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Reactions of (Silyl)(silylene)tungsten and -molybdenum Complexes with Sulfur Reagents

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Summary: Reaction of (silyl)(silylene)tungsten complex $Cp^*(OC)_2W(SiMe_3)({=}SiMes_2)$ (**1**) *with sulfur reagents,* S_8 *and ethylene sulfide* **4***, afforded cyclic carbene tungsten complex* $Cp^*(S)W\{{=}C(SiMe_3)C({=}O)OSi(Mes)_2S\}$ (**3**) *via C=O bond fission of a carbonyl ligand and 1,2-migration of the* $SiMe_3$ *group from W to the resulting carbene carbon. In contrast to the tungsten complex, reaction of (silyl)(silylene)molybdenum complex* $Cp^*(OC)_2Mo(SiMe_3)({=}SiMes_2)$ (**2**) *with* **4** *gave* η^2*-thiocarbonyl complex* $Cp^*(S)Mo[\{\eta^2\text{-}S{=}C(SiMe_3)\}C({=}O)OSi(Mes)_2S]$ (**5**)*, which would be formed by addition of a sulfur atom to the Mo=C bond of a molybdenum analogue of* **3**.

The reaction of transition metal carbene complexes $L_nM{=}CR_2$ with sulfur reagents has been investigated intensively, which afforded a variety of sulfur-containing metal complexes and organic compounds via the initial formation of η^1- or η^2-thiocarbonyl-coordinated complexes by addition of sulfur to the M=C bond.[1−3] In contrast to the carbene complexes, only two examples have been reported so far on the reaction of heavier congeners of carbene complexes, namely, silylene and germylene complexes $L_nM{=}ER_2$ (E = Si, Ge) with sulfur reagents.[4,5] The reaction of germylene complexes $P_2Pd{=}Ge\{N(SiMe_3)_2\}_2$ (P_2 = $2PEt_3$, $2PPh_3$, $Ph_2P(CH_2)_2PPh_2$) with COS afforded metallacycles containing Pd, Ge, and S atoms via addition of S to the Pd=Ge bond.[4] As opposed to the germylene complex, the reaction of silylene Os complex $[Cp^*(Me_3P)_2Os{=}Si^iPr_2][B(C_6F_5)_4]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with elemental sulfur caused the elimination of the silylene fragment to give $[Cp^*(Me_3P)_2Os{-}S{-}S{-}Os(PMe_3)_2Cp^*][B(C_6F_5)_4]_2$ and unidentified organosilicon compounds.[5]

We have reported the synthesis, structure, and properties of (silyl)(silylene) complexes $L_nM(SiR_3)({=}SiR_2)$ (M = Mo, W, Fe; R = alkyl, aryl).[6] These complexes are categorized as silylene complexes, but show unique reactivity attributable to the cooperation of the silyl and silylene ligands in the complexes, such as 1,3-R group shift from the silyl to the silylene ligand and 1,2-silyl shift from the metal to the silylene ligand. This prompted us to investigate the reactivity of (silyl)(silylene) complexes with sulfur reagents. In this paper, we report the reaction of (silyl)(silylene)tungsten and -molybdenum complexes $Cp^*(OC)_2M(SiMe_3)({=}SiMes_2)$ (**1**, M = W; **2**, M = Mo; Mes = 2,4,6-$(CH_3)_3C_6H_2$) with sulfur reagents. This reaction did not cause silylene elimination, as mentioned above for the silylene Os complex,[5] but gave a cyclic carbene complex and its sulfur adduct in which the silylene fragment remains in the metallacycle core. Bond fission of a carbonyl ligand also took place during the reaction to form the carbene ligand.

