Evidence for Intramolecular C–H Bond Activation and the Formation of a "Tucked-In" Complex of Hexamethylbenzene at a Tantalum(III) Center

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Abstract: The reactions of the d^2 tantalum complex $(\eta^6\text{-}C_6Me_6)Ta(OR)_2Cl$ (**1**, OR = 2,6-diisopropylphenoxide) with 3,3-dimethyl-1-butyne and 3-chloropropene provide the η^1-pentamethylbenzyl compounds $(E)\text{-}(\eta^1\text{-}C_6Me_5CH_2)Ta(CH{=}CH\text{-}(CMe_3))(OR)_2Cl$ (**3**) and $(\eta^1\text{-}C_6Me_5CH_2)Ta(CH_2CH_2CH_2Cl)(OR)_2Cl$ (**5**), respectively. Both complexes are proposed to have arisen through the intermediacy of an unprecedented d^0 "tucked-in" hexamethylbenzene compound, viz. $(\eta^6,\eta^1\text{-}C_6Me_5CH_2)Ta(H)(OR)_2Cl$ (**4**). The intramolecular metalation of a methyl C–H bond in **1** and the existence of a hydride intermediate are also inferred from various deuterium labeling and kinetic studies. The metalated hexamethylbenzene can be functionalized selectively as demonstrated in the iodination of **3** to form $C_6(CH_3)_5CH_2I$ and (E)-CHI=CH(CMe$_3$).

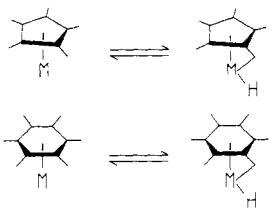
Intramolecular C–H bond activation in pentamethylcyclopentadienyl ligands (η^5-C_5Me_5), when coordinated to f-element or early d-block metals, is a well-documented process[1] which has provided new, fundamental knowledge[1c] in metalloorganic chemistry. The so-called "tucked-in" complexes which result from these intramolecular metalations may arise through distinctive mechanistic pathways, including the following: C–H oxidative addition to a d^2 metal, as observed in the thermolysis of $(\eta^5\text{-}C_5Me_5)_2Ti$ and generalized in Scheme I;[2] from addition of the C–H bond across a metal–carbon double bond;[3] from C–*H* addition to a departing hydrocarbon[4] or hydride[5] ligand; or, C–H addition to a benzyne moiety.[6] To the best of our knowledge, no analogous intramolecular metalation has been observed in a complex of hexamethylbenzene (η^6-C_6Me_6), Scheme I. Herein we report the first evidence for such a reaction and demonstrate its synthetic utility.

Results and Discussion

$(\eta^6\text{-}C_6Me_6)Ta(OR)_2Cl$ (**1**, OR = 2,6-diisopropylphenoxide) can be prepared in high yield from $Ta(OR)_2Cl_3{\cdot}OEt_2$, 2 equiv of Na/Hg, and 3 equiv of 2-butyne.[7] The arene ligand in **1** can be displaced smoothly by ethylene (35 psi) to provide the yellow metalacyclopentane compound $(CH_2CH_2CH_2CH_2)Ta(OR)_2Cl$ (**2**).[8] With this metalacyclization reaction as a precedent, we turned to alkynes as substrates with a view to prepare tantallacyclopentadienes.[9]

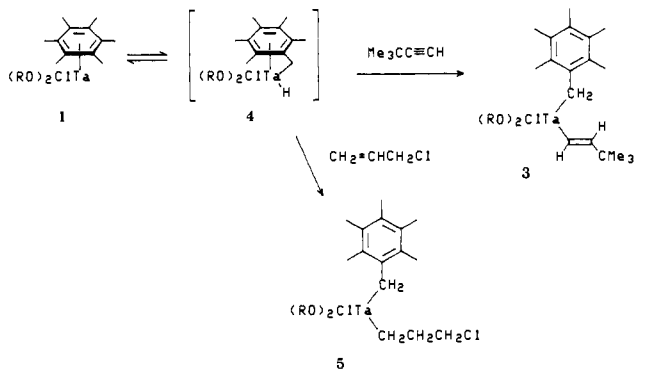
The reaction of **1** with an excess of 3,3-dimethyl-1-butyne (6 equiv in Et_2O, room temperature, 48 h) provides a pale yellow solid after the removal of all volatiles in vacuo. Sublimation produces ca. a 10% yield of hexamethylbenzene; pale yellow compound **3** which remains can be recrystallized from Et_2O/pentane (−40 °C, 60% yield). From ^1H and ^{13}C NMR we formulate compound **3** as the η^1-pentamethylbenzyl complex $(E)\text{-}(\eta^1\text{-}C_6Me_5CH_2)Ta(CH{=}CH(CMe_3))(OR)_2Cl$, Scheme II. The most likely mechanism for the formation of **3** involves the in-

