ORGANOMETALLICS

Communication

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(η^3-α-Silabenzyl)tungsten Complexes: An Isolable Intermediate for Interconversion between a Silylene Complex and a Silyl Complex through 1,2-Aryl Migration

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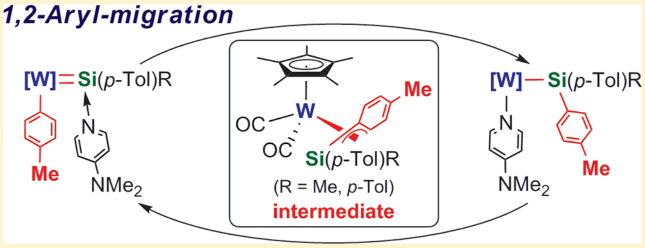
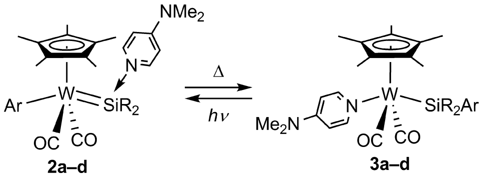
Supporting Information

ABSTRACT: η^3-α-Silabenzyl complexes Cp*W(CO)$_2${η^3(*Si,C,C*)-Si(*p*-Tol)$_2$R} (**1a**, R = Me; **1b**, R = *p*-Tol; Cp* = η^5-C$_5$Me$_5$, *p*-Tol = *p*-tolyl), the first silicon analogues of η^3-benzyl complexes, were synthesized by abstraction of DMAP (4-(dimethylamino)pyridine) with BPh$_3$ either from (aryl)(DMAP·silylene)tungsten complexes **2a**,**b** at room temperature or from (arylsilyl)(DMAP)tungsten complexes **3a**,**b** under irradiation. Complex **1** was demonstrated to be a key intermediate for the interconversion between **2** and **3** and to serve as a synthetic equivalent for both base-free silylene complexes and coordinatively unsaturated silyl complexes.



1,2-Group migration between transition-metal and silicon atoms in metal—silicon complexes is considered to play important roles in metal-mediated scrambling of substituents on organosilanes.[1,2] A typical example is the interconversion between silyl complexes and silylene complexes. Thus, 1,2-migration of a group on the silicon atom to the metal center in a silyl complex affords a silylene complex and vice versa. In particular, 1,2-migration of a hydrocarbyl group between the metal center and the silicon atom is attractive because the reaction involves intramolecular activation or formation of a chemically robust Si—C bond[3] and therefore can be applied to the synthesis of organosilicon compounds. However, this type of 1,2-migration is still limited,[2] and its detailed mechanism is largely uncertain. To elucidate the mechanism and develop new reactions involving the 1,2-migration, the most effective approach is the isolation and structure determination of the reaction intermediate. We now report the isolation and characterization of an intermediate in the 1,2-migration of an aryl group.

We recently found the interconversion between (aryl)(base·silylene)tungsten complexes and (arylsilyl)(base)tungsten complexes via reversible 1,2-aryl migration (eq 1).[4] Thus,



(1)

