Articles

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

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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 $(PhSiH_2)_2-CH_2$ 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 $1 \rightarrow 4$ 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^tCH₂)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 Cp₂Ta(=CH₂)CH₃ 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 d² Ta(III) center, followed by CH₄ elimination and alkylidene transfer and insertion steps.³ The formation of d^0 Cp*₂Ta(H)(CH₃)SiH₃ (Cp* = pentamethylcyclopentadienyl) from the reaction of Cp*₂Ta(H)=CH₂ with SiH₄ was found to occur via oxidative addition of SiH₄ to $d^2 Cp^*{}_2Ta-CH_3$, which is in equilibrium with $Cp^*{}_2$ - $Ta(H)=CH_2$.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

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

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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 Cpfree, high-oxidation-state alkylidene complexes. We have chosen alkylidene complexes containing phosphine ligands (RCH₂)Ta(PMe₃)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 ¹H spectra). ²⁹Si, ³¹P, and ²H chemical shifts were referenced to SiMe₄, external 85% H_3PO_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. TaCl₅ (Strem) was sublimed before use. PMe₃ (Aldrich) and 1.0 M anhydrous HCl in Et₂O (Aldrich) were used as received. H₂SiMePh (Gelest) and H₂SiPh₂ (Aldrich) were dried over activated molecular sieves and stored under nitrogen. Me_3SiCH_2MgCl ,⁹ $(Bu^tCH_2)_3Ta=CHBu^t$,^{1a,b} $(Bu^tCH_2)Ta=CHBu^t$,^{1a,b} (Bu^tCH_2)Ta=CHB $(PMe_3)_2$ [=CHBu^t]₂ (2),^{1c} (Me₃SiCH₂)Ta(PMe₃)₂[=CHSiMe₃]₂ (3),¹⁰ and D₂SiMePh¹¹ were prepared by the literature procedures. (PhSiH₂)₂CH₂ was prepared by a procedure similar to that in the literature.¹² Elemental analyses were performed by E + R Microanalytical, Parsippany, NJ.

Preparation of (Me₃SiCH₂)₃Ta(PMe₃)[=CHSiMe₃] (1). The following is a modified procedure from the previously reported synthesis.¹³ A slurry of 5.0 g (0.014 mol) of TaCl₅ in 75 mL of hexanes at -20 °C was treated dropwise with 41.0 mL of a Me₃SiCH₂MgCl solution in Et₂O (1.7 M, 0.070 mol).

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current procedure, CH₂Cl₂ was used in lieu of CH₂Br₂ to react with 2 equiv of H₂SiClPh and Mg/Zn dust to give (PhSiH₂)₂CH₂ in 43% yield. (13) Rupprecht, G. A. Ph.D. Thesis, Massachusetts Institute of Technology, 1979.

The mixture turned green, then green-yellow, and finally bright yellow as (Me₃SiCH₂)₅Ta was produced. The reaction was monitored carefully by ¹H NMR until complete conversion to $(Me_3SiCH_2)_5Ta^{14}$ 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 MgCl₂. PMe₃ (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 MgCl₂, concentrated, and cooled to -20 °C, producing 7.8 g (92%) of 1 as bright orange crystals. NMR: ¹H NMR (benzene- d_6 , 250.1 MHz, 23 °C) δ 6.17 (s, 1H, =CHSiMe₃), 0.89 (d, 9H, ${}^{2}J_{H-P} = 4.4$ Hz, PMe₃), 0.30 (s, 9H, =CHSiMe₃), 0.27 (s, 27H, CH₂Si*Me*₃), 0.24 (s, 6H, CH₂SiMe₃); ¹³C{¹H} NMR (benzene-d₆, 62,9 MHz, 23 °C) δ 251.8 (=CHSiMe₃), 77.3 (CH₂-SiMe₃), 15.9 (d, ${}^{1}J_{C-P} = 8.6$ Hz, PMe₃), 3.6 (=CHSiMe₃), 3.0 (CH₂SiMe₃).

