ORGANOMETALLICS

Synthesis, Structure, and Reactions of a $(\eta^3 - \alpha - \alpha)$ silabenzyl)molybdenum Complex: A Synthetic Equivalent of a **Coordinatively Unsaturated Silvl Complex**

Takashi Komuro, Yuto Kanno, and Hiromi Tobita*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Supporting Information

ABSTRACT: The $(\eta^3 - \alpha - \text{silabenzyl})$ molybdenum complex Cp*Mo- $(CO)_{2}\{\eta^{3}(Si,C,C)-Si(p-Tol)_{3}\}$ (1; $Cp^{*} = \eta^{5}-C_{5}Me_{5}, p-Tol = p-C_{6}H_{4}Me$) was synthesized in high yield by removal of 4-(dimethylamino)pyridine (DMAP) from the (arylsilyl)(DMAP)molybdenum complex Cp*Mo- $(CO)_2(DMAP){Si(p-Tol)_3}$ (2) with BPh₃. The precursor, complex 2, was readily prepared by reaction of the (DMAP)(methyl)molybdenum complex $Cp*Mo(CO)_2(DMAP)Me(3)$ with tri-*p*-tolylsilane (HSi(*p*-Tol)₃) through methane elimination. Study on the reactivity of 1 toward DMAP



and nitrile revealed that complex 1 serves as a synthetic equivalent of the 16-electron silvl complex $Cp*Mo(CO)_{2}{Si(p-Tol)_{3}}$. Thus, complex 1 reacted with DMAP quantitatively at room temperature to reproduce arylsilyl complex 2 through dissociation of the arene carbon atoms coordinated to molybdenum. Complex 1 also reacted with acetonitrile at room temperature to give the N-silyliminoacyl complex $Cp^*Mo(CO)_2\{\eta^2(C,N)-C(Me)=NSi(p-Tol)_3\}$ (4) exclusively via cleavage of the Mo-C(arene) bonds followed by insertion of nitrile into the Mo-Si bond.

INTRODUCTION

Reactive transition-metal complexes with a metal-silicon bond such as silylene complexes and coordinatively unsaturated silyl complexes play important roles in the synthesis of organosilicon compounds.¹ These complexes are presumed to be key intermediates in metal-mediated transformations of organosilanes such as hydrosilylation of unsaturated organic molecules, dehydrogenative silvlation of organic molecules, dehydrogenative coupling of hydrosilanes, scrambling of the substituents of silanes, etc.¹ Therefore, in order to elucidate detailed reaction mechanisms for these transformations of organosilanes, basic studies on the synthesis and reactions of reactive metal-silicon complexes are indispensable.

We have recently succeeded in the synthesis of a new type of reactive metal-silicon complex, i.e., the $(\eta^3 - \alpha - \text{silabenzyl})$ tungsten complexes $Cp^*W(CO)_2\{\eta^3(Si,C,C)-Si(p-Tol)_2R\}$ (A; R = Me, p-Tol), which adopt an unusual η^3 coordination of one silicon and two aromatic carbon atoms to the tungsten center.² These complexes have been demonstrated to be key intermediates in the interconversion between DMAP-stabilized $(aryl)(silylene)tungsten complexes Cp*W(CO)_2(p-Tol) =$ Si(p-Tol)R·DMAP} (B) and (arylsilyl)(DMAP)tungsten complexes $Cp*W(CO)_2(DMAP){Si(p-Tol)_2R}$ (C) through 1,2-migration of an aryl group (eq 1).^{2,3} A study on the reactivity



toward nitrogen-containing molecules revealed that complexes A serve as synthetic equivalents for both base-free silylene complexes and coordinatively unsaturated silyl complexes (Scheme 1).² Thus, reactions of A with DMAP afforded

Scheme 1. Reactions of $(\eta^3 - \alpha - \text{silabenzyl})$ tungsten Complexes A with DMAP and Acetonitrile



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(aryl)(silylene·DMAP)tungsten complexes **B** via cleavage of the coordinated Si–C(aryl) bond, whereas **A** (R = *p*-Tol) reacted with acetonitrile to give the η^2 -*N*-silyliminoacyl complex Cp*W(CO)₂{ $\eta^2(C,N)$ -C(Me)=NSi(*p*-Tol)₃} (D) through dissociation of the coordinated aryl group followed by insertion of nitrile into the W–Si bond.

In this work, we synthesized the molybdenum analogue of η^3 - α -silabenzyl complex A (R = p-Tol), i.e., Cp*Mo- $(CO)_2\{\eta^3(Si,C,C)-Si(p-Tol)_3\}$ (1). Although the covalent radius of molybdenum is about the same as that of tungsten according to the recent reports by Pyykkö et al. (single-bond covalent radii, Mo = 1.38 Å, W = 1.37 Å; double-bond covalent radii, Mo = 1.21 Å, W = 1.20 Å),⁴ molybdenum uses much smaller d orbitals (4d orbitals) for the construction of coordinate bonds with ligands in comparison with those of tungsten (5d orbitals). Therefore, it is expected that the structure and reactivity of molybdenum complex 1 are fairly different from those of the tungsten analogue A (R = p-Tol)because of the significant change of orbital interaction between the metal center and the η^3 - α -silabenzyl ligand.⁵ This speculation turned out to be consistent with the results of this work: in contrast with the reactions of tungsten complexes A depicted in Scheme 1^2 , we found that both reactions of molybdenum complex 1 with DMAP and acetonitrile favor initial formation of silyl complexes through cleavage of the Mo-C(arene) bonds. Thus, 1 predominantly serves as a synthetic equivalent of the 16-electron silyl complex Cp*Mo- $(CO)_2$ {Si(*p*-Tol)₃}.

RESULTS AND DISCUSSION

Synthesis and Characterization of (DMAP)(methyl) molybdenum Complex 3. The (DMAP)(methyl)molybdenum complex $Cp^*Mo(CO)_2(DMAP)Me$ (3), which is the precursor of (DMAP)(silyl) complex 2 in this research (vide infra), was synthesized by a method analogous to that for the synthesis of the tungsten analogue $Cp^*W(CO)_2(DMAP)Me$ (E).^{3b} Thus, 3 was obtained in 62% yield by treatment of the acetonitirile(methyl)molybdenum complex $Cp^*Mo(CO)_2(NCMe)Me$,^{5a} prepared as the main product by photoirradiation of $Cp^*Mo(CO)_3Me$ in acetonitrile, with DMAP in toluene at room temperature (eq 2).



