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Reaction of Molybdenocene and Tungstenocene Derivatives with the Divalent Silicon Species $SiN^tBuCHCHN^tBu$ and $(C_5Me_5)_2Si$

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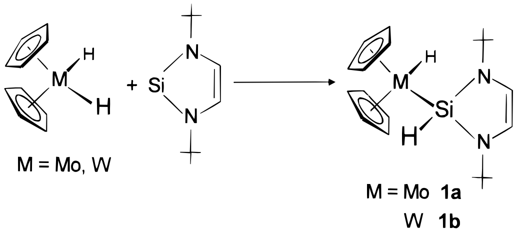
The divalent organosilicon compounds $(C_5Me_5)_2Si$ (Cp^*_2Si) and $\overline{SiN^tBuCHCHN}{}^tBu$ ($SiL^N{}_2$) have been compared concerning their reactivity toward metallocene derivatives of molybdenum and tungsten. While Cp^*_2Si does not react with Cp_2MH_2 (M = Mo, W), either thermally or photochemically, the reaction of $SiL^N{}_2$ with Cp_2MH_2 leads via silanediyl insertion to $Cp_2M(H)(SiL^N{}_2H)$ (M = Mo (**1a**), W (**1b**)). Irradiation of a mixture of $Cp_2Mo(PEt_3)$ and Cp^*_2Si yields only decomposition products, whereas photolysis of equimolar amounts of $Cp_2Mo(PEt_3)$ and $SiL^N{}_2$ results in the formation of the silanediyl complex $Cp_2Mo(SiL^N{}_2)$ (**2**). **2** is extremely moisture sensitive and easily adds one molecule of water to yield the metallosilanol $Cp_2Mo(H)(SiL^N{}_2OH)$ (**3**). **1a** and **2** have been characterized by X-ray crystallography. **2** is the first molybdenum silanediyl complex with a tricoordinated silicon atom. The silicon−molybdenum interaction in **2** has to be described as a dative bond from the silicon to the metal atom.

Introduction

Only few papers in the literature have dealt with the reactivity of divalent silicon species toward transition-metal complexes. In previous studies we examined the behavior of decamethylsilicocene (Cp^*_2Si) toward ClAu(CO),[1] $Ti(NMe_2)_4$,[2] and $HMn(CO)_5$.[3] Berry et al.[4] have reported on the insertion of $SiMe_2$ into a tantalum−hydrogen bond. Denk and West[5,67] have described the reactions of 1,3-di-*tert*-butyl-1,3,2-diazasilol-2-ylidene ($SiL^N{}_2$) with the transition-metal carbonyl compounds $MesCr(CO)_3$ (Mes = 2,4,6-trimethylphenyl), $Fe_2(CO)_9$, and $Ni(CO)_4$, whereas Lappert et al.[8] reported on the reaction of $Si[(NCH_2Bu^t)_2C_6H_4\text{-}1,2]$ with $MCl_2(PPh_3)_2$ (M = Ni, Pt) and with $Ni(cod)_2$. Tilley et al.[9] have investigated the reaction of Mes_2Si with $Pt(PR_3)_2$ complexes. In the course of our investigations we have compared the reactivity of Cp^*_2Si and $SiL^N{}_2$ toward molybdenocene and tungstenocene derivatives.

Results and Discussion

The reactivity of decamethylsilicocene is characterized by the oxidation of the Si(II) center to Si(IV) and the change of the hapticity of the Cp* ligand ($\eta^5 \rightarrow \eta^1$). Therefore, we expected Cp^*_2Si to react with Cp_2MH_2 (M = Mo, W) to form $Cp_2M(H)(SiCp^*_2H)$, but no reaction was observed, either by thermal treatment (5 days, 110 °C) or by prolonged irradiation. In contrast, the reaction of $SiL^N{}_2$ with Cp_2MoH_2 takes place at room temperature and affords yellow crystals of $Cp_2Mo(H)(SiL^N{}_2H)$ (**1a**) (eq 1). For the analogous insertion of $SiL^N{}_2$ into a W−H bond of Cp_2WH_2 irradiation or prolonged heating is necessary to yield yellow $Cp_2W(H)(SiL^N{}_2H)$ (**1b**) (eq 1). Compounds **1a** and **1b** show the typical properties of bent-sandwich complexes of the type $Cp_2M(H)(SiR_3)$ (M = Mo, W).[10] The facile insertion of $SiL^N{}_2$ into an M−H bond of Cp_2MH_2 (M = Mo, W) is attributed to the good accessibility of the silicon atom in the 2-fold-coordinated silanediyl complex, whereas the inertness of the π-complex Cp^*_2Si toward these metallocene dihydrides pre-