Preparation of (Me₃SiCH₂)Ta(PMe₃)₂[=CHBu^t]₂ (6). A solution of 1.24 g of (^tBuCH₂)₃Ta=CHBu^t (2.67 mmol) in 20 mL of toluene at -60 °C was treated dropwise with 12.6 mL of HCl in Et₂O (0.21 M, 2.6 mmol). The HCl/Et₂O was prepared by diluting 2.6 mL of 1.0 M HCl in Et₂O with 10 mL of Et₂O. The resulting solution of (Bu^tCH₂)₄TaCl^{1d} was then treated with 0.60 mL of PMe₃ (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-(PMe₃)₂[=CHBu^t]₂.^{1c} Me₃SiCH₂MgCl in Et₂O (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^tCH₂)₃Ta=CHBu^t). NMR: ¹H NMR (benzene d_6 , 250.1 MHz, 23 °C) δ 7.27 (s, 1H, =CHBu^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, =CHCMe₃), 0.27 (s, 9H, CH₂SiMe₃), -0.27 (t, 2H, ${}^{3}J_{H-P} = 20.1$ Hz, CH_2SiMe_3 ; ¹³C{¹H} NMR (benzene- d_6 , 62,9 MHz, 23 °C) δ 273.1, 242.2 (=CHBut), 47.4, 44.1 (=CHCMe₃), 37.3 (CH₂-SiMe₃), 35.3, 34.3 (=CHC*Me*₃), 19.3 (t, ${}^{1}J_{C-P} = 11.6$ Hz, P*Me*₃), 5.2 (CH₂SiMe₃). Anal. Calcd for $C_{20}H_{49}SiP_2Ta$: C, 42.85; H, 8.81. Found: C, 42.84; H, 8.82.

Preparation of (Me₃SiCH₂)₃Ta[=C(SiMe₃)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 H₂SiMePh 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 ¹H NMR) amount of $(Me_3SiCH_2)_4Ta_2(\mu$ -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: ¹H NMR (benzene-d₆, 250.1 MHz, 23 °C) δ 7.20-7.90 (m, 5H, SiHMePh), 4.90 (q, 1H, ${}^{3}J_{H-H} = 3.6$ Hz, SiHMePh), 1.20 (d, 3H, ${}^{2}J_{H-H} = 12.1$ Hz, $CH_{a}H_{b}SiMe_{3}$), 0.92 (d, 3H, $CH_{a}H_{b}$ -SiMe₃), 0.80 (d, 3H, SiHMePh), 0.30 (s, 9H, =CSiMe₃), 0.19 (s, 27H, CH₂Si*Me*₃); ¹³C{¹H} NMR (benzene-*d*₆, 62.9 MHz, 23 °C) δ 240.6 (=*C*SiMe₃), 137.6, 135.3, 129.5, 128.0 (SiHMe*Ph*), 89.6 (CH2SiMe3), 5.0 (=CSiMe3), 2.7 (CH2SiMe3), -1.9 (SiH-MePh); $^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6 , 79.5 MHz, 27 °C) δ 0.08 (CH₂SiMe₃), -13.2 (=CSiMe₃), -49.9 (=CSiHMePh). Data for **4b**: ¹H NMR (benzene-*d*₆, 250.1 MHz, 23 °C) δ 7.20–7.90 (m, 10H, SiHPh₂), 5.07 (s, 1H, SiHPh₂), 1.19 (s, 6H, CH₂SiMe₃), 0.31 (s, 9H, =CSiMe₃), 0.19 (s, 27H, CH₂SiMe₃); ¹³C{¹H} NMR (benzene-*d*₆, 62.9 MHz, 23 °C) δ 238.2 (=*C*SiMe₃), 137.5, 136.5, 129.7, 128.1 (SiHPh₂), 90.7 (CH₂SiMe₃), 5.19 (=CSiMe₃), 2.72

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 (CH_2SiMe_3) ; ²⁹Si{¹H} NMR (benzene- d_6 , 79.5 MHz, 27 °C) δ 0.37 (CH₂SiMe₃), -13.1 (=CSiMe₃), -48.3 (=CSiHPh₂).

