1504 *Organometallics* **2001,** *20,* 1504−1514

Articles

Reactions of Tantalum Alkylidene Complexes with Silanes. Synthesis and Characterization of Novel Metallasilacyclodiene Complexes and Kinetic and Mechanistic Studies of Their Formation

Jonathan B. Diminnie, Jaime R. Blanton, Hu Cai, Keith T. Quisenberry, and Ziling Xue*

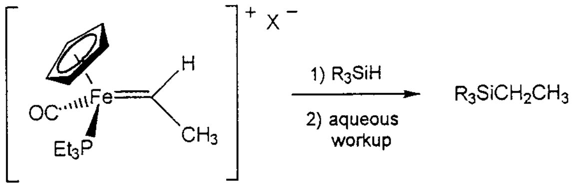
Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

Received June 5, 2000

The reactions of tantalum alkylidene complexes $(RCH_2)_3Ta(L){=}CHR$ (**1**) and $RCH_2Ta(L)_2[{=}CHR]_2$ (**3**) ($R = SiMe_3$, $L = PMe_3$) with phenylsilanes $H_2SiR'Ph$ ($R' = Me, Ph$) and $(PhSiH_2)_2CH_2$ were found to produce bis(silyl)-substituted alkylidene complexes $(RCH_2)_3Ta{=}CR(SiHR'Ph)$ (**4**) and novel metallasilacyclobutadiene and metalladisilacyclohexadiene complexes. Reaction of the mixed-ligand trimethylsilylmethyl neopentylidene complex $RCH_2Ta(L)_2[{=}CHBu^t]_2$ (**6**) with $H_2SiMePh$ also yielded a metallasilacyclobutadiene complex, but reaction of the neopenyl neopentylidene complex $Bu^tCH_2Ta(L)_2[{=}CHBu^t]_2$ (**2**) with $H_2SiMePh$ yielded unidentified products. Deuterium-labeling and kinetic studies of the conversion of **1** → **4** were found to be consistent with a dissociative mechanism. The structures of the novel metallacyclic complexes **5a**, **5b**, **7**, and **8** were determined by X-ray crystallography.

Early transition metal alkylidene complexes have been the subject of enthusiastic study since the first alkylidene complex, $(Bu^tCH_2)_3Ta{=}CHBu^t$, was prepared by Schrock in 1973.[1] Alkylidene complexes have been widely studied for their roles in effecting reactions such as alkene and alkyne metathesis as well as olefin polymerization.[2] However, the reactivity of alkylidene complexes toward silanes is a relatively unexplored area. The complex $Cp_2Ta({=}CH_2)CH_3$ was found to react with $H_2SiBu^t_2$ to give $Cp_2Ta(H){=}CHSiHBu^t_2$ through a mechanism involving oxidative addition of the silane to a d^2 Ta(III) center, followed by CH_4 elimination and alkylidene transfer and insertion steps.[3] The formation of d^0 $Cp^*_2Ta(H)(CH_3)SiH_3$ (Cp^* = pentamethylcyclopentadienyl) from the reaction of $Cp^*_2Ta(H){=}CH_2$ with SiH_4 was found to occur via oxidative addition of SiH_4 to d^2 $Cp^*_2Ta{-}CH_3$, which is in equilibrium with $Cp^*_2Ta(H){=}CH_2$.[4] In contrast, the reactions of some other carbene complexes with silanes led to insertion reactions of the carbene moiety into the Si−H bond to yield alkyl silanes (Scheme 1).[5] Mechanistic studies revealed that these reactions involved direct insertion of the carbene unit into the Si−H bond[5a] and that the cleavage of the Si−H bond and the formation of the new C−Si and C−H bonds were concerted.[5c] To our knowledge, no such direct reactions of silanes with the M═CHR moiety of an early transition metal alkylidene complex have been observed.[6]

Scheme 1



We are interested in the reactions of alkylidene complexes with silanes as part of our studies of the

---

(1) (a) Schrock, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 6796. (b) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359. (c) Fellmann, J. D.; Schrock, R. R.; Rupprecht, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5752. (d) Fellmann, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964.

(2) (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (c) Breslow, D. S. *Prog. Polym. Sci.* **1993**, *18*, 1141. (d) Sundararajan, G. *J. Sci. Ind. Res.* **1994**, *53*, 418.

(3) Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* **1990**, *9*, 2952.

(4) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

(5) (a) Scharrer, E.; Brookhart, M. *J. Organomet. Chem.* **1995**, *497*, 61. (b) Mak, C. C.; Tse, M. K.; Chan, K. S. *J. Org. Chem.* **1994**, *59*, 3585. (c) Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *Tetrahedron Lett.* **1997**, *38*, 229. (d) Fischer, E. O.; Dötz, K. H. *J. Organomet. Chem.* **1972**, *36*, C4.

(6) For reactions of metal complexes with silanes and silyl chemistry, see, for example: (a) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175. (b) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z.; Eds.; Wiley: New York, 1989; Part 2, p 1415. (c) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z.; Eds.; Wiley: New York, 1991; p 245 and p 309. (d) Eisen, M. S. In *The Chemistry of Organic Silicon Compounds*, Vol. 2; Rappoport, Z.; Apeloig, Y.; Eds.; Wiley: New York, 1998; Part 3, p 2037. (e) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363.

10.1021/om000476r CCC: $20.00
Publication on Web 03/22/2001

reactions of silanes with coordinated ligands.[7] We are particularly interested in how H−Si bonds in silanes react with the π-bonds in the M═CHR moiety of Cp-free, high-oxidation-state alkylidene complexes. We have chosen alkylidene complexes containing phosphine ligands (RCH$_2$)Ta(PMe$_3$)$_2$[═CHR′]$_2$, in the hope that such ligands would help stabilize the resulting reaction products. In this paper, we report the synthesis and characterization of novel bis(silyl)-substituted alkylidene, metallasilacyclobutadiene, and metalladisilacyclohexadiene complexes and kinetic and mechanistic studies of the reactions of an alkylidene complex with silanes. Preliminary results have been reported.[8]

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere with the use of either standard Schlenk techniques or a glovebox. All solvents were purified by distillation from potassium/benzophenone ketyl. Benzene-d_6 and toluene-d_8 were dried over activated molecular sieves and stored under nitrogen. NMR spectra were recorded on a Bruker AC-250, AMX-400, or Varian INOVA 600 Fourier transform spectrometer and were referenced to solvents (residual protons in the ^{1}H spectra). ^{29}Si, ^{31}P, and ^{2}H chemical shifts were referenced to SiMe$_4$, external 85% H$_3$PO$_4$, and external toluene-d_8, respectively. Mass spectra were recorded on a VG ZAB-EQ hybrid high-performance mass spectrometer at an ionization voltage of 70 eV. TaCl$_5$ (Strem) was sublimed before use. PMe$_3$ (Aldrich) and 1.0 M anhydrous HCl in Et$_2$O (Aldrich) were used as received. H$_2$SiMePh (Gelest) and H$_2$SiPh$_2$ (Aldrich) were dried over activated molecular sieves and stored under nitrogen. Me$_3$SiCH$_2$MgCl,[9] (Bu^{t}CH$_2$)$_3$Ta═CHBu^t,[1a,b] (Bu^{t}CH$_2$)Ta(PMe$_3$)$_2$[═CHBu^t]$_2$ (**2**),[1c] (Me$_3$SiCH$_2$)Ta(PMe$_3$)$_2$[═CHSiMe$_3$]$_2$ (**3**),[10] and D$_2$SiMePh[11] were prepared by the literature procedures. (PhSiH$_2$)$_2$CH$_2$ was prepared by a procedure similar to that in the literature.[12] Elemental analyses were performed by E + R Microanalytical, Parsippany, NJ.

Preparation of (Me$_3$SiCH$_2$)$_3$Ta(PMe$_3$)[═CHSiMe$_3$] (1). The following is a modified procedure from the previously reported synthesis.[13] A slurry of 5.0 g (0.014 mol) of TaCl$_5$ in 75 mL of hexanes at −20 °C was treated dropwise with 41.0 mL of a Me$_3$SiCH$_2$MgCl solution in Et$_2$O (1.7 M, 0.070 mol). The mixture turned green, then green-yellow, and finally bright yellow as (Me$_3$SiCH$_2$)$_5$Ta was produced. The reaction was monitored carefully by ^{1}H NMR until complete conversion to (Me$_3$SiCH$_2$)$_5$Ta[14] was achieved, at which time the solvents were removed in vacuo. The yellow residue was taken up in hexanes at 0 °C and filtered to remove MgCl$_2$. PMe$_3$ (1.7 mL, 0.017 mol) was then added by syringe, and the solution was heated to 50 °C for 1 h, during which time a bright orange color developed. At this time NMR showed the conversion to **1** to be complete, and the solution was filtered to remove any remaining MgCl$_2$, concentrated, and cooled to −20 °C, producing 7.8 g (92%) of **1** as bright orange crystals. NMR: ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 6.17 (s, 1H, ═C*H*SiMe$_3$), 0.89 (d, 9H, $^{2}J_{H-P}$ = 4.4 Hz, P*Me*$_3$), 0.30 (s, 9H, ═CHSi*Me*$_3$), 0.27 (s, 27H, CH$_2$Si*Me*$_3$), 0.24 (s, 6H, C*H*$_2$SiMe$_3$); ^{13}C{^{1}H} NMR (benzene-d_6, 62,9 MHz, 23 °C) δ 251.8 (═*C*HSiMe$_3$), 77.3 (*C*H$_2$SiMe$_3$), 15.9 (d, $^{1}J_{C-P}$ = 8.6 Hz, P*Me*$_3$), 3.6 (═CHSi*Me*$_3$), 3.0 (CH$_2$Si*Me*$_3$).

Preparation of (Me$_3$SiCH$_2$)Ta(PMe$_3$)$_2$[═CHBu^t]$_2$ (6). A solution of 1.24 g of (^{t}BuCH$_2$)$_3$Ta═CHBu^t (2.67 mmol) in 20 mL of toluene at −60 °C was treated dropwise with 12.6 mL of HCl in Et$_2$O (0.21 M, 2.6 mmol). The HCl/Et$_2$O was prepared by diluting 2.6 mL of 1.0 M HCl in Et$_2$O with 10 mL of Et$_2$O. The resulting solution of (Bu^{t}CH$_2$)$_4$TaCl[1d] was then treated with 0.60 mL of PMe$_3$ (5.8 mmol, excess) and warmed to room temperature with stirring. After 4 h NMR spectra of the resulting orange solution showed complete conversion to ClTa(PMe$_3$)$_2$[═CHBu^t]$_2$.[1c] Me$_3$SiCH$_2$MgCl in Et$_2$O (2.8 mL, 1.12 M, 3.1 mmol) was then added to the solution. After 1 h, the volatiles were removed by vacuum, and the yellow-brown residue was extracted with 30 mL of pentane. The pentane solution was then filtered, concentrated, and cooled to −20 °C, yielding three crops of orange crystals totaling 0.743 g (49.9% yield based on (Bu^{t}CH$_2$)$_3$Ta═CHBu^t). NMR: ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 7.27 (s, 1H, ═C*H*Bu^t), 1.44 (s, 1H, ═C*H*Bu^t), 1.26 (t, 18H, $^{2}J_{H-P}$ = 2.7 Hz, P*Me*$_3$), 1.25 (s, 18H, ═CHC*Me*$_3$), 0.27 (s, 9H, CH$_2$Si*Me*$_3$), −0.27 (t, 2H, $^{3}J_{H-P}$ = 20.1 Hz, C*H*$_2$SiMe$_3$); ^{13}C{^{1}H} NMR (benzene-d_6, 62,9 MHz, 23 °C) δ 273.1, 242.2 (═*C*HBu^t), 47.4, 44.1 (═CH*C*Me$_3$), 37.3 (*C*H$_2$SiMe$_3$), 35.3, 34.3 (═CHC*Me*$_3$), 19.3 (t, $^{1}J_{C-P}$ = 11.6 Hz, P*Me*$_3$), 5.2 (CH$_2$Si*Me*$_3$). Anal. Calcd for C$_{20}$H$_{49}$SiP$_2$Ta: C, 42.85; H, 8.81. Found: C, 42.84; H, 8.82.

