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ARTICLES

Preparation and Use of $Ta(CD_2Bu^t)_5$ To Probe the Formation of $(Bu^tCD_2)_3Ta{=}CDBu^t$. Kinetic and Mechanistic Studies of the Conversion of Pentaneopentyltantalum to the Archetypical Alkylidene Complex

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Abstract: Pentaneopentyltantalum, $Ta(CH_2Bu^t)_5$ (**1**), was directly observed earlier in the formation of the archetypical alkylidene complex $(Bu^tCH_2)_3Ta{=}CHBu^t$ (**2**) from the reaction of either $(Bu^tCH_2)_3TaCl_2$ (**3**) with 2 equiv of Bu^tCH_2Li or $(Bu^tCH_2)_4TaCl$ (**4**) with 1 equiv of Bu^tCH_2Li. $Ta(CH_2Bu^t)_5$ (**1**) was, however, short-lived, and its ^1H NMR resonances were mixed with those of $(Bu^tCH_2)_3Ta{=}CHBu^t$ (**2**), Bu^tCH_2Li, $(Bu^tCH_2)_3TaCl_2$ (**3**), $(Bu^tCH_2)_4TaCl$ (**4**), and CMe_4 in a fairly narrow region. In the current work, deuterium-labeled $Ta(CD_2Bu^t)_5$ (**1-d_{10}**) has been prepared from the reactions of $(Bu^tCD_2)_3TaCl_2$ (**3-d_6**) with 2 equiv of Bu^tCD_2Li as well as $(Bu^tCD_2)_4TaCl$ (**4-d_8**) with 1 equiv of Bu^tCD_2Li. Due to a kinetic isotope effect, $Ta(CD_2Bu^t)_5$ (**1-d_{10}**) has a much longer life than **1**. In addition, there are fewer peaks in the ^1H NMR spectra of $Ta(CD_2Bu^t)_5$ (**1-d_{10}**). ^2H NMR spectroscopy can also be used to characterize **1-d_{10}**. These properties provide an opportunity to identify and study **1-d_{10}** in detail. Kinetic studies of the $Ta(CD_2Bu^t)_5$ (**1-d_{10}**) → $(Bu^tCD_2)_3Ta{=}CDBu^t$ (**2-d_7**) and $Ta(CH_2Bu^t)_5$ (**1**) → $(Bu^tCH_2)_3Ta{=}CHBu^t$ (**2**) conversions yield a kinetic isotope effect (KIE) = 14.1(0.8) at 273 K. In addition, kinetic studies of the **1-d_{10} → 2-d_7** conversion at 273−298 K give $\Delta H^‡_D = 21.1(1.5)$ kcal/mol and $\Delta S^‡_D = -4(6)$ eu for the α-deuterium abstraction reaction.

Introduction

Metal complexes containing a metal carbon double bond (carbenes) have been of intense current interest.[1,2] Two types of carbene complexes are known: electron-rich, low oxidation state transition metal complexes (Fischer-type)[1c,g−i,3] and electron-deficient, high oxidation state transition metal complexes (Schrock-type, also called alkylidene complexes).[1d,e,q,3] Since Hérrison and Chauvin proposed the catalytic olefin metathesis mechanism involving M=CHR species,[4] studies of metal carbene chemistry have led to the development of Mo and W catalysts by the Schrock group[5] and Ru catalysts by the Grubbs group.[6] One particular complex that has played a crucial role in metal carbene chemistry is $(Bu^tCH_2)_3Ta{=}CHBu^t$ (**2**).[7] It was the first isolated and characterized high oxidation state alkylidene complex,[7a,b] and this discovery led to the development of a new field in organometallic chemistry.[1d,e,3,7] Studies of this and other Ta alkylidene complexes have also helped the design and synthesis of the most active alkylidene olefin metathesis catalysts.[5]

$(Bu^tCH_2)_3Ta{=}CHBu^t$ (**2**) was initially prepared from the reaction of $(Bu^tCH_2)_3TaCl_2$ (**3**) with 2 equiv of Bu^tCH_2Li,[7a] and additional studies suggested that the first step in the reaction was the

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(1) (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (b) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117. (c) Fischer, E. O. *NATO ASI Ser., Ser. C* **1989**, *269*, 1. (d) Schrock, R. R. *Dalton Trans.* **2001**, 2541. (e) Schrock, R. R. *Chem. Commun.* **2005**, 2773. (f) Mindiola, D. J. *Acc. Chem. Res.* **2006**, *39*, 813. (g) Doetz, K. H.; Minatti, A. In *Transition Metals for Organic Synthesis*, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley-VCH: New York, 2004; Vol. 1, pp 397−425. (h) Gomez-Gallego, M.; Mancheno, M. J.; Sierra, M. A. *Acc. Chem. Res.* **2005**, *38*, 44. (i) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **2002**, *37*, 137. (j) Doyle, M. P. *Top. Organomet. Chem.* **2004**, *13*, 203. (k) Yong, B. S.; Nolan, S. P. *Chemtracts* **2003**, *16*, 205. (l) Kaesz, H. D.; Jensen, C. M. *Polyhedron* **1988**, *7*, 1035. (m) Casey, C. P. *Reactive Intermediates*; Wiley: New York, 1985; Vol. 3, pp 109−150. (n) Pamplin, C. B.; Legzdins, P. *Acc. Chem. Res.* **2003**, *36*, 223. (o) Hoveyda, A. H.; Gillingham, D. G.; Van Veldhuizen, J. J.; Kataoka, O.; Garber, S. B.; Kingsbury, J. S.; Harrity, J. P. A. *Org. Biomol. Chem.* **2004**, *2*, 8. (p) Caulton, K. G. *J. Organomet. Chem.* **2001**, *617*−*618*, 56. (q) Giesbrecht, G. R.; Gordon, J. C. *Dalton Trans.* **2004**, 2387. (r) Thieuleux, C.; Coperet, C.; Dufaud, V.; Marangelli, C.; Kuntz, E.; Basset, J. M. *J. Mol. Catal. A* **2004**, *213*, 47. (s) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592.

