Synthesis and Characterization of (Me$_3$ECH$_2$)$_2$Ta(=CHEMe$_3$)Si(SiMe$_3$)$_3$ (E = C, Si). Kinetic and Mechanistic Studies of the Formation of a Silyl Alkylidene Complex through Preferential Silane Elimination

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Silyl alkylidene complexes (Me$_3$ECH$_2$)$_2$Ta(=CHEMe$_3$)Si(SiMe$_3$)$_3$ (E = C, **1**; E = Si, **2**), which are free of anionic π-ligands such as cyclopentadienyl (Cp), were prepared through the reactions of (Me$_3$ECH$_2$)$_3$TaCl$_2$ with 2 equiv of LiSi(SiMe$_3$)$_3$(THF)$_3$. An unprecedented preferential elimination of silane HSi(SiMe$_3$)$_3$ leads to the formation of the alkylidene bonds in **1** and **2**. An intermediate (Me$_3$SiCH$_2$)$_3$Ta(Cl)Si(SiMe$_3$)$_3$ (**9**) was observed in the formation of **2**. **9** was found to react with LiSi(SiMe$_3$)$_3$(THF)$_3$ and LiCH$_2$SiMe$_3$ to form **2** and (Me$_3$SiCH$_2$)$_3$Ta=CHSiMe$_3$ (**6**), respectively. The reaction of **9** with LiSi(SiMe$_3$)$_3$(THF)$_3$ to form the *silyl alkylidene* complex **2** follows a pathway *different* from the reaction of (Me$_3$ECH$_2$)$_4$-TaCl (E = C, Si) with LiCH$_2$EMe$_3$ to form *alkyl alkylidene* complexes (Me$_3$ECH$_2$)$_2$-Ta=CHEMe$_3$. The decomposition of **9** was found to follow first-order kinetics, with $\Delta H^{\ddagger}$ = 17.2(1.0) kcal/mol and $\Delta S^{\ddagger}$ = −4(4) eu, and give an unstable dimeric alkylidene complex (Me$_3$SiCH$_2$)$_4$(Cl)$_2$Ta(=CHSiMe$_3$)$_2$ (**12**). The reaction between **9** and LiSi(SiMe$_3$)$_3$(THF)$_3$ to form **2** and HSi(SiMe$_3$)$_3$ was observed to follow first-order kinetics, and the reaction rates were independent of the concentration of LiSi(SiMe$_3$)$_3$(THF)$_3$. In addition, the rates of this reaction (k_2) are almost equal to the rates of the decomposition of **9** (k_1). These results are consistent with the presence of "(Me$_3$SiCH$_2$)$_2$Ta(=CHSiMe$_3$)Cl" as an intermediate in the conversion of **9** to **2**. Kinetic and mechanistic studies of the formation of **2** will be discussed. A thermodynamic analysis of the preferential silane elimination shows that this preference may *not* be thermodynamic in origin, and could be attributed to a kinetic effect.

Introduction

Early-transition-metal silyl chemistry is currently a field of increasing interest.[1] The studies in this area have been focused mostly on silyl compounds supported by Cp or analogous anionic π-ligands.[1] The presence

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of such ligands in, *e.g.,* Cp$_2$Zr(SiR$_3$)R′,[1f] thermally labile Cp$_2$Ta(=CH$_2$)SiH^{t}Bu$_2$ (*in situ* at −70 °C),[1b] and Cp$_2$W(η^2-Me$_2$Si=SiMe$_2$)[1k] is believed to contribute to the enhanced stabilities of these silyl compounds. The study of early-transition-metal silyl complexes that are free from anionic π-ligands, on the other hand, is a relatively new area.[2] The few known Cp-free early-transition-metal silyl complexes, such as V(CO)$_6$SiH$_3$,[2a] (Me$_3$-CO)$_3$MSi(SiMe$_3$)$_3$ (M = Zr, Hf),[2i] and (Me$_3$P)$_3$W(H)$_2$I-(SiMe$_3$),[2j] usually contain carbonyls, alkoxides, or phosphines as supporting ligands. We have been interested in early-transition-metal silyl alkyl, alkylidene, and alkylidyne compounds free from Cp, CO, alkoxides, or phosphines as ancillary ligands. We report here the syntheses and characterization of silyl alkylidene complexes (Me$_3$ECH$_2$)$_2$Ta(=CHEMe$_3$)Si(SiMe$_3$)$_3$ (E = C, **1**; E = Si, **2**). These complexes represent, to our knowl-

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edge, the first *stable* silyl alkylidene compounds of the early transition metals.[3]

The mechanistic pathways to Schrock-type alkylidene complexes have been subjects of intense interest.[4] In the formation of $(Me_3CCH_2)_3Ta=CHCMe_3$ (**3**) from the reaction of $(Me_3CCH_2)_3TaCl_2$ with 2 equiv of $LiCH_2$-CMe_3, three paths were postulated with $(Me_3CCH_2)_4$-TaCl (**4**) as an intermediate.[4b–g] In one path, **4** was converted to "$(Me_3CCH_2)_2Ta(=CHCMe_3)Cl$" which further reacted with Me_3CCH_2Li to give **3**; *i.e.*, the alkylidene bond $Ta=CHCMe_3$ was formed before the Cl^- substitution. The second path involved an α-hydrogen abstraction by $LiCH_2CMe_3$. In the third path, **4** reacted with Me_3CCH_2Li to form "$(Me_3CCH_2)_5Ta$" (**5**) which then underwent an intramolecular α-hydrogen abstraction to form **3**; the Cl^- substitution occurred before the formation of the alkylidene bond $Ta=CHCMe_3$. We recently reported the observation of **4** and **5** as the precursors to $(Me_3CCH_2)_3Ta=CHCMe_3$ (**3**).[5] In the formation of the analogous $(Me_3SiCH_2)_3Ta=CHSiMe_3$ (**6**) from the reaction of $(Me_3SiCH_2)_3TaCl_2$ with 2 equiv of Me_3SiCH_2Li, we similarly observed $(Me_3SiCH_2)_4TaCl$ (**7**) and isolated $(Me_3SiCH_2)_5Ta$ (**8**) as the intermediates. Our kinetic and mechanistic studies pointed to the third pathway in the formation of the *alkyl alkylidene complexes* **3** and **6**.[5]

In addition to the synthesis and characterization of $(Me_3ECH_2)_2Ta(=CHEMe_3)Si(SiMe_3)_3$ (E = C, **1**; E = Si, **2**), we report here our studies on the formation of *silyl alkylidene complex* **2**. *In contrast to the formation of the alkyl alkylidene complexes **3** and **6**, the formation of **2** was found to follow the first pathway.* $(Me_3SiCH_2)_3$-$Ta(Cl)Si(SiMe_3)_3$ (**9**) undergoes silane elimination to give "$(Me_3SiCH_2)_2Ta(=CHSiMe_3)Cl$" and then subsequent Cl^- substitution by $Si(SiMe_3)_3^-$ to form the silyl alkylidene complex. Our studies here offer a comparison of different reactivities of alkyl and silyl ligands.

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere with the use of either a drybox or standard Schlenk techniques. 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 N_2. NMR spectra, unless noted, were recorded at 23 °C on a Bruker AC-250 or AMX-400 Fourier transform spectrometer. ^1H and ^{13}C NMR chemical shifts were referenced to solvents (residual protons in the ^1H spectra). ^{29}Si chemical shifts were referenced to $SiMe_4$. $TaCl_5$ (Strem) was used without further purification. Me_3SiCH_2MgCl,[6] $LiSi(SiMe_3)_3(THF)_3$,[7] (Me_3-

$CCH_2)_3TaCl_2$,[4b] and $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ (**10**)[8] were prepared by the literature procedures. The elemental analyses were performed by Desert Analytics (Tucson, AZ).