Preparation of (Me$_3$SiCH$_2$)$_3$Ta[═C(SiMe$_3$)SiHRPh] (R = Me, 4a; Ph, 4b). A solution of 0.90 g (1.5 mmol) of **1** in 30 mL of hexanes was treated dropwise with a solution of 0.20 g (1.6 mmol) of H$_2$SiMePh in 5 mL of hexanes. The reaction mixture was then stirred for 18 h at room temperature, during which time the color changed from orange to red-orange. Removal of solvent yielded ca. 0.9 g of a red-orange oil of **4a**, which also contained a small (<5% by ^{1}H NMR) amount of (Me$_3$SiCH$_2$)$_4$Ta$_2$(μ-CSiMe$_3$)$_2$. Attempts to crystallize the compound were unsuccessful, and the instability of **4a** in solution precluded attempts to obtain analytically pure samples for microanalysis. A similar result was obtained for **4b**. Data for **4a**: ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 7.20−7.90 (m, 5H, SiHMe*Ph*), 4.90 (q, 1H, $^{3}J_{H-H}$ = 3.6 Hz, Si*H*MePh), 1.20 (d, 3H, $^{2}J_{H-H}$ = 12.1 Hz, CH_aH$_b$SiMe$_3$), 0.92 (d, 3H, CH$_a$$H_b$SiMe$_3$), 0.80 (d, 3H, SiH*Me*Ph), 0.30 (s, 9H, ═CSi*Me*$_3$), 0.19 (s, 27H, CH$_2$Si*Me*$_3$); ^{13}C{^{1}H} NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 240.6 (═*C*SiMe$_3$), 137.6, 135.3, 129.5, 128.0 (SiHMe*Ph*), 89.6 (*C*H$_2$SiMe$_3$), 5.0 (═CSi*Me*$_3$), 2.7 (CH$_2$Si*Me*$_3$), −1.9 (SiH*Me*Ph); ^{29}Si{^{1}H} NMR (benzene-d_6, 79.5 MHz, 27 °C) δ 0.08 (CH$_2$*Si*Me$_3$), −13.2 (═C*Si*Me$_3$), −49.9 (═C*Si*HMePh). Data for **4b**: ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 7.20−7.90 (m, 10H, SiH*Ph*$_2$), 5.07 (s, 1H, Si*H*Ph$_2$), 1.19 (s, 6H, C*H*$_2$SiMe$_3$), 0.31 (s, 9H, ═CSi*Me*$_3$), 0.19 (s, 27H, CH$_2$Si*Me*$_3$); ^{13}C{^{1}H} NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 238.2 (═*C*SiMe$_3$), 137.5, 136.5, 129.7, 128.1 (SiH*Ph*$_2$), 90.7 (*C*H$_2$SiMe$_3$), 5.19 (═CSi*Me*$_3$), 2.72

---

(7) (a) Liu, X.; Wu, Z.; Peng, Z.; Wu, Y.; Xue, Z. *J. Am. Chem. Soc.* **1999**, *121*, 5350. See also: (b) Xue, Z. *Comments Inorg. Chem.* **1996**, *18*, 223. (c) Chen, T.; Xue, Z. *Chin. J. Inorg. Chem.* **1999**, *15*, 413. (d) Xue, Z.; Li, L.; Hoyt, L. K.; Diminnie, J. B.; Pollitte, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2169. (e) Li, L.; Diminnie, J. B.; Liu, X.; Pollitte, J. L.; Xue, Z. *Organometallics* **1996**, *15*, 5231. (f) McAlexander, L. H.; Hung, M.; Li, L.; Diminnie, J. B.; Xue, Z.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1996**, *15*, 3520. (g) Wu, Z.; Diminnie, J. B.; Xue, Z. *Organometallics* **1998**, *17*, 2917. (h) Wu, Z.; McAlexander, L. H.; Diminnie, J. B.; Xue, Z. *Organometallics* **1998**, *17*, 4853. (i) Chen, T.; Wu, Z.; Li, L.; Sorasaenee, K. R.; Diminnie, J. B.; Pan, H.; Guzei, I. A.; Rheingold, A. L.; Xue, Z. *J. Am. Chem. Soc.* **1998**, *120*, 13519. (j) Liu, X.; Li, L.; Diminnie, J. B.; Yap, G. P. A.; Rheingold, A. L.; Xue, Z. *Organometallics* **1998**, *17*, 4597. (k) Wu, Z.; Diminnie, J. B.; Xue, Z. *Inorg. Chem.* **1998**, *37*, 6366. (l) Wu, Z.; Diminnie, J. B.; Xue, Z. *Organometallics* **1999**, *18*, 1002. (m) Choi, S.-H.; Lin, Z.; Xue, Z. *Organometallics* **1999**, *18*, 5488. (n) Wu, Z.; Diminnie, J. B.; Xue, Z. *J. Am. Chem. Soc.* **1999**, *121*, 4300.

(8) Diminnie, J. B.; Xue, Z. *J. Am. Chem. Soc.* **1997**, *119*, 12657.

(9) (a) Whitmore, F. C.; Sommer, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 481. (b) Moorhouse, S.; Wilkinson, G. *J. Organomet. Chem.* **1973**, *52*, C5. (c) Moorhouse, S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1974**, 2187.

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

(11) Watanabe, H.; Ohsawa, N.; Sudo, T.; Hirakata, K.; Nagai, Y. *J. Organomet. Chem.* **1977**, *128*, 27.

(12) Zech, J.; Schmidbaur, H. *Chem. Ber.* **1990**, *123*, 2087. In the current procedure, CH$_2$Cl$_2$ was used in lieu of CH$_2$Br$_2$ to react with 2 equiv of H$_2$SiClPh and Mg/Zn dust to give (PhSiH$_2$)$_2$CH$_2$ in 43% yield.

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

(14) Li, L.; Hung, M.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 12746.

(CH$_2$Si*Me*$_3$); ^{29}Si{^{1}H} NMR (benzene-d_6, 79.5 MHz, 27 °C) δ 0.37 (CH$_2$*Si*Me$_3$), −13.1 (=C*Si*Me$_3$), −48.3 (=C*Si*HPh$_2$).

Preparation of Metallasilacyclobutadiene Complexes. Synthesis of 5a. A solution of 0.204 g (0.344 mmol) of (Me$_3$SiCH$_2$)Ta(PMe$_3$)$_2$[=CHSiMe$_3$]$_2$ (**3**) in 10 mL of hexanes was treated with 0.044 g (0.35 mmol) of H$_2$SiMePh in 5 mL of hexanes. The solution was stirred at room temperature for 3 h, during which time the color changed from bright orange to yellow. The solution was then concentrated and cooled to −20 °C, producing 0.190 g (78%) of **5a** as yellow crystals. NMR: ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 7.17−7.86 (m, 5H, SiMe*Ph*), 1.12 (d, 9H, $^2J_{H-P}$ = 6.6 Hz, P*Me*$_3$), 1.00 (s, 3H, Si*Me*Ph), 0.88 (d, 9H, $^2J_{H-P}$ = 6.7 Hz, P*Me*$_3$), 0.35 (s, 18H, =CSi*Me*$_3$), 0.25 (s, 9H, CH$_2$Si*Me*$_3$), −0.46 (t, 2H, $^3J_{H-P}$ = 16.0 Hz, C*H*$_2$SiMe$_3$); ^{13}C{^{1}H} NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 255.1 (=*C*SiMe$_3$), 145.8, 136.3, 127.8, 127.2 (SiMe*Ph*), 50.4 (*C*H$_2$SiMe$_3$), 17.9 (d, $^1J_{C-P}$ = 12.5 Hz, P*Me*$_3$), 17.6 (d, $^1J_{C-P}$ = 12.9 Hz, P*Me*$_3$), 5.9 (=CSi*Me*$_3$), 5.8 (Si*Me*Ph), 5.8 (CH$_2$Si*Me*$_3$); ^{29}Si{^{1}H} NMR (benzene-d_6, 79.5 MHz, 27 °C) δ 0.40 (CH$_2$*Si*Me$_3$), −15.4 (=C*Si*Me$_3$), −76.8 (*Si*MePh); ^{31}P{^{1}H} NMR (benzene-d_6, 162.0 MHz, 27 °C) δ −4.51 (d, $^2J_{P-P}$ = 125 Hz), −7.03 (d). The ^{13}C resonance assignments were confirmed by the use of ^{13}C−^{1}H HETCOR NMR. Anal. Calcd for C$_{25}$H$_{55}$P$_2$Si$_4$Ta: C, 42.24; H, 7.80. Found: C, 42.11; H, 7.69.

Synthesis of 5b. A solution of 0.199 g (0.336 mmol) of **3** in 10 mL of hexanes was treated dropwise with 0.070 g (0.38 mmol) of H$_2$SiPh$_2$ in 5 mL of hexanes. The reaction solution was stirred for 4 h, during which time the color changed from bright orange to yellow. The solution was then concentrated and cooled to −20 °C, producing 0.114 g of **5b** as yellow needles (44.0% yield). NMR: ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 7.09−7.89 (m, 10H, Si*Ph*$_2$), 0.94 (t, 18H, $^2J_{H-P}$ = 3.14 Hz, P*Me*$_3$), 0.41 (s, 18H, =CSi*Me*$_3$), 0.26 (s, 9H, CH$_2$Si*Me*$_3$), −0.41 (t, 2H, $^3J_{H-P}$ = 15.8 Hz, C*H*$_2$SiMe$_3$); ^{13}C{^{1}H} NMR (benzene-d_6, 62,9 MHz, 23 °C) δ 255.4 (=*C*SiMe$_3$), 143.3, 137.4, 128.0, 127.1 (Si*Ph*$_2$), 52.5 (*C*H$_2$SiMe$_3$), 17.5 (t, $^1J_{C-P}$ = 11.3 Hz, P*Me*$_3$), 6.55 (=CSi*Me*$_3$), 5.83 (CH$_2$Si*Me*$_3$); ^{29}Si{^{1}H} NMR (benzene-d_6, 79.49 MHz, 27 °C) δ 0.70 (CH$_2$*Si*Me$_3$), −16.6 (=C*Si*Me$_3$), −75.5 (*Si*Ph$_2$); ^{31}P{^{1}H} NMR (benzene-d_6, 162.0 MHz, 27 °C) δ −6.72. Anal. Calcd for C$_{30}$H$_{57}$P$_2$Si$_4$Ta: C, 46.61; H, 7.43. Found: C, 46.45; H, 7.49.