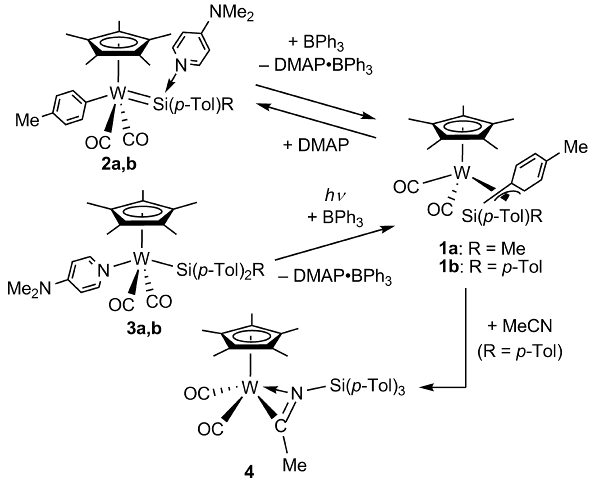
the DMAP-stabilized aryl silylene complexes Cp*W(CO)$_2$(Ar)(=SiR$_2$·DMAP) (**2a**, R$_2$ = Me(*p*-Tol), Ar = *p*-Tol; **2b**, R = Ar = *p*-Tol; **2c**, R = Me, Ar = Ph; **2d**, R = Me, Ar = *p*-Tol) thermally isomerize to arylsilyl DMAP complexes Cp*W(CO)$_2$(DMAP)(SiR$_2$Ar) (**3a**, R$_2$ = Me(*p*-Tol), Ar = *p*-Tol; **3b**, R = Ar = *p*-Tol; **3c**, R = Me, Ar = Ph; **3d**, R = Me, Ar = *p*-Tol) through 1,2-migration of an aryl group from tungsten to silicon. On the other hand, photoirradiation to silyl complexes **3a**—**d** induces the reverse reaction to reproduce silylene complexes **2a**—**d**.[4b] Kinetic study on the thermal isomerization of **2a**—**d** to **3a**—**d** revealed its large positive entropy of activation, implying that the rate-determining step involves dissociation of DMAP from **2a**—**d**.[4b] Therefore, to generate and isolate the DMAP-free intermediate in the interconversion, we examined the abstraction of DMAP from **2a**,**b** with BPh$_3$, which is known as an effective Lewis acid for abstraction of pyridine.[5]

Reaction of silylene complexes **2a**,**b** with BPh$_3$ in toluene at room temperature led to abstraction of DMAP in **2a**,**b** to give the first η^3-α-silabenzyl complexes Cp*W(CO)$_2${η^3(*Si,C,C*)-Si(*p*-Tol)$_2$R} (**1a**, R = Me; **1b**, R = *p*-Tol) and DMAP·BPh$_3$ (Scheme 1). The byproduct DMAP·BPh$_3$ was removed by precipitation in hexane. Product **1a** was obtained as a brown oil (crude yield: 89%), while **1b** was isolated as reddish brown crystals in 43% yield.

A single-crystal X-ray analysis revealed that **1b** adopts a three-legged piano-stool structure having an unprecedented η^3-α-silabenzyl ligand that is a silicon analogue of the η^3-benzyl ligand (Figure 1). The η^3-α-silabenzyl ligand in **1b** takes an exo geometry. The W—Si bond distance (2.5257(12) Å) lies between those of silylene complex **2a** (2.505(4) Å)[4b] and silyl complex **3b** (2.6110(13) Å)[4b] and is slightly shorter than that of a related (η^3-1-silaallyl)tungsten complex Cp*W(CO)$_2${η^3(*Si,C,C*)-Me$_2$SiCHCMe$_2$} (2.571(1) Å).[6] Two W—C(aryl) distances (W—C3 = 2.416(4) Å and W—C4 = 2.564(4) Å) are similar to the corresponding distances of the (η^3-

Received: January 8, 2013
Published: January 24, 2013

Scheme 1. Formation and Reactions of (η^3-α-Silabenzyl)tungsten Complexes 1a,b



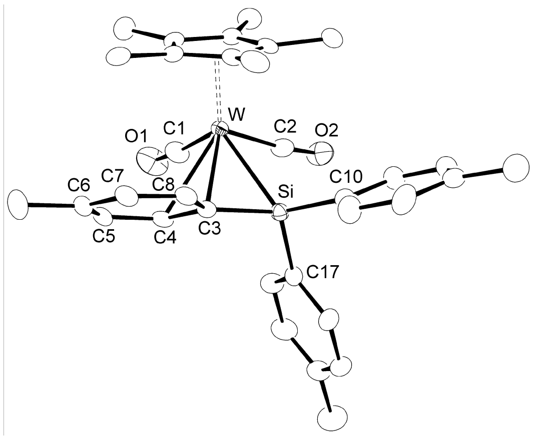
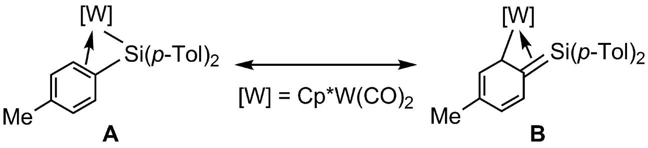