Treatment of **1** with S_8 in THF at 25 °C for 5 h afforded cyclic carbene tungsten complex $Cp^*(S)W\{{=}C(SiMe_3)C({=}O)OSi(Mes)_2S\}$ (**3**) in 65% yield (eq 1). Complex **3** was also obtained by the reaction of **1** with excess ethylene sulfide **4**, although a longer reaction time was required for completion (C_6D_6, rt, 26 days). Crystal structure analysis of **3** (Figure 1) revealed the three-legged piano-stool geometry at the metal, two of which constitute a metallacyclohexene fragment. The W=C(32) bond distance (1.935(4) Å) is at the shorter limit for those of typical W=C double bonds in the metallacyclic compounds (1.94−2.14 Å)[7] and within the range of the usual $W{=}C{-}SiMe_3$ double bonds (1.87−1.96 Å).[8] The

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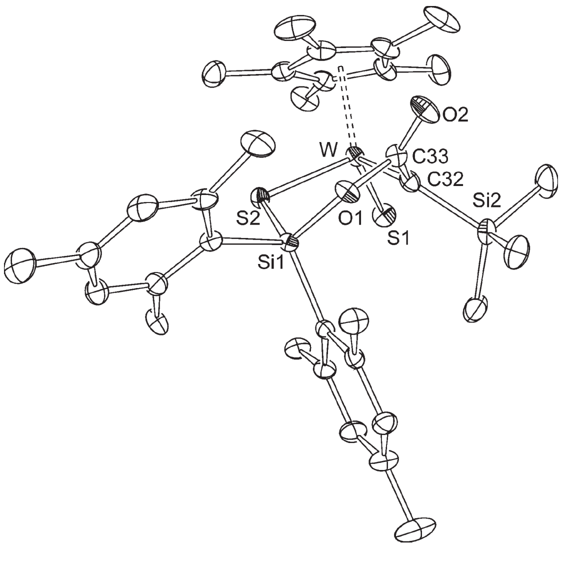
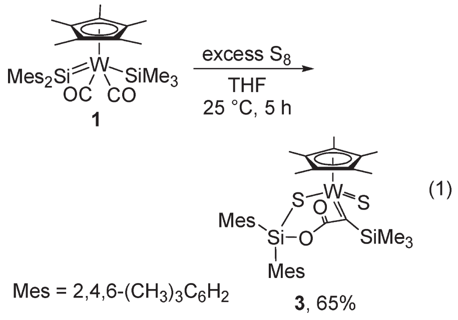
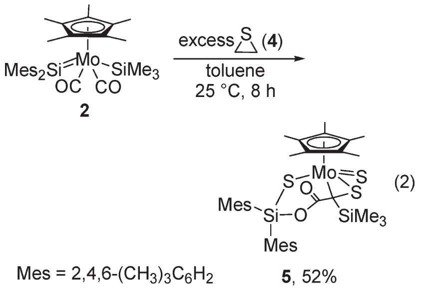


Figure 1. ORTEP drawing of **3** (50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): W−C(32) 1.935(4), W−S(1) 2.1476(13), W−S(2) 2.3784(16), S(1)−W−S(2) 110.12(5), S(1)−W−C(32) 104.31(13), W−C(32)−Si(2) 127.7(2), W−C(32)−C(33) 119.9(3), Si(2)−C(32)−C(33) 112.3(3).

sum of the three bond angles around C(32) is 360(1)°, which implies the sp^2 hybridization of C(32). The W=S(1) (2.1476(13) Å) and W−S(2) (2.3784(16) Å) bond distances are comparable to those of the usual W=S (2.13−2.16 Å)[9] and W−S (2.26−2.52 Å)[9b,d,10] bonds, respectively. The structure of **3** is also supported by spectroscopic data. The ^{13}C NMR spectrum showed resonances for the carbene and ester carbonyl carbons at 264 and 169 ppm, respectively, which are within the reported chemical shift ranges corresponding to W=*C*(SiMe$_3$) (235−276 ppm)[8] and W−C−*C*O$_2$R (163−181 ppm),[11] respectively. In the IR spectrum, stretching absorptions for the ester carbonyl and W=S were observed at 1676 and 489 cm^{-1}, respectively.[9,11] The ^{1}H NMR spectrum at 293 K showed a broad signal around 2.8 ppm, which is assignable to *o*-Me of the Mes groups. The signal varied from four sharp singlet signals at 213 K to two sharp singlet signals at 313 K. These spectral changes are attributable to the restricted rotation of the *ipso*-C−Si bond of Mes groups.



