η³-Silapropargyl/Alkynylsilyl Molybdenum Complexes: Synthesis, Structure, and Reactivity toward Methanol

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Transition-metal η³-propargyl/allenyl complexes have attracted considerable interest because of their unique structural features and reactivity toward polar reagents.[1] However, their silicon analogues, η³-silapropargyl complexes, have not been synthesized, although Rosenthal and co-workers[2] previously reported the silapropargyl/silaallenyl-like complexes Cp₂M(η²-*trans*-HMe₂SiCCR) (M = Ti, R = ᵗBu; M = Zr, R = SiMe₂H) with an agostic Si−H−M interaction. In our recent attempt to synthesize the η³-silapropargyl tungsten complex Cp*(CO)₂W(η³-Ph₂SiCCᵗBu) by the reaction of Cp*(CO)₂(MeCN)WMe with HPh₂SiC≡CᵗBu, we obtained the novel acetylide−silylene complex Cp*(CO)₂W(SiPh₂)(CCᵗBu), which is a structural isomer of the expected silapropargyl complex.[3]

To clarify the bonding nature and relative stability of these two types of complexes, Sakaki and co-workers[4,5] performed detailed theoretical studies of Cp(CO)₂M(SiR₂)(CCR′) and Cp(CO)₂M(η³-R₂SiCCR′) (M = W, Mo). They revealed that the metal center controls the relative stability of the complexes: the W center favors Cp(CO)₂M(SiH₂)(CCH), while the Mo center favors Cp(CO)₂M(η³-H₂SiCCH),[5] suggesting the possibility of isolating η³-silapropargyl/alkynylsilyl molybdenum complexes. Encouraged by this interesting finding, we examined the reactions of the acetonitrile molybdenum complex Cp*(CO)₂(MeCN)MoMe (**1**) with alkynylsilanes HPh₂SiC≡CR (**2a**, R = ᵗBu; **2b**, R = ⁱPr) and found that the reactions indeed gave the expected complexes Cp*(CO)₂Mo(η³-Ph₂SiCCR) (**3a** and **3b**, respectively). Herein, we describe their synthesis, structure, and reactivity toward methanol.

The reaction of **1** with **2a** in toluene-*d₈* at room temperature resulted in the rapid, clean formation of Cp*(CO)₂Mo(η³-Ph₂SiCCᵗBu) (**3a**) along with the generation of MeCN and CH₄ (Scheme 1). The corresponding reaction of **2b** gave the isopropyl

Scheme 1
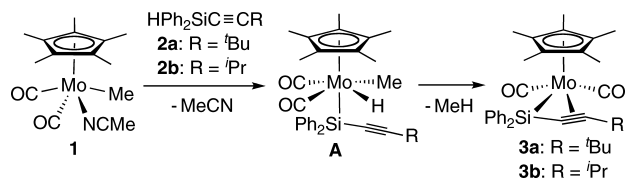
analogue **3b**. From preparative-scale reactions, **3a** and **3b** were isolated as air-sensitive orange and yellow solids in 56 and 51% yields, respectively. The structures of **3a** and **3b** were determined by X-ray analyses (Figure 1) and showed similar bonding parameters for the Mo−Si−C1−C2 skeletons. The Mo1−Si1 bond lengths [**3a**, 2.5249(10) Å; **3b**, 2.5221(9) Å] are in the range of typical Mo−Si single bonds (2.513−2.670 Å),[6] and the C1−C2 bond lengths [**3a**, 1.251(4) Å; **3b**, 1.254(4) Å] lie between those of C−C double and triple bonds, as in the case of the corresponding bond in η³-propargyl complexes.[1] The Si1−C1 bond lengths [**3a**, 1.806(3) Å; **3b**, 1.795(3) Å] are between Si−C single- and double-bond lengths,[7] showing some double-bond character. The theoretical
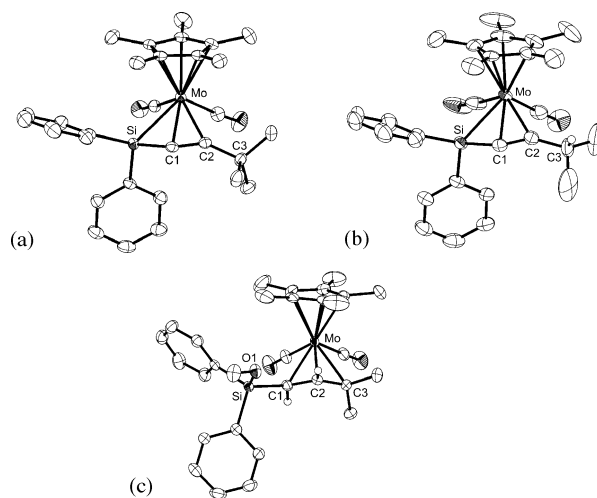
Figure 1. Molecular structures of (a) **3a**, (b) **3b**, and (c) **7**.