Figure 1. Molecular structure of **1b** (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): W−Si = 2.5257(12), W−C1 = 1.949(6), W−C2 = 1.926(5), W−C3 = 2.416(4), W−C4 = 2.564(4), Si−C3 = 1.834(5), Si−C10 = 1.867(5), Si−C17 = 1.867(5), C3−C4 = 1.429(6), C3−C8 = 1.451(7), C4−C5 = 1.430(7), C5−C6 = 1.359(7), C6−C7 = 1.427(7), C7−C8 = 1.355(7); Si−W−C1 = 109.54(16), Si−W−C2 = 65.25(15), Si−W−C3 = 43.50(11), Si−W−C4 = 65.28(11), C1−W−C2 = 83.8(2), C1−W−C3 = 102.31(18), C1−W−C4 = 70.17(19), C2−W−C3 = 106.60(18), C2−W−C4 = 110.17(18), C3−W−C4 = 33.19(15), W−Si−C3 = 65.07(14), W−Si−C10 = 119.02(15), W−Si−C17 = 124.92(16), C3−Si−C10 = 118.9(2), C3−Si−C17 = 114.5(2), C10−Si−C17 = 108.4(2), Si−C3−C4 = 114.0(4).

benzyl)tungsten complex Cp*W(CO)$_2${η^3(C,C,C)-C(p-Tol)H-(BEt$_2$)} (W−C$_\beta$ = 2.374(9) Å and W−C$_\gamma$ = 2.552(9) Å),[7] indicating the coordination of the two aromatic carbons C3 and C4 to the tungsten center in **1b**. Bond alternation is observed for the C−C bonds in the aryl ring other than the coordinated C3−C4 bond (C4−C5 = 1.430(7) Å, C5−C6 = 1.359(7) Å, C6−C7 = 1.427(7) Å, C7−C8 = 1.355(7) Å). Similar bond alternation was also reported for η^3-benzyl complexes.[7,8] The Si−C3 bond distance (1.834(5) Å) is slightly shorter than the other two Si−C bonds (1.867(5) Å) and lies between typical Si−C single-bond distances (1.86−1.91 Å)[9] and coordinated Si=C double-bond distances in η^2-silene complexes (1.78(2)−1.810(6) Å).[10] This indicates the existence of some double-bond character at the Si−C3 bond. The sum of the bond angles around the silicon atom (341.8(3)°) is similar to that of the η^3-1-silaallyl complex Cp*W(CO)$_2${η^3(Si,C,C)-Me$_2$SiCHCMe$_2$} (346.3°)[6] and lies midway between the tetrahedral (329°) and trigonal (360°) valence angles, implying some contribution of sp^2 hybridization at the silicon atom. On the basis of these observations, complex **1b** can be drawn as a resonance of two canonical forms: the η^2-arene silyl form **A** and the aryl η^2-silene form **B** (Scheme 2).

