Synthesis and Structure of a Base-stabilized Silyl(silylene)tantalum Complex

Hidenori Koshikawa, Masaaki Okazaki,[†] Shun-ichi Matsumoto, Keiji Ueno,[††] Hiromi Tobita,* and Hiroshi Ogino[†††]
Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578
[†]*International Research Center for Elements Science, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011*
[††]*Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu 376-8515*
[†††]*Miyagi Study Center, The University of the Air, Sendai 980-8577*

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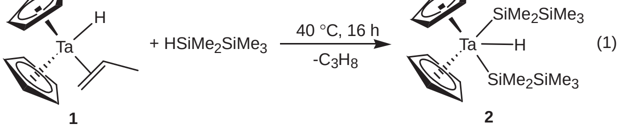
Thermal reaction of $Cp_2Ta(\eta^2\text{-}C_3H_6)$ with $HSiMe_2SiMe_2OMe$ in toluene at 60 °C gave $Cp_2Ta\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ (7%) and $Cp_2TaH(SiMe_2SiMe_2OMe)_2$ (8%). The former methoxy-stabilized silyl(silylene) complex was characterized by X-ray diffraction study.

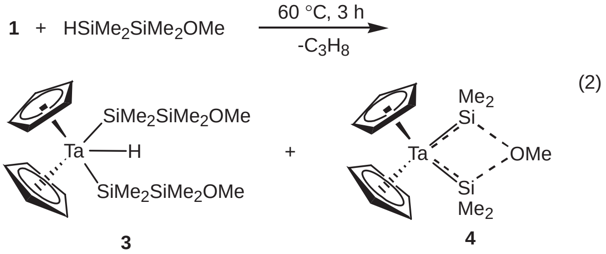
Over the past few decades, transition-metal silylene complexes with metal–silicon double bonds have attracted much interest as silicon analogues of carbene complexes, and as possible intermediates in various transformation reactions of organosilicon compounds.[1] Until now, a wide variety of silylene complexes have been synthesized as not only a base-stabilized form but also a base-free form.[2] To our best knowledge, all these examples are Fischer-type ones, in which the metal–silicon bond is polarized in a $M^{\delta-}\text{–}Si^{\delta+}$ manner.[3] Theoretical studies on early transition metal–silylene complexes have been reported by Nakatsuji et al.[4] They concluded that the Schrock-type metal–silylene complex $L_nNb{=}SiR_2$ is more stable than the Fischer-type $L_nM{=}SiR_2$ (M = Fe and Cr), although silylene complexes of group 5 transition metals have not been prepared yet. We herein report the synthesis and structure of methoxy-bridged silyl(silylene)tantalum complex.

Heating a toluene solution of *endo*-$Cp_2Ta(H)(\eta^2\text{-}C_3H_6)$[5] (**1**) and $HSiMe_2SiMe_3$ at 40 °C for 16 h gave a yellow solid of $Cp_2Ta(H)(SiMe_2SiMe_3)_2$ (**2**) in 85% yield (eq 1).[6] Monitoring the reaction by NMR indicated the evolution of propane. The existence of the Ta–H moiety was indicated by ^{1}H NMR (benzene-d_6, δ −3.03) and IR spectroscopic data (Nujol, $\nu_{Ta\text{–}H}$ 1797 cm^{-1}). In the $^{29}Si\{^1H\}$ NMR spectrum (benzene-d_6), the signals of a disilanyl ligand are observed at δ −14.9 and −8.7, although their assignment is not clear.



Klazinga and Teuben reported the reaction of *endo*-$Cp_2Ta(H)(\eta^2\text{-}C_3H_6)$ with CO giving $Cp_2Ta(C_3H_7)(CO)$ exclusively, indicating that the initial step is the insertion of propene into the Ta–H bond.[5] The reaction in eq 1 would start from the same reaction, leading to the coordinatively unsaturated species, $[Cp_2Ta(C_3H_7)]$. Successive oxidative addition–reductive elimination processes give **2**. In order to isolate the silyl(silylene) complex generated by the reductive elimination of $HSiMe_2SiMe_3$ from **2** followed by 1,2-migraion of the silyl group, **2** was treated with 4-dimethylaminopyridine (DMAP), which has been recognized as a useful base for stabilization of silylene complexes.[2] However, this was not the case. Heating the solution at 80 °C gave a complicated mixture containing $HSiMe_2SiMe_3$. No evidence was obtained for the formation of the DMAP-stabilized silyl(silylene) complex.