Preparation of $(Me_3SiCH_2)_3TaCl_2$. The synthesis described here is a modified procedure from the reported synthesis through a reaction between $TaCl_5$ and $(Me_3SiCH_2)_2$-Zn.[6b,c] A stirred solution of $TaCl_5$ (3.5 g, 9.77 mmol) in 80 mL of hexanes at −78 °C was treated with a 1.50 M solution of Me_3SiCH_2MgCl (20 mL, 30 mmol). After the addition was complete, the reaction mixture was warmed to 30 °C and stirred for 1 h, at which time ^1H NMR spectra showed the reaction to be complete. The solvents were then removed, and the residue was extracted with 70 mL of hexanes and filtered. The filtrate was evaporated to give a yellow solid, which was sublimed at 60 °C to give 4.84 g of $(Me_3SiCH_2)_3TaCl_2$ (yield 94% from $TaCl_5$).

Preparation of $(Me_3CCH_2)_2Ta(=CHCMe_3)Si(SiMe_3)_3$ (1). A solution of $(Me_3CCH_2)_3TaCl_2$ (3.02 g, 6.49 mmol) in 30 mL of toluene was added with vigorous stirring to a solution of $LiSi(SiMe_3)_3(THF)_3$ (6.11 g, 12.97 mmol) in 60 mL of toluene at −20 °C. The color of the solution changed slowly first to brown and then orange. The solution was allowed to warm to room temperature. After the solution was stirred for another 3 h, the solvent was removed in vacuo. Then the reaction mixture was pumped (1×10^{-4} mmHg) overnight to remove $HSi(SiMe_3)_3$. The residue was dissolved in a small amount of hexanes and recrystallized at −20 °C, yielding 3.05 g of orange crystals (4.76 mmol, 73% yield). Anal. Calcd for $C_{24}H_{59}Si_4Ta$: C, 44.98; H, 9.29. Found: C, 43.82; H, 9.41.[9] Molecular weight (cryoscopic in cyclohexane): Calcd, 641; found, 637. NMR: ^1H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 1.65 (1H, =C*H*), 1.52 (2H, CH$_a$*H*$_b$, $^2J_{H-H}$ = 12.2 Hz), 1.50 (9H, =CHC*Me₃*), 1.16 (18H, CH₂C*Me₃*), 0.41 (27H, Si*Me₃*), −0.44 (2H, C*H*$_a$H$_b$); $^{13}C\{^1H\}$ NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 263.1 (=*C*H, $^1J_{C-H}$ = 80.5 Hz), 144.8 (*C*H₂, $^1J_{C-H}$ = 101.9 Hz), 48.6 (=CH*C*Me₃), 38.1 (CH₂*C*Me₃), 35.1 (CH₂C*Me₃*), 34.7 (=CHC*Me₃*), 4.0 (Si*Me₃*, $^1J_{C-H}$ = 119.6 Hz, $^1J_{Si-C}$ = 44 Hz); $^{29}Si\{^1H\}$ NMR (benzene-d_6, 79.5 MHz, 23 °C) δ −5.30 (*Si*Me₃), −53.47 (*Si*SiMe₃).

Preparation of $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ (2). A solution of $(Me_3SiCH_2)_3TaCl_2$ (8.00 g, 15.23 mmol) in 80 mL of hexanes was added with vigorous stirring to a solution of $LiSi(SiMe_3)_3(THF)_3$ (14.74 g, 31.30 mmol) in 100 mL of hexanes at 0 °C. The color of the solution changed first to purple-red and then orange. The solution was allowed to warm to room temperature. After the solution was stirred for 35 min, the solvent was removed in vacuo. The NMR of the reaction mixture showed the products were **2**, $HSi(SiMe_3)_3$, and a small amount of $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ (**10**). The mixture was pumped (1×10^{-4} mmHg) overnight to remove $HSi(SiMe_3)_3$ and then dissolved in a small amount of hexanes. Recrystallization at −20 °C gave 7.52 g of orange crystals (10.9 mmol, 72% yield). Anal. Calcd for $C_{21}H_{59}Si_7Ta$: C, 36.61; H, 8.64. Found: C, 36.21; H, 8.71. NMR: ^1H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 6.42 (s, 1H, =C*H*SiMe₃), 0.80 (d, 2H, Me₃-SiC*H*$_a$H$_b$, $^2J_{H-H}$ = 11.8 Hz), 0.39 (s, 27H, SiSi*Me₃*, $^1J_{Si-H}$ = 6.5 Hz), 0.38 (s, 9H, =CHSi*Me₃*), 0.22 (s, 27H, CH₂Si*Me₃*, $^1J_{Si-H}$ = 6.5 Hz), −0.35 (d, 2H, Me₃SiCH$_a$*H*$_b$); $^{13}C\{^1H\}$ NMR (benzene-d_6, 62.9 MHz, 23 °C) δ 263.4 (=*C*HSiMe₃, $^1J_{C-H}$ = 94.5 Hz), 114.5 (*C*H₂SiMe₃, $^1J_{C-H}$ = 103.3 Hz), 3.8 (SiSi*Me₃*, $^1J_{C-H}$ =

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119.7 Hz), 3.3 (=CHSi*Me*₃, $^1J_{C-H}$ = 118.4 Hz), 2.9 (CH₂Si*Me*₃, $^1J_{C-H}$ = 118.6 Hz); ²⁹Si{¹H} NMR (benzene-*d*₆, 79.5 MHz, 23 °C) δ −0.06 (CH₂*Si*Me₃), −5.68 (Si*Si*Me₃), −11.23 (=CH*Si*Me₃), −38.90 (*Si*SiMe₃).

Preparation of (Me₃CCH₂)₃Ta(Cl)Si(SiMe₃)₃ (11). The unstable compound **11** was prepared by the addition of 0.073 mL of anhydrous HCl (1.0 M, in Et₂O) to 50 mg of (Me₃CCH₂)₂-Ta(=CHCMe₃)Si(SiMe₃)₃ (**1**, 0.078 mmol) in 1 mL of Et₂O at −78 °C. Purple compound **11** was formed instantaneously. **11** was found to decompose above −90 °C to HSi(SiMe₃)₃ and other unidentified products. ¹H NMR (toluene-*d*₈, 400.1 MHz, −90 °C): δ 2.32 (s, 6H, C*H*₂), 1.22 (s, 27H, C*Me*₃), 0.41 (s, 27H, Si*Me*₃).
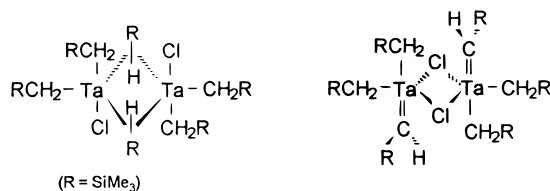
Preparation of (Me₃SiCH₂)₃Ta(Cl)Si(SiMe₃)₃ (9). A solution of 50 mg of **2** (0.073 mmol) in 1 mL of Et₂O was cooled to −78 °C, and anhydrous HCl (0.073 mL, 1.0 M, in Et₂O) was added dropwise by syringe. The solution turned purple immediately. The volatiles were removed under vacuum at −78 °C to give a purple solid of thermally unstable complex **9**. It can also be prepared in situ in hexanes or toluene by similar methods. NMR: ¹H NMR (toluene-*d*₈, 400.1 MHz, −50 °C) δ 2.30 (s, 6H, C*H*₂), 0.38 (s, 27H, SiSi*Me*₃), 0.28 (s, 27H, CH₂Si*Me*₃); ¹³C{¹H} NMR (toluene-*d*₈, 100.6 MHz, −50 °C) δ 121.9 (*C*H₂), 3.8 (SiSi*Me*₃), 1.70 (CH₂Si*Me*₃).

