Silylidyne Complexes

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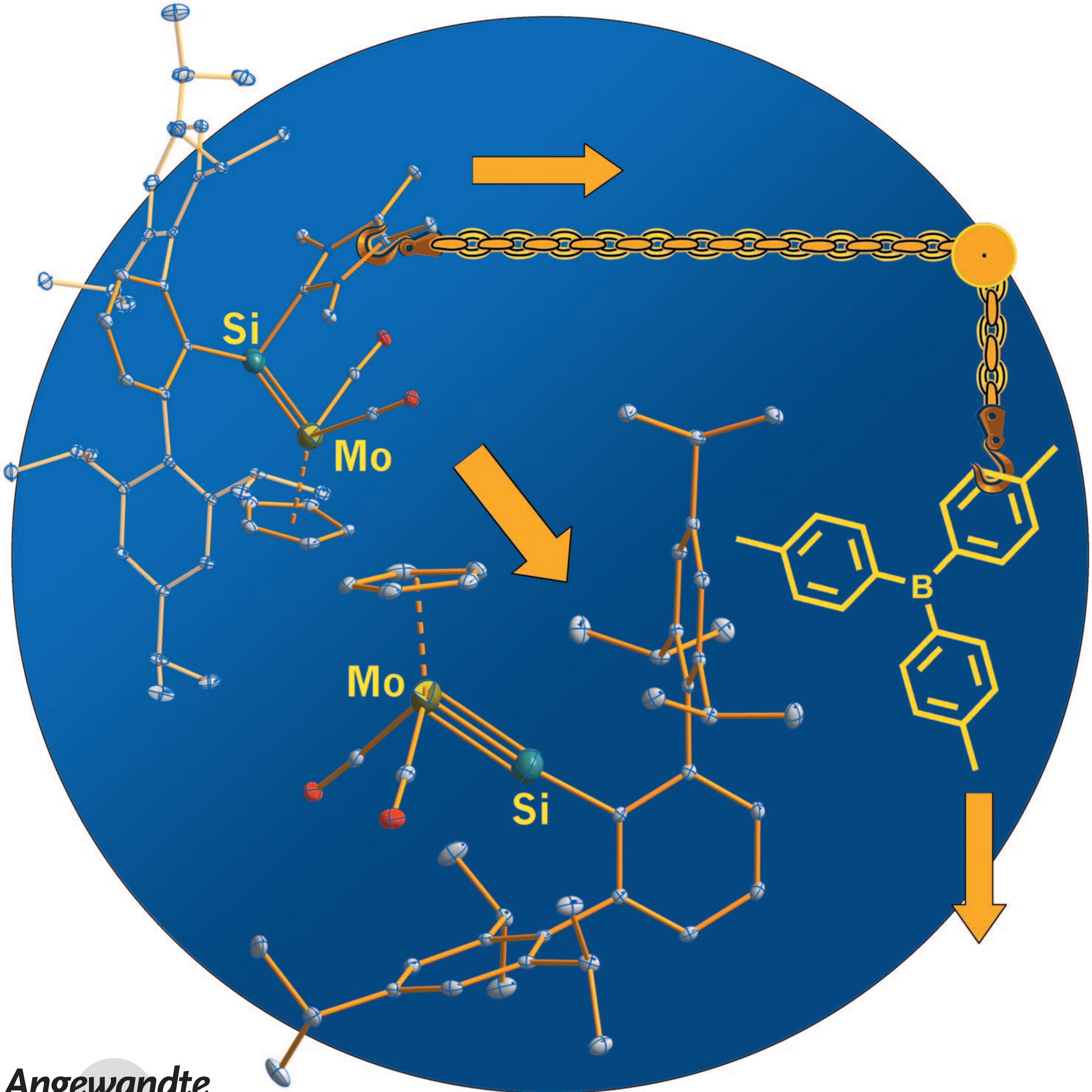
Metal–Silicon Triple Bonds: The Molybdenum Silylidyne Complex [Cp(CO)$_2$Mo$\equiv$Si-R]**