Synthesis of 7. A solution of 0.548 g of (Me$_3$SiCH$_2$)Ta(PMe$_3$)$_2$[=CHBu^t]$_2$ (**6**, 0.978 mmol) in 10 mL of pentane was treated with 0.236 mL of H$_2$SiMePh (1.93 mmol) in 2 mL of pentane. The solution was stirred for 2 h, during which time the color changed from yellow-orange to orange. Concentration and cooling of the solution to −20 °C yielded 0.249 g of **7** as yellow crystals (37.5%). NMR: ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 7.10−8.00 (m, 5H, Si*Ph*Me), 1.40 (s, 18H, =CC*Me*$_3$), 1.18 (d, 9H, $^2J_{H-P}$ = 6.2 Hz, P*Me*$_3$), 1.12 (s, 3H, SiPh*Me*), 1.09 (br d, 9H, $^2J_{H-P}$ = 6.3 Hz, P*Me*$_3$), 0.28 (s, 9H, CH$_2$Si*Me*$_3$), −0.46 (br t, 2H, $^3J_{H-P}$ = 15.2 Hz, C*H*$_2$SiMe$_3$); ^{13}C{^{1}H} NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 271.9 (=*C*Bu^t), 145.4, 138.0, 127.1, 126.5 (SiMe*Ph*), 51.0 (*C*H$_2$SiMe$_3$), 47.9 (=C*C*Me$_3$), 37.3 (=CC*Me*$_3$), 18.5 (overlapping d, P*Me*$_3$), 5.95 (CH$_2$Si*Me*$_3$), 3.82 (Si*Me*Ph). Anal. Calcd for C$_{27}$H$_{55}$P$_2$Si$_2$Ta: C, 47.78; H, 8.17. Found: C, 47.76; H, 8.18.

Reaction of (Bu^{t}CH$_2$)Ta(PMe$_3$)$_2$[=CHBu^t]$_2$ (2) with H$_2$SiMePh. Complex **2** (0.029 g, 0.053 mmol) was dissolved in benzene-d_6 in an NMR tube. H$_2$SiMePh (0.025 g, 0.20 mmol) was added to the NMR tube. NMR spectra of the solution showed the products to be H$_2$, neopentane (CMe$_4$), PMe$_3$, and other unidentified species. Another attempt in hexanes with 0.191 g of **2** and 0.050 g of H$_2$SiMePh gave, after removal of solvent, a red oil whose NMR spectra were similar to those observed above.

Synthesis of the Metalladisilacyclohexadiene Complex 8. A solution of 0.860 g (1.45 mmol) of **3** in 15 mL of pentane was treated dropwise with a solution of 0.378 g (1.65 mmol) of (PhSiH$_2$)$_2$CH$_2$ in 2 mL of pentane. The solution was stirred for 16 h, during which time the color changed from bright orange to yellow-orange. The solution was concentrated and cooled to −20 °C, yielding 0.119 g of **8** as yellow crystals (10.0%). Data for **8**: ^{1}H NMR (toluene-d_8, 400.1 MHz, 27 °C) δ 7.13−7.75 (m, 10H, SiH*Ph*), 5.82 (m, 2H, Si*H*Ph), 1.41 (m, 1H, Si−C*H*$_a$H$_b$−Si), 1.38 (2 overlapping d, 18H, P*Me*$_3$), 0.88 (m, 1H, Si−CH$_a$*H*$_b$−Si), 0.22 (s, 9H, CH$_2$Si*Me*$_3$), 0.039 (s, 18H, =CSi*Me*$_3$), −0.58 (br t, 2H, $^3J_{H-P}$ = 15.6 Hz, C*H*$_2$SiMe$_3$); ^{13}C{^{1}H} NMR (toluene-d_8, 100.6 MHz, 27 °C) δ 262.7 (=*C*SiMe$_3$), 145.4, 135.3, 128.5, 127.7 (*Ph*), 67.1 (*C*H$_2$SiMe$_3$), 18.6 (d, $^1J_{C-P}$ = 21.1 Hz, P*Me*$_3$), 16.7 (br d, $^1J_{C-P}$ = 21.1 Hz, P*Me*$_3$), 13.7 (Si−*C*H$_2$−Si), 6.22 (=CSi*Me*$_3$), 5.24 (CH$_2$Si*Me*$_3$); ^{29}Si{^{1}H} NMR (toluene-d_8, 79.5 MHz, 27 °C) δ 10.5 (CH$_2$*Si*Me$_3$), −11.9 (*Si*−CH$_2$−*Si*), −19.3 (=C*Si*Me$_3$); ^{31}P{^{1}H} NMR (toluene-d_8, 162.0 MHz, 27 °C) δ 3.07 (d, $^2J_{P-P}$ = 155.8 Hz), −0.21 (d). The assignment of two overlapping doublets for the PMe$_3$ groups in the ^{1}H spectrum was confirmed by an HMQC (heteronuclear multiple quantum coherence) experiment. Anal. Calcd for C$_{31}$H$_{61}$P$_2$Si$_5$Ta: C, 45.57; H, 7.52. Found: C, 45.53; H, 7.53.

Reaction of 1 with D$_2$SiMePh and Analysis of the Hydrogen Gas Produced in This Reaction by Mass Spectrometry. To **1** (0.0303 g, 0.0501 mmol) dissolved in 0.4 mL of toluene-d_8 in an NMR tube was added 20.0 μL (0.143 mmol) of D$_2$SiMePh. The tube was then placed on an NMR spectrometer which had been preheated to 50 °C, and the reaction was monitored by NMR. After 20 min all of **1** had been consumed, and the products were identified as **4a-*d*$_1$** and PMe$_3$. HDSiMePh, H$_2$SiMePh, and a trace amount of **4a** were also identified. Data for **4a-*d*$_1$**: ^{1}H NMR (toluene-d_8, 400.1 MHz, 50 °C) δ 7.20−7.81 (m, 5H, Si*Ph*MeD), 1.10 (d, 3H, $^2J_{H-H}$ = 12.1 Hz, C*H*$_a$H$_b$SiMe$_3$), 0.91 (d, 3H, CH$_a$*H*$_b$SiMe$_3$), 0.75 (s, 3H, SiPh*Me*D), 0.26 (s, 9H, =CSi*Me*$_3$), 0.18 (s, 27H, CH$_2$Si*Me*$_3$); ^{13}C{^{1}H} NMR (toluene-d_8, 100.6 MHz, 50 °C) δ 241.1 (=*C*SiMe$_3$), 137.8, 135.3, 129.7, 128.0 (SiDMe*Ph*), 89.7 (*C*H$_2$SiMe$_3$), 5.0 (=CSi*Me*$_3$), 2.8 (CH$_2$Si*Me*$_3$), −1.8 (SiD*Me*Ph); ^{2}H NMR (toluene, 61.42 MHz, 27 °C) δ 4.92 (br s, Si*D*MePh). In a separate experiment with 0.045 g of **1**, 0.6 mL of toluene-d_8, and 47 μL (0.33 mmol) of D$_2$SiMePh, 4,4′-dimethylbiphenyl (3.0 mg, 0.016 mmol, Aldrich) was added to the solution at the beginning of the reaction as internal standard for NMR studies. After the reaction, ^{1}H NMR at 600 MHz revealed the presence of ca. 0.0065 mmol (0.088 equiv) of H$_2$SiMePh and 0.024 mmol (0.33 equiv) of HDSiMePh in the product mixture. The resonance of *H*DSiMePh is 0.010 ppm upfield-shifted from that of *H*$_2$SiMePh as a result of isotopic shift.

Three samples were prepared for analysis of hydrogen gas. In sample A, a J. Young valved NMR tube was charged with a solution of 0.045 g (0.074 mmol) of **1** in 0.6 mL of toluene-d_8 and 9.5 μL (0.068 mmol) of D$_2$SiMePh. The solution was immediately frozen in liquid nitrogen, and the tube was evacuated to remove nitrogen. The Teflon valve on the tube was then sealed, and the solution allowed to thaw and kept at 23 °C for 25 min, at which time gas evolution from the solution had ceased. The solution was frozen again in liquid nitrogen, and the tube connected to the mass spectrometer. The gaseous products were then pumped into the mass spectrometer. In sample B, a J. Young valved NMR tube was charged with a solution of 0.045 g (0.074 mmol) of **1** in 0.6 mL of toluene-d_8 and 47 μL (0.33 mmol) of D$_2$SiMePh. The procedure was repeated to obtain the mass spectrum of the gaseous products.

In sample C, a solution of 0.045 g (0.074 mmol) of **1** in 0.65 mL of toluene-d_8 and 47 μL (0.33 mmol) of D$_2$SiMePh was placed in a precalibrated J. Young valved NMR tube to give 2.51 mL of headspace. The tube was then immediately placed in liquid N$_2$ to freeze the solution. In this process, part of the headspace was cooled as well. N$_2$ in the tube was then removed in vacuo. H$_2$ at 1 atm was added to the tube to fill the headspace. The solution was then allowed to thaw and kept at 23 °C for 25 min, at which time gas evolution from the solution had ceased. The solution was frozen again in liquid N$_2$, and the tube was connected to the mass spectrometer to

Table 1. Crystallographic Information for 5a, 5b, 7, and 8

	5a	5b	7	8
formula	$C_{25}H_{55}P_2Si_4Ta$	$C_{30}H_{57}P_2Si_4Ta$	$C_{27}H_{55}P_2Si_2Ta$	$C_{31}H_{61}P_2Si_5Ta$
fw	710.94	773.01	678.78	817.14
cryst size (mm)	0.30× 0.20 × 0.20	0.36 × 0.20 × 0.05	0.30 × 0.22 × 0.05	0.32 × 0.26 × 0.20
temp (K)	173(2)	173(2)	173(2)	173(2)
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$Pnma$
lattice params	$a = 10.647(3)$ Å $b = 17.757(6)$ Å $c = 18.686(5)$ Å $\alpha = 90°$ $\beta = 96.91(3)°$ $\gamma = 90°$	$a = 12.199(5)$ Å $b = 16.428(5)$ Å $c = 19.526(6)$ Å $\alpha = 90°$ $\beta = 93.96(3)°$ $\gamma = 90°$	$a = 10.154(3)$ Å $b = 10.998(3)$ Å $c = 16.492(5)$ Å $\alpha = 101.92(2)°$ $\beta = 91.86(2)°$ $\gamma = 111.98(2)°$	$a = 10.667(3)$ Å $b = 17.314(4)$ Å $c = 25.591(5)$ Å $\alpha = 90°$ $\beta = 90°$ $\gamma = 90°$
volume, Å^3	3507(2)	3904(2)	1658.8(8)	4726(2)
Z	4	4	2	4
density(calc) (g/cm^3)	1.346	1.315	1.359	1.148
μ (mm^{-1})	3.374	3.037	3.495	2.536
F(000)	1456	1584	696	1680
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
θ range (deg)	2.10−22.55	1.62−22.54	2.05−22.54	2.07−22.55
index ranges	$h, k, \pm l$	$h, k, \pm l$	$h, \pm k, \pm l$	$h, k, \pm l$
no. of unique reflns	4617 ($R_{int} = 0.0352$)	5120 ($R_{int} = 0.0499$)	4355 ($R_{int} = 0.0384$)	3230 ($R_{int} = 0.0744$)
no. of params varied	289	334	289	208
R indices	0.0504 (wR2 = 0.1240)	0.0606 (wR2 = 0.1111)	0.0450 (wR2 = 0.0901)	0.0583 (wR2 = 0.1669)
goodness-of-fit on F^2	1.030	1.077	1.019	1.035

pump the gaseous products into the spectrometer. After the reaction, 4,4′-dimethylbiphenyl (4.1 mg, 0.022 mmol, Aldrich) was added to the solution as internal standard for subsequent NMR studies. ^{1}H NMR at 600 MHz of the product mixture showed the presence of ca. 0.0081 mmol (0.11 equiv) of $H_2SiMePh$ and 0.074 mmol (1.0 equiv) of HDSiMePh.