Preparation of Metallasilacyclobutadiene Complexes. Synthesis of 5a. A solution of 0.204 g (0.344 mmol) of (Me₃-SiCH₂)Ta(PMe₃)₂[=CHSiMe₃]₂ (3) in 10 mL of hexanes was treated with 0.044 g (0.35 mmol) of H₂SiMePh 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: ¹H NMR (benzene- d_6 , 250.1 MHz, 23 °C) δ 7.17–7.86 (m, 5H, SiMe*Ph*), 1.12 (d, 9H, ${}^{2}J_{H-P} = 6.6$ Hz, P*Me*₃), 1.00 (s, 3H, Si*Me*Ph), 0.88 (d, 9H, ${}^{2}J_{H-P} = 6.7$ Hz, P*Me*₃), 0.35 (s, 18H, = CSiMe₃), 0.25 (s, 9H, CH₂SiMe₃), -0.46 (t, 2H, ${}^{3}J_{H-P} = 16.0$ Hz, CH₂SiMe₃); ¹³C{¹H} NMR (benzene-d₆, 62.9 MHz, 23 °C) δ 255.1 (=*C*SiMe₃), 145.8, 136.3, 127.8, 127.2 (SiMe*Ph*), 50.4 (CH_2SiMe_3) , 17.9 (d, ${}^{1}J_{C-P} = 12.5$ Hz, PMe₃), 17.6 (d, ${}^{1}J_{C-P} =$ 12.9 Hz, PMe₃), 5.9 (=CSiMe₃), 5.8 (SiMePh), 5.8 (CH₂SiMe₃); ²⁹Si{¹H} NMR (benzene-*d*₆, 79.5 MHz, 27 °C) δ 0.40 (CH₂SiMe₃), -15.4 (=CSiMe₃), -76.8 (SiMePh); ³¹P{¹H} NMR (benzene d_6 , 162.0 MHz, 27 °C) δ -4.51 (d, ${}^2J_{P-P} = 125$ Hz), -7.03 (d). The ¹³C resonance assignments were confirmed by the use of ¹³C-¹H HETCOR NMR. Anal. Calcd for C₂₅H₅₅P₂Si₄Ta: 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 H₂SiPh₂ 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: ¹H NMR (benzene-d₆, 250.1 MHz, 23 °C) δ 7.09–7.89 (m, 10H, SiPh₂), 0.94 (t, 18H, ²J_{H-P} = 3.14 Hz, PMe₃), 0.41 (s, 18H, =CSiMe₃), 0.26 (s, 9H, CH₂SiMe₃), -0.41 (t, 2H, ${}^{3}J_{H-P} = 15.8$ Hz, $CH_{2}SiMe_{3}$); ${}^{13}C{}^{1}H{}$ NMR (benzened₆, 62,9 MHz, 23 °C) δ 255.4 (=CSiMe₃), 143.3, 137.4, 128.0, 127.1 (SiPh₂), 52.5 (CH₂SiMe₃), 17.5 (t, ¹J_{C-P} = 11.3 Hz, PMe₃), 6.55 (=CSiMe₃), 5.83 (CH₂SiMe₃); ²⁹Si{¹H} NMR (benzene-d₆, 79.49 MHz, 27 °C) & 0.70 (CH₂SiMe₃), -16.6 (=CSiMe₃), -75.5 (*Si*Ph₂); ³¹P{¹H} NMR (benzene-*d*₆, 162.0 MHz, 27 °C) δ −6.72. Anal. Calcd for C₃₀H₅₇P₂Si₄Ta: C, 46.61; H, 7.43. Found: C, 46.45; H, 7.49.

Synthesis of 7. A solution of 0.548 g of (Me₃SiCH₂)Ta-(PMe₃)₂[=CHBu^t]₂ (6, 0.978 mmol) in 10 mL of pentane was treated with 0.236 mL of H₂SiMePh (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: ¹H NMR (benzene- d_6 , 250.1 MHz, 23 °C) δ 7.10-8.00 (m, 5H, Si*Ph*Me), 1.40 (s, 18H, = CCMe₃), 1.18 (d, 9H, ²J_{H-P} = 6.2 Hz, PMe₃), 1.12 (s, 3H, SiPh*Me*), 1.09 (br d, 9H, ${}^{2}J_{H-P} = 6.3$ Hz, P*Me*₃), 0.28 (s, 9H, CH_2SiMe_3), -0.46 (br t, 2H, ${}^3J_{H-P} = 15.2$ Hz, CH_2SiMe_3); ${}^{13}C_{-1}$ {¹H} NMR (benzene- d_6 , 62.9 MHz, 23 °C) δ 271.9 (=*C*Bu^t), 145.4, 138.0, 127.1, 126.5 (SiMePh), 51.0 (CH₂SiMe₃), 47.9 (= CCMe₃), 37.3 (=CCMe₃), 18.5 (overlapping d, PMe₃), 5.95 (CH₂-SiMe₃), 3.82 (SiMePh). Anal. Calcd for C₂₇H₅₅P₂Si₂Ta: C, 47.78; H, 8.17. Found: C, 47.76; H, 8.18.