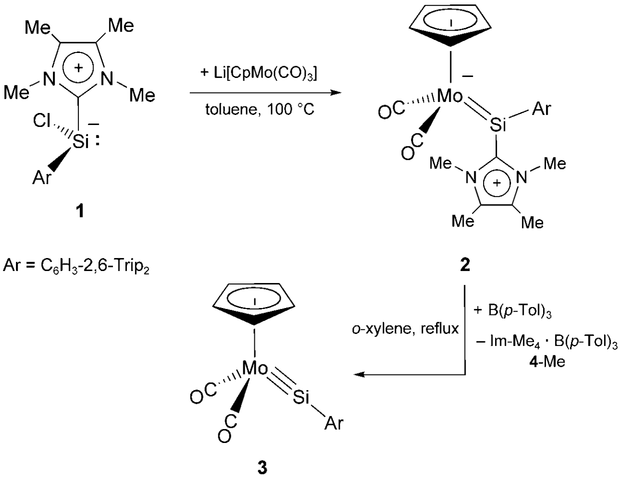
Alexander C. Filippou, Oleg Chernov, Kai W. Stumpf, and Gregor Schnakenburg*



Transition metal alkylidyne complexes are among the most important organometallic compounds. The great utility of these compounds in organometallic and organic chemistry was highlighted by E. O. Fischer and R. R. Schrock in their Nobel lectures.[1,2] Numerous stoichiometric and catalytic transformations have been accomplished with these complexes[3] since their discovery in 1973.[4] In comparison, silicon analogues of the alkylidyne complexes are presently unknown,[5,6] thereby emphasizing the marked difference between silicon and carbon in forming multiple bonds. A series of compounds featuring metal–germanium, metal–tin, or metal–lead triple bonds have been obtained by reacting carbonyl metalates[7] or dinitrogen and homoleptic phosphane complexes of molybdenum and tungsten[8] with organo Group 14 element(II) halides.[9] Extension of this efficient process to silicon analogues was hampered to date by the absence of any suitable organosilicon(II) halide precursors. In fact, the isolation of transition metal silylidyne complexes is one of the most challenging unresolved targets in organosilicon chemistry.

Recent studies in our group have shown that N-heterocyclic carbenes can be used to stabilize aryl silicon(II) chlorides.[10] The synthetic potential of these compounds is demonstrated herein by the isolation of the first complex featuring a metal–silicon triple bond.

Heating a toluene solution of SiRCl(Im-Me$_4$) (**1**: R = C$_6$H$_3$-2,6-Trip$_2$, Im-Me$_4$ = tetramethylimidazol-2-ylidene)[10] with Li[CpMo(CO)$_3$][11] at 100 °C was accompanied by a color change from yellow over brown-green to brown. Monitoring of the reaction progress by IR spectroscopy revealed a rapid conversion of **1** into the silylidene complex **2**, which was isolated after recrystallization from a toluene/hexane mixture as a dark-brown, air-sensitive solid in 51 % yield (Scheme 1).[12]



Scheme 1. Stepwise synthesis of the silylidyne complex **3**.

