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Ansa Complexes

Intramolecular Activation of a Disila[2]molybdenocenophanedihydride: Synthesis and Structure of a [1],[1]Metalloarenophane**

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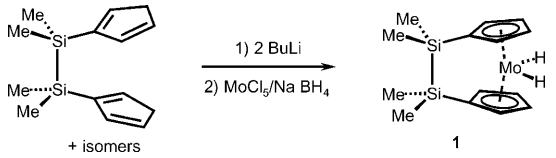
Metallocenophanes have attracted increasing attention in recent years, as strained ansa complexes have become pivotal precursors for organometallic polymers prepared by ring-opening polymerization (ROP), whereas unstrained metallocenophanes, especially those derived from Group 4 metals, serve as catalysts for olefin polymerization.[1]

The structural and electronic properties and the particular reactivity of ansa complexes are in the focus of current research. The reactivity of the E–C_{ipso} bond (E = bridging element, C_{ipso} = *ipso* carbon atom of the cyclopentadienyl ring) is of major importance for ROP, which can be induced thermally, by interaction with nucleophiles, or by late-transition-metal catalysts.[1a–e] Furthermore, ligand exchange reactions, which play a role in catalytic processes,[1f–h,2] as well as haptotropic shifts of cyclopentadienyl ligands under different conditions[3] are being intensely studied.

[2]Metallocenophanes, which are not commonly susceptible to ROP owing to their lower molecular strain, nevertheless attracted considerable attention because of their pronounced propensity to oxidatively add to coordinatively unsaturated complexes of late-transition-metal elements through the bridging E–E (E = B, Si, Sn) moiety. Owing to the facile activation of the E–E bond by, for example, Pd^0 and Pt^0, subsequent insertions of various unsaturated organic substrates have been achieved. In 1992, Manners and co-workers reported the first Pd-catalyzed insertion of alkynes into the Si–Si bridge of tetramethyldisila[2]ferrocenophane,[4] Herberhold et al. described in 1997 the first oxidative addition of a Pt^0 fragment into the Sn–Sn bridge of an ansaferrocene and the subsequent insertion of an alkyne,[5] whereas our group accomplished oxidative additions of Pt^0 fragments as well as homogeneously and heterogeneously catalyzed insertions of alkynes and diazobenzene into B–B and Si–Si bonds of various [2]metalloarenophanes.[6]

Motivated by this facile activation of the E–E bridge, we wondered whether a corresponding oxidative addition can be achieved intramolecularly and turned our attention to tetramethyldisila[2]molybdenocenophanedihydride (**1**) as a promising starting material. Herein we report the synthesis and full characterization of this species and its conversion into an unprecedented twofold-bridged [1],[1]metalloarenophane.

Compound **1** was synthesized by dilithiation of 1,2-bis(cyclopentadienyl)tetramethyldisilane in toluene/diethyl ether (9:1) at 0 °C and subsequent reaction with $MoCl_5$ at −78 °C in the presence of $NaBH_4$ as a reducing agent in THF/hexane (4:1) (Scheme 1).



Scheme 1. Synthesis of **1**.

The very air-sensitive but moisture-stable compound **1** was obtained as a yellow solid in 29% yield and was characterized by multinuclear NMR spectroscopy in solution. Two characteristic virtual triplets for the C_5H_4 ligands at δ = 4.72 and 4.70 ppm, one singlet for the methyl groups at δ = 0.17 ppm, and one signal for the hydrogen atoms at δ = −8.20 ppm are observed in the ^{1}H NMR spectrum, thus indicating C_{2v} symmetry in solution. These chemical shifts are in the same range as those of the unbridged 1,1′-bis(trimethylsilylcyclopentadienyl)molybdenumdihydride (δ = 4.57 (C_5H_4), 4.27 (C_5H_4), 0.17 ($SiMe_3$), −8.93 ppm (MoH_2)).[7] In the ^{29}Si NMR spectrum, one resonance at δ = −14.76 ppm for the two equivalent silicon nuclei of **1** is detected, which is in the range characteristic for disila[2]metalloarenophanes of the early transition metals (δ = −12.67 to −20.2 ppm).[6d,8]

Irradiation of a solution of **1** in [D_6]benzene afforded **3** with concomitant evolution of gaseous H_2. Monitoring the reaction by ^{1}H NMR spectroscopy revealed the absence of any soluble byproducts, thus indicating quantitative conversion. In accordance with the known reactivity of the parent [(η^5-C_5H_5)Mo($H)_2$] (**4**), photolysis of **1** is believed to generate a 16-electron species by loss of hydrogen.[9] This highly reactive intermediate **2**, however, could not be observed, but immediately reacted to the final product **3** with addition of the bridging Si–Si unit to the Mo center (Scheme 2).

