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Direct Observation of $(Me_3ECH_2)_5Ta$ (E = C, Si) as the Precursors to $(Me_3ECH_2)_3Ta{=}CHEMe_3$ and $(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2$. Kinetic and Mechanistic Studies of the Formation of Alkylidene and Alkylidyne Ligands[†]

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Abstract: Pentaalkyl complexes $(Me_3ECH_2)_5Ta$ (E = C (**1**), Si (**2**)) were found to convert to alkyl alkylidene compounds $(Me_3ECH_2)_3Ta{=}CHEMe_3$ (E = C (**3**), Si (**4**)) with the elimination of EMe_4. Np_5Ta (**1**, Np = Me_3CCH_2) was observed as an intermediate to **3** in both the reaction of Np_3TaCl_2 with 2 equiv of NpLi and the reaction of Np_4TaCl (**5**) with 1 equiv of NpLi. In addition to **1**, **5** was also observed as an intermediate in the reaction between Np_3TaCl_2 and 2 equiv of NpLi. Ns_5Ta (**2**, Ns = Me_3SiCH_2) was synthesized and isolated. Its quantitative conversion to **4** follows first-order kinetics. The further conversion of **4** to a bridged-alkylidyne complex $Ns_2Ta(\mu\text{-}CSiMe_3)_2TaNs_2$ (**7**) follows second-order kinetics. The activation parameters are $\Delta H_1^{\ddagger} = 21.6$ (1.4) kcal/mol and $\Delta S_1^{\ddagger} = -5(5)$ eu for the conversion **2** → **4** and $\Delta H_2^{\ddagger} = 6.2(0.3)$ kcal/mol and $\Delta S_2^{\ddagger} = -61.6(0.8)$ eu for **4** → **7**. Based on these results we propose mechanistic pathways for the formation of the alkylidene and bridged-alkylidyne complexes.

The study of pentaalkyl complexes of niobium and tantalum, where the metals have a d^0 electron configuration, has played an important role in organometallic chemistry.[1−4] Alkyl ligands were found to undergo an α-hydrogen abstraction process which can give alkylidene complexes of these metals.[1−4] This discovery by Schrock has led to the development of a new field of organometallic chemistry, largely in an effort to understand the reactivities of alkylidene ligands, catalytic olefin metathesis, and olefination of ketones by alkylidene complexes.[3−6]

The initial synthesis of a neopentylidene complex $Np_3Ta{=}CHCMe_3$ (Np = Me_3CCH_2, **3**) was the result of an attempted synthesis of a pentaalkyl complex "Np_5Ta" (**1**).[1−3,4a] Currently there is no firm conclusion regarding the mechanisms of the formation of the alkylidene complexes $(Me_3ECH_2)_3Ta{=}CHEMe_3$ (E = C, Si). In the synthesis of **3** from the reaction of Np_3TaCl_2 with 2 equiv of NpLi, a thermally unstable complex Np_4TaCl (**5**) is believed to be an intermediate and its formation is suggested to be the rate-determining step.[2,3a−c] Schrock and Fellmann postulate two paths for the conversion of **5** to **3**.[2] In one path, **5** is converted to "$Np_2Ta(Cl)({=}CHCMe_3)$" (**6**) which further reacts with NpLi to give **3**. In another path, **3** is formed from **5** by formal dehydrohalogenation. Several thermally unstable pentaalkyl derivatives of tantalum, $Ta(CH_2R)_5$ (R = H,[7−9] Ph,[8−9] 4-methylbenzyl[10]), have been reported, which decompose via α-hydrogen abstraction to give unidentified residues and methane, toluene, and *p*-xylene, respectively.[7−10]

In the studies involving the analogous Me_3SiCH_2- (Ns) ligand, Mowat and Wilkinson isolated a dimeric bridged-alkylidyne complex of $Ns_2Ta(\mu\text{-}CSiMe_3)_2TaNs_2$ (**7**) in the reaction of $TaCl_5$ with 5 equiv of the Grignard reagent NsMgCl followed by crystallization.[11] Later Rupprecht and Schrock found that the reaction between Ns_3TaCl_2[12] and Ns_2Mg(dioxane) led to an unstable alkylidene complex $Ns_3Ta{=}CHSiMe_3$ (**4**) which decomposes under heating to the bridged-alkylidyne complex **7**.[3b,13]

In our recent study of tantalum silyl alkylidene complexes $(Me_3ECH_2)_2Ta({=}CHEMe_3)[Si(SiMe_3)_3]$ (E = C,[14a] Si[14b]), we found that the bridged-alkylidyne compound **7** was formed as a byproduct in the synthesis of $(Me_3SiCH_2)_2Ta({=}CHSiMe_3)[Si(SiMe_3)_3]$ from the reaction between Ns_3TaCl_2 and 2 equiv of $LiSi(SiMe_3)_3(THF)_3$. In a subsequent investigation of this process and **7**, we discovered that a pentaalkyl

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[†] Dedicated to Professor Malcolm H. Chisholm on the occasion of his 50th birthday.

