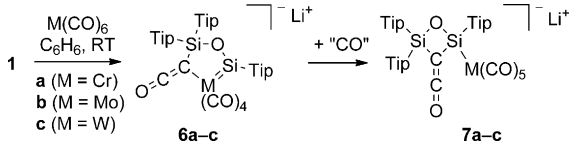


Scheme 2. Proposed intermediates during the formation of **2**.

by prearrangement through coordination of lithium cations to the ethynolato ends of two molecules of **[4/4′]**. Two "Si(Tip)$_2$" fragments would complete the reaction sequence by [1+2] cycloaddition to one ethynolato/ketenylidene moiety and insertion into the C–O bond of the other to give the final product **2**. DFT calculations on simplified anionic model systems of **[3]**, **[4]**, **[4/4′]**, **[4′]$_2$**, and **[5]** (Me instead of Tip; see the Supporting Information) confirm the plausibility of the postulated mechanism, although some of the involved barriers are with up to 30.5 kcal mol^{-1} too high for a reaction at room temperature. Fully aware that the mechanistic considerations must remain tentative on the basis of the available data, we assume that the incorporation of the experimental substituents and countercations could solve the discrepancy, albeit at an exponentially increased computational cost. We therefore sought to gather experimental data to support the mechanistic proposal.

We expected that an early transition metal as countercation instead of Li$^+$ might sufficiently stabilize **[3]** or **[4]**. Ketenylidenes, similar to the C=C=O moiety in **[4]**, have been characterized as intermediates of the reductive cleavage of CO by coordinatively unsaturated transition-metal complexes.[7,27] Ketenylidene complexes of Zr^{IV} and Hf^{IV} have been generated by Zr^{II}- and Hf^{II}-assisted reductive coupling of metal-coordinated carbonyls.[28] Manganese carbonyls are known to convert into η^2-ketene complexes by reaction with carbene precursors.[29] Notably, even surface carbide species on Fischer–Tropsch catalysts have been proposed to form CCO fragments in the presence of CO.[30] On this basis, we

decided to investigate the reactivity of disilenide **1** toward Group 6 metal hexacarbonyls, which could not only stabilize a postulated intermediate, but would also supply the required two equivalents of CO. Indeed, the reaction of **1** with $M(CO)_6$ (M = Cr, Mo, W) in benzene initially resulted in uniform products in all three cases. An X-ray diffraction study on single crystals of the tungsten derivative (see below) allowed the identification of the series as η^1-ketenyl-functionalized silylene complexes **6a–c** (Scheme 3).[20]



Scheme 3. Formation of ketenyl-ligated Group 6 metal–silylene complexes **6a–c** by the reduction of metal-coordinated CO by disilenide **1** (Tip = 2,4,6-iPr$_3$C$_6$H$_3$).

The donor-free silylene centers in complexes **6a–c** showed diagnostic signals[31] in the ^{29}Si NMR spectra at +320.39 (**6a**; M = Cr), +313.01 (**6b**; M = Mo), and +296.11 ppm (**6c**; M = W; $^1J_{Si-W}$ = 138 Hz). In addition, the metal-coordinated ketenyl carbon atoms gave rise to characteristic ^{13}C NMR resonances between −10 to −20 ppm.[32] However, only the tungsten derivative **6c** could be isolated by crystallization from toluene upon addition of [12]crown-4 as cation-sequestering agent.