Kinetic Studies of the Conversion of 1→4a and 1→4a-*d*$_1$. In a glovebox an NMR tube was charged with **1** (12.8−45.0 mg) and 4,4′-dimethylbiphenyl (2.8−9.5 mg, an internal standard), which were then dissolved in 400 μL of toluene-d_8. $H_2SiMePh$ or $D_2SiMePh$ was then added to the NMR tube via calibrated micropipet so as to make $[H_2SiMePh]_0/[\mathbf{1}]_0$ between 5.34 and 34.8 and $[D_2SiMePh]_0/[\mathbf{1}]_0$ between 5.00 and 35.1. The contents of the NMR tube were then mixed, and the tube was cooled to −78 °C. The sample was then placed on an NMR spectrometer which had been precooled to 10 °C, and NMR spectra were recorded. The concentration of **1** was determined by integration with respect to the internal standard 4,4′-dimethylbiphenyl.

In kinetic studies involving excess PMe_3, **1** (28.1 mg, 0.0465 mmol), 4,4′-dimethylbiphenyl (1.3 mg), and 420 μL (396 mg) of toluene-d_8 were placed in an NMR tube. PMe_3 (97 μL, 71 mg, 0.94 mmol) and $H_2SiMePh$ (34 μL, 30 mg, 0.25 mmol) were then added to this solution at 24 °C to make $[H_2SiMePh]_0/[\mathbf{1}]_0$ approximately 5.4. The reaction was conducted at 24 °C and monitored by ^{1}H and ^{13}C NMR. In a control experiment, **1** (28.6 mg, 0.0473 mmol) and 4,4′-dimethylbiphenyl (5.1 mg) were dissolved in 536 μL (504 mg) of toluene-d_8. $H_2SiMePh$ (34 μL, 30 mg, 0.25 mmol) was then added at 24 °C to make $[H_2SiMePh]_0/[\mathbf{1}]_0$ approximately 5.3. This reaction at 24 °C was monitored by ^{1}H NMR.

X-ray Crystal Structure Determinations of 5a, 5b, 7, and 8. All crystal structures were determined on a Siemens R3m/V diffractometer fitted with a Nicolet LT-2 low-temperature device. Suitable crystals were coated with Paratone oil (Exxon) and mounted under a stream of nitrogen at −100 °C. The unit cell parameters and orientation matrix were determined from a least-squares fit of at least 25 reflections obtained from a rotation photograph and an automatic peak search routine. The refined lattice parameters and other pertinent crystallographic information are given in Table 1.[15]

Intensity data were measured with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Background counts were measured at the beginning and end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured after every 97 reflections. The intensity data were corrected for Lorentz and polarization effects and for absorption using an empirical absorption correction based upon ψ scans.

The structures were solved by direct methods using the Siemens SHELXTL 93 (versions 5.0 and 5.10) software packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and introduced into the refinement as fixed contributors with isotropic U values of 0.08 Å^2.

Results and Discussion

Synthesis of Disilyl-Substituted Alkylidene Complexes. The addition of a solution of $H_2SiR'Ph$ (R′ = Me, Ph) to a solution of the alkylidene complex $(Me_3SiCH_2)_3Ta(PMe_3){=}CHSiMe_3$ (**1**)[13] resulted in the evolution of H_2 and the nearly quantitative conversion (by NMR) of **1** to the disilyl-substituted alkylidene complex $(Me_3SiCH_2)_3Ta[{=}C(SiMe_3)SiHR'Ph]$ (R′ = Me, **4a**; Ph, **4b**) (Scheme 2). The reaction of the silane occurred exclusively with the alkylidene (${=}CHSiMe_3$) ligand, and the resulting complexes **4a**,**b** were found to be unreactive toward excess silane. No reaction was observed between **1** and $HSiPh_3$ at room temperature.

Spectroscopic properties of **4a**,**b** are consistent with the structure assignments. The alkylidene resonances of **4a** and **4b** occur at 240.6 and 238.2 ppm, respectively, in the $^{13}C\{^1H\}$ NMR spectra, and appear as singlets in the ^{1}H-gated-decoupled ^{13}C spectra. The α-H resonances of the methylene groups of the (Me_3SiCH_2-) groups in **4a** are diastereotopic and appear as two doublets in the ^{1}H spectrum due to the stereogenic Si center in the ${=}C(SiMe_3)Si^*HMePh$ moiety.

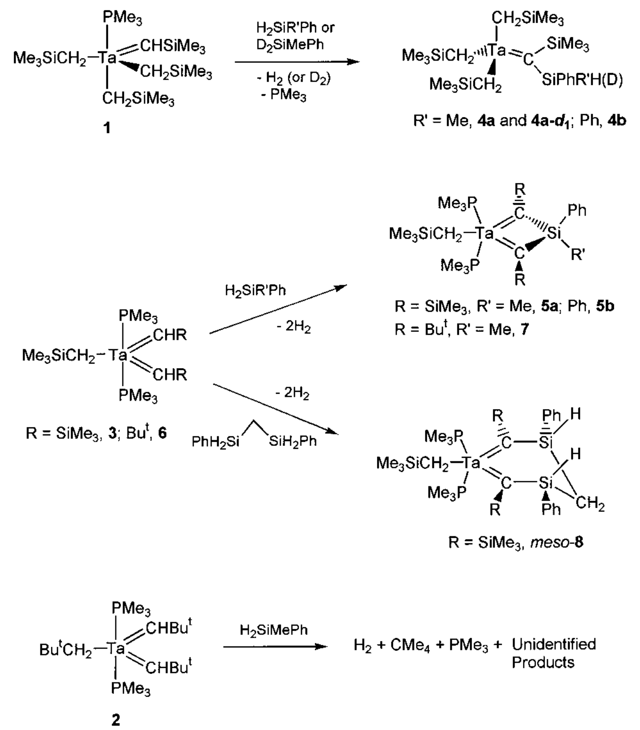
Workup of the reaction mixture to produce **4a** yielded a red oil of reasonably pure **4a** (>95% by ^{1}H NMR). However, all attempts to isolate analytically pure samples of this compound were unsuccessful, as **4a** was found to slowly decompose in solution. When monitored by NMR in benzene-d_6, **4a** slowly decomposed through $SiMe_4$ elimination; however a solution of **4a** in benzene could be frozen and stored at −20 °C for several weeks without significant decomposition.

Synthesis of Novel Metallasilacyclobutadiene Complexes. Addition of $H_2SiR'Ph$ (R′ = Me, Ph) to

---

[15] See the Supporting Information for details.

Scheme 2



$(Me_3SiCH_2)Ta(PMe_3)_2[{=}CHSiMe_3]_2$ (**3**) led to the evolution of H_2 and the formation of novel 1,1′-metalla-3-silacyclobutadiene complexes $(Me_3SiCH_2)Ta(PMe_3)_2[{=}C(SiMe_3)SiPhR'C(SiMe_3)]$ ($R' = Me$, **5a**; Ph, **5b**) (Scheme 2). Again, preferential reactions with the alkylidene ligands were observed, and the products were inert to excess silane. In contrast to **4**, no decomposition of complexes **5a**,**b** in both solution and solid state was observed over a long period of time, and **5a**,**b** are soluble in a variety of aromatic, aliphatic, and ethereal solvents. No reaction was observed between **3** and $HSiPh_3$, $HSiBu^tPh_2$, or $H_2SiBu^t_2$.

The structures of **5a**, **5b**, **7**, and **8** are novel and to our knowledge represent the first examples of 1,1-metalla*sila*cyclobuta*diene* complexes. A number of metallasilacyclobut*ane* complexes have been synthesized and structurally characterized,[16] and a large number of conjugated metallacyclobutadiene complexes are known;[17] however, to our knowledge, **5a** and **5b** represent the first cyclobutadiene complexes in which both double bonds are localized exclusively on the metal atom.[18]

The spectroscopic properties of **5a**,**b** support the structure assignments. The $^{13}C\{^1H\}$ NMR resonances of the alkylidene ligands range from 250.3 to 255.4 ppm and appear as singlets in the ^1H-gated-decoupled ^{13}C spectra. The phosphine ligands in **5a** are chemically inequivalent, resulting in the appearance of two doublets in the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra. This is consistent with a trigonal bipyramidal structure with axial phosphine ligands and a planar metallasilacyclobutadiene ring with the Ph and Me ligands above and below the ring, thus making the phosphine ligands chemically inequivalent. The two phosphine ligands in **5b** are equivalent, leading to virtually coupled triplets in the ^1H and $^{13}C\{^1H\}$ spectra and a singlet in the $^{31}P\{^1H\}$ spectrum. The methylene resonances of the Me_3SiCH_2- ligands in **5a**,**b** appear as triplets in the ^1H NMR spectra. The structural assignments of **5a** and **5b** were confirmed by X-ray crystallography, which is discussed below.

The preferential reactions of the alkylidene ligands, rather than the alkyl ligands, of **3** with H_2SiPhR' were unexpected. To probe whether such a preference was general, the reactions of the neopentyl analogue of **3**, $(Bu^tCH_2)Ta(PMe_3)_2[{=}CHBu^t]_2$ (**2**),[1c] and the mixed-ligand trimethylsilylmethyl neopentylidene complex $(Me_3SiCH_2)Ta(PMe_3)_2[{=}CHBu^t]_2$ (**6**) with $H_2SiMePh$ were studied. The reaction of **6** with $H_2SiMePh$ also generated H_2 and a metallasilacyclobutadiene complex **7** (Scheme 2). However, the reaction of **2** with $H_2SiMePh$ gave as products H_2, CMe_4, PMe_3, and a mixture of unidentified complexes. Spectroscopic properties of **7** are similar to those of **5a**. The alkylidene carbon resonance occurs at 271.9 ppm in the $^{13}C\{^1H\}$ NMR spectrum and appears as a singlet in the ^1H-gated-decoupled ^{13}C spectrum. The phosphine ligands are chemically inequivalent and appear as two doublets in both the ^1H and $^{13}C\{^1H\}$ spectra. However, one of the two phosphine signals in the ^1H spectrum is broad, indicating a fluxional process involving one of the two phosphine ligands. The structure of **7** was confirmed by X-ray crystallography.