Reaction of (Bu^tCH_2)Ta(PMe_3)_2[=CHBu^t]_2 (2) with H₂SiMePh. Complex 2 (0.029 g, 0.053 mmol) was dissolved in benzene- d_6 in an NMR tube. H₂SiMePh (0.025 g, 0.20 mmol) was added to the NMR tube. NMR spectra of the solution showed the products to be H₂, neopentane (CMe₄), PMe₃, and other unidentified species. Another attempt in hexanes with 0.191 g of 2 and 0.050 g of H₂SiMePh 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 (PhSiH₂)₂CH₂ 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: ¹H NMR (toluene-d₈, 400.1 MHz, 27 °C) δ 7.13-7.75 (m, 10H, SiHPh), 5.82 (m, 2H, SiHPh), 1.41 (m, 1H, Si-CH_aH_b-Si), 1.38 (2 overlapping d, 18H, PMe₃), 0.88 (m, 1H, Si-CH_aH_b-Si), 0.22 (s, 9H, CH₂SiMe₃), 0.039 (s, 18H, =CSiMe₃), -0.58 (br t, 2H, ${}^{3}J_{H-P} = 15.6$ Hz, CH₂SiMe₃); ${}^{13}C$ -{¹H} NMR (toluene-*d*₈, 100.6 MHz, 27 °C) δ 262.7 (=*C*SiMe₃), 145.4, 135.3, 128.5, 127.7 (Ph), 67.1 (CH₂SiMe₃), 18.6 (d, ¹J_{C-P} = 21.1 Hz, PMe₃), 16.7 (br d, ${}^{1}J_{C-P}$ = 21.1 Hz, PMe₃), 13.7 (Si- CH_2 -Si), 6.22 (=CSiMe₃), 5.24 (CH₂SiMe₃); ²⁹Si{¹H} NMR (toluene-d₈, 79.5 MHz, 27 °C) & 10.5 (CH₂SiMe₃), -11.9 (Si-CH₂-Si), -19.3 (=CSiMe₃); ³¹P{¹H} NMR (toluene-d₈, 162.0 MHz, 27 °C) δ 3.07 (d, ${}^{2}J_{P-P} = 155.8$ Hz), -0.21 (d). The assignment of two overlapping doublets for the PMe₃ groups in the ¹H spectrum was confirmed by an HMQC (heteronuclear multiple quantum coherence) experiment. Anal. Calcd for C₃₁H₆₁P₂Si₅Ta: C, 45.57; H, 7.52. Found: C, 45.53; H, 7.53.

Reaction of 1 with D₂SiMePh 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 μ L (0.143) mmol) of D₂SiMePh. 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 $4a \cdot d_1$ and PMe₃. HDSiMePh, H₂SiMePh, and a trace amount of 4a were also identified. Data for 4a-d₁: ¹H NMR (toluene-d₈, 400.1 MHz, 50 °C) δ 7.20–7.81 (m, 5H, Si*Ph*MeD), 1.10 (d, 3H, $^{2}J_{H-H}$ = 12.1 Hz, CH_aH_bSiMe₃), 0.91 (d, 3H, CH_aH_bSiMe₃), 0.75 (s, 3H, SiPhMeD), 0.26 (s, 9H, =CSiMe₃), 0.18 (s, 27H, CH₂SiMe₃); ¹³C{¹H} NMR (toluene- d_8 , 100.6 MHz, 50 °C) δ 241.1 (= CSiMe₃), 137.8, 135.3, 129.7, 128.0 (SiDMePh), 89.7 (CH₂-SiMe₃), 5.0 (=CSiMe₃), 2.8 (CH₂SiMe₃), -1.8 (SiDMePh); ²H NMR (toluene, 61.42 MHz, 27 °C) δ 4.92 (br s, SiDMePh). In a separate experiment with 0.045 g of 1, 0.6 mL of toluene- d_8 , and 47 µL (0.33 mmol) of D₂SiMePh, 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, ¹H NMR at 600 MHz revealed the presence of ca. 0.0065 mmol (0.088 equiv) of H₂SiMePh and 0.024 mmol (0.33 equiv) of HDSiMePh in the product mixture. The resonance of HDSiMePh is 0.010 ppm upfield-shifted from that of H₂SiMePh 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 μ L (0.068 mmol) of D₂SiMePh. 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-d₈ and 47 µL (0.33 mmol) of D₂SiMePh. 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 μ L (0.33 mmol) of D₂SiMePh 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 N₂ to freeze the solution. In this process, part of the headspace was cooled as well. N₂ in the tube was then removed in vacuo. H₂ 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 N₂, and the tube was connected to the mass spectrometer to