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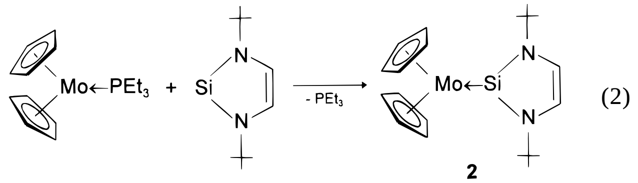
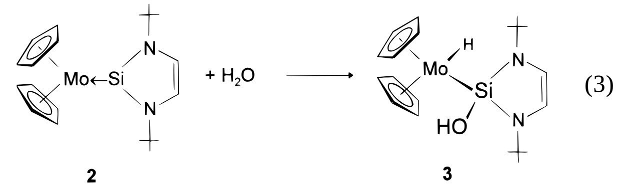
sumably is caused by the 10-fold coordination and the effective shielding of the Si atom by the bulky Cp* ligands.[11]

Divalent silicon compounds can be regarded as two-electron-donating ligands due to their lone pair at the silicon atom. Thus, Cp*$_2$Si and SiL$^N{}_2$ should act as σ-donating ligands in reaction with 16-valence-electron (16-VE) complexes such as Cp$_2$Mo. A useful precursor for molybdocene is the phosphane adduct Cp$_2$Mo(PEt$_3$).[12] Under thermal conditions no reaction between Cp*$_2$Si and Cp$_2$Mo(PEt$_3$) takes place. The educts are recovered quantitatively. Irradiation of the mixture only results in the formation of unspecific decomposition products. Again, the bulky Cp* ligands prohibit a clean reaction. In contrast, photolytic treatment of a stoichiometric amount of Cp$_2$Mo(PEt$_3$) and SiL$^N{}_2$ in hexane leads to the formation of deep red Cp$_2$Mo(SiL$^N{}_2$) (**2**) (eq 2). Compound **2** is extremely air and moisture sensitive,



as reflected by an isolated yield of only 73%, though NMR-tube experiments show a quantitative ligand exchange reaction.

The controlled hydrolysis of **2** in hexane affords yellow Cp$_2$Mo(H)(SiL$^N{}_2$OH) (**3**) via a regiospecific addition of one molecule H$_2$O to the molybdenum silicon bond (eq 3).



The silyl complex **1a** and the silanediyl complex **2** have been characterized by X-ray diffractometry. The corresponding ORTEP plots are shown in Figures 1 and 2, respectively. Crystallographic data are given in Table 1; selected bond lengths are collected in Table 2.

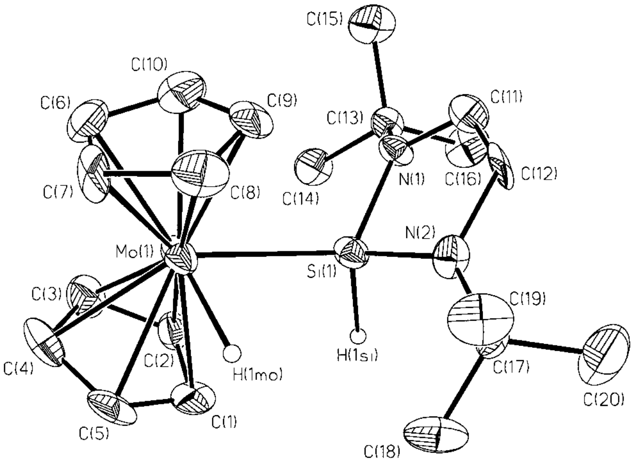


Figure 1. ORTEP drawing of **1a** with thermal ellipsoids shown at the 50% probability level.

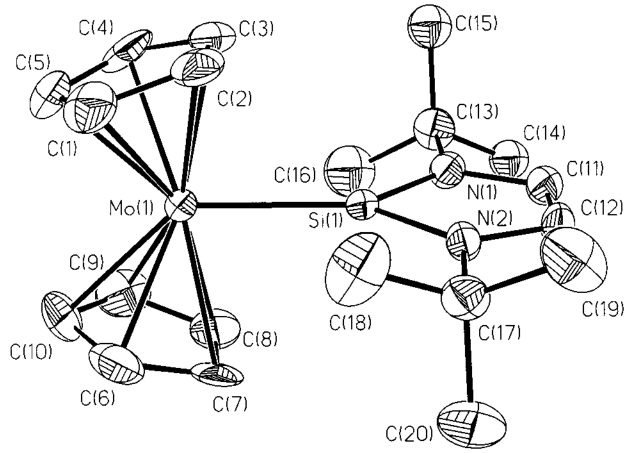


Figure 2. ORTEP drawing of **2** with thermal ellipsoids shown at the 50% probability level.

