Organosilicon Chemistry

Metal–Silicon Triple Bonds: Nucleophilic Addition and Redox Reactions of the Silylidyne Complex [Cp(CO)₂Mo=Si-R]**

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Recent developments in the chemistry of low-valent maingroup element compounds have revealed that N-heterocyclic carbenes (NHC) are particularly suitable to stabilize silicon centers in low oxidation states.^[1] Remarkable achievements include the syntheses of stable NHC adducts of Si₂,^[2] SiX₂ (X = Cl, Br),^[3] silanones,^[4] and Si(R)Cl (R = *m*-terphenyl).^[5] The latter compounds were shown to be useful precursors for the preparation of complexes containing metal–silicon multiple bonds as exemplified by the synthesis of the first silylidyne complex, [Cp(CO)₂Mo \equiv Si-R] (1).^[6] Compound 1 offers, as silicon analogue of metal alkylidyne complexes,^[7] new perspectives in organosilicon chemistry. The high synthetic potential of 1 is demonstrated here by a series of reactions providing access to new complexes containing metal–silicon double and single bonds. 143 °C, respectively. Chlorosilylidene complexes are very rare^[10] and azidosilylidene complexes as **3** have not been reported to date highlighting the synthetic potential of **1**. Moreover, complex **1** undergoes selective addition reactions with carbon-centered nucleophiles. For example, addition of one equivalent of LiMe to a solution of **1** in diethylether at -60 °C was accompanied by a rapid color change from redbrown to orange and afforded cleanly the methylsilylidene complex salt **4**, which was isolated as a yellow, air-sensitive, thermolabile diethylether solvate in 75% yield.^[9,11] The crystal structures of **2** and **3** were determined by single-crystal X-ray diffraction analyses^[12] and revealed the presence of well separated tetraalkylammonium cations and silylidene complex anions.^[13] The most striking bonding features of the

Complex 1 contains an electrophilic silicon center and reacts smoothly with various anionic nucleophiles to give unprecedented anionic silvlidene complexes (Scheme 1).^[8] For example, treatment of 1 with $(NMe_4)Cl$ in 1,2dimethoxyethane (DME) afforded selectively the bright orange chlorosilylidene complex salt 2 in 72 % yield, and reaction of 1 with $(NEt_4)N_3$ gave the orange azidosilvlidene complex salt 3 in quantitative yield (Scheme 1).^[9] Compounds 2 and 3 were isolated as very air-sensitive solids, which decompose on heating at 122-126°C and



Scheme 1. Nucleophilic addition and redox reactions of 1.

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Prochnicki and H. Spitz for recording the solution NMR spectra, Dr. B. Lewall for the electroanalytical studies, and A. Martens for the elemental analyses. $Cp = \eta^{s} - C_{s}H_{s}$; $R = C_{6}H_{3}$ -2,6-Trip₂, Trip = 2,4,6triisopropylphenyl.

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three-legged piano-stool complex anions (Figures 1 and 2) are: a) the short Mo–Si distances (**2**, 2.300(1) Å; **3**, 2.287(1) Å), which compare well with the Mo–Si double bond lengths of other molybdenum arylsilylidene complexes (Mo–Si 2.288(2)–2.3872(7) Å),^[6,10a,14] b) the trigonal planar coordination of the silicon atoms (sum of angles at Si: **2**, 359.4°; **3**, 359.6°); c) the nearly upright conformation of the silylidene ligand with the *m*-terphenyl group pointing towards the cyclopentadienyl ring;^[15] d) the considerably widened Mo-Si-C_{aryl} angle (**2**, 145.0(1)°; **3**, 142.2(1)°), which can be attributed to the large steric demand of the *m*-terphenyl substituent; and e) the small Cl/N_{azide}-Si-C_{aryl} angle (**2**,



Figure 1. Diamond plot of the structure of the silylidene complex anion in 2-toluene. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo–Si 2.300(1), Mo–C37 1.930(4), Mo–C38 1.900(4), Si–Cl 2.145(1), Si–Cl 1.909(4), C37–O1 1.176(5), C38–O2 1.188(5); Mo-Si-Cl 145.0(1), Mo-Si-Cl 120.81(5), Cl-Si-Cl 93.6(1), Si-Mo-C37 79.5(1), Si-Mo-C38 85.8(1), C37-Mo-C38 83.8(2).