(2) (a) Yu, X.-H.; Morton, L. A.; Xue, Z.-L. *Organometallics* **2004**, *23*, 2210. (b) Blanton, J. R.; et al. *J. Mol. Catal. A* **2002**, *190*, 101. (c) Xue, Z.-L. *Comments Inorg. Chem.* **1996**, *18*, 223. (d) Diminnie, J. B.; et al. *Pure Appl. Chem.* **2001**, *73*, 331. (e) Morton, L. A.; Chen, S.-J.; Qiu, H.; Xue, Z.-L. *J. Am. Chem. Soc.* **2007**, *129*, 7277. (f) Morton, L. A.; Wang, R.-T.; Yu, X.-H.; Campana, C. F.; Guzei, I. A.; Yap, G. P. A.; Xue, Z.-L. *Organometallics* **2006**, *25*, 427. (g) Chen, T.-N.; Zhang, X.-H.; Wang, C.-S.; Chen, S.-J.; Wu, Z.-Z.; Li, L.-T.; Sorasaenee, K. R.; Diminnie, J. B.; Pan, H.-J.; Guzei, I. A.; Rheingold, A. L.; Wu, Y.-D.; Xue, Z.-L. *Organometallics* **2005**, *24*, 1214. (h) Morton, L. A.; Zhang, X.-H.; Wang, R.; Lin, Z.; Wu, Y.-D.; Xue, Z.-L. *J. Am. Chem. Soc.* **2004**, *126*, 10208. (i) Diminnie, J. B.; Blanton, J. R.; Cai, H.; Quisenberry, K. T.; Xue, Z.-L. *Organometallics* **2001**, *20*, 1504. (j) Choi, S.-H.; Lin, Z.-Y.; Xue, Z.-L. *Organometallics* **1999**, *18*, 5488. (k) Liu, X.-Z.; Li, L.-T.; Diminnie, J. B.; Yap, G. P. A.; Rheingold, A. L.; Xue, Z.-L. *Organometallics* **1998**, *17*, 4597. (l) Diminnie, J. B.; Xue, Z.-L. *J. Am. Chem. Soc.* **1997**, *119*, 12657. (m) Diminnie, J. B.; Hall, H. D.; Xue, Z.-L. *Chem. Commun.* **1996**, 2383. (n) Li, L.-T.; Diminnie, J. B.; Liu, X.-Z.; Pollitte, J. L.; Xue, Z.-L. *Organometallics* **1996**, *15*, 3520. (o) Li, L.-T.; Xue, Z.-L.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1995**, *14*, 4992. (p) Xue, Z.-L.; Li, L.-T.; Hoyt, L. K.; Diminnie, J. B.; Pollitte, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 2169.

(3) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley: New York, 2005.

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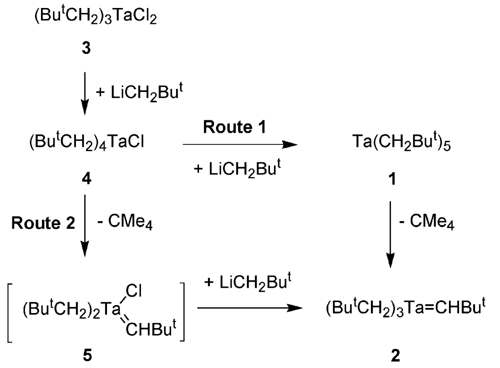
Scheme 1

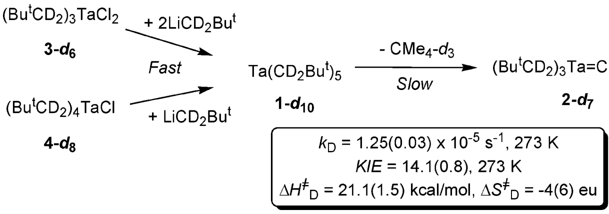


substitution of a chloride ligand in **3** to yield $(Bu^tCH_2)_4TaCl$ (**4**).[7a,b] Two paths were postulated for the conversion of **4** to **2** (Scheme 1).[7b] One route involves the initial formation of pentaneopentyltantalum $Ta(CH_2Bu^t)_5$ (**1**), followed by α-H abstraction between two alkyl ligands to give $(Bu^tCH_2)_3Ta=CHBu^t$ (**2**) (route 1). The other route involves initial α-H abstraction in $(Bu^tCH_2)_4TaCl$ (**4**) to give "$(Bu^tCH_2)_2Ta(=CHBu^t)Cl$" (**5**), followed by substitution of the Cl^- ligand in **5** to yield **2**.

Previous study of the mechanistic pathways in the formation of $(Bu^tCH_2)_3Ta=CHBu^t$ (**2**) led to direct observation of $Ta(CH_2Bu^t)_5$ (**1**) in the NMR spectra of the reactions of $(Bu^tCH_2)_3TaCl_2$ (**3**) with 2 equiv of Bu^tCH_2Li and $(Bu^tCH_2)_4TaCl$ (**4**) with 1 equiv of Bu^tCH_2Li.[8] $Ta(CH_2Bu^t)_5$ (**1**) was, however, short-lived, and its ^1H NMR peaks at 233 K are in a small region (0.8−1.5 ppm) that is crowded with peaks of $(Bu^tCH_2)_3TaCl_2$ (**3**), axial and equatorial ligands in $(Bu^tCH_2)_4TaCl$ (**4**), Bu^tCH_2Li, $(Bu^tCH_2)_3Ta=CHBu^t$ (**2**), and CMe_4, leading to partial overlap of NMR peaks.[8] No kinetic study of the α-H abstraction reaction in $Ta(CH_2Bu^t)_5$ (**1**) yielding the archetypical alkylidene complex, $(Bu^tCH_2)_3Ta=CHBu^t$ (**2**), was performed. The observation of $Ta(CH_2Bu^t)_5$ (**1**), and the slow α-H abstraction reaction in $(Bu^tCH_2)_4TaCl$ (**4**) [to yield "$(Bu^tCH_2)_2Ta(=CHBu^t)Cl$" (**5**)][8b] in comparison to the relatively quick formation of $(Bu^tCH_2)_3Ta=CHBu^t$ (**2**) from the reaction of $(Bu^tCH_2)_4TaCl$ (**4**) with 1 equiv of Bu^tCH_2Li led us to suggest that route 1 in Scheme 1 is the path to give **2**.[8]