In contrast to the tungsten complex **1**, the reaction of molybdenum complex **2** with excess **4** in toluene for 8 h did not afford the corresponding carbene complex but Mo-(η^2-S=C) cyclic complex Cp*(S)Mo[{η^2-S=C(SiMe$_3$)}-C(=O)OSi(Mes)$_2$S] (**5**) in 52% yield (eq 2). Elemental analysis is consistent with the composition of **5**. The crystal structure analysis clearly revealed the Mo-(η^2-S=C) cyclic structure of **5** shown in Figure 2; however, the low quality of the crystal hampered a detailed discussion (R_w = 0.1547). The spectroscopic data also support the structure of **5**. The ^{13}C NMR resonances assignable to the Mo-(η^2-S=C) and ester carbonyl carbons were observed at 89 and 177 ppm, respectively, which are within the usual ranges of chemical shift values in Mo-(η^2-S=C) (80−103 ppm)[12] and Mo−C−*C*O$_2$R (171−178 ppm),[13] respectively. The IR spectrum showed the stretching absorptions of ester carbonyl and Mo=S at 1701 and 485 cm^{-1}, respectively.[13,14] Complex **5** showed two sharp singlet signals assignable to the *o*-Me groups at 2.96 and 2.90 ppm in the ^{1}H NMR spectrum at 293 K, indicating free rotation of the *ipso*-C−Si bond of the Mes groups.



Complex **5** seems to form by addition of a sulfur atom to the Mo=C bond of a Mo analogue of complex **3**, although such a complex was not detected during the reaction of complex **2** with excess **4** in C$_6$D$_6$. Attempts to synthesize the Mo analogue of complex **3** by sulfur abstraction from complex **5** with excess PMe$_3$[15] in C$_6$D$_6$ at 25 °C failed and resulted in complete consumption of complex **5** with the formation of a mixture of S=PMe$_3$ and unidentified complexes. Efforts of sulfur addition to complex **3** to provide a W analogue of complex **5** were also unsuccessful. The reaction of complex **3** with excess S$_8$ in C$_6$D$_6$ at 25 °C for 26 days

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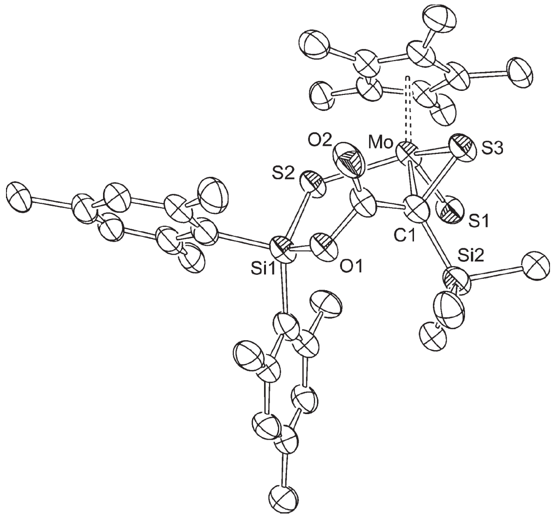

Figure 2. ORTEP drawing of **5** (50% probability level). Hydrogen atoms are omitted for clarity.

caused a 10% decomposition of complex **3** without any isolable products. These results exhibited significant differences in the sulfur affinity between Mo=C and W=C bonds. A tendency similar to our results was also reported in the sulfur addition reaction of ferrocenyl aminocarbene molybdenum and tungsten complexes. Thus, carbene molybdenum complexes reacted readily (~5 min) to give the corresponding thioamide complexes, while tungsten analogues required a much longer reaction time (~24 h).[3f]

It should be noted that the transformation proceeds via a C=O bond fission of one carbonyl ligand[16] and migration of the $SiMe_3$ group to the resulting carbene carbon. The conversion would start by addition of a sulfur atom to the M=Si bond to give a M−Si−S three-membered complex that is similar to that observed for the reaction of germylenepalladium complexes with COS.[4] However, the detailed formation mechanism of complexes **3** and **5** is unclear at present. Mechanistic aspects as well as reactions with other group 16 elements are under investigation.

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Supporting Information Available: Text, tables, figures, and a CIF file on experimental details and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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