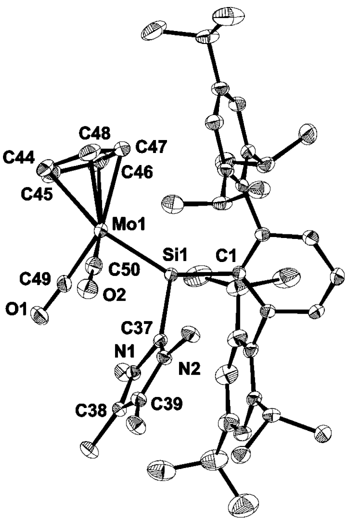


Figure 1. DIAMOND plot of the molecular structure of the silylidene complex **2**. Thermal ellipsoids are set at 50% probability, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (values in square brackets are of the second independent molecule of **2** found in the asymmetric unit): Mo1–Si1 2.3474(6) [2.3430(6)], Mo1–C49 1.917(2) [1.906(2)], Mo1–C50 1.936(2) [1.938(3)], Si1–C1 1.918(2) [1.922(2)], Si1–C37 1.943(2) [1.945(2)]; Mo-Si1-C1 145.71(6) [144.92(6)], Mo-Si1-C37 111.08(6) [111.58(6)], C1-Si-C37 99.64(8) [101.12(8)], Si1-Mo1-C49 90.67(6) [91.36(7)], Si1-Mo1-C50 82.43(7) [82.53(8)], C49-Mo1-C50 78.80(9) [80.2(1)].

Complex **2** was fully characterized, and its molecular structure was determined by single-crystal X-ray diffraction (Figure 1).[13,14] The three-legged piano-stool complex features a Mo=Si double bond (2.345 Å), which lies in the range of Mo=Si bonds reported for molybdenum arylsilylidene complexes (d(Mo=Si) = 2.288(2)–2.3872(7) Å).[5b,15,16] The silylidene ligand has a trigonal planar coordinated silicon center (sum of angles at Si = 357.0°) and it adopts an upright conformation, with the m-terphenyl group pointing towards the cyclopentadienyl ring.[17] The angles at silicon differ markedly; the Mo-Si-C$_{\mathrm{Ar}}$ angle is considerably widened to 145.3° owing to the large steric demand of the m-terphenyl substituent; the C$_{\mathrm{Ar}}$-Si-C$_{\mathrm{carbene}}$ angle is lowered to 100.4°, which reflects the low tendency of silicon for hybridization.[18] The Si–C$_{\mathrm{carbene}}$ bond of **2** (1.944 Å) compares well with that of **1** (1.963(2) Å)[10] and is only slightly longer than the Si–C$_{\mathrm{Ar}}$ bond of **2** (1.920 Å) and **1** (1.937(2) Å), thus indicating the presence of a rather strong C$_{\mathrm{carbene}}$–Si donor–acceptor interaction.[19]

Further structural information is provided by the IR and NMR spectra of **2**. The IR spectrum of **2** in toluene has two ν(CO) absorption bands at considerably lower wavenumbers (1859 and 1785 cm^{-1}) than those of **3** (1937 and 1875 cm^{-1} in toluene), which indicates that the silylidene ligand in **2** is a

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[*] Prof. Dr. A. C. Filippou, O. Chernov, K. W. Stumpf,
Dr. G. Schnakenburg
Institut für Anorganische Chemie, Universität Bonn
Gerhard-Domagk-Strasse 1, 53121 Bonn (Germany)
E-mail: filippou@uni-bonn.de
Homepage: http://www.filippou.chemie.uni-bonn.de

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considerably weaker π-acceptor ligand than the silylidyne ligand in **3**. The ^{1}H and ^{13}C{^{1}H} NMR spectra reveal a C_s symmetric structure of the silylidene complex in solution, and that rotation of the *m*-terphenyl substituent about the Si–C_{Ar} bond is fast on the NMR timescale at room temperature. The most distinctive signal in the ^{13}C{^{1}H} NMR spectrum of **2** is that of the silicon-bonded $C_{carbene}$ atom ($\delta = 165.3$ ppm), which appears considerably upfield to that of Im-Me$_4$ ($\delta = 212.7$ ppm),[20] but at similar position to that of **1** ($\delta = 166.7$ ppm).[10] The ^{29}Si{^{1}H} NMR spectrum of **2** has a characteristic downfield-shifted signal at $\delta = 201.8$ ppm, which compares well with those of the molybdenum arylsilylidene complexes [(η^5-C_5Me_5)(dmpe)Mo(H){Si(R)Ar}] (R = H, Cl, Me; Ar = Ph, Mes; $\delta = 182$–250 ppm).[5b,15a] All the spectroscopic data and bonding parameters suggest that **2** is a new type of silylidene complex, which is best described by the zwitterionic structure depicted in Scheme 1.