Scheme 2. Two Canonical Forms of 1b



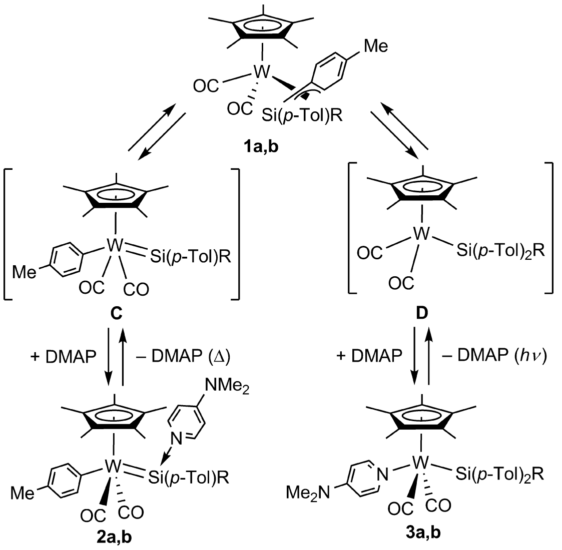
The NMR spectroscopic data for **1a,b** are consistent with their molecular structures having the η^3-α-silabenzyl ligand. The ^{1}H NMR spectrum of **1b** at room temperature shows two sets of two doublet signals for ortho and meta aromatic protons of the p-tolyl groups with 1:2 intensity ratio at 6.73 (ortho), 6.44 (meta) ppm and 7.80 (ortho), 7.03 (meta) ppm.[11] The first two signals are shifted upfield in comparison with the last two signals and with those of silyl complex **3b** (7.05−8.26 ppm).[4b] This upfield shift is attributable to the η^2 coordination of the aryl ring to the metal. A similar upfield shift of signals of aromatic protons was observed in the (η^3-benzyl)tungsten complex Cp*W(CO)$_2${η^3(C,C,C)-C(p-Tol)H(BEt$_2$)} (5.49−6.76 ppm).[7] Each of the ^{13}C{^{1}H} NMR spectra of **1a,b** shows one characteristic signal assignable to the carbon bound to silicon in the coordinating p-tolyl group of the silabenzyl ligand at 70.2 (**1a**) and 69.6 ppm (**1b**). The signal is shifted upfield in comparison with the corresponding carbon of the (η^3-benzyl)tungsten complex CpW(CO)$_2${η^3(C,C,C)-C(p-Tol)H(BEt$_2$)} (84.8 ppm).[7] The ^{29}Si{^{1}H} NMR spectra of **1a,b** exhibit signals at 8.8 (**1a**) and 9.5 ppm (**1b**) with ^{183}W satellites ($^1J_{\mathrm{WSi}}$ = 18 (**1a**) and 21 Hz (**1b**)). The chemical shifts of these signals lie between those of silyl complexes **3a,b** (17.8 (**3a**) and 24.3 ppm (**3b**))[4b] and that of the (η^2-silene)tungsten complex Cp$_2$W{η^2(Si,C)-Me$_2$Si=CH$_2$} (−15.7 ppm).[10a] This is attributable to some contribution of the aryl η^2-silene form **B** of **1b** and also the corresponding form of **1a**. Similar ^{29}Si chemical shifts have been reported for the η^3-1-silaallyl complexes Cp*W(CO)$_2${η^3(Si,C,C)-Me$_2$SiCHCR$_2$} (13.8 (R = H) and 8.8 ppm (R = Me)).[6]

The NMR spectra also demonstrate the existence of some dynamic behaviors of **1a,b** in solution. As mentioned above, only two doublets of the η^2-coordinated aryl ring protons in **1b** were observed in the ^{1}H NMR spectrum at room temperature. This observation suggests that the fast exchange between ortho positions and between meta positions is achieved by facile migration of the tungsten fragment between two η^2-C−C coordination sites in the p-tolyl group of the silabenzyl ligand. In the ^{13}C NMR spectrum of **1b**, only one signal for two carbonyl ligands is observed at 227.3 ppm. Only one set of the signals of two uncoordinated p-tolyl groups of **1b** was also observed in both the ^{1}H and ^{13}C NMR spectra. These observations indicate that the dynamic behavior of **1b** involves exchange between the CO ligands and between the uncoordinated p-tolyl groups. Low-temperature NMR spectroscopic measurements showed that this dynamic behavior of **1b** is very fast. Thus, upon cooling of a toluene-d_8 solution of **1b**, the ^{1}H NMR spectra (700 MHz) exhibited broadening of the four ArH signals and the methyl signal of the uncoordinated *p*-tolyl substituents. Especially, the *o*-ArH signal (6.65 ppm at room temperature) broadened most significantly and finally disappeared at −70 °C. Interestingly, in the ^{1}H NMR spectrum of **1a**, four upfield-shifted doublets assignable to the aromatic protons in the η^2-coordinated *p*-tolyl group are observed at 6.16, 6.40, 6.50, and 6.73 ppm at room temperature. Since a fast exchange similar to that in **1b** is also expected for **1a**, this observation indicates that two ortho and two meta positions in **1a** are kept inequivalent, respectively, during the fast exchange. This is attributable to the existence of two different substituents on the silicon atom and the absence of rotation around the coordinated Si−C bond.

On the basis of the aforementioned observations, we suggest that a possible mechanism of the dynamic behavior involves ring slippage of the coordinated *p*-tolyl group on the Cp*W(CO)$_2$ moiety without rotation around the coordinated Si−C bond.