	5a	5b	7	8
formula	C ₂₅ H ₅₅ P ₂ Si ₄ Ta	C ₃₀ H ₅₇ P ₂ Si ₄ Ta	C ₂₇ H ₅₅ P ₂ Si ₂ Ta	$C_{31}H_{61}P_2Si_5Ta$
fw	710.94	773.01	678.78	817.14
cryst size (mm)	0.30 imes 0.20 imes 0.20	0.36 imes 0.20 imes 0.05	0.30 imes 0.22 imes 0.05	0.32 imes 0.26 imes 0.20
temp (K)	173(2)	173(2)	173(2)	173(2)
cryst syst	monoclinic	monoclinic	tr <u>i</u> clinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	<i>P</i> 1	Pnma .
lattice params	a = 10.647(3) Å	a = 12.199(5) Å	a = 10.154(3) A	a = 10.667(3) A
	b = 17.757(6) Å	b = 16.428(5) Å	b = 10.998(3) Å	b = 17.314(4) Å
	c = 18.686(5) A	c = 19.526(6) A	c = 16.492(5) A	c = 25.591(5) A
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 101.92(2)^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 96.91(3)^{\circ}$	$\beta = 93.96(3)^{\circ}$	$\beta = 91.86(2)^{\circ}$	$\beta = 90^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 111.98(2)^{\circ}$	$\gamma = 90^{\circ}$
volume, A 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
$\mu \text{ (mm}^{-1}\text{)}$	3.374	3.037	3.495	2.536
F(000)	1456	1584	696	1680
scan type	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
Ø range (deg)	2.10-22.55	1.62-22.54	2.05 - 22.54	2.07 - 22.55
index ranges	$n, K, \pm I$	$n, K, \pm I$ 5120 ($B = 0.0400$)	$n, \pm K, \pm I$	$(D, K, \pm I)$
no. of unique refins	$4017 (R_{int} = 0.0352)$	$5120 (R_{int} = 0.0499)$	$4355 (R_{int} = 0.0384)$	$3230 (R_{int} = 0.0744)$
Dindiana	203 0.0504 (mD2 - 0.1240)	334 0.0606 (mD9 - 0.1111)	403 0.0450 (mD2 - 0.0001)	400 0.0592 (mD9 - 0.1660)
κ mances of fit on E^2	0.0504 (WKZ = 0.1240)	0.0000 (WK2 = 0.1111)	0.0450 (WK2 = 0.0901)	0.0583 (WKZ = 0.1669)
goouness-or-fit off T	1.000	1.077	1.013	1.000

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. ¹H NMR at 600 MHz of the product mixture showed the presence of ca. 0.0081 mmol (0.11 equiv) of H_{2} -SiMePh and 0.074 mmol (1.0 equiv) of HDSiMePh.

Kinetic Studies of the Conversion of 1→4a and 1→4ad₁. 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-d₈. H₂SiMePh or D₂SiMePh was then added to the NMR tube via calibrated micropipet so as to make [H₂SiMePh]₀/[1]₀ between 5.34 and 34.8 and [D₂SiMePh]₀/[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 PMe₃, **1** (28.1 mg, 0.0465 mmol), 4,4'-dimethylbiphenyl (1.3 mg), and 420 μ L (396 mg) of toluene-*d*₈ were placed in an NMR tube. PMe₃ (97 μ L, 71 mg, 0.94 mmol) and H₂SiMePh (34 μ L, 30 mg, 0.25 mmol) were then added to this solution at 24 °C to make [H₂SiMePh]₀/[**1**]₀ approximately 5.4. The reaction was conducted at 24 °C and monitored by ¹H and ¹³C NMR. In a control experiment, **1** (28.6 mg, 0.0473 mmol) and 4,4'-dimethylbiphenyl (5.1 mg) were dissolved in 536 μ L (504 mg) of toluene-*d*₈. H₂SiMePh (34 μ L, 30 mg, 0.25 mmol) was then added at 24 °C to make [H₂SiMePh]₀/[**1**]₀ approximately 5.3. This reaction at 24 °C was monitored by ¹H 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 K α 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

(15) See the Supporting Information for details.

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 Å².

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 (Me₃-SiCH₂)₃Ta(PMe₃)=CHSiMe₃ (1)¹³ resulted in the evolution of H_2 and the nearly quantitative conversion (by NMR) of 1 to the disilyl-substituted alkylidene complex (Me₃SiCH₂)₃Ta[=C(SiMe₃)SiHR'Ph] (R' = Me, 4a; Ph, 4b) (Scheme 2). The reaction of the silane occurred exclusively with the alkylidene (=CHSiMe₃) ligand, and the resulting complexes 4a,b were found to be unreactive toward excess silane. No reaction was observed between 1 and HSiPh₃ 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 ¹³C{¹H} NMR spectra, and appear as singlets in the ¹H-gated-decoupled ¹³C spectra. The α -H resonances of the methylene groups of the (Me₃SiCH₂-) groups in **4a** are diastereotopic and appear as two doublets in the ¹H spectrum due to the stereogenic Si center in the =C(SiMe₃)Si*HMePh moiety.