Observation of 9 in the Reaction of (Me₃SiCH₂)₃TaCl₂ with 1 equiv of LiSi(SiMe₃)₃(THF)₃. A stirred solution of LiSi(SiMe₃)₃(THF)₃ (13 mg, 0.029 mmol) in 0.5 mL of Et₂O at −78 °C was treated dropwise with a solution of 15 mg of (Me₃-SiCH₂)₃TaCl₂ (0.029 mmol) in 0.5 mL of Et₂O. The solution changed to a deep purple-brownish color. The solvent was then removed at −78 °C. The NMR spectra (−50 °C) of the remaining solid showed the presence of the unstable **9** and (Me₃SiCH₂)₂(Cl)₂Ta₂(=CHSiMe₃)₂ (**12**).[10]

Kinetic Studies of the Decomposition of (Me₃SiCH₂)₃Ta-(Cl)Si(SiMe₃)₃ (9) to 12. **9** was synthesized *in situ* as described above by adding 1 equiv of HCl into the solution of **2** in Et₂O at −78 °C. A portion of the solution containing **9** was transferred into another flask, and the solvent was removed by vacuum at ca. −50 °C. The purple compound **9** and 4,4′-dimethylbiphenyl (1.1−4.1 mg, an internal standard) were then dissolved in toluene-*d*₈ at −50 to −60 °C to make [**9**]₀ between 0.0026 and 0.018 M and the internal standard at 0.015−0.036 M. The solution was transferred at −50 to −60 °C to a J. Young valve NMR tube. The NMR spectra were taken at 227 ± 1, 233 ± 1, 238 ± 1, 244 ± 1, 249 ± 1, and 255 ± 1 K. The concentrations of **9** were calculated from the integrations of its ¹H NMR peaks with respect to the internal standard 4,4′-dimethylbiphenyl.

The rate constants were obtained from at least two separate experiments at a given temperature, and their averages are listed. The *maximum* random uncertainty in the rate constants was combined with the estimated systematic uncertainty, ca. 5%.[11] The total uncertainties in the rate constants

were used in the Eyring plots and error propagation calculations. The estimated uncertainty in the temperature measurements for an NMR probe was 1 K. The activation enthalpies (Δ*H*‡) and entropies (Δ*S*‡) were calculated from an unweighted nonlinear least-squares procedure contained in the SigmaPlot Scientific Graph System, which is available from Jandel Corp. The uncertainties in Δ*H*‡ and Δ*S*‡ were computed from the error propagation formulas derived from the Eyring equation by Girolami and co-workers.[12]

Reaction of 9 with LiSi(SiMe₃)₃(THF)₃ and Kinetic Studies of the Reaction. Compound **9** was synthesized as described above from 65 mg of **2** (0.094 mmol in 1 mL of Et₂O) and anhydrous HCl (0.094 mL, 1.0 M in Et₂O) at −78 °C. LiSi-(SiMe₃)₃(THF)₃ (44 mg, 0.094 mmol) in 1 mL of Et₂O was added to the purple solution at −78 °C. The solution was allowed to warm to room temperature, and the color gradually changed from purple to orange. NMR analysis showed the products to be HSi(SiMe₃)₃ and **2**.

In kinetic studies, the thermally unstable compound **9** was prepared at ca. −50 °C with the use of the procedures described above. LiSi(SiMe₃)₃(THF)₃ and 4,4′-dimethylbiphenyl (1.5−3.0 mg, an internal standard) were dissolved in toluene-*d*₈. The toluene-*d*₈ was then added to the purple compound **9** at −50 °C (the concentration of the internal standard was between 0.015 and 0.027 M). The reaction with an excess of LiSi-(SiMe₃)₃(THF)₃ was monitored by NMR at 238 ± 1 and 244 ± 1 K. The concentrations of **9** were calculated from the integrations of its NMR peaks with respect to the internal standard 4,4′-dimethylbiphenyl. The reaction products were **2** and HSi(SiMe₃)₃ along with unreacted LiSi(SiMe₃)₃(THF)₃.

Formation of (Me₃SiCH₂)₃(Cl)₂Ta₂(=CHSiMe₃)(≡CSiMe₃) (13). The unstable compound was observed in the decomposition of (Me₃SiCH₂)₄(Cl)₂Ta₂(=CHSiMe₃)₂ (**12**)[10] at 238 ± 1 K. **12** had been prepared *in situ*, by our procedure published earlier,[10] from the addition of 0.113 mL of anhydrous HCl (1.0 M, in Et₂O) to 50 mg of (Me₃SiCH₂)₄Ta₂(*μ*-CSiMe₃)₂[8] (**10**, 0.057 mmol) in Et₂O at −78 °C. The decomposition of **12** at 238 K was found to form **13**, which was characterized by ¹H, ¹³C, and ¹H−¹³C HETCOR NMR. **13** is thermally unstable and decomposes above −20 °C. NMR: ¹H NMR (toluene-*d*₈, 400.1 MHz, −50 °C) δ 4.68 (s, 1H, Me₃SiC*H*=), 1.94 (d, 1H, Me₃SiC*H*ₐHᵦ, $^2J_{H-H}$ = 10.4 Hz), 1.91 (d, 1H, Me₃SiC*H*cHd, $^2J_{H-H}$ = 10.4 Hz), 1.79 (d, 1H, Me₃SiCHₐ*H*ᵦ), 1.44 (d, 1H, Me₃SiC*H*ₑHf, $^2J_{H-H}$ = 13.4 Hz), 1.13 (d, 1H, Me₃SiHc*H*d), 1.01 (d, 1H, Me₃SiCHₑ*H*f), 0.42 (s, 9H, *Me*₃SiCH=), 0.36 (s, 18H, *Me*₃SiCH₂), 0.34 (s, 9H, *Me*₃SiCH₂), 0.21 (s, 9H, *Me*₃SiC≡); ¹³C NMR (toluene-*d*₈, 100.6 MHz, −50 °C) δ 376.4 (Me₃Si*C*≡), 237.4 (Me₃Si*C*H=, $^1J_{C-H}$ = 104.3 Hz), 91.5 (Me₃Si*C*H₂, $^1J_{C-H}$ = 110.8 Hz), 91.2 (Me₃Si*C*H₂, $^1J_{C-H}$ =108.3 Hz), 78.3 (Me₃Si*C*H₂, $^1J_{C-H}$ = 110.8 Hz), 4.3 (*Me*₃SiC≡, $^1J_{C-H}$ = 120.4 Hz), 3.5 (*Me*₃SiCH=, $^1J_{C-H}$ = 119.0 Hz), 3.0 (*Me*₃SiCH₂, $^1J_{C-H}$ = 118.9 Hz), 2.1 (*Me*₃SiCH₂, $^1J_{C-H}$ = 119.4 Hz). The assignment of the ¹H and ¹³C NMR resonances of **13** was based on those of **10** and **12** and its ¹H−¹³C HETCOR NMR.

X-ray Crystal Structure Determinations for 1 and 2. The crystal structures of **1** and **2** were obtained at 163 and 173 K, respectively, on a Siemens R3m/V diffractometer fitted with a Nicolet LT-2 low-temperature device. Suitable crystals of **1** and **2** were coated with Paratone oil (Exxon) and mounted under a stream of nitrogen. **1** was found to crystallize in the trigonal system with space group *P*3. A total of 3820 reflections were collected, of which 2452 were determined to be unique. The structure was solved using the Siemens SHELX-TL PLUS (VMS) proprietary software package. The tantalum was found by the Patterson method, and other atoms were located from a Fourier map and refined using the full-matrix least-squares method to *R* (w*R*) = 6.31 (7.90)%. The tantalum, silicon, and eight of the nine carbon atoms in the three −SiMe₃

(10) (a) Li, L.; Xue, Z.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 4992. (b) There are two possible structures for (Me₃-SiCH₂)₄(Cl)₂Ta₂(=CHSiMe₃)₂ (**12**) that are consistent with its NMR spectra and reactivities.