Figure 2. Diamond plot of the structure of the silylidene complex anion in 3·2(toluene) pentane. Hydrogen atoms were omitted and the 2,4,6-tris(isopropyl)phenyl rings were faded for clarity. Selected bond lengths [Å] and angles [°]: Mo–Si 2.287(1), Mo–C37 1.922(5), Mo–C38 1.929(5), Si–N1 1.801(4), Si–C1 1.919(4), N1–N2 1.217(5), N2–N3 1.124(6); Mo-Si-C1 142.2(1), Mo-Si-N1 126.3(1), N1-Si-C1 91.1(2), Si-Mo-C37 90.9(1), Si-Mo-C38 81.4(1), C37-Mo-C38 83.3(2).

 $93.6(1)^{\circ}$; **3**, $91.1(2)^{\circ}$), which reflects the low tendency of the doubly-bonded silicon atom for hybridization.

The Si–Cl bond of **2** (2.145(1) Å) is slightly shorter than that of the Si^{II} chloride Si(R)Cl(Im-Me₄) (2.1836(8) Å; $\mathbf{R} = C_6H_3$ -2,6-Trip₂; Im-Me₄ = tetramethylimidazol-2-ylidene),^[5] but considerably longer than that of the arylchlorosilane

 $Si(C_6H_3-2,6-Trip_2)H_2Cl$ (2.032(8) Å),^[16] or other typical organic chlorosilanes (2.023 Å),^[17] indicating a strongly polarized Si-Cl bond in 2. Indirect evidence for the polarization of the Si-Cl bond of 2 is also provided by the IR and ¹H NMR spectra, which show that **2** dissociates to some extent in toluene or benzene solutions to give 1 and (NEt₄)Cl. The dissociation equilibrium depends on the solvent and is fully shifted in THF or DME to 2. In comparison, complex 3 contains a less polar Si– N_{azide} bond and does not dissociate to 1 and $(NMe_4)N_3$ in toluene or benzene solutions at similar concentrations. The lower polarity of the $Si-N_{azide}$ bond in 3 is also indicated by the bonding parameters: the Si-Nazide bond of **3** (1.801(4) Å) is only slightly longer than that of $Si(N_3)_4$ $((Si-N)_{calcd} 1.735 \text{ Å})^{[18]}$ or other tetracoordinate azidosilanes (1.760(3)–1.814(2) Å),^[19] and the difference between the N_{α} - N_{β} (1.217(5) Å) and N_{β} -N_y bond length (1.124(6) Å) of the azide group in $3 (\Delta(NN) = 9.3 \text{ pm})$ compares well with that of Si(N₃)₄ (Δ (NN)_{calcd} = 9.0 pm).^[18] The Mo–CO bond lengths of **2** (1.915(15) Å)^[20] and **3** (1.926(4) Å)^[20] are much shorter than those of [Mo(CO)₆] (2.063(3) Å)^[21] or **1** (1.971(3) Å)^[6,20] and indicate a considerably stronger metal-carbonyl back bonding in 2 and 3 in full agreement with the IR spectra (see below).

The IR and NMR spectra corroborate the structures of the silvlidene complex salts 2–4. Thus, the ${}^{29}Si{}^{1}H$ NMR spectra of 2-4 display a distinctive downfield-shifted signal at $\delta = 228.2, 228.5, \text{ and } 138.0 \text{ ppm}, \text{ respectively. The }^{29}\text{Si NMR}$ chemical shifts of the silvlidene complexes 2-4 lie between that of the silvlidyne complex 1 ($\delta = 320.1$ ppm) and those of the silvl complexes 5 and 6 ($\delta = 27.4$ and 50.8 ppm, respectively). Further structural information is provided by the ¹H and ${}^{13}C{}^{1}H$ NMR spectra, which reveal that complexes 2–4 are on average C_s symmetric in solution. The NMR spectra also show, that rotation of the *m*-terphenyl substituent about the Si-Carvl bond is fast on the NMR timescale at room temperature. The IR spectrum of 3 in DME shows a distinctive, very strong $v_{as}(N_3)$ absorption band at 2109 cm⁻¹. Furthermore, the solution IR spectra of all silvlidene complexes show in DME two very strong v(CO) absorption bands, which appear at considerably lower wavenumbers (2, 1840 and 1762 cm⁻¹; **3**, 1826 and 1756 cm⁻¹; **4**, 1824 and 1695 cm⁻¹) than those of 1 (1937 and 1875 cm⁻¹ in toluene) and of the zwitterionic silylidene complex [Cp(CO)₂Mo=Si(C₆H₃-2,6- $Trip_2$)(Im-Me₄)] (1859 and 1785 cm⁻¹ in toluene).^[6] This suggests that the σ -donor/ π -acceptor ratio increases in the ligand series $SiR^+ < SiR(Im-Me_4)^+ < Si(R)Cl < Si(R)N_3 <$ Si(R)Me leading to a strengthening of the metal-carbonyl back bonding.