Workup of the reaction mixture to produce **4a** yielded a red oil of reasonably pure **4a** (>95% by ¹H 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 SiMe₄ 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



 $(Me_3SiCH_2)Ta(PMe_3)_2$ [=CHSiMe_3]₂ (**3**) led to the evolution of H₂ and the formation of novel 1,1'-metalla-3-silacyclobutadiene complexes $(Me_3SiCH_2)Ta(PMe_3)_2$ [=

PMe₂

 $C(SiMe_3)SiPhR'C(SiMe_3)]$ (R' = Me, **5a**; Ph, **5b**) (Scheme

The structures of **5a**, **5b**, **7**, and **8** are novel and to our knowledge represent the first examples of 1,1metalla*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 ¹³C{¹H} NMR resonances of the alkylidene ligands range from 250.3 to 255.4 ppm and appear as singlets in the ¹H-gated-decoupled ¹³C spectra. The phosphine ligands in 5a are chemically inequivalent, resulting in the appearance of two doublets in the ¹H, ${}^{13}C{}^{1}H$, and ${}^{31}P{}^{1}H$ 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 ¹³C $\{^{1}H\}$ spectra and a singlet in the ³¹P-{¹H} spectrum. The methylene resonances of the Me₃-SiCH₂- ligands in **5a**,**b** appear as triplets in the 1 H 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 H₂SiPhR' were unexpected. To probe whether such a preference was general, the reactions of the neopentyl analogue of **3**, (Bu^tCH₂)Ta(PMe₃)₂[=CHBu^t]₂ (2),^{1c} and the mixedligand trimethylsilylmethyl neopentylidene complex $(Me_3SiCH_2)Ta(PMe_3)_2$ [=CHBu^t]₂ (6) with H₂SiMePh were studied. The reaction of 6 with H₂SiMePh also generated H₂ and a metallasilacyclobutadiene complex 7 (Scheme 2). However, the reaction of 2 with H₂SiMePh gave as products H₂, CMe₄, PMe₃, 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 ¹³C{¹H} NMR spectrum and appears as a singlet in the ¹H-gated-decoupled ¹³C spectrum. The phosphine ligands are chemically inequivalent and appear as two doublets in both the ¹H and ${}^{13}C{}^{1}H$ 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 PMe3 followed by loss of SiMe4 to give a mixture of decomposition products whose NMR spectra were similar to those from the reaction of 2 with H₂SiMePh. 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 PMe₃ ligands in the ¹H NMR spectrum of 7), resulting in a pseudo-tetrahedral complex, which further decomposes by loss of SiMe₄ (possibly via γ -H abstraction from a –Bu^t group) to give unidentified products. It is therefore likely that the reaction of 2 with H₂SiMePh may also form a metallasilacyclobutadiene complex, which then rapidly loses PMe₃ followed by CMe₄ to give a product mixture similar to that from the decomposition of 7.

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 HSiPh₃, HSiBu^tPh₂, or H₂SiBu^t₂.

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Synthesis of the Metalladisilacyclohexadiene Complex 8. The unexpected formation of metallasilacyclobutadiene complexes 5a,b from the reactions of 3 with H₂SiR'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 (H₂PhSi)₂CH₂,¹² 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 (PhH₂Si)₂CH₂ 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 $^{13}\text{C}\{^{1}\text{H}\}$ spectrum, and this signal appears as a singlet in the ¹H-gated-decoupled ¹³C spectrum. The phosphine ligands are chemically inequivalent and lead to two doublets in the ${}^{1}H$, ${}^{13}C{}^{1}H$, and ${}^{31}P{}^{1}H$ 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 PMe₃ 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)(PMe₃)₂,^{19a} and 1.932-(9) Å in [Ta(=CHBu^t)(CH₂Bu^t)(PMe₃)₂]₂(μ -N₂)^{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 d⁰ makes any metal–silicon bonding interaction unlikely. The silicon atom of the metallasilacyclobutadiene ring exhibits

distorted tetrahedral geometry, with bond angles ranging from $96.7(5)^\circ$ to $115.9(6)^\circ$.

