

Multiple Metal–Carbon Bonds. 8.^{1a} Preparation, Characterization, and Mechanism of Formation of the Tantalum and Niobium Neopentylidene Complexes, $M(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$

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Abstract: The reaction between $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and 2 mol of $\text{LiCH}_2\text{CMe}_3$ in pentane gives thermally stable $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ (**1**) in quantitative yield. The rate-determining step is believed to be formation of thermally unstable $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$ (**7**) (which can be prepared from **1** and HCl at -78°C). **7** reacts very rapidly with $\text{LiCH}_2\text{CMe}_3$ compared to the rate at which $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ reacts. In the absence of $\text{LiCH}_2\text{CMe}_3$ **7** decomposes to thermally unstable $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{Cl})(\text{CHCMe}_3)$ (**8**) above ca. -10°C (in noncoordinating solvents); **8** can be trapped as (inter alia) $\text{TaCp}(\text{CH}_2\text{CMe}_3)_2(\text{CHCMe}_3)$. We postulate that **1** forms from **7** via **8** (path A) and directly from **7** by formal dehydrohalogenation, possibly via short-lived $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$ (path B). All postulates are supported by deuterium labeling results. A deuterium isotope effect for the α -hydrogen abstraction reaction leading to **1** was shown to be 2.7 ± 0.2 . Thermally unstable $\text{Nb}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ (**2**) can be prepared similarly. The reactions of **1** and **2** are characteristic of the neopentylidene ligand being nucleophilic but the final products suggest that Ta and Nb prefer to bind to elements more electronegative than carbon; e.g., **1** and CH_3CN give *E* and *Z* isomers of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{CH}_3)\text{C}=\text{CHCMe}_3]$ (**6a**). All five-coordinate complexes of formally Nb(V) and Ta(V) are believed to be trigonal bipyramids with the most electronegative substituents in the axial positions. This structure and steric crowding are both believed to be important factors in determining when α -hydrogen atom abstraction to give alkylidene complexes occurs; we postulate that a relatively more nucleophilic axial alkyl α -carbon atom will remove a relatively more acidic proton from an equatorial alkyl α -carbon atom in a trigonal bipyramidal intermediate.

Introduction

Transition metal alkyl complexes in which the alkyl contains one to three β -hydrogen atoms often decompose fairly readily by β -hydride elimination.² This decomposition pathway is blocked if no β -hydrogen atoms are available. Methyl, benzyl, or neopentyl complexes, for example, are therefore normally more stable thermally. Yet many of these, particularly early transition metal permethyl complexes like TiMe_4 and NbMe_5 , are also unstable and decompose to give primarily, if not exclusively, the alkane, ostensibly by " α -hydride elimination".^{2,3} However, direct evidence for a process of this type has been scant⁴ and no primary alkylidene complexes⁵ have been detected.

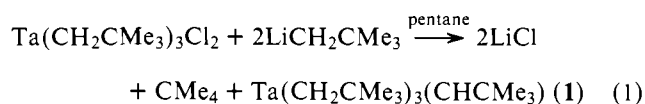
An attempt to prepare $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$ from $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and $\text{LiCH}_2\text{CMe}_3$ in pentane produced instead the first example of a primary alkylidene complex, $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ (**1**), reportedly by α -hydrogen atom abstraction³ in hypothetical $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$. More detailed examination of this deceptively simple reaction, including a deuterium labeling study, has still not provided a definitive answer as to how **1** forms but has at least narrowed the possibilities (the above being one). In the process we have explored some reactions of **1** and $\text{Nb}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ (**2**) with electrophiles which will probably be characteristic of early transition metal nucleophilic alkylidene complexes. These studies have also led us to conclude that the chemistry of d^0 Nb(V) and Ta(V) alkyl complexes is probably closely related to organophosphorus, arsenic, or antimony chemistry. We therefore postulate certain details of the α -hydrogen atom abstraction reaction with this analogy in mind.

Results

Preparation and Properties of $M(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$, $M = \text{Ta}$ (1**) or Nb (**2**).** $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ is best prepared from yellow $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and 2 mol of $\text{LiCH}_2\text{CMe}_3$ in pentane at 25°C . The reaction is surprisingly slow (15–30 min to completion) and free of side products; after

LiCl is removed by filtration, **1** can be isolated in quantitative yield by removing pentane in vacuo. Diethyl ether is also a suitable solvent for the above reaction; the rate in this case is comparatively rapid (<5 min to completion). In neither solvent can **1** be prepared in good yield directly by adding 5 mol of $\text{LiCH}_2\text{CMe}_3$ to TaCl_5 , at -78 or 25°C . For example, after adding $\text{LiCH}_2\text{CMe}_3$ to TaCl_5 in ether at -78°C and warming to 25°C , only a 5% yield of **1** was present as shown by quantitative GLC determination of *cis*- and *trans*- β -*tert*-butylstyrene formed on addition of excess benzaldehyde to the reaction mixture.⁷ Adding 5 mol of $\text{Me}_3\text{CCH}_2\text{MgCl}$ to TaCl_5 in ether at 25°C , removing solvent, and subliming the crude reaction product *does* give a high yield of **1** (50–85%). However, **1** is not formed rapidly at 25°C (5% after mixing, 30% in 24 h in refluxing ether) but only in the sublimation apparatus at higher temperatures. Much poorer yields were obtained in a "direct" preparation of **1** from TaCl_5 employing $\text{Me}_3\text{CCH}_2\text{MgBr}$, partially at least because mixed chloride/bromide complexes like $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{ClBr}$ are known to form under these conditions and decompose more readily than those containing only chlorides.⁸

The organic product in all the above preparations, neopentane, was identified by GLC/mass spectroscopy and ^1H NMR comparison with an authentic sample. Quantitative GLC showed that 1.0 mol per Ta evolves on reaction of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and 2 $\text{LiCH}_2\text{CMe}_3$ in pentane. Therefore, the reaction proceeds as in eq 1.



$\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ is extremely soluble in organic solvents (ca. 5 g dissolves in 5 mL of pentane at 25°C) and can be crystallized as orange, elongated octahedra only from concentrated saturated hydrocarbon solutions at -30°C . It is quite volatile and readily sublimes at temperatures slightly

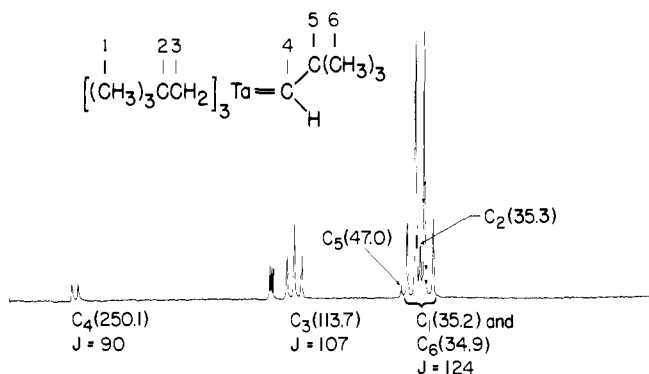


Figure 1. The gated decoupled 22.63-MHz ^{13}C spectrum of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{ChCMe}_3)$ (**1**) in C_6D_6 .

above its melting point (71 °C) in vacuo (1 μ). It can even be distilled in vacuo in a short-path apparatus. It reacts readily with water and oxygen (in air it turns into an orange oil instantly), protic solvents, and, in general, unsaturated organic functionalities like carbonyls,⁷ nitriles, and olefins.⁸ It can be stored for several weeks at 25 °C under N_2 (it turns brown slowly over several months) and indefinitely at -30 °C under N_2 . It decomposes in ~8 h at 100 °C (neat) to as yet unidentified products.

$\text{Nb}(\text{CH}_2\text{CMe}_3)_3(\text{ChCMe}_3)$ is best prepared from $\text{Nb}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and 2 mol of $\text{LiCH}_2\text{CMe}_3$ in pentane at -78 °C. ($\text{Nb}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ has not been reported in the literature; it resembles $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ in its physical characteristics except that it decomposes on attempted sublimation.) It can be isolated as waxy, red crystals by removing pentane in vacuo. It resembles **1** in many ways (solubility, sensitivity to oxygen, etc.) but decomposes extensively in C_6D_6 at 25 °C in 6 h (according to ^1H NMR) and on attempted sublimation at 70 °C. Elemental analyses have not been practical for this reason but its ^{13}C and ^1H NMR spectra at low temperature (vide infra) leave little doubt that its formulation is correct. So far it has not been possible to prepare **2** directly from NbCl_5 with $\text{Me}_3\text{CCH}_2\text{MgCl}$ or $\text{LiCH}_2\text{CMe}_3$.

Characterization of $\text{M}(\text{CH}_2\text{CMe}_3)_3(\text{ChCMe}_3)$. A molecular weight measurement in benzene (freezing point depression) gave a value of 472 (calcd 464) for **1**. A stable dimeric formulation with bridging ChCMe_3 groups can therefore be discarded. The mass spectrum of **1** is consistent with these data; it shows a parent ion at m/e 464.2857 (calcd 464.2821) but no peaks above this value.

Treating **1** in hexane with 5 mol of DCl gave 90% of the theoretical 4 mol of neopentane which by mass spectroscopy was shown to be a mixture of 26% $-d_0$, 57% $-d_1$, and 17% neopentane- d_2 (error $\approx \pm 3\%$; see Experimental Section). A similar deuterolysis of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ gave 91% of the theoretical neopentane which was shown to consist of 19% $-d_0$ and 81% neopentane- d_1 though using excess $\text{C}_2\text{H}_5\text{OD}$ in place of a stoichiometric amount of DCl gave a high yield of 95% neopentane- $-d_1$. The source of neopentane- $-d_0$ in the experiments employing a stoichiometric amount of DCl is most likely HCl formed by H/D exchange with traces of water. The fact that the ratio of $-d_1$ to neopentane- $-d_2$ formed on treatment of **1** with DCl is close to 3 is consistent with the proposal that **1** is $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{ChCMe}_3)$.

The ^1H NMR spectrum of **1** in C_6D_6 shows four singlets at τ 8.09, 8.57, 8.85, and 9.16 vs. Me_4Si in the ratio of 1:9:27:6. The τ 8.09 peak is virtually absent in the spectrum of " $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CDCMe}_3)$ " (vide infra), consistent with its assignment as the unique neopentylidene α proton. The ^1H NMR spectrum of **2** is similar to that of **1**: τ 7.00 (1), 8.59 (9), 8.88 (27), and 9.07 (6) in C_6D_6 vs. Me_4Si . The chemical shift of the neopentylidene α proton in each case is much higher than

that in monocyclopentadienyl complexes (e.g., τ 3-4 in $\text{MCp}(\text{CHCMe}_3)\text{Cl}_2$; $\text{M} = \text{Nb}$ or Ta)⁹ which is in turn significantly higher than in biscyclopentadienyl complexes (e.g., τ -1 to 0 in $\text{MCp}_2(\text{CHCMe}_3)\text{Cl}$ or $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$; $\text{M} = \text{Nb}$ or Ta).^{1a,10} We do not yet have sufficient data to say which, if any, is a "normal" chemical shift for an alkylidene α proton. Since the α -carbon atom is almost certainly π bonded to the metal,¹¹ an α proton (like, but to a lesser extent than a hydride ligand) is quite susceptible to changes in electron density near the metal. Chemical shifts therefore almost certainly will vary widely.