(R = SiMe₃)

This complex may contain either alkylidene or Cl⁻ as bridging ligands. Schrock and co-workers have reported several dimeric alkylidene complexes [M(CHCMe₃)LX₃]₂ (M = Nb, Ta; L = a tertiary phosphine; X = Cl, Br). Neutron diffraction studies have shown that[Ta(CHCMe₃)-(PMe₃)Cl₃]₂ contains two bridging halide ligands. See: Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G. A.; Fellmann, J. D. *J. Am. Chem. Soc.* **1979**, *101*, 1593. Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.

(11) See ref 5a for the procedures to estimate errors in rate constants.
(12) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.
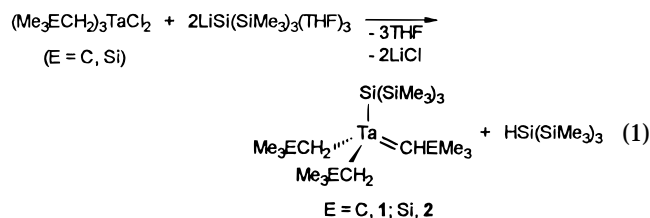
Table 1. Crystal Data for 1 and 2

|	compd	
	1	**2**
formula	$C_{24}H_{59}Si_4Ta$	$C_{21}H_{59}Si_7Ta$
fw	641.0	684.2
cryst size (mm³)	$0.35 \times 0.20 \times 0.20$	$0.80 \times 0.50 \times 0.20$
cryst system	trigonal	rhombohedral
space group	$P3$	$R3$
lattice params (Å)	$a = 16.292(2)$	$a = 16.373(2)$
	$c = 11.373(2)$	$c = 12.111(3)$
V (Å³)	2614.4(7)	2811.8(11)
Z	3	3
d(calcd) (g/cm³)	1.221	1.212
μ(Mo Kα) (cm^{-1})	32.56	31.25
$F(000)$	819	1053
temp (K)	163	173
scan type	$2\theta - \omega$	ω
$2\theta_{max}$ (deg)	45.0	45.0
index ranges	$\pm h, k, -l$	$\pm h, k, l$
unique reflcns	2452	871
params varied	182	88
final R indices		
R [$F > 4\sigma(F)$]	0.0631	0.0459
wR (all data)	0.0790	0.0588
goodness-of-fit	1.37	1.69

groups were anisotropically refined. No attempt was made to locate or calculate the hydrogen atoms. Crystal data for **1** are summarized in Table 1. **2** was found to crystallize in the rhombohedral system with space group $R3$. A total of 4064 reflections were collected, of which 871 were determined to be unique. The structure was solved using the Siemens SHELXTL PLUS (VMS) proprietary software package by direct methods. Refinements were done using the full-matrix least-squares method to R (wR) = 4.59 (5.88)%. The tantalum, silicon, and carbon atoms were anisotropically refined. The hydrogen atoms of the methyl groups were placed in calculated positions and introduced into the refinement as fixed contributors with isotropic U values of 0.08 Å². Crystal data for **2** are summarized in Table 1.

Results and Discussion

Syntheses of the Silyl Alkylidene Complexes $(Me_3ECH_2)_2Ta(=CHEMe_3)Si(SiMe_3)_3$ (E = C, 1; E = Si, 2). The oxygen- and moisture-sensitive compounds **1** and **2** are synthesized by the reactions shown in eq 1.

$(Me_3ECH_2)_3TaCl_2$ + $2LiSi(SiMe_3)_3(THF)_3$ $\xrightarrow[\text{- 2LiCl}]{\text{- 3THF}}$

(E = C, Si)

$$Me_3ECH_2 \overset{Si(SiMe_3)_3}{\underset{Me_3ECH_2}{\underset{\diagup}{\overset{\diagdown}{Ta}}}} \hspace{-0.3em}=\hspace{-0.2em} CHEMe_3 + HSi(SiMe_3)_3 \quad (1)$$

E = C, 1; Si, 2

The lithium silylating reagent $LiSi(SiMe_3)_3(THF)_3$ (2 equiv) reacts instantaneously with 1 equiv of the trialkyltantalum dichloride $(Me_3ECH_2)_3TaCl_2$ (E = C, Si) to form **1** and **2**, respectively, and 1 equiv of the corresponding silane $HSi(SiMe_3)_3$ in high yield. A preferential silane elimination reaction led to the formation of the alkylidene bonds in **1** and **2**. No alkanes, chloroalkanes, or chlorosilanes are observed. Such preferential elimination of a silane over alkanes to form alkylidene bonds is, to our knowledge, unprecedented.[13] When monitored by ^{1}H NMR at 23 °C, both reactions go to completion instantaneously in almost quantitative yield. Workup of the reaction mixture (*i.e.*, removal of solvent, extraction of the residue with hexanes, and filtration) gave a mixture of $HSi(SiMe_3)_3$ and **1** or **2**. A
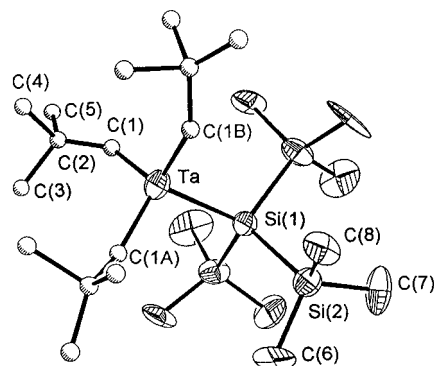
Figure 1. ORTEP diagram of $(Me_3CCH_2)_2Ta(=CHCMe_3)Si(SiMe_3)_3$ (**1**). One of three symmetry-independent, but chemically equivalent, molecules is shown. Thermal ellipsoids are drawn at the 20% probability level.
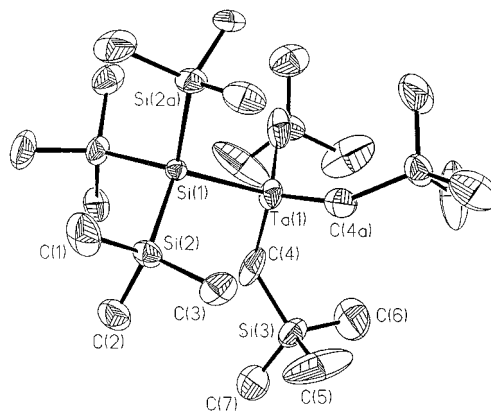
Figure 2. ORTEP diagram of $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ (**2**), showing 20% probability thermal ellipsoids.

small amount of a byproduct $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ (**10**) was observed in the formation of **2**. The silane was removed at 23 °C by an oil-diffusion pump (10^{-4} mmHg). Subsequent crystallization at −20 °C gave crystals of **1** and **2** which were characterized by NMR. The NMR of **1** and **2** are consistent with the structure assignments. In both compounds, there are large chemical shift differences between the diastereotopic H_a and H_b atoms of the $Me_3ECH_aH_b$ groups (1.96 ppm for **1** and 1.15 ppm for **2**). The α-carbon resonances of these ligands in the ^{1}H-gated-decoupled ^{13}C NMR at both 23 and −70 °C appear as triplets. In both compounds, the equality of the $^1J(C-H_a)$ and $^1J(C-H_b)$ coupling constants rules out the possibility of an agostic CH_a-Ta interaction. It appears that the chemical shift differences in **1** and **2** are due to the diamagnetic anisotropy of the metal−carbon multiple bonds. One interesting comparison is that the reaction of $(Me_3CCH_2)_3TaCl_2$ with 2 equiv of the silylating reagent $LiSi(SiMe_3)_3(THF)_3$ to form the silyl alkylidene complex **1** is much faster than its reaction with 2 equiv of an alkylating reagent Me_3CCH_2Li to form the alkyl alkylidene compound $(Me_3CCH_2)_3Ta=CHCMe_3$ (**3**). The former reaction is completed in a few seconds at 23 °C while the latter requires 20−30 min of stirring.[4b]

Crystal and Molecular Structures of 1 and 2. The molecular structures of **1** and **2** are shown in

(13) (a) Elimination of HSiMe₃ has been reported in the decomposition of $(C_5Me_5)Ta(SiMe_3)Me_3$: Arnold, J.; Shina, D. N.; Tilley, T. D.; Aria, A. M. *Organometallics* **1986**, *5*, 2037. (b) Syntheses of carbene M=C bonds were reported[2g] by cleavage of M−Si bonds in anionic silyl complexes through 1,2-elimination of halosilanes.