The molecular structure of **6c** in the solid state was determined by X-ray crystallography (Figure 2). The C1-Si2-O1-Si1 framework acts as a monoanionic bidentate chelating ligand coordinated to the $W(CO)_4$ fragment, thereby forming a five-membered metallacycle. The lithium cation is coordinated by two [12]crown-4 equivalents to form a solvent-separated ion pair. The divalent Si1 is coordinated to the W center at a Si1–W1 distance of 2.4356(13) Å, which is in the typical range for tungsten–silylene complexes.[31d,e] The sum of angles at Si1 (ΣSi1 = 360.0°) further confirms significant Si=W bond character, also in line with the large $^1J_{Si-W}$ coupling constant of **6c** ($^1J_{Si-W}$ = 138 Hz). The anionic ketenyl moiety coordinates to tungsten at a W1–C1 distance of 2.375(4) Å, which is significantly longer than reported W–C_{ketene} bond lengths,[32] suggesting a relatively weak interaction as a result of the geometric constrains of the metallacycle. C1 is only slightly pyramidal with ΣC1 = 358.98°, which hints to a certain ynolate character of the ketenyl unit, comparable to the resonance structure **[4′]** of the postulated intermediate of the formation of **2**. Indeed, the angle Si2-C1-C2 is with 129.8(4)° significantly wider than the ideal 120° expected for sp^2 hybrids, although, the C1–C2 and C2–O2 distances in **6c** of 1.270(6) Å and 1.189(6) Å, respectively, fall within the range of reported double bonds of ketenes.[32]

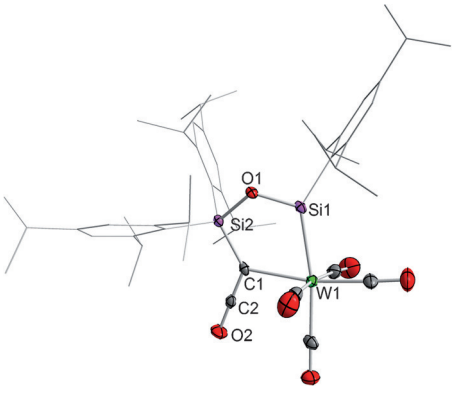
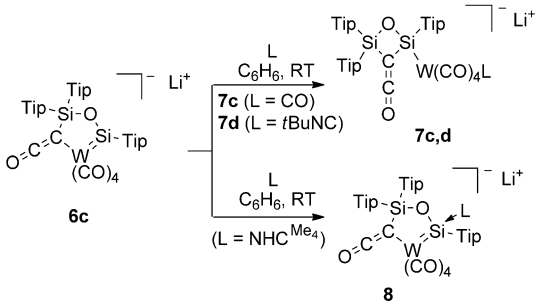


Figure 2. Molecular structure in the solid state of the anionic part of **6c**. Thermal ellipsoids at 50%. Countercation, hydrogen atoms, solvent molecules, and [([12]crown-4)Li]$^+$ omitted for clarity. Selected bond lengths [Å]: Si2–C1 1.818(5), Si2–O1 1.690(3), O1–Si1 1.626(3), C1–W1 2.375(4), Si1–W1 2.4356(13), C1–C2 1.270(6), C2–O2 1.189(6).

The formation of the silylene complexes **6a–c** can be rationalized by invoking precisely the same anionic intermediates as postulated in the mechanism for the generation of **2**. The Group 6 metal centers can reasonably be expected to stabilize the transient silylenoid **[3]** to such an extent that $Si(Tip)_2$ extrusion becomes unfavorable. Instead, cyclization of the ligand system to **[5]** followed by insertion of the coordinatively unsaturated metal center into the adjacent Si-$C_{ketenyl}$ bond would give **6a–c**. However, in [D_6]benzene, the silylene complexes **6a–c** slowly convert into more stable complexes **7a–c** with strongly high-field-shifted ^{29}Si NMR resonances (**7a**: +75.74, −21.82; **7b**: +66.97, −22.18; **7c**: +48.71, −21.70 ppm) accompanied by the formation of an insoluble black residue (Scheme 3). The chromium derivative crystallized from hexane as olive-colored crystals in 48% yield. An X-ray diffraction study on single crystals resulted in a data set of low, but still sufficient quality to unambiguously confirm the constitution of **7a** (see the Supporting Information). Apparently, the incorporation of an additional CO ligand (originating from decomposition of part of the starting material **6a**) reverses the postulated ring expansion and regenerates the four-membered siloxane ligand **[5]**.

