Silicon-Containing Carbene Complexes. 15.[1] A Strong W···H···Si Interaction in the 16-Electron Carbene Complex $(CO)_4WC(NMe_2)SiHMes_2$

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Received March 1, 1994®

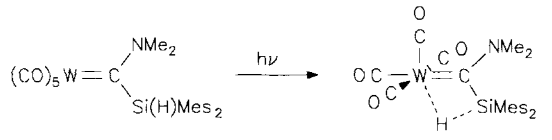
Summary: Upon photolysis of the carbene complex $(CO)_5WC(NMe_2)SiHMes_2$ (Mes = mesityl), a CO ligand is eliminated and the stable 16-electron carbene complex $(CO)_4WC(NMe_2)SiHMes_2$ is obtained. In this complex there is an agostic interaction of the Si–H bond with the tungsten atom. This is manifested by the very small coupling constant J(SiH) of 106 Hz and the location of the hydrogen atom in a bridging position between silicon and tungsten in the X-ray structure analysis. The W···H···Si interaction results in a strong distortion of the carbene ligand. The W–C(carbene)–Si angle is reduced to 87.8(6)°, and the sum of the C–Si–C angles is 351.1°.

The M,H,Si three-center interactions by which silanes $HSiR_3$ interact with coordinatively unsaturated transition-metal complexes (L_nM) in the early stages of oxidative-addition reactions are well understood.[2] In contrast to the η^2-coordination of $HSiR_3$, *agostic* M,H,Si interactions, i.e., *intra*molecular, chelating interactions in mononuclear complexes of the type L_nM–X–SiR_2–H, are rare.[3]

The first complex of this type, $MeCp(CO)MnPPh_2(CH_2)_2SiMe_2H$,[4] is not typical, because the large distance between the Si–H group and the phosphine allows an interaction geometrically similar to that in the nonchelated complexes $MeCp(CO)(R_3P)Mn(\eta^2\text{-}HSiR_3)$. Three examples were found very recently in which Si–H groups in β-positions with regard to the metal center are involved in the M,H,Si three-center interactions. In $\{Zr[N(SiHMe_2)_2]_2Cl\ (\mu\text{-}Cl)\}_2$ a very weak β-SiH interaction of one of the N–$SiHMe_2$ groups was indicated by the Zr–H and Zr–Si distances.[5] Unfortunately, no SiH coupling constants were measured. In $[(PCy)_3(SiHMes)_3]Cr(CO)_3$ (Cy = C_6H_{11}, Mes = mesityl) the triphosphatrisilacyclohexane ligand is coordinated to the metal atom via two phosphorus atoms and one η^2-SiH group.[6] The SiH coupling constant of this group (135.7 Hz) is 75–90 Hz lower than ^1J(SiH) of the "normal" SiH groups of the heterocycle. An even more advanced stage of a β-SiH addition to a metal center was found in the complexes $Cp_2(X)ZrNBu^tSiMe_2H$ (X = H, F, Cl, Br, I),[7] as judged by the small SiH coupling constants of only 113.2 (X = H) to 135.4 Hz (X = F) and the acute Zr–N–Si bond angles (95.1° for X = H and 99.1° for X = Cl).

We have now found a strong β-SiH interaction in Fischer-type silyl carbene complexes. In earlier work, we obtained the stable 16-electron complexes $(CO)_4WC(NR_2)SiPh_{3-x}Me_x$ (x = 0–2) upon thermolysis of the corresponding 18-electron carbene complexes $(CO)_5WC(NR_2)SiPh_{3-x}Me_x$.[8] The X-ray structure analysis of $(CO)_4WC(NC_5H_{10})SiPh_3$ showed this complex to be intramolecularly stabilized by a weak agostic interaction of the *ipso* carbon of one phenyl group with the tungsten atom. The W–C(ipso) distance (268.8 (8) pm) was larger than, for instance, the W–C distances in W(0) complexes with π-olefin ligands, and the W–$C_{carbene}$–Si angle was reduced to 101.2(4)°.

Upon photolysis of the carbene complex $(CO)_5WC(NMe_2)SiHMes_2$ (**1**), recently prepared by standard methods,[1] a CO ligand was eliminated, and the 16-electron carbene complex **2** was obtained (eq 1).[9] Photolysis of the 18-electron carbene complex turned out to be more effective than thermolysis, because thermolysis also resulted in decomposition to a substantial degree.