Table 2. Selected Interatomic Distances and Angles for 1[a]

(a) Intramolecular Distances (Å)			
Ta–Si(1)	2.680(15)	Ta–C(1)	1.97(5)
Ta′–Si′(1)	2.651(14)	Ta′–C′(1)	2.00(3)
Ta″–Si″(1)	2.559(16)	Ta″–C″(1)	2.21(4)
Si(1)–Si(2)	2.367(11)	Si′(1)–Si′(2)	2.330(11)
Si″(1)–Si″(2)	2.353(12)	C(1)–C(2)	1.47(8)
C′(1)–C′(2)	1.55(4)	C″(1)–C″(2)	1.39(16)

(b) Intramolecular Bond Angles (deg)			
Si(1)–Ta–C(1)	105.4(12)	C(1)–Ta–C(1A)	113.2(12)
Si′(1)–Ta′–C′(1)	105.3(9)	C′(1)–Ta′–C′(1A)	113.3(10)
Si″(1)–Ta″–C″(1)	105.9(8)	C″(1)–Ta″–C″(1A)	112.7(9)
Ta–Si(1)–Si(2)	111.0(4)	Ta′–Si′(1)–Si′(2)	111.0(4)
Ta″–Si″(1)–Si″(2)	111.8(4)	Ta–C(1)–C(2)	149(3)
Ta″–C′(1)–C′(2)	145(2)	Ta″–C″(1)–C″(2)	135(2)

[a] There are three independent molecules; the intermolecular distances and angles of the three molecules are listed.

**Table 3. Selected Interatomic Distances and Angles for 2**

(a) Intramolecular Distances (Å)			
Ta(1)–Si(1)	2.611(7)	Ta(1)–C(4)	2.03(4)
Si(1)–Si(2)	2.349(7)	Si(3)–C(4)	1.87(3)

(b) Intramolecular Bond Angles (deg)			
Si(1)–Ta(1)–C(4)	105.4(6)	C(4)–Ta(1)–C(4A)	113.2(8)
Ta(1)–Si(1)–Si(2)	110.8(2)	Si(2)–Si(1)–Si(2A)	108.2(2)
C(4)–Si(3)–C(5)	113(2)	C(4)–Si(3)–C(6)	112(3)
C(4)–Si(3)–C(7)	112(2)	Ta(1)–C(4)–Si(3)	131.8(13)

Scheme 1. Preparation of 11 and 9
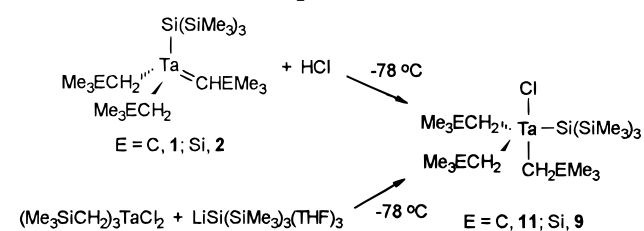
Figures 1 and 2. Selected bond lengths and angles are listed in Tables 2 and 3. Crystallographically imposed 3-fold rotation axes containing the Si–Ta bonds in both complexes result in a disorder between the alkylidene and the two alkyl ligands. The average Ta–C bond length in **1** is 1.97(3) Å, and the average Ta–C bond length in **2** is 2.03(4) Å. In comparison, the Ta–C and Ta=C bond lengths in [Ta(=CHBu[t])(CH$_2$Bu[t])(PMe$_3$)$_2$]$_2$-(μ-N$_2$) are 2.285(10) and 1.932(9) Å, respectively,[14a] and the Ta–C and Ta=C bond lengths in Ta(=CHSiMe$_3$)-(CH$_2$SiMe$_3$)(OC$_6$H$_3$tBu$_2$-2,6)$_2$ are 2.17(2) and 1.89(3) Å, respectively.[14b] In both **1** and **2** the –Si(SiMe$_3$)$_3$ and alkyl(alkylidene)–Ta moieties are arranged in a staggered conformation. Such a conformation has been observed in (Me$_3$ECH$_2$)$_3$TiSi(SiMe$_3$)$_3$ (E = C, Si)[5,15] and (Bu^{t}O)$_3$ZrSi(SiMe$_3$)$_3$.[2i] The geometries of these moieties in both **1** and **2** are pseudotetrahedral, with bond angles ranging from 105.4(12) to 113.2(14)° in **1** and 105.4(6) to 113.2(8)° in **2**. The Ta–Si distances of 2.559(16)– 2.680(15) Å in **1** and 2.611(7) Å in **2** are comparable to many previously reported values[16] but are shorter than that in Cp$_2$Ta(PMe$_3$)(Si^{t}Bu$_2$H).[16b] The molecular weight

(14) (a) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 2899. Turner, H. W.; Fellmann, J. D.; Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 7809. (b) Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 7338.
(15) McAlexander, L. K.; Hung, M.; Li, L.; Diminnie, J. D.; Xue, Z.; Yap, G. P. A.; Rheingold, A. L. Submitted for publication in *Organometallics*.

Scheme 2. Observed Reactions Involving 9
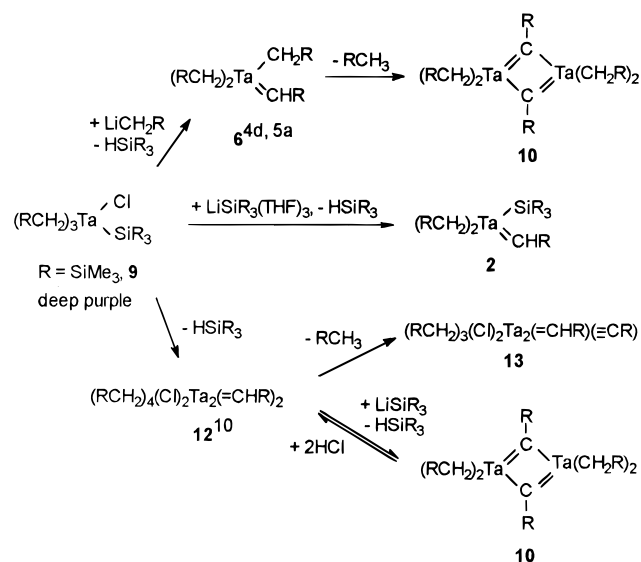
of **1**, as determined by cryoscopy in cyclohexane, indicates that **1** exists as a monomer in solution.

Formation of (Me$_3$ECH$_2$)$_3$Ta(Cl)Si(SiMe$_3$)$_3$ (E = C, 11; E = Si, 9). When **1** or **2** was reacted with 1 equiv of anhydrous HCl at −78 °C, a thermally unstable purple complex (Me$_3$ECH$_2$)$_3$Ta(Cl)Si(SiMe$_3$)$_3$ (E = C, **11**; E = Si, **9**) was immediately formed (Scheme 1). In the reaction of (Me$_3$SiCH$_2$)$_3$TaCl$_2$ with *1 equiv* of LiSi-(SiMe$_3$)$_3$(THF)$_3$ at −78 °C, a purple solution was observed. The analysis of the purple solution by NMR showed that it was a mixture of **9** and a dimeric bis-(alkylidene) compound (Me$_3$SiCH$_2$)$_4$(Cl)$_2$Ta$_2$(=CHSiMe$_3$)$_2$ (**12**), which we had observed as the product of the addition of HCl to the bis(alkylidyne) compound (Me$_3$-SiCH$_2$)$_4$Ta$_2$(μ-CSiMe$_3$)$_2$ (**10**).[10]

Compound **11** was found to decompose above −90 °C to form HSi(SiMe$_3$)$_3$ and unidentified products. However, compound **9**, probably due to the steric factor, is relatively more stable than **11**, which makes it possible to conduct studies of the reactions of **9**.

