Silyl alkylidene complexes free of anionic π ligands $(Me_3ECH_2)_2Ta(=CHEMe_3)(SiPh_2Bu^t)$ (E = C, Si): PMe_3-promoted conversions to bis(alkylidene) complexes through preferential silane elimination

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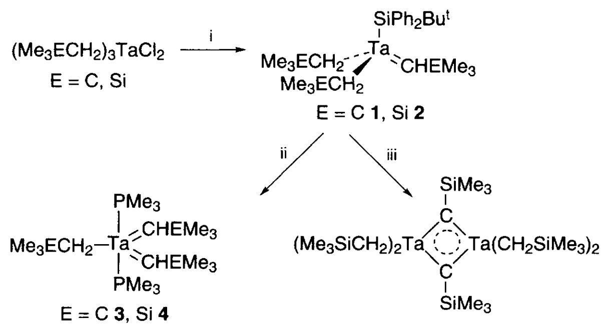
Silyl alkylidene complexes $(Me_3ECH_2)_2Ta(=CHEMe_3)(SiPh_2Bu^t)$ (E = C 1, Si 2) react with PMe_3 to form bis(alkylidene) complexes $(Me_3ECH_2)Ta(PMe_3)_2(=CHEMe_3)_2$ (E = C 3, Si 4; 4 is structurally characterized) *via* preferential silane elimination, but 2 thermally decomposes to an alkyl alkylidyne compound $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$.

Early-transition-metal silyl chemistry is currently a field of increasing interest.[1] We have been studying early-transition-metal silyl complexes that are free of anionic π ligands, such as cyclopentadienyl,[2a–c] with a two-fold interest: (*a*) the use of silyl complexes, *e.g.* $(RCH_2)_2Ta(=CHR)(SiR'_3)$, as models for the possible intermediates $(RCH_2)_2Ta(=CHR)(SiH_3)$ in the proposed reactions of $(RCH_2)_3Ta{=}CHR$ with SiH_4 to form metal silicides $TaSi_n$;[2d] (*b*) the synthesis, characterization, and reactivity of this new family of cyclopentadienyl free silyl complexes. Here, we report the synthesis and reactivities of the thermally unstable silyl alkylidene complexes $(Me_3ECH_2)_2Ta(=CHEMe_3)(SiPh_2Bu^t)$ (E = C **1**, Si **2**). Both **1** and **2** react with 2 equiv. of PMe_3 to give bis(phosphine)bis(alkylidene) complexes $(Me_3ECH_2)Ta(PMe_3)_2(=CHEMe_3)_2$ (E = C **3**,[3] Si **4**). Yet, in the absence of PMe_3, **2** converts to a bridging dimeric bis(alkylidyne) compound $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$.[4]

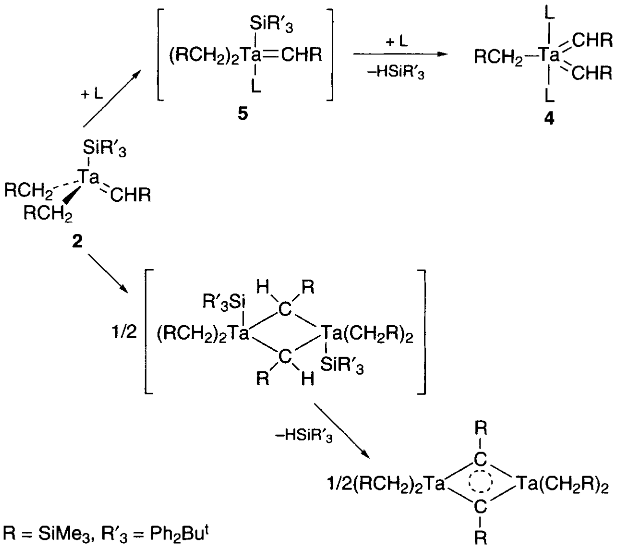
The reaction of 2 equiv. of the lithium silylating reagent $LiSiPh_2Bu^t(thf)_2$[5] with trialkyltantalum dichloride gives **1** and **2** (Scheme 1). The silyl alkylidene complexes **1** and **2** were found to be thermally unstable. **1** decomposes slowly over the course of several hours at room temperature by loss of $HSiPh_2Bu^t$ (as monitored by ^1H NMR) to give as yet unidentified products. **2** decomposes within minutes of its formation at room temperature to give $HSiPh_2Bu^t$ and $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$. In both cases decomposition is observed to occur *via* a preferential silane elimination over alkane elimination. In comparison, the analogous complexes $(Me_3ECH_2)_2(=CHEMe_3)Si(SiMe_3)_3$ (E = C, Si) were found to be stable at room temperature.[2a–c] Both compounds **1** and **2** are stable for much longer periods of time at −50 °C and have been characterized at this temperature by ^1H, $^{13}C\{^1H\}$, and ^{13}C–^1H HETCOR NMR;† the $Ta{=}C\mathit{H}EMe_3$ resonances of the alkylidene groups in **1** and **2** were observed at δ 2.84 (**1**) and 7.41 (**2**) in the ^1H NMR spectrum as well as at δ 268.0 (**1**) and 271.1 (**2**) in the ^{13}C NMR spectrum.