The structure of **5b** is similar to **5a** (Figure 2). As in **5a**, the tantalum atom exhibits distorted trigonal bipyramidal geometry with the PMe₃ 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-SiMe₃ 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 PMe₃ 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 PMe₃ ligand followed by SiMe₄ 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 Me₃SiCH₂- ligand in **7** is $135.7(5)^{\circ}$, which is wider than that $(121.2(6)^\circ)$ 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 SiMe₃ group *exo* to the ring in **5a**,**b** may help to stabilize these complexes toward decomposition. It is well established that a silvl 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 Me₃SiCH₂- 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 PMe₃ 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- $(3)-93.3(5)^{\circ}$). This large angle causes the *exo*-SiMe₃ groups [Si(1)Me₃] to be in closer proximity to the Me₃-SiCH₂- ligand, which in turn leads to a considerable

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

widening of the Ta–C–Si angle $(147(2)^{\circ})$ in the Me₃-SiCH₂– ligand.

Deuterium Labeling Studies of the Conversion of 1 to 4a. To further study the reaction of 1 with H₂-SiMePh to give the disilyl-substituted alkylidene complex 4a, the reaction of 1 with the deuterated silane D₂SiMePh was investigated. Monitoring the reaction of 1 with D₂SiMePh by NMR showed the product to be (Me₃SiCH₂)₃Ta[=C(SiMe₃)SiDMePh] (4a-d₁) (Scheme 2). In addition, when 2.1 equiv of D₂SiMePh was used for the reaction, the formation of HDSiMePh and H₂-SiMePh 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 D₂SiMePh was also observed to be slower than that of **1** with H₂-SiMePh; 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 D₂SiMePh to give HDSiMePh and H₂SiMePh was unexpected, and the reaction was thus monitored by ²H NMR to investigate whether the hydrogen incorporation into D₂SiMePh was due to exchange of deuterium in D₂SiMePh with protons in the alkyl ligands (Me₃SiCH₂-) 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.

were those from D_2 SiMePh, H*D*SiMePh (overlapping signals), and (Me₃SiCH₂)₃Ta[=C(SiMe₃)Si*D*MePh].¹⁵ This result rules out the possibility that hydrogen incorporation into D₂SiMePh is the result of exchange of deuterium in D₂SiMePh with protons in the alkyl ligands of **1**. In a separate experiment, ¹H NMR spectra of a D₂-SiMePh solution in toluene- d_8 showed no exchange of the residual hydrogen in toluene- d_8 with D₂SiMePh after 3 h at 50 °C.

The gaseous products from the reaction of **1** with ca. 1 equiv of $D_2SiMePh$ 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 $D_2SiMePh$



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

(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 D₂SiMePh, ¹H NMR at 600 MHz showed the presence of 0.088 equiv of H₂SiMePh and 0.33 equiv of HDSiMePh. In the third experiment, the gaseous products from the reaction of **1** with 4.5 equiv of D₂SiMePh under excess H₂ (sample C) were analyzed as well by mass spectrometry. The MS showed the products to be D₂, HD, and H₂ in a 24.5(0.1):13.4(0.1):62.1(0.1) ratio.¹⁵ ¹H NMR at 600 MHz of this reaction mixture revealed the presence of approximately 1.0 equiv of HDSiMePh and 0.11 equiv of H₂SiMePh. The results from samples A and B showed that D_2 is the major product in the reaction, and the ratios of D₂, HD, and H₂ changed slightly when D₂SiMePh/1 ratios varied from ca. 1 to 5. The result in sample C with added H₂ in the reaction mixture indicated that products and H₂ 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 H₂SiMePh and D₂SiMePh 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 H₂SiMePh was conducted in the presence of HSiPh₃ (which had been found to be unreactive toward 1), no crossover disilanes PhMeHSiSiPh₃ 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 PMe₃ 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-



proximation (d[1a]/dt = 0) gives^{21a}

$$[\mathbf{1a}] = \frac{k_1[\mathbf{1}]}{k_{-1}[\text{PMe}_3] + k_2[\text{H}_2\text{SiMePh}]}$$
(1)

and

$$\nu = -d[\mathbf{1}]/dt = \frac{k_1 k_2 [H_2 SiMePh][\mathbf{1}]}{k_{-1} [PMe_3] + k_2 [H_2 SiMePh]}$$
(2)

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

$$k_{\text{obs}} = \frac{k_1 k_2 [\text{H}_2 \text{SiMePh}]}{k_{-1} [\text{PMe}_3] + k_2 [\text{H}_2 \text{SiMePh}]}$$
(3)

which may also be expressed in a linear form

$$\frac{1}{k_{\rm obs}} = \frac{k_{-1} [\rm PMe_3]}{k_1 k_2 [\rm H_2 SiMePh]} + \frac{1}{k_1}$$
(4)