Given the critical importance of $(Bu^tCH_2)_3Ta=CHBu^t$ (**2**) in the Schrock-type, high oxidation state transition metal carbene chemistry, and its role in the development of olefin metathesis catalysts, we have sought to provide unambiguous evidence of the presence of $Ta(CH_2Bu^t)_5$ (**1**) as the precursor to the formation of $(Bu^tCH_2)_3Ta=CHBu^t$ (**2**), and to confirm the assignment of the NMR resonances of **1**. In addition, we are interested in the kinetics of the α-H abstraction reaction of $Ta(CH_2Bu^t)_5$ (**1**), leading to the formation of the first characterized M=C bond in high oxidation state metal complexes. We have reasoned that, if the α-hydrogen atoms in $Ta(CH_2Bu^t)_5$ (**1**) are replaced by deuterium atoms to give $Ta(CD_2Bu^t)_5$ (**1-d_{10}**), the lifetime of **1-d_{10}** would be much longer due to a kinetic isotope effect in the α-H/D abstraction, assuming the rate of formation of **2**/$(Bu^tCD_2)_3Ta=CDBu^t$ (**2-d_7**) depends in part on the α-H/D abstraction. The longer lifetime of $Ta(CD_2Bu^t)_5$ (**1-d_{10}**) would provide an opportunity to observe and characterize this important intermediate. In addition, only the methyl resonances in $(Bu^tCD_2)_3TaCl_2$ (**3-d_6**), $(Bu^tCD_2)_4TaCl$ (**4-d_8**), Bu^tCD_2Li, $(Bu^tCD_2)_3Ta=CDBu^t$ (**2-d_7**) would be observed in the ^1H NMR spectrum of the reaction between $(Bu^tCD_2)_3TaCl_2$ (**3-d_6**) and Bu^tCD_2Li. In other words, there would be only half of the number of the peaks in the ^1H NMR spectrum of the mixture containing $Ta(CD_2Bu^t)_5$ (**1-d_{10}**) as in the mixture containing $Ta(CH_2Bu^t)_5$ (**1**). Use of **1-d_{10}** would also allow its observation and characterization by deuterium NMR spectroscopy. The $-CD_2-$ peak of $Ta(CD_2Bu^t)_5$ (**1-d_{10}**) in the ^2H NMR spectrum would help confirm the assignment of the $-CH_2-$ resonances of **1**. In addition to measuring a kinetic isotope effect of the α-H/D abstraction in **1**/**1-d_{10}**, we have also reasoned that $Ta(CD_2Bu^t)_5$ (**1-d_{10}**) would provide a unique opportunity to study in detail the kinetics of the formation of the archetypical alkylidene complex, and allow us to measure the activation enthalpy ($\Delta H^{\ddagger}_D$) and entropy ($\Delta S^{\ddagger}_D$) of this reaction. We have prepared in situ $Ta(CD_2Bu^t)_5$ (**1-d_{10}**) and characterized it by NMR spectroscopy. The kinetics of α-H abstraction in $Ta(CH_2Bu^t)_5$ (**1**) at 273 K and α-D abstraction in **1-d_{10}** at 273−298 K have also been studied. These studies are reported here.

Scheme 2



Results and Discussion

Preparation of $Ta(CD_2Bu^t)_5$ (1-d_{10}) and Its Conversion to $(Bu^tCD_2)_3Ta=CDBu^t$ (2-d_7). $Ta(CD_2Bu^t)_5$ (**1-d_{10}**) was prepared from either $(Bu^tCD_2)_3TaCl_2$ (**3-d_6**) and 2 equiv of Bu^tCD_2Li or $(Bu^tCD_2)_4TaCl$ (**4-d_8**) and 1 equiv of Bu^tCD_2Li in toluene-d_8 for ^1H NMR spectroscopy or in toluene (with a small amount of toluene-d_8) for ^2H NMR spectroscopy (Scheme 2). Chloride substitutions in both reactions were found to be faster than the α-deuterium abstraction in $Ta(CD_2Bu^t)_5$ (**1-d_{10}**). Since **4-d_8** is unstable, subsequent studies focused on the reaction of $(Bu^tCD_2)_3TaCl_2$ (**3-d_6**) with Bu^tCD_2Li.

^1H NMR spectra of the reaction between $(Bu^tCD_2)_3TaCl_2$ (**3-d_6**) and 2 equiv of Bu^tCD_2Li to give $(Bu^tCD_2)_3Ta=CDBu^t$ (**2-d_7**) are given in Figure 1. Both $(Bu^tCD_2)_4TaCl$ (**4-d_8**) and $Ta(CD_2Bu^t)_5$ (**1-d_{10}**) were observed as intermediates. The peaks at 1.30 and 1.09 ppm were assigned to the equatorial and axial methyl groups, respectively, in $(Bu^tCD_2)_4TaCl$ (**4-d_8**). The intensities quickly reached a maximum about 30 min after the start of the reaction at 293 K and then started to decrease as the monochloride **4-d_8** was converted to $Ta(CD_2Bu^t)_5$ (**1-d_{10}**). At 283 K, a single peak at 1.25 ppm was assigned to the methyl groups in **1-d_{10}**. This peak is close to that of the methyl groups in $Ta(CH_2Bu^t)_5$ (**1**) at 1.27 ppm at 258 K.[8] After the Bu^tCD_2Li

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(4) (a) Hérrison, J. L.; Chauvin, Y. *Makromol. Chem.* **1971**, *141*, 161. (b) Chauvin, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3741 (Nobel Lecture).

(5) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748 (Nobel Lecture).

(6) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760 (Nobel Lecture).

(7) (a) Schrock, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 6796. (b) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359. (c) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (d) Schrock, R. R. in *Reactions of Coordinated Ligands*; Braterman, P. S.; Ed.; Plenum: New York, 1986. (e) Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249. (f) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

(8) (a) Li, L.; Hung, M.; Xue, Z. *J. Am. Chem. Soc.* **1995**, *117*, 12746. (b) Li, L. Ph.D. Dissertation, The University of Tennessee, Knoxville, TN, 1996.

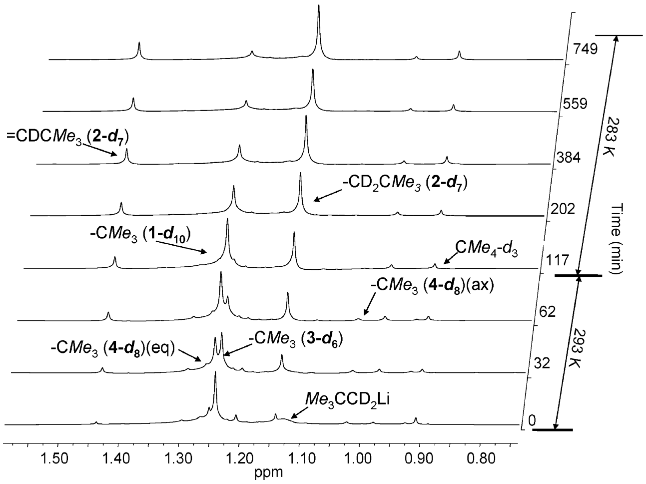

Figure 1. ^{1}H NMR spectra of the reaction between $(\mathrm{Bu^tCD_2})_3\mathrm{TaCl_2}$ (**3-d_6**) and 2 equiv of $\mathrm{Bu^tCD_2Li}$ to give $(\mathrm{Bu^tCD_2})_3\mathrm{Ta{=}CDBu^t}$ (**2-d_7**) in toluene-d_8. $(\mathrm{Bu^tCD_2})_4\mathrm{TaCl}$ (**4-d_8**) and $\mathrm{Ta(CD_2Bu^t)_5}$ (**1-d_{10}**) were observed as intermediates. The solution was maintained at 293 K until $\mathrm{Bu^tCD_2Li}$ disappeared, and then held at 283 K until the reaction was complete.