Scheme I



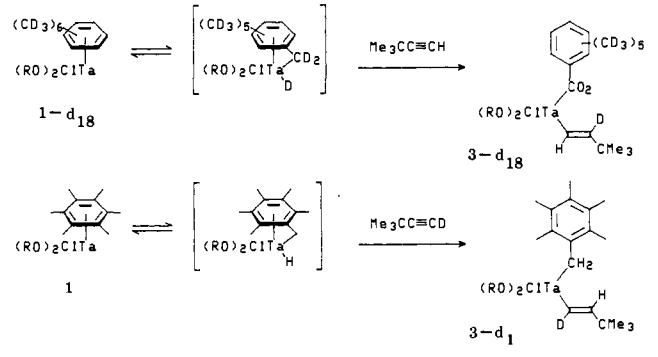
Scheme II

(RO = 2,6-Diisopropylphenoxide)



Scheme III

(RO = 2,6-Diisopropylphenoxide)



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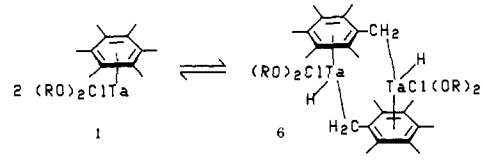
termediacy of the d^0 "tucked-in" or metalated compound, $(\eta^6,\eta^1\text{-}C_6Me_5CH_2)Ta(H)(OR)_2Cl$ (**4**), postulated in Scheme II, and the subsequent alkyne insertion into the metal–hydride bond.[10]

The reaction of the hexamethylbenzene-d_{18} complex with 3,3-dimethyl-1-butyne further implicates a hydride intermediate as well as eliminating exogenous sources of hydrogen, Scheme III. Thus, $(\eta^6\text{-}C_6(CD_3)_6)Ta(OR)_2Cl$ (**1-d_{18}**, prepared by using $CD_3C{\equiv}CCD_3$) reacts with $HC{\equiv}CCMe_3$ to yield *only* (*E*)-$(\eta^1\text{-}C_6(CD_3)_5CD_2)Ta(CH{=}CD(CMe_3))(OR)_2Cl$ (**3-d_{18}**). Conversely, $(\eta^6\text{-}C_6Me_6)Ta(OR)_2Cl$ and $DC{\equiv}CCMe_3$ react to provide (*E*)-$(\eta^1\text{-}C_6Me_5CH_2)Ta(CD{=}CH(CMe_3))(OR)_2Cl$ (**3-d_1**) as the only product, Scheme III. Proposed intermediate **4** has not been detected spectroscopically and therefore is most likely generated in very low concentration. Given the unusual bonding of the arene ligand in compound **1**,[7] we cannot as yet preclude this reaction involving a tucked-in $(\eta^{n<6},\eta^1\text{-}C_6Me_5CH_2)$ intermediate.[11] However, the reaction of **1-d_{18}** with $HC{\equiv}CCMe_3$, in the presence of 1 equiv of C_6Me_6, provides only **3-d_{18}** and no all-protio **3**, thus eliminating the possibility of complete dissociation of the arene ligand, followed by *inter*molecular C–H bond oxidative addition.

