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Metal–Silicon Triple Bonds: Nucleophilic Addition and Redox Reactions of the Silylidyne Complex [Cp(CO)$_2$Mo≡Si-R]**

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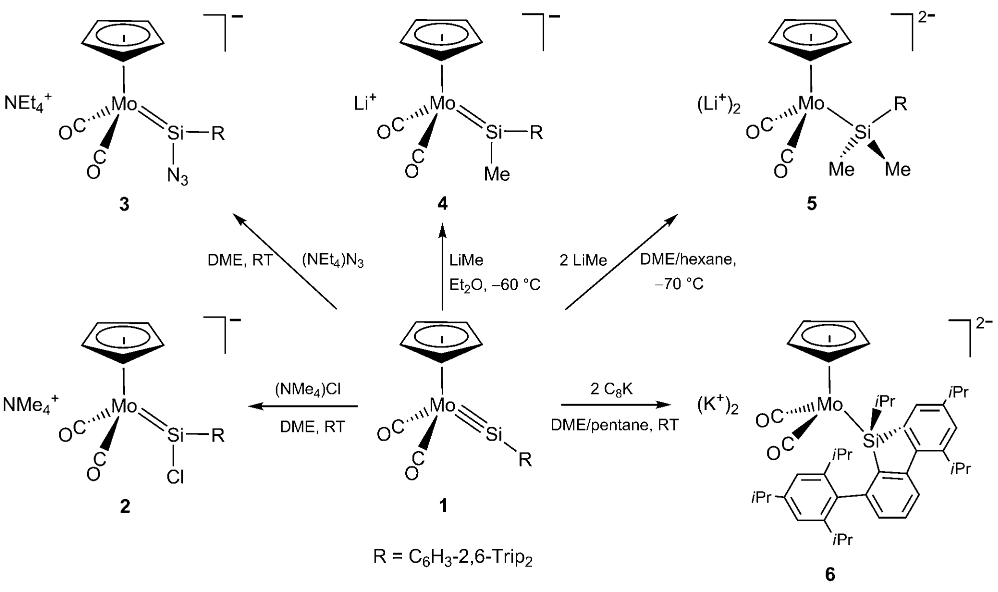
Recent developments in the chemistry of low-valent main-group element compounds have revealed that N-heterocyclic carbenes (NHC) are particularly suitable to stabilize silicon centers in low oxidation states.[1] Remarkable achievements include the syntheses of stable NHC adducts of Si_2,[2] SiX_2 (X = 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)$_2$Mo≡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.



Scheme 1. Nucleophilic addition and redox reactions of **1**.

Complex **1** contains an electrophilic silicon center and reacts smoothly with various anionic nucleophiles to give unprecedented anionic silylidene complexes (Scheme 1).[8] For example, treatment of **1** with (NMe$_4$)Cl in 1,2-dimethoxyethane (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 azidosilylidene 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 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 red-brown 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 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**,

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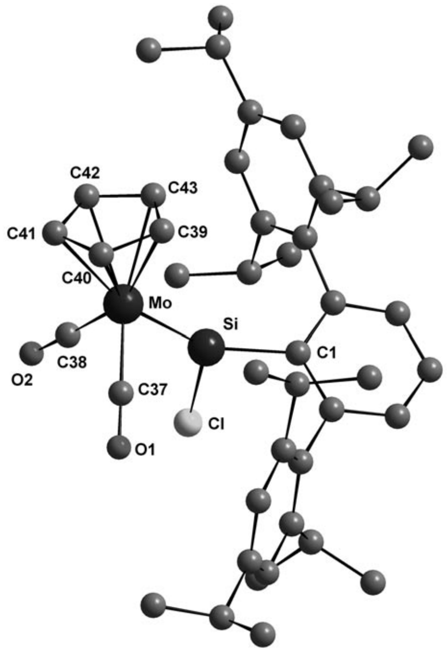

Figure 1. Diamond plot of the structure of the silylidene complex anion in **2**·toluene. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo–Si 2.300(1), Mo–C37 1.930(4), Mo–C38 1.900(4), Si–Cl 2.145(1), Si–C1 1.909(4), C37–O1 1.176(5), C38–O2 1.188(5); Mo-Si-C1 145.0(1), Mo-Si-Cl 120.81(5), Cl-Si-C1 93.6(1), Si-Mo-C37 79.5(1), Si-Mo-C38 85.8(1), C37-Mo-C38 83.8(2).

