

Reactions of Alkyl Alkylidene Complexes with Silanes. Synthesis and Characterization of Novel Tantalum 1,1-Metallasilacyclobutadiene and Disilyl-Substituted Alkylidene Complexes

Jonathan B. Diminnie and Ziling Xue*

Department of Chemistry, The University of Tennessee
Knoxville, Tennessee 37996-1600

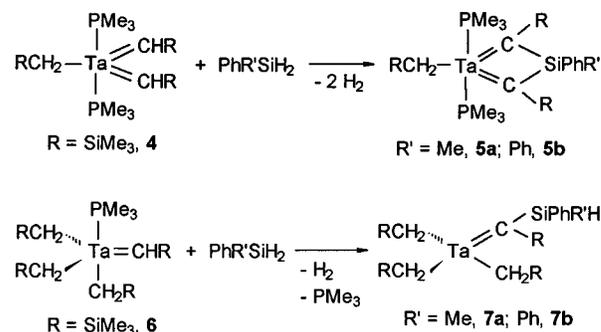
Received July 11, 1997

We have been investigating cyclopentadienyl (Cp)-free silyl alkylidene complexes of tantalum as models for possible reactive intermediates in the reactions of alkyl alkylidene complexes $(RCH_2)_3Ta=CHR$ with SiH_4 .^{1,2} Recently, we reported the synthesis and characterization of thermally unstable silyl alkylidene complexes $(Me_3ECH_2)_2Ta(=CHEMe_3)SiPh_2Bu^t$ (E = C, **1**; Si, **2**), which react with PMe_3 to form bis(phosphine) bis(alkylidene) complexes $(Me_3ECH_2)_2Ta(PMe_3)_2(=CHEMe_3)_2$ (E = C, **3**; Si, **4**; **3** has been previously prepared by Schrock and co-workers³). In order to further study the reaction of silane with alkyl alkylidene complexes, we investigated the reactions of tantalum alkylidene complexes containing phosphine supporting ligands with silanes $PhR'SiH_2$ ($R' = Ph, Me$), in the hope that phosphine might help stabilize the resulting products.

When a solution of $PhR'SiH_2$ (1 equiv) was added to a solution of **4**, we were surprised to find immediate H_2 evolution from the solution⁴ and formation of a novel metallasilacyclobutadiene complex (**5**, Scheme 1).⁵ Similarly, addition of a solution of $PhR'SiH_2$ to a solution of $(Me_3SiCH_2)_3Ta(PMe_3)=CHSiMe_3$ (**6**)⁶ resulted in a nearly quantitative conversion (by NMR) of **6** to $(Me_3SiCH_2)_3Ta[=C(SiMe_3)SiPhR'H]$ (**7**),⁵ again with evolution of H_2 . The reaction of the silane with **4** and **6** occurred *exclusively* with the $=CHSiMe_3$ ligands, and the resulting products **5** and **7** were inert toward further reaction with excess silane. In contrast, Berry and co-workers have observed that $Cp_2Ta(=CH_2)CH_3$ reacts with tBu_2SiH_2 to give $Cp_2Ta(H)=CHSiHBu^t_2$ through a mechanism involving oxidative addition of the silane to a d^2 center, followed by CH_4 elimination and alkylidene transfer and insertion steps.^{7a} Bercaw and co-workers have reported that the formation of d^0 $Cp^*Ta(H)(CH_3)SiH_3$ ($Cp^* =$ pentamethylcyclopentadienyl) from the reaction of d^0 $Cp^*_2Ta(H)=CH_2$ with SiH_4 is through the oxidative addition of SiH_4 to d^2 $Cp^*_2Ta-CH_3$, which is in equilibrium with $Cp^*_2Ta(H)=CH_2$.^{7b} It is interesting to point out that no reaction was observed between **4** and tBu_2SiH_2 in benzene- d_6 , even at 65 °C.⁸

Spectroscopic properties of **5** and **7** are consistent with the structure assignments.⁵ The ^{13}C NMR alkylidene resonances of **5a,b** and **7a,b** range from 238.2 to 255.4 ppm and appear as