Scheme 1 *Reagents and conditions*: i, $2LiSiPh_2Bu^t(thf)_2$, $-2LiCl$, −2 thf, $-HSiPh_2Bu^t$; ii, $2PMe_3$, $-HSiPh_2Bu^t$; iii, E = Si, $-HSiPh_2Bu^t$

Reaction of either **1** or **2** (generated *in situ* at −70 °C) with 2 equiv. of PMe_3 results in the formation of **3** or **4** in good yields, along with 1 equiv. of $HSiPh_2Bu^t$.‡ Again, preferential silane elimination is observed. It is interesting that silane elimination from **2** in the absence of PMe_3 yields a product having *two* alkyl and *one* alkylidyne ligands, while silane elimination from **2** during reaction with PMe_3 yields a product with *one* alkyl and *two* alkylidene ligands. No reaction was observed between **1** and bulkier PPh_3. Schrock and coworkers have reported that the reaction of a neopentyl neopentylidene complex $(Me_3CCH_2)_3Ta{=}CHCMe_3$ with PR_3 (R_3 = Me_3, Me_2Ph) gives **3**.[3]

In the absence of PMe_3, the thermal decomposition of **2** may take a path that involves the initial dimerization of **2** through the coordination of the alkylidene bonds (Scheme 2),[6] followed by an α-hydrogen abstraction between the silyl ligands and the bridging alkylidene ligand to give the bridging alkylidyne compound. However, the initial coordination of L (PMe_3) may make the intermediate $(RCH_2)_2Ta(=CHR)(SiR'_3)L$ **5** less electron deficient and sterically bulky (thus making the dimerization of **5** unfavourable). Subsequent α-hydrogen abstraction between the silyl ligand and an alkyl ligand and the coordination of the second L gives the bis(alkylidene) compound **4**. It is less likely that an α-hydrogen abstraction occurs between the silyl ligand and the alkylidene ligand in **5** to give an alkylidyne bis(alkyl) intermediate '$(RCH_2)_2Ta(\equiv CR)L_2$', followed by an α-hydrogen exchange between an alkyl and the alkylidyne ligands. No such exchange was observed in $Ta(=CHCMe_3)_2(CD_2CMe_3)L_2$.[3a] The reactivities of the silyl alkylidene complexes **1** and **2** discussed here are novel. To our knowledge,



Scheme 2

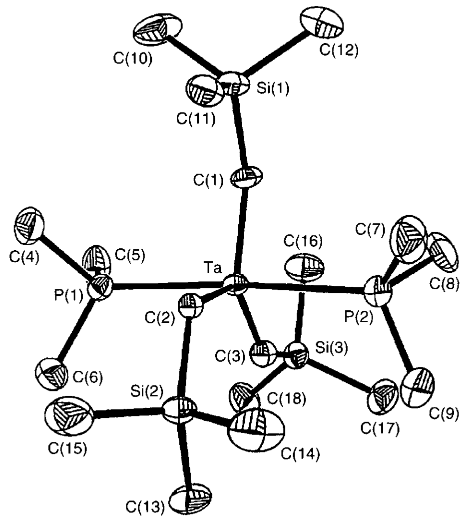


Fig. 1 ORTEP view of **4** showing 30% probability ellipsoids. The alternate positions for the disordered carbons C(2) and C(3) are omitted for clarity. Selected bond distances (Å) and angles (°): Ta–P(1) 2.583(2), Ta–P(2) 2.581(2), Ta–C(1) 1.998(8), Ta–C(2) 2.21(2), Ta–C(3) 1.95(2); P(1)–Ta–P(2) 175.73(7), Si(1)–C(1)–Ta 133.7(5), Si(2)–C(2)–Ta 124.6(12), Si(3)–C(3)–Ta 142.0(12), P(1)–Ta–C(1) 91.9(2), P(1)–Ta–C(2) 88.8(6), P(1)–Ta–C(3) 90.4(6), P(2)–Ta–C(1) 91.8(2), P(2)–Ta–C(2) 91.6(6), P(2)–Ta–C(3) 86.0(6), C(1)–Ta–C(2) 114.0(6), C(2)–Ta–C(3) 129.3(8), C(1)–Ta–C(3) 116.8(6).

this is the first case in which the formation of an alkyl alkylidyne compound, through the thermal decomposition of **2**, and phosphine-promoted formation of a bis(alkylidene) complex from the same complex are observed.