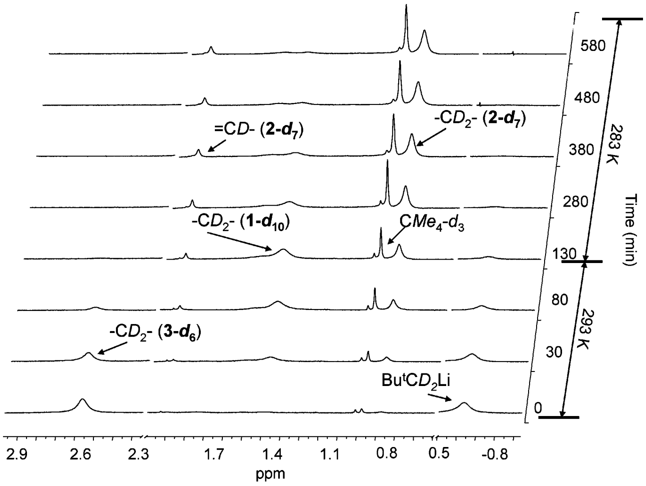

Figure 2. ^{2}H NMR spectra of the reaction between $(\mathrm{Bu^tCD_2})_3\mathrm{TaCl_2}$ (**3-d_6**) and 2 equiv of $\mathrm{Bu^tCD_2Li}$ to give $(\mathrm{Bu^tCD_2})_3\mathrm{Ta{=}CDBu^t}$ (**2-d_7**) in toluene. The solution was maintained at 293 K until $\mathrm{Bu^tCD_2Li}$ disappeared, and then held at 283 K until the reaction was complete.

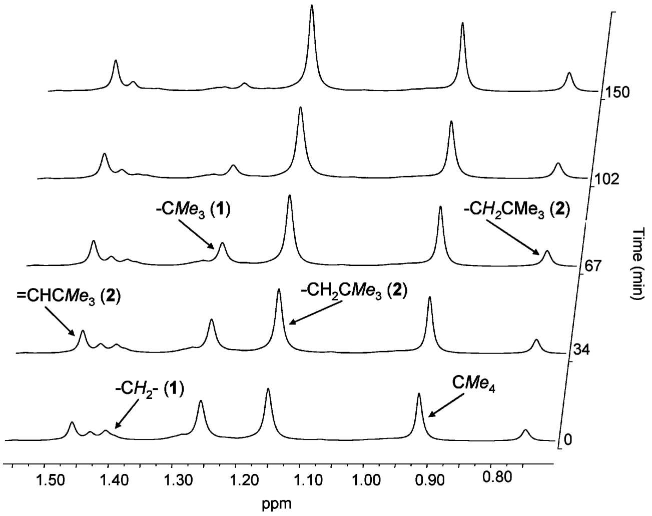

Figure 3. ^{1}H NMR spectra of the conversion of $\mathrm{Ta(CH_2Bu^t)_5}$ (**1**) → $(\mathrm{Bu^tCH_2})_3\mathrm{Ta{=}CHBu^t}$ (**2**) in toluene-d_8 at 273 K. The solution was initially maintained at 233 K until $\mathrm{Bu^tCH_2Li}$ disappeared. The reaction $\mathrm{Ta(CH_2Bu^t)_5}$ (**1**) → $(\mathrm{Bu^tCH_2})_3\mathrm{Ta{=}CHBu^t}$ (**2**) was then conducted at 273 K. The reaction was quenched by cooling the NMR tube to 233 K at the end of each time period, and the spectra were taken at 233 K.[9]

peak at 1.12 ppm disappeared and the conversion of $(\mathrm{Bu^tCD_2})_3\mathrm{TaCl_2}$ (**3-d_6**) and $(\mathrm{Bu^tCD_2})_4\mathrm{TaCl}$ (**4-d_8**) to **1-d_{10}** was complete, the NMR probe was set to a desired temperature to observe the conversion of **1-d_{10}** to $(\mathrm{Bu^tCD_2})_3\mathrm{Ta{=}CDBu^t}$ (**2-d_7**). Kinetic studies of the formation of **2-d_7** are discussed below.

The reaction of $(\mathrm{Bu^tCD_2})_3\mathrm{TaCl_2}$ (**3-d_6**) with 2 equiv of $\mathrm{Bu^tCD_2Li}$ to give $(\mathrm{Bu^tCD_2})_3\mathrm{Ta{=}CDBu^t}$ (**2-d_7**) was also monitored by ^{2}H NMR spectroscopy. The reactants **3-d_6** and $\mathrm{Bu^tCD_2Li}$, intermediates $(\mathrm{Bu^tCD_2})_4\mathrm{TaCl}$ (**4-d_8**) and $\mathrm{Ta(CD_2Bu^t)_5}$ (**1-d_{10}**), and product **2-d_7** are expected to give resonances for their α-D atoms. ^{2}H NMR spectra of the reaction are given in Figure 2. At 283 K, the $-\mathrm{C}D_2-$ groups of $\mathrm{Ta(CD_2Bu^t)_5}$ (**1-d_{10}**) were observed at 1.39 ppm. This peak is close to the peak at 1.42 ppm in the ^{1}H NMR spectrum at 258 K for the $-\mathrm{C}H_2-$ groups in $\mathrm{Ta(CH_2Bu^t)_5}$ (**1**),[8] supporting the assignment of this resonance in ^{1}H NMR spectra. The $-\mathrm{C}D_2-$ peak of **1-d_{10}** reaches its maximum at approximately the same time as the methyl groups (1.25 ppm) in $\mathrm{Ta(CD_2Bu^t)_5}$ (**1-d_{10}**) in the ^{1}H NMR spectra. These observations are consistent with the assignment of the $-\mathrm{C}D_2-$ and $-\mathrm{C}Me_3$ resonances in the NMR spectra to the same complex, **1-d_{10}**.

In the ^{13}C NMR spectra at 268 K, the $-C\mathrm{D_2}-$ peak of $\mathrm{Ta(CD_2Bu^t)_5}$ (**1-d_{10}**) was observed as a quintet at 114.8 ppm with a coupling constant $J_{\mathrm{C-D}}$ of 15.9 Hz. In comparison, the $-C\mathrm{H_2}-$ peak of $\mathrm{Ta(CH_2Bu^t)_5}$ (**1**) was observed at 115.9 ppm with $J_{\mathrm{C-H}}$ of 105.6 Hz at 258 K.[8]