Scheme 1



singlets in the gated-decoupled ^{13}C spectra. The molecular structures of **5a,b** have been determined by X-ray crystallography and are found to be similar. The structure of **5a** is shown in Figure 1.⁹ Complex **5a** exhibits distorted trigonal bipyramidal geometry around the tantalum center, with the PMe_3 ligands occupying axial positions. The $Ta=C$ bond distances of 1.947(12) and 1.962(12) Å are consistent with those observed for other alkylidene complexes of tantalum (1.998(8) and 1.95(2) Å in **4**,² 1.932(7) and 1.955(7) Å in $Ta(=CHBu^t)_2$ -(mesityl)(PMe_3)₂,¹⁰ and 1.932(9) Å in $[Ta(=CHBu^t)(CH_2Bu^t)(PMe_3)_2]_2(\mu-N_2)$ ¹¹). The metallasilacyclobutadiene ring in **5a** is planar (average deviation from least-squares plane = 0.007 Å), which brings the silicon atom in close proximity to the tantalum center ($Ta-Si$ distance of 2.607(3) Å); however, the fact that the metal center is formally d^0 makes any metal-silicon bonding interaction unlikely.¹² The silicon atom of the metallasilacyclobutadiene ring in **5a** exhibits distorted tetrahedral geometry, with bond angles ranging from 96.7(5)° to 115.9(6)°. The structure of **5a** is novel, and to our knowledge represents the first example of a 1,1-metallasilacyclobutadiene complex. A number of metallasilacyclobutane complexes have been synthesized and structurally characterized by Marks, Girolami, Wilkinson, Petersen, and others,^{13–16} and a large number of conjugated metallacyclobutadiene complexes are known;¹⁷ however, to our knowledge, complexes **5a,b** represent the first cyclobutadiene complexes in which both double bonds are localized exclusively on the metal atom.¹⁸

When the reaction of **6** with excess deuterated silane $PhMeSiD_2$ (2–5 equiv) was monitored by NMR, the predominant product was identified as $(Me_3SiCH_2)_3Ta=[C(SiPhMeD)SiMe_3]$ (**7a-d1**),⁵ along with a trace amount of **7a**. $PhMeSiHD$ and $PhMeSiH_2$ were also observed in the reaction mixture. The possibility of H incorporation into $PhMeSiD_2$ occurring by exchange with the Me_3SiCH_2 -ligands of **6** was investigated by

(1) (a) Xue, Z.; Li, L.; Hoyt, L. K.; Diminnie, J. B.; Pollitte, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2169. (b) Li, L.; Diminnie, J. B.; Liu, X.; Pollitte, J. L.; Xue, Z. *Organometallics* **1996**, *15*, 3520. (c) Xue, Z. *Comments Inorg. Chem.* **1996**, *18*, 223. (d) Li, L.; Hung, M.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 12746. (e) For a review of transition metal silyl complexes, see: Tilley, T. D. In *The Silicon Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapters 9 and 10. Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351.

(2) Diminnie, J. B.; Hall, H. D.; Xue, Z. *J. Chem. Soc., Chem. Commun.* **1996**, 2383.

(3) Fellmann, J. D.; Schrock, R. R.; Rupprecht, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5752.

(4) A signal is observed at 4.47 ppm (relative to C_6D_5H at 7.15 ppm), whose chemical shift is identical to that of H_2 in benzene- d_6 prepared independently.

(5) See the Supporting Information for experimental and spectroscopic details.

(6) Rupprecht, G. A. Ph.D. Thesis, Massachusetts Institute of Technology, 1979.

(7) (a) Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* **1990**, *9*, 2952. (b) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

(8) After a benzene- d_6 solution of **4** and excess tBu_2SiH_2 was heated for 24 h at 65 °C, a 5% thermal decomposition of **4** to $(Me_3SiCH_2)_4Ta_2(\mu-CSiMe_3)_2$ ¹⁹ had occurred; however, no reaction with tBu_2SiH_2 was observed.

(9) Crystal data for **5a**: monoclinic, $P2_1/n$ (No. 14), $a = 10.647(3)$ Å, $b = 17.757(6)$ Å, $c = 18.686(5)$ Å, $\beta = 96.91(3)^\circ$, $V = 3507(2)$ Å³, $Z = 4$, $R(R_wF^2) = 5.04$ (12.40)% with 4617 unique reflections with $F > 2.0\sigma(F)$, GOF = 1.03, number of parameters refined = 289.