The molecular structure of the new compound **4** has been determined by X-ray crystallography (Fig. 1).§ **4** adopts a trigonal-bipyramidal geometry in the solid state, with the $\mathrm{PMe_3}$ ligands occupying axial positions. There is a positional disorder involving the α-carbon atoms of the alkyl and one of the alkylidene ligands [C(2) and C(3) in Fig. 1, respectively]. In addition, the Si–C–Ta angles of the two alkylidene ligands differ from each other significantly [133.7(5)° for Si(1)–C(1)–Ta *vs.* 142.0(12)° for Si(3)–C(3)–Ta].§ A similar distortion is observed in a bis(neopentylidene) complex $\mathrm{(mes)Ta(PMe_3)_2({=}CHBu^t)_2}$ (mes = mesityl),[7] and may be attributed to an α-agostic interaction between the distorted alkylidene proton and the metal.

Studies are continuing of the reaction of **1** and **2** with $\mathrm{PMe_3}$ to give **3** and **4**, and also to further probe the reactivity of these alkylidene silyl complexes.

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Footnotes

† NMR for **1**: ^{1}H ([$^2\mathrm{H_8}$]toluene, 400.1 MHz, −50 °C) δ 7.89–7.23 (m, 10 H, $\mathrm{Si}Ph_2\mathrm{Bu^t}$), 2.84 (s, 1 H, $\mathrm{{=}C}H\mathrm{Bu^t}$), 1.39 (s, 9 H, $\mathrm{SiPh_2C}Me_3$), 1.35 (s, 9 H, $\mathrm{{=}CHC}Me_3$), 1.05 (s, 18 H, $\mathrm{CH_2C}Me_3$), 1.02 (d, 2 H, $\mathrm{CH_a}H_\mathrm{b}\mathrm{Bu^t}$), 0.16 (d, 2 H, $\mathrm{C}H_\mathrm{a}\mathrm{H_bBu^t}$, $^2J_\mathrm{HH}$ 12.8 Hz). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ ([$^2\mathrm{H_8}$]toluene, 100.6 MHz, −50 °C) δ 268.0 ($\mathrm{{=}}C\mathrm{HBu^t}$, $^1J_\mathrm{C-H}$ 87.0 Hz), 145.4 ($C\mathrm{H_2Bu^t}$, $^1J_\mathrm{CH}$ 106.6 Hz), 144.6, 137.6, 137.3, 136.7 ($\mathrm{Si}Ph_2\mathrm{Bu^t}$), 47.7 ($\mathrm{{=}CH}C\mathrm{Me_3}$), 37.7 ($\mathrm{CH_2}C\mathrm{Me_3}$), 34.5 ($\mathrm{CH_2C}Me_3$, $^1J_\mathrm{CH}$ 123.7 Hz), 33.7 ($\mathrm{SiPh_2C}Me_3$), 30.4 ($\mathrm{{=}CHC}Me_3$, $^1J_\mathrm{CH}$ 125.7 Hz), 21.8 ($\mathrm{SiPh_2}C\mathrm{Me_3}$). NMR for **2**: ^{1}H ([$^2\mathrm{H_8}$]toluene$_8$, 400.1 MHz, −50 °C) δ 7.41 (s, 1 H, $\mathrm{{=}C}H\mathrm{SiMe_3}$), 7.80–7.24 (m, 10 H, $\mathrm{Si}Ph_2\mathrm{Bu^t}$), 1.32 (s, 9 H, $\mathrm{SiPh_2C}Me_3$), 0.86 (d, 2 H, $\mathrm{CH_a}H_\mathrm{b}\mathrm{SiMe_3}$), 0.35 (s, 9 H, $\mathrm{{=}CHSi}Me_3$), 0.11 (s, 18 H, $\mathrm{CH_2Si}Me_3$), −0.32 (d, 2 H, $\mathrm{C}H_\mathrm{a}\mathrm{H_bSiMe_3}$, $^2J_\mathrm{HH}$ 11.6 Hz). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ ([$^2\mathrm{H_8}$]toluene, 100.6 MHz, −50 °C) δ 271.1 ($\mathrm{{=}}C\mathrm{HSiMe_3}$, $^1J_\mathrm{CH}$ 90.8 Hz), 145.6, 138.6, 137.9, 126.7 ($\mathrm{Si}Ph_2\mathrm{Bu^t}$), 106.2 ($C\mathrm{H_2SiMe_3}$, $^1J_\mathrm{CH}$ 96.8 Hz), 30.5 ($\mathrm{SiPh_2C}Me_3$, $^1J_\mathrm{CH}$ 125.8 Hz), 22.5 ($\mathrm{SiPh_2}C\mathrm{Me_3}$), 4.9 ($\mathrm{{=}CHSi}Me_3$), 3.1 ($\mathrm{CH_2Si}Me_3$, $^1J_\mathrm{CH}$ 115.6 Hz).