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complex $\mathrm{Ns_5Ta}$ (**2**) could be synthesized through the reactions either between $\mathrm{TaCl_5}$ and 5 equiv of NsMgCl or between $\mathrm{Ns_3TaCl_2}$ and 2 equiv of NsLi. The thermally unstable **2** eliminates 1 equiv of $\mathrm{Me_4Si}$ to quantitatively form **4**. The alkylidene complex **4** further undergoes an α-hydrogen elimination to give **7**.[3b,13] We also observed both $\mathrm{Np_4TaCl}$ (**5**) and $\mathrm{Np_5Ta}$ (**1**) in the formation of $\mathrm{Np_3Ta{=}CHCMe_3}$ (**3**) through the reaction of $\mathrm{Np_3TaCl_2}$ with 2 equiv of NpLi. The studies of these processes are presented here.

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 $\mathrm{N_2}$. NMR spectra, unless noted, were recorded at 23 °C on a Bruker AC-250 or AMX-400 Fourier transform spectrometer. $\mathrm{TaCl_5}$ (Strem) was used without further purification. NsMgCl,[12b] $\mathrm{Ns_3TaCl_2}$,[12b] NsLi,[15a,b] $\mathrm{Np_3TaCl_2}$,[2] and NpLi[2] were prepared by the literature procedures.

The rate constants were obtained from at least two separate experiments at a given temperature. The rate constants are the averages of the separate experiments. The *maximum* random uncertainty in the rate constants for each reaction was combined with the estimated systematic uncertainties, ca. 5%.[16a,b] The total uncertainties in the rate constants were used in the Eyring plots and in the following error propagation calculations. The estimated uncertainties in the temperature measurements for an NMR probe (used in the k_1 determinations) and for a circulation bath (used in the k_2 determinations) were 1 and 0.1 K, respectively. The activation enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) 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 $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were computed from the error propagation formulas derived from the Eyring equation by Girolami and co-workers.[16a]

The standard-state concentration for a second-order reaction is 1 M (mol/L). This concentration was used in the calculation of the activation enthalpy and entropy.[16c-f]

NMR Study of the Formation of $\mathrm{Np_3Ta{=}CHCMe_3}$ (3). (a) From $\mathrm{Np_3TaCl_2}$ and NpLi. $\mathrm{Np_3TaCl_2}$ (40.0 mg, 0.0860 mmol) and NpLi (13.4 mg, 0.172 mmol), each dissolved in toluene-d_8 at −15 °C, were mixed and transferred to an NMR tube (total volume = 0.691 mL) at −15 °C. The yellow solution was kept at −78 °C until use. The ^{1}H and ^{13}C NMR spectra of the solution were then taken at −40 °C. The reaction was conducted at 5.0 °C and quenched at −40 °C at the end of each time period to take the ^{1}H and ^{13}C NMR spectra.

(b) From $\mathrm{Np_4TaCl}$ (5) and NpLi. **5** in $\mathrm{Et_2O}$ was prepared by the literature method at −78 °C from 50 mg of $\mathrm{Np_3Ta{=}CHCMe_3}$ (**3**, 0.11 mmol) and 1.0 M HCl/$\mathrm{Et_2O}$.[2] After removal of the solvent $\mathrm{Et_2O}$ at −50 °C, the yellow product $\mathrm{Np_4TaCl}$ was redissolved in toluene-d_8 at −78 °C and added to NpLi (8.4 mg, 0.11 mmol) which had been dissolved in toluene-d_8 at −78 °C to give 0.611 mL of a yellow solution. The reaction was conducted at 0.0 °C and quenched at −40 °C at the end of each time period to take the ^{1}H and ^{13}C NMR spectra.

5 (toluene-d_8, −50 °C, **5e** equatorial, **5a** axial):[2] ^{1}H NMR (400.1 MHz) δ 2.31 (6H, CH_2, **5e**), 1.33 (27H, CH_3, **5e**), 1.10 (9H, CH_3, **5a**), 0.78 (2H, CH_2, **5a**); ^{13}C{^{1}H} NMR (100.6 MHz) δ 145.3 (CH$_2$, **5a**), 115.6 (CH$_2$, **5e**), 40.0 (CCH$_3$, **5a**), 34.9 (CCH$_3$, **5e**), 34.8 (CH$_3$, **5e**), 33.8 (CH$_3$, **5a**). The ^{1}H NMR indicates the Cl− ligand is on the axial position.

1: ^{1}H NMR (toluene-d_8, 400.1 MHz, −15 °C) δ 1.42 (2H, CH_2), 1.27 (9H, CH_3); ^{13}C{^{1}H} NMR (toluene-d_8, 100.6 MHz, −15 °C) δ 115.9 (CH$_2$, $^1J_{C-H}$ = 105.6 Hz), 36.5 (CCH$_3$), 35.2 (CH$_3$, $^1J_{C-H}$ = 124.4 Hz).