(10) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930.

(11) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 2899. Turner, H. W.; Fellmann, J. D.; Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 7809.

(12) Our preliminary *ab initio* quantum mechanics calculations support this conclusion. Wu, Y.-D.; Xue, Z. Unpublished results.

(13) Tikkanen, W. R.; Liu, J. Z.; Egan, J. W., Jr.; Petersen J. L. *Organometallics* **1984**, *3*, 825.

(14) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357.

(15) Behling, T.; Girolami, G. S.; Wilkinson, G. J. *Chem. Soc., Dalton Trans.* **1984**, 877.

(16) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

(17) For a review of metallacyclobutadiene complexes, see: (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988; Chapter 7. (b) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281 and references therein.

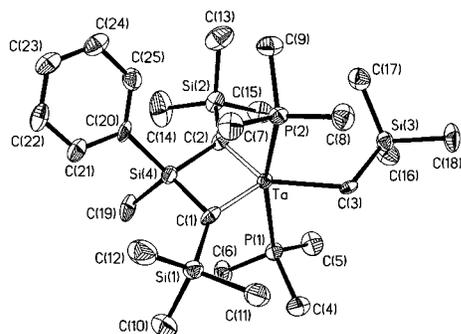
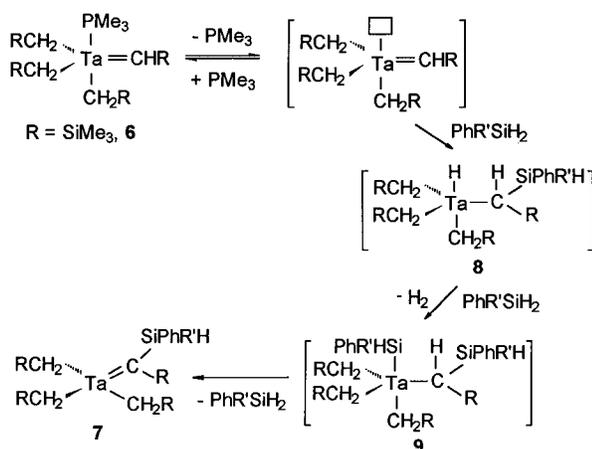


Figure 1. ORTEP of **5a**, showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Ta–C(1) 1.947(12), Ta–C(2) 1.962(12), Ta–C(3) 2.285(11), Ta–P(1) 2.605(3), Ta–P(2) 2.665(3), C(1)–Si(4) 1.901(11), C(2)–Si(4) 1.900(11), C(1)–Si(1) 1.832(12), C(2)–Si(2) 1.819(11), P(1)–Ta–P(2) 161.97(10), P(1)–Ta–C(3) 80.7(3), P(2)–Ta–C(3) 85.6(3), C(1)–Ta–C(2) 93.1(4), C(1)–Ta–C(3) 134.4(4), C(2)–Ta–C(3) 132.5(4), C(1)–Si(4)–C(2) 96.7(5), Ta–C(1)–Si(4) 85.3(5), Ta–C(2)–Si(4) 84.9(5).