Complex **3** was thermally unstable at room temperature in C_6D_6 solution ($t_{1/2} = ca. 76$ h at 25 °C) but was characterized by NMR and IR spectroscopy. The ¹H NMR spectrum of **3** shows a signal assignable to the methyl ligand at 0.54 ppm. This chemical shift is similar to that of the tungsten analogue E (0.52 ppm).^{3b} Two signals attributable to the carbonyl ligands were observed at 254.2 and 269.7 ppm in the ¹³C{¹H} NMR spectrum of **3**. The IR spectrum of **3** in C_6D_6 shows two

absorption bands due to the symmetric and antisymmetric CO vibrations at 1905 and 1807 cm⁻¹, respectively, where the intensity of the former absorption is slightly stronger than that of the latter absorption. These observations indicate that the CO ligands in **3** were located at mutually *cis* positions on the metal center. This geometry is the same as that of the tungsten analogue E.^{3b}

Synthesis of (arylsilyl)(DMAP)molybdenum Complex 2. (DMAP)(methyl)molybdenum complex 3 reacted with tri-*p*-tolylsilane (HSi(*p*-Tol)₃) in toluene at room temperature to give the (DMAP)(silyl)molybdenum complex Cp*Mo- $(CO)_2(DMAP){Si(p-Tol)_3}$ (2) as yellow crystals in 69% isolated yield (eq 3). A possible mechanism for the formation



of **2** involves (1) dissociation of DMAP in **3** followed by Si–H oxidative addition of $HSi(p-Tol)_3$, (2) reductive elimination of methane from the resulting (hydrido)(methyl)(silyl)molybde-num complex F, and (3) coordination of DMAP to the metal center (eq 3).

This reaction of molybdenum complex 3 sharply contrasts with that of the tungsten analogue **E** with $HSi(p-Tol)_3$, which leads to the (aryl)(DMAP-silylene)tungsten complex Cp*W- $(CO)_2(p-Tol)$ {=Si(p-Tol)₂·DMAP} (**B**; R = p-Tol) through 1,2-migration of a p-tolyl group from the silicon atom to the metal center.^{3b} Silylene complex **B** (R = p-Tol) is thermally unstable and is converted into the (arylsilyl)(DMAP)tungsten complex $Cp^*W(CO)_2(DMAP){Si(p-Tol)_3} (C; R = p-Tol)$ on heating at 40 °C in toluene through 1,2-aryl migration from tungsten to silicon.^{3b} Therefore, silylene complex B (R = p-Tol) and silvl complex C (R = p-Tol) can be regarded as the kinetically controlled product and the thermodynamically controlled product, respectively, of the reaction of E with $HSi(p-Tol)_3$. On the other hand, in the ¹H NMR monitored reaction of molybdenum complex 3 with $HSi(p-Tol)_3$ (1:2) molar ratio) in C_6D_6 at room temperature, we did not observe any signals assignable to the (aryl)(silylene)molybdenum complex $Cp*Mo(CO)_2(p-Tol)$ =Si(p-Tol)₂·DMAP} (G) in the reaction mixture but observed weak signals of η^3 - α silabenzyl complex 1 (vide infra) as a transient species. This difference in reactivity on a change of the central metal implies that the stability of the hypothetical aryl(silylene)molybdenum complex G is considerably lower than that of the tungsten analogue **B** (R = p-Tol). This is attributable to less effective π back-donation from the metal center to the silvlene silicon atom in molybdenum complex G caused by the smaller orbital overlap between a 4d orbital of molybdenum and the vacant 3p orbital of the silylene silicon atom in comparison with that in the tungsten analogue **B** (R = p-Tol).

Characterization of (arylsilyl)(DMAP)molybdenum Complex 2. Single-crystal X-ray analysis revealed that 2 adopts a four-legged piano-stool geometry composed of η^{5} - C_5Me_5 , silyl, DMAP, and two carbonyl ligands (Figure 1 and Table 1). The silyl ligand and the DMAP ligand are located at



Figure 1. ORTEP drawing of $Cp*Mo(CO)_2(DMAP){Si(p-Tol)_3}$ (2). Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) in $Cp*Mo(CO)_2(DMAP){Si(p-Tol)_3}$ (2)

Mo-Si	2.6218(10)	Mo-N1	2.255(3)
Mo-C1	1.965(4)	Mo-C2	1.933(4)
Si-Mo-N1	133.20(8)	Si-Mo-C1	70.03(10)
Si-Mo-C2	70.68(10)	N1-Mo-C1	79.65(13)
N1-Mo-C2	83.83(13)	C1-Mo-C2	104.23(15)

mutually *trans* positions. This molecular structure is similar to that of the tungsten analogue $Cp*W(CO)_2(DMAP){Si(p-Tol)_3} (C, R = p-Tol).^{3b}$

The Mo–Si bond distance (2.6218(10) Å) is relatively long in the range of normal Mo–Si single-bond distances (2.480(2)-2.6815(13) Å).⁶ This elongation is attributable to the steric repulsion between the Cp*Mo(CO)₂(DMAP) fragment and the Si(*p*-Tol)₃ ligand in **2**: some interatomic distances between methyl carbon atoms in the C₅Me₅ ligand and aromatic carbon atoms in two *p*-tolyl groups, i.e., C10···C37 (3.493(6) Å), C11···C37 (3.604(7) Å), C17···C36 (3.621(7) Å), and C18···C36 (3.595(7) Å), are shorter than the sum (3.7 Å) of the van der Waals radius of the methyl group (2.0 Å) and the half-thickness of the plane of an aromatic ring (1.7 Å).⁷

The ¹H NMR spectrum of **2** in C_6D_6 at room temperature shows two sets of signals assignable to *p*-tolyl groups on silicon with a 1:2 intensity ratio, indicating the existence of hindered rotation around the Mo–Si bond on the NMR time scale. This hindered rotation in **2** is attributable to the steric repulsion between the Cp*Mo(CO)₂(DMAP) fragment and the Si(*p*-Tol)₃ ligand (vide supra). A similar hindered rotation around a Mo–Si bond has been reported by Berry et al. for the molybdenum complexes bearing a bulky Si(*t*-Bu)₂H ligand: (η^5 -C₅H₄R)₂Mo(H){Si(*t*-Bu)₂H} (R = H, Me).⁸ In the ¹³C{¹H} NMR spectrum of **2**, two carbonyl ligands show only one signal at 249.1 ppm because of the mutual *trans* arrangement of them. The ²⁹Si{¹H} NMR spectrum of **2** shows a signal at 34.7 ppm, which is shifted more downfield than that of HSi(*p*-Tol)₃ (–17.9 ppm) and is comparable with those of typical (silyl) molybdenum complexes with a SiR₃ (R₃ = Me₃, Et₃, MePh₂) ligand (27.0–35.2 ppm).^{8,9} The ²⁹Si signal is also shifted more downfield than that of the tungsten analogue C (R = *p*-Tol) (24.3 ppm)^{3b} by 10.4 ppm. The latter trend is similar to that observed for the molybdenum and tungsten complexes of Cp₂M(H)(SiMe₃) (Cp = η^{5} -C₅H₅, M = Mo (27.0 ppm) and W (0.5 ppm)).⁸

The IR spectrum of **2** exhibits two $\nu_{\rm CO}$ bands at 1892 (symmetric) and 1805 cm⁻¹ (antisymmetric). The intensity of the latter band is stronger than that of the former, which is consistent with the mutual *trans* arrangement of the two carbonyl ligands in **2**. Also, these absorption bands are shifted to higher wavenumbers in comparison with each of the corresponding bands of the tungsten analogue C (R = *p*-Tol) (1874 and 1786 cm⁻¹, respectively),^{3b} which implies the weaker back-donation from the metal center to the CO ligands in **2** in comparison with that in C (R = *p*-Tol).