The intramolecular metalation of a methyl C–H bond of **1** is also inferred from its reaction with 3-chloropropene, Scheme II. This reaction does not proceed as cleanly as the alkyne reaction, under similar conditions, but the metalated ligand is readily trapped, and $(\eta^1\text{-}C_6Me_5CH_2)Ta(CH_2CH_2CH_2Cl)(OR)_2Cl$ (**5**) can be isolated in ca. 50% yield. Although the ^1H NMR spectrum of **5** is consistent with structures other than that depicted in Scheme II, this formulation alone accounts for both the NMR data *and* the products obtained upon deuteriolysis of **5**. Thus, the reaction of **5** with excess D_2O (1:9 v/v in acetone) produces $DCH_2CH_2CH_2Cl$ (bp 46–47 °C, observed by ^1H NMR in the reaction volatiles) and a near quantitative yield (^1H NMR) of sublimable hexamethylbenzene-d_1, $C_6(CH_3)_5(CH_2D)$, and DO-2,6-*i*-$Pr_2C_6H_3$.

In more firmly establishing how compounds like **3** might arise, we note that a simple crossover experiment, e.g., the reaction of the alkyne trap with an equimolar mixture of $(\eta^6\text{-}C_6(CD_3)_6)Ta(OR)_2Cl$ (**1-d_{18}**) and $(\eta^6\text{-}C_6(CH_3)_6)Ta(OR)_2Cl$ (**1-d_0**), will *not* allow a distinction between inter- vs intramolecular C–H activation (reaction 1) since both the hydride (or deuteride) and the η^1-



(1)

$C_6(CH_3)_5CH_2$ (or $\eta^1\text{-}C_6(CD_3)_5CD_2$) ligands are transferred in a pairwise fashion in this process. In the unlikely event that a *nonpairwise* transfer were possible, the trapping experiment would produce an equimolar mixture of compounds **3**, **7**, **8**, and **3-d_{18}**.

$(\eta^1\text{-}C_6(CH_3)_5CH_2)Ta(CH{=}CH(CMe_3))(OR)_2Cl$, **3**

$(\eta^1\text{-}C_6(CH_3)_5CH_2)Ta(CH{=}CD(CMe_3))(OR)_2Cl$, **7**

$(\eta^1\text{-}C_6(CD_3)_5CD_2)Ta(CH{=}CH(CMe_3))(OR)_2Cl$, **8**

$(\eta^1\text{-}C_6(CD_3)_5CD_2)Ta(CH{=}CD(CMe_3))(OR)_2Cl$, **3-$d_{18}$**

In this case, it would be necessary to distinguish between the mixture of these four compounds and a 50:50 mixture of $(\eta^1\text{-}C_6(CH_3)_5CH_2)Ta(CH{=}CH(CMe_3))(OR)_2Cl$ (**3**) and $(\eta^1\text{-}C_6(CD_3)_5CD_2)Ta(CH{=}CD(CMe_3))(OR)_2Cl$ (**3-d_{18}**) produced by any other mechanism. Since the vinyl resonances of **3** would be indistinguishable by NMR from **8** and those of **3-d_{18}** indistinguishable from **7**, and since mixtures from any pathway would exhibit the same aryl resonances, a simple crossover experiment cannot address this question.

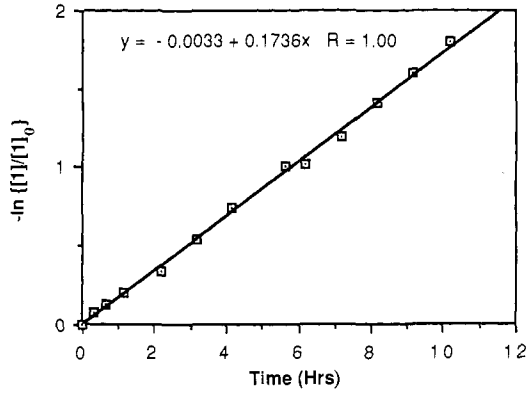


Figure 1. Plot of $-\ln\{[\mathbf{1}]/[\mathbf{1}]_{t=0}\}$ vs time at 25 °C for the first-order disappearance of $(\eta^6\text{-}C_6Me_6)Ta(OR)_2Cl$ (**1**) in its reaction with excess of 3,3-dimethyl-1-butyne.