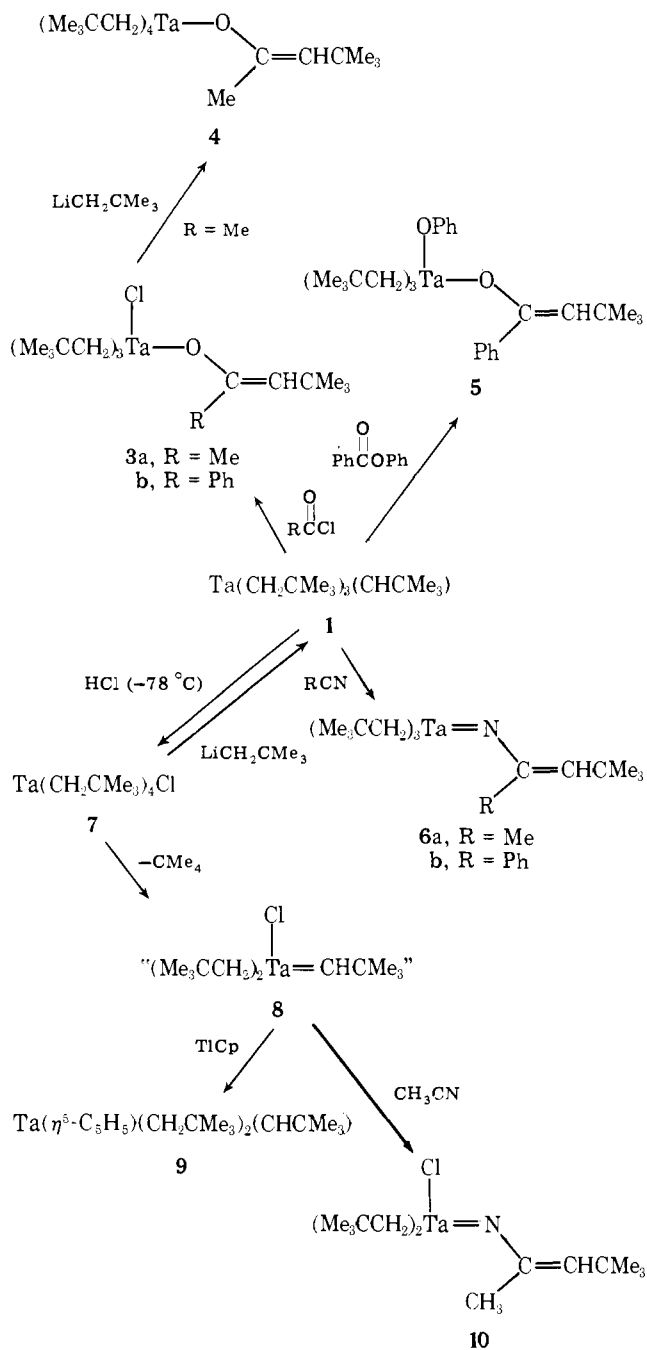
The ^{13}C spectrum of **1** in C_6D_6 (gated decoupled) shows a peak with the appropriate multiplicity for each of the six types of carbon atoms (Figure 1). The neopentylidene α -carbon atom resonance is found far downfield of the others, at the upper end of the range where the resonance for the α -carbon atom in Fischer-type carbene complexes is normally found.¹⁴ $^1J_{\text{CH}\alpha}$ for this and the neopentyl α -carbon atoms both seem anomalously low (90 and 107 Hz, respectively) for (formally) olefinic¹¹ and aliphatic carbon atoms, respectively.¹⁵ But since one can easily assign too great a significance to $^1J_{\text{CH}}$, as Gil has pointed out,¹⁶ we do not want to attempt to interpret these results in detail at this time. We might point out, however, that $\text{M}-\text{C}_\alpha-\text{C}_\beta$ bond angles are rather large (ca. 130°) for CH_2CMe_3 ligands in known examples¹⁷ and even larger (ca. 150°) for $=\text{CHCMe}_3$ ligands.^{13b}

The ^{13}C spectrum of **2** in toluene- d_8 at -50 °C is similar to that of **1** with the following exceptions. The signal for the neopentyl α -carbon atoms is markedly broadened in the gated decoupled or ^1H decoupled spectrum; the $^1J_{\text{CH}\alpha}$ value could just be discerned in the former (~101 Hz). The neopentylidene α -carbon atom resonance could only be found in the ^1H decoupled spectrum (at 246 ppm, ~600 Hz wide); evidently it is too broad in the gated decoupled spectrum. In comparison the neopentyl α -carbon atom resonance is ~350 Hz wide in the decoupled spectrum. The broadening of each signal is due to coupling of the α -carbon atom to ^{93}Nb . The neopentyl and neopentylidene ligands probably do not interconvert by proton transfer from the former to the latter since this process is slow on the NMR time scale in **1** ($\Delta G^\ddagger \approx 28$ kcal, vide infra). The fact that the neopentylidene α -carbon atom resonance is significantly broader than the neopentyl α -carbon atom resonance therefore suggests it is more strongly coupled to ^{93}Nb , as one might expect if it were π bonded to Nb.

Some Reactions of **1 and **2** Consistent with the Neopentylidene α -Carbon Atom Being Nucleophilic.** Orange **1** in pentane reacts with acetyl chloride at 25 °C to give a pale yellow solution from which nearly white, sublimable, pentane-soluble crystals of a product which analyzes as the sum of the reactants can be obtained. The following evidence suggests that this product is a mixture of *E* and *Z* isomers of **3a** (Scheme 1).

The ^1H NMR spectrum of **3a** shows primarily one isomer ($\geq 90\%$). It has a characteristic quartet resonance at τ 4.57 ($J = 1.1$ Hz, 1 H) and a doublet resonance at τ 8.08 (3 H) in addition to singlets of areas 6, 27, and 9 at τ 8.14, 8.79, and 8.94, respectively. Irradiating the low-field quartet collapses the τ 8.08 doublet to a singlet. For convenience we assign the *E* configuration to this isomer since we cannot argue convincingly one way or the other based on any data in hand. The olefinic resonance for *Z*-**3a** is found at τ 5.56 and (at 270 MHz) the olefinic methyl resonance at τ 8.07 and the neopentyl methyl resonance at τ 8.76; the *E* and *Z* neopentyl methylene protons and the *E* and *Z* olefinic *tert*-butyl protons are apparently coincident. Recrystallization of sublimed **3a** gives pure *E*-**3a**.

The gated decoupled ^{13}C spectrum of the **3a** mixture clearly shows the two olefinic carbon atoms in *E*-**3a** at 126 (d, $^1J_{\text{CH}} = 150$ Hz) and 154 ppm (s) downfield of Me_4Si and in *Z*-**3a** at 122 (d, $^1J_{\text{CH}} = 148$ Hz) and 152 ppm (s) downfield of

Scheme I. Some Reactions of **1** Consistent with the Neopentylidene α -Carbon Atom Being Nucleophilic

Me_4Si . $^1J_{\text{CH}}$ in each case is in the range expected for an olefinic carbon atom.¹⁸

The infrared spectrum of **3a** shows a medium-strength peak at 1655 cm^{-1} which may be ascribed to a $\nu_{\text{C}=\text{C}}$ stretching mode; its greater than normal intensity is due to an oxygen atom being bonded to the olefinic carbon atom (as in vinyl ethers^{19a}). Its mass spectrum shows no parent ion but a peak at m/e 507.3056 (calcd 507.3007) corresponding to the parent ion less Cl.

Base hydrolysis of **3a** gives a mixture of $\text{Me}_3\text{CCH}_2\text{OH}$ and $\text{Me}_3\text{CCH}_2\text{C}(=\text{O})\text{CH}_3$. These products were identified by GLC/mass spectroscopy in this case and by GLC isolation followed by ^1H NMR in others below (see Experimental Section).

3a reacts slowly with $\text{LiCH}_2\text{CMe}_3$ in pentane to give $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{enolate})$ (**4**, Scheme I). Its ^1H NMR spectrum shows major peaks similar to those of *E*-**3a** at τ 4.71 (1), 8.08 (3), 8.38 (8), 8.73 (36), and 8.90 (9), and its infrared

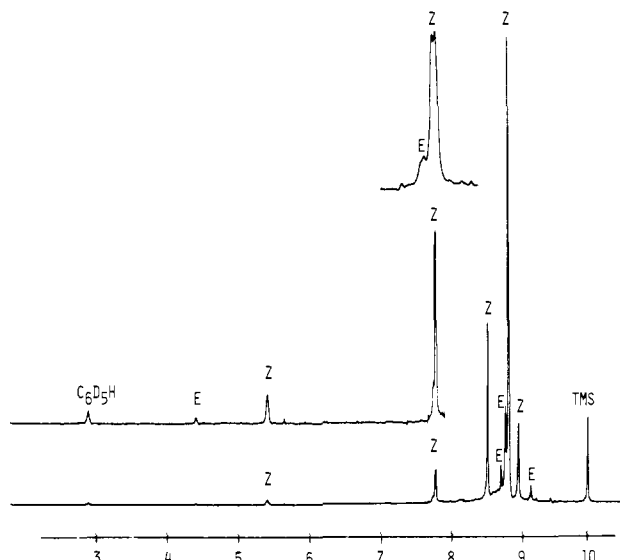


Figure 2. The 90-MHz ^1H NMR spectrum of a 1:6 mixture of (*E*)- and (*Z*)- $\text{Ta}(\text{CH}_2\text{CMe}_3)_3[\text{N}(\text{Me})\text{C}=\text{CHCMe}_3]$ (**3a**).

spectrum a peak at 1635 cm^{-1} . The highest peak in its mass spectrum is the same as that for **3a**. **4** decomposes slowly at 25°C (days) or in about 1 h at 75°C in benzene. Neopentane was identified by ^1H NMR and GLC but the organometallic product has not yet been characterized.

The reaction between **1** and benzoyl chloride in pentane gave a pale yellow oil whose ^1H NMR spectrum was consistent with a 4:6 mixture of *E*- and *Z*-**3b**. The olefinic protons at τ 4.30 (*E*-**3b**) and 5.22 are now sharp singlets. When the reaction is done in diethyl ether the isolated product (57%) is $\geq 95\%$ white, crystalline *Z*-**3b**.

Normally **1** reacts with esters (e.g., ethyl acetate or formate) in a Wittig sense.⁷ Phenyl benzoate, however, is one anomaly since it gives white, crystalline **5** in 85% isolated yield. This isolated product is pure *E*-**5**.

Acetonitrile reacts vigorously with **1** to give essentially a quantitative yield of approximately a 3:1 mixture of *E*- and *Z*-**6a** (by ^1H NMR); Figure 2 shows the ^1H NMR spectrum of a partially purified sample enriched in the *Z* isomer. No solid product can be isolated readily from common organic solvents (even pentane) but from acetonitrile at -30°C pale yellow *Z*-**6a** can be had after three or four recrystallizations of the mixture. It can be freed of acetonitrile by sublimation. It slowly decomposes in room light to give as yet unidentified products. *E*- and *Z*-**6a** cosublime as a yellow oil and hydrolyze to give neopentyl methyl ketone and neopentyl alcohol.

The reaction of **1** with benzonitrile gives a similar yellow oil, a 1:9 mixture of *E*- and *Z*-**6b**. Recrystallization from acetonitrile followed by sublimation gave pure *Z*-**6b** as a yellow oil.

At -78°C (in toluene, pentane, or ether) **1** reacts instantly with 1 mol of HCl to give a bright yellow solution. The ^1H NMR spectrum in toluene- d_8 at -20°C shows that no neopentane is present and the product gives rise to only two slightly broadened singlet resonances at τ 8.08 and 8.74 in a ratio of 2:9. The -50°C 22.63-MHz ^{13}C NMR spectrum is consistent with a complex containing three neopentyl groups of one type (C_α at 115.9 ppm, C_γ at 35.2 ppm) and one of another (C_α at 145.8 ppm, C_γ at 35.0 ppm), and no neopentylidene α -carbon atom. At -20°C the C_γ signals have coalesced and the C_α signals are broad and slightly shifted toward each other. We propose that the product of this reaction is trigonal bipyramidal $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$ (**7**) in which the neopentyl groups begin to equilibrate on the ^1H NMR time scale at ca. -10°C . We cannot be certain that they equilibrate intramolecularly (see

Discussion) even though this is almost certainly the case for complexes such as $\text{Ta}(\text{CH}_2\text{Ph})_5$ in which only one benzyl H_α resonance is observed at room temperature.²⁰

$\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$ can be isolated as yellow crystals from pentane at -78°C . The solid is not stable at 25°C for more than a few minutes under nitrogen. In toluene- d_8 **7** begins to decompose above about -10°C to give neopentane (by ^1H NMR and GLC). The organometallic products are **1**, $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$, and other unidentified solubles and a brown precipitate. In the presence of TiCp , however, **9**, a thermally stable, yellow oil, which can also be prepared from $\text{TaCpCl}_2(\text{CHCMe}_3)$,⁹ can be isolated. Since TiCp is very mild (it does not react with $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$, for example), and the yield of **9** high, we propose that $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{Cl})(\text{CHCMe}_3)$ (**8**) is the decomposition product which initially forms from **7** and which reacts with TiCp to give **9**.

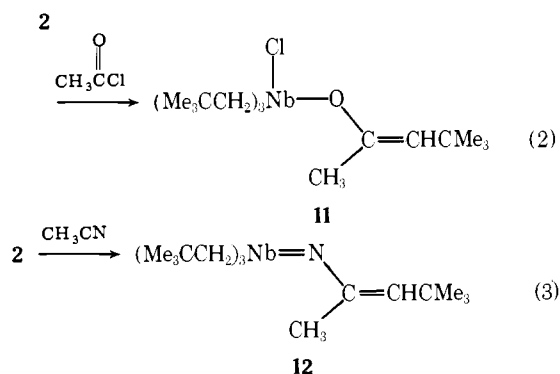
Additional evidence for **8** comes from the decomposition of **7** in the presence of acetonitrile to give a mixture of *E*- and *Z*-**10** (a yellow oil). Fractional crystallization from acetonitrile at -30°C gives the pure *E* isomer (cf. *Z*-**6a**), a sublimable yellow oil.