Synthesis of $(\eta^3 - \alpha$ -silabenzyl)molybdenum Complex 1. Reaction of 2 with BPh₃, an effective Lewis acid for removal of a pyridine molecule,¹⁰ in toluene at room temperature led to formation of the $\eta^3 - \alpha$ -silabenzyl complex Cp*Mo-(CO)₂{ $\eta^3(Si,C,C)$ -Si(*p*-Tol)₃} (1) and the adduct DMAP·BPh₃ (eq 4). Complex 1 was isolated in 83% yield as reddish purple



crystals. This reaction is considered to proceed through initial dissociation of DMAP, which was readily trapped with BPh₃ to form the adduct DMAP·BPh₃, followed by π coordination of one of the *p*-tolyl groups on silicon to the coordinatively unsaturated molybdenum center.

In contrast with the reaction in eq 4, the formation of tungsten η^3 - α -silabenzyl complexes **A** by the reaction of arylsilyl complexes **C** with BPh₃ requires photoirradiation.² This is possibly because the coordination of DMAP to tungsten in **C** is stronger than that of molybdenum complex **2**.

Crystal Structure of $(\eta^3 - \alpha - silabenzyl)$ molybdenum **Complex 1.** The molecular structure of 1, bearing a η^3 - α silabenzyl ligand, was unequivocally determined by a singlecrystal X-ray analysis (Figure 2 and Table 2). Similarly to the tungsten analogue A (R = p-Tol),² the η^3 - α -silabenzyl ligand in 1 takes an exo geometry. The Mo-Si distance (2.5172(8) Å) is typical of single bonds and is comparable with those for $(\eta^3$ silapropargyl)molybdenum complexes Cp*Mo- $(CO)_{2}\{\eta^{3}(Si,C,C)-Ph_{2}SiCCR\}$ (R = t-Bu, 2.5249(10) Å; R = *i*-Pr, 2.5221(9) Å) with a related $\eta^3(Si,C,C)$ -coordinated organosilicon moiety.^{5a} The Mo-C3 and Mo-C4 distances in 1 (2.452(3) and 2.646(3) Å, respectively) are longer than the corresponding Mo–C_{β} and Mo–C_{γ} distances for the (η^3 benzyl)molybdenum complex CpMo(CO)₂{ $\eta^{3}(C,C,C)$ -CH₂(p-Tol)} (Mo-C_{β} = 2.364(5) Å, Mo-C_{γ} = 2.480(6) Å),¹¹ but similarly long distances have been reported for a molybdenum complex with a η^3 -PPh₃ ligand, [CpMo(CO)₂{ $\eta^3(P,C,C)$ -PPh₃}](BAr'₄) (Mo-C_{β} = 2.566(9) Å, Mo-C_{γ} = 2.645(9) Å; Ar' = 3,5-bis(trifluoromethyl)phenyl).¹² The elongation of the Mo–C distances for 1 is attributable to the steric repulsion between the η^3 - α -silabenzyl ligand and the Cp*Mo(CO)₂ moiety, especially that between one methyl group (C30) of the Cp* ligand and ring carbons of the silabenzyl ligand. Thus,



Figure 2. ORTEP drawing of $Cp*Mo(CO)_2\{\eta^3(Si,C,C)-Si(p-Tol)_3\}$ (1). Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) in $Cp*Mo(CO)_2{\eta^3(Si,C,C)-Si(p-Tol)_3}$ (1)

	a a a a a (a)		
Mo-Si	2.51/2(8)	Mo-CI	1.924(3)
Mo-C2	1.944(3)	Mo-C3	2.452(3)
Mo-C4	2.646(3)	Si-C3	1.850(3)
Si-C10	1.868(3)	Si-C17	1.873(3)
C3-C4	1.424(4)	C3-C8	1.435(4)
C4-C5	1.417(4)	C5-C6	1.373(4)
C6-C7	1.422(4)	C7-C8	1.359(4)
Si-Mo-C1	64.53(9)	Si-Mo-C2	109.11(10)
Si-Mo-C3	43.68(7)	Si-Mo-C4	64.70(7)
C1-Mo-C2	83.62(14)	С3-Мо-С4	32.16(9)
Mo-Si-C3	66.28(9)	Mo-Si-C10	119.06(10)
Mo-Si-C17	125.44(10)	C3-Si-C10	119.00(14)
C3-Si-C17	113.69(13)	C10-Si-C17	107.87(13)

the C6···C30, C7···C30, and C8···C30 interatomic distances (3.540(4), 3.339(4), and 3.585(5) Å) are much shorter than the sum of the van der Waals radii of the methyl group and the aromatic ring plane.⁷ The C–C bonds in the aryl ring other than the coordinated C3–C4 bond alternate, i.e., C3–C8 = 1.435(4) Å, C4–C5 = 1.417(4) Å, C5–C6 = 1.373(4) Å, C6–C7 = 1.422(4) Å, and C7–C8 = 1.359(4) Å, indicating the existence of bond localization in the aromatic ring. Similar bond alternations have been observed for the tungsten analogue **A** (R = p-Tol)² and for the (η ³-benzyl)molybdenum complex CpMo(CO)₂{ η ³(*C*,*C*,*C*)-CH₂(*p*-Tol)}.¹¹

The structure of complex 1 can be drawn as a resonance of two canonical forms, i.e., $(\eta^2$ -arene)(silyl)molybdenum form H and $(aryl)(\eta^2$ -silene)molybdenum form I (Scheme 2), on the basis of the following structural features. The Si–C3 bond distance (1.850(3) Å) is slightly shorter than the other two Si–C bonds (1.868(3) and 1.873(3) Å) and lies between typical

Scheme 2. Two Possible Canonical Forms of $(\eta^3 - \alpha - silabenzyl)$ molybdenum Complex 1



Si-C single-bond distances $(1.86-1.91 \text{ Å})^{13}$ and coordinated Si=C double-bond distances in η^2 -silene complexes (1.78(2)-1.810(6) Å).¹⁴ The sum of the bond angles around the silicon atom $(340.6(2)^\circ)$ is similar to that of the tungsten analogue **A** (R = *p*-Tol) $(341.8(3)^\circ)^2$ and lies midway between the tetrahedral (329°) and trigonal (360°) valence angles, implying some contribution of sp² hybridization at the silicon atom.