studies by Sakaki and co-workers showed that the π conjugation between the Si and C atoms of the H₂SiCCH group in Cp(CO)₂M(η³-H₂SiCCH) is very weak and that its electronic structure is intermediate between those of η³-silapropargyl and alkynylsilyl groups,[4,5] indicating that the contribution of a silaallenyl structure is minor relative to that of an allenyl structure in an η³-propargyl complex. The calculated Si−C and C−C lengths in Cp(CO)₂Mo(η³-H₂*Si*CCᵗBu), 1.814 and 1.263 Å, respectively,[5] are very close to the above-mentioned Si−C1 and C1−C2 lengths in **3a** and **3b**.

In the ¹³C NMR spectra of **3a** and **3b** at room temperature, a single CO signal and one set of Ph carbon signals were observed, and these signals decoalesced into two CO signals and two sets of Ph signals at −90 °C.[8] These spectral changes indicate the existence of the stereochemical inversion process of the metal center, which is also evidenced by the decoalescence of a doublet (1.32 ppm, 6H, rt) due to the CH*Me₂* protons of **3b** into two doublets (1.26 and 1.58 ppm, 3H each, −90 °C). The ¹³C signals at 51.4 and 129.0 ppm at −90 °C were assigned to the C1 and C2 carbons, respectively, of the Si−C1−C2−ⁱPr moiety in **3b** on the basis of their correlation with the C*H*Me₂ proton signal in the HMBC spectrum. Interestingly, no ²⁹Si resonance was detected for **3b** at room temperature, while a sharp resonance appeared at 46.2 ppm upon cooling to −90 °C. In contrast, a ²⁹Si resonance was clearly observed at 23.6 ppm for **3a** at room temperature. These observations suggest the interconversion between **3b** and a trace amount of its isomer, for which the acetylide−silylene complex Cp*(CO)₂Mo(SiPh₂)(CCⁱPr) may be a candidate.

A plausible mechanism for formation of **3a,b** is shown in Scheme 1. The Si−H bond in **2a,b** is activated by the coordinatively unsaturated complex Cp*(CO)₂MoMe generated from **1** to give **A**, which undergoes reductive elimination of methane and coordination of the alkynyl moiety to the metal center to form **3a,b**. The

corresponding reaction sequence was shown for the formation of the tungsten complex $Cp(CO)_2W(\eta^3\text{-}H_2SiCCH)$ in Sakaki's theoretical study.[4]

When **3a** was treated with methanol in toluene-d_8 at room temperature, a rapid reaction took place to give the stable four-membered cyclic complex **5a**, whose structure was fully characterized by NMR spectroscopy and X-ray analysis, which showed the E configuration for the double bond (Scheme 2).[8] In the ^{1}H NMR

Scheme 2
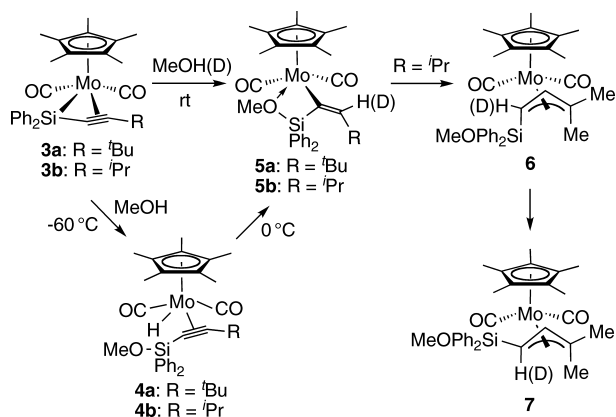
spectrum, a characteristic vinylic CH signal appeared at 6.60 ppm. The reaction of **3b** with methanol first gave metallacycle **5b**, which was characterized on the basis of the similarity of its spectroscopic data with those of **5a** (e.g., a vinylic CH signal at 6.25 ppm for **5b**). As the reaction was monitored by ^{1}H NMR spectroscopy, the consecutive conversion of **5b** to η^3-allyl complexes **6** and **7** was observed. The structure of the final product **7** was established by X-ray analysis (Figure 1), which showed the exo−syn configuration of the η^3-allyl moiety. The structure of **6** was characterized by NMR spectra, which were very similar to those of **7**, and the exo configuration was confirmed by the observation of an NOE between the central allyl proton and the Cp* protons. In the reaction of **3b** with MeOD at room temperature, selective deuterium incorporation at the vinylic position in **5b** and at the terminal allylic position in **6** and **7** (~92% D) was observed.