In contrast to complexes **5a**,**b**, which are stable in solution, **7** was found to be unstable in solution, decomposing by loss of PMe_3 followed by loss of $SiMe_4$ to give a mixture of decomposition products whose NMR spectra were similar to those from the reaction of **2** with $H_2SiMePh$. One possibility for the lower stability of **7** in solution may be due to increased steric crowding around the Ta center caused by the $-Bu^t$ groups on the alkylidene ligands; a C$-$C bond (ca. 1.54 Å) is shorter than a C$-$Si bond (ca. 1.85 Å), resulting in the two groups *exo* to the metallasilacyclobutadiene ring being closer to the metal center. This may lead to the dissociation of a phosphine ligand (as is supported by the broadened signal for one of the PMe_3 ligands in the ^1H NMR spectrum of **7**), resulting in a pseudo-tetrahedral complex, which further decomposes by loss of $SiMe_4$ (possibly via γ-H abstraction from a $-Bu^t$ group) to give unidentified products. It is therefore likely that the reaction of **2** with $H_2SiMePh$ may also form a metallasilacyclobutadiene complex, which then rapidly loses PMe_3 followed by CMe_4 to give a product mixture similar to that from the decomposition of **7**.

---

[16] (a) Tikkanen, W. R.; Liu, J. Z.; Egan, J. W.; Petersen, J. L. *Organometallics* **1984**, *3*, 825. (b) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357. (c) Behling, T.; Girolami, G. S.; Wilkinson, G.; Somerville, R. G.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 877. (d) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

[17] For reviews of metallacyclobutadiene complexes, see: (a) Wigley, D. E.; Gray, S. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 5, p 57. (b) Nugent, W. A.; Mayer, J. M. *Metal–Ligand Multiple Bonds*; Wiley: New York, 1988; Chapter 7. (c) Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281, and references therein.

[18] A number of metallacyclo*penta*diene and -triene complexes have been reported. For examples see: (a) Albers, M. O.; de Waal, D. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680. (b) Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218. (c) Hessen, B.; Teuben, J. H. *J. Organomet. Chem.* **1989**, *367*, C18.

Synthesis of the Metalladisilacyclohexadiene Complex 8. The unexpected formation of metallasilacyclobutadiene complexes **5a**,**b** from the reactions of **3** with $H_2SiR'Ph$ prompted us to study whether such chemistry could be extended to the reactions of alkylidene complexes with compounds containing more than one silyl functionality. The reactions of such compounds, such as a disilylmethane $(H_2PhSi)_2CH_2$,[12] which contain two reactive groups, could possibly lead to the formation of oligomeric, cyclic, or polymeric complexes in which the disilylmethane moiety could bridge two metal centers, as well as to the formation of a metalladisilacyclohexadiene complex. We therefore studied the reactivity of $(PhH_2Si)_2CH_2$ toward **3**.

The reaction of $PhSiH_2CH_2SiH_2Ph$ with **3**, when conducted in an NMR tube in benzene-d_6 and monitored by ^1H NMR, was found to immediately produce H_2 and other products. Increasing the scale of the reaction in pentane and cooling the reaction mixture to −20 °C led to the isolation of a 1,1′-metalla-3,5-disilacyclohexadiene complex **8** in low yield (Scheme 2). No further products could be isolated from the reaction mixture.

Crystals of **8** were found by X-ray crystallography to be those of a *meso*-isomer, in which both phenyl rings on the two stereogenic Si atoms are occupying pseudoequatorial positions on the metalladisilacyclohexadiene ring. The NMR spectroscopic properties of crystals of **8** are in agreement with the structure assignment of the *meso*-isomer. The alkylidene carbons appear at 262.7 ppm in the $^{13}C\{^1H\}$ spectrum, and this signal appears as a singlet in the ^1H-gated-decoupled ^{13}C spectrum. The phosphine ligands are chemically inequivalent and lead to two doublets in the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra. The silane protons appear as a multiplet at 5.82 ppm, and the methylene protons as multiplets at 0.88 and 1.41 ppm. **8** has an extremely low solubility in benzene, but surprisingly is soluble in toluene.

X-ray Crystal Structures of 5a, 5b, 7, and 8. Slow cooling of solutions of **5a**,**b** in hexanes and **7** and **8** in pentane, respectively, produced crystals suitable for analysis by X-ray crystallography. Crystal data, results of analyses, and bond distances and angles are given in Tables 1 and 2.[15] The molecular structures of **5a**, **5b**, **7**, and **8** are shown in Figures 1−4.

Complex **5a** exhibits distorted trigonal bipyramidal geometry around the tantalum center, with the PMe_3 ligands occupying axial positions (Figure 1). 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 **3**, 1.932(7) and 1.955(7) Å in $Ta(=CHBu^t)_2(mesityl)(PMe_3)_2$,[19a] and 1.932(9) Å in $[Ta(=CHBu^t)(CH_2Bu^t)(PMe_3)_2]_2(\mu\text{-}N_2)$[19b,c]). The metallasilacyclobutadiene ring is planar (average deviation from the 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. The silicon atom of the metallasilacyclobutadiene ring exhibits distorted tetrahedral geometry, with bond angles ranging from 96.7(5)° to 115.9(6)°.

The structure of **5b** is similar to **5a** (Figure 2). As in **5a**, the tantalum atom exhibits distorted trigonal bipyramidal geometry with the PMe_3 ligands occupying axial positions. The Ta=C bond distances of 1.951(12) and 1.977(12) Å are similar to those listed above. The metallasilacyclobutadiene ring is also planar, and the silicon atom of the ring exhibits distorted tetrahedral geometry, with bond angles ranging from 97.7(6)° to 115.7(6)°. Again, the planar nature of the ring brings the Si atom in close contact to the Ta center (Ta−Si distance of 2.599(4) Å).

The structure of **7** is similar to **5a**, except that the *exo*-$SiMe_3$ groups of the metallasilacyclobutadiene ring are replaced by $-Bu^t$ groups (Figure 3). Again, the Ta atom has a distorted trigonal bipyramidal geometry with axial PMe_3 ligands, and the Ta=C bond distances of 1.952(9) and 1.953(8) Å are consistent with the presence of two alkylidene moieties. Despite the instability of **7** in solution, in which it decomposes by loss of a PMe_3 ligand followed by $SiMe_4$ elimination, there is little in the structure of **7** to indicate increased steric strain around the Ta center. The Ta−P distances of 2.621(3) and 2.628(3) Å are similar to those in **5a** and **5b**, which range from 2.596(4) to 2.664(3) Å. The Ta−C−Si angle of the Me_3SiCH_2- ligand in **7** is 135.7(5)°, which is wider than that (121.2(6)°) in **5a**, but less than that (137.8(7)°) in **5b**. The Ta−Si distance of 2.621(3) Å is slightly longer than those in **5a**,**b**. It is therefore unclear from the solid-state structure of **7** why this complex is unstable in solution, while complexes **5a**,**b** are stable in solution. It is possible that the instability of **7** is perhaps the result of a combination of steric and electronic effects caused by the nature of the *exo*-R group on the metallasilacyclobutadiene ring; the presence of a $SiMe_3$ group *exo* to the ring in **5a**,**b** may help to stabilize these complexes toward decomposition. It is well established that a silyl substituent helps to stabilize adjacent metal−carbon bonds.[20] The lack of silyl substituents *exo* to the metallasilacyclobutadiene ring in **7** may contribute to the lower stability of this complex in solution.

Analysis of the structure of the crystals of **8** revealed them to be that of a *meso*-isomer (Figure 4), in which the metalladisilacyclohexadiene ring is in a half-chair conformation, and the Ph rings on the ring Si atoms were found to occupy pseudoequatorial positions. The molecule was found to exhibit crystallographically imposed mirror symmetry, with the Me_3SiCH_2- ligand disordered over the mirror plane. This ligand was therefore refined as two mirror images with site occupancy factors of 0.5. The Ta atom exhibits distorted trigonal bipyramidal geometry, with the PMe_3 ligands occupying axial positions. The Ta=C distances of 1.985(15) and 1.985(14) Å are again consistent with other alkylidene complexes of tantalum. The C=Ta=C bond angle of 113.0(8)° is much wider than those in the metallasilacyclobutadiene complexes **5a**,**b** and **7** (91.9(3)−93.3(5)°). This large angle causes the *exo*-$SiMe_3$ groups $[Si(1)Me_3]$ to be in closer proximity to the Me_3SiCH_2- ligand, which in turn leads to a considerable

---

[19] (a) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930. (b) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 2899. (c) 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.

[20] Fleming, I. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon: New York, 1979; Vol. 3, Part 13, p 541.