The Mo-Si and Mo-C3 bond distances (2.5172(8) and 2.452(3) Å, respectively) are comparable to the corresponding distances for the tungsten analogue A (R = p-Tol) (2.5257(12)) and 2.416(4) Å, respectively), whereas the Mo-C4 bond distance (2.646(3) Å) is longer than the corresponding distance for A (R = p-Tol; 2.564(4) Å) by ca. 0.08 Å.² This implies that the coordination of the aromatic carbon atom at the γ position in 1 is weaker than that for tungsten complex A (R = p-Tol). This bond weakening is attributable to a smaller contribution of the (aryl)(η^2 -silene)molybdenum canonical form I (Scheme 2) for 1 in comparison with the corresponding canonical form for A (R = p-Tol). In accord with the aforementioned observation, it is expected that the η^2 -coordinated arene moiety in molybdenum complex 1 is more labile than that in tungsten complexes A. This is consistent with the result that reactions of 1 with DMAP and nitrile exclusively proceed through dissociation of the η^2 -arene moiety (vide infra).

Spectroscopic Data for $(\eta^3 - \alpha - silabenzyl)$ molybdenum **Complex 1.** The NMR spectroscopic analysis for 1 also demonstrates a molecular structure bearing the η^3 - α -silabenzyl ligand. The ¹H NMR spectrum of **1** at room temperature shows two sets of two doublet signals assignable to ortho and meta aromatic protons of the *p*-tolyl groups with a 1:2 intensity ratio at 7.02 (ortho), 6.52 ppm (meta) and 7.84 (ortho), 7.04 ppm (meta).¹⁵ The first two signals are shifted upfield in comparison with the last two signals and with those of $HSi(p-Tol)_3$ (7.61) and 7.03 ppm). This upfield shift is attributable to the η^2 coordination of the aryl ring to the metal. A similar upfield shift of ¹H NMR signals of aromatic protons was also observed in the tungsten analogue A (R = p-Tol): 6.73 (*ortho*), 6.44 (*meta*) ppm for the protons of the coordinated aromatic ring and 7.80 (ortho), 7.03 (meta) ppm for the protons of the uncoordinated aromatic rings.²

The ¹³C{¹H} NMR spectrum of 1 at room temperature exhibits a signal at 79.6 ppm, which is assignable to the siliconbound ipso carbon in the coordinated p-tolyl group of the silabenzyl ligand. This chemical shift is similar to that of the corresponding ¹³C signals for tungsten complexes A (70.2 (R =Me) and 69.6 ppm (R = p-Tol)).² In the same ¹³C NMR spectrum of 1, a single broad signal attributable to the ortho carbon atoms in the coordinated *p*-tolyl group was observed at 124.7 ppm, whereas in the low-temperature ¹³C NMR spectrum of 1 in toluene- d_8 at -90 °C (vide infra) the ortho carbon signal appears as two separated broad resonances at 101.6 and 140.7 ppm. The former signal is shifted considerably upfield in comparison with the latter signal and also with the signal assignable to the ortho carbon atoms of the uncoordinated *p*-tolyl groups for 1 (136.4 ppm at -90 °C), indicating the coordination of an ortho carbon atom in the silabenzyl ligand to the metal center. Similar upfield-shifted resonances of coordinated ipso and ortho carbons have been reported for the η^3 -PPh₃ complex [CpMo(CO)₂{ $\eta^3(P,C,C)$ -PPh₃}](BAr'₄) (81.5 (*ipso*) and 90.0 ppm (*ortho*)).¹² Therefore, the aforementioned ¹³C NMR data for 1 support the η^2 coordination of a C–C unsaturated bond in the *p*-tolyl group of the η^3 - α -silabenzyl ligand.

The ²⁹Si{¹H} NMR spectrum of **1** at room temperature exhibits a signal at 15.8 ppm, which is shifted downfield in comparison with those of tungsten complexes **A** (8.8 (R = Me) and 9.5 ppm (R = *p*-Tol)).² This trend is similar to that observed for the ²⁹Si NMR data of silyl complex **2** (vide supra). The chemical shift of the ²⁹Si signal of **1** is between that of silyl complex **2** (34.7 ppm) and those of typical η^2 -silene complexes (from -20.77 to 6.14 ppm),^{14,16} indicating some contribution of the (aryl)(η^2 -silene)molybdenum canonical form **I** in **1** (Scheme 2). Similar ²⁹Si NMR chemical shifts have also been reported for related (η^3 -1-silaallyl)tungsten complexes Cp*W-(CO)₂{ $\eta^3(Si,C,C)$ -Me₂SiCHCR₂} (13.8 (R = H) and 8.8 ppm (R = Me)).¹⁷

The IR spectrum of **1** shows $\nu_{CO,sym}$ and $\nu_{CO,asym}$ bands at 1873 and 1807 cm⁻¹, respectively, with nearly the same intensity. This supports the mutual *cis* arrangement of the two carbonyl ligands in **1**. The wavenumbers of these bands are almost identical with the corresponding wavenumbers for the tungsten analogue **A** (R = *p*-Tol) (1873 and 1805 cm⁻¹, respectively),² indicating that the degree of π back-donation from the metal to the CO ligands in **1** is comparable with that for **A** (R = *p*-Tol). This is in contrast with the previously described trend of CO stretching frequencies between silvl complexes **2** and **C** (R = *p*-Tol), where the degree of the corresponding π back-donation of **2** is weaker than that for tungsten complex **C** (R = *p*-Tol).

Dynamic Behavior of $(\eta^3 - \alpha - \text{silabenzyl})$ molybdenum Complex 1 in Solution. An NMR spectroscopic analysis of 1 in solution demonstrates the existence of some dynamic behaviors. As mentioned above, in the ¹H NMR spectrum of 1 in C_6D_6 at room temperature, each set of two *ortho* and two *meta* protons of the η^3 - α -silabenzyl ligand and also two uncoordinated *p*-tolyl groups appears equivalently on the NMR time scale. A similar spectroscopic feature was observed for the tungsten analogue \hat{A} (R = *p*-Tol).² The ¹³C{¹H} NMR spectrum of 1 in C_6D_6 at room temperature also shows only one set of signals assignable to the ortho and meta carbons in the silabenzyl ligand at 124.7 and 125.6 ppm, respectively, where the former signal is broadened ($\Delta \nu_{1/2} = 8$ Hz).¹⁵ In the same spectrum, a single ¹³C signal assignable to CO ligands of 1 was observed at 234.6 ppm, indicating that the two carbonyl ligands also exchange quickly on the NMR time scale.