Preparation of $\mathrm{Ns_5Ta}$ (2). (a) From $\mathrm{TaCl_5}$ and NsMgCl. A 1.18 M solution of NsMgCl in ether (59 mL, 70 mmol) was added with vigorous stirring to $\mathrm{TaCl_5}$ (5.0 g, 14 mmol) in 40 mL of hexane at −78 °C. The color of the solution changed slowly first to light brown, then to colorless, and finally to yellow during slow warming to −10 °C. The solution was stirred at −10 to −5 °C for another 2 h. At this point, the ^{1}H NMR spectrum showed the reaction was complete. The solvents were then removed in vacuo below 0 °C. The residue was extracted with hexane and filtered below 0 °C. The filtrate was concentrated to ca. 40 mL below 0 °C and cooled slowly to −78 °C. Yellow microcrystals then gradually appeared. After remaining at −78 °C for 1 h, the supernatant solution was filtered away. The bright yellow microcrystals were washed with cold hexane twice at −78 °C and dried under vacuum to give 4.30 g (7.0 mmol, 50% yield) of **2**.

(b) From $\mathrm{Ns_3TaCl_2}$ and NsLi. A solution of NsLi (0.394 g, 4.2 mmol) in 10 mL of pentane at −35 °C was added with stirring to $\mathrm{Ns_3TaCl_2}$ (1.0 g, 2.1 mmol) dissolved in ca. 20 mL of pentane at −35 °C. The color of the solution changed from yellow to bright yellow in 5 min at −10 °C. The ^{1}H NMR spectrum showed the reaction was complete in 20 min at −10 °C. Crystallization at −78 °C gave 0.65 g (1.1 mmol, 56% yield) of bright yellow solid **2**.

The assignment of resonances for **2** is based on the known resonances of $\mathrm{Me_3SiCH_2}$− in **4**[13] and **7**.[11a] **2**: ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 0.95 (2H, CH_2), 0.25 (9H, CH_3, $^2J_{Si-H}$ = 6.0 Hz); ^{13}C{^{1}H} (benzene-d_6, 62.9 MHz, 23 °C) δ 92.1 (CH$_2$, $^1J_{C-H}$ = 105.9 Hz, $^1J_{C-Si}$ = 42.1 Hz), 3.1 (CH$_3$, $^1J_{C-H}$ = 118.3 Hz, $^1J_{C-Si}$ = 50.6 Hz).

Preparation of $\mathrm{Ns_3Ta{=}CHSiMe_3}$ (4). $\mathrm{Ns_5Ta}$ (**2**) was prepared according to the procedure described above. Then a hexane solution containing **2** was diluted to [**2**] = 0.06 M. This was used to prevent the dimerization of product **4** to form **7**. The solution was then heated at 52 °C for 45 min. The ^{1}H NMR spectra of the orange solution showed **4** with a very small amount of $\mathrm{Ns_2Ta(\mu\text{-}CSiMe_3)_2TaNs_2}$ (**7**). Complex **4** can be kept at −20 °C in this dilute hexane solution for more than one month. Removing the solvent gave a dark orange oil, which solidified at −20 °C within a week to form **7**.

4: ^{1}H NMR (benzene-d_6, 250.1 MHz, 23 °C) δ 5.75 (1H, $\mathrm{Me_3SiC}H{=}$), 0.42 (6H, $\mathrm{Me_3SiC}H_2$), 0.34 (9H, Me_3SiCH=, $^2J_{Si-H}$ = 6.52 Hz), 0.19 (27H, Me_3SiCH$_2$, $^2J_{Si-H}$ = 6.48 Hz); ^{13}C{^{1}H} (benzene-d_6, 62.9 MHz, 23 °C) δ 240.7 ($\mathrm{Me_3Si}C$H=, $^1J_{C-H}$ = 99.6 Hz), 85.9 ($\mathrm{Me_3Si}C$H$_2$, $^1J_{C-H}$ = 107.0 Hz), 3.4 (Me_3SiCH=, $^1J_{C-H}$ = 118.2 Hz), 2.5 (Me_3SiCH$_2$, $^1J_{C-H}$ = 118.5 Hz).

Kinetic Study of the Decomposition of $\mathrm{Ns_5Ta}$ (2) to $\mathrm{Ns_3Ta{=}CHSiMe_3}$ (4). Samples of **2** (21.8−41.7 mg), 4,4′-dimethylbiphenyl (4.0−6.8 mg, an internal standard), and benzene-d_6 were weighed and dissolved in NMR tubes to make solutions with [**2**]$_0$ between 0.0493 and 0.137 M and the internal standard at 0.036−0.070 M. The handling of the thermally unstable **2** at 23 °C should be brief to limit its decomposition to **4** and **7**. The concentrations of **2** were calculated from the integration with respect to the internal standard 4,4′-dimethylbiphenyl. The NMR spectra were taken at 301 ± 1, 305 ± 1, 310 ± 1, 315 ± 1, 320 ± 1, and 325 ± 1 K. The rate of decomposition was independent of the presence of small amounts of LiCl, $\mathrm{MgCl_2}$, and some other unknown impurities.