Table 2. Selected Interatomic Distances and Angles for 5a, 5b, 7, and 8

Interatomic Distances (Å)							
5a				**7**			
Ta−P(1)	2.605(3)	Ta−P(2)	2.664(3)	Ta−P(1)	2.621(3)	Ta−P(2)	2.605(3)
Ta−C(1)	1.955(13)	Ta−C(2)	1.969(12)	Ta−C(1)	1.953(8)	Ta−C(2)	1.952(9)
Ta−C(3)	2.289(12)	Si(1)−C(1)	1.824(13)	Ta−C(3)	2.271(9)	Ta−Si(1)	2.628(3)
Si(2)−C(2)	1.811(12)	Si(3)−C(3)	1.879(12)	P(1)−C(22)	1.796(9)	P(2)−C(25)	1.831(10)
Si(4)−C(1)	1.904(12)	Si(4)−C(2)	1.905(12)	Si(1)−C(1)	1.902(9)	Si(1)−C(2)	1.885(8)
Si(4)−C(19)	1.899(13)	Si(4)−C(20)	1.889(13)	Si(1)−C(12)	1.879(9)	Si(1)−C(13)	1.908(9)
				Si(2)−C(3)	1.898(9)	Si(2)−C(19)	1.885(11)
				C(1)−C(4)	1.542(12)	C(2)−C(8)	1.534(12)
5b				**8**			
Ta−P(1)	2.596(4)	Ta−P(2)	2.631(4)	Ta−P(1)	2.608(6)	Ta−P(2)	2.624(6)
Ta−C(1)	1.977(12)	Ta−C(2)	1.951(12)	Ta−C(1)	1.985(15)	Ta−C(1A)	1.985(14)
Ta−C(3)	2.282(12)	Ta- -Si(4)	2.599(4)	Ta−C(2)	2.23(3)	Si(1)−C(1)	1.847(15)
P(1)−C(4)	1.797(14)	P(2)−C(7)	1.81(2)	Si(2)−C(2)	1.87(3)	Si(3)−C(1)	1.854(14)
Si(1)−C(1)	1.816(13)	Si(2)−C(2)	1.823(13)	Si(3)−C(3)	1.873(12)	Si(3)−C(14)	1.880(18)
Si(4)−C(1)	1.886(13)	Si(4)−C(2)	1.865(13)				
Si(4)−C(19)	1.901(13)	Si(4)−C(25)	1.899(13)				
Bond Angles (deg)							
5a							
C(1)−Ta−C(2)	93.3(5)	C(1)−Ta−C(3)	134.2(5)	C(3)−Si(3)−C(18)	112.0(6)	C(1)−Si(4)−C(2)	97.1(6)
C(2)−Ta−C(3)	132.4(5)	C(1)−Ta−P(1)	90.1(4)	C(1)−Si(4)−C(19)	115.0(6)	C(1)−Si(4)−C(20)	114.0(6)
C(2)−Ta−P(1)	101.0(4)	C(3)−Ta−P(1)	80.7(3)	C(2)−Si(4)−C(19)	116.2(6)	C(2)−Si(4)−C(20)	111.9(6)
C(1)−Ta−P(2)	91.0(4)	C(2)−Ta−P(2)	96.9(4)	Si(1)−C(1)−Si(4)	130.4(7)	Si(2)−C(2)−Si(4)	127.9(7)
C(3)−Ta−P(2)	85.6(3)	Si(4)−C(1)−Ta	85.0(5)	P(1)−Ta−P(2)	161.96(11)	C(1)−Si(1)−C(12)	115.0(6)
Si(2)−C(2)−Ta	146.8(7)	Si(4)−C(2)−Ta	84.6(5)	C(2)−Si(2)−C(13)	113.0(6)	C(3)−Si(3)−C(16)	114.4(6)
Si(3)−C(3)−Ta	121.2(6)	Si(1)−C(1)−Ta	144.6(7)	C(3)−Si(3)−C(17)	111.3(6)		
5b							
C(1)−Ta−C(2)	91.9(5)	C(1)−Ta−C(3)	146.0(5)	Si(3)−C(3)−Ta	137.8(7)	C(19)−Si(4)−C(25)	103.5(5)
C(2)−Ta−C(3)	122.0(5)	C(1)−Ta−P(1)	90.0(4)	C(2)−Ta−P(1)	98.8(4)	C(3)−Ta−P(1)	84.7(3)
C(4)−P(1)−Ta	117.1(5)	C(7)−P(2)−C(8)	102.4(9)	C(1)−Ta−P(2)	93.3(4)	C(2)−Ta−P(2)	99.6(4)
C(7)−P(2)−Ta	115.3(6)	C(1)−Si(1)−C(10)	114.0(7)	C(3)−Ta−P(2)	82.3(3)	P(1)−Ta−P(2)	161.25(12)
C(2)−Si(2)−C(13)	114.7(7)	C(3)−Si(3)−C(16)	113.0(7)	Si(1)−C(1)−Si(4)	133.9(7)	Si(1)−C(1)−Ta	141.4(7)
C(1)−Si(4)−C(2)	97.7(6)	C(1)−Si(4)−C(19)	115.7(6)	Si(4)−C(1)−Ta	84.5(5)	Si(2)−C(2)−Si(4)	135.4(7)
C(1)−Si(4)−C(25)	113.9(6)	C(2)−Si(4)−C(19)	113.6(6)	Si(2)−C(2)−Ta	138.5(7)	Si(4)−C(2)−Ta	85.8(5)
				C(2)−Si(4)−C(25)	113.0(6)		
7							
C(1)−Ta−C(2)	91.9(3)	C(1)−Ta−C(3)	146.4(3)	C(1)−Si(1)−C(2)	95.7(4)	C(1)−Si(1)−C(12)	113.2(4)
C(2)−Ta−C(3)	121.7(3)	C(1)−Ta−P(1)	94.0(3)	C(1)−Si(1)−C(13)	117.9(4)	C(2)−Si(1)−C(12)	116.0(4)
C(1)−Ta−P(2)	93.9(3)	C(2)−Ta−P(1)	100.4(3)	C(2)−Si(1)−C(13)	112.3(4)	C(12)−Si(1)−C(13)	102.6(4)
C(2)−Ta−P(2)	96.6(3)	C(3)−Ta−P(1)	81.7(3)	C(3)−Si(2)−C(19)	112.3(5)	C(4)−C(1)−Si(1)	126.5(6)
C(3)−Ta−P(2)	82.2(3)	P(1)−Ta−P(2)	160.99(8)	C(4)−C(1)−Ta	147.6(6)	Si(1)−C(1)−Ta	85.9(3)
C(22)−P(1)−Ta	119.2(4)	C(25)−P(2)−Ta	113.0(4)	C(8)−C(2)−Si(1)	130.3(7)	C(8)−C(2)−Ta	142.9(6)
				Si(1)−C(2)−Ta	86.4(3)	Si(2)−C(3)−Ta	135.7(5)
8							
C(1)−Ta−C(1A)	113.0(8)	C(1)−Ta−C(2)	131.7(10)	C(12)−P(2)−Ta	112.9(8)	C(1)−Si(1)−C(4)	108.0(8)
C(1A)−Ta−C(2)	115.3(11)	C(1)−Ta−P(1)	94.1(4)	C(1)−Si(3)−C(3)	113.9(8)	C(1)−Si(3)−C(14)	118.2(7)
C(1A)−Ta−P(1)	94.1(4)	C(2)−Ta−P(1)	82.6(7)	C(3)−Si(3)−C(14)	101.9(9)	Si(1)−C(1)−Si(3)	112.8(8)
C(2A)−Ta−P(1)	82.6(7)	C(1)−Ta−P(2)	93.0(4)	Si(1)−C(1)−Ta	126.0(7)	Si(3)−C(1)−Ta	120.6(8)
C(1A)−Ta−P(2)	93.0(4)	C(2)−Ta−P(2)	84.8(7)	Si(3)−C(3)−Si(3A)	113.0(11)	C(15)−C(14)−Si(3)	121.8(19)
P(1)−Ta−P(2)	167.25(18)	C(10)−P(1)−Ta	114.8(9)	Si(2)−C(2)−Ta	147(2)	C(2)−Si(2)−C(7)	116.7(13)

widening of the Ta−C−Si angle (147(2)°) in the Me_3SiCH_2- ligand.

Deuterium Labeling Studies of the Conversion of 1 to 4a. To further study the reaction of **1** with $H_2SiMePh$ to give the disilyl-substituted alkylidene complex **4a**, the reaction of **1** with the deuterated silane $D_2SiMePh$ was investigated. Monitoring the reaction of **1** with $D_2SiMePh$ by NMR showed the product to be $(Me_3SiCH_2)_3Ta[{=}C(SiMe_3)SiDMePh]$ (**4a-d_1**) (Scheme 2). In addition, when 2.1 equiv of $D_2SiMePh$ was used for the reaction, the formation of HDSiMePh and $H_2SiMePh$ was also observed; at larger excesses of silane (>10 equiv), only HDSiMePh was found in the reaction solution by NMR. The reaction of **1** with $D_2SiMePh$ was also observed to be slower than that of **1** with $H_2SiMePh$; the latter was nearly complete after a few hours at room temperature, while the former reaction took 1 day to go to completion. This observation was confirmed by kinetic studies of this reaction, which are discussed below. The incorporation of hydrogen into the excess deuterated silane $D_2SiMePh$ to give HDSiMePh and $H_2SiMePh$ was unexpected, and the reaction was thus monitored by ^{2}H NMR to investigate whether the hydrogen incorporation into $D_2SiMePh$ was due to exchange of deuterium in $D_2SiMePh$ with protons in the alkyl ligands (Me_3SiCH_2-) of **1**. No incorporation of deuterium into the alkyl ligands of the product **4a-d_1** was observed, and the only deuterium signals observed

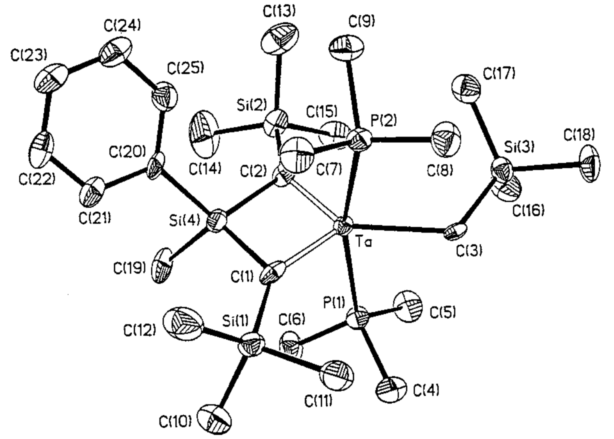


Figure 1. ORTEP diagram of **5a** showing 50% ellipsoids.

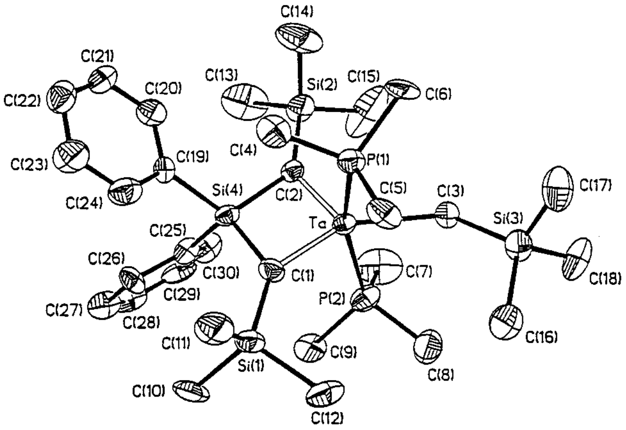


Figure 2. ORTEP diagram of **5b** showing 50% ellipsoids.

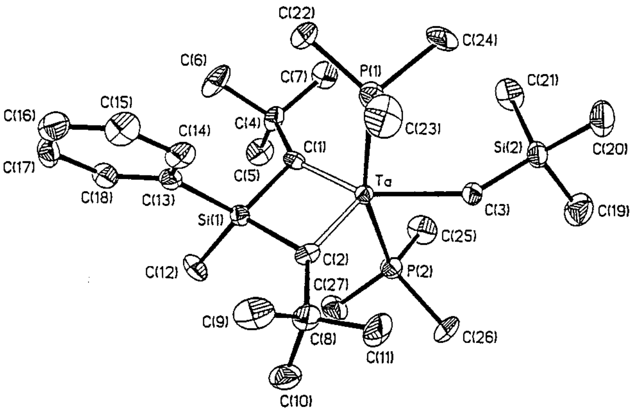


Figure 3. ORTEP diagram of **7** showing 50% ellipsoids.

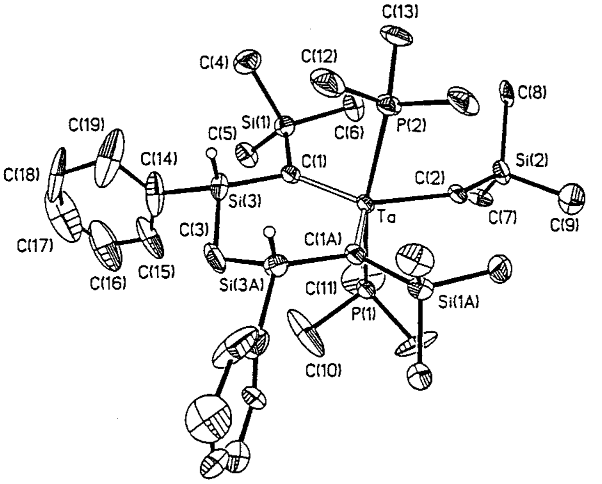


Figure 4. ORTEP diagram of **8** showing 30% ellipsoids.