Furthermore, low-temperature 1H and ${}^{13}C\{{}^1H\}$ NMR spectroscopic measurements for 1 in toluene- d_8 revealed that the dynamic behavior was very fast (see Figures S1-S5 in the Supporting Information). When a toluene- d_8 solution of 1 was cooled, the ¹H NMR spectra (700 MHz) showed broadening of the four ArH signals of the coordinated and uncoordinated ptolyl substituents and the methyl signal of the latter substituents. Especially, the ortho ArH signal of the silabenzyl ligand (6.93 ppm at room temperature) broadened most significantly and finally disappeared at -70 °C. The ${}^{13}C{}^{1}H{}$ NMR spectrum (176 MHz) of 1 in toluene- d_8 at room temperature exhibited only one signal for the two CO ligands at 234.4 ppm and a broad signal assignable to the ortho carbon of the η^3 - α -silabenzyl ligand at 124.2 ppm. At -30 °C, the CO signal broadened, and the ortho carbon signal apparently disappeared because of significant broadening. Finally, the ¹³C{¹H} NMR spectrum of 1 at -90 °C showed two sets of two separated broad resonances attributable to the ortho carbons and CO signals at 101.6, 140.7 ppm and at 229.4, 239.9 ppm, respectively.

These NMR spectroscopic observations indicate that the dynamic behavior of 1 entails exchange between each of two *ortho* positions and two *meta* positions in the η^3 - α -silabenzyl ligand and also exchange between two uncoordinated *p*-tolyl groups on silicon and between two CO ligands. Although these data are insufficient to clarify the mechanism of the dynamic behavior of 1, we suggest that a possible mechanism of the dynamic behavior involves ring slippage of the coordinated *p*-tolyl group on the Cp*Mo(CO)₂ moiety without rotation around the coordinated Si–C bond (see Scheme S1 in the Supporting Information). The same mechanism has been proposed for tungsten complexes A.²

Reactions of $(\eta^3 - \alpha$ -silabenzyl)molybdenum Complex 1 with DMAP and Acetonitrile. To compare the reactivity of molybdenum complex 1 with that of tungsten complexes A (Scheme 1),² we examined reactions of 1 with nitrogencontaining organic molecules (DMAP and acetonitrile), revealing that 1 can serve as a synthetic equivalent of the 16electron silvl complex Cp*Mo(CO)₂{Si(p-Tol)₃}. Thus, treatment of complex 1 with DMAP in toluene at room temperature produced silvl complex 2 in 99% yield through dissociation of the coordinated aromatic carbons of the silabenzyl ligand in 1 (Scheme 3). This result indicates that the reaction in eq 4 is

Scheme 3. Reactions of $(\eta^3 - \alpha - \text{silabenzyl})$ molybdenum Complex 1 with DMAP and Acetonitrile



reversible. In contrast, the reaction of $(\eta^3 - \alpha \text{-silabenzyl})$ tungsten complexes **A** with DMAP gave DMAP-stabilized (aryl)-(silylene)tungsten complexes **B** as the kinetically controlled products almost quantitatively (Scheme 1).² As has been previously described, this difference of reactivity on a change of the metal center is attributable to the lower stability of (aryl)(silylene)molybdenum complex **G** in comparison with that of the tungsten analogue **B** (R = p-Tol).

Complex 1 smoothly reacted with excess acetonitrile (2 equiv) in toluene at room temperature to give the η^2 -*N*-silyliminoacyl complex Cp*Mo(CO)₂{ $\eta^2(C,N)$ -C(Me)==NSi-(*p*-Tol)₃} (4) in 86% yield (Scheme 3). This reaction pattern is the same as that of the tungsten analogue **A** (R = *p*-Tol), which reacts with acetonitrile to give the corresponding η^2 -*N*-silyliminoacyl complex **D** (Scheme 1).²

The X-ray crystal structure analysis of 4 (Figure 3 and Table 3) revealed that 4 adopts a pseudo three-legged piano-stool geometry composed of η^{5} -C₅Me₅, η^{2} -N-silyliminoacyl, and two



Figure 3. ORTEP drawing of $Cp*Mo(CO)_2\{\eta^2(C,N)-C(Me)=NSi(p-Tol)_3\}$ (4). Thermal ellipsoids are drawn at the 50% probability level, and all hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) in $Cp*Mo(CO)_{2}\{\eta^{2}(C,N)-C(Me)=NSi(p-Tol)_{3}\}$ (4)

Mo–N Mo–C2	2.2242(13) 1.9660(19)	Мо-С1 Мо-С3	1.9373(19) 2.0906(16)
Si–N	1.7556(14)	N-C3	1.254(2)
N-Mo-C1	110.69(6)	N-Mo-C2	93.58(6)
N-Mo-C3	33.62(6)	C1-Mo-C2	77.35(8)
C1-Mo-C3	88.69(7)	C2-Mo-C3	114.07(7)
Mo-N-Si	152.00(8)	Mo-N-C3	67.34(9)
Mo-C3-N	79.05(10)	Si-N-C3	140.10(12)
N-C3-C4	130.59(16)		

carbonyl ligands. The Mo–C3, Mo–N, and N–C3 distances (2.0906(16), 2.2242(13), and 1.254(2) Å, respectively) of the Mo–N–C three-membered ring in 4 are similar to the corresponding distances of the (*N*-silyliminoacyl)molybdenum complex Cp*Mo[κ^4 Si,H,N,C-xantsil(H){N=C(t-Bu)}](CO) (Mo–C = 2.073(3) Å, Mo–N = 2.236(2) Å, and N–C = 1.262(4) Å).¹⁸

The ${}^{13}C{}^{1}H$ NMR spectrum of 4 shows a signal assignable to the iminoacyl carbon at 236.4 ppm, and this chemical shift is almost identical with that for the tungsten analogue D (235.2 ppm).¹⁹ However, the signal is shifted considerably downfield in comparison with those (189.7-199.2 ppm) of iminoacyl carbons in the (N-alkyliminoacyl)molybdenum complexes $Cp'Mo(CO)_{2}{\eta^{2}(C,N)-C(R')=NR''}$ ($Cp' = \eta^{5}-C_{5}H_{5}, \eta^{5}-C_{5}H_{5}$ C_5H_4Me , η^5 - C_5Me_5 ; R' = Me, Et; R'' = Me, Et, *i*-Pr, *t*-Bu).²⁰ The IR spectrum of 4 shows a C=N stretching absorption band at 1647 cm^{-1} . This band is shifted to lower wavenumbers in comparison with those of the (N-alkyliminoacyl)molybdenum complexes $Cp'Mo(CO)_2\{\eta^2(C,N)-C(R')=NR''\}$ (1693–1732 cm⁻¹).²⁰ These results indicate the existence of a significant contribution of the (amido)(carbene)molybdenum canonical form K in addition to the (alkyl)-(imino)molybdenum canonical form J in the bonding mode of $\stackrel{•}{4}$ illustrated in Scheme 4. This trend is characteristic of *N*-silyliminoacyl complexes.¹⁹ On the other hand, the C=N stretching absorption band of 4 is shifted slightly to a higher wavenumber region in comparison with that of the tungsten analogue D (1620 cm^{-1}) .¹⁹ This is attributable to a stronger contribution of the (amido)(carbene)tungsten canonical form





in complex **D**, possibly due to the stronger π back-donation from the tungsten center to the iminoacyl carbon atom. The ²⁹Si{¹H} NMR spectrum of **4** shows a signal at -15.9 ppm, a chemical shift is close to that of the tungsten analogue **D** (-17.9 ppm),¹⁹ indicating that the Si(*p*-Tol)₃ group is bound to the iminoacyl nitrogen.