Kinetic Study of the Decomposition of $\mathrm{Ns_3Ta{=}CHSiMe_3}$ (4) to $\mathrm{Ns_2Ta(\mu\text{-}CSiMe_3)_2TaNs_2}$ (7). The transformation of **4** to the bridged-alkylidyne complex **7** was studied after **2** was fully converted to **4**. Crystalline **2** (70.2−85.3 mg) and 4,4′-dimethylbiphenyl (14.7−19.0 mg, an internal standard) were dissolved in toluene-d_8 in NMR tubes to give solutions with [**2**]$_0$ between 0.137 and 0.229 M. The tube was kept in a 60 °C circulation bath for about 1 h until the NMR spectra showed the complete conversion of **2** to **4**. The NMR tube was then placed in a hot bath with temperature at 40.0 ± 0.1, 60.0 ± 0.1, 80.0 ± 0.1, and 100.0 ± 0.1 °C to start the kinetic measurement. At the end of each time period, the NMR tube was removed from the circulation bath and placed in an ice bath to quench the decomposition. The ^{1}H NMR spectra were taken at 23 °C within a 15-min period before

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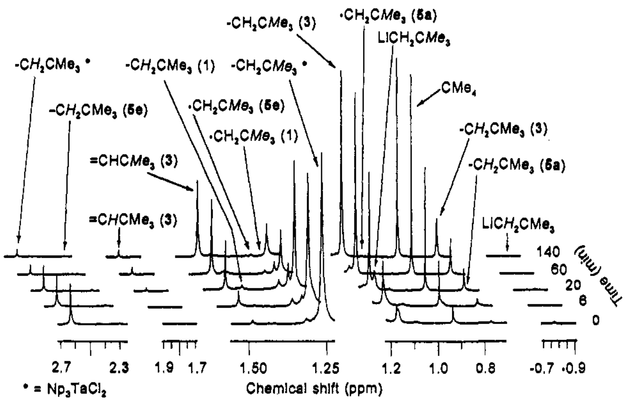


Figure 1. ^{1}H NMR (toluene-d_8) spectra of the conversions in the presence of 2 equiv of NpLi: $Np_3TaCl_2 \rightarrow Np_4TaCl$ (**5**) $\rightarrow Np_5Ta$ (**1**) $\rightarrow Np_3Ta{=}CHCMe_3$ (**3**). The solution was maintained at 5.0 °C for the reactions. The reactions were quenched by cooling to −40 °C at the end of each time period, and the spectra were then taken at −40 °C.

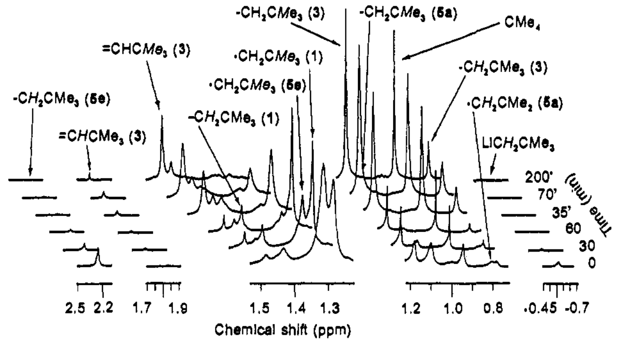


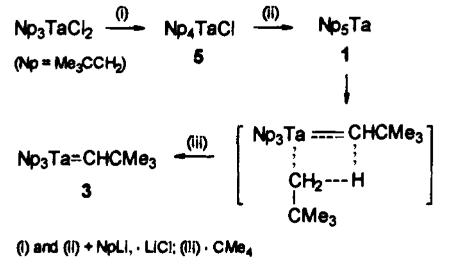
Figure 2. ^{1}H NMR (toluene-d_8) spectra of the conversions in the presence of 1 equiv of NpLi: **5** → **1** → **3**. The solution was maintained at −40 °C until NpLi disappeared. Then the reaction **1** → **3** was conducted at 0.0 °C. The reactions were quenched by cooling to −40 °C at the end of each time period, and the spectra were then taken at −40 °C.

the NMR tube was placed back in the circulation bath. No decomposition at 23 °C within the 15-min period was detected by NMR. The concentrations of **4** were calculated based on the integrations of its NMR resonances with respect to that of the internal standard. Other experiments (not discussed in this paper) show that the conversion of **4** to **7** deviates from second-order kinetics and occurs more quickly if the precursor **2** is prepared in situ. Evidently, impurities present when **2** is synthesized can catalyze the conversion of **4** to **7**. Therefore, the data shown in Figure 6 were obtained with the use of crystalline samples of **2**.

Results and Discussion

Formation of Np_5Ta (1) and Its Conversion to $Np_3Ta{=}CHCMe_3$ (3). The ^{1}H spectra of the reaction of Np_3TaCl_2 with 2 equiv of NpLi to the alkylidene complex **3** are shown in Figure 1. Np_4TaCl (**5**), previously reported by Schrock and Fellmann,[2] was identified as an intermediate in the system. The peaks at 1.42 and 1.27 ppm in Figure 1 are assigned to the previously unknown compound Np_5Ta (**1**). The assignment for **1** is based on its ^{1}H and ^{13}C NMR and its reactivities. In one such reaction between Np_3TaCl_2 and 2 equiv of NpLi, the maximum concentration of **1** was 3.5% of the theoretical maximum concentration (0.124 M). The presence of **1** as a precursor to **3** is also observed in the reaction between Np_4TaCl (**5**) and 1 equiv of NpLi, as monitored by the ^{1}H NMR spectra in Figure 2. As the intensities of the resonances of **5** decrease, the intensity of the resonances of **1** first increase and then decrease as it is converted to form **3** and CMe_4. In one such reaction between Np_4TaCl and NpLi, the maximum concentration of **1** was 60% of the theoretical maximum concentration (0.176 M). The results presented here indicate the mechanistic pathway shown in Scheme 1 for the formation of the Schrock-type alkylidene complex **3** from the reaction of Np_3TaCl_2 with NpLi.