7 decomposes considerably more slowly in 1:1 acetonitrile-pentane (or toluene, ether, benzene, etc.) at 25°C (several hours by ^1H NMR in $\text{CD}_3\text{CN}-\text{C}_6\text{D}_6$) than in pentane or toluene alone. Possibly it is stabilized in polar solvents by loss of Cl^- to give $\text{Ta}(\text{CH}_2\text{CMe}_3)_4^+$. Some evidence that this is the case is the result of an attempt to form $[\text{Ta}(\text{CH}_2\text{CMe}_3)_4]^+\text{BF}_4^-$ from **7** and TlBF_4 in acetonitrile-ether solution. TiCl formed within minutes but the only isolable organometallic product was pentane-soluble, white $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{F}_2$. Consistent with this result is the finding that treatment of **1** with 1 mol of $\text{HBF}_4\cdot\text{ether}$ in ether at -78°C also gave only $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{F}_2$. Apparently $[\text{Ta}(\text{CH}_2\text{CMe}_3)_4]^+$ readily removes F^- from BF_4^- , then exchanges a second CH_2CMe_3 ligand for F in BF_3 .

The reaction of **7** with $\text{LiCH}_2\text{CMe}_3$ to give **1** is also consistent with (but, of course, does not prove) intermediacy of **8**.

We believe that most, if not all, of the reactions with **1** shown in Scheme I would be successful with $\text{Nb}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ (**2**). The only two we tried were: **2** reacts with acetyl chloride to give **11** (eq 2) and with acetonitrile to give **12** (eq 3). Each is analogous in almost every way with **3a** and

$\text{Nb}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$



6a, respectively, the exception being that **11** and **12** are somewhat less stable thermally.

Finally, we should note that none of the above reactions could reasonably involve one of the neopentyl ligands rather than the neopentylidene ligand in the primary step; the latter is clearly more nucleophilic as the reaction with HCl demonstrates. It has also been shown⁸ that $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ readily reacts with acetonitrile to give a mixture of (*E*)- and (*Z*)- $\text{TaCpCl}_2[\text{N}(\text{CH}_3)\text{C}=\text{CHCMe}_3]$.

Scrambling Processes Involving 1. $[(\text{Me}_3\text{CCH}_2)_3\text{Ta}\equiv\text{CCMe}_3]\cdot\text{LiTMEDA}$ ¹⁷ reacts with $\text{CF}_3\text{CO}_2\text{D}$ in pentane

at -78°C to give a moderate yield of **1**. Mass spectroscopy shows **1** to be $\sim 90\%$ d_1 and $\sim 10\%$ d_0 . The percent D initially on the neopentylidene α -carbon atom can be determined by mass spectroscopic analysis of diisobutylene- $3-d_0$ and $-3-d_1$ formed on reaction of **1-d**₁ with acetone.⁷ One sample contained 72% $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CDCMe}_3)$ and a second 81% $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CDCMe}_3)$; the remainder in each case is presumably a mixture of **1-d**₀ ($\sim 10\%$ of the total) and $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{CHDCMe}_3)(\text{CHCMe}_3)$ (18 and 9% of the total, respectively). The percent $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CDCMe}_3)$ in the first decreased to 58 and 47% after heating for 103 and 240 min at 75°C in C_6D_6 , and in the second to 44% in 300 min at 75°C . The ^1H NMR spectra of each sample showed that $<5\%$ had decomposed to give neopentane during this time. One can calculate an average first-order rate constant for converting $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CDCMe}_3)$ to $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{CHDCMe}_3)(\text{CHCMe}_3)$ (see Experimental Section) and from it ΔG^\ddagger_{348} using the Eyring equation; we find $\Delta G^\ddagger_{348} = 27.8 \pm 0.2 \text{ kcal mol}^{-1}$.

We would like to believe that this scrambling process is strictly intramolecular, unlike a superficially similar α -proton scrambling process in $\text{Me}_3\text{P}=\text{CH}_2$ ($\Delta G^\ddagger_{373} \approx 18 \text{ kcal mol}^{-1}$)²¹ which may not only be intermolecular but catalyzed by traces of acid.²³ If this is true then a neopentyl α -hydrogen atom must transfer to the more basic neopentylidene α -carbon atom more easily (a nondestructive process) than the neopentylidene (or neopentyl) α -hydrogen atom transfers to a neopentyl α -carbon atom. The latter is very likely one of the steps involved in the decomposition of **1** at higher temperatures.

A second type of scrambling process is that in which neopentyl groups in **1** exchange with those in $\text{LiCH}_2\text{CMe}_3$. For example, the neopentyllithium recovered by fractional crystallization after stirring $\text{LiCD}_2\text{CMe}_3$ (3 mol) with **1** in pentane for 15 min was shown to be a 1:1 mixture of $\text{LiCH}_2\text{CMe}_3$ and $\text{LiCD}_2\text{CMe}_3$ by ^1H NMR while the ^1H NMR spectrum of a similar mixture in C_6D_6 showed that the intensity of the neopentyl methylene peak in **1** (at τ 9.16) decreased by $\sim 50\%$ while that ascribed to the single neopentylidene α proton (at τ 8.09) was unchanged. Presumably $\text{LiTa}(\text{CH}_2\text{CMe}_3)_4(\text{CHCMe}_3)$, in which Li would probably be bound to one or more α -carbon atoms, is the short-lived intermediate. It has not been isolated; only $\text{LiCH}_2\text{CMe}_3$ crystallizes out on cooling a 1:1 mixture of **1** and $\text{LiCH}_2\text{CMe}_3$ in pentane. An attempt to form a Li-TMEDA salt in pentane gave neopentane and $[(\text{Me}_3\text{CCH}_2)_3\text{Ta}\equiv\text{CCMe}_3]\cdot\text{Li}(\text{TMEDA})$ ¹⁷ immediately.

Deuterium Labeling Studies. Deuterium labeling studies provide four important clues to how **1** forms.

$\text{Ta}[\text{CD}_2\text{CMe}_3]_3\text{Cl}_2$ was treated with 2 mol per Ta of $\text{LiCD}_2\text{CMe}_3$ in alumina-dried spectrograde hexane in a Vycor flask (flame dried in vacuo).²⁴ After 6 h the volatile components were transferred in vacuo and the residue treated with 1 mol of acetone to give 2,4,4-trimethyl-2-pentene- d_x (diisobutylene- d_x)⁷ which was similarly isolated by bulb/bulb transfer in vacuo. Neopentane- d_x and diisobutylene- d_x were analyzed by mass spectroscopy. The diisobutylene was $\geq 98\%$ $3-d_1$. The neopentane- d_x was labeled as shown in Table I.

Three of the most obvious ways neopentane can form is by homolytic scission of the metal-carbon bond followed by abstraction of H (or D) from the solvent, abstraction of a γ -hydrogen atom by Me_3CCD_2 (97%) or Me_3CCDH (3%), or abstraction of an α hydrogen (or deuterium) by Me_3CCD_2 (97%) or Me_3CCDH (3%). The results seem to rule out the first as a major pathway, since that using hexane solvent does not differ to an experimentally significant extent from that where toluene- d_8 is the solvent.²⁵ The second must also not be a major decomposition pathway since the majority of the neopentane is d_3 . The third is the most consistent interpretation. For example, the theoretical neopentane- d_x mixture

Table I. The Isotopic Distribution in Neopentane Formed in the Preparation of $\text{Ta}(\text{CD}_2\text{CMe}_3)_3(\text{CDCMe}_3)$

	% d_0	% d_1	% d_2	% d_3
Neopentane- d_x (hexane)	0	~0	15	85
Neopentane- d_x (toluene- d_8) ^a	0	4	13	83
Calcd ^b	0	0.1	6.4	93.5

^a The reaction of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and $2\text{LiCH}_2\text{CMe}_3$ in toluene- d_8 gave only neopentane- d_0 . ^b Assuming 97% α, α - d_2 and 3% α - d_1 neopentyl groups (see Experimental Section) and random α -abstraction among five with $k_H/k_D = 3$.^{27,28} The experimental k_H/k_D is 2.7 ± 0.2 (see later section).

which would form by random abstraction of α -D (or H) from one of five neopentyl groups by the α -carbon atom of a second assuming $k_H/k_D = 3$ (Table I) at least demonstrates that about half the observed neopentane- d_2 could arise from starting materials containing ca. 3% neopentyl- d_1 groups. The remaining neopentane- d_2 we believe arises from proton sources on the Vycor surface.²⁴ This systematic error almost certainly will skew all results toward protoneopentane (vide infra). Nevertheless, we believe that these data show sufficiently accurately that *H (or D) on a neopentyl α -carbon atom only is used to form neopentane*.

One possible intermediate in the reaction to give **1**, by analogy with $\text{Ta}(\text{CH}_3)_5$ and $\text{Ta}(\text{CH}_2\text{C}_6\text{H}_5)_5$,²⁰ is $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$. This possibility can be tested by comparing the labeled neopentane and diisobutylene (obtained as before by treating **1**- d_x with acetone) obtained from the reaction between $\text{Ta}(\text{CD}_2\text{CMe}_3)_3\text{Cl}_2$ and 2 mol of $\text{LiCH}_2\text{CMe}_3$ (expt B, Table II) with that from the reaction between $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{CD}_2\text{CMe}_3)\text{Cl}_2$ and 2 mol of $\text{LiCD}_2\text{CMe}_3$ (expt A). [The labels have not previously scrambled in $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{CD}_2\text{CMe}_3)\text{Cl}_2$ since hydrolysis with excess methanol in toluene at 60 °C for 1 h gave a mixture of 64% neopentane- d_0 , 34% neopentane- d_2 , and 2% neopentane- d_1 .] If $\text{Ta}(\text{neopentyl})_5$ were a discrete intermediate in which all neopentyl groups equilibrate then each should give the same neopentane- d_x and diisobutylene- d_x mixture. However, the differences (Table II) are greater than experimental error (estimated to be $\pm 3\%$; see Experimental Section), and would seem to indicate that pentaneopentyltantalum is not a discrete intermediate, i.e., if it is, its lifetime is too short to allow all five neopentyl groups to equilibrate. Any process which scrambles neopentyl groups (by Ta/Li exchange, for example, vide supra) is equivalent and therefore cannot invalidate this conclusion.

Before considering alternatives we should point out that results such as those for experiments A and B in Table II are inherently inadequate for studying the mechanism of forming **1** in detail, primarily for four reasons: (1) a significant amount of each neopentane is always formed; (2) the differences between A and B are not as great as one might wish; (3) errors due to spurious proton sources on the glass could be serious;²⁴ and (4) since neopentyl scrambles between **1** and Li neopentyl at a rate on the order of formation of **1**, the isotopic distribution of the lithium reagent almost certainly changes during the course of the reaction. [This is confirmed by the results of experiment D in Table II. The recovered $\text{LiCH}_2\text{CMe}_3$ was not d_0 , but 18–19% d_2 , as shown by hydrolysis with excess CH_3OD to give 18% neopentane- d_3 (plus 8% d_0 , 69% d_1 , and 6% d_2) and with excess CH_3OH to give 19% neopentane- d_2 (plus 79% d_0 , 2% d_1 , 0% d_3). This is the amount predicted by complete scrambling of the neopentyl groups.] However, these data can be used selectively and do allow one to reach two other important conclusions.

The first derives from experiment C (Table II). When a deficiency of lithium reagent is used only 0.5 mol of **1**- d_x forms

Table II. Isotopically Labeled Neopentanes Generated on Preparing Labeled **1** in Hexane at 25 °C (Vycor Flasks)^a

Expt	Method	% d_0	% d_1	% d_2	% d_3
A	$\text{Ta}(\text{CD}_2\text{CMe}_3)_3\text{Cl}_2/$ $(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2/$ $2\text{LiCD}_2\text{CMe}_3$ ^b	16	4	71	9
B	$\text{Ta}(\text{CD}_2\text{CMe}_3)_3\text{Cl}_2/$ $2\text{LiCH}_2\text{CMe}_3$ ^c	19 (17)	13 (17)	47 (45)	21 (21)
C	$\text{Ta}(\text{CD}_2\text{CMe}_3)_3\text{Cl}_2/$ $1\text{LiCH}_2\text{CMe}_3$	17	18	47	18
D	$\text{Ta}(\text{CD}_2\text{CMe}_3)_3\text{Cl}_2/$ $10\text{LiCH}_2\text{CMe}_3$ ^d	24 (24)	17 (18)	48 (48)	11 (10)
E	$\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2/$ $1\text{LiCD}_2\text{CMe}_3$ ^e	40	3	57	~0
F	$\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2/$ $2\text{LiCD}_2\text{CMe}_3$	40	3	55	2

^a Experiments in Vycor flasks were reproducible to $\pm 3\%$.²⁴ Numbers in parentheses are the results of another identical experiment.

^b The diisobutylene formed by treating the product with acetone was 87% d_0 , 13% d_1 . ^c The diisobutylenes formed by treating the product with acetone were 67 (66)% d_0 and 33 (34)% d_1 . ^d Methanolysis of recovered LiR gave 73% d_0 , 1% d_1 , and 26% neopentane- d_2 . ^e Methanolysis of recovered TaR_3Cl_2 gave no detectable neopentane- d_2 .