Transition-metal silyl complexes are a well-studied class of compounds.^[22] The majority of silyl complexes are neutral. Anionic transition metal silyl complexes are less common and have been shown to be useful building blocks in coordination chemistry.^[23] In comparison, dianionic silyl complexes are extremely rare and structural characterization has been lacking so far.^[24] The silylidyne complex **1** enables general synthetic access to dianionic silyl complexes by two routes. The first route involves double addition of strong nucleophiles to the electrophilic silicon center of **1**. For example, treatment of **1** with two equivalents of LiMe in DME/hexane

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(1:4) at -70 °C followed by warming to room temperature affords selectively the silyl complex salt **5**, which was isolated as a yellow, extremely air-sensitive DME/hexane solvate in 88% yield (Scheme 1).^[9] The second approach to dianionic silyl complexes was discovered studying the redox properties of **1**. In fact, reduction of **1** with slightly more than two equivalents of potassium graphite in DME/pentane (1:1) resulted in an unusual insertion of silicon into the C–C bond of one of the peripheral 2,6-positioned isopropyl substituents to give the silafluorenyl complex **6**. The dianionic silyl complex **6** was isolated as an orange, highly air-sensitive dipotassium salt in 90% yield (Scheme 1).

Cyclic voltammetric studies of 1 provided further insight into this C-C bond activation reaction induced by electron transfer. They showed that the silvlidyne complex 1 undergoes in THF at ambient temperature an irreversible reduction at $E_{p}^{c}(1) = -2060 \text{ mV}$ to give probably a silafluorenyl radical anion, which then takes up a second electron at $E_{\rm p}^{\rm c}(2) = -2270 \,{\rm mV}$ to give the silafluorenyl complex dianion **6** (potentials vs. the $[Fe(C_5Me_5)_2]/[Fe(C_5Me_5)_2]^+$ redox couple/ 0.1M (NBu₄)PF₆ in THF; scan rate = 100 mV s^{-1}).^[9,25] The complex salts 5 and 6 were fully characterized.^[9] The IR spectra of DME solutions of 5 and 6 display two very strong v(CO) absorption bands at comparable low energy (5: 1677 and 1589 cm⁻¹; **6**: 1685 and 1593 cm⁻¹) as those of highly reduced metal carbonyls (e.g. $[M(CO)_4]^{3-}$ (M = Mn, Re); $v(CO) = 1670, 1690 \text{ cm}^{-1}; [M(CO)_3]^{3-} (M = \text{Rh}, \text{Ir}); v(CO) =$ 1664, 1666 cm⁻¹).^[26] The ²⁹Si 1 H NMR spectra of **5** and **6** show a distinctive ²⁹Si NMR signal at $\delta = 27.4$ ppm and 50.8 ppm, respectively. The ²⁹Si NMR chemical shifts of 5 and 6 are typical for transition metal silyl complexes, which usually display ²⁹Si NMR signals in the range of -50 to +70 ppm.^[22,27] The ¹H and ¹³C{¹H} NMR spectra of **5** show a single set of resonance signals for the *m*-terphenyl substituent and one CO signal at $\delta = 248.9$ ppm, as expected for an overall $C_{\rm s}$ symmetric silvl complex dianion, in which rotation of the *m*-terphenyl substituent about the Si-C_{arvl} single bond is fast on the NMR time scale. In comparison, 6 contains a stereogenic silicon center, which renders the methyl groups of all isopropyl substituents diastereotopic, and gives rise to two CO signals in the ¹³C{¹H} NMR spectrum at $\delta = 245.7$ and 248.3 ppm.^[9] The CO signals of the dianionic silyl complexes 5 and 6 appear in the ¹³C{¹H} NMR spectra at even lower field than those of the anionic silvlidene complexes 2–4 ($\delta = 240.4$ – 243.2 ppm) indicating an even stronger metal-carbonyl backbonding in 5 and 6 than in 2-4, which is further demonstrated by the position of the v(CO) absorption bands in the IR spectra and the Mo-C and C-O bond lengths (see below).