The Reactions Involving (Me$_3$SiCH$_2$)$_3$Ta(Cl)Si-(SiMe$_3$)$_3$ (9). These reactions are summarized in Scheme 2. **9** was found to react with another 1 equiv of LiSi(SiMe$_3$)$_3$(THF)$_3$ to give (Me$_3$SiCH$_2$)$_2$Ta(=CHSiMe$_3$)-Si(SiMe$_3$)$_3$ (**2**) through preferential elimination of silane HSi(SiMe$_3$)$_3$. In the formation of **2** from the reaction of (Me$_3$SiCH$_2$)$_3$TaCl$_2$ with *2 equiv* of Li(THF)$_3$Si(SiMe$_3$)$_3$ at −78 °C, the unstable intermediate **9** and a small amount of **11** were also observed before **9** reacted further to produce **2**.

The thermally unstable complex **9** was found to react with LiCH$_2$SiMe$_3$ to form the alkyl alkylidene complex **6** by elimination of silane HSi(SiMe$_3$)$_3$. **6** further decomposes, through alkane elimination, to form a dimeric bis(alkylidyne) complex **10**, as we have recently reported.[5] It is interesting to note that the conversion **9 → 6** involves a preferential silane elimination reaction,

(16) Some reported Ta–Si distances: (a) 2.624(12)–2.633(2) Å in Cp$_2$Ta(H)(SiMe$_2$H) and 2.639 (4) Å in Cp$_2$Ta(PMe$_3$)(SiMe$_3$). Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1991**, *10*, 3648. (b) 2.631-(2)–2.684(1) Å in Cp$_2$Ta(CO)(SiR$_3$) (R$_3$ = Me$_3$, ^{t}Bu$_2$H) and 2.740 Å in Cp$_2$Ta(PMe$_3$)(Si^{t}Bu$_2$H). Jiang, Q.; Pestana, D. C.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 3679. (c) 2.651(4) Å in Cp$_2$Ta-(H)$_2$SiPhMe$_2$. Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701. (d) 2.669(4) Å in (C$_5$Me$_5$)Ta(SiMe$_3$)Cl$_3$. See ref 13a.
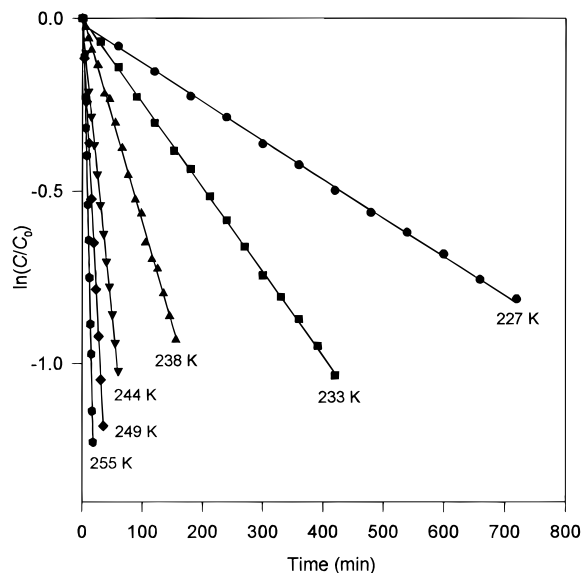
Figure 3. Kinetics plots of the decomposition of **9** to **12**.

Table 4. Measured Rate Constants k_1 for the Decomposition of 9 to 12[a]

T (K)	$10^4(k_1 \pm \delta k_{1(ran)})$ (s^{-1})	T (K)	$10^4(k_1 \pm \delta k_{1(ran)})$ (s^{-1})
227 ± 1	0.192 ± 0.005	244 ± 1	2.72 ± 0.08
233 ± 1	0.407 ± 0.001	249 ± 1	5.72 ± 0.11
238 ± 1	1.03 ± 0.02	255 ± 1	12.0 ± 0.4

[a] The total uncertainty $\delta k_{1(tot)}/k_1$ of 6% was calculated from random uncertainty $\delta k_{1(ran)}/k_1 = 3.3\%$ and systematic uncertainty $\delta k_{1(sys)}/k_1 = 5\%$; the rate constants are listed as $k_1 \pm \delta k_{1(tot)}$.

which is *followed* by an alkane elimination in the conversion **6 → 10**.

The decomposition of **9** was found to produce **12**, which decomposes further to give an alkylidene alkylidyne complex **13**. Again preferential silane elimination is involved; the first step in the conversion **9 → 13** occurs through preferential silane elimination and dimerization to **12**, which is followed by alkane elimination to form **13** from **12**. If LiSi(SiMe$_3$)$_3$(THF)$_3$ is present, **12** reacts with the lithium silyl compound to form **10**, as we have recently reported.[10]

The decomposition of **9** to **12** was observed to follow first-order kinetics. Plots of $\ln(C/C_0)$ vs t at six different temperatures are shown in Figure 3. The rate constants at these temperatures were calculated from the slope $= -k_1$ and are listed in Table 4. An Eyring plot of $\ln(k_1/T)$ vs $1/T$ is shown in Figure 4. The activation parameters thus derived for the decomposition of **9** are $\Delta H^{\ddagger} = 17.2(1.0)$ kcal/mol and $\Delta S^{\ddagger} = -4(4)$ eu.

In order to find out whether the decomposition of **9** was the rate-determining step in the formation of **2** and HSi(SiMe$_3$)$_3$, we studied the kinetics of the reaction of **9** with LiSi(SiMe$_3$)$_3$(THF)$_3$ at 238 and 244 K. Excess LiSi(SiMe$_3$)$_3$(THF)$_3$ (between 2- and 17-fold) was used in these kinetic studies to investigate if the concentration of LiSi(SiMe$_3$)$_3$(THF)$_3$ affected the reaction rates. The reaction was found to follow first-oder kinetics.[17] The measured rate constants k_2 for the reaction are listed in Table 5. These rate constants k_2 [(1.04–1.12) $\times$ 10^{-4} s^{-1} at 238 K and (2.67–2.83) $\times$ 10^{-4} s^{-1} at 244 K] were found to be almost equal to the

(17) See Supporting Information for plots of $\ln(C/C_0)$ vs t at 238 and 244 K for the reaction of **9** with Li(THF)$_3$Si(SiMe$_3$)$_3$ at different concentrations of Li(THF)$_3$Si(SiMe$_3$)$_3$.
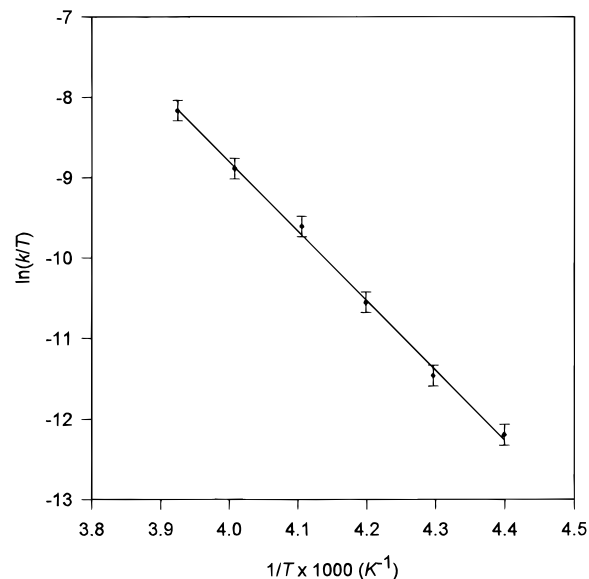
Figure 4. Eyring plot of the decomposition of **9** to **12**.