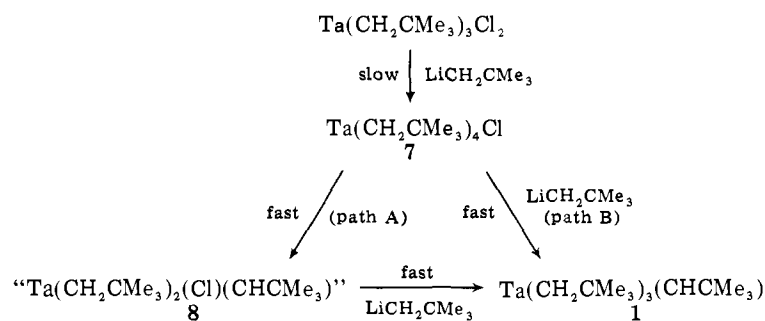
(by ¹H NMR) and the isotopic distribution in the evolved neopentane differs insignificantly from that evolved in B. Most importantly, the unreacted material is identical with the starting $\text{Ta}(\text{CD}_2\text{CMe}_3)_3\text{Cl}_2$ by ¹H NMR. Therefore, the *first step of the reaction must be the slowest*. The same conclusion follows based on the results of two analogous experiments, E and F in Table II.

Finally, the results of experiments B, C, and D show fairly clearly (outside experimental error) that *the label in excess lithium reagent turns up in neopentane*; as the amount of $\text{LiCH}_2\text{CMe}_3$ increases from 1 to 2 to 10 mol per Ta, neopentane- d_0 increases from ~17% (B and C) to 24% (D) while neopentane- d_3 decreases from 18–21% (B and C) to 11% (D). Either CH_2CMe_3 on Li exchanges with CD_2CMe_3 on Ta during the rapid phase of the reaction (but before neopentane forms) or an attacking CH_2CMe_3 group, before it loses its identity by scrambling, removes α -H (or D) from a neopentyl group bound to Ta. This may (but need not necessarily) involve discrete $\text{Ta}(\text{neopentyl})_4(\text{neopentyl}')$ in which neopentyl' is the attacking group which has not yet scrambled with the other neopentyl ligands.

An important result which is needed in such labeling experiments is the kinetic deuterium isotope effect. This can be determined unambiguously by treating $\text{Ta}(\text{CHDCMe}_3)_3\text{Cl}_2$ with 2 mol of LiCHDCMe_3 in pentane, then cleaving off the neopentylidene ligand in the product with acetone⁷ and determining the ratio of $\text{Me}_2\text{C}=\text{CDCMe}_3$ to $\text{Me}_2\text{C}=\text{CHCMe}_3$ by mass spectroscopy. (We can confidently predict that the rate of scrambling of α hydrogens in (e.g.) $\text{Ta}(\text{CHDCMe}_3)_3(\text{CDCMe}_3)$ would be slow; see previous section.) The value of k_H/k_D so determined is 2.7 ± 0.2 . Note that the isotope effect estimated from the rates of decomposition of TaMe_5 and $\text{Ta}(\text{benzyl})_5$ was about 3.²⁰

Postulated Mechanism of Forming **1.** We believe that the first, and slowest, step of the reaction between five-coordinate $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and $\text{LiCH}_2\text{CMe}_3$ gives $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$ (**7**, Schemes I and II). Since so far we have not been able to show conclusively that **7** forms from $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and $\text{LiCH}_2\text{CMe}_3$ in pentane it must disappear rapidly at 25 °C. This can be tested by comparing the relative rates of reaction of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and **7** with $\text{LiCH}_2\text{CMe}_3$. To do so we followed the production of LiCl in each case (see Experimental Section) and assumed that this rate is the same as the rate of forming **1**. In the reaction of 1 mmol of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$

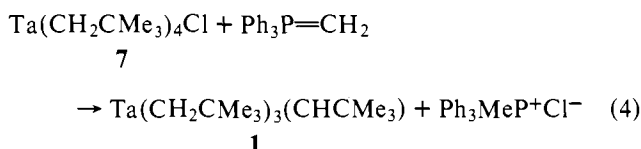
Scheme II. The Most Plausible Mechanism of Forming 1



and 2 mmol of $\text{LiCH}_2\text{CMe}_3$ in 50 mL of heptane at 22 °C half the theoretical amount of LiCl forms in 25–30 min. In contrast, a reaction employing 1 mmol of $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$ and 1 mmol of $\text{LiCH}_2\text{CMe}_3$ in 50 mL of heptane at 22 °C was virtually complete in 10 min. Clearly, therefore, the rate of forming **1** from $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$ is much greater (say ten times) than the rate of forming **1** from $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$, a conclusion also drawn from the results of labeling studies in the previous section. Evidently a weaker nucleophile, $\text{Me}_3\text{CCH}_2\text{MgCl}$, reacts comparatively slowly with $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$, and $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ therefore forms only at higher temperatures.

All subsequent steps are fast. One possible path (A, Scheme II) seems likely in view of the studies of the decomposition of **7** to give postulated **8**, which, being only four coordinate, probably reacts rapidly with another mol of $\text{LiCH}_2\text{CMe}_3$ to give **1**. We favor this alternative if the solvent is a nonpolar one like pentane but still cannot exclude some contribution from path B.

The main reasons for insisting that path B is plausible even in pentane, are the facts that neopentane- d_0 should not be formed in experiment B (Table II) and the amount of neopentane- d_0 formed in experiments B, C, and D (Table II) increases in that order. Neither should be true if only path A obtains. It is possible that neopentane- d_0 arises from proton sites on the glass.²⁴ However, this cannot be a major or sole source since $\text{Ph}_3\text{P}=\text{CH}_2$ also reacts with **7** (in ether) to give $\text{Ph}_3\text{MeP}^+\text{Cl}^-$ and **1** in 76% yield (eq 4). Therefore, one also cannot postulate that the neopentane- d_0 arises solely by

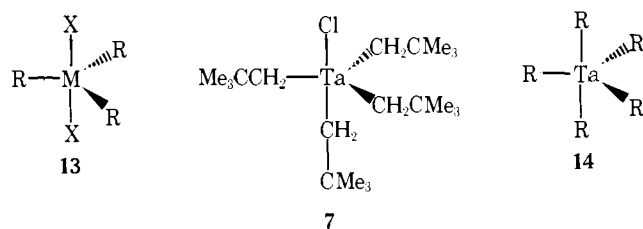


exchange between Li and Ta during the rapid phase of the reaction. Adding LiMe to **7** gives only a small yield of **1** (ca. 20% by ^1H NMR); we propose that the major product is thermally unstable $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{Me})(\text{CHCMe}_3)$, either by loss of neopentane from $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{Me})$ or by substituting Cl by Me in $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{Cl})(\text{CHCMe}_3)$ (**8**). Unfortunately no experiment distinguishes between formation of short-lived $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$ and dehydrohalogenation of **7** by $\text{LiCH}_2\text{CMe}_3$ (i.e., neopentane forms before LiCl leaves the coordination sphere) as the better description of path B.

We cannot determine the relative contributions of paths A and B. The fact that we can isolate **7**, and it reacts rapidly with $\text{LiCH}_2\text{CMe}_3$, of course does not help resolve this question. Almost certainly their relative contributions will change with the solvent and the temperature. We feel that a system such as $\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{OR})$ (**4**, Scheme I), which smoothly evolves neopentane, will ultimately be a good model for intramolecular α abstraction. Understanding the role of the lithium reagent will be much more difficult.

Discussion

Structures. Solubilities and molecular weight measurements for $\text{MR}_x\text{Cl}_{5-x}$ complexes of Nb and Ta suggest that these species are monomers unless R is small (e.g., R = Me) and $x = 1$.^{2a} In that case monomeric MRCl_4 , like NbCl_5 , is probably in equilibrium in solution with a dimer containing bridging chloride ligands. Though x-ray structures of monomeric five-coordinate Ta(V) and Nb(V)(d^0) alkyl complexes have not been determined, we can predict that they will be similar to those of analogous organophosphorus(V), arsenic(V), or antimony(V) compounds, that is, trigonal bipyramids with the most electronegative ligands in the axial positions.³¹ For example, MR_3X_2 complexes, which, like those of Sb,^{31a} are quite common (M = Nb or Ta; R = Me, CH_2Ph , CH_2CMe_3 ; X = Br, Cl, F, OR, etc.), almost certainly have the structure **13**. Therefore, in a molecule such as **7** or **14**, where an alkyl ligand



is located in an axial position, we can also predict that (1) the $\text{M}-\text{C}_{\text{ax}}$ bond length will be 0.1–0.2 Å longer than the $\text{M}-\text{C}_{\text{eq}}$ bond length and (2) the axial carbon atoms will be more negative than the equatorial carbon atoms.^{31b,c} Some evidence for the latter is the finding that **7** and $\text{Ta}(\text{CH}_2\text{Ph})_5$ react rapidly with anhydrous HCl to give TaR_3Cl_2 ; further cleavage is slower but once initiated proceeds all the way to TaCl_5 .⁸ Evidence for the former consists of the fact that $\text{Ta}(\text{CH}_2\text{CMe}_3)_3[\text{OC}(\text{Me})=\text{CHCMe}_3]\text{Cl}$ loses Cl to give the same parent ion as $\text{Ta}(\text{CH}_2\text{CMe}_3)_4[\text{OC}(\text{Me})=\text{CHCMe}_3]$.

A second feature which may be important only by virtue of the preferred arrangement of ligands in (e.g.) **13** is that in five-coordinate complexes containing two or three alkyl ligands, the angle between them will always be about 120°. In those containing four or five (e.g., **4**, **7**, or **14**) an axial alkyl is surrounded by three equatorial alkyls at 90° to it. Were the axial alkyl ligand to leave and take an α -hydrogen atom with it, not only would the six available equatorial α -hydrogen atoms be close by but the pseudotetrahedral product easily formed as the three equatorial ligands move toward the void.

Four-coordinate complexes are probably all pseudotetrahedral and from our present point of view do not deserve any special comment.

Steric Crowding. One reason why molecules like **4** or **7** evolve alkane readily while (e.g.) $\text{Ta}(\text{CH}_2\text{Ph})_5$ ²⁰ only slowly eliminates toluene may be steric crowding. This can take two forms, interligand and intraligand. Interligand crowding in **7**, for example, could encourage loss of Cl^- to give tetrahedral

$[\text{Ta}(\text{CH}_2\text{CMe}_3)_4]^+\text{Cl}^-$ or loss of axial CH_2CMe_3 and an α -hydrogen atom on equatorial CH_2CMe_3 to give tetrahedral **8**, in each case because the $\text{Ta}-\text{L}_{\text{axial}}$ bond length ($\text{L} = \text{Cl}$ or CH_2CMe_3) is probably slightly longer and therefore weaker than in a relatively uncrowded molecule like $\text{Ta}(\text{CH}_2\text{Ph})_5$. Alternatively, repulsion between R groups on CH_2R ligands can lead to larger than normal $\text{M}-\text{C}_\alpha-\text{C}_\beta$ angles with consequences similar to those resulting from intraligand crowding.

Intraligand crowding could be measured as that fraction of the larger than normal $\text{M}-\text{C}_\alpha-\text{C}_\beta$ angle in CH_2R ligands attributable solely to repulsion between M and R. Clearly this will be impossible to separate from interligand effects. Each is important since the α -hydrogen atoms probably become more acidic as the $\text{M}-\text{C}_\alpha-\text{C}_\beta$ angle increases, a form of "steric assistance".^{32a} A good example of this phenomenon is the reaction of $\text{Ph}_3\text{P}^+\text{CH}_2\text{CMe}_3\text{I}^-$ with $\text{Ph}_3\text{P}=\text{CH}_2$ to give $\text{Ph}_3\text{P}=\text{CHCMe}_3$ and $\text{Ph}_3\text{P}^+\text{MeI}^-$,^{32b} in spite of the fact that the protons in methyl groups are normally more acidic than those on a secondary carbon atom ($\text{Ph}_3\text{P}=\text{CHCH}_3 + \text{Ph}_3\text{P}^+(\text{CH}_3) \rightarrow \text{Ph}_3\text{P}^+(\text{CH}_2\text{CH}_3) + \text{Ph}_3\text{P}=\text{CH}_2$).³³ Of course, inductive effects due to a phenyl group on C_α (as in benzyl) also increase the acidity of H_α . Neither effect is present when the alkyl ligand is CH_3 and this may be one reason why α -hydrogen abstraction of the type we are observing here is at present undocumented for methyl complexes. Of course, there is considerable evidence for an intermolecular version in TaMe_5 .²⁰

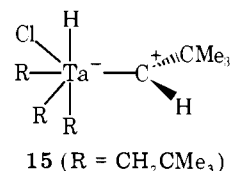
A rough idea of how crowded a molecule is and therefore whether it will be stable toward α -hydrogen atom abstraction or not can be had by calculating an angle (α_i) at the metal center which defines an area the i th ligand occupies (in two dimensions) and summing over all ligands.³⁴ For about 20 stable complexes $\Sigma\alpha_i$ falls in the range 420 – 545° ; for example, $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ (545°), TaCp_2Me_3 (498°),^{1a} $\text{Ta}(\text{CH}_2\text{Ph})_5$ (505°),²⁰ $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ (468°), $\text{TaCp}_2(\text{CH}_2\text{Ph})(\text{CHPh})$ ¹⁰ (473°), and $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ ⁹ (443°). For unstable or as yet unobserved "precursors" to known complexes $\Sigma\alpha_i$ exceeds 550° ; for example, $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$ (565°), $\text{TaCp}_2(\text{CH}_2\text{Ph})_3$ (567°), $\text{TaCp}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_2$ (560°), and $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{Ph})_3\text{Cl}$ (578°). The fact that $\Sigma\alpha_i = 585^\circ$ for $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$ is of course consistent with the fact that it, like $[\text{Ta}(\text{CH}_2\text{CMe}_3)_4(\text{CHCMe}_3)]^-$ (the postulated intermediate in neopentyl group exchange between **1** and $\text{LiCH}_2\text{CMe}_3$), is probably short lived at best.