The bond dissociation enthalpy $D^o(0)$ and Gibbs free dissociation energy $\Delta G_D{}^o(298)$ required to cleave the Si–$C_{carbene}$ bond of **2** was calculated to be 62.1 and 1.2 kJ mol^{-1}, respectively.[21,22] Both values are smaller than the respective values of **1** ($D^o(0) = 94.3$ kJ mol^{-1}, $\Delta G_D{}^o(298) = 28.1$ kJ mol^{-1}),[10] which suggests that dissociation of the N-heterocyclic carbene Im-Me$_4$ from **2** might occur to some extent at elevated temperatures and in the presence of a suitable carbene trapping agent may lead to the silylidyne complex **3**. Indeed, reaction of **2** with one equivalent of the triarylborane B(C_6H_4-4-Me)$_3$ in refluxing *o*-xylene afforded selectively the silylidyne complex **3** and the carbene–borane adduct Im-Me$_4$•B(C_6H_4-4-Me)$_3$ (**4**-Me; Scheme 1).[12] Complex **3** was easily separated from the adduct **4**-Me upon fractional crystallization from pentane and was isolated as a brick-red, air-sensitive solid in 53 % yield.

The molecular structure of **3** was determined by single-crystal X-ray diffraction (Figure 2).[13] The almost C_s-symmetric three-legged piano-stool complex[23] is isostructural with the germanium analogue [Cp(CO)$_2$Mo≡Ge–C_6H_3-2,6-Trip$_2$].[7b] It features an almost linearly coordinated silicon center (Mo-Si-C_{Ar} = 173.49(8)°) and a very short Mo–Si bond (2.2241(7) Å), which is 12 pm shorter than the Mo–Si double bond of **2**. The Mo–Si bond length of **3** compares well with the calculated Mo–Si bond lengths of the hypothetical silylidyne complexes [Cp(CO)$_2$Mo≡Si–R] (R = H: 2.213 Å, R = Me: 2.229 Å)[24] and the Mo–Si bond length of [(η^5-C_5Me_5)(dmpe)(H)MoSiMes][B(C_6F_5)$_4$] (2.219(2) Å).[5b]

The IR and NMR spectra support the structure of complex **3**. The ^{29}Si{^{1}H} NMR spectrum of **3** has a distinctive signal that is considerably downfield (at $\delta = 320.1$ ppm) to that of **2** ($\delta = 201.8$ ppm). The IR spectrum of **3** in toluene has two ν(CO) bands (1937 and 1875 cm^{-1}) that appear at almost the same position as those of the germylidyne complex [Cp(CO)$_2$Mo≡Ge-C_6H_3-2,6-Mes$_2$] (1930 and 1875 cm^{-1} in nujol),[7a] but at considerably lower wavenumbers than those of the alkylidyne complex [Cp(CO)$_2$Mo≡C–C_6H_3-2,6-Me$_2$] (1992 and 1919 cm^{-1} in CH_2Cl_2).[25] This result indicates that metal–carbonyl back-bonding is stronger in the complexes [Cp(CO)$_2$Mo≡E–R] (E = Si, Ge). It also suggests that silylidyne and germylidyne ligands have a similar σ-donor/π-acceptor ratio, which is however larger than that of alkylidyne ligands. Further evidence for the stronger metal–carbonyl back-bonding in [Cp(CO)$_2$Mo≡E–C_6H_3-2,6-Trip$_2$] (E = Si, Ge) is provided by the downfield-shifted ^{13}C NMR signal of the carbonyl ligands (E = Si (**3**): $\delta = 231.1$ ppm, E = Ge: $\delta = 231.4$ ppm[7b]) than that of [Cp(CO)$_2$Mo≡C–C_6H_3-2,6-Me$_2$] ($\delta = 228.7$ ppm).[25]