Silyl(silylene) complexes have been synthesized as four-membered ring compounds by introducing the internal base such as methoxy and diethylamino groups.[2a,7] Thermal reactions of *endo*-$Cp_2Ta(H)(\eta^2\text{-}C_3H_6)$ with $HSiMe_2SiMe_2OMe$ in benzene-d_6 at 60 °C for 3 h gave $Cp_2TaH(SiMe_2SiMe_2OMe)_2$ (**3**) and $Cp_2Ta\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ (**4**) in 33 and 23% NMR yields, respectively (eq 2). Further heating of the mixture did not affect the molar ratio of the products. The large scale reaction allowed the isolation of **3** and **4** in 8 and 7% yields, respectively.[8]



The spectroscopic feature of **3** is quite similar to that of **2**. The ^{1}H NMR spectrum (benzene-d_6) shows five signals at δ −3.10 (1H, TaH), 0.33 (12H, SiMe$_2$), 0.53 (12H, SiMe$_2$), 3.33 (6H, OMe), and 4.64 (10H, Cp), which is in good agreement with the structure of **3**. The existence of Ta–H is also supported by IR spectrum (Nujol), showing a band at 1789 cm^{-1} ($\nu_{Ta\text{–}H}$). The ^{29}Si NMR spectrum (benzene-d_6) shows signals at δ −9.9 and 19.5. Complex **4** exhibits a downfield-shifted ^{29}Si NMR signal at δ 127.8. The ^{29}Si NMR chemical shift is characteristic of the base-stabilized silylene complexes.[2] In the ^{1}H NMR spectrum of **4** in benzene-d_6, three signals are observed at δ 0.37 (12H, SiMe$_2$), 2.73 (3H, OMe), and 4.28 (10H, Cp), which is consistent with the structure having a mirror plane composed of tantalum, oxygen, and two silicon atoms. Moreover, the upfield shift of the ^{1}H NMR signal for the methoxy group (δ 2.73) is characteristic of methoxy-bridged silyl(silylene) complexes.[7]

Cooling the hexane solution of **4** at −50 °C allowed the growth of yellow crystals suitable for X-ray diffraction study. Molecular structure of **4** is depicted in Figure 1.[9] According to the Cambridge Crystallographic Database (version 5.26), the Ta–Si distance of 2.605(1) and 2.597(1) Å is the shortest yet reported for tantalum complexes with Cp or substituted cyclopentadienyl ligands (2.62–2.74 Å). The Si–O bonds in **4** (1.873(4) and 1.891(4) Å) are much longer than a normal silicon–oxygen single bond (1.63 Å), and is the longest yet reported for me-

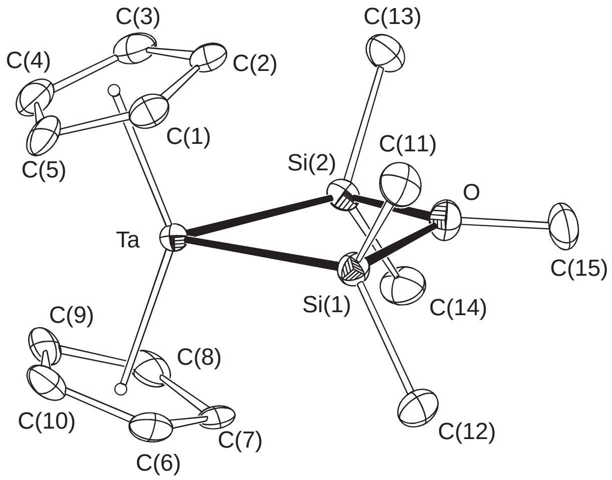
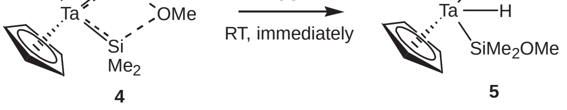


Figure 1. Molecular Structure of **4**. The thermal ellipsoids are at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ta–Si(1) = 2.605(1), Ta–Si(2) = 2.597(1), Si(1)–O = 1.873(4), Si(2)–O = 1.891(4), Si(1)–Ta–Si(2) = 67.30(4), Ta–Si(1)–C(11) = 124.3(2), Ta–Si(1)–C(12) = 125.5(2), C(11)–Si(1)–C(12) = 102.5(3), Ta–Si(2)–C(13) = 125.0(2), Ta–Si(2)–C(14) = 126.0(2), C(13)–Si(2)–C(14) = 101.9(2).