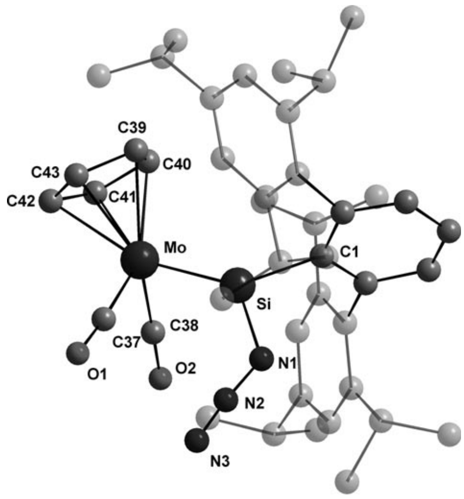

Figure 2. Diamond plot of the structure of the silylidene complex anion in **3**·2(toluene)·pentane. Hydrogen atoms were omitted and the 2,4,6-tris(isopropyl)phenyl rings were faded for clarity. Selected bond lengths [Å] and angles [°]: Mo–Si 2.287(1), Mo–C37 1.922(5), Mo–C38 1.929(5), Si–N1 1.801(4), 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)°; **3**, 91.1(2)°), 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-Me_4) (2.1836(8) Å; R = C_6H_3-2,6-$Trip_2$; Im-Me_4 = 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 ^{1}H NMR spectra, which show that **2** dissociates to some extent in toluene or benzene solutions to give **1** and (NEt_4)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–N_{azide} bond of **3** (1.801(4) Å) is only slightly longer than that of $Si(N_3)_4$ ($(Si\text{–}N)_{calcd}$ 1.735 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_γ bond length (1.124(6) Å) of the azide group in **3** (Δ(NN) = 9.3 pm) compares well with that of $Si(N_3)_4$ ($\Delta(NN)_{calcd}$ = 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 silylidene 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, and 138.0 ppm, respectively. The ^{29}Si NMR chemical shifts of the silylidene complexes **2**–**4** lie between that of the silylidyne complex **1** ($\delta = 320.1$ ppm) and those of the silyl complexes **5** and **6** ($\delta = 27.4$ and 50.8 ppm, respectively). Further structural information is provided by the ^{1}H 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–C_{aryl} bond is fast on the NMR timescale at room temperature. The IR spectrum of **3** in DME shows a distinctive, very strong $\nu_{as}(N_3)$ absorption band at 2109 cm^{-1}. Furthermore, the solution IR spectra of all silylidene complexes show in DME two very strong ν(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 $[Cp(CO)_2Mo{=}Si(C_6H_3\text{-}2,6\text{-}Trip_2)(Im\text{-}Me_4)]$ (1859 and 1785 cm^{-1} in toluene).[6] This suggests that the σ-donor/π-acceptor ratio increases in the ligand series $SiR^+ < SiR(Im\text{-}Me_4)^+ < Si(R)Cl < Si(R)N_3 < Si(R)Me$ 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

(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 silylidyne complex **1** undergoes in THF at ambient temperature an irreversible reduction at $E_p^c(1) = -2060$ mV to give probably a silafluorenyl radical anion, which then takes up a second electron at $E_p^c(2) = -2270$ mV to give the silafluorenyl complex dianion **6** (potentials vs. the $[Fe(C_5Me_5)_2]/[Fe(C_5Me_5)_2]^+$ redox couple/ 0.1 M $(NBu_4)PF_6$ 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 ν(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); ν(CO) = 1670, 1690 cm^{-1}; $[M(CO)_3]^{3-}$ (M = Rh, Ir); ν(CO) = 1664, 1666 cm^{-1}).[26] The $^{29}Si\{^1H\}$ NMR spectra of **5** and **6** show a distinctive ^{29}Si NMR signal at $\delta = 27.4$ ppm and 50.8 ppm, respectively. The ^{29}Si NMR chemical shifts of **5** and **6** are typical for transition metal silyl complexes, which usually display ^{29}Si NMR signals in the range of −50 to +70 ppm.[22,27] The ^{1}H and $^{13}C\{^1H\}$ 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_s symmetric silyl complex dianion, in which rotation of the *m*-terphenyl substituent about the Si−C$_{aryl}$ 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 $^{13}C\{^1H\}$ 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 $^{13}C\{^1H\}$ NMR spectra at even lower field than those of the anionic silylidene complexes **2**–**4** ($\delta = 240.4$–243.2 ppm) indicating an even stronger metal–carbonyl back-bonding in **5** and **6** than in **2**–**4**, which is further demonstrated by the position of the ν(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 of two silafluorenyl complex dianions through short K···O isocarbonyl bridges (K2−O1 2.627(6) Å, K2−O2# 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−C$_{arene}$ 3.080(8)–3.329(8) Å).[32,33] Isocarbonyl bridging leads in **6**·1.5 (DME)·0.5 (Et$_2$O) 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 (Et$_2$O) 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 silylidene complexes **2** and **3**, but shorter than the Mo−Si single bonds of all silyl complexes reported so far (2.487–2.669 Å).[35]