Thus under conditions of excess H₂SiMePh, one would expect to observe pseudo-first-order kinetics in [1]. When $[H_2SiMePh] \gg [PMe_3]$, the silane terms in the rate expression (eq 3) would become dominant and the observed rate would simplify to $k_{obs} \approx k_1$. In other words, one would observe saturation kinetics at large H₂-SiMePh excesses. Also, a plot of $1/k_{obs}$ vs $[PMe_3]/[H_2-$ SiMePh] 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 PMe₃ is produced. If the average concentrations of silane and PMe₃ are $[Silane]_{av} = [Silane]_0 + [Si$ $lane]_{end}$ and $[PMe_3]_{av} = [1]/2$, eq 4 then approximates to

$$\frac{1}{k_{\rm obs}} = \frac{k_{-1} [\rm PMe_3]_{\rm av}}{k_1 k_2 [\rm H_2 SiMePh]_{\rm av}} + \frac{1}{k_1}$$
(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: Diminnie et al.

$$d[\mathbf{1}]/dt = k_3[\mathbf{1}][\mathbf{H}_2 \text{SiMePh}]$$
(6)

For reactions conducted with an excess of H₂SiMePh, pseudo-first-order kinetics are expected (eq 7)

$$k_{\rm obs} = k_3 [\rm H_2 SiMePh]$$
(7)

Kinetic studies were performed with $[H_2SiMePh]_0/[1]_0$ ranging from 5.34 to 34.8 and [D₂SiMePh]₀/[1]₀ ranging from 5.00 to 35.1. In these studies, [PMe₃]_{av} ranges from 0.0174 to 0.0575 M in the reactions with H₂SiMePh and 0.0348 to 0.0785 M in the reactions with D₂SiMePh.¹⁵ For each [Silane]_{av}/[PMe₃]_{av} ratio, the experiment was repeated with different [Silane]₀ and [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 $1/k_{obs}$ vs $[PMe_3]_{av}$ [H₂SiMePh]_{av} and [PMe₃]_{av}/[D₂SiMePh]_{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 PMe₃ from 1 prior to the reaction of **1** with H₂SiMePh. From the plots of $1/k_{obs}$ vs $[PMe_3]_{av}/[H_2SiMePh]_{av}$, a value of $k_1 = 5.45(10) \times$ 10⁻² min⁻¹ was obtained. In addition, from the slopes of the plots shown in Figure 5, a kinetic isotope effect value k_{2H}/k_{2D} 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 PMe₃. The presence of excess PMe₃ is thus expected to significantly slow the reaction. Kinetic studies of the reaction of **1** with 5.4 equiv of H₂SiMePh in the presence of 20 equiv of PMe₃ at 24 °C gave $k_{obs} = 8.1 \times 10^{-4}$ min⁻¹.¹⁵ In comparison, the control experiment in the absence of added PMe₃ at 24 °C gave $k_{obs}' = 1.5 \times 10^{-2}$ 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 $[H_2SiMePh]_0$ and k_{obs} vs $[H_2SiMePh]_{av}$ 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-H₂ 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 PMe₃ 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 [PMe₃]_{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 silvl 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 H₂SiMePh or HDSiMePh and $4a \cdot d_1$. The mechanism shown in path A-1 is thus consistent with the observed dissociativemechanism from the kinetic studies and also accounts for the preferential formation of D_2 and the proton incorporation into the unreacted D₂SiMePh 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

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the Si-Ta-C"-H moiety (C" = C(SiDMePh)R) of opposite regiochemistry.

The observations of hydrogen scrambling in products when H₂ 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 H₂ (or HD) to give HD (or D₂) and **9**- d_1 . This process may lead to increased percentage of HD in sample C when the reaction was conducted under H₂. Path A-3 in Scheme 4, followed by the exchange HD + D₂SiMePh \Rightarrow D₂ + 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 D₂SiMePh, 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 phenylcontaining 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 phenylcontaining silanes H_xSiPh_{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-

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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 nucleo-

philic 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.

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Supporting Information Available: ²H NMR spectrum of the reaction mixture of **1** with D₂SiMePh, mass spectra (MS) of the hydrogen gas produced from the reaction of **1** with D₂SiMePh, kinetic plots of the reactions of **1** with H₂SiMePh and D₂SiMePh, a list of rate constants for the reactions of **1** with H₂SiMePh and D₂SiMePh, plots of k_{obs} vs [H₂SiMePh]₀ and k_{obs} vs [H₂SiMePh]_{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.

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