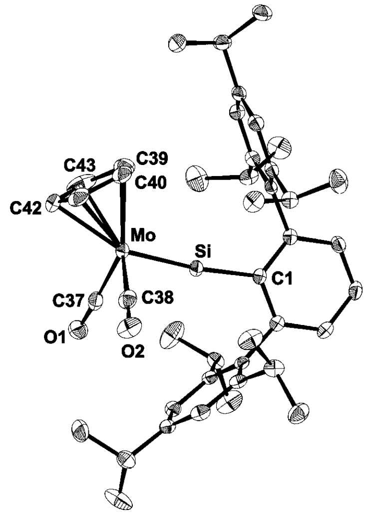

Figure 2. DIAMOND plot of the molecular structure of the silylidyne complex **3**. Thermal ellipsoids are set at 50 % probability, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo–Si 2.2241(7), Mo–C37 1.968(3), Mo–C38 1.973(3), Si–C1 1.859(2); Mo-Si-C1 173.49(8), Si-Mo-C37 90.56(7), Si-Mo-C38 89.63(8), C37-Mo-C38 87.0(1).

The thermochemical parameters for the carbene transfer reaction of **2** with the borane B(C_6H_4-4-Me)$_3$ to give **3** and **4**-Me were computed.[21,22] Formation of the silylidyne complex **3** is an exergonic process ($\Delta G_R{}^o(298) = -39.0$ kJ mol^{-1}), which is favored by both the reaction enthalpy ($\Delta H_R{}^o(298) = -21.8$ kJ mol^{-1}) and the reaction entropy ($\Delta S_R{}^o(298) = 57.7$ J mol^{-1} K^{-1}). The negative reaction enthalpy results from the higher bond dissociation enthalpy $D^o(0)$ of the carbene–borane adduct **4**-Me (88.4 kJ mol^{-1}) than that of **2** (62.1 kJ mol^{-1}) and suggests that triarylboranes, such as B(C_6H_4-4-Me)$_3$, should be useful N-heterocyclic carbene abstracting agents owing to the formation of a rather strong B–$C_{carbene}$ bond.

The isolation of the silylidyne complex **3** shows the potential of the carbene adduct **1** as a source for the generation of unprecedented compounds featuring silicon multiple bonds. Studies are currently in progress to explore this potential and the chemistry of the silylidyne complex **3**.

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Keywords: molybdenum · silicon · silylidene complexes · silylidyne complexes · triple bonds

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[13] Brown crystals of **2**·toluene were grown from an oversaturated toluene solution at ambient temperature. Orange-red crystals of **3**·*n*-pentane were obtained upon cooling a pentane solution from room temperature to −60 °C, and colorless crystals of **4**-H formed upon slow evaporation of a concentrated toluene solution at room temperature. CCDC 760807 (**2**·toluene), 760808(**3**·*n*-pentane), and 764217 (**4**-H) 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.

[14] Two independent molecules of **2** with very similar geometric parameters were found in the asymmetric unit of **2**·toluene. The mean values x_m of the individual bonding parameters of the two molecules were used for the discussion of the structure. The individual bonding parameters are given in the legend of Figure 1 and the Supporting Information.

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[17] The upright conformation of the silylidene ligand in **2** is best indicated by the dihedral angle of 10.9° between the silylidene ligand plane (least-square plane passing through the atoms Mo, Si, C_{Ar}, and $C_{carbene}$) and the plane defined by the atoms Si, Mo, and C_g, where C_g denotes the center of gravity of the cyclopentadienyl ring. Several isolobal metal–cyclopentadienyl carbene complexes also feature an upright conformation of the carbene ligand: a) A. C. Filippou, D. Wössner, G. Kociok-Köhn, I. Hinz, *J. Organomet. Chem.* **1997**, *541*, 333 and references therein.