Kinetic Studies of the Conversion of $\mathrm{Ta(CH_2Bu^t)_5}$ (1) to $(\mathrm{Bu^tCH_2})_3\mathrm{Ta{=}CHBu^t}$ (2) and $\mathrm{Ta(CD_2Bu^t)_5}$ (1-d_{10}) to $(\mathrm{Bu^tCD_2})_3\mathrm{Ta{=}CDBu^t}$ (2-d_7). The reaction of $\mathrm{Bu^tCH_2Li}$ with $(\mathrm{Bu^tCH_2})_4\mathrm{TaCl}$ (**4**), prepared in situ from $(\mathrm{Bu^tCH_2})_3\mathrm{Ta{=}CHBu^t}$ (**2**) and HCl,[7b] yielded $\mathrm{Ta(CH_2Bu^t)_5}$ (**1**).[8] Two methods were used to collect kinetic data for the α-H abstraction reaction of the short-lived $\mathrm{Ta(CH_2Bu^t)_5}$ (**1**) at 273 K. In one method, the solution was maintained at 233 K until $\mathrm{Bu^tCH_2Li}$ disappeared.[8] Then the reaction $\mathrm{Ta(CH_2Bu^t)_5}$ (**1**) → $(\mathrm{Bu^tCH_2})_3\mathrm{Ta{=}CHBu^t}$ (**2**) was conducted at 273 K, and at the end of each time period the reaction was quenched by cooling the NMR tube containing the solution to 233 K. ^{1}H spectra were then taken at 233 K (Figure 3).[9] In another method, the reaction of $\mathrm{Bu^tCH_2Li}$ with $(\mathrm{Bu^tCH_2})_4\mathrm{TaCl}$ (**4**) was conducted in an NMR tube at 273 K, and kinetic data were collected after $(\mathrm{Bu^tCH_2})_4\mathrm{TaCl}$ (**4**) disappeared. These two methods were found to give similar kinetic plots.

The α-H abstraction reaction of $\mathrm{Ta(CH_2Bu^t)_5}$ (**1**) to yield the alkylidene complex $(\mathrm{Bu^tCH_2})_3\mathrm{Ta{=}CHBu^t}$ (**2**) was found to follow first-order kinetics. A plot of $\ln(C/C_0)$ vs t at 273 K is given in Figure 4. The rate constant for the α-H abstraction reaction at 273 K from the aforementioned two methods is $k_{\mathrm{H}} = 1.76(0.06) \times 10^{-4}\ \mathrm{s^{-1}}$ [half-life $t_{1/2} = 66(2)$ min]. We reported earlier the observation of $\mathrm{Ta(CH_2SiMe_3)_5}$ (**6**) and its conversion through α-H abstraction to alkylidene complex $(\mathrm{Me_3SiCH_2})_3\mathrm{Ta{=}CHSiMe_3}$ (**7**) and then to bridging alkylidyne complex $(\mathrm{Me_3SiCH_2})_2\mathrm{Ta}(\mu\text{-}\mathrm{CSiMe_3})_2\mathrm{Ta(CH_2SiMe_3)_2}$ (**8**) (Scheme 3).[8] $\mathrm{Ta(CH_2SiMe_3)_5}$ (**6**) and $(\mathrm{Me_3SiCH_2})_3\mathrm{Ta{=}CHSiMe_3}$ (**7**) containing β-Si atoms are analogs of $\mathrm{Ta(CH_2CMe_3)_5}$ (**1**) and

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(9) Some of the spectra in the studies reported in ref 8 were used to obtain kinetic data in the current work.

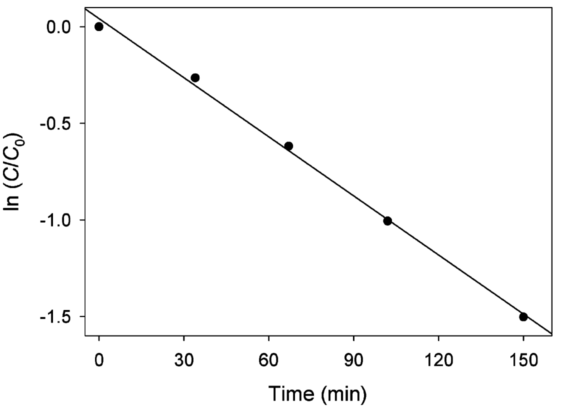
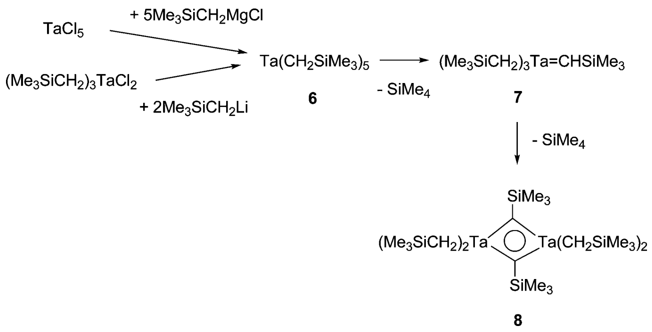


Figure 4. Kinetic plot of the conversion of $Ta(CH_2Bu^t)_5$ (**1**) to $(Bu^tCH_2)_3Ta{=}CHBu^t$ (**2**) at 273 K.

Scheme 3



$(Me_3CCH_2)_3Ta{=}CHCMe_3$ (**2**). Kinetic studies of the **6** → **7** conversion showed that it is much slower than the **1** → **2** conversion. The **6** → **7** conversion was investigated between 301.0 and 326.5 K yielding $\Delta H^{\ddagger}_{H} = 21.6(1.4)$ kcal/mol and $\Delta S^{\ddagger}_{H} = -5(5)$ eu.[8] The rate constants for the conversion of **6** → **7** range from $1.028(0.008) \times 10^{-4}$ s^{-1} [$t_{1/2} = 112(1)$ min] at 301.0 K to $1.83(0.02) \times 10^{-3}$ s^{-1} [$t_{1/2} = 6.3(0.1)$ min] at 326.5 K. Extrapolation of the rate constants at 301.0−326.5 K to 273 K using the Eyring equation yields a rate constant of 2.65×10^{-6} s^{-1} ($t_{1/2} = 4.36 \times 10^3$ min or 72.7 h) for the **6** → **7** conversion. Given the rate constant of $1.76(0.06) \times 10^{-4}$ s^{-1} for the $Ta(CH_2Bu^t)_5$ (**1**) → $(Bu^tCH_2)_3Ta{=}CHBu^t$ (**2**) conversion, the α-H abstraction reaction of the neopentyl complex $Ta(CH_2CMe_3)_5$ (**1**) is about 66.4 times faster than that of its *β*-Si analogue $Ta(CH_2SiMe_3)_5$ (**6**) at 273 K. This difference is perhaps not surprising given that $Ta(CH_2CMe_3)_5$ (**1**) is expected to be much more crowded than $Ta(CH_2SiMe_3)_5$ (**6**). A typical C−C bond length is 1.54 Å versus a typical C−Si bond length of 1.89 Å.