Scheme 1



In the alternate possible mechanistic pathway,[2] the thermally unstable Np_4TaCl (**5**) first undergoes an α-hydrogen abstraction to form "$Np_2Ta(Cl)({=}CHCMe_3)$" (**6**). **6** then reacts with NpLi to form **3**. A reasonable assumption is that forming **6** is the first step in the thermal decomposition of **5**. The decomposition of **5** was observed to follow first-order kinetics.[17a] This thermal decomposition was found to be much slower than the reaction of **5** with NpLi. The extrapolated half-life for the decomposition of **5** at −40 °C is 1.12×10^5 min. However, the reaction between NpLi and **5** at −40 °C was virtually complete in about 80 min. The route involving "$Np_2Ta(Cl)({=}CHCMe_3)$" (**6**) as the precursor to **3** is thus unlikely.[17b]

Both the direct observation of Np_4TaCl (**5**) and Np_5Ta (**1**) and the kinetic studies on the decomposition of **5** point to the mechanistic pathways shown in Scheme 1. When the reactions shown in Scheme 1 were conducted at 23 °C, **1** could be identified by its ^{1}H and ^{13}C NMR. However, the ^{1}H and ^{13}C NMR of **5** were broad and the intensities of its resonances were weak. Conducting the reactions at 5.0 °C and subsequently quenching the consecutive reactions at −40 °C before taking the NMR spectra (Figure 1) clearly revealed the presence of **5** and **1** as the intermediates leading to the formation of **3**.

Synthesis and Isolation of Ns_5Ta (2). **2** could be synthesized either from $TaCl_5$ and 5 equiv of NsMgCl in ethyl ether or from yellow Ns_3TaCl_2 and 2 equiv of NsLi in pentane (eqs 1 and 2). The reactions are fast at room temperature and are

$$TaCl_5 + 5NsMgCl \xrightarrow{Et_2O} \underset{\mathbf{2}}{Ns_5Ta} + 5MgCl_2 \qquad (1)$$

$$Ns_3TaCl_2 + 2NsLi \xrightarrow{pentane} \underset{\mathbf{2}}{Ns_5Ta} + 2LiCl \qquad (2)$$

almost quantitative except for the presence of small amounts of $Ns_3Ta{=}CHSiMe_3$ (**4**) and $Ns_2Ta(\mu\text{-}CSiMe_3)_2TaNs_2$ (**7**), as demonstrated by the tests conducted in NMR tubes. Low-temperature synthesis and purification are crucial to inhibiting the further conversion of **2** to **4** and **7**. Crystallization at −78 °C led to the formation of microcrystals of **2**.

2 is very soluble in hydrocarbon solvents. The yellow crystals of **2** can be stored at −20 °C under N_2 for several days without noticeable decomposition. About 10% of yellow crystalline **2** was found to have converted to **7** in five weeks of storage at −20 °C with repeated brief exposures (20 min each) to 23 °C during sample transfers in a drybox under N_2. However, heating of solid **2** at 50 °C under vacuum led to the quick formation of

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[17] (a) The activation parameters for the thermal decomposition of **5** are: $\Delta H^{\ddagger} = 18.3(0.7)$ kcal/mol and $\Delta S^{\ddagger} = -11(3)$ eu, which were obtained from the kinetic measurements between 283.2 and 303.2 K. See supporting information. (b) There is a slim possibility that NpLi induces the conversion of **5** to **6** at a faster rate.

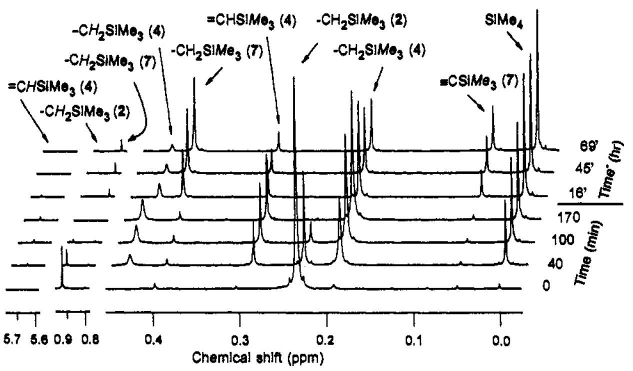

Figure 3. ^{1}H NMR (toluene-d_8) spectra of the conversions Ns_5Ta (**2**) → Ns_3Ta=CHSiMe$_3$ (**4**) → $Ns_2Ta(\mu$-CSiMe$_3)_2TaNs_2$ (**7**). During the conversion of **2** to **4**, the first four spectra were taken *in situ* at 42.0 °C. Then the solution was heated to 95.0 °C to study the conversion of **4** to **7**. The reaction was quenched by cooling to 0 °C at the end of 16′, 45′, and 69′ h, respectively, of heating at 95 °C. The last three spectra were then taken at 23 °C. The temperature difference causes the shifts in the resonances between the first four spectra at 42.0 °C and the last three spectra at 23 °C.