[18] Various metal tetrelylidene complexes of the general formula [$L_nM{=}E(Ar)X$] (L_n = ligand sphere; M = Fe, Mo, W, Re, Pt; E = Si, Ge, Sn; Ar = 2,6-$Mes_2C_6H_3$, 2,6-$Trip_2C_6H_3$; X = singly-bonded substituent) featuring trigonal planar coordinate Group 14 element centers have been isolated in our group recently. In all cases, the C_{Ar}-E-X angles were found by single-crystal X-ray diffraction studies to be considerably smaller than 120°, ranging from 85° to 100°. The small C_{Ar}-E-X angles indicate that the Group 14 element centers use hybrid orbitals of high p character for the bonding to the substituents Ar and X.

[19] The interplane angle of 74.0° between the imidazol-2-ylidene least-square plane and the silylidene ligand plane (Ref. [17]) reveals that the Im-Me_4 substituent is arranged almost orthogonally to the silicon coordination plane. In comparison, the *m*-terphenyl substituent is slightly tilted to minimize the intramolecular repulsion between the peripheral Trip groups and the Cp and Im-Me_4 groups. The tilting is evidenced by the interplane angle of 38.6° between the central aryl ring plane of the *m*-terphenyl substituent and the silylidene ligand plane.

[20] N. Kuhn, T. Kratz, *Synthesis* **1993**, 561.

[21] All quantum chemical calculations were carried out at the B3LYP level of theory. The basis set TZVPP was used for the Mo and Si atoms, and the basis set 6-31G* for the other atoms. Details of the computational methods, tables of selected calculated and experimental bonding parameters for **2**, **3**, **4**-H, and **4**-Me, illustrations of the calculated structures of **2**, **3**, and **4**-Me, and their cartesian atomic coordinates are given in the Supporting Information.

[22] $D^o(0)$ is the enthalpy of the dissociation of **2** or **4**-Me at 0 K to give the products **3** and Im-Me_4 or B(C_6H_4-4-Me)$_3$ and Im-Me_4, respectively, and includes the correction for the zero-point vibrational energies. $\Delta G_D{}^o(298)$ is the Gibbs free energy of the dissociation of **2** or **4**-Me to give the products **3** and Im-Me_4 or

$B(C_6H_4\text{-}4\text{-Me})_3$) and Im-$Me_4$ at 298 K, respectively. $\Delta G_{\mathrm{R}}{}^{\circ}(298)$ is the Gibbs free energy and $\Delta H_{R}{}^{\circ}(298)$ the enthalpy of the reaction of **2** with $B(C_6H_4\text{-}4\text{-Me})_3$ to give **3** and **4**-Me at 298 K. $\Delta G_{\mathrm{R}}{}^{\circ}(298) = \Delta G_{\mathrm{D}}{}^{\circ}(298)$ (**2**)$-\Delta G_{\mathrm{D}}{}^{\circ}(298)$ (**4**-Me). $\Delta G_{\mathrm{D}}{}^{\circ}(298)$ (**2**) and $\Delta G_{\mathrm{D}}{}^{\circ}(298)$ (**4**-Me) were calculated to be 1.2 and 40.2 $\mathrm{kJ\,mol^{-1}}$, respectively. $\Delta H_{\mathrm{R}}{}^{\circ}(298) = D^{\circ}(298)$ (**2**)$-D^{\circ}(298)$ (**4**-Me), where $D^{\circ}(298)$ (**2**) is the enthalpy of the dissociation of **2** to give **3** and Im-Me_4 at 298 K, and $D^{\circ}(298)$ (**4**-Me) is the enthalpy of the dissociation of **4**-Me to give $B(C_6H_4\text{-}4\text{-Me})_3$ and Im-Me_4 at 298 K. $D^{\circ}(298)$ (**2**) and $D^{\circ}(298)$ (**4**-Me) were calculated to be 60.7 and 82.5 $\mathrm{kJ\,mol^{-1}}$, respectively.

[23] The silylidyne ligand adopts an upright conformation in which the interplane angle between the central aryl ring plane of the *m*-terphenyl substituent and the plane passing through the atoms Si, Mo, and C_g (center of gravity of the Cp ring) is 6.4°.

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