Decomposition of $Ta(CH_2Ph)_5$ (**9**), another pentaalkyl complex free of *β*-H atoms, has also been studied.[10] This decomposition leads to unknown species, and no NMR signal attributed to "$(PhCH_2)_3Ta{=}CHPh$" was observed in the decomposition process. Kinetic studies of the decomposition of $Ta(CH_2Ph)_5$ (**9**) at 313 K gave a rate constant of $(3.8-4.3) \times 10^{-5}$ s^{-1} ($t_{1/2} = 269-304$ min).[10] This decomposition of $Ta(CH_2Ph)_5$ (**9**) is about 10 times slower than that of $Ta(CH_2SiMe_3)_5$ (**6**) at 313 K. Kinetic studies of the decomposition involving $Ta(CH_2CMe_3)_5$ (**1**) were conducted at temperatures much lower than those involving $Ta(CH_2SiMe_3)_5$ (**6**) and $Ta(CH_2Ph)_5$ (**9**). Yet it is reasonable to show that decomposition rates of the three complexes are $Ta(CH_2CMe_3)_5$ (**1**) > $Ta(CH_2SiMe_3)_5$ (**6**) > $Ta(CH_2Ph)_5$ (**9**).

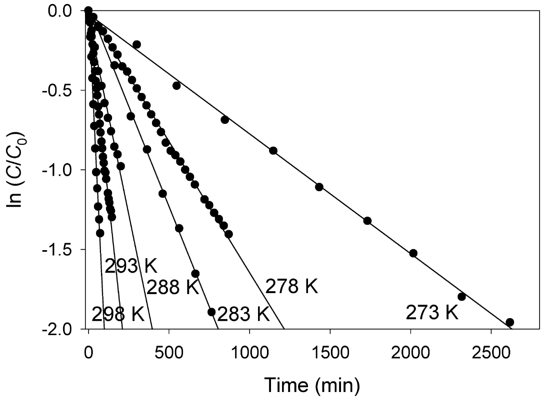


Figure 5. Kinetic plots of the conversion of **1-*d*$_{10}$** → **2-*d*$_7$**.

Table 1. Measured Rate Constants *k* for the **1-*d*$_{10}$** → **2-*d*$_7$** Conversion[a]

T (K)	k (δk_{ran}) × 10^5 (s^{-1})
273(1)	1.25 (0.03)
278(1)	2.17 (0.12)
283(1)	4.28 (0.08)
288(1)	8.4 (0.3)
293(1)	16.9 (1.4)
298(1)	34.8 (1.5)

[a] The total uncertainty $\delta k/k$ of 0.095 was calculated from $\delta k_{ran}/k = 0.081$ and $\delta k_{sys}/k = 5\%$.[17]

The current work to observe $Ta(CD_2Bu^t)_5$ (**1-*d*$_{10}$**) and its conversion to $(Bu^tCD_2)_3Ta{=}CDBu^t$ (**2-*d*$_7$**) by ^1H and ^2H spectroscopy provides clear evidence that pentaneopentyltantalum (**1**) is an intermediate to the alkylidene complex **2**. The use of the D-labeled complex also offers the opportunity to further probe kinetics of the formation of the alkylidene complex $(Bu^tCD_2)_3Ta{=}CDBu^t$ (**2-*d*$_7$**) including kinetic isotope effect (KIE).

Kinetic studies of the conversion of $Ta(CD_2Bu^t)_5$ (**1-*d*$_{10}$**) to $(Bu^tCD_2)_3Ta{=}CDBu^t$ (**2-*d*$_7$**) were conducted after $(Bu^tCD_2)_4TaCl$ (**4-*d*$_8$**) and $(Bu^tCD_2)_3TaCl_2$ (**3-*d*$_6$**) had disappeared in ^1H NMR spectra. At this time, no more **1-*d*$_{10}$** was expected to form, and the time was counted as $t = 0$ min. The α-D abstraction reaction of $Ta(CD_2Bu^t)_5$ (**1-*d*$_{10}$**) to $(Bu^tCD_2)_3Ta{=}CDBu^t$ (**2-*d*$_7$**) was found to follow first-order kinetics. Plots of $\ln(C/C_0)$ vs t at six different temperatures between 273 and 298 K are shown in Figure 5. The rate constants at these temperatures are listed in Table 1. An Eyring plot of $\ln(k_D/T)$ vs $1000/T$ is shown in Figure 6. The activation parameters derived for the conversion of **1-*d*$_{10}$** to **2-*d*$_7$** are $\Delta H^{\ddagger}_{D} = 21.1(1.5)$ kcal/mol, $\Delta S^{\ddagger}_{D} = -4(6)$ eu, and $\Delta G^{\ddagger}_{D,273K} = 22(3)$ kcal/mol. Near-zero or negative values for $\Delta S^{\ddagger}$ have been observed in C−H bond activation reactions where concerted four-center transition states, especially those involving cyclometalation, are proposed.[11] $\Delta G^{\ddagger}_{H,273K}$ for the α-hydrogen abstraction reaction of $Ta(CH_2Bu^t)_5$ (**1**) may

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(10) Malatesta, V.; Ingold, K. U.; Schrock, R. R. *J. Organomet. Chem.* **1978**, *152*, C53.

(11) (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.-L. *J. Am. Chem. Soc.* **1991**, *113*, 6082.

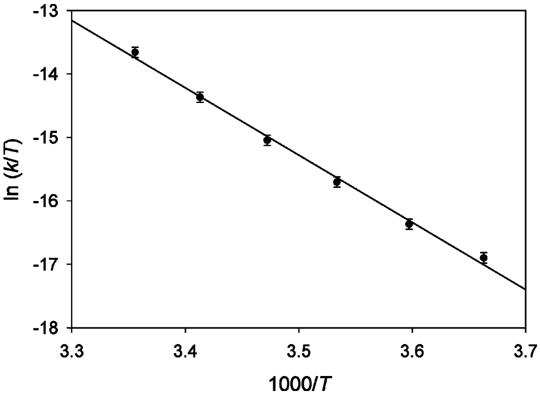

Figure 6. Eyring plot of the conversion of **$1\text{-}d_{10}$** → **$2\text{-}d_7$**.

be estimated from the KIE = 14.1(0.8) at 273 K and the Eyring equation: $RT\ln(k_H/k_D) = \Delta G^{\ddagger}_D - \Delta G^{\ddagger}_H$, yielding $\Delta G^{\ddagger}_{H,273K} = 21(3)$ kcal/mol. In the calculation here, the C−H/C−D stretching frequency is assumed to disappear in the transition state to break the bond.[12] The activation free energy for the α-hydrogen abstraction reaction of $\mathrm{Ta(CH_2SiMe_3)_5}$ (**6**), in comparison, is estimated to be $\Delta G^{\ddagger}_{H,273K} = 23(3)$ kcal/mol.[8]

The KIE in the current work is larger than usual. Such large KIEs have been observed in hydrogen abstraction reactions[13] and electrophilic protonolysis of transition metal complexes.[14] Larger KIE values have also been attributed to the tunneling effect for lighter H atoms, leading to the faster C−H bond breaking reaction.[13a,14,15] The tunneling effect is reportedly more prominent for sterically crowded molecules.[15d] Given the instability of $\mathrm{Ta(CH_2Bu^t)_5}$ (**1**) and $\mathrm{Ta(CD_2Bu^t)_5}$ (**$1\text{-}d_{10}$**) and limited experimental data in the current work, it is not feasible at present to obtain KIE values over a larger temperature range for the **1** → **2** conversion to study the tunneling effect.[16]