The yellow-orange solid **3** proved to be highly air- and moisture-sensitive. Its characterization by multinuclear NMR spectroscopy in solution revealed a lower molecular symmetry of C_2 compared to the C_{2v}-symmetrical precursor **1**. In the ^{1}H NMR spectrum four signals were observed for the C_5H_4

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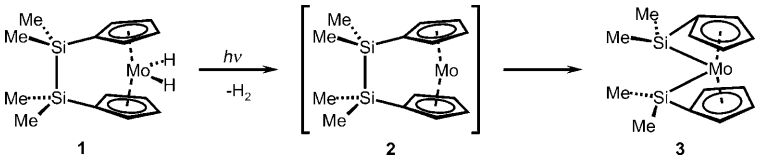

Scheme 2. Synthesis of **2**.

rings at $\delta = 4.49$, 4.38, 4.16, and 4.10 ppm and two signals for the $SiMe_2$ groups at $\delta = 0.40$ and 0.29 ppm. In the ^{29}Si NMR spectrum one resonance was detected at $\delta = -109.05$ ppm, which is significantly further upfield than that of **1**. Likewise, average ^{29}Si NMR shifts of complexes $[L_xMo{-}SiR_3]$ (R = alkyl, aryl) range from 35.2 to 27.0 ppm and thus are also much further downfield.[10] The pronounced upfield shift observed for **3** indicates considerable molecular strain, as reported for silacyclopropanes, which typically display ^{29}Si NMR resonances between $\delta = -43.9$ and -56.8 ppm, which are shifted considerably upfield from those of tetraalkylsilanes ($\delta = 10.48$ to -1.55 ppm).[11]

For both complexes **1** and **3**, recrystallization from diethyl ether an $-30\,^{\circ}C$ yielded single crystals suitable for X-ray diffraction analysis; both compounds crystallize in the triclinic space group $P\bar{1}$ (Figures 1 and 2).

The C_5H_4 rings in complex **1** are η^5-coordinated and arranged almost eclipsed (C1-Si1-Si2-C11 0.89(8)°). The tilt angle $\alpha = 30.48(6)^{\circ}$ (angle between the planes of the C_5H_4 rings) and the distortion $\delta = 154.38^{\circ}$ ($X_{Cp}1$-M-$X_{Cp}2$, X_{Cp} = centroid of the cyclopentadienyl ring) are comparable to the parameters of the unbridged complex **4** ($\alpha = 34.21^{\circ}$, $\delta = 152.22^{\circ}$).[12] Likewise, the Si–Si separation of 2.3329(7) Å and all other pertinent structural parameters are in the expected ranges.[8a]

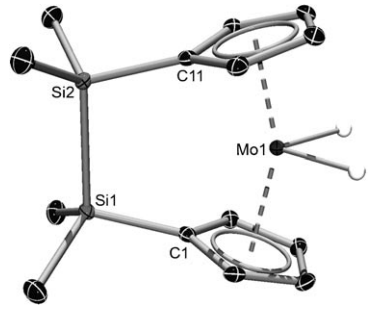

Figure 1. Molecular structure of **1**. The C-bonded hydrogen atoms are omitted for clarity, and the Mo-bonded hydrogen atoms are computed. Selected bond lengths [Å] and angles [°]: Mo–$X_{Cp}1$ 1.952(8), Mo–$X_{Cp}2$ 1.954(8), Si1–C1 1.8809(17), Si2–C11 1.8799(17), Si1–Si2 2.3329(7); $X_{Cp}1$-Mo-$X_{Cp}2$ 154.38.