Table 5. Measured Rate Constants k_2 for the Reactions of 9 with LiSi(SiMe$_3$)$_3$(THF)$_3$[a]

expt	T (K)	C_0 (M)	C_0' (M)	$10^4 k_2$ (s^{-1})	$10^4(k_1 \pm \delta k_{1(tot)})$ (s^{-1})[b]
1	238 ± 1	0.0057	0.098	1.04	1.03 ± 0.06
2	238 ± 1	0.0063	0.013	1.12	
3	244 ± 1	0.0049	0.046	2.83	2.72 ± 0.16
4	244 ± 1	0.0026	0.027	2.67	

[a] C_0, initial concentration of (Me$_3$SiCH$_2$)$_3$Ta(Cl)Si(SiMe$_3$)$_3$ (**9**); C_0', initial concentration of Li(THF)$_3$Si(SiMe$_3$)$_3$. [b] See Table 4 for a detailed list of k_1. The total uncertainty $\delta k_{1(tot)}$ is used here.

rate constants k_1 for the decomposition of **9** to **12** [1.03-(6) $\times$ 10^{-4} s^{-1} at 238 K and 2.72(16) $\times$ 10^{-4} s^{-1} at 244 K] and independent of the concentration of LiSi(SiMe$_3$)$_3$-(THF)$_3$.

Preferential Silane Elimination. Even though there have been few comparisons of metal–silicon vs metal–carbon bond strengths,[18,19] recent experimental[16b,20] and theoretical studies[21a] of M–Si and M–C bonding energetics provide a more detailed picture of metal–silyl bonding and reactivity. These investigations indicate that early-transition-metal (especially d^0)–silicon bonds are weaker than metal–hydrocarbyl bonds. Marks and co-workers have shown that M–Si bond disruption enthalpies (BDEs) involving d^0 early transition metals are about 14–17 kcal mol^{-1} smaller than those of the corresponding metal hydrocarbyl
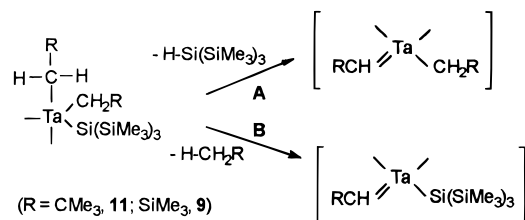
(18) For recent articles and reviews on bonding energies of organometallic compounds, see: (a) *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990. (b) Martinho Simões, J. A.; Beauchamp, J. M. *Chem. Rev.* **1990**, *90*, 629. (c) *Energetics of Organometallic Species*; Martinho Simões, J. A., Ed.; NATO ASI Series C; Kluwer Academic Publishers: Boston, MA, 1992; Vol. 367. (d) Nolan, S. P. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; VCH: New York, 1994; p 307 and references therein.

(19) For bonding energies of silicon compounds, see: (a) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (b) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 1, Chapter 5, p 371.

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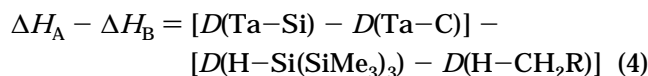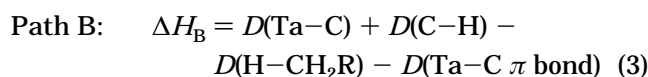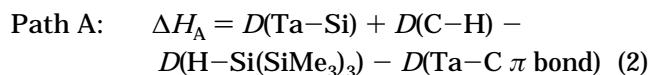
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Scheme 3. Competing Silane (Path A) and Alkane (Path B) Elimination Pathways for $(RCH_2)_3Ta(Cl)Si(SiMe_3)_3$ (R = CMe$_3$, 11; R = SiMe$_3$, 9)


Scheme 4. *Proposed* Pathways in the Formation of Alkylidene Compounds

$[ER'_3 = CH_2R$ or $Si(SiMe_3)_3; R = CMe_3, SiMe_3]$

bonds.[20]   In $Cp_2Zr(Me)Si(SiMe_3)_3$, *e.g.*, the Zr–Si bond [56(5) kcal mol^{-1}] is 10 kcal mol^{-1} weaker than the Zr–Me bond [66(5) kcal mol^{-1}].[20a]   Berry and co-workers also conclude, through their thermodynamic measurement of arene addition to $Cp_2Ta(PMe_3)SiMe_3$ (d^2) complex to yield $Cp_2Ta(PMe_3)Ar$ products, that the Ta–Ph BDE is about 5.4 kcal mol^{-1} larger than the Ta–Si BDE.[16b]   Koga and Morokuma, through their ab initio molecular orbital calculations, reported that the Zr–C bond in $Cl_2Zr(CH_3)H$ is 11.7–14.3 kcal mol^{-1} stronger than the Zr–Si bond in $Cl_2Zr(SiH_3)H$.[21a]   The stronger M–C bonds in early-transition-metal complexes have been attributed to larger electronegativity differences between M and C in metal alkyl complexes than those between M and Si in metal silyl complexes.[21]

However, a thermodynamic analysis of silane vs alkane elimination from $(RCH_2)_3Ta(Cl)Si(SiMe_3)_3$ (**11**, **9**) in the current work indicates that the silane elimination may *not* be thermodynamically favorable, even though M–Si bonds are weaker.   The smaller Ta–Si BDE is offset by the smaller H–Si BDE in $HSi(SiMe_3)_3$. In Scheme 3, the competing silane (path A) and alkane (path B) elimination pathways are shown.   The enthalpies of the two reactions are as follows:

Path A: $\Delta H_A = D(\text{Ta–Si}) + D(\text{C–H}) - D(\text{H–Si(SiMe}_3)_3) - D(\text{Ta–C } \pi \text{ bond})$ (2)

Path B: $\Delta H_B = D(\text{Ta–C}) + D(\text{C–H}) - D(\text{H–CH}_2R) - D(\text{Ta–C } \pi \text{ bond})$ (3)

$\Delta H_A - \Delta H_B = [D(\text{Ta–Si}) - D(\text{Ta–C})] - [D(\text{H–Si(SiMe}_3)_3) - D(\text{H–CH}_2R)]$ (4)

Here $D(\text{C–H})$ is the BDE of the α-C–H bond in TaCH$_2$R and $D(\text{Ta–C } \pi \text{ bond})$ is the BDE of the π bond in Ta=CHR.   The BDE of the H–Si in H–Si(SiMe$_3$)$_3$ is 79.0(1.0) kcal mol^{-1}.[19,22a]   The BDE's of a C–H bond in CMe$_4$ and SiMe$_4$ are 99.7(1.2) and 99.2(1.2) kcal mol^{-1}, respectively.[19,22b]   Combining these BDE's with the largest difference between the BDE's of M–Si and M–C bonds reported so far (-17 kcal mol^{-1})[20a] for eq 4 yields 3.2–3.7 kcal mol^{-1}.   In other words, the silane elimination is thermodynamically slightly less favored than the alkane elimination by at least 3 kcal mol^{-1}; the preferential silane elimination may *not* be driven by thermodynamics.   Our preliminary ab initio quantum mechanics calculations of the reactivities of $MCl_x(CH_3)_y(SiH_3)_z$ (M = Nb, Ta) are consistent with the thermodynamic
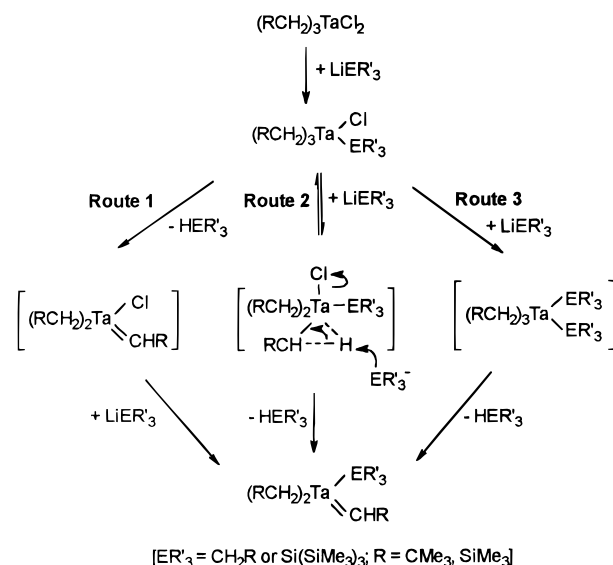
analysis here and show that CH$_4$ elimination is usually thermodynamically more favorable than SiH$_4$ elimination.[23]   The preferential silane elimination could be attributed to a kinetic effect: the calculated activation free energy is lower for silane elimination than for methane elimination by about 4–5 kcal mol^{-1}.[23]