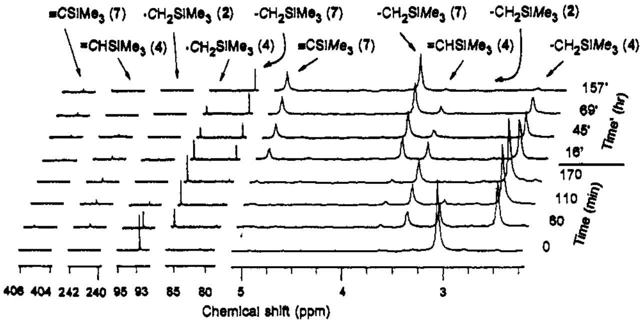

Figure 4. $^{13}C\{^1H\}$ NMR (toluene-d_8) spectra of the conversions **2** → **4** → **7**. The spectra at 0, 60, 110, and 170 min were taken *in situ* at 42.0 °C. The solution was then heated to 95.0 °C to study the conversion of **4** to **7**. The reaction was quenched by cooling to 0 °C at the end of 16′, 45′, 69′, and 157′ h, respectively, of heating at 95 °C. The spectra were then taken at 23 °C. The temperature difference causes the shifts in the resonances between the first four spectra at 42.0 °C and the last four spectra at 23 °C.

Table 1. Measured Rate Constants k_1 for the Conversion **2** → **4**[a]

T (K)	$(k_1 \pm \delta k_{1(\mathrm{ran})}) \times 10^4$ (s^{-1})
301.0 ± 1.0	1.028 ± 0.008
306.1 ± 1.0	1.8538 ± 0.0002
311.2 ± 1.0	3.51 ± 0.07
316.3 ± 1.0	6.09 ± 0.03
321.4 ± 1.0	10.4 ± 0.4
326.5 ± 1.0	18.3 ± 0.2

[a] The total uncertainty $\delta k_1/k_1$ of 6.2% was calculated from $\delta k_{1(\mathrm{ran})}/k_1$ = 3.6% and $\delta k_{1(\mathrm{sys})}/k_1$ = 5%.[16b]

alkylidene complex **4** and a small amount of **7**. The structural assignment for the thermally unstable **2** is based on its ^{1}H and ^{13}C NMR and its reactivities.

Conversions of Ns_5Ta (2) to Ns_3Ta=CHSiMe$_3$ (4) and $Ns_2Ta(\mu$-CSiMe$_3)_2TaNs_2$ (7). The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of the conversions are shown in Figures 3 and 4, respectively. As the intensities of the resonances of **2** decrease at 316.3 K, resonances corresponding to Me_3SiCH_2–, Me_3SiCH= of **4** first increase in intensity. After the pentaalkyl complex **2** is almost fully decomposed to alkylidene **4**, the intensities of the resonances of **4** start to decrease as it is converted to form **7**.

The conversion of **2** → **4** is observed to follow first-order kinetics. Plots of ln(C/C_0) vs t at six different temperatures

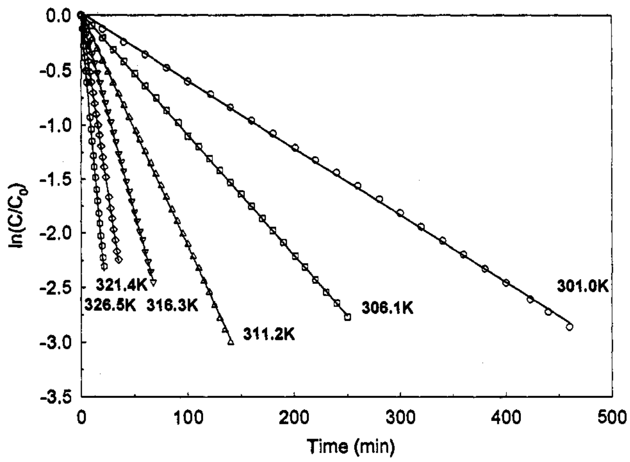

Figure 5. Kinetics plots of the conversion of **2** → **4**.

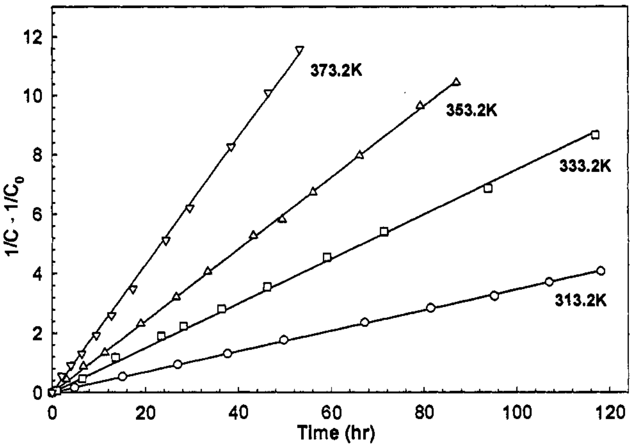

Figure 6. Kinetics plots of the conversion of **4** → **7**.