Based on $\Sigma\alpha_i$ alone one might even predict that $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$ is a minor intermediate; $\Sigma\alpha_i$ for $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$ already exceeds 550° . It would also have to be true, however, that $\text{Ta}(\text{CH}_2\text{CMe}_3)_4\text{Cl}$ decomposes more rapidly than $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$ forms. Although this is entirely reasonable, we should also note that $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and excess LiOCMe_3 react in ether to give *only* $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{OCMe}_3)\text{Cl}$ while $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and 1 mol of KOOCMe_3 in toluene give *only* $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{OCMe}_3)_2$;⁸ these results will be reported in detail in a future publication.

Of course this approach is limited to closely related species. Gross exceptions will almost certainly be found if the coordination number or geometry, the nature of the electronegative ligand(s), or the $\text{M}-\text{C}_\alpha-\text{C}_\beta$ angle changes. For example, $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{OCMe}_3)_2$ is very stable thermally. Clearly structural considerations outlined in the previous section are at least equally important; a neopentyl ligand essentially never occupies an axial site in $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{OCMe}_3)_2$.

α -Hydrogen Abstraction. It would be difficult if not impossible to describe an intramolecular α -hydrogen abstraction process in a neutral molecule in detail. A simplified description, on the other hand, at least can serve as a starting point for future experiments and discussions.

One possible interpretation is that an α -hydrogen atom (a "hydride") transfers to the metal to give an alkylidene hydride complex which then reductively eliminates neopentane. Why this process should be *accelerated* in a crowded environment is not obvious, *unless* reductive elimination of the alkane is rate determining and the alkyl ligand in equilibrium with an alkylidene and a hydride ligand. Green⁴ has proposed such an equilibrium in the case of hypothetical $[\text{WCp}_2(\text{CH}_3)]^{++}$; however, it is also possible that the α proton transfers to the cyclopentadienyl ligand, a type of reaction postulated in reactions of similar cyclopentadienyl complexes. A similar equilibrium between $\text{Os}_3(\text{CO})_{10}(\text{CH}_3)\text{H}$ and $\text{Os}_3(\text{CO})_{10}(\text{CH}_2)\text{H}_2$ (in which the methylene ligand is believed to be *bridging*) further suggests that α -hydride elimination is, in some circumstances, entirely plausible.³⁵ Returning to the $\text{M}(\text{V})$ case, however, we find that the only adequate description of the d^0 , $\text{Ta}(\text{V})$ alkylidene hydride complex formed from **7** is **15**, almost certainly an unfavorable, relatively high energy



situation; an electropositive metal like $\text{Ta}(\text{V})$ would not prefer to be formally negatively charged relative to a carbon ligand. We might therefore postulate that " α elimination" is *strictly* possible only when the metal is initially in less than its maximum oxidation state and does not occur in the cases we are talking about.

A second, more consistent interpretation is that a more weakly bound, more basic axial alkyl α -carbon atom removes a more acidic α proton from an equatorial alkyl ligand. There are several facts which indirectly support this proposition: (1) the resulting neopentylidene α -carbon atom (in **1** and other alkylidene complexes of this genre) is nucleophilic, apparently more nucleophilic than the neopentyl α -carbon atom; e.g., **1** reacts with HCl to give **7**, not **8**; (2) *cationic* $\text{Ta}(\text{V})$ alkyl complexes (e.g., $[\text{TaCp}_2\text{Me}_2]^+\text{BF}_4^-$, ref 1a) can be deprotonated to give complexes which also contain a nucleophilic alkylidene ligand [in this case $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$]. Of course, this postulate is also consistent with the fact that alkyl ligands in $\text{M}(\text{V})$ complexes are powerful nucleophiles (the metals can be fully alkylated only with lithium or magnesium reagents) and the $\text{M}(\text{V})$ d^0 alkyl complexes are probably trigonal bipyramids. We should note that some phosphoranes probably form by loss of alkane from a $\text{P}(\text{V})$ pentaalkyl (e.g., $\text{Ph}_3\text{P}=\text{CH}_2$ from $\text{Ph}_4\text{P}(\text{CH}_3)$ axial)³⁶, the main group analogue of the α -hydrogen abstraction reaction proposed here. Finally, the isotope effect (2.7 ± 0.2) is close to that observed for deprotonation of $[\text{TaCp}_2\text{Me}_2]^+$ (3.4 ± 0.3).^{1a} We believe that the effect arises in the rate-determining α -hydrogen abstraction step²⁰ but cannot prove it here.³⁷ The isotope effect we do observe of course cannot actually be used to probe the nature of the α -hydrogen abstraction reaction.

A slightly different variation on the above postulate is that the alkyl leaves as R^- and abstracts H^+ from a neighboring α -carbon atom more rapidly than it abstracts H^+ from anywhere else in the system. If a metal-carbon bond breaks most easily, an isotope effect in the rate-determining step^{20,37} could arise only if TaR were in equilibrium with $[\text{Ta}^-][\text{R}^+]$ prior to abstraction of α - H^+ (or D^+), or if the reaction were a radical chain. The latter does not seem likely, though the former would be difficult to distinguish from the acid/base interpretation above in which a proton transfers smoothly from one α -carbon atom to another.

The only documented example of a related postulated intramolecular hydrogen atom abstraction process is the de-

composition of $M(\eta^5\text{-C}_5\text{H}_5)_3(\text{C}_4\text{H}_9)$ ($M = \text{U}$ or Th) to give butane and $[M(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-}\eta^1, \eta^4\text{-C}_5\text{H}_4)]_2$; for $\text{U}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{D}_5)_2(\text{C}_4\text{H}_9)$ $k_{\text{H}}/k_{\text{D}}$ was found to be 8 ± 1 .²⁹ Quite likely α -abstraction or " α -elimination"³³ processes are fairly common² but the resulting alkylidene complexes (or other related reaction products) are normally too unstable to isolate.

General Comments. Complexes **1** and **2** might be called transition metal ylides^{31d} since they are formally isostructural to and polarized the same way as main group 5 ylides like $\text{Ph}_3\text{P}=\text{CH}_2$. However, we prefer to call them (nucleophilic) alkylidene complexes in order to distinguish them from "carbene" complexes which have heteroatoms (O, N, S, etc.) bound to C_α —we feel they will be substantially and inherently more reactive toward unsaturated organic functionalities—and to avoid yet further confusion over nomenclature. Their ¹³C NMR spectra illustrate that resonances characteristic of carbene-type α -carbon atoms bound to transition metals are found in the 200–400-ppm region regardless of the formal charge on the α -carbon atom. It will almost certainly be true to some extent, however, that the formal charge on the α -carbon atom will determine where in this region a resonance will be found. We do not believe it coincidental that the neopentylidene C_α resonances in **1** and **2** are found at the upper end of this region while that in $(\text{CO})_5\text{WPh}_2$ is found at 358 ppm³⁸ and in $[\text{FeCp}(\text{CO})_2(\text{CHPh})]^+$ at 342 ppm ($^1J_{\text{CH}} = 146$ Hz).³⁹

The extraordinary stability of **1** probably can be ascribed primarily to the facts that (1) the lowest energy reaction, α -hydrogen transfer from a neopentyl α -carbon atom to the neopentylidene α -carbon atom, is degenerate, and (2) bimolecular reactions, for example, combination of the two neopentylidene fragments to give di-*tert*-butylethylene, are probably unfavorable for steric reasons (cf. methylene^{1a}).

The reactions which ultimately lead to enolate and unsaturated imido complexes (Scheme I) suggest that electropositive Ta(V) prefers to bind to elements more electronegative than carbon, given the opportunity. Their reaction with the carbonyl function in $\text{RC}(\text{O})\text{R}'$ to give $[\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{O})]_x$ and $\text{RR}'\text{C}=\text{CHCMe}_3$ is another example of this tendency.⁷ One might suspect, therefore, that such complexes would in general be good "sources" of the alkylidene fragment. In at least one other case so far, selective insertion of neopentylidene into olefinic C–H bonds, is this tendency evident.⁹

Experimental Section

All manipulations were done in a N_2 -filled Vacuum Atmospheres HE43-2 drybox. Solvents were dried by passing them through Linde 4A molecular sieve columns. Metal halides were purchased from standard sources and sublimed before use. Acetonitrile was distilled from P_2O_5 .

1. Preparation of Alkylating Reagents. (a) Preparation of $\text{LiCH}_2\text{CMe}_3$. A mixture of neopentyl chloride (100 g) and ca. 30 g (excess) of finely chopped Li wire (1% Na) in ca. 1 L of hexane was stirred and refluxed under argon for 1 week. The LiCl and excess Li were removed by filtration through a medium porosity glass fritted Buchner funnel and the neopentyllithium isolated from the filtrate by cooling and by reducing the volume in vacuo, yield 50–60 g (70–80%) of white, crystalline $\text{LiCH}_2\text{CMe}_3$. It may be sublimed at 150 °C, 1 μ .

¹H NMR (C_6D_6): τ 8.87 (s), 10.67 (s), 9:2 ratio.

(b) Preparation of $\text{LiCD}_2\text{CMe}_3$ and LiCHDCMe_3 . The reduction of 100 g of pivaloyl chloride with 20 g of LiAlD_4 in ether gave 58 g of $\text{Me}_3\text{CCD}_2\text{OH}$ (77% yield) by distillation. This was converted to the bromide with $\text{P}(\text{C}_4\text{H}_9)_3\text{Br}_2$ in DMF,⁴⁰ yield 70 g (71%, distilled). A 14-g sample and 4 g of Li dispersion (1% Na, Lithium Co., filtered and washed with pentane) were placed in 125 mL of pentane under argon and stirred and refluxed for 11 days. The mixture was filtered and 4.0 g of $\text{LiCD}_2\text{CMe}_3$ isolated from the filtrate as in (a). A sample

was hydrolyzed with methanol to give 97% neopentane- d_2 and 3% neopentane- d_1 .

LiCHDCMe_3 was prepared similarly from pivaldehyde.

(c) Preparation of $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$, $\text{Zn}(\text{CD}_2\text{CMe}_3)_2$, and $\text{Zn}(\text{CHDCMe}_3)_2$. The Grignard reagent was prepared by refluxing a stirred solution of 100 g of $\text{Me}_3\text{CCH}_2\text{Cl}$ in 1 L of ether containing 40 g (excess) of Mg turnings. The solution was cooled to 0 °C and 64 g of ZnCl_2 (dried with SOCl_2) added slowly as a solid so that the temperature did not exceed 30 °C, followed by 1 L of ether. The mixture was stirred overnight and filtered through a 3000-mL medium-porosity glass fritted Buchner funnel the next day. Distillation of the filtrate (27 mm) gave 60 g (61%) of $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$ (bp 82 °C at 27 mm).

¹H NMR (C_6D_6): τ 8.83 (s), 9.43 (s), 9:2 ratio.

$\text{Zn}(\text{CD}_2\text{CMe}_3)_2$ and $\text{Zn}(\text{CHDCMe}_3)_2$ were prepared from ZnCl_2 , dioxane and 2 mol of Li neopentyl in ether at 25 °C. The solution was filtered and the solvent removed in vacuo leaving a ca. 65% yield of dineopentylzinc.

(d) Preparation of $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$ (dioxane). $\text{Me}_3\text{CCH}_2\text{MgCl}$ in ether was prepared as in (c). Dioxane (125 mL) was added the next day and MgCl_2 (dioxane) filtered off with difficulty. The filtrate was evaporated to a semisolid which was triturated with pentane. Filtration gave 70 g (58%) of $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$ (dioxane) which can be purified by sublimation at 125 °C and 1 μ .

Anal. Cl: found <0.3. ¹H NMR ($\text{THF}-d_8$): τ 6.44 (s, 8), 9.03 (s, 18), 10.37 (s, 4).

2. Preparation of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$, $\text{Ta}(\text{CD}_2\text{CMe}_3)_3\text{Cl}_2$, and $\text{Ta}(\text{CHDCMe}_3)_3\text{Cl}_2$. TaCl_5 (20.0 g) and $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$ (18.0 g) were stirred for 12 h in 300 mL of pentane. The ZnCl_2 was removed by filtration and yellow crystals were isolated from the filtrate by cooling and reducing the volume in vacuo, yield 22 g (85%). It may be sublimed at 110 °C and 1 μ .