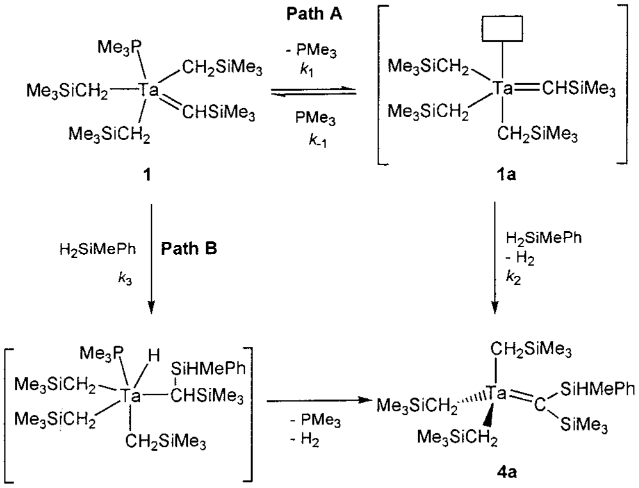
were those from *D*$_2$SiMePh, H*D*SiMePh (overlapping signals), and (Me$_3$SiCH$_2$)$_3$Ta[=C(SiMe$_3$)Si*D*MePh].[15] This result rules out the possibility that hydrogen incorporation into D$_2$SiMePh is the result of exchange of deuterium in D$_2$SiMePh with protons in the alkyl ligands of **1**. In a separate experiment, ^{1}H NMR spectra of a D$_2$SiMePh solution in toluene-*d*$_8$ showed no exchange of the residual hydrogen in toluene-*d*$_8$ with D$_2$SiMePh after 3 h at 50 °C.

The gaseous products from the reaction of **1** with ca. 1 equiv of D$_2$SiMePh were analyzed by mass spectrometry. The mass spectrum of sample A showed the products to be D$_2$, HD, and H$_2$ in an 86.6(0.3):12.5(0.3):0.86(0.03) ratio (by total ion current).[15] In another experiment when **1** reacted with 4.5 equiv of D$_2$SiMePh (sample B), the mass spectrum showed the gaseous products to be D$_2$, HD, and H$_2$ in an 89.6(1.2):9.1(1.1):1.26(0.01) ratio.[15] In such a reaction between **1** and 4.5 equiv of D$_2$SiMePh, ^{1}H NMR at 600 MHz showed the presence of 0.088 equiv of H$_2$SiMePh and 0.33 equiv of HDSiMePh. In the third experiment, the gaseous products from the reaction of **1** with 4.5 equiv of D$_2$SiMePh under excess H$_2$ (sample C) were analyzed as well by mass spectrometry. The MS showed the products to be D$_2$, HD, and H$_2$ in a 24.5(0.1):13.4(0.1):62.1(0.1) ratio.[15] ^{1}H NMR at 600 MHz of this reaction mixture revealed the presence of approximately 1.0 equiv of HDSiMePh and 0.11 equiv of H$_2$SiMePh. The results from samples A and B showed that D$_2$ is the major product in the reaction, and the ratios of D$_2$, HD, and H$_2$ changed slightly when D$_2$SiMePh/**1** ratios varied from ca. 1 to 5. The result in sample C with added H$_2$ in the reaction mixture indicated that products and H$_2$ added to the system undergo hydrogen scrambling.

Kinetic Studies of the Conversion of 1 to 4a and Mechanistic Considerations of This Conversion. To further investigate the reaction of phenyl-containing silanes with alkylidene complexes, kinetic studies of the reactions of **1** with H$_2$SiMePh and D$_2$SiMePh at 10 °C were performed. During the NMR studies of this reaction, no disilanes such as PhMeHSiSiHMePh or polysilanes were observed. In addition, when the reaction of **1** with H$_2$SiMePh was conducted in the presence of HSiPh$_3$ (which had been found to be unreactive toward **1**), no crossover disilanes PhMeHSiSiPh$_3$ were observed. Thus it is unlikely that a mechanism involving silyl radicals is involved in this reaction, as such a mechanism is expected to involve disilane formation through combination of silyl radicals as one of the chain termination steps. We therefore focused our attention on two possible reaction pathways, which are shown in Scheme 3. The first pathway (path A) involves the loss of a PMe$_3$ ligand to open a coordination site on the tantalum center, followed by addition of the silane to the Ta=C bond, leading to products. The second pathway (path B) would involve an addition of the silane to the Ta=C alkylidene bond, followed by loss of phosphine and conversion to products. When monitored by NMR, no intermediates were observed in the conversion of **1** to **4a**.

If the dissociative mechanism in path A (Scheme 3) were operative in this reaction, a steady-state ap-

Scheme 3



proximation (d[**1a**]/dt = 0) gives[21a]

$$[\mathbf{1a}] = \frac{k_1[\mathbf{1}]}{k_{-1}[\mathrm{PMe_3}] + k_2[\mathrm{H_2SiMePh}]} \quad (1)$$

and

$$v = -\mathrm{d}[\mathbf{1}]/\mathrm{d}t = \frac{k_1k_2[\mathrm{H_2SiMePh}][\mathbf{1}]}{k_{-1}[\mathrm{PMe_3}] + k_2[\mathrm{H_2SiMePh}]} \quad (2)$$

or $v = k_{\mathrm{obs}}[\mathbf{1}]$ where

$$k_{\mathrm{obs}} = \frac{k_1k_2[\mathrm{H_2SiMePh}]}{k_{-1}[\mathrm{PMe_3}] + k_2[\mathrm{H_2SiMePh}]} \quad (3)$$

which may also be expressed in a linear form

$$\frac{1}{k_{\mathrm{obs}}} = \frac{k_{-1}[\mathrm{PMe_3}]}{k_1k_2[\mathrm{H_2SiMePh}]} + \frac{1}{k_1} \quad (4)$$

Thus under conditions of excess $H_2SiMePh$, one would expect to observe pseudo-first-order kinetics in [**1**]. When [$H_2SiMePh$] ≫ [PMe_3], the silane terms in the rate expression (eq 3) would become dominant and the observed rate would simplify to $k_{\mathrm{obs}} \approx k_1$. In other words, one would observe saturation kinetics at large $H_2SiMePh$ excesses. Also, a plot of $1/k_{\mathrm{obs}}$ vs [PMe_3]/[$H_2SiMePh$] would be linear (eq 4), yielding values for k_1 and k_{-1}/k_2.[21b] In the reactions shown in Scheme 2, 1 equiv of PMe_3 is produced. If the average concentrations of silane and PMe_3 are $[\mathrm{Silane}]_{\mathrm{av}} = [\mathrm{Silane}]_0 + [\mathrm{Silane}]_{\mathrm{end}}$ and $[\mathrm{PMe_3}]_{\mathrm{av}} = [\mathbf{1}]/2$, eq 4 then approximates to

$$\frac{1}{k_{\mathrm{obs}}} = \frac{k_{-1}[\mathrm{PMe_3}]_{\mathrm{av}}}{k_1k_2[\mathrm{H_2SiMePh}]_{\mathrm{av}}} + \frac{1}{k_1} \quad (5)$$

If the reaction proceeded by the associative mechanism shown in path B of Scheme 3, and if the first step was rate controlling, a much simpler rate expression would be obtained:

$$\mathrm{d}[\mathbf{1}]/\mathrm{d}t = k_3[\mathbf{1}][\mathrm{H_2SiMePh}] \quad (6)$$

For reactions conducted with an excess of $H_2SiMePh$, pseudo-first-order kinetics are expected (eq 7)

$$k_{\mathrm{obs}} = k_3[\mathrm{H_2SiMePh}] \quad (7)$$

Kinetic studies were performed with $[\mathrm{H_2SiMePh}]_0/[\mathbf{1}]_0$ ranging from 5.34 to 34.8 and $[\mathrm{D_2SiMePh}]_0/[\mathbf{1}]_0$ ranging from 5.00 to 35.1. In these studies, $[\mathrm{PMe_3}]_{\mathrm{av}}$ ranges from 0.0174 to 0.0575 M in the reactions with $H_2SiMePh$ and 0.0348 to 0.0785 M in the reactions with $D_2SiMePh$.[15] For each $[\mathrm{Silane}]_{\mathrm{av}}/[\mathrm{PMe_3}]_{\mathrm{av}}$ ratio, the experiment was repeated with different $[\mathrm{Silane}]_0$ and $[\mathbf{1}]_0$. Under these conditions the disappearance of **1** with time was found to obey first-order kinetics,[15] as is shown in the kinetic plots. Values for the observed rate constants are given in the Supporting Information. Plots of $1/k_{\mathrm{obs}}$ vs $[\mathrm{PMe_3}]_{\mathrm{av}}/[\mathrm{H_2SiMePh}]_{\mathrm{av}}$ and $[\mathrm{PMe_3}]_{\mathrm{av}}/[\mathrm{D_2SiMePh}]_{\mathrm{av}}$ were found to be linear (Figure 5), as would also be expected from the dissociative mechanism rate law (eq 5). Such an observation is consistent with the mechanistic pathway path A shown in Scheme 3, in which there is a dissociative mechanism involving loss of PMe_3 from **1** prior to the reaction of **1** with $H_2SiMePh$. From the plots of $1/k_{\mathrm{obs}}$ vs $[\mathrm{PMe_3}]_{\mathrm{av}}/[\mathrm{H_2SiMePh}]_{\mathrm{av}}$, a value of $k_1 = 5.45(10) \times 10^{-2}\ \mathrm{min}^{-1}$ was obtained. In addition, from the slopes of the plots shown in Figure 5, a kinetic isotope effect value $k_{2\mathrm{H}}/k_{2\mathrm{D}}$ was calculated to be 1.87. The magnitude of this kinetic isotope effect is consistent with the formation of or the breaking of a silicon−deuterium bond in the rate-controlling step and is similar to that (1.5) observed in a kinetic study of the reactions of an iron carbene complex with silanes (Scheme 1).[5c]

Path A (Scheme 3) involves initial dissociation of PMe_3. The presence of excess PMe_3 is thus expected to significantly slow the reaction. Kinetic studies of the reaction of **1** with 5.4 equiv of $H_2SiMePh$ in the presence of 20 equiv of PMe_3 at 24 °C gave $k_{\mathrm{obs}} = 8.1 \times 10^{-4}\ \mathrm{min}^{-1}$.[15] In comparison, the control experiment in the absence of added PMe_3 at 24 °C gave $k_{\mathrm{obs}}' = 1.5 \times 10^{-2}\ \mathrm{min}^{-1}$, which is ca. 19 times larger than k_{obs}.[15] These observations are consistent with path A.

The likelihood of path B was also investigated. Plots of k_{obs} vs $[\mathrm{H_2SiMePh}]_0$ and k_{obs} vs $[\mathrm{H_2SiMePh}]_{\mathrm{av}}$ did not reveal the linear relationship as defined in eq 7 for path B,[15] suggesting that path B is unlikely the pathway in the reaction between **1** and $H_2SiMePh$.