This prompted us to investigate the possibility of displacing the ketenylidene ligand systematically. Indeed, exposure of **6c** to either 1 atm of CO or one equivalent of isonitrile gives complex **7c** (L = CO, also obtained by heating of **6c**, albeit in lower yield, see above) and **7d** (L = tBuNC), respectively (Scheme 4).[20] The liberated ketenylidene donor site intramolecularly coordinates to the silylene moiety instead. The isonitrile complex **7d** exhibited ^{29}Si NMR shifts at +55.78 ppm ($^1J_{Si-W}$ = 116 Hz) and



Scheme 4. Ligand displacement in **6c** affording complexes **7c** (L = CO), **7d** (L = tBuNC), and **8** (L = $NHC^{Me}{}_4$ = 1,3,4,5-tetramethylimidazol-2-ylidene).

−23.31 ppm, very similar to those of the corresponding CO derivatives **7a–c**. In the ^{13}C NMR spectra, characteristic resonances for ketenyl moiety are observed (**7c**: 16.52 ppm (*C*=C=O), 164.76 ppm (C=*C*=O); **7d**: 16.81 ppm (*C*=C=O), 165.46 ppm (C=*C*=O)). The X-ray diffraction studies on single crystals of **7c** (Figure 3) and **7d** (Supporting Information) confirmed the coordination of an additional ligand to tungsten under formation of the monodentate ligand **[5]**. The lengths of Si−C bonds in the four-membered rings of **7c** differ significantly: Si2-C1 (1.869(4) Å) is significantly shorter than Si1-C1 (1.961(4) Å), suggesting that Si1 retains a certain silylene character. This is reminiscent of the observation by Bacereido et al. that a phospha ylidic ketenyl moiety, if at all, interacts only very weakly with a Lewis acidic boryl group in β position.[33]

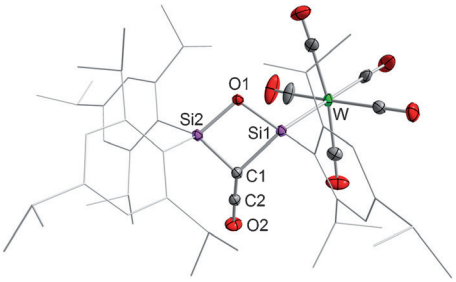


Figure 3. Molecular structure in the solid state of anionic **7c**. Thermal ellipsoids at 30%. Hydrogen atoms, solvent molecules, and lithium cation omitted for clarity. Selected bond lengths [Å]: Si2–C1 1.869(4), Si2–O1 1.649(2), O1–Si1 1.723(2), C1–Si1 1.961(4), Si1–W1 2.6008(9), C1–C2 1.259(5), C2–O2 1.192(5).

Conversely, the reaction of **6c** with one equivalent of a N-heterocyclic carbene (NHC^{Me}_4 = 1,3,4,5-tetramethylimidazol-2-ylidene) resulted in the coordination of the NHC^{Me}_4 to the donor-free silylene ligand, affording **8** in near quantitative yield as a pale-yellow crystalline material (Scheme 4). The now base-stabilized[34] silylene complex **8** was unambiguously identified by multinuclear NMR spectroscopy, UV/Vis, IR, and combustion analyses, and X-ray diffraction on single crystals (Supporting Information). The ^{29}Si NMR spectrum of **8** showed resonances at 31.12 and −20.92 ppm; the former is notably shifted to higher field by approximately 270 ppm, compared to the corresponding signal of the base-free precursor **6c**.

In summary, the Si=Si bond of disilenide **1** is indeed able to provide the reduction potential that is necessary for the complete cleavage of the strongest bond in chemistry, the C≡O bond. The selective formation of **2** from the reaction of **1** with CO in the absence of transition-metal compounds can be explained by the occurrence of the same intermediates as during the corresponding reactions with Group 6 carbonyls, providing an impressive case of transition-metal-like behavior of a low-valent main group compound.[8]

Keywords: carbon monoxide · C–C coupling · ketenylidenes · reduction · silylene complexes

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[20] Experimental and computational details are supplied in the Supporting Information (X-ray structure determination, complete analytical data, mechanistic considerations). CCDC 1024836 (**2**), 1024833 (**6c**), 1024834 (**8**), 1024837 (**7d**), 1024838 (**7c**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
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