A plausible formation mechanism of 4 involves (1) substitution of the coordinated aromatic carbons in 1 with acetonitrile to generate (arylsilyl)(nitrile)molybdenum complex L and (2) insertion of the coordinated C=N bond of nitrile into the Mo–Si bond in L (Scheme 3). The related migratory insertion of nitrile into a metal–silyl bond to produce an η^2 -*N*-silyliminoacyl complex has been reported by Bergman, Brookhart, et al. for rhodium complexes²¹ and by Nakazawa et al. for an iron complex.²²

CONCLUSION

The $(\eta^3 - \alpha - \text{silabenzyl})$ molybdenum complex Cp*Mo- $(CO)_{2}$ { $\eta^{3}(Si,C,C)$ -Si(p-Tol)_{3}} (1) was synthesized by the DMAP-removal reaction from (arylsilyl)(DMAP)molybdenum complex $Cp*Mo(CO)_2(DMAP){Si(p-Tol)_3}$ (2) with BPh₃. The $\eta^3(Si,C,C)$ coordination of the silabenzyl ligand in 1 was confirmed by an X-ray crystallographic analysis, where the coordination of the aromatic carbon at the γ position of the silabenzyl ligand is considerably weaker than that of the tungsten analogue A (R = p-Tol).² The reactions of 1 with DMAP and acetonitrile exclusively proceeded through dissociation of the η^2 -coordinated aromatic carbons in the silabenzyl ligand. The result of the reaction of 1 with DMAP that reproduces **2** is very different from that of (η^3 - α -silabenzyl) tungsten complexes A, which gives DMAP-stabilized (aryl)-(silylene)tungsten complexes $Cp^*W(CO)_2(p-Tol) = Si(p-Tol)$ Tol) $R \cdot DMAP$ (B) as the kinetically controlled products. These results indicate that $\eta^3 - \alpha$ -silabenzyl complex 1 solely serves as a synthetic equivalent of the 16-electron triarylsilyl complex $Cp*Mo(CO)_{2}{Si(p-Tol)_{3}}$. The molybdenum analogue of complex **B** (R = p-Tol), i.e., the hypothetical silvlene complex G, appears to be less stable than B possibly because the d orbitals of molybdenum (4d orbitals) that are used mainly for bonding with silicon are smaller in size than those of tungsten (5d orbitals), which causes less effective π backdonation from the metal center to the silvlene silicon in G. Further studies on the reactivity of 1 toward other organic molecules and on its application to catalytic reactions are in progress.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under dry argon or nitrogen in a glovebox or using a high-vacuum line and standard Schlenk techniques.

Materials. Benzene- d_{60} toluene, toluene- d_{80} hexane, and acetonitrile were dried over CaH₂, vacuum-transferred, and stored under argon over 3 Å (for acetonitrile) or 4 Å (for other solvents) molecular sieves in a glovebox. BPh₃ (Strem Chemicals) was used as received. Cp*Mo(CO)₃Me was prepared according to the literature method.²³

Physical Measurements. ¹H, ¹³C{¹H}, and ²⁹Si{¹H} NMR spectra were recorded on a Bruker AVANCE-300, Bruker AVANCE III 400, JEOL JNM-ECA 700, or JEOL JNM-ECA 600 Fourier transform spectrometer. Chemical shifts are reported in parts per million. Coupling constants (I) and line widths at half-height $(\Delta \nu_{1/2})$ are given in Hz. ²⁹Si{¹H} NMR measurements were performed using the DEPT pulse sequence. The residual proton (C6D5H, 7.15 ppm; $C_6D_5CD_2H$, 2.09 ppm) and the carbon resonances (C_6D_{64} 128.0 ppm; $C_6D_5CD_3$, 20.4 ppm) of deuterated solvents were used as internal references for ¹H and ¹³C resonances, respectively. Aromatic protons and carbons are abbreviated as ArH and ArC, respectively. Pyridyl protons and carbons are abbreviated as pyH and pyC, respectively. The ¹H signals of pyridyl protons of DMAP in Cp*Mo- $(CO)_2(DMAP){Si(p-Tol)_3}$ (2) and $Cp*Mo(CO)_2(DMAP)Me$ (3) appeared as AA'XX' multiplets, but coupling constants of the signals could not be determined because the peak tops of each signal were poorly resolved. ²⁹Si{¹H} NMR chemical shifts were referenced to SiMe₄ (0 ppm) as an external standard. The NMR data were collected at room temperature unless indicated otherwise. Infrared spectra were measured on a C₆D₆ solution placed between KBr plates in a liquid cell or on a KBr pellet using a Horiba FT-730 or Horiba FT-720 spectrometer. The UV-visible spectrum of Cp*Mo(CO)₂{ $\eta^{3}(Si,C,C)$ - $Si(p-Tol)_3$ (1) was acquired on a Shimadzu MultiSpec-1500 spectrometer at room temperature. High-resolution mass spectra (HRMS) and mass spectra were recorded on a Hitachi M-2500S spectrometer operating in the electron impact (EI) mode or on a JEOL JMS-T100GCV spectrometer operating in the field desorption (FD) mode. Measurements of some NMR and mass spectra and elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Tohoku University.

Synthesis of Cp*Mo(CO)₂(DMAP)Me (3). The title compound was synthesized by modifying a literature method for the synthesis of the tungsten analogue $Cp^*W(CO)_2(DMAP)Me(E)$.^{3b} An acetonitrile (7 mL) solution of Cp*Mo(CO)₃Me (86 mg, 0.26 mmol) in a Pyrex tube (20 mm o.d.) with a Teflon vacuum valve was irradiated for 30 min with a 450 W medium-pressure Hg lamp immersed in a water bath (ca. 5 °C). During the photoreaction, the mixture was degassed after 10 and 20 min of irradiation to remove generated carbon monoxide by a conventional freeze-pump-thaw cycle on a vacuum line. The reaction mixture containing Cp*Mo(CO)₂(NCMe)Me^{5a} as the main product was transferred into a Schlenk tube and evaporated to dryness under reduced pressure. The residue was dissolved in toluene (2 mL), and the solution was added to a solid of DMAP (35 mg, 0.29 mmol). The mixture was stirred at room temperature for 70 min. The reaction mixture was concentrated to three-fourths volume, and then hexane (2 mL) was slowly layered on it. After crystals were precipitated, the mother liquor was removed by a syringe, and the crystals were washed with hexane $(1 \text{ mL} \times 3)$. Purple crystals of 3 (68 mg, 0.16 mmol) were obtained in 62% yield. Mp: 133 °C dec. ¹H NMR (300 MHz, C_6D_6): δ 0.54 (s, 3H, MoMe), 1.74 (s, 15H, Cp*), 1.97 (s, 6H, NMe₂), 5.50-5.56 (m, 2H, pyH), 7.88-7.94 (m, 2H, pyH). ¹³C{¹H} NMR (75.5 MHz, C_6D_6): δ 5.4 (MoMe), 10.6 (C_5Me_5) , 38.0 (NMe₂), 102.9 (C_5Me_5), 107.2, 153.4, 154.5 (pyC), 254.2, 269.7 (CO). IR (C_6D_6 , cm⁻¹): 1905 (s, $\nu_{CO,sym}$), 1807 (m, $\nu_{\rm CO,asym}$). HRMS (FD): m/z calcd for $[C_{20}H_{28}N_2O_2Mo]^+$ 426.1199, found 426.1197. Anal. Calcd for C20H28N2O2Mo: C, 56.60; H, 6.65; N, 6.60. Found: C, 56.39; H, 6.53; N, 6.37.