Both compounds **1a** and **2** are complexes of the bent-sandwich type, but there are significant differences. The most striking features are the surroundings of the silicon atoms. In compound **1a** the Si atom is coordinated in a distorted-tetrahedral fashion; in **2** the coordination is trigonal planar. The bond lengths within the C$_2$N$_2$Si ring system suggest an aromatic delocalization for the cyclic six-π-electron system in the SiL$^N{}_2$ unit of **2**, whereas in **1a** localized single and double bonds are found (Table 2). This interpretation is supported by the ^{1}H NMR shifts of the methyne protons of the C$_2$N$_2$-Si ring. Due to the aromatic ring current in **2** the resonance is shifted to low field compared to the corresponding protons in **1a** (6.58 ppm vs 5.92 ppm). Concerning these parameters complex **2** behaves quite similarly to the free silanediyl SiL$^N{}_2$.[7]

There arises the question concerning the nature of the interaction between molybdenum and silicon in **1a** and in **2**. In **1a** it is a simple single bond indicated by a Mo−Si distance of 2.538(3) Å, which is in good agreement with structurally characterized Cp$_2$Mo(H)(SiR$_3$) compounds.[10e−h] In the silanediyl complex **2** the Mo−Si bond is significantly shorter, 2.4125(13) Å. In fact, this is the shortest Mo−Si bond observed so far. It is ca. 0.05 Å shorter than the shortest Mo−Si bond known to date (Cp$_2$Mo(H)(SiBr$_3$)^{10f}) and is also ca. 0.05 Å shorter than the Mo−Si bond in (CO)$_5$Mo═SiH$_2$ (estimated by CASSCF calculations).[13] This might lead to the interpretation of the Mo−Si interaction as a double bond. On the other hand, a distance of only 2.3 Å or less is expected for a

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Table 1. Crystallographic Data for 1a and 2

	1a	2
empirical formula	$C_{20}H_{32}MoN_2Si$	$C_{20}H_{30}MoN_2Si$
fw	424.51	422.49
cryst color, habit	yellow, irregular	dark red, plates
cryst size, mm^3	0.30 × 0.20 × 0.20	0.40 × 0.20 × 0.10
temp, K	173	173
wavelength, Å	Mo Kα, 0.710 73 (graphite monochromator)	Mo Kα, 0.710 73 (graphite monochromator)
space group	$P2_1/c$	Cc
unit cell dimens		
a, Å	9.499(2)	10.1598(5)
b, Å	24.664(7)	19.8694(10)
c, Å	9.740(3)	11.0164(3)
β, deg	118.60(2)	116.610(1)
V, Å^3	2003.5(9)	1988.3(2)
Z	4	4
density (calcd), Mg/m^3	1.407	1.411
θ range for data collecn, deg	1.65−25.00	2.05−27.23
no. of rflns collected	3755	9374
no. of indep rflns	3533 (R_{Int} = 0.1060)	4091 (R_{Int} = 0.0330)
abs cor	semiempirical from ψ scans	semiempirical from equivalents
final $R(F)$ ($I > 2\sigma(I)$)	0.0830 (1696)	0.0421 (3839)
$R_w(F^2)$ (all data)	0.2246	0.1058
no. of params	223	214
largest diff peak and hole, e Å^{-3}	1.032 and −0.784	1.720 and −1.515
diffractometer used	Siemens P2(l)	Siemens SMART CCD
programs used	Siemens SHELXTL plus/SHELXL-97	Siemens SHELXTL plus/SHELXL-97
structure refinement	full-matrix least-squares on F^2	full-matrix least-squares on F^2

Table 2: Selected Bond Lengths (Å) and Angles (deg) in 1a, 2, and SiL$^N{}_2$

	1a	2	SiL$^N{}_2$[17]
Si−Mo	2.538(3)	2.4125(13)	
Si−N	1.773(9)	1.748(5)	1.753(5)
1.784(9)			
N−C	1.398(14)	1.397(7)	1.400(9)
1.416(14)			
C−C	1.30(2)	1.344(8)	1.347(2)
N−Si−N	89.8(4)	90.0(2)	90.5(10)
C−N−Si	108.6(7)	111.2(4)	[a]
108.6(8)	111.1(4)		
N−C−C	116.0(11)	113.9(5)	114.1(5)
115.1(10)	113.8(5)		

[a] Not mentioned.