‡ 1.001 g (1.91 mmol) of $\mathrm{(Me_3SiCH_2)_3TaCl_2}$ in 20 ml of $\mathrm{Et_2O}$ was added slowly to 1.567 g (4.01 mmol) $\mathrm{LiSiPh_2Bu^t(thf)_2}$ in 20 ml of $\mathrm{Et_2O}$ at −70 °C. The resulting dark red solution was stirred for 20 min at this temperature, and 0.60 ml of $\mathrm{PMe_3}$ (5.7 mmol) was added by syringe. The solution was allowed to warm to room temperature, filtered, concentrated, and cooled to −60 °C, yielding 0.626 g of microcrystalline **4** [55.5% based on $\mathrm{(Me_3SiCH_2)_3TaCl_2}$]. NMR: ^{1}H ($\mathrm{C_6D_6}$, 250.1 MHz, 23 °C) δ 7.92 (s, 1 H, $\mathrm{{=}C}H\mathrm{SiMe_3'}$), 7.06 (s, 1 H, $= \mathrm{C}H\mathrm{SiMe_3}$), 1.18 (t, 18 H, $\mathrm{PMe_3}$, $^2J_\mathrm{HP}$ 2.95 Hz), 0.34 (br s, 9 H, $\mathrm{{=}CHSi}Me_3'$), 0.22 (s, 9 H, $\mathrm{CH_2Si}Me_3$), 0.16 (br s, 9 H, $\mathrm{{=}CHSi}Me_3$), −0.33 (t, 2 H, $\mathrm{C}H_2\mathrm{SiMe_3}$, $^3J_\mathrm{HP}$ 19.8 Hz). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ ($\mathrm{C_6D_6}$, 62.9 MHz, 23 °C) δ 258.0 ($\mathrm{{=}}C\mathrm{HSiMe_3'}$, $^1J_\mathrm{CH}$ 97.7 Hz), 252.1 ($\mathrm{{=}}C\mathrm{HSiMe_3}$, $^1J_\mathrm{CH}$ 99.6 Hz), 50.3 ($C\mathrm{H_2SiMe_3}$, $^1J_\mathrm{CH}$ 106.9 Hz), 18.4 (t, $\mathrm{PMe_3}$, $^1J_\mathrm{CP}$ 12.0 Hz), 5.22 ($\mathrm{CH_2Si}Me_3$), 4.1 ($\mathrm{{=}CHSi}Me_3'$), 3.7 ($\mathrm{{=}CHSi}Me_3$). ^{31}P ($\mathrm{C_6D_6}$, 36.21 MHz, 23 °C) δ −2.31. ^{29}Si ([$^2\mathrm{H_8}$]toluene, 79.5 MHz, 23 °C) δ −3.10 ($\mathrm{CH_2SiMe_3}$), −15.65 ($\mathrm{{=}CHSiMe_3}$). Anal. Calc for $\mathrm{C_{18}H_{49}P_2Si_3Ta}$: C, 36.47; H 8.33. Found: C, 36.73; H, 8.18%. Similar reaction of $\mathrm{PMe_3}$with **1** at 0 °C in an NMR tube in [$^2\mathrm{H_8}$]toluene gave a quantitative yield of **3**[3] by ^{1}H and ^{13}C NMR.

§ *Crystal data* for **4**: monoclinic, space group $P2_1/n$, a = 10.504(4), b = 16.699(6), c = 16.848(7) Å, β = 91.84(3)°, Mo-Kα radiation. 4503 (3886 unique) reflections were collected at −100 °C on a Siemens R3m/V diffractometer fitted with a Nicolet LT-2 low-temperature device. The structure was solved by direct methods using the Siemens SHELXTL 93 (Version 5.0) proprietary software package. Full-matrix least-squares refinements on F^2 to $R[R_\mathrm{w}(F^2)]$ = 0.0333 [0.1123]. A two-site disorder involving the α-carbons of the alkyl and disorted alkylidene ligands was resolved using site occupancy factors of 0.5. The alternative angles for Si(2)–C(2)–Ta and Si(3)–C(3)–Ta in Fig. 1 are 122.2(11) and 144.2(13)°, respectively. Hydrogen atoms for the methyl groups were placed in calculated positions and introduced into the refinement as fixed contributors with isotropic U_{ij} values of 0.08 Å^2. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallogaphic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/227.

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