Experimental Section

All manipulations were preformed under a dry nitrogen or argon atmosphere with the use of either a drybox or standard Schlenk techniques. Ether, toluene, and toluene-d_8 were dried over potassium/benzophenone, distilled, and stored under N_2. Benzene-d_6 was dried over activated molecular sieves, stored under N_2, and used in the identification of several complexes after their synthesis. NMR spectra were recorded on a Bruker AMX-400 Fourier transform spectrometer and were referenced to solvents. In the case of ^{2}H NMR spectra, a small amount of toluene-d_8 was added to toluene for reference. $\mathrm{Bu^tCD_2Br}$,[7b,11g,18] $\mathrm{(Bu^tCD_2)_3TaCl_2}$ (**$3\text{-}d_6$**),[7b] and $\mathrm{Bu^tCD_2Li}$[7b] were prepared by the literature procedures. $\mathrm{ZnCl_2}$ was dried by refluxing with $\mathrm{SOCl_2}$.[7b] $\mathrm{Ta(CH_2Bu^t)_4Cl}$ (**4**) was prepared in situ from **2** and HCl.[7b] DCl and HCl in ether (1.0 M) were purchased from Aldrich. They were each diluted to 0.10 M with ether before use.

The rate constants were the average of at least two separate experiments at each temperature. The *maximum* random uncertainty in the rate constants for each reaction was combined with the estimated systematic uncertainties, ca. 5%.[17] The total uncertainties in the rate constants were used in the Eyring plots and in the following error propagation calculations. The estimated uncertainty in the temperature measurements for an NMR probe (used in the k determinations) was 1 K. The activation enthalpies ($\Delta H^{\ddagger}_D$) and entropies ($\Delta S^{\ddagger}_D$) were calculated from an unweighted nonlinear least-squares procedure contained in the SigmaPlot Scientific Graph System. The uncertainties in $\Delta H^{\ddagger}_D$ and $\Delta S^{\ddagger}_D$ were computed from the error propagation formulas derived from the Eyring equation by Girolami and co-workers.[19]

Preparation of $\mathrm{Zn(CD_2Bu^t)_2}$. $\mathrm{Zn(CD_2Bu^t)_2}$ was prepared earlier from $\mathrm{Bu^tCD_2Li}$ and $\mathrm{ZnCl_2}$•dioxane.[7b] In the current work, it was directly prepared from $\mathrm{Bu^tCD_2MgBr}$ and $\mathrm{ZnCl_2}$. The Grignard reagent $\mathrm{Bu^tCD_2MgBr}$ was prepared by adding $\mathrm{Bu^tCD_2Br}$ (20.37 g, 133.1 mmol) dropwise to Mg turnings (3.251 g, 133.8 mmol) in ether (50 mL). Several drops of $\mathrm{BrCH_2CH_2Br}$ were used to initiate the reaction, and the solution was refluxed for 20 h at 45 °C. Filtration gave a solution of $\mathrm{Bu^tCD_2MgBr}$ in ether (75 mL, 0.95 M, 71 mmol, 53% yield). The concentration of the Grignard solution was determined by adding 1.0 mL of the solution into distilled water to form Mg(OH)Br and $\mathrm{CMe_3CD_2H}$. Titration of the aqueous Mg(OH)Br solution using 0.096 M HCl gave the concentration of the $\mathrm{Bu^tCD_2MgBr}$ solution.

The solution of $\mathrm{Bu^tCD_2MgBr}$ was added slowly to $\mathrm{ZnCl_2}$ (4.62 g) in ether (40 mL) at −20 °C, and stirred for 2 days at room temperature. Filtration, removal of ether, and distillation of the product yielded $\mathrm{Zn(CD_2Bu^t)_2}$ (5.019 g, 23.74 mmol, 70% yield), which was then used to make $\mathrm{(Bu^tCD_2)_3TaCl_2}$ (**$3\text{-}d_6$**) according to the literature procedures.[7b]

In Situ Preparation of $\mathrm{Ta(CD_2Bu^t)_5}$ ($1\text{-}d_{10}$) and Its Conversion to $\mathrm{(Bu^tCD_2)_3Ta{=}CDBu^t}$ ($2\text{-}d_7$). 1. Preparation of $\mathrm{Ta(CD_2Bu^t)_5}$ ($1\text{-}d_{10}$) from the Reaction between $\mathrm{(Bu^tCD_2)_3TaCl_2}$ ($3\text{-}d_6$) and $\mathrm{Bu^tCD_2Li}$. $\mathrm{(Bu^tCD_2)_3TaCl_2}$ (**$3\text{-}d_6$**) (40.0 mg, 0.0849 mmol) and $\mathrm{Bu^tCD_2Li}$ (17 mg, 0.21 mmol)[20] were each dissolved in toluene-d_8 at −78 °C. They were mixed in an NMR tube (total volume = 4.0 mL) at −78 °C, giving a dark yellow solution. The sample was kept at −78 °C until ready for use. ^{1}H NMR spectra of the solution were taken at 10 °C.

The reaction between $\mathrm{(Bu^tCD_2)_3TaCl_2}$ (**$3\text{-}d_6$**) and $\mathrm{Bu^tCD_2Li}$ was conducted similarly in toluene containing a small amount of toluene-d_8. ^{2}H NMR spectra of the solution were collected using toluene-d_8 as internal standard. **$1\text{-}d_{10}$**: ^{1}H NMR (toluene-d_8, 399.7 MHz, 10 °C) δ 1.25 (s, 45H, $Me_3\mathrm{CCD_2}$); ^{2}H NMR (toluene, 61.4 MHz, 10 °C) δ 1.39 (s, 10D, $\mathrm{Me_3CC}D_2$); ^{13}C{^{1}H} NMR (toluene-d_8, 100.5 MHz, −5 °C) δ 114.8 (quintet, $\mathrm{Me_3C}C\mathrm{D_2}$, $J_{C-D} = 15.9$ Hz), 36.3 ($\mathrm{Me_3}C\mathrm{CD_2}$), 35.2 ($Me_3\mathrm{CCD_2}$). **$2\text{-}d_7$**: ^{1}H NMR (toluene-$d_8$, 399.7 MHz, 10 °C) δ 1.44 (s, 9H, $Me_3\mathrm{CCD}{=}$), 1.14 (s, 27H, $Me_3\mathrm{CCD_2}$); ^{2}H NMR (toluene, 61.4 MHz, 10 °C) δ 1.90 (s, 1D, $\mathrm{Me_3CC}D{=}$), 0.88 (s, 6D, $\mathrm{Me_3CC}D_2$); ^{13}C{^{1}H} NMR (toluene-d_8, 100.5 MHz, −5 °C) δ 248.7 (t, $\mathrm{Me_3C}C\mathrm{D}{=}$, $J_{C-D} = 14.1$ Hz), 112.3 (quintet,

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(12) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140.