Synthesis of Cp*Mo(CO)₂(DMAP){Si(*p*-Tol)₃} (2). Cp*Mo-(CO)₂(DMAP)Me (3; 34 mg, 0.080 mmol) and HSi(*p*-Tol)₃ (48 mg, 0.16 mmol) were dissolved in toluene (4 mL), and the solution was stirred for 90 min at room temperature. After concentration of the reaction mixture, hexane (3 mL) was slowly layered on the concentrated solution. On standing at room temperature, yellow crystals precipitated. Removing the mother liquor, washing the crystals with hexane (1 mL × 2), and drying under vacuum afforded yellow crystals of **2** in 69% yield (39 mg, 0.055 mmol). Mp: 136 °C dec. ¹H NMR (300 MHz, C₆D₆): δ 1.64 (s, 15H, Cp*), 1.97 (s, 6H, NMe₂), 2.02 (s, 3H, C₆H₄Me), 2.23 (s, 6H, C₆H₄Me × 2), 5.44–5.51 (m, 2H, pyH), 7.04 (d, ³J_{HH} = 7.8 Hz, 2H, ArH), 7.21 (d, ³J_{HH} = 7.8 Hz, 4H, ArH), 8.16 (d, ³J_{HH} = 7.8 Hz, 4H, ArH), 8.19–8.27 (m, 4H, ArH +

pyH). ¹³C{¹H} NMR (75.5 MHz, C_6D_6): δ 10.9 (C_5Me_5), 21.37, 21.44 (C_6H_4Me), 38.0 (NMe₂), 103.1 (C_5Me_5), 107.9 (pyC), 135.6, 136.1, 136.8, 137.2, 138.5, 141.3, 144.2 (ArC), 153.7, 157.6 (pyC), 249.1 (CO). One aromatic carbon signal could not be observed due to the overlap with the signal of benzene- d_6 . ²⁹Si{¹H} NMR (59.6 MHz, C_6D_6): δ 34.7. IR (KBr pellet, cm⁻¹): 1892 (w, $\nu_{CO,sym}$), 1805 (s, $\nu_{CO,asym}$). HRMS (FD): m/z calcd for [$C_{40}H_{46}N_2O_2SiMo$]⁺ 712.2377, found 712.2379. Anal. Calcd for $C_{40}H_{46}N_2O_2SiMo$: C, 67.59; H, 6.52; N, 3.94. Found: C, 67.61; H, 6.56; N, 3.98.

Synthesis of Cp*Mo(CO)₂{ η^3 (Si,C,C)-Si(p-Tol)₃} (1). Cp*Mo-(CO)₂(DMAP){Si(p-Tol)₃} (2; 150 mg, 0.211 mmol) and BPh₃ (46 mg, 0.19 mmol) were dissolved in toluene (5 mL), and the solution was stirred at room temperature for 18 h. The dark red reaction mixture was evaporated to dryness under vacuum. To the residue was added hexane (5 mL), and then the mixture was stirred at room temperature for 8 h. DMAP·BPh3 was precipitated as a colorless solid. The mixture was filtered to remove DMAP·BPh₃, and the reddish purple filtrate was concentrated under vacuum. When the concentrated solution was cooled to -35 °C, reddish purple crystals were precipitated. Removing the mother liquor, washing the crystals with hexane, and drying under vacuum afforded reddish purple crystals of 1 in 83% yield based on BPh3 (93 mg, 0.16 mmol). Mp: 160 °C dec. ¹H NMR (400 MHz, C_6D_6): δ 1.52 (s, 15H, Cp*), 1.98 (s, 3H, $C_6H_4Me(\text{silabenzyl}))$, 2.06 (s, 6H, $C_6H_4Me)$, 6.52 (d, ³J = 7.8 Hz, 2H, meta-ArH(silabenzyl)), 7.02 (d, ³J = 7.8 Hz, 2H, ortho-ArH-(silabenzyl)), 7.04 (d, ³J = 8.2 Hz, 4H, meta-ArH), 7.84 (d, ³J = 8.2 Hz, 4H, ortho-ArH).^{15 1}H NMR (700 MHz, 203 K, toluene- d_8): δ 1.51 (s, 15H, Cp*), 1.99 (s, 3H, C₆H₄Me(silabenzyl)), 2.05 (br s, $\Delta \nu_{1/2}$ = 9.6 Hz, 6H, C₆H₄Me), 6.41 (br, $\Delta v_{1/2}$ = 19 Hz, 2H, meta-ArH(silabenzyl)), 6.98 (br, 4H, meta-ArH), 7.85 (br d, ³J = 7.0 Hz, 4H, ortho-ArH). The ortho-ArH(silabenzyl) signal is too broad to be observed, indicating that the signal is nearly decoalesced. The line width at half-height of the broad signal at 6.98 ppm could not be determined due to partial overlap with a signal of the residual protons of toluene- d_8 . ¹³C{¹H} NMR (75.5 MHz, C_6D_6): δ 10.0 (C_5Me_5), 21.4 (C₆H₄Me), 21.8 (C₆H₄Me(silabenzyl)), 79.6 (ipso-ArC(silabenzyl)), 100.7 (C_5Me_5), 124.7 (br, $\Delta \nu_{1/2} = 8$ Hz, ortho-ArC(silabenzyl)), 125.6 (meta-ArC(silabenzyl)), 129.1 (meta-ArC), 130.9 (ipso-ArC), 136.6 (ortho-ArC), 139.7 (para-ArC), 142.1 (para-ArC(silabenzyl)), 234.6 (CO).¹⁵ ¹³C{¹H} NMR (176 MHz, 183 K, toluene- d_8) δ 9.7 (C₅Me₅), 21.3 (br, $\Delta \nu_{1/2} = 11$ Hz, C₆H₄Me), 21.7 (C₆H₄Me(silabenzyl)), 77.2 (*ipso*-ArC(silabenzyl)), 100.1 (C_5 Me₅), 101.6 (br, $\Delta \nu_{1/2}$ = ca. 190 Hz, ortho-ArC(silabenzyl)), 129.5 (ipso-ArC), 136.4 (br, $\Delta \nu_{1/2}$ = 41 Hz, ortho-ArC), 139.7 (para-ArC), 140.7 (br, ortho-ArC(silabenzyl)), 141.3 (para-ArC(silabenzyl)), 229.4 (br, $\Delta \nu_{1/2}$ = ca. 190 Hz, CO), 239.9 (br, $\Delta v_{1/2}$ = ca. 180 Hz, CO). Other aromatic carbon signals could not be observed due to the overlap with signals of toluene- d_8 . The line width at half-height of the broad signal at 140.7 ppm could not be determined because of partial overlap with the aromatic carbon signals at 139.7 and 141.3 ppm. ²⁹Si{¹H} NMR (59.6 MHz, C₆D₆): δ 15.8. IR (KBr pellet, cm⁻¹): 1873 (s, $\nu_{CO,sym}$), 1807 (s, $\nu_{CO,asym}$). UV– vis $(\lambda_{max}, nm (\epsilon, M^{-1} cm^{-1}), hexane)$: 250 sh (25000), 329 (7200), 377 sh (4800). EI-MS (70 eV): m/z 590 (M⁺, 33), 534 (M⁺ - 2 CO, 100). HRMS (EI): m/z calcd for $[C_{33}H_{36}O_2SiMo]^+$ 590.1533, found 590.1539. Anal. Calcd for C33H36O2SiMo: C, 67.33; H, 6.16. Found: C, 67.36; H, 6.22