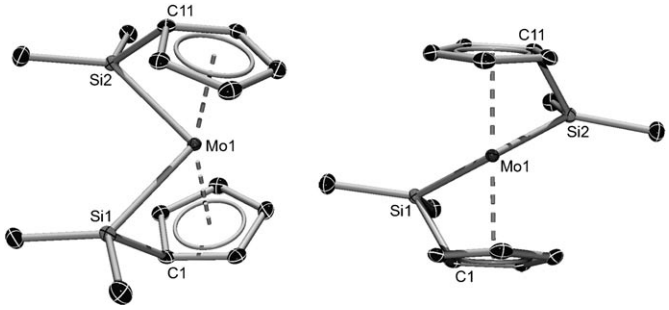

Figure 2. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo–$X_{Cp}1$ 1.942(6), Mo–$X_{Cp}2$ 1.941(6), Si1–C1 1.8528(14), Si2–C11 1.8570(14), Si1–Mo1 2.4915(4), Si2–Mo1 2.4866(4); $X_{Cp}1$-Mo-$X_{Cp}2$ 154.38, C1-Si1-Mo1 61.15(4), C11-Si2-Mo1 61.13(4).

The structural parameters of **3** reveal the presence of significant molecular strain. Thus, the tilt angle $\alpha = 20.48(7)^{\circ}$ and the distortion $\delta = 159.41^{\circ}$ of **3** exhibit a pronounced deviancy from the parameters of **1** and **4**, although the Mo–X_{Cp} distances for the η^5-coordinated cyclopentadienyl ligand of **3** (1.942(6), 1.941(6) Å) are comparable to those of **1** (1.952(8), 1.954(8) Å) and **4** (1.942, 1.942 Å).[12] The Mo–Si separations of 2.4915(4) and 2.4866(4) Å are conspicuously small and mark the very low end of distances commonly observed for Mo–Si single bonds (2.4919(12) to 2.604(1)).[10b,c] Likewise, the C_{ipso}-Si-Mo angles of 61.15(4) and 61.13(4)° are remarkable, as they indicate a significant deviation from tetrahedral geometry at the four-coordinate silicon atoms. Furthermore, the angles β between the Si–C_{ipso} bond axes and the planes of the C_5H_4 ligands (48.7 and 48.9°) display pronounced distortion. Another indication for strong molecular strain is the torsion between the Si1-Mo1-Si2 plane and the $X_{Cp}1$-Mo1-$X_{Cp}2$ plane of 64.0° rather than 90° as expected for unbridged derivatives.

The presence of two single bridging atoms linking each cyclopentadienyl ring to the metal center constitutes a highly unusual structural motif in metallocene chemistry. To our knowledge, only one corresponding bis(dicarba)[2],[2]metallocenophane $[(\eta^1\text{-}CH_2CH_2)_2(\eta^5\text{-}C_5H_4)_2Mo]$ has been reported. This compound, which is not accessible by conventional methods but only in ca. 50 % yield by co-condensation of molybdenum atoms and spiro[2.4]hepta-4,6-diene, displays, however, an undistorted molecular geometry ($\alpha = 30.79^{\circ}$, $\delta = 152.45^{\circ}$, $\beta = 23^{\circ}$) matching those of **1** and the parent complex **4**.[13] Furthermore, a variety of fulvene complexes, particularly of early transition metals, displaying ligands of the type $C_5R_4{=}CR'_2$ (R = H, Me; R′ = H, various organic groups), has been described. Experimental and theoretical studies revealed the coordination mode of the fulvene ligand to lie between a dianionic η^1, η^5 and an olefinic η^6 coordination, and thus in case of the former, these compounds bear a certain similarity to the title compound.[14]

The facile yet unprecedented intramolecular activation of the Si–Si bridge in disila[2]molybdenocenophanedihydride gave access to a novel, highly strained disila[1],[1]metallocenophane. The presence of two single-atom bridges between the Cp rings and the central metal ion marks a highly unusual structural motif in metallocene chemistry, the reactivity of which is currently under investigation.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry argon with common Schlenk techniques. 1,2-Bis(cyclopentadienyl)tetramethyldisilane[15] was synthesized according to lit-

erature procedures and lithiated as described previously.[16] NMR spectra were recorded on a Bruker Avance 500 NMR Spectrometer at 500.13 MHz (^{1}H), 125.77 MHz (^{13}C{^{1}H}), and 99.36 MHz (^{29}Si) with tetramethylsilane as the external standard. Elemental analyses (C, H) were performed on a Leco Instruments Elemental Analyzer, type CHNS 932. Irradiation was carried out with a Hg/Xe arc lamp (500 W) equipped with IR filters, irradiating at 210–600 nm.