The observed kinetic isotope effect indicates that a Si−H bond formation or bond cleavage occurs in the rate-controlling step of the reaction. The deuterium-labeling studies showed that D_2 was the major gaseous product in the reaction of **1** with excess $D_2SiMePh$, and the percentage of D_2 in the D_2−HD-H_2 mixtures increased slightly when $D_2SiMePh$ was raised from 1- to 5-fold. In addition, hydrogen incorporation into excess $D_2SiMePh$ to yield HDSiMePh was also observed, and hydrogen scrambling clearly occurs in the products.

While the mechanism of the conversion of **1** to **4a** is not clear, these observations offer some clues as to the possible mechanistic pathways in this reaction. The kinetic studies indicate that PMe_3 initially dissociates from **1** to give an intermediate complex **1a** with an open coordination site for the approach of silane. The silane then reacts with the alkylidene ligand to yield a deu-

---

(21) (a) Jordan, R. B. *Reaction Mechanisms of Inorganic and Organometallic Systems*; Oxford University Press: New York, 1991; p 31. (b) For an example of the approaches here, see: Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 2669.

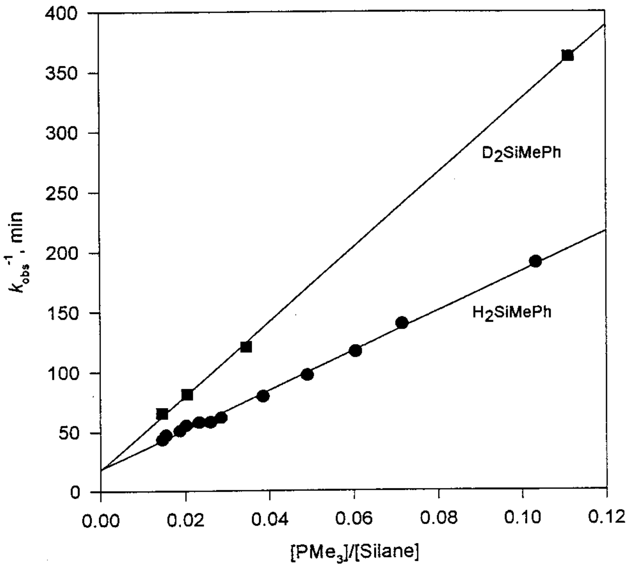
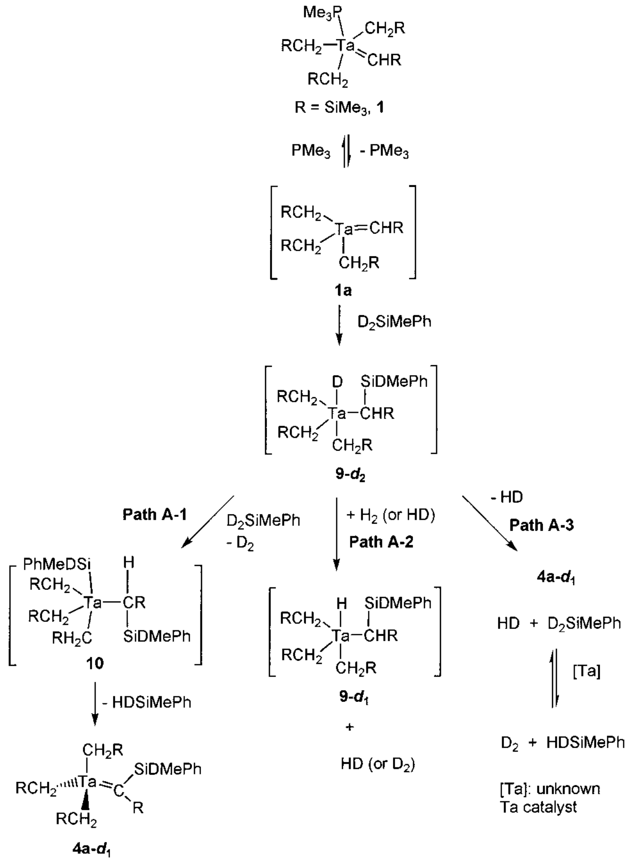


Figure 5. Plot of k_{obs}^{-1} vs [PMe$_3$]$_{av}$/[Silane]$_{av}$.

teride intermediate **9-*d*$_2$**, possibly through nucleophilic attack on the silane by the π-electron density of the alkylidene bond. The alkylidene ligands of Schrock alkylidene complexes have been shown to be nucleophilic in nature, and reactions of alkylidene complexes with olefins and ketones are also believed to involve some degree of nucleophilic attack on the olefin and ketone by the alkylidene ligand.[2] Similar reactions of alkyl or amido complexes with silanes to give metal hydride complexes and alkylsilanes or amidosilanes have recently been reported.[7a,22]

At least the three processes in Scheme 4 may occur in the next step. The ratio D$_2$/HD = 86.6(0.3)/12.5(0.3) when D$_2$SiMePh/**1** = ca. 1 suggested that **9-*d*$_2$** may then react with a second silane molecule through a dehydrogenative coupling reaction to yield D$_2$ and a silyl intermediate **10**. Such reactions of hydride complexes with silanes have been proposed in the dehydrogenative polymerization of silanes.[23] The silyl ligand in **10** then undergoes α-hydrogen abstraction to give H$_2$SiMePh or HDSiMePh and **4a-*d*$_1$**. The mechanism shown in path A-1 is thus consistent with the observed dissociative-mechanism from the kinetic studies and also accounts for the preferential formation of D$_2$ and the proton incorporation into the unreacted D$_2$SiMePh to give HDSiMePh in the deuterium labeling studies. It should be noted that this pathway (path A-1) first requires H−SiHMePh addition to the Ta═C bond to give the H−Ta−C′−Si moiety (C′ = CHR) and at the last step requires the elimination of H−SiDMePh from **10** with the Si−Ta−C″−H moiety (C″ = C(SiDMePh)R) of opposite regiochemistry.

Scheme 4



The observations of hydrogen scrambling in products when H$_2$ was added indicate that path A-2 and path A-3 may occur in the system. In path A-2, the deuteride ligand in **9-*d*$_2$** undergoes σ-bond metathesis with H$_2$ (or HD) to give HD (or D$_2$) and **9-*d*$_1$**. This process may lead to increased percentage of HD in sample C when the reaction was conducted under H$_2$. Path A-3 in Scheme 4, followed by the exchange HD + D$_2$SiMePh $\rightleftharpoons$ D$_2$ + HDSiMePh, may explain the observed hydrogen scrambling process. Another process that may occur is a σ-bond metathesis reaction involving the α-C and H atoms of the Ta═CHR ligand in **1a** and the incoming D$_2$SiMePh, yielding HD and **4a-*d*$_1$** as products. Subsequent scrambling as shown in path A-3 may lead to the observed product hydrogen isotope distributions.

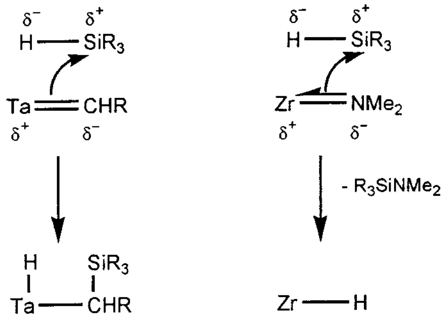
It is interesting to note that the reaction of phenyl-containing silanes with **1** may proceed through a step involving some degree of nucleophilic attack on the silicon center of the incoming silane molecule by the π-electron density of the alkylidene ligand, leading to the formation of a product **4** in which a new carbon−silicon bond is formed. Similar chemistry was observed in the reaction of zirconium amide complexes Zr(NMe$_2$)$_4$ and Zr(NMe$_2$)$_3$[SiR$_3$][7k] (R$_3$ = SiMe$_3$) with phenyl-containing silanes H$_x$SiPh$_{4-x}$ (x = 2, 3) to yield amidosilanes and unstable zirconium hydride complexes (Scheme 5).[7a] These amide complexes possess some degree of π-character (d−p π-bonds) in the N−Zr bonds through interaction of the lone pair on the nitrogen atom of the amide ligand with the unfilled d-orbitals on the zirco-

---

[22] Voskoboynikov, 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.

[23] (a) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (b) Xin, S. X.; Harrod, J. F. *J. Organomet. Chem.* **1995**, *499*, 181. (c) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *Polyhedron* **1995**, *14*, 45. (d) Corey, J. Y.; Zhu, X. H.; Bedard, T. C.; Lange, L. D. *Organometallics* **1991**, *10*, 924. (e) Hengge, E.; Gspaltl, P.; Pinter, E. *J. Organomet. Chem.* **1996**, *521*, 145. (f) Banovetz, J. P.; Suzuki, H.; Waymouth, R. M. *Organometallics* **1993**, *12*, 4700. (g) Spaltenstein, E.; Palma, P.; Kreutzer, K. A.; Willoughby, C. A.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 10308. (h) Verdaguer, X.; Lange, U. E. W.; Reding, M. T.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 6784. (i) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564.

Scheme 5



nium atom (Scheme 5). The d−p π-bonds may also be involved in the nucleophilic attack on the silicon center of an incoming silane molecule in the reactions of silanes with the zirconium amide complexes, leading to the formation of a silicon−nitrogen bond and a metal hydride (Scheme 5).[7a] It should be also pointed out that such reactivity is also in agreement with the formal bond polarities of the reactants in both the alkylidene/silane and amide/silane systems: the metal−carbon and metal−nitrogen bonds are both polarized with a partial negative charge on the carbon and nitrogen atoms, respectively, while the Si−H bond of the silane is polarized with a partial negative charge on the hydrogen atom (the Pauling electronegativities of silicon and hydrogen being 1.8 and 2.1, respectively). Such nucleophilic attack of the π-electron density of the alkylidene ligand in **1** on the incoming silane may explain the observed preferential reaction of only the alkylidene ligands, and not the alkyl ligands, of **1**, **3**, and **6** with silane.

Acknowledgment is made to the National Science Foundation (CHE-9904338, NSF Young Investigator program CHE-9457368, and Research Experiences for Undergraduates (REU) program), Camille Dreyfus Teacher-Scholar program, and DuPont Young Professor program for financial support of this research. The authors also thank Dr. Albert A. Tuiman for help with mass spectroscopy experiments, Karen T. Welch and Dr. Hongjun Pan for assistance with ^{1}H NMR at 600 MHz, and referees for insightful suggestions.

Supporting Information Available: ^{2}H NMR spectrum of the reaction mixture of **1** with $D_2SiMePh$, mass spectra (MS) of the hydrogen gas produced from the reaction of **1** with $D_2SiMePh$, kinetic plots of the reactions of **1** with $H_2SiMePh$ and $D_2SiMePh$, a list of rate constants for the reactions of **1** with $H_2SiMePh$ and $D_2SiMePh$, plots of k_{obs} vs $[H_2SiMePh]_0$ and k_{obs} vs $[H_2SiMePh]_{av}$, and a complete list of the crystallographic data for **5a**, **5b**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000476R