Reaction of $(\eta^3 - \alpha$ -silabenzyl)molybdenum Complex 1 with DMAP. Complex 1 (30 mg, 0.051 mmol) and DMAP (9 mg, 0.07 mmol) were dissolved in toluene (3 mL), and the solution was stirred at room temperature for 50 min. The orange reaction mixture was evaporated under vacuum. The residue was washed with hexane (1 mL \times 3) and dried under vacuum to give a yellow powder of Cp*Mo(CO)₂(DMAP){Si(p-Tol)₃} (2) in 99% yield (36 mg, 0.051 mmol). The product was identified as 2 by comparison of its ¹H NMR and IR spectra with those of a sample synthesized from 3 in the previous section. The purity of the obtained 2 was confirmed by elemental analysis. Anal. Calcd for C₄₀H₄₆N₂O₂SiMo: C, 67.59; H, 6.52; N: 3.94. Found: C, 67.97; H, 6.60; N: 4.16.

Reaction of $(\eta^3-\alpha$ -silabenzyl)molybdenum Complex 1 with Acetonitrile. To a solid sample of complex 1 (27 mg, 0.046 mmol)

was added acetonitrile (5 μ L, d = 0.782 g mL⁻¹, 0.09 mmol), and the mixture was dissolved in toluene (3 mL). The solution was stirred at room temperature for 70 min. The resulting red solution was evaporated under vacuum. The residue (red oil) was washed with hexane $(1 \text{ mL} \times 3)$ and dried under vacuum to give a red powder of $Cp*Mo(CO)_{2}{\eta^{2}(C,N)-C(Me)=NSi(p-Tol)_{3}}$ (4) in 86% yield (25) mg, 0.040 mmol). Mp: 147 °C dec. ¹H NMR (300 MHz, C_6D_6): δ 1.74 (s, 15H, Cp*), 2.06 (s, 9H, C₆H₄Me), 2.50 (s, 3H, N=CMe), 7.05 (d, ${}^{3}J_{HH} = 7.8$ Hz, 6H, ArH), 7.63 (d, ${}^{3}J_{HH} = 7.8$ Hz, 6H, ArH). ¹³C{¹H} NMR (75.5 MHz, C_6D_6): δ 11.1 (C_5Me_5), 21.4 (C_6H_4Me), 25.1 (N=CMe), 105.2 (C₅Me₅), 129.3, 130.0, 136.2, 140.6 (ArC), 236.4 (N=CMe). The CO signals could not be observed probably because of dynamic behavior involving inversion of the chiral metal center in 4, which led to exchange between the CO ligands.¹ ²⁹Si{¹H} NMR (59.6 MHz, C_6D_6): δ –15.9. IR (KBr pellet, cm⁻¹): 1917 (s, $\nu_{CO,svm}$), 1817 (s, $\nu_{CO,asvm}$), 1647 (w, ν_{CN}). EI-MS (70 eV): m/z 631 (M⁺, 6), 534 (M⁺ – 2 CO – MeCN, 100). Anal. Calcd for C35H39NO2SiMo: C, 66.76; H, 6.24; N, 2.22. Found: C, 67.14; H, 6.40; N, 2.39.

X-ray Crystal Structure Determination. Selected crystallographic data for 1, 2, and 4 are listed in Table S1 (see the Supporting Information). X-ray quality single crystals were obtained from hexane at -35 °C (for 1 and 4.0.5(hexane) as reddish purple platelike crystals and red platelike crystals, respectively) and from THF at -35 °C (for 2.1.5THF as yellow prismatic crystals). In the case of 4.0.5hexane, a large single crystal was cut to a suitable size $(0.35 \times 0.35 \times 0.33 \text{ mm}^3)$. Intensity data for the analysis were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71069 Å) under a cold nitrogen stream (T = 150 K (for 1 and 4) or 223 K (for 2)). Numerical absorption corrections were applied to the data. The structures were solved by the Patterson method using the DIRDIF-99 or DIRDIF-2008 program²⁴ and refined by full matrix least-squares techniques on all F^2 data with SHELXL-97.25 Except for the carbon and oxygen atoms of the THF molecules, the solvent of crystallization, in 2.1.5THF, anisotropic refinements were applied to all non-hydrogen atoms. The carbon and oxygen atoms of these THF molecules were isotropically refined, and no hydrogen atoms on the carbon atoms were included. In the case of 2.1.5THF, a THF molecule was disordered over two sites related to each other by an inversion center. The hydrogen atom on the coordinated ortho aromatic carbon C4 in 1 was found on the difference Fourier map and was refined isotropically. Other hydrogen atoms were placed at calculated positions. All calculations were carried out using Yadokari-XG 2009.²⁶ CCDC reference numbers: 932045 (1), 932046 (2), and 932047 (4). Crystallographic data are available in the Supporting Information as a CIF file.

ASSOCIATED CONTENT

S Supporting Information

A scheme illustrating a possible mechanism of the dynamic behavior of 1 (Scheme S1), figures depicting variable-temperature ¹H and ¹³C{¹H} NMR spectra of 1 (Figures S1–S5), a table giving selected X-ray crystallographic data for 1, 2, and 4 (Table S1), and a CIF file giving X-ray crystallographic data for 1, 2, and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for H.T.: tobita@m.tohoku.ac.jp.

Notes

The authors declare no competing financial interest.

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