1 2 (1)

Some spectroscopic properties of the SiH-substituted 16-electron carbene complex **2**[9] are distinctly different from those of the previously prepared derivatives $(CO)_4WC(NR_2)SiPh_{3-x}Me_x$.[8] The ν(CO) bands of **2** (2021 m, 1966 w, 1939 s, 1923 vs, 1888 s cm^{-1} in petroleum ether) are between those of **1** (2055 m, 1970 w, 1934 vs, 1926 vs cm^{-1}) and $(CO)_4WC(NMe_2)SiPh_3$ (2013 w, 1931 s, 1914 vs, 1860 m cm^{-1}). These data indicate that **2** is less electron

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® Abstract published in *Advance ACS Abstracts,* April 1, 1994.

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(9) All operations were carried out under an atmosphere of dry Ar. A diethyl ether solution of **1**[1] was irradiated at –20 °C with a 160-W UV lamp. Through the solution is bubbled a weak stream of dry Ar to remove CO. The reaction is monitored by IR spectroscopy and stopped when all ν(CO) bands of **1** have disappeared (about 1 h). The solvent is then removed *in vacuo* and the residue chromatographed at –20 °C with a petroleum ether/ether mixture (2:1) on silica. The first zone contains unreacted **1** and the second **2**. Removal of the solvent *in vacuo* gives an orange-red solid, which is washed with pentane at 0 °C: yield, 67%; mp 134 °C dec. ^{1}H NMR (C_6D_6, 200 MHz): δ 6.58 (s, 4H, $C_6\mathit{H}_2Me_3$), 3.00 (s, 3H, (*Z*)-NCH_3), 2.59 (s, 3H, (*E*)-NCH_3), 2.26 (s, 12H, *o*-CH_3), 2.02 (s, 6H, *p*-CH_3), –2.40 (s, 1H, SiH, *J*(SiH) = 106 Hz, *J*(WH) = 34 Hz). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ –89.3 (d, *J*(SiH) = 106 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz): δ 216.90, 214.68, and 204.61 (CO), 145–129 ($\mathit{C}_6H_2Me_3$), 53.67 ((*Z*)-NCH_3), 52.65 ((*E*)-NCH_3), 23.58 (*o*-CH_3), 20.93 (*p*-CH_3). Anal. Found (calcd): C, 48.73 (48.47); H, 4.82 (4.72); N, 2.18 (2.26).

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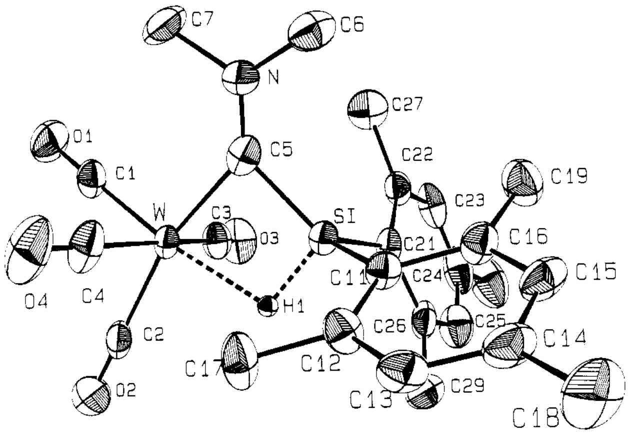


Figure 1. ORTEP drawing of **2**. Important bond distances (in pm) and angles (in deg) are as follows: W–C(1) = 194(1), W–C(2) = 200(1), W–C(3) = 202(1), W–C(4) = 204(1), W–C(5) = 214(1), W–H(1) = 210(10), W–Si = 277.6(3), C(5)–N = 131(1), C(5)–Si = 185(1), Si–H(1) = 150(10), Si–C(11) = 188(1), Si–C(21) = 188(1); C(1)–W–H(1) = 172(3), C(1)–W–C(5) = 103.6(6), C(2)–W–C(5) = 160.8(6), C(3)–W–C(5) = 99.1(5), C(4)–W–C(5) = 90.5(6), C(3)–W–C(4) = 168.5(7), W–C(5)–N = 140(1), W–C(5)–Si = 87.8(6), N–C(5)–Si = 131(1), C(5)–Si–C(11) = 119.3(6), C(5)–Si–C(21) = 118.4(6), C(5)–W–H(1) = 97(4), C(11)–Si–C(21) = 113.4(5), C(11)–Si–H(1) = 104(4), C(21)–Si–H(1) = 99(4).