thoxy-bridged silyl(silylene) complexes (1.79–1.84 Å).[7] These structural features are consistent with the bonding scheme of **4** having unsaturated Ta–Si bonds and dative O–Si bonds. The sums of the bond angles of three bonds around the Si(1) and Si(2) atoms except the O–Si dative bonds are 352.3 and 352.9°, respectively, implying the considerable contribution of the π interaction between the sp^2-hybridized Si atoms and the tantalum center. The Ta–Si(1)–O–Si(2) four-membered ring is almost planar: Dihedral angle between the planes defined by Ta–Si(1)–Si(2) and Si(1)–Si(2)–O is 174.3°.

Complex **4** is the first silylene complex having group 5 transition metal.[10] The reactivity is of great interest. A preliminary reactivity study of **4** was carried out with MeOH. Addition of 2.1 equiv. of MeOH to a benzene solution of **4** resulted in an immediate reaction, and after workup, complex **5** was obtained as a yellow solid in 90% yield.[11] The $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR signal (δ 68.5) in benzene-d_6 was shifted to the higher field compared with that of **4**. The ^{1}H NMR spectrum (benzene-d_6) shows four signals at δ −4.74 (1H, TaH), 0.50 (12H, $SiMe_2$), 3.41 (6H, OMe), and 4.57 (10H, Cp), supporting the structure of **5**. The reaction of **4** with MeOH is considered to be initiated by nucleophilic attack of MeOH to the silylene silicon atom.



(3)

In summary, we succeeded in the synthesis and X-ray characterization of the group 5 transition metal silylene complex **4** for the first time. Further reactivity studies of **4** toward various nucleophiles and electrophiles are under active investigation.

References and Notes

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4 H. Nakatsuji, M. Hada, and K. Kondo, *Chem. Phys. Lett.*, **196**, 404 (1992).

5 A. H. Klazinga and J. H. Teuben, *J. Organomet. Chem.*, **165**, 31 (1979).

6 A Pyrex tube (20 mmϕ) was charged with **1** (345 mg, 0.974 mmol), $HSiMe_2SiMe_3$ (592 mg, 4.47 mmol), and toluene (20 mL). The tube was connected to a vacuum line and flame-sealed under vacuum. The sample was heated at 40 °C for 16 h and opened under N_2 in a glovebox. Volatiles were removed under reduced pressure and the residue was extracted with hexane. Cooling of the concentrated extract at −50 °C gave a yellow solid of **2**. Yield: 477 mg (85%).

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8 A Pyrex tube (20 mmϕ) was charged with **1** (379 mg, 1.06 mmol), $HSiMe_2SiMe_2OMe$ (473 mg, 3.19 mmol), and toluene (25 mL). The tube was connected to a vacuum line and flame-sealed under vacuum. The sample was placed in an oil bath and heated at 60 °C for 6 h. The tube was then opened under N_2 in a glovebox. Volatiles were removed under reduced pressure and the residue was extracted with hexane (30 mL). Cooling of the concentrated hexane solution (20 mL) at −50 °C gave a yellow solid of **3** (53 mg, 8%). Cooling of the further concentrated mother liquid (10 mL) gave a yellow solid of **4** (35 mg, 7%).

9 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-279047. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

10 For the rare earth elements, silylene complexes have been reported: a) X. Cai, B. Gerhus, P. B. Hitchcock, and M. F. Lappert, *Can. J. Chem.*, **78**, 1484 (2000). b) W. J. Evans, J. M. Perotti, J. W. Ziller, D. F. Moser, and R. West, *Organometallics*, **22**, 1160 (2003).

11 An NMR tube (5 mmϕ) was charged with **4** (10 mg, 0.022 mmol), MeOH (1.6 mg, 0.050 mmol), and benzene-d_6 (0.35 mL). The tube was connected to a vacuum line and flame-sealed under vacuum. NMR monitoring of the reaction indicated the immediate and quantitative formation of **5**. The tube was opened under N_2 in a glovebox. Evaporation of the solution gave **5** (9 mg) in 90% yield.

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