Anal. Calcd for $\text{TaC}_{15}\text{H}_{33}\text{Cl}_2$: C, 38.72; H, 7.14; Cl, 15.24; Ta, 38.89. Found: C, 38.47; H, 7.14; Cl, 15.71; Ta, 40.08. ¹H NMR (C_6D_6): τ 7.38 (s, 6), 8.75 (s, 27). ¹³C NMR (CD_2Cl_2 , ¹H decoupled): δ 115 (C_α), 34.8 (C_β), 34.6 (C_γ). Mol wt (cryoscopic in benzene): calcd 465; found 487.

$\text{Ta}(\text{CD}_2\text{CMe}_3)_3\text{Cl}_2$ was prepared similarly from $\text{Zn}(\text{CD}_2\text{CMe}_3)_2$. Methanolysis in toluene gave 97% neopentane- d_2 and 3% neopentane- d_1 .

$\text{Ta}(\text{CHDCMe}_3)_3\text{Cl}_2$ was prepared similarly from $\text{Zn}(\text{CHDCMe}_3)_2$. Its ¹H NMR spectrum showed a 1:1:1 triplet ($J_{\text{HD}} \approx 1.6$ Hz) of relative area 1.0 for H_α .

3. Preparation of $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ and $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{CD}_2\text{CMe}_3)\text{Cl}_2$. To TaCl_5 (4.0 g, slight excess) in 20 mL of toluene was added very slowly with vigorous stirring 2.1 g of $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$ in 10 mL of toluene. The ZnCl_2 was removed by filtration and the toluene removed from the filtrate in vacuo leaving a yellow-green oil. The oil was taken up in ca. 10 mL of pentane to which some activated carbon (Darco) was added. Filtration gave a canary yellow solution which crystallized on removing pentane in vacuo, then melted to an oil again at 25 °C. The ¹H NMR spectrum showed 5% $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ to be present. $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ can be isolated as yellow needles (which melt at room temperature) by low-temperature crystallization from pentane.

¹H NMR (τ , C_6D_6): 7.08 (s, 4), 8.88 (s, 18).

$\text{LiCD}_2\text{CMe}_3$ (0.14 g) was added to 0.76 g of $\text{Ta}(\text{CH}_2\text{CMe}_3)_2\text{Cl}_3$ in pentane at –78 °C followed by warming to room temperature. The mixture was filtered, the filtrate's volume halved, and the solution stood at –30 °C for 4 h to give 0.25 g of $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{CD}_2\text{CMe}_3)\text{Cl}_2$ with ¹H NMR peaks at τ 7.38 and 8.75 in the ratio of 4:27. Hydrolysis with methanol gave a 2:1 mixture of neopentane- d_0 and neopentane- d_2 (64% d_0 , 34% d_2 , 2% d_1).

4. Preparation of $\text{Nb}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$. $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$ (dioxane) (4.7 g) was added rapidly to 5.0 g of NbCl_5 in 100 mL of ether. The solution was stirred for 1 min and filtered and all solvent removed from the filtrate in vacuo. The residue was extracted with 20 mL of pentane and filtered and the filtrate evaporated to ca. 5 mL and stood at –30 °C for 16 h to give 1.6 g of orange $\text{Nb}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ (35% vs Mg). Larger scale reactions gave lower yields.

Anal. Calcd for $\text{NbC}_{15}\text{H}_{33}\text{Cl}_2$: C, 47.75; H, 8.83; Cl, 18.79. Found: C, 47.81; H, 8.76; Cl, 18.73; Mg, <0.02. ¹H NMR (C_6D_6): τ 6.40 (br s, 6), 8.70 (s, 27).

5. Preparation of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ (1**).** (a) From $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and $\text{LiCH}_2\text{CMe}_3$. Stirring 30.0 g of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ and 10.08 g of $\text{LiCH}_2\text{CMe}_3$ in 200 mL of pentane

gave a yellow solution in which lithium chloride was evident after a few minutes as the color began to darken to orange. The solution warmed up slowly (the pentane sometimes boils when the solution is as concentrated as described here) over a period of 1 h. After 4 h the lithium chloride was filtered off (5.52 g, theory 5.48 g) and the filtrate's volume reduced to ca. 30 mL and stood overnight at -30°C . Orange octahedra (9.3 g) were filtered off and further crops gathered similarly from the filtrate for a total of 24.3 g of product. Stripping the final filtrate gave 4.1 g of "crude" product which was, however, indistinguishable from the crystallized product by ^1H NMR; total yield 28.4 g (95%).

(b) From TaCl_5 and $\text{MeCCH}_2\text{MgCl}$. A 1.56 M solution of $\text{Me}_3\text{CCH}_2\text{MgCl}$ (100 mL) was added over 0.5 h to a stirred solution of TaCl_5 (11.1 g) in 500 mL of diethyl ether at room temperature. Any solid TaCl_5 rapidly dissolved as the reaction proceeded through stages characterized by greenish-yellow, yellow, and finally, orange-brown colors. The final solution contained some magnesium chloride, which was removed by filtration. All solvent was removed in vacuo and the residue sublimed at 90°C and $\sim 1\ \mu$ to give 7.0 g (49%) of deep orange nuggets on the water-cooled probe. This must be done in two stages as the first crude product splatters on melting and for some time thereafter. The reason is that $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ forms rapidly (evolving neopentane) only under sublimation conditions. In refluxing ether it forms slowly (ca. 30% in 24 h).

The reaction has successfully been scaled up tenfold (2 L total reaction volume) to give 75 g (54%) of the product.

The Grignard must be standardized carefully in order to avoid adding too little and risk contaminating the final product with residual $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$. A careful sublimation of such a mixture at 80°C and ca. $1\ \mu$ will leave most of the $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ behind.

Anal. Calcd for $\text{TaC}_{20}\text{H}_{43}$: C, 51.72; H, 9.33; Ta, 38.95. Found: C, 51.39; H, 9.31; Ta, 41.22. ^1H NMR (C_6D_6): τ 8.09 (s, 1), 8.57 (s, 9), 8.85 (s, 27), 9.16 (s, 6). ^{13}C NMR (downfield from Me_4Si , C_6D_6 , gated decoupled): 250 (d, $J = 90$ Hz, neopentylidene C_α), 114 (t, $J = 107$ Hz, neopentyl C_α), 35.2 (q, $J = 124$ Hz, neopentyl C_γ), 34.9 (q, $J = 124$ Hz, neopentylidene C_γ), 35.3 (s, neopentyl C_β), 47.0 ppm (s, neopentylidene C_β); see Figure 1. Mass spectrum: parent ion at 464.2857 (calcd 464.2821). Mol wt (cryoscopic in C_6H_6): 472. Mp 71°C (sealed capillary).

6. Preparation of $\text{Nb}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ (2). A stirred solution of $\text{Nb}(\text{CH}_2\text{CMe}_3)_3\text{Cl}_2$ (0.75 g) in 50 mL of pentane at -78°C was treated dropwise with a solution of 0.31 g of $\text{LiCH}_2\text{CMe}_3$ in 20 mL of pentane. The LiCl (0.19 g, theory 0.17 g) was filtered from the red solution after warming to 25°C . Wine-red $\text{Nb}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ (0.67 g, 83%) remained after removing all volatiles in vacuo. About half the time only an oil could be obtained. The compound is temperature sensitive and does not survive more than a few hours at 25°C . It was identified by its ^1H and ^{13}C NMR spectra (see below and text) and by its reaction with acetone to give 2,4,4-trimethyl-2-pentene essentially quantitatively.

^1H NMR (toluene- d_8): τ 6.98 (1, s), 8.58 (9, s), 8.89 (27, s), 9.07 (6, s). ^{13}C NMR (toluene- d_8 , ^1H decoupled, -50°C): 246 (broad, neopentylidene C_α), 96.9 (broad, neopentyl C_α), 47.5 (neopentylidene C_β), 34.5 (neopentyl C_β), 34.2 (neopentyl C_γ), 32.8 (neopentylidene C_γ); (gated decoupled) 96.9 (t, $J = 101$ Hz), 47.5 (s), 34.5 (s), 34.2 (q, $J = 124$ Hz), 32.8 ppm (q, $J = 124$ Hz).

7. Preparation of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CDCMe}_3)$ and Scrambling of D among All α -Carbon Atoms. A mixture of 5.7 mL of 1.6 M butyllithium in hexane and 1.0 g of N,N,N',N' -tetramethylethylenediamine (TMEDA) in 20 mL of hexane was allowed to stand for 10 min, then added to 4.17 g of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ dissolved in 20 mL of hexane at -78°C . The deep orange color lightened to yellow-orange on warming to 25°C . On removing hexane in vacuo, tiny, yellow-orange crystals formed and were filtered off when the total volume was about 7 mL, yield 4.1 g (78%) of $[\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CCMe}_3)]\cdot\text{Li}(\text{TMEDA})^{17}$ (this product will be fully described in a separate publication).

A solution of 5.86 g of $[\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CCMe}_3)]\cdot\text{Li}(\text{TMEDA})$ in 100 mL of pentane was cooled to -78°C and 0.75 mL of $\text{CF}_3\text{CO}_2\text{D}$ in 50 mL of pentane added dropwise with stirring. The solution was warmed to room temperature and filtered the next day to give 0.39 g of white solid (theory for LiCO_2CF_3 1.04 g). Removing part of the solvent in vacuo gave 1.5 g of starting material. Solvent was removed in vacuo from the remaining solution and the orange residue was sublimed at 75°C ($1\ \mu$) to give 380 mg of the title compound (11% yield vs. Ta based on starting material consumed).

A mass spectrum of the product showed a parent peak due to $\text{TaC}_{20}\text{H}_{42}\text{D}$ at 465.2862 (465.2886 calcd) and one due to $\text{TaC}_{20}\text{H}_{43}$ with 12% the former's intensity corresponding to 11% of the mix. Accordingly a ^1H NMR spectrum showed that the neopentylidene α -proton peak had an area corresponding to ~ 0.1 proton. A sample (130 mg) was treated with 21 mL of acetone in pentane and the resulting diisobutylene analyzed by GLC/mass spectroscopy: found, 12% $\text{Me}_2\text{C}=\text{CHCMe}_3$, 88% $\text{Me}_2\text{C}=\text{CDCMe}_3$. We assume 11% $1-d_0$ is formed after exchange of D^+ in $\text{CF}_3\text{CO}_2\text{D}$ with traces of H^+ and the difference between diisobutylene- d_0 (which varies from one experiment to another) and $1-d_0$ is the percent $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{CHDCMe}_3)(\text{CHCMe}_3)$. In the following experiment, however, we assume that the amount of $1-d_0$ is negligible; the error so introduced is far smaller than the variation in k .

The % deuterium on the neopentylidene α -carbon atom in a similarly prepared sample (72% d_1), after heating in benzene at 75°C for 130 and 240 min, had decreased to 58 and 47%, respectively, as determined by the mass spectrum of the diisobutylene obtained on reaction with acetone. In another sample 81% d_1 decreased to 44% in 300 min at 75°C . Less than 5% decomposition of each sample occurred during this time period according to the ^1H NMR spectra. If $\text{A} = \text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CDCMe}_3)$ and $\text{B} = \text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{CHDCMe}_3)(\text{CHCMe}_3)$ then $\ln \{([A]_0 K_{\text{eq}} - [\text{B}]) / ([A]_0 K_{\text{eq}} - [\text{B}]_0)\} = -(k_1 + k_2)t$ where $[A]_0$ and $[B]_0$ are the concentrations of A and B at $t = 0$, $K_{\text{eq}} = 6$, k_1 is the first-order rate constant for $\text{A} \rightarrow \text{B}$, and $k_2 (= k_1/6)$ is the rate constant for $\text{B} \rightarrow \text{A}$. The values for k_1 from the above data are 3.04, 3.37, and $3.84 \times 10^{-5} \text{ s}^{-1}$, which give values for ΔG^\ddagger_{348} of 27.85, 27.78, and 27.69 kcal mol^{-1} or $\Delta G^\ddagger_{348} = 27.8 \pm 0.2 \text{ kcal mol}^{-1}$.

8. Preparation of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}[\text{O}(\text{Me})\text{C}=\text{CHCMe}_3]$ (3a). $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ (1.5 g, 3.23 mmol) was dissolved in 40 mL of pentane and 0.23 mL (3.25 mmol) of acetyl chloride added dropwise. In 2 min the orange solution turned pale yellow. After 1 h the solvent was removed in vacuo leaving a yellow, crystalline solid. The product was then sublimed at 75°C and $0.5\ \mu$, yield 1.5 g (86%). Hydrolysis with excess 1N NaOH gave $\text{Me}_3\text{CCH}_2\text{OH}$ and $\text{Me}_3\text{C}-\text{CH}_2\text{C}(=\text{O})\text{CH}_3$ by GLC/mass spectroscopy.