To obtain mechanistic information on the formation of **5b**, the reaction of **3b** with methanol was monitored by low-temperature ^{1}H NMR spectroscopy. When the temperature was increased to −60 °C from −90 °C, the formation of (methoxysilyl)alkyne hydride complex **4b** was observed as a major product (~75%), and it was converted to **5b** upon warming to 0 °C. The structure of **4b** was characterized by low-temperature NMR spectra.[8] A characteristic hydride signal was detected at −3.86 ppm, and the signals of the coordinated alkyne carbons were observed at 77.1 and 134.8 ppm. The corresponding complex **4a** was detected in the low-temperature reaction of **3a** with methanol, as indicated by a hydride signal at −3.88 ppm and alkyne carbon signals at 79.6 and 143.4 ppm for **4a** at −60 °C.

A possible mechanism for the reaction of **3a,b** with methanol is illustrated in Scheme 3. Nucleophilic attack of methanol at the silicon center of **3a,b** causes Si−Mo bond cleavage to form **4a,b**, which undergoes alkyne insertion into the Mo−H bond followed by coordination of the methoxy oxygen to the resulting unsaturated metal center to produce **5a,b**. Similar four-membered metallacycle formation was observed in the reaction of the silaallyl tungsten complex with methanol.[9] Dissociation of the methoxy ligand in **5a,b** regenerates **B**, and coordination of the alkene moiety to the metal center may form 1-metallacyclopropene (η^2-vinyl) complex

Scheme 3
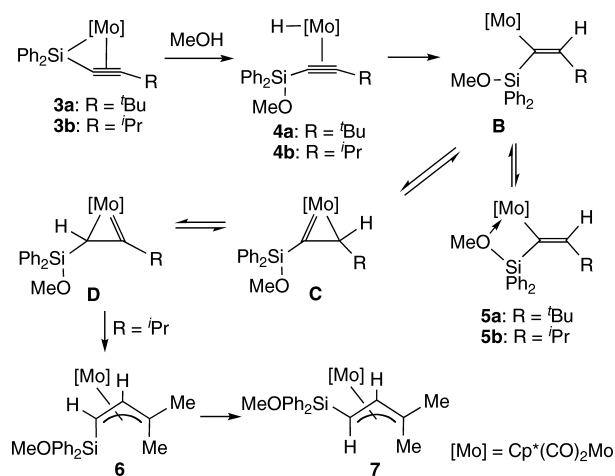
C, which leads to **D** via a 1,2-H shift. In this system, **5a** is suggested to be thermodynamically more stable than **C** and **D**. In the case of R = ^iPr, the 1,2-H shift of the CHMe$_2$ in **D** can open the way to η^3-allyl complex **6**, which undergoes slow isomerization to **7** to relieve steric repulsion between the silyl and methyl groups in the allyl ligand. It has been shown that the alkyne hydride complex $[Cp^*(CO)_2ReH(\eta^2\text{-MeCCMe})]^+$, which is isoelectronic with **4a,b**, is transformed into the η^3-allyl complex $[Cp^*(CO)_2Re(\eta^3\text{-MeHC-}CHCH_2)]^+$ via the observable 1-metallacyclopropene complex $[Cp^*(CO)_2Re(\eta^2\text{-CMeCHMe})]^+$.[10]

In summary, a novel η^3-silapropargyl/alkynylsilyl complex was successfully synthesized using molybdenum as a metal center in accordance with the theoretical prediction,[5] and its structure and reactivity toward methanol were elucidated. Further studies of the reactivity of the silapropargyl complex and the possibility of its equilibration with an acetylide−silylene complex are in progress.

Supporting Information Available: Experimental details, spectroscopic data, and X-ray crystallographic data for **3a**, **3b**, **5a**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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