We have, however, examined the reaction of **1** with a large excess of 3,3-dimethyl-1-butyne (an effective constant concentration) and found the disappearance of **1** to be a first-order process over at least 3 half-lives, Figure 1. Whether a preequilibrium between **1** and **4** (Scheme II) exists as we propose or whether **1** → **4** → **3** are first-order reactions with k_1 and k_2, this observation *precludes* the alkyne trap reacting directly with the tuck-in dimer **6** produced in an *inter*molecular process, reaction 1. These kinetic data, combined with the fact that the reaction **1** → **4** (in the absence of alkyne) is not observed under our reaction conditions, provide additional evidence for the pathways shown in Scheme II and III.

The present data do not allow a definitive formulation of the existence or absence of a π interaction between the pentamethylbenzyl ligand and the d^0 metal centers in **3** and **5**. Although the ^{13}C NMR resonances of the $C_6Me_5CH_2$ ring carbons closely parallel those in the related $(\eta^1\text{-}C_6H_5CH_2)$ ligand in tantalum(V) compounds,[12] this feature is not diagnostic. In addition, any arene $\pi \rightarrow \pi^*$ transitions which might prove useful are masked by intense LMCT bands and $\pi \rightarrow \pi^*$ bands from the phenoxide ligands.[13] However, we propose that this π bonding has been completely disrupted (Scheme II and III) for the following reasons. Firstly, *all* known η^6-arene compounds of niobium and tantalum contain metals in the $d^{n\geq 2}$ oxidation state, suggesting a required back-bonding component in these complexes.[7,14] Secondly, by examining the steric demands of bulky phenoxide ligands in similar compounds, one might predict a labilization of the π bonded portion of a tucked-in ligand, based solely upon steric constraints.[15]

The potential utility of this metalation reaction for the selective functionalization of hexaalkylbenzenes is evident from the deuteriolysis reaction above and from the reaction of **3** with I_2, reaction 2. The iodination proceeds smoothly in diethyl ether to provide $C_6(CH_3)_5CH_2I$ and (*E*)-CHI=CH(CMe_3) in >85% isolated yield. Reaction 2 represents a functionalization which is impossible to

(10) (a) Our assignment of the olefinic proton resonances in compound **3** is opposite to that reported for the vinyl derivatives of the group 4 metallocenes: see Experimental Section. These group 4 compounds are also prepared by the insertion of an alkyne into an M–H bond, ref 10b. (b) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *27*, 373.

(11) See, for example, various complexes containing the $(\eta^4\text{-}C_6R_6)$ ligand: (a) Boncella, J. M.; Green, M. L. H.; O'Hare, D. *J. Chem. Soc., Chem. Commun.* **1986**, 618. (b) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347. (c) Huttner, G.; Lange, S.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 556.

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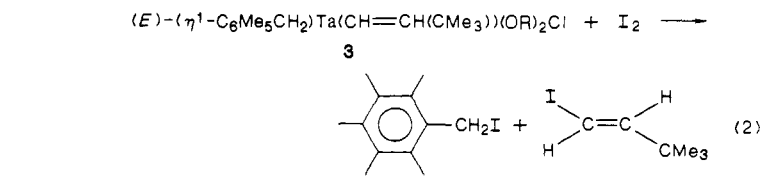
(15) See, for example: (a) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502. (b) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *Polyhedron* **1987**, *6*, 1765.



achieve in a *selective* fashion by traditional free-radical substitution pathways.[16]

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[17] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were purified under N_2 by standard techniques[18] and transferred to the drybox without exposure to air. In all preparations, OR = 2,6-diisopropylphenoxide.

Starting Materials. Tantalum(V) chloride (resublimed) was purchased from Alfa and used as received. 3-Chloropropene was purchased from Aldrich and distilled under nitrogen before use. 2-Butyne and 3,3-dimethyl-1-butyne were obtained from Farchan Laboratories and passed down a short (5-cm) column of activated alumina (at ca. −10 °C) prior to use. Di-*n*-butyl ether (Alfa) was dried over Na sand for 2 days and vacuum distilled before use. *n*-Butyllithium (1.6 M in hexanes) was obtained from Aldrich, and iodomethane-d_3 was purchased from MSD Isotopes and used without further purification. $Ta(OR)_2Cl_3{\cdot}OEt_2$ was prepared as previously described.[7]

Physical Measurements. ^1H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded at probe temperature on a Bruker WM-250 spectrometer in C_6D_6 solvent. Chemical shifts are referenced to protio solvent impurities (δ 7.15) and are reported in ppm downfield of Me_4Si. Multiplicities for ^{13}C resonances (when reported) were obtained from off-resonance decoupled spectra. All microanalytical samples were handled under nitrogen and were combusted with WO_3 (Desert Analytics, Tucson, AZ).