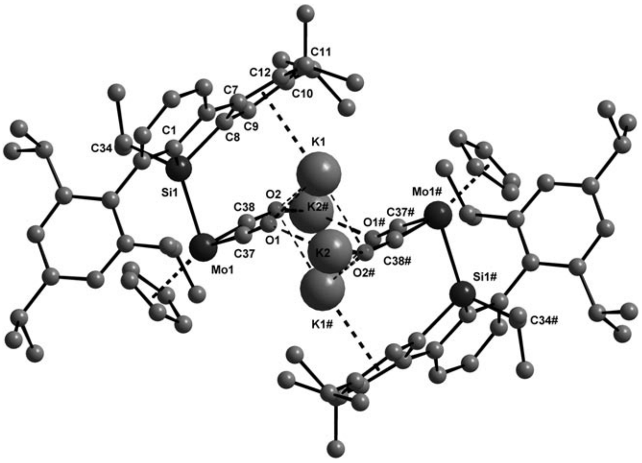

Figure 3. Diamond plot of the structure of the one independent contact ion-pair dimer of **6**·1.5 (DME)·0.5 (Et$_2$O). Hydrogen atoms and the DME and Et$_2$O molecules bonded to K2 and K2# were omitted for clarity. Selected distances [Å] and angles [°]: K1–O1 2.806(7), K1–O2 2.950(7), K1–O2# 2.913(6), 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).

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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[9] The Supporting Information contains the syntheses and analytical and spectroscopic data of complexes **2**–**6**. All compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR and ^{29}Si NMR spectroscopies, and the ^{1}H and ^{13}C NMR signals were unequivocally assigned by a combination of H,H-COSY, HMQC, HMBC, and DEPT experiments. The Supporting Information contains also details of the cyclic voltammetric studies of **1**.

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[12] Orange single crystals of **2**·toluene and **3**·2(toluene)·pentane were obtained upon diffusion of pentane into a toluene solution of **2** at room temperature and a toluene solution of **3** at −16 °C, respectively. Orange single crystals of **6**·1.5 DME·0.5 Et_2O were obtained upon addition of diethylether into a solution of **6** in DME at ambient temperature. CCDC 800704 (**2**·toluene), 800705 (**3**·2(toluene)·pentane), and 800706 (**6**·1.5 (DME)·0.5 (Et_2O)) 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.

[13] The shortest interionic contacts exist in **2** and **3** between the hydrogen atoms of the ammonium cations and the carbonyl oxygen atoms of the anions (**2**: H45B···O1 2.313 Å, H47C···O2 2.434 Å; **3**: H48A···O2 2.504 Å). These CH···O contacts are shorter than the sum of the van der Waals radii of hydrogen and oxygen (2.70 Å) and lie close to the range of short CH···O contacts (2.045–2.399 Å) found in various neutron diffraction crystal structures: R. Taylor, O. Kennard, *J. Am. Chem. Soc.* **1982**, *104*, 5063.

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[29] In the second independent ion-pair dimer of **6**·1.5 (DME)·0.5 (Et_2O) the corresponding potassium cations K4 and K4# are coordinated by two chelating DME ligands. The structure of the second independent ion-pair dimer of **6**·1.5 (DME)·0.5 (Et_2O) with selected bonding parameters is depicted in the Supporting Information.

[30] The $K{-}O_{carbonyl}$ distances of **6**·1.5 (DME)·0.5 (Et_2O) compare well with those of other potassium carbonyl metalates: a) E. Hey-Hawkins, H. G. von Schnering, *Chem. Ber.* **1991**, *124*, 1167; b) V. Kirin, P. W. Roesky, *Eur. J. Inorg. Chem.* **2004**, 1045.

[31] The chair-like conformation of the three planes is indicated by the dihedral angle between plane 1 and plane 2, and plane 2 and plane 3 of 47.9°.

[32] The $K{-}C_{arene}$ distances in **6**·1.5 (DME)·0.5 (Et_2O) compare well with those found in other arene complexes of K^+; selected references: a) P. B. Hitchcock, M. F. Lappert, G. A. Lawless, B. Royo, *J. Chem. Soc. Chem. Commun.* **1993**, 554, and references therein; b) L. Pu, M. O. Senge, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1998**, *120*, 12682; c) G. K. Fukin, S. V. Linde-

man, J. K. Kochi, *J. Am. Chem. Soc.* **2002**, *124*, 8329, and refs. therein.

[33] The asymmetric coordination of the potassium cation K1 (K1#) is also evidenced by its distance from the arene ring C7–C12 (K1–C_f 2.855(2) Å), which is shorter than the distance from the arene ring center (K1–C_g 2.865(4) Å) (C_f denotes the foot of the potassium-to-ring normal and C_g the center of the arene ring; C_f–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).