Mechanistic Pathway to the Silyl Alkylidene Complex 2.   Three possible pathways for the reactions of $(RCH_2)_3Ta(Cl)ER'_3$ [ER'$_3$ = CH$_2$R, Si(SiMe$_3$)$_3$; R = CMe$_3$, SiMe$_3$] with LiER'$_3$ to form alkylidene complexes $(RCH_2)_2Ta(=CHR)ER'_3$ are listed in Scheme 4.   Such pathways were postulated for the reaction of $(Me_3CCH_2)_3TaCl_2$ with LiCH$_2$CMe$_3$ to form $(Me_3CCH_2)_3Ta=CHCMe_3$.[4b–g]   In route 1, the first step is an intramolecular α-hydrogen abstraction reaction by the ER'$_3$ ligand to eliminate HER'$_3$ and form an intermediate "$(RCH_2)_2Ta(=CHR)Cl$" containing an alkylidene bond.   Subsequent Cl$^-$ substitution by ER'$_3^-$ leads to the formation of the alkyl alkylidene or silyl alkylidene complex $(RCH_2)_2Ta(=CHR)ER'_3$.   In other words, the alkylidene bond forms *before* the Cl$^-$ substitution in route 1.   Route 2 involves a pre-equilibrium of $(RCH_2)_3Ta(ER'_3)Cl$ with an α-agostic isomer, which reacts with the added ER'$_3^-$ via intermolecular hydrogen abstraction to form the product $(RCH_2)_2Ta(=CHR)ER'_3$.   In route 3, the first step is the Cl$^-$ substitution to form a pentacoordinated $(RCH_2)_3Ta(ER'_3)_2$, followed by an α-hydrogen abstraction reaction to form $(RCH_2)_2Ta(=CHR)ER'_3$.   The alkylidene bond is formed *after* the Cl$^-$ substitution in route 3.

In route 1 (Scheme 4), if the first step in the reaction of $(RCH_2)_3Ta(Cl)ER'_3$ (α-hydrogen abstraction) is rate-determining, the reaction would follow first-order kinetics.   The rate constants to form $(RCH_2)_2Ta(=CHR)ER'_3$ should be the same as the rates of the decomposition of $(RCH_2)_3Ta(Cl)ER'_3$ and independent of the concentration of LiER'$_3$.   If route 2 or 3 is the pathway to $(RCH_2)_2Ta(=CHR)ER'_3$, the reaction of $(RCH_2)_3Ta(Cl)ER'_3$ with LiER'$_3$, as measured by the disappearance of $(RCH_2)_3Ta(Cl)ER'_3$, would be faster than the competitive decomposition of $(RCH_2)_3Ta(Cl)ER'_3$.   In addition, neither

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**Scheme 5. Mechanistic Pathways to the Silyl
Alkylidene Complex 2 and the Byproduct 10**
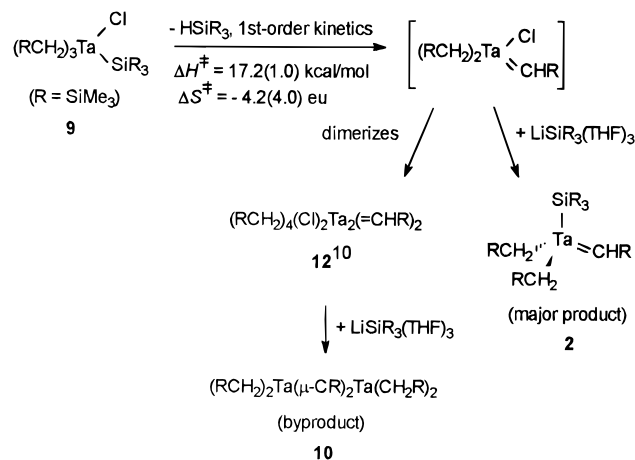
reaction in route 2 or 3 may follow first-order kinetics. Thus the reactivities of $(RCH_2)_3Ta(Cl)ER'_3$ and kinetic studies of its decomposition and reactions with $LiER'_3$ would provide information regarding the formation of the alkylidene complex.

In the current studies, the decomposition of $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ (**9**) was found to follow first-order kinetics (Figures 3 and 4) and give a dimeric bis(alkylidene) complex **12** (Scheme 2). In addition, the rates of the reaction of **9** with $LiSi(SiMe_3)_3(THF)_3$ are almost equal to the rates of the decomposition of **9** and independent of the concentration of $LiSi(SiMe_3)_3(THF)_3$. These observations are consistent with route 1 in Scheme 4 being the pathway to the formation of the silyl alkylidene complex **2**. The mechanistic pathways to the silyl alkylidene complex **2** and the byproduct **10** are shown in Scheme 5. The first step in the conversion of **9** to **2** is the rate-determining decomposition of **9** to give an unidentified intermediate "$(Me_3SiCH_2)_2Ta(=CHSiMe_3)Cl$". "$(Me_3SiCH_2)_2Ta(=CHSiMe_3)Cl$" either reacts with $LiSi(SiMe_3)_3(THF)_3$ to form the major product **2** (>95% yield) or dimerizes to give $(Me_3SiCH_2)_4(Cl)_2Ta_2(=CHSiMe_3)_2$ (**12**). **12** further reacts with $LiSi(SiMe_3)_3(THF)_3$ to give the minor byproduct $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ (**10**).[10] Thus in the formation of the *silyl alkylidene complex* **2** from **9**, the preferential silane

elimination to give the alkylidene bond precedes the Cl⁻ substitution.

In contrast, our recent studies showed that $(Me_3ECH_3)_4TaCl$ (E = C, **4**; E = Si, **7**) follows *a different pathway* (route 3 in Scheme 4) to form the *alkyl alkylidene complexes* $(Me_3ECH_3)_3Ta=CHEMe_3$ (**3** and **6**).[5] The Cl⁻ ligands are replaced to give $Ta(CH_2EMe_3)_5$. Subsequent alkane elimination leads to the formation of **3** or **6**; the alkylidene bonds are formed *after* the Cl⁻ substitution. The reasons for the different reactivities between $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ (**9**) and $(Me_3ECH_2)_4TaCl$ (**4** and **7**) are not clear. Steric factors perhaps play an important role here. The silyl ligand $Si(SiMe_3)_3$ is quite bulky and may make routes 2 and 3 in Scheme 3 unfavorable and route 1 the low-energy and preferred pathway instead.

Our studies reported here demonstrate that, similar to the α-hydrogen abstraction between alkyl ligands, a silyl group could react with the α-hydrogen of an alkyl ligand leading to the formation of alkylidene bonds. However, the reactivities of silyl ligands could be unique; silane elimination could be preferential to alkane elimination in metal alkyl silyl complexes, and the formation of a silyl alkylidene complex could follow a pathway different from that of alkyl alkylidene compounds.

Supporting Information Available: Complete lists of the crystallographic data for **1** and **2** (data collection parameters, atomic coordinates and thermal parameters, bond distances and angles) and plots of $\ln(C/C_0)$ vs t at 238 and 244 K for the reaction of **9** with $LiSi(SiMe_3)_3(THF)_3$ at different concentrations of $LiSi(SiMe_3)_3(THF)_3$ (17 pages). Ordering information is given on any current masthead page.