(between 301.0 and 326.5 K) are shown in Figure 5. The rate constants at these temperatures are listed in Table 1. An Eyring plot of ln(k_1/T) vs 1/T is shown in Figure 7. The activation parameters thus derived for the conversion of **2** of **4** are $\Delta H_1^\ddagger$ = 21.6(1.4) kcal/mol and $\Delta S_1^\ddagger$ = −5(5) eu.[18] Both near-zero and negative values for $\Delta S^\ddagger$ have been observed in C–H bond activation processes where concerted four-center transition states, especially those involving cyclometalation, are proposed.[19] The rate constants for the conversion from **2** to **4** at 311.2 and 316.3 K are 3.512 × 10^{-4} and 6.087 × 10^{-4} s^{-1}, respectively. In comparison, the rate of decomposition for $Ta(CH_2Ph)_5$ at 313 K was found to be 3.8 × 10^{-5}–4.3 × 10^{-5} s^{-1}.[9]

A second-order reaction is observed for the conversion of **4** to **7** with the elimination of SiMe$_4$. The plots 1/C − 1/C_0 vs t for temperatures between 313 K and 373 K are shown in Figure 6. The rate constants at these temperatures are listed in Table 2. An Eyring plot of ln(k_2/T) vs 1/T is shown in Figure 7. The activation parameters for this second-order reaction thus derived are $\Delta H_2^\ddagger$ = 6.2(0.3) kcal/mol and $\Delta S_2^\ddagger$ = −61.6(0.8) eu.

Small $\Delta H^\ddagger$ and large negative $\Delta S^\ddagger$ values have been observed in *associative* reactions that follow second-order kinetics.[20] In the current conversion from a monomeric Ns_3Ta=CHSiMe$_3$ (**4**) to a dimeric $Ns_2Ta(\mu$-CSiMe$_3)_2TaNs_2$ (**7**), the second-order

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[18] The error in the value of $\Delta S_1^\ddagger$ is large enough that its sign cannot be positively determined.

[19] (a) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210. (b) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805. (c) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (d) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (e) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153. (f) Buchwald, S. L.; Nielson, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171. (g) Caulton, K. G.; Chisholm, M. H.; Streib, W. E.; Xue, Z. *J. Am. Chem. Soc.* **1991**, *113*, 6082.

Table 2. Measured Rate Constants k_2 for the Conversion **4** → **7**[a]

T (K)	$(k_2 \pm \delta k_{2(\mathrm{ran})}) \times 10^6$ (M$^{-1}\cdot$s^{-1})
313.2 ± 0.1	9.75 ± 0.11
333.2 ± 0.1	20.5 ± 0.3
353.2 ± 0.1	33.8 ± 0.3
373.2 ± 0.1	60.2 ± 0.6

[a] The total uncertainty $\delta k_2/k_2$ of 5.2% was calculated from $\delta k_{2(\mathrm{ran})}/k_2 = 1.5\%$ and $\delta k_{2(\mathrm{sys})}/k_2 = 5\%$.[16b]

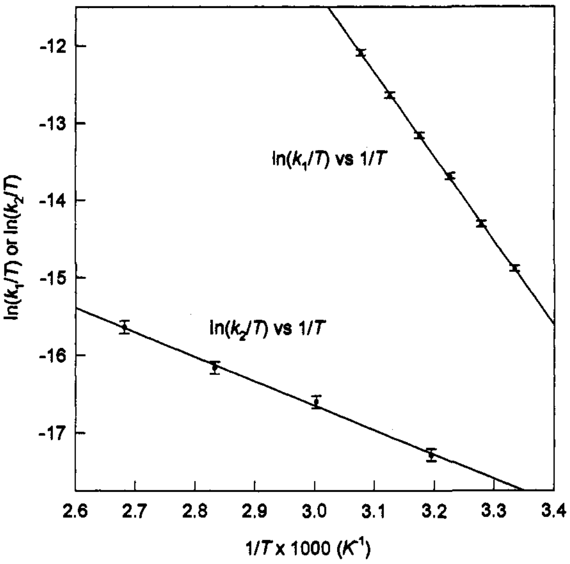
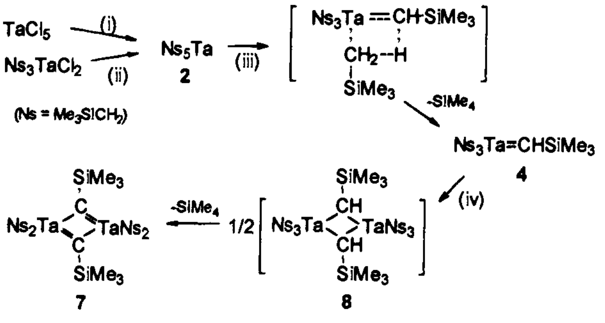


Figure 7. Eyring plots of the conversions of **2** → **4** and **4** → **7**.