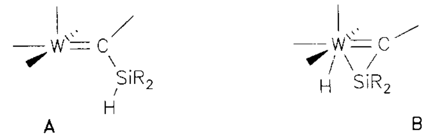
deficient than the known 16-electron complexes $(CO)_4WC(NR_2)SiPh_{3-x}Me_x$. The NMR data of the SiH group provide strong evidence that the electron deficiency at the metal is reduced by an agostic interaction: in the ^1H NMR spectrum the signal of the SiH group is dramatically shifted from 6.56 ppm in **1**[1] to −2.40 ppm in **2** and the ^{29}Si NMR signal from −30.1 ppm in **1** to −89.31 ppm. The chemical shift of the SiH group is in the typical range of transition-metal hydrides rather than silicon hydrides. Changes in ^{29}Si NMR shifts are generally difficult to interpret. Although the ^{13}C NMR resonance of the carbene carbon was not observed for **2**, the signal of the related complex $(CO)_4WC(NC_4H_8)SiHMes_2$ (δ 275.8 compared to δ 283.2 in $(CO)_5WC(NC_4H_8)SiHMes_2$) indicates that this carbon atom still is a typical carbene carbon atom.

The strongest evidence for a W,H,Si three-center bond comes from the coupling constant $J(SiH)$ (106 Hz), which is 109 Hz lower than in the corresponding 18-electron complex **1**! This is the smallest coupling constant in a M,H,Si three-center bond to date. The SiH addition in **2** to the metal is therefore probably more advanced than in any other known complex. Correspondingly, the carbene ligand is rather distorted. The W–C(carbene)–Si angle in **2** (Figure 1)[10] is reduced to 87.8°, compared with 113.1(4)° in **1**. The sum of the C–Si–C angles is increased from 342.6° in **1** to 351.1° in **2**; i.e., the substituents at silicon (excluding the hydrogen atom) are increasingly planarized. The W–C(carbene) distance is the same as in the other structurally characterized 16-electron carbene complex $(CO)_4WC(NC_5H_4)SiPh_3$, while the C(carbene)–Si distance is slightly shorter (185(1) pm, compared with 187.7(9) pm).

A similar agostic interaction in a carbene complex was found in $[Tp'(CO)_2W{=}C(Ph)CH_2R]BF_4$ (Tp′ = hydridotris(3,5-dimethylpyrazolyl); R = H, Me), where the *β-CH* group interacts with the metal.[11] The carbene ligand of the methyl derivative (R = H) shows a distortion (W–C(carbene)–C(methyl) = 91(1)°) similar to that in **2**.

The *β*-elimination of C–H bonds leading to olefins is one of the principal reactions in organometallic chemistry. Although several examples for the generation of silene[12] or silanimine complexes[13] by *β*-SiH migration are known, *β*-SiH eliminations do not play as an important role as *β*-CH eliminations. *β*-Si–H bonds are considered to be less activated, because the concomitant formation of silenes or disilenes makes the whole process disadvantageous. The *β*-hydrogen transfer probably occurs via a multicenter transition state, in which the M,H,Si interaction is similar to that in **2** or other complexes with an agostic *β*-SiH group.

Bonding in the carbene complex **2** corresponds to an intermediate stage of the hydrogen transfer from a nonstabilized 16-electron complex (**A**) to a metallasilacyclopropene (**B**).



It is worth noting that in **2** the (*β*) Si–H bond is more easily activated than the (*α*) C(carbene)–Si bond. Migration of the silyl group in **1** would result in the silyl carbyne complex $(CO)_4(Mes_2HSi)W{\equiv}CNMe_2$. Such a rearrangement was found for the corresponding stannyl complex $(CO)_5Cr{=}C(NEt_2)SnPh_3$[14] and was also postulated to explain the thermolysis products of *alkoxy*(silyl)carbene complexes $(CO)_5M{=}C(OR)SiPh_3$ (M = Cr, Mo, W).[15]

Acknowledgment. This work was supported by the Volkswagen-Foundation and the Fonds der Chemischen Industrie.

Supplementary Material Available: Listings of the final atomic coordinates, thermal parameters, bond lengths, and bond angles for **2** (6 pages). Ordering information is given on any current masthead page.

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[10] Crystals of **2** were obtained from ether/pentane. Crystallographic data (213 K): orthorhombic, space group $P2_12_12_1$; a = 1186.2(4) pm, b = 1764.5(7) pm, c = 1222.7(9) pm, V = 2559(3) pm^3, Z = 4, d_{calcd} = 1.61 g cm^{-3}. A total of 6808 independent reflections were measured at 213 K (2° ≤ 2θ ≤ 48°, Mo Kα radiation, λ = 71.069 pm) on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods (SHELXS 86) using 4708 decay- and absorption-corrected reflections ($F_o \geq 3\sigma(F_o)$); R = 0.054, R_w = 0.061. The agostic hydrogen atom (H(1)) was located from a difference Fourier map and isotropically refined.

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