Scheme 2

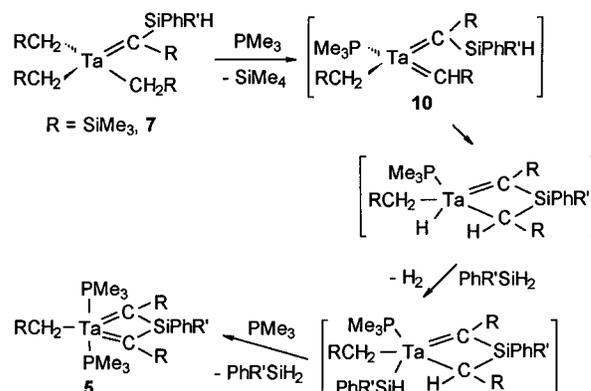


monitoring a solution containing PhMeSiD_2 and $(\text{Me}_3\text{SiCH}_2)_4\text{Ta}_2(\mu\text{-CSiMe}_3)_2$,¹⁹ which we had found to be inert toward reaction with PhMeSiH_2 . No such H/D exchange was observed by ^1H NMR over 2.5 h at 50 °C, ruling out exchange with residual protons in the solvent and suggesting that exchange with $-\text{CH}_2\text{SiMe}_3$ ligands would be unlikely. In addition, analysis of the gaseous products from the reaction with PhMeSiD_2 by mass spectrometry showed the predominant product to be D_2 , with some HD also present.⁵ These observations lead us to propose a possible mechanism for the formation of **7** (Scheme 2). The silane first reacts by addition across the Ta=C bond to form a hydride (deuteride) intermediate **8**, which then reacts with a second equivalent of silane, producing H_2 (D_2) and a silyl intermediate **9**. Complex **9** then undergoes α -hydrogen abstraction by the $-\text{SiPhR}'\text{H}$ ligand to yield **7**, reforming the silane in the process. With $\text{PhR}'\text{SiD}_2$, this final step would yield $\text{PhR}'\text{SiHD}$, which could further react to form $\text{PhR}'\text{SiH}_2$, consistent with the results obtained from the reaction with PhMeSiD_2 .

(18) Metallacyclopentadiene and -trienene complexes have been reported; see, e.g.: (a) Johnson, E. S.; Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 7685. (b) Hessen, B.; Teuben, J. H. *J. Organomet. Chem.* **1989**, *367*, C18.

(19) Mowat, W.; Wilkinson, G. *J. Chem. Soc. Dalton Trans.*, **1973**, 1120.

Scheme 3



Workup of the reaction mixture to produce **7** yields a red oil of reasonably pure (>95% by ^1H NMR) **7**. However, all attempts to isolate analytically pure samples of this compound were unsuccessful, as **7** was found to be thermally unstable. When monitored by NMR in benzene- d_6 , **7** slowly decomposed through SiMe_4 elimination; however, a solution of **7** in benzene could be frozen and stored at -20 °C for several weeks without significant decomposition. When the reaction to form **7** is monitored by NMR, a partial conversion of **7** to **5**, along with formation of SiMe_4 , is observed after several days; **5** is not observed during the formation of **7**. A possible mechanism for this conversion is shown in Scheme 3. Reactions similar to those shown in Scheme 3 may be involved in the conversion of **4** to **5**: attack of one of the alkylidene ligands to produce H_2 and **10**, followed by intramolecular attack of the alkylidene $-\text{SiPhR}'\text{H}$ group on the second alkylidene as proposed above to give **5**, with a small excess of silane acting as a catalyst.

The preferential reaction of the alkylidene ligands, rather than the alkyl ligands, of **4** and **6** with $\text{PhR}'\text{SiH}_2$ was unexpected. In order to probe whether such a preference is general, the reaction of the neopentyl analog **3** with PhMeSiH_2 was investigated. Surprisingly, no H_2 was observed; rather, a considerable amount of CMe_4 formed, along with a mixture of unidentified products.²⁰ It therefore appears that the silicon atoms in the $-\text{CH}_2\text{SiMe}_3$ and $=\text{CHSiMe}_3$ ligands of **4** may exert an important influence over the course of the reactions of silanes with alkylidene complexes.²¹ Kinetic studies are currently underway to further probe the possible mechanistic pathways of these reactions.

Acknowledgment is made to the NSF Young Investigator Award program (CHE-9457368), the DuPont Young Professor Award, the donors of the Petroleum Research Fund (28044-G3), administered by the American Chemical Society, and the Camille Dreyfus Teacher-Scholar Award for financial support of this research. We thank Professor Gregory Girolami for helpful discussion regarding the crystal structures of **5a,b** and Dr. Al Tuinman for assistance in obtaining mass spectra.

Supporting Information Available: Experimental and spectroscopic data for **5** and **7**; crystal structure of **5b** along with crystallographic and structural data for **5a,b** (23 pages). See any current masthead page for ordering and Internet access instructions.

JA972302F

(20) There was a report of the reactions of lanthanide alkyl complexes with silanes to produce alkylsilanes and metal hydride complexes. Voskoboinikov, A. Z.; Parshina, I. N.; Shestakova, A. K.; Butin, K. P.; Beletskaya, I. P.; Kuz'mina, L. G.; Howard, J. A. K. *Organometallics* **1997**, *16*, 4041.

(21) It is well-known that silicon stabilizes an adjacent carbon–metal bond. Fleming, I. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon: New York, 1979; Vol. 3, Chapter 13, p 541.