Reaction of η^3-α-silabenzyl complexes **1a,b** with DMAP in toluene produced silylene complexes **2a,b** almost quantitatively (Scheme 1). Since **2a,b** are converted into silyl complexes **3a,b** by thermal reactions (eq 1),[4] **2a,b** and **3a,b** can be regarded as the kinetically controlled products and the thermodynamically controlled products, respectively, of the reactions of **1a,b** with DMAP. On the other hand, photoirradiation of a mixture of silyl complexes **3a,b** and BPh$_3$ in C$_6$D$_6$ led to the formation of silabenzyl complexes **1a,b** as the main product (Scheme 1). This reaction possibly proceeds through (1) dissociation of the DMAP molecule in **3a,b** by photoirradiation, (2) reaction of DMAP with BPh$_3$ to give DMAP·BPh$_3$, and (3) coordination of a *p*-tolyl group on silicon to tungsten. These results strongly support that **1a,b** are important and isolable intermediates in the interconversion between **2a,b** and **3a,b** via 1,2-aryl migration. Thus, as illustrated in Scheme 3, intermediates **1a,b** in this interconversion are formed by thermal dissociation of DMAP in **2a,b** to generate base-free aryl silylene complexes **C** followed by 1,2-migration of the *p*-tolyl ligand to the silylene silicon atom or by photoinduced dissociation of DMAP in **3a,b** to generate coordinatively unsaturated arylsilyl complexes **D** followed by coordination of a *p*-tolyl group on silicon to tungsten.

Scheme 3. Probable Mechanism of the Interconversion between Aryl Silylene Complexes 2a,b and Arylsilyl DMAP Complexes 3a,b through η^3-α-Silabenzyl Complexes 1a,b



Complexes **1a,b** are considered to serve as synthetic equivalents for both reactive silyl and silylene complexes. A tentative study of the reaction of **1b** with acetonitrile gave the *N*-silyliminoacyl complex Cp*W(CO)$_2${η^2(*C,N*)-C(Me)═NSi-(*p*-Tol)$_3$} (**4**)[12] in 55% yield (Scheme 1). This reaction apparently proceeds through a nitrile silyl complex via dissociation of the η^2-coordinated *p*-tolyl group. This is in contrast with the aforementioned reaction of **1a,b** with DMAP, where silylene complexes **2a,b** were quantitatively produced. This is probably attributable to the difference in the Lewis basicity and coordinating ability of the substrates and also due to the smaller steric hindrance around the silicon atom in comparison with the metal center in **1a,b**. Thus, the DMAP molecule, which is a stronger Lewis base and is bulkier than acetonitrile, is likely to attack at the silylene silicon atom. These results demonstrate the potential utility of η^3-α-silabenzyl complexes in general as the synthetic equivalents for reactive transition-metal complexes.

In conclusion, we newly synthesized and characterized (η^3-α-silabenzyl)tungsten complexes **1a,b** with an unusual η^3(*Si,C,C*) coordination of the silabenzyl ligand. Complexes **1a,b** were demonstrated to be key intermediates in the interconversion between DMAP-stabilized aryl silylene complexes **2a,b** and arylsilyl DMAP complexes **3a,b** through 1,2-aryl migration. The study of the reactions of complexes **1a,b** with nitrogen-containing substrates, i.e., DMAP and MeCN, revealed that **1a,b** serve as synthetic equivalents for both base-free silylene complexes and coordinatively unsaturated silyl complexes. Further investigations into the reactivity of **1a,b** toward other organic molecules are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving synthetic procedures and characterization data for **1a,b** and a table and a CIF file giving X-ray crystallographic data for **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid for Scientific Research (Nos. 22350024, 20750040, and 23750053) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We are grateful to Mr. Shinichiro Yoshida (Tohoku University) for his help with the low-temperature NMR spectroscopic measurements of **1b**. We also acknowledge the Research and Analytical Center for Giant Molecules, Tohoku University, for spectroscopic measurements and elemental analysis.

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(11) Assignment of ^{1}H NMR signals for ortho and meta aromatic protons of the *p*-tolyl groups in **1b** was confirmed by ^{1}H−^{13}C HSQC and ^{1}H−^{13}C HMBC spectra (see the Supporting Information).

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