Scheme 2[22]



(i) + 5NsMgCl, − 5MgCl$_2$; (ii) + 2NsLi, − 2LiCl;
(iii) $\Delta H_1^\ddagger$ = 21.6 (1.4) kcal/mol, $\Delta S_1^\ddagger$ = − 5 (5) e.u.;
(iv) $\Delta H_2^\ddagger$ = 6.2 (0.3) kcal/mol, $\Delta S_2^\ddagger$ = − 61.6 (0.8) e.u.

kinetics observed, the small $\Delta H_2^\ddagger$, and the unusually large negative $\Delta S_2^\ddagger$ values suggest that dimerization of **4** to an intermediate "Ns$_3$Ta(μ-CHSiMe$_3$)$_2$TaNs$_3$" (**8**) is an intergral part of the mechanism. Dimerization to **8**, followed by rate-determining α-hydrogen abstraction steps, constitutes one pathway, but rate-determining dimerization is more plausible in view of the characteristic activation parameters. The results of current studies are summarized in Scheme 2.

The reaction between Np$_3$TaCl$_2$ and 2 equiv of NpLi to form Np$_3$Ta=CHCMe$_3$ at 23 °C requires 15–30 min to complete.[1,2] The fast formation of Ns$_5$Ta (**2**) from the reaction of Ns$_3$TaCl$_2$ with 2 equiv of NsLi may be the result of reduced steric crowding around the metal centers in Ns$_3$TaCl$_2$ and **2**. Compared with the neopentyl ligands, the methyl groups in (trimethylsilyl)methyl ligands are farther away from the tantalum atoms. Such increased distances perhaps make the accommodation of five Me$_3$SiCH$_2$− ligands relatively easier in Ns$_5$Ta (**2**) than in Np$_5$Ta (**1**) and the isolation of **2** possible. Neither Np$_5$Ta (**1**) nor Ns$_5$Ta (**2**) is thermodynamically favorable with respect to the four-coordinated (Me$_3$ECH$_2$)$_3$Ta=CHEMe$_3$ (E = C (**3**), Si (**4**)), thus undergoing the elimination of EMe$_4$ to form **3** and **4**, respectively. Similar elimination and conversion have been reported in the formation of an antimony ylide compound Ns$_3$Sb=CHSiMe$_3$ from Ns$_5$Sb.[21]

The relatively reduced steric crowding around the Ta atoms when they are coordinated by Ns− or bridging (trimethylsilyl)-methylene ligands may lead to the formation of the *proposed* bridged-alkylidene intermediate "Ns$_3$Ta(μ-CHSiMe$_3$)$_2$TaNs$_3$" (**8**).[22] In contrast, the steric crowding in the neopentyl neopentylidene analog Np$_3$Ta=CHCMe$_3$ makes bi-molecular reactions unfavorable, as described by Schrock and Fellmann.[2] The large negative $\Delta S_3^\ddagger$ value clearly suggests that dimerization of **4** to form **8** occurs prior to or during the rate-determining step in the formation of **7**. The α-hydrogen elimination between the hydrogen atoms of the bridged-alkylidene ligands and the terminal alkyl ligands produces the bridged-alkylidyne complex **7**. The presence of small amounts of unknown impurities in these systems was found to catalyze the formation of **7** from **4**. In such instances clean second-order kinetic behavior was not observed.

Our studies present the proposed mechanistic pathways in the formation of the Schrock-type alkylidene complexes (Me$_3$ECH$_2$)$_3$Ta=CHEMe$_3$ (**3**, **4**) and the further conversion of **4** to the bridged-alkylidyne complex **7**, indicating that Np$_5$Ta (**1**) and Ns$_5$Ta (**2**) are the precursors to **3** and **4**, respectively. The formation of the alkylidene bonds in **3** and **4** occurs through α-hydrogen abstraction between two alkyl ligands in the pentaalkyl complexes (Me$_3$ECH$_2$)$_5$Ta (**1** and **2**). In the environment of reduced steric crowding in (Me$_3$SiCH$_2$)$_3$Ta=CHSiMe$_3$ (**4**), the molecules dimerize, perhaps through the bridging alkylidene bonds leading to the formation of the bridged-alkylidyne complex (Me$_3$SiCH$_2$)$_2$Ta(μ-CSiMe$_3$)$_2$Ta(CH$_2$SiMe$_3$)$_2$ (**7**).

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Supporting Information Available: Experimental procedure for the kinetic study of the decomposition of Np$_4$TaCl (**5**), kinetics plot and Eyring plot of the decomposition, and table of the rate constants of the decomposition (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the internet; see any current masthead page for ordering information and Internet access instructions.

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[21] Schmidbaur, H.; Hasslberger, G. *Chem. Ber.* **1978**, *111*, 2702.

[22] The bridging alkylidene ligands in **8** could be asymmetric.