1: In a dry ice/ethanol bath, $MoCl_5$ (0.455 g, 1.67 mmol) was covered with −78 °C cold hexane (10 mL), and −78 °C cold THF (25 mL) was slowly added with stirring. The resulting auburn solution was added dropwise to a vigorously stirred suspension of $[(Me_2Si)_2(C_5H_4)_2Li_2]$ (1.29 g, 5.00 mmol) and $NaBH_4$ (0.165 g, 4.35 mmol) in THF (15 mL) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and was treated in a ultrasonic bath for 2 h. All volatile components of the yellow-red suspension were removed in vacuo, and the residue was extracted with toluene (30 mL). The solvent of the brown solution was removed in vacuo, and the yellow-brown crude product was washed with hexane and dried in vacuo. Yield: 0.168 g (0.491 mmol, 29 % based on $MoCl_5$). Single crystals for X-ray diffraction analysis were obtained by recrystallization from diethyl ether at −30 °C. ^{1}H NMR (500.13 MHz, C_6D_6): $\delta = 4.72$ (vt, 4H, C_5H_4), 4.70 (vt, 4H, C_5H_4), 0.17 (s, 12H, SiMe_2), −8.20 ppm (s, 2H, MoH); ^{13}C NMR (C_6D_6): $\delta = 82.51$ (C_5H_4), 80.29 (C_5H_4), 80.05 (C_{ipso}), −1.95 ppm (SiMe_2); ^{29}Si NMR: $\delta = -14.76$ ppm ($SiMe_2$). Elemental analysis (%) calcd for $C_{14}H_{22}Si_2Mo$: C 49.10, H 6.48; found: C 48.98, H 6.48.

3: A solution of **1** (170 mg, 0.50 mmol) in toluene (30 mL) was irradiated in a quartz-glass tube. Gas evolution was observed. After 15 h all volatiles were removed in vacuo to obtain a crude yellow-brown solid. Recrystallization from hexane afforded **3** as a yellow solid (127 mg, 0.37 mmol, 75 %). Single crystals for X-ray diffraction analysis were obtained by recrystallization from diethyl ether at −30 °C. ^{1}H NMR (500.13 MHz, C_6D_6): $\delta = 4.49$ (vt, 2H, C_5H_4), 4.38 (vt, 2H, C_5H_4), 4.16 (vt, 2H, C_5H_4), 4.10 (vt, 2H, C_5H_4), 0.40 (s, 6H, SiMe_2), 0.29 ppm (s, 6H, SiMe_2); ^{13}C NMR (C_6D_6): $\delta = 82.00$ (C_5H_4), 81.53 (C_5H_4), 81.45 (C_5H_4), 79.86 (C_{ipso}), 75.69 (C_5H_4), 1.40 (SiMe_2), 0.67 ppm (SiMe_2); ^{29}Si NMR: $\delta = -109.05$ ppm ($SiMe_2$). Elemental analysis (%) calcd for $C_{14}H_{20}Si_2Mo$: C 49.40, H 5.92; found: C 48.98, H 6.04.

The crystal data for **1** and **3** were collected on a Bruker X8 APEX diffractometer with a CCD area detector and multilayer-mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the Shelx software package (G. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122), and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure-factor calculations. **1**: $C_{14}H_{22}MoSi_2$, $M_r = 342.44$, yellow block, $0.34 \times 0.19 \times 0.17$ mm^3, triclinic, space group $P\bar{1}$, $a = 7.7080(9)$, $b = 8.6056(10)$, $c = 11.5869(12)$ Å, $\alpha = 85.928(5)$, $\beta = 86.092(5)$, $\gamma = 73.772(5)$°, $V = 735.16(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.547$ g cm^{-3}, $\mu = 1.032$ mm^{-1}, $F(000) = 352$, $T = 100(2)$ K, $R_1 = 0.0231$, $wR^2 = 0.0670$, 4441 independent reflections [$2\theta \leq 65.4$°] and 165 parameters. **3**: $C_{14}H_{20}MoSi_2$, $M_r = 680.84$, yellow plate, $0.23 \times 0.22 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$, $a = 7.8059(3)$, $b = 8.1254(3)$, $c = 11.7444(4)$ Å, $\alpha = 82.931(1)$°, $\beta = 77.930(1)$, $\gamma = 77.967(1)$, $V = 709.96(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.592$ g cm^{-3}, $\mu = 1.069$ mm^{-1}, $F(000) = 348$, $T = 100(2)$ K, $R_1 = 0.0225$, $wR^2 = 0.0560$, 3717 independent reflections [$2\theta \leq 63.48$°] and 158 parameters. CCDC-693086 and 693087 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.

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