(13) (a) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (b) Slaughter, L. M.; Wolczanski, P. T.; Klinckman, T. R.; Cundari, T. R. *J. Am. Chem. Soc.* **2000**, *122*, 7953. (c) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

(14) Bercaw, J. E.; Chen, G. S.; Labinger, J. A.; Lin, B.-L. *J. Am. Chem. Soc.* **2008**, *130*, 17654.

(15) (a) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*: Wiley: New York, 1980; pp 140−152. (b) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; pp 270−289. (c) *Isotope Effects in Chemistry and Biology*; Kohen, A., Limbach, H.-H., Eds.; CRC Press: Boca Raton, FL, 2006. (d) Lewis, E. S.; Funderburk, L. *J. Am. Chem. Soc.* **1967**, *89*, 2322.

(16) (a) Doering, W. v. E.; Keliher, E. J.; Zhao, X. *J. Am. Chem. Soc.* **2004**, *126*, 14206. (b) Doering, W. v. E.; Zhao, X. *J. Am. Chem. Soc.* **2006**, *128*, 9080. (c) Doering, W. v. E.; Keliher, E. J. *J. Am. Chem. Soc.* **2007**, *129*, 2488.

(17) The systematic uncertainties δk_{sys} were estimated based on the subjective judgment of the sensitivities of the NMR integration to the changes in concentrations. The total uncertainties δk were calculated from $\delta k = (\delta k_{ran}^2 + \delta k_{sys}^2)^{1/2}$ (δk_{ran} = random uncertainty). See: Taylor. J. R. *An Introduction to Error Analysis*; University Science Books: Mill Valley, CA, 1982; Chapter 4.

(18) Wiley, G. A.; Rein, B. M.; Hershkowitz, R. L. *Tetrahedron Lett.* **1964**, *5*, 2509.

(19) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

(20) Some excess of $\mathrm{Bu^tCD_2Li}$ was used to ensure complete conversion of $\mathrm{(Bu^tCD_2)_3TaCl_2}$ (**$3\text{-}d_6$**) to $\mathrm{Ta(CD_2Bu^t)_5}$ (**$1\text{-}d_{10}$**). When exactly 2 equiv of $\mathrm{Bu^tCD_2Li}$ was used in the reaction, the same intermediates, including **$1\text{-}d_{10}$**, and products were observed. A slight excess of **$3\text{-}d_6$**, however, was left after the reaction, probably as a result of a trace amount of moisture and error of the analytical balance.

Me_3CCD_2, $J_{C-D} = 16.2$ Hz), 47.0 ($Me_3CCD{=}$), 34.9 (Me_3CCD_2), 34.8 (Me_3CCD_2), 34.6 ($Me_3CCD{=}$).

2. Preparation of $Ta(CD_2Bu^t)_5$ (1-d_{10}) from the Reaction between $(Bu^tCD_2)_4TaCl$ (4-d_8) and Bu^tCD_2Li. $(Bu^tCD_2)_4TaCl$ (**4**-d_8) was prepared from $(Bu^tCD_2)_3Ta{=}CDBu^t$ (**2**-d_7) and DCl (0.10 M, ether). $(Bu^tCD_2)_3Ta{=}CDBu^t$ (**2**-d_7, 30 mg, 0.064 mmol) was added to a flask in ether (10 mL). DCl (0.64 mL, 0.10 M, ether) was added slowly at −78 °C. The mixture was stirred for 30 min, and then solvent was removed. The solid was redissolved in toluene-d_8 and kept at −78 °C. An NMR tube was prepared with Bu^tCD_2Li (5.6 mg, 0.070 mmol) in toluene-d_8 and cooled to −78 °C.[20] The unstable $(Bu^tCD_2)_4TaCl$ (**4**-d_8) was quickly added to the NMR tube, and the sample was kept at −78 °C until ready for use. ^1H NMR spectra of the solution were taken at 0 °C.

Kinetic Studies of the Conversion of $Ta(CD_2Bu^t)_5$ (1-d_{10}) to $(Bu^tCD_2)_3Ta{=}CDBu^t$ (2-d_7). $(Bu^tCD_2)_3TaCl_2$ (**3**-d_6, 40.0 mg, 0.085 mmol) and Bu^tCD_2Li (17 mg, 0.21 mmol)[20] were dissolved in toluene-d_8 in separate NMR tubes. Bibenzyl (20−25 mg, an internal standard) was added to the solution of **3**-d_6. The samples were kept at −78 °C. The solution of **3**-d_6/bibenzyl was added to that of Bu^tCD_2Li and kept at −78 °C until use. Initial NMR spectra were taken at 293 K until the peaks of $(Bu^tCD_2)_3TaCl_2$ (**3**-d_6) and Bu^tCD_2Li had disappeared. Then, ^1H NMR spectra were taken at the end of each time period at 273(1), 278(1), 283(1), 288(1), 293(1), and 298(1) K for kinetic measurements until the conversion of **1**-d_{10} to $(Bu^tCD_2)_3Ta{=}CDBu^t$ (**2**-d_7) was complete.

Kinetic Studies of the Conversion of $Ta(CH_2Bu^t)_5$ (1) to $(Bu^tCH_2)_3Ta{=}CHBu^t$ (2). In the first method, $(Bu^tCH_2)_4TaCl$ (**4**)[7b] in toluene-d_8 at −78 °C was mixed with Bu^tCH_2Li in toluene-d_8 at −78 °C. The solution was kept in the precooled NMR spectrometer at −40 °C until Bu^tCH_2Li disappeared.[8] The reaction was then conducted at 0.0 °C in a circulation bath and quenched at −40 °C at the end of each time period to take ^1H spectra. After **4** disappeared, subsequent ^1H spectra and the peaks of $Ta(CH_2Bu^t)_5$ (**1**) were used in the kinetic studies.[9]

In the second method, **4**, prepared in situ from **2** (60.0 mg, 0.129 mmol) and HCl (1.40 mL, 0.10 M, ether) at −78 °C,[7b] was redissolved in toluene-d_8 at −78 °C and then added to a solution of Bu^tCH_2Li (12 mg, 0.15 mmol) and bibenzyl (20 mg, internal standard) in toluene-d_8 at −78 °C. The NMR tube containing the mixture was then placed into an NMR spectrometer precooled to 0 °C. The reaction was conducted at 0 °C and ^1H spectra were taken directly at this temperature and were used for kinetic studies.

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Supporting Information Available: Complete refs 2b and 2d and ^{13}C NMR spectra of **1**-d_{10} and **2**-d_7. This material is available free of charge via the Internet at http://pubs.acs.org.

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