Anal. Calcd for $\text{TaC}_{22}\text{H}_{46}\text{ClO}$: C, 48.65; H, 8.55; Cl, 6.53. Found: C, 48.61; H, 8.39; Cl, 6.76. ^1H NMR (C_6D_6): *E* isomer, τ 4.57 (1, q, $J \approx 1$ Hz), 8.08 (3, d, $J \approx 1$ Hz), 8.14 (6, s), 8.79 (27, s), 8.94 (9, s). *Z* isomer (in mixture at 270 MHz): τ 5.56 (1, q, $J \approx 1$ Hz), 8.07 (3, d, $J \approx 1$ Hz), 8.14 (6, s), 8.76 (27, s), 8.94 (9, s). ^{13}C NMR (gated decoupled, from Me_4Si , C_6D_6): *E* isomer, τ 154.5 (s, olefinic C_α), 126.1 (d, $J = 150$ Hz, olefinic C_β), 102.0 (t, $J = 113$ Hz, neopentyl C_α), 35.4 (q, $J = 124$ Hz, neopentyl C_γ), 34.8 (s, neopentyl C_β), 31.8 (q, $J = 126$ Hz, methyl of olefinic *tert*-butyl group), 18.2 ppm (q, $J = 126$ Hz, olefinic methyl); tertiary carbon of olefinic *tert*-butyl group not located. *Z* isomer: τ 152 (s, olefinic C_α), 122.8 (d, $J = 148$ Hz, olefinic C_β), 105.2 (t, $J \approx 120$ Hz, neopentyl C_α), 23.8 (q, $J \approx 129$ Hz, olefinic methyl); others not located. The mass spectrum shows no parent ion but a peak at m/e 507.3056 corresponding to M^+ minus Cl (calcd 507.3007), and a second major peak at m/e 471 corresponding to M^+ minus C_5H_{11} (not mass measured). IR (Nujol): 1655 cm^{-1} , medium ($\nu_{\text{C}=\text{C}}$).

9. Preparation of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}[\text{O}(\text{Ph})\text{C}=\text{CHCMe}_3]$ (3b). $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ (1.5 g, 3.23 mmol) was dissolved in 25 mL of Et_2O and 0.45 g (3.23 mol) of benzoyl chloride was added directly to the stirring solution. After stirring overnight the volume of the solvent was reduced in vacuo to 5 mL and stood at -30°C for 1 h to yield 1.12 g of crude **3b**. Recrystallization of the crude material from pentane gave white crystals of $>95\%$ **Z-3b**.

In pentane a similar reaction gave a yellow oil on removing the solvent, a 4:6 mixture of *E*- and *Z-3b* by ^1H NMR.

^1H NMR (C_6D_6): *E* isomer, τ 2.8 (complex Ph resonance), 4.30 (1, s), 8.28 (6, s), 8.89 (27, s), 9.08 (9, s). *Z* isomer, τ 2.8 (complex Ph resonance), 5.22 (1, s), 8.22 (6, s), 8.68 (9, s), 8.85 (27, s). IR (Nujol): 1655 cm^{-1} , medium ($\nu_{\text{C}=\text{C}}$).

10. Preparation of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3[\text{O}(\text{Me})\text{C}=\text{CHCMe}_3]$ (4). $\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Cl}[\text{O}(\text{CH}_3)\text{C}=\text{CHCMe}_3]$ (2.63 g) was dissolved in pentane and 0.39 g of $\text{LiCH}_2\text{CMe}_3$ added as a solid with stirring. After 1 h 0.20 g of LiCl (theory 0.20 g) was filtered off and the solvent removed in vacuo leaving 2.67 g of a yellow oil (95% yield) which solidified in a few minutes at 25°C . The compound was too unstable for accurate elemental analysis; it turned into a gum after 1–2 days.

^1H NMR (major isomer, C_6D_6): τ 4.71 (1, q, $J \approx 1$ Hz), 8.08 (3,

d, $J \approx 1$ Hz), 8.38 (8, s), 8.73 (36, s), 8.90 (9, s). The mass spectrum shows an M^+ minus C_5H_{11} peak at 507.3056 (calcd 507.3007). IR (Nujol): 1635 cm^{-1} , medium ($\nu_{C=C}$).

11. Preparation of Ta(CH₂CMe₃)₃(OPh)[O(Ph)C=CHCMe₃] (5). Ta(CH₂CMe₃)₃(CHCMe₃) (1.5 g, 3.23 mmol) was dissolved in 50 mL of Et₂O and 0.64 g of phenyl benzoate added as a solid to the stirred reaction mixture. After stirring for 1 day the volume was reduced to 15 mL and the solution stood at -30°C overnight to give white crystals, yield 1.32 g (85%). Hydrolysis of a 1.32-g sample with 1 N HCl gave 0.38 g of a colorless oil which was purified by dissolving in pentane, passing the solution through alumina, then removing the solvent in vacuo. The ¹H NMR spectrum [τ 2.2 (2, m, H ortho), 2.7 (3, m, H meta and para), 7.2 (2, s), 8.8 (9, s)] and infrared spectrum ($\nu_{C=O}$ at 1685 cm^{-1}) are consistent with neopentyl phenyl ketone.

Anal. Calcd for TaC₃₃H₅₃O₂: C, 59.81; H, 8.05. Found: C, 59.85; H, 8.14. ¹H NMR (C₆D₆): τ 2.8 (10, m), 3.22 (1, s), 8.55 (6, s), 8.88 (27, s), 8.96 (9, s). IR (Nujol): 1649 cm^{-1} m ($\nu_{C=C}$).

12. Preparation of Ta(CH₂CMe₃)₃[N(Me)C=CHCMe₃] (6a). Ta(CH₂CMe₃)₃(CHCMe₃) (2.0 g, 4.3 mmol) was added slowly as a solid to 10 mL of stirred CH₃CN. This reaction is quite vigorous. After stirring for 2 h the solution was filtered through a medium-porosity frit and the filtrate stood at -30°C overnight. The supernatant was decanted from the yellow crystals (1.7 g) and the remaining solvent was removed in vacuo. The product, now a partially crystalline oil, is, by ¹H NMR, a 1:4 *E/Z* mixture containing weakly coordinated acetonitrile ($\nu_{CN} \approx 2280\text{ cm}^{-1}$, weak; $\tau(\text{CH}_3\text{CN})$ 9.4), which causes the chemical shifts of several peaks to vary from sample to sample by ca. 1 ppm. [The acetonitrile is lost when the oil is sublimed (see Figure 2).] Two or three recrystallizations give pure *Z*-6a as a pale yellow, crystalline, acetonitrile adduct. Fractional sublimation at 71°C and $1\ \mu$ for 1 h yields a crystalline, acetonitrile-free product; an oil remained behind. *E*-6a has not yet been obtained free of *Z*-6a.

A 2-mmol sample of 6a in ether was poured into aqueous NaOH. Two organic products were identified by GLC/mass spectroscopy and by preparative GLC isolation and identification by IR and NMR. The minor product was neopentyl alcohol (identical with an authentic sample), the major methyl neopentyl ketone [¹H NMR in CDCl₃ τ 7.65 (s, 2), 7.86 (s, 3), 8.95 (s, 9); IR 1710 cm^{-1} s ($\nu_{C=O}$)].

¹H NMR (C₆D₆): *E* isomer, τ 4.36 (m, 1, $J \approx 1$ Hz), 7.76 (d, 3, $J \approx 1$ Hz), 8.74 (s, 9), 8.79 (s, 27), 9.18 (s, 6). *Z* isomer, τ 5.38 (q, 1, $J = 1.1$ Hz), 7.80 (d, 3, $J = 1.1$ Hz), 8.55 (s, 9), 8.85 (s, 27), 8.98 (s, 6). IR (*Z*-6a, Nujol): 1610 cm^{-1} m ($\nu_{C=C}$).

13. Preparation of Ta(CH₂CMe₃)₃[N(Ph)C=CH₂CMe₃] (6b). An orange solution of Ta(CH₂CMe₃)₃(CHCMe₃) (1.0 g in 20 mL of ether), on addition of a solution of 0.22 g of benzonitrile in 3 mL of ether, turned yellow. Removing all solvent left a yellow oil whose ¹H NMR spectrum showed it to be $\geq 90\%$ the *Z* isomer. Recrystallization from acetonitrile followed by sublimation at 71°C and $1\ \mu$ for 1 h yield 0.40 g of nitrile-free *Z*-6a as a yellow oil. Hydrolysis with 1 N HCl gave two organic products, neopentyl alcohol and neopentyl phenyl ketone, according to GLC/mass spectroscopy.

¹H NMR (C₆D₆): *Z* isomer, τ 2.2 (m, 2, H ortho), 2.8 (m, 3, H meta and para), 4.87 (s, 1), 8.42 (s, 9), 8.83 (s, 27) merged with 8.85 (s, 6). *E* isomer, olefinic proton at τ 4.01. IR (neat oil): 1590 cm^{-1} m ($\nu_{C=C}$).

14. Preparation of Ta(CH₂CMe₃)₄Cl (7). A solution of 0.93 g of Ta(CH₂CMe₃)₃(CHCMe₃) in 15 mL of pentane was cooled to -78°C and 45 mL of anhydrous HCl added slowly by syringe. The solution turned brilliant yellow and on standing (especially when more concentrated) deposited yellow crystals of pure Ta(CH₂CMe₃)₄Cl in 1–2 h at -78°C . Ta(CH₂CMe₃)₄Cl decomposes at $> -10^\circ\text{C}$ in aromatic or aliphatic hydrocarbons but is more stable in the presence of acetonitrile (see text). The solid decomposes at 25°C under nitrogen. It can also be prepared in situ similarly in, for example, toluene or diethyl ether.

¹H NMR (toluene-*d*₈, -20°C): τ 7.9 (br s, 2), 8.75 (br s, 9). The ¹H NMR spectrum is temperature dependent but this behavior has not been investigated fully as yet. ¹³C NMR (toluene-*d*₈, -20°C , gated decoupled, 67.89 MHz): 144.6 (axial neopentyl C_α, $J_{CH} \approx 105$ Hz), 116.9 (equatorial neopentyl C_α, $J_{CH} = 112$ Hz), 40.3 (axial neopentyl C_β), 35.2 (equatorial neopentyl C_γ, $J_{CH} = 123$ Hz), 35.5 (equatorial neopentyl C_β), 34.4 ppm (axial neopentyl C_γ, $J_{CH} \approx 121$ Hz).

15. Trapping 8 as Ta(η^5 -C₅H₅)(CH₂CMe₃)₂(CHCMe₃) (9). Ta(CH₂CMe₃)₄Cl (1 mmol) was generated as in 14 in 50 mL of toluene at -78°C . TIC₅H₅ (0.30 g, 11% excess) was added at -78°C

and the solution was warmed to -10°C and stirred for 1 h, then 0°C for 5 h, then 25°C for 36 h. The yellow solution was stripped to an oil which was dissolved in pentane. After filtering, the pentane was removed in vacuo to give a quantitative yield of 9 as a sublimable yellow oil.

An identical product can be made quantitatively by adding 2 mol of LiCH₂CMe₃ to TaCp(CHCMe₃)Cl₂⁹ in ether at -78°C .⁸

¹H NMR (C₆D₆): τ 4.41 (s, 5, Cp), 4.94 (s, 1, neopentylidene H_α), 8.40 (d, 2, $J = 12$ Hz, neopentyl H_α), 8.73 (s, 9, neopentylidene CH₃), 8.82 (s, 18, neopentyl CH₃), 10.47 (d, 2, $J = 12$ Hz, neopentyl H'α).

16. Trapping 8 as Ta(CH₂CMe₃)₂Cl[N(Me)C=CHCMe₃] (10). A 2-mmol sample of Ta(CH₂CMe₃)₄Cl in 15 mL of pentane was prepared from Ta(CH₂CMe₃)₃(CHCMe₃) and HCl at -78°C (see 14). The solvent was removed in vacuo at -78°C and 2 mL of acetonitrile added to the dry residue of Ta(CH₂CMe₃)₄Cl. Ta(CH₂CMe₃)₄Cl is nearly insoluble in CH₃CN at low temperatures but after stirring for 2 h at 25°C the residue had dissolved and the colorless supernatant turned orange. The solution was filtered and the filtrate stood at -30°C overnight to give orange crystals (0.4 g) which turned tacky at 25°C . Sublimation of half the product at 70°C and $1\ \mu$ gave pure, acetonitrile-free *E*-10 as a yellow oil on the 0°C probe.

¹H NMR (C₆D₆): *E* isomer, τ 4.40 (q, 1, $J = 1.2$ Hz), 7.79 (d, 3, $J = 1.2$ Hz), 8.77 (s, 9), 8.84 (s, 18), 9.08 (s, 4). IR (neat): 1655 cm^{-1} m ($\nu_{C=C}$).

17. Preparation of Nb(CH₂CMe₃)₃[N(Me)C=CHCMe₃]. Nb(CH₂CMe₃)₃(CHCMe₃) (0.15 g) was added slowly as a solid to 1.5 mL of acetonitrile. The brown solution was filtered and stood at -30°C overnight. The supernatant was removed from the crystals which were recrystallized similarly from 1 mL of acetonitrile. The product is a 2:3 mixture of *E* and *Z* isomers which contain excess acetonitrile ($> \tau$ 9, variable; here τ 9.15).