Mo=Si double bond on the basis of the covalent radii.[14] The geometric arrangement of the Cp_2Mo[15] and the SiL$^N{}_2$[7,16] fragments and the corresponding frontier orbitals in the solid state shows that a bonding interaction between the HOMO of the Cp_2Mo fragment and the vacant p orbital at the Si atom is impossible, because these orbitals are perpendicular to each other (Figure 3). Therefore, a Mo=Si double bond cannot be formed. It is more reasonable to regard the silanediyl SiL$^N{}_2$ as a two-electron-donating ligand forming a dative bond to the electronically and coordinatively unsaturated Cp_2-Mo fragment without any π-back-donation from the metal to the silicon atom (cf. eqs 2 and 3). This description corresponds to a polar Mo−Si bond, which is reflected both in the chemical reactivity (regiospecific addition of water to **2**; eq 3) and in the spectroscopic properties. The ^{29}Si NMR shift is 139.3 ppm, which is 61 ppm to low field from the free silanediyl SiL$^N{}_2$ (78.3 ppm[17]), indicating a distinct silicenium cation character.

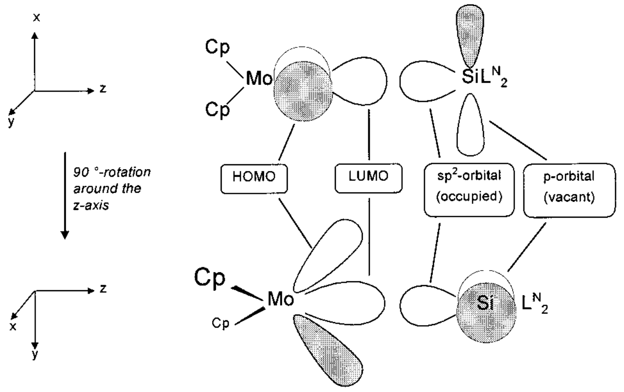

Figure 3. Geometric arrangement of the frontier orbitals of the Cp_2Mo[15] and SiL$^N{}_2$ [7,16] fragments in **2**.

Conclusions

In this contribution we have described the reactivity of the divalent silicon species $Cp^*{}_2Si$ and SiL$^N{}_2$ toward Cp_2MH_2 (M = Mo, W) and $Cp_2Mo(PEt_3)$. $Cp^*{}_2Si$ is shown to be rather inert toward these metallocene derivatives, which is attributed to the effective shielding of the Si(II) center by the bulky Cp* ligands. In contrast. the Si atom in SiL$^N{}_2$ is accessible quite easily. With the dihydrides an insertion reaction occurs and the silyl complexes $Cp_2M(H)(SiL^N{}_2H)$ (M = Mo (**1a**), W (**1b**)) are formed, while the reaction with $Cp_2Mo(PEt_3)$ yields the first molybdenum silanediyl complex with a tricoordinated silicon atom (**2**). Compounds **1a** and **2** have been characterized by X-ray crystallography. The Mo−Si interaction in **1a** is shown to be a Mo−Si single bond, whereas in **2** the Mo−Si interaction consists of dative coordination from the silicon to the metal atom.

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Experimental Section

General Data. All manipulations were carried out under a purified argon atmosphere using standard vacuum techniques. The solvents were commercially available and were purified by conventional means and distilled immediately prior to use. Cp_2MoH_2,[18] Cp_2WH_2,[18] and $Cp_2Mo(PEt_3)$[19] were prepared according to literature methods. Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld. The NMR spectra were recorded in benzene-d_6 using a Bruker Avance DRX 500 spectrometer (^{1}H, 500.1 MHz; ^{13}C{^{1}H}, 125.8 MHz; ^{29}Si{^{1}H}, 99.1 MHz). Chemical shifts are reported in ppm and are referenced to benzene as internal standard. IR data were measured as KBr pellets or in Nujol using a Bruker Vektor 22-FT-spectrometer.