Compound **6** crystallizes in the space group $P\bar{1}$ and is composed of two independent, centrosymmetric ion-pair dimers containing two molybdenum silafluorenyl dianions and four potassium cations (Figure 3).^[12] Each ion-pair dimer is hold together by electrostatic interactions between the potassium cations and the carbonyl oxygen atoms, which are typical of alkali metal salts of metal carbonyl anions and isocarbonyl compounds.^[28] Two potassium cations (K2 and K2#) are bound to one diethylether (K2–O3 2.715(13) Å) and one chelating DME ligand (K2–O4 2.827(9) Å, K2–O5 2.639(9) Å)^[29] and link the molybdenum dicarbonyl moieties



Figure 3. Diamond plot of the structure of the one independent contact ion-pair dimer of **6**·1.5 (DME)·0.5 (Et₂O). Hydrogen atoms and the DME and Et₂O molecules bonded to K2 and K2# were omitted for clarity. Selected distances [Å] and angles [°]: K1–O1 2.806(7), K1–O2 2.950(7), K1–O2# 2.913(6), K1–C7 3.329(8), K1–C8 3.151(8), K1–C9 3.080(8), K1–C10 3.144(8), K1–C11 3.173(9), K1–C12 3.259(9), K2–O1 2.627(6), K2–O2# 2.652(7), Mo1–Si1 2.480(2), Mo1–C37 1.910(9), Mo1–C38 1.891(11), Si1–C1 1.934(9), Si1–C8 1.920(9), Si1–C34 1.944(9), C37–O1 1.204(11), C38–O2 1.220(11); Mo1-Si1-C1 121.8(3), Mo1-Si1-C8 115.6(3), Mo1-Si1-C34 119.9(3), C1-Si1-C8 87.2(4), C1-Si1-C34 102.4(4), C8-Si1-C34 104.3(4).

of two silafluorenyl complex dianions through short K-O isocarbonyl bridges (K2–O1 2.627(6) Å, K2-02# 2.652(7) Å)^[30] to form a twelve-membered ring, which consists of three planes arranged in a chair-like conformation (plane 1: Mo1, C37, O1, C38, O2; plane 2: O1, K2, O2#, O1#, K2#, O2; plane 3: Mo1#, C37#, O1#, C38#, O2#).^[31] The other two potassium cations (K1, K1#) are located above and below the central ring plane (plane 2), display slightly longer interionic contacts to three carbonyl O atoms (K1-O1 2.806(7) Å, K1-O2 2.950(7) Å, K1-O2# 2.913(6) Å),^[30] and are coordinated in an asymmetric fashion to the C-C bond activated arene ring (K-Carene 3.080(8)-3.329(8) Å).[32,33] Isocarbonyl bridging leads in 6.1.5 (DME).0.5 (Et₂O) to even shorter Mo–C_{carbonyl} bonds (1.900 Å) than those of 2 (1.915 Å) and 3 (1.926 Å) and correspondingly to even longer C-O bonds (1.208 Å) than those of **2** (1.182 Å) and **3** (1.181 Å).^[34] Finally, the silafluorenyl complex anions in 6.1.5 (DME).0.5 (Et₂O) feature a distorted tetrahedral coordinated silicon center and a Mo-Si single bond (2.480(2) Å), which is ca. 20 pm longer than the Mo-Si double bonds of the silvlidene complexes 2 and 3, but shorter than the Mo-Si single bonds of all silvl complexes reported so far (2.487–2.669 Å).^[35]

The general, expandable access to unprecedented anionic silylidene complexes and dianionic silyl complexes presented in this work illustrates the high synthetic potential of the silylidyne complex **1** resulting from the high polarity of the Mo–Si triple bond. Further studies are currently underway to explore the scope of this new chemistry.

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potassium-to-ring normal and C_g the center of the arene ring; $C_f \mathcal{-} C_g = 0.233$ Å).

- [34] The mean bond lengths of **2**, **3**, and the two independent ion-pair dimers of **6** are given in brackets.
- [35] The median value of Mo–Si single bond lengths is 2.5595 Å according to a CSD survey of molybdenum silyl complexes (14.09.2010).