¹H NMR (C₆D₆): *E* isomer, τ 3.95 (br s, 1), 7.62 (d, 3, $J \approx 2$ Hz), 8.69 (s, 27), 8.72 (s, 9). *Z* isomer, τ 5.23 (br s, 1), 7.69 (d, 3, $J \approx 2$ Hz), 8.50 (s, 9), 8.79 (s, 27). Only one broad singlet assignable to neopentyl methylene protons in either isomer was seen at τ 8.63. IR (Nujol): 1600 cm^{-1} br, m ($\nu_{C=C}$).

18. Preparation of Nb(CH₂CMe₃)₃[O(Me)C=CHCMe₃] (12). LiCH₂CMe₃ (0.312 g, 4 mmol) in 25 mL of pentane was added to a 50-mL pentane solution of Nb(CH₂CMe₃)₃Cl₂ (0.754 g, 2 mmol) at -78°C followed by warming to 25°C for 15 min. The solution containing Nb(CH₂CMe₃)₃(CHCMe₃) was cooled to -78°C and 0.156 g of acetyl chloride added. Lithium chloride was filtered off and most of the pentane removed in vacuo (volume ≈ 5 mL). The product (greenish-yellow needles) was filtered off after standing at -30°C overnight and identified by comparison of its ¹H NMR and infrared spectrum (virtually identical) with that of Ta(CH₂CMe₃)₃[O(Me)C=CHCMe₃] (3a). It is $\geq 95\%$ the *E* isomer.

¹H NMR (C₆D₆): τ 4.60 (poor q, 1, $J \approx 1$ Hz), 7.43 (br s, 6), 8.15 (poor d, 3, $J \approx 1$ Hz), 8.77 (s, 27), 8.98 (s, 9). IR (Nujol): 1645 cm^{-1} m ($\nu_{C=C}$).

19. On the Reaction of Ta(CH₂CMe₃)₃(CHCMe₃) with HBF₄ and Ta(CH₂CMe₃)₄Cl with TIBF₄. Attempts to Prepare [Ta(CH₂CMe₃)₄]⁺BF₄⁻. (a) Reaction of Ta(CH₂CMe₃)₃(CHCMe₃) with HBF₄. Ta(CH₂CMe₃)₃(CHCMe₃) (1.5 g, 3.2 mmol) was dissolved in 20 mL of CH₂Cl₂ and 0.5 mL (2X excess) of HBF₄·OEt₂ (Aldrich) added to the stirred solution at -78°C . After 20 min it was warmed to room temperature. The solvent was removed in vacuo and the residue sublimed at 60 – 70°C ($1\ \mu$) for 4 h to yield 0.4 g (29%) of Ta(CH₂CMe₃)₃F₂.

(b) Reaction of Ta(CH₂CMe₃)₄Cl with TIBF₄. Ta(CH₂CMe₃)₄Cl (1 mmol) was generated as in 14 in 20 mL of Et₂O. TIBF₄ (0.29 g, 1 mmol) was added as a solid to the solution at -78°C followed by 3 mL of CH₃CN. The solution was warmed to room temperature and stirred for 1 h. The solution was filtered to yield 0.21 g of a white solid (theory for TiCl 0.24 g) and the solution was stripped to a yellow solid. The solid was extracted with pentane and the mixture filtered. The solvent was removed in vacuo and the residue sublimed at 60 – 70°C ($1\ \mu$) for 4 h to yield 0.15 g (35%) of Ta(CH₂CMe₃)₃F₂.

Anal. Calcd for TaC₁₅H₃₃F₂: C, 41.67; H, 7.69. Found: C, 41.13; H, 7.91. ¹H NMR (C₆D₆): τ 8.26 (t, 6, $J_{H,F} \approx 6.5$ Hz), 8.87 (s, 27).

20. Reaction of Ta(CH₂CMe₃)₄Cl with Ph₃P=CH₂. Ta(CH₂CMe₃)₃(CHCMe₃) (0.46 g, 1 mmol) was dissolved in 50 mL of ether. Ta(CH₂CMe₃)₄Cl was generated by the addition of 0.78 mL of a 2.1 M solution of HCl in ether at -78°C ; 0.28 g (1 mmol) of

Table III. *tert*-Butyl Ions in the Mass Spectra of Neopentanes^a

<i>m/e</i>	55	56	57	58	59	60	61	Ref
Neopentane- <i>d</i> ₀	3.01 ^b	4.17 ^c	100.00	0.13				43,44 ^d
Neopentane- <i>d</i> ₁	1.38	4.48	35.07	100.00	0.13			Calcd
Neopentane- <i>d</i> ₂	1.00	2.14	34.60	3.29	100.00	0.13		Calcd
Neopentane- <i>d</i> ₃	1.00	1.39	32.66	3.30	2.71	100.00	0.13	Calcd
Neopentane- <i>d</i> ₃ (96.8%)			32.2	2.4	6.0	100.00	0.3	<i>e</i>
Neopentane- <i>d</i> ₂ (97.6%)			33.3	5.7	100.00	0.3		<i>f</i>
Neopentane- <i>d</i> ₁ (96.7%)		4.1	38.4	100.00	0.1			<i>g</i>
Neopentane- <i>d</i> ₃ (hexane)			33.8	3.3	17.7	100.00	0.1	Table I
Expt A			76.6	10.9	100.00	12.5		Table II

^a All corrected for ¹³C. ^b An average of 2.85⁴⁴ and 3.15⁴³ corrected. ^c An average of 4.38⁴⁴ and 4.20⁴³ corrected. ^d *m/e* 54 (0.22) and 59 (0.07) are considered negligible. ^e Prepared by treating LiCD₂CMe₃ with excess CH₃OD. ^f Prepared by treating LiCD₂CMe₃ with excess CH₃OH. ^g Prepared by treating LiCH₂CMe₃ with excess CH₃OD.

Table IV. Results of the Kinetic Experiments

Trial ^a	Time, min ^b	Filtering time, min ^c	mmol LiCl ^d
1	33.1	6.2	1.11
2	23.8	7.7	0.82
3	43.1	6.3	1.39
4	65.5	11.0	1.94
5	35.7	11.3	1.31
6	23.6	7.2	1.31
7	11.5	3.0	0.99

^a Runs 1–6 are Ta(CH₂CMe₃)₃Cl₂ and 2LiCH₂CMe₃. Run 7 is Ta(CH₂CMe₃)₄Cl and LiCH₂CMe₃. ^b Time is the average time between the start and the end of the filtration. ^c Filtration time varied from run to run and probably is the greatest source of error. ^d LiCl titrated with 35.4 ± 0.1 mM AgNO₃.

Ph₃P=CH₂ dissolved in 20 mL of ether was added dropwise at –78 °C. After stirring for 2 h at –78 °C it was warmed to room temperature. The brown solution was filtered leaving a light brown solid (0.22 g, theory for Ph₃P⁺MeCl[–] 0.31 g) identified as Ph₃P⁺MeCl[–] by IR comparison with an authentic sample. The filtrate's solvent was removed in vacuo and the tarry residue was extracted with 3 × 10 mL of pentane. The pentane was removed to yield 0.35 g of Ta(CH₂CMe₃)₃(CHCMe₃) (76%), identified by ¹H NMR.

21. Determination of Neopentane-*d*_x Mix by Mass Spectroscopy. The cracking pattern of neopentane is well known. The parent ion is too weak to be observed and the highest molecular weight ion is due to C₄H₉⁺. The *tert*-butyl ion appears to be stable with no evidence for carbon skeletal regrouping.⁴² We have assumed during all of these studies that neopentane-*d*₂ is solely D₂HCC(CH₃)₃, neopentane-*d*₃ solely D₃CC(CH₃)₃, etc.

The spectrum for neopentane^{43,44} is shown in Table III. The spectrum of neopentane-*d*₁, -*d*₂, and -*d*₃ calculated from this data (assuming no isotope effect for C–D vs. C–H cleavage and a 57 peak 32% the size of the higher molecular weight fragment; cf. 76% CMe₃(¹³CH₃), 24% CMe₃ from Me₃C(¹³CH₃)⁴²) is normalized to 100.0 for *m/e* 58, 59, and 60, respectively.

The spectra for experimental samples of neopentane-*d*₁, -*d*₂, and -*d*₃ are similar; clearly there is not significant H/D scrambling. The isotopic purity is calculated to be approximately 97% in each case. The errors are clearly greatest for *d*₀, which is obtained by difference; in this case they amount to less than ±3%; this is a reasonable experimental error which we have assumed throughout this study.

The isotopic distribution in the neopentanes obtained from the reaction of Ta(CD₂CMe₃)₃Cl₂ and 2LiCD₂CMe₃ (Table I) is calculated similarly (e.g., Table III, eighth entry).

More complex mixtures are not significantly more difficult to evaluate (see last entry, Table II). One assumes that the highest mass peak in the ¹³C corrected data set corresponds to the amount of that isotope (arbitrary units, unnormalized), then subtracts the appropriate theoretical amount from all lower mass peak totals; three such operations give the amounts of neopentane-*d*₃, -*d*₂, and -*d*₁. The amount remaining in the *m/e* 57 column is due to neopentane-*d*₀; however, this must be normalized by multiplying by 0.75 since an *m/e* 57 fragment from neopentane-*d*₀ is generated four times out of four but neopentane-*d*₁, -*d*₂, or -*d*₃ gives *m/e* 58, 59, and 60 fragments, respectively, only three times out of four. For example, the last entry in Table III

reduces to 22.9 (57), 6.3 (58), 100.0 (59), and 12.5 (60) or 16% *d*₀, 4% *d*₁, 71% *d*₂, and 9% *d*₃ (Table II).

The mass spectrum of neopentane was determined by GC/mass spectroscopy under conditions where the GC peak was sharp. Therefore, differently labeled neopentanes did not separate to any significant extent. In several experiments the labeled neopentane was collected and examined by conventional mass spectroscopy on a different spectrometer; the results agreed within ±2%.

22. Rate of Reaction of Ta(CH₂CMe₃)₃Cl₂ vs. Ta(CH₂CMe₃)₄Cl with LiCH₂CMe₃ in Heptane. The heptane used in these experiments was washed with 5% HNO₃ in H₂SO₄, rinsed with water, distilled, dried over 4A series, and purged with nitrogen. AgNO₃ (Mallinckrodt) and Bacteriological Dextrin (Eastman) were used as received. Reagent grade KCl (Baker) was dried at 150 °C for 24 h and stored in a desiccator. Anhydrous LiCl was obtained from the reaction of Ta(CH₂CMe₃)₃Cl₂ and LiCH₂CMe₃ in pentane. Following the procedure⁴⁵ for halide analyses (adsorption method) a stock solution of AgNO₃ was prepared using both LiCl and KCl as primary standards. All titrations were buffered with 10 drops of 1 M acetate buffer (pH 5.5). Dichlorofluorescein in ethyl alcohol was the adsorption indicator.

Ta(CH₂CMe₃)₃Cl₂ (0.465 g, 1 mmol) was dissolved in 30 mL of heptane in a three-necked 100-mL flask fitted with a N₂ inlet, dropping funnel, and a fine fritted Schlenk filter. LiCH₂CMe₃ (0.160 g) was dissolved in 20 mL of heptane and placed in the dropping funnel. The reaction vessel was immersed in an insulated water bath maintained at 22 °C. The neopentyllithium solution was added rapidly and after the required time interval the solution was filtered. The isolated LiCl was washed once with 20 mL of pentane and dried in vacuo. The LiCl was dissolved in 50 mL of H₂O and titrated with standardized AgNO₃ using the above procedure. The results are outlined in Table IV (runs 1–6).

Ta(CH₂CMe₃)₃(CHCMe₃) (1, 0.465 g, 1.0 mmol) was dissolved in 20 mL of ether and the solution cooled to –78 °C; 0.78 mL of a 1.29 *m* solution of HCl in ether was added to the stirred solution. After 20 min all volatiles were removed in vacuo and the residue dissolved in 20 mL of heptane. After warming to –20 °C a solution of 80 mg of LiCH₂CMe₃ in 30 mL of heptane at 25 °C was added rapidly as the vessel was placed in the bath (at 23 °C; final *T* 22 °C). Upon addition of the LiCH₂CMe₃ the solution became cloudy immediately and did not change throughout the run. The LiCl was isolated and titrated using the above procedures. The result is listed in Table IV (run 7).

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References and Notes

- (1) (a) Part 7: R. R. Schrock and P. R. Sharp, *J. Am. Chem. Soc.*, **100**, 2389 (1978); (b) Alfred P. Sloan Foundation Fellow, 1976–1978.
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- (3) By analogy with "β-hydride elimination", this description implies that an α-hydrogen atom migrates to the metal to give a complex containing a hydride and an alkylidene ligand. In contrast, the term "α-hydrogen atom

- abstraction" has been used to describe a situation in which the α -hydrogen atom could be removed by some other atom, e.g., the α -carbon atom of another alkyl ligand. These two processes are virtually indistinguishable in all cases known to date.
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