Preparation of $Cp_2Mo(H)(SiL^N{}_2H)$ (1a). A toluene solution (20 mL) of Cp_2MoH_2 (240 mg, 1.05 mmol) and $SiL^N{}_2$ (210 mg, 1.07 mmol) was stirred for 14 h at room temperature. The solution was reduced to ca. 5 mL under vacuum. Crystallization at −30 °C yielded yellow crystals of **1a** (320 mg, 0.64 mmol, 47%): ^{1}H NMR δ −7.86 (s, 1H, MoH), 1.42 (s, 18H, CH_3), 4.31 (s, 10H, C_5H_5), 5.92 (s, 2H, CH=CH), 7.96 (s, $^1J_{SiH}$ = 187 Hz, 1H, SiH); ^{13}C NMR 30.8 ($C(CH_3)_3$), 51.6 ($C(CH_3)_3$), 79.7 (C_5H_5), 117.1 (CH=CH);^{29}Si NMR 43.6; IR (KBr) ν_{SiH} 1975 cm^{-1}. Anal. Calcd for $C_{20}H_{32}MoN_2Si$: C, 56.59; H, 7.60; N, 6.60. Found: C, 56.59; H, 7.27; N, 6.56.

Preparation of $Cp_2W(H)(SiL^N{}_2H)$ (1b). A hexane solution (20 mL) of Cp_2WH_2 (210 mg, 0.66 mmol) and $SiL^N{}_2$ (390 mg, 1.99 mmol) was irradiated with a 150 W mercury arc lamp for 19 h. After irradiation, volatiles were removed, and excess $SiL^N{}_2$ was sublimed at 70 °C/0.1 mbar. The yellow residue was recrystallized from 20 mL of hexane at −60 °C to yield **1b** as a yellow solid (310 mg, 0.60 mmol, 91%): ^{1}H NMR δ −11.50 (s, $^1J_{WH}$ = 78.4 Hz, 1H, WH), 1.42 (s, 18H, CH_3), 4.21 (s, 10H, C_5H_5), 5.90 (s, 2H, CH=CH), 8.34 (s, $^1J_{SiH}$ = 182 Hz, 1H, SiH); ^{13}C NMR 30.7 ($C(CH_3)_3$), 51.4 ($C(CH_3)_3$), 76.2 (C_5H_5), 116.7 (CH=CH);^{29}Si NMR 21.4; IR (KBr) ν_{SiH} 1975 cm^{-1}. Anal. Calcd for $C_{20}H_{32}N_2SiW$: C, 46.88; H, 6.29; N, 5.47. Found: C, 46.11; H, 6.26; N, 5.12.

Preparation of $Cp_2Mo(SiL^N{}_2)$ (2). A hexane solution (20 mL) of $Cp_2Mo(PEt_3)$ (290 mg, 0.84 mmol) and $SiL^N{}_2$ (165 mg, 0.84 mmol) was irradiated with a 150 W mercury arc lamp for 3.5 h. The solution was reduced to ca. 10 mL under vacuum. Crystallization at −30 °C yielded deep red crystals of **2** (250 mg, 0.62 mmol, 74%): ^{1}H NMR δ 1.48 (s, 18H, CH_3), 4.09 (s, 10H, C_5H_5), 6.59 (s, 2H, CH=CH); ^{13}C NMR 32.9 ($C(CH_3)_3$), 55.0 ($C(CH_3)_3$), 69.0 (C_5H_5), 118.5 (CH=CH);^{29}Si NMR 139.3. Anal. Calcd for $C_{20}H_{30}MoN_2Si$: C, 56.86; H, 7.16; N, 6.63. Found: C, 56.39; H, 7.15; N, 6.29.

Preparation of $Cp_2Mo(H)(SiL^N{}_2OH)$ (3). To a hexane solution (10 mL) of $Cp_2Mo(SiL^N{}_2)$ (30 mg, 0.071 mmol) was added a drop of water. The mixture was shaken for 15 s. The color changed immediately from deep red to yellow. Volatiles were removed under vacuum. The residue was recrystallized from hexane to afford **3** as a yellow solid (25 mg, 0.057 mmol, 80%): ^{1}H NMR δ −7.54 (s, 1H, MoH), 1.48 (s, 18H, CH_3), 1.75 (s, 1H, OH), 4.41 (s, 10H, C_5H_5), 6.01 (s, 2H, CH=CH); ^{13}C NMR 32.0 ($C(CH_3)_3$), 51.6 ($C(CH_3)_3$), 79.6 (C_5H_5), 115.2 (CH=CH);^{29}Si NMR 35.8; IR (Nujol) ν_{OH} 3606 cm^{-1}. Anal. Calcd for $C_{20}H_{32}MoON_2Si$: C, 54.53; H, 7.32; N, 6.36. Found: C, 54.63; H, 7.38; N, 6.19.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and selected bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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