Preparations. (η^6-C_6Me_6)Ta(OR)$_2$Cl (1). To a −40 °C solution of 2.0 g (2.8 mmol) of $Ta(OR)_2Cl_3{\cdot}OEt_2$ in 20 mL of diethyl ether was added 0.66 mL (8.4 mmol) of 2-butyne and 1.89 mL of 0.5% Na/Hg amalgam (5.6 mmol). This reaction mixture was shaken vigorously for 5–10 min over which time the color changed to a deep blue. After filtering the mixture through Celite, the solvent was removed under reduced pressure to provide a blue solid. This solid was washed thoroughly with cold (−20 °C) pentane and dried in vacuo, giving 1.54 g (2.1 mmol, 75%) of bright blue **1**. Compound **1** prepared by this method was sufficiently pure for use in the following reactions, but analytically pure samples can be obtained by recrystallization from Et_2O/pentane at −40 °C: ^1H NMR 7.10–6.91 (A_2B multiplet, 6 H, H_{aryl}), 3.19 (spt, 4 H, $^3J_{HH}$ = 6.8 Hz, C*H*Me$_2$), 2.02 (s, 18 H, C$_6$*Me*$_6$), 1.19 (d, 24 H, $^3J_{HH}$ = 6.8 Hz, CH*Me*$_2$); ^{13}C NMR δ 156.7 (s, C_{ipso}), 136.7 (s, C_{ortho}), 123.6 (d, C_{meta}), 122.3 (d, C_{para}), 120.6 (s, *C*$_6$Me$_6$), 26.2 (d, *C*HMe$_2$), 24.8 (q, CH*Me*$_2$), 16.2 (q, C$_6$*Me*$_6$). Anal. Calcd for $C_{36}H_{52}ClO_2Ta$: C, 58.97; H, 7.15. Found: C, 59.18; H, 7.29.

(*E*)-(η^1-$C_6Me_5CH_2$)Ta(CH=CH(CMe$_3$))(OR)$_2$Cl (3). To a solution of 1.0 g (1.36 mmol) of **1** in 20 mL of diethyl ether was added 1.0 mL (8.16 mmol) of 3,3-dimethyl-1-butyne. The solution was stirred for 48 h over which time it gradually became yellow. The solvent was removed under reduced pressure to yield a yellow oily solid. The small amount of hexamethylbenzene formed during the reaction was removed by sublimation at 50 °C, 10^{-3} Torr. The resulting solid was washed with a small amount of cold (−20 °C) pentane and dried in vacuo, yielding 0.67 g (0.82 mmol, 60%) of pale yellow **3**. Analytically pure samples can be obtained by recrystallization from Et_2O/pentane at −40 °C: ^1H NMR δ 7.18–6.98 (A_2B multiplet, 6 H, H_{aryl}), 6.85 (d, 1 H, $^3J_{HH}$ = 18.1 Hz, TaCH=C*H*(CMe$_3$)), 5.44 (d, 1 H, $^3J_{HH}$ = 18.1 Hz, TaC*H*=CH-(CMe$_3$)), 3.54 (spt, 4 H, C*H*Me$_2$), 3.50 (s, 2 H, C*H*$_2$C$_6$Me$_5$), 2.22 (s, 3 H, *p*-CH$_3$), 1.92 and 1.87 (s, 6 H each, *o*- and *m*-CH$_3$), 1.35 and 1.34 (d, 12 H each, CH*Me*$_2$), 0.88 (s, 9 H, TaCH=CH(C*Me*$_3$)); ^{13}C NMR δ 182.0 (d, *C*H=CH(CMe$_3$)), 159.3 (d, CH=*C*H(CMe$_3$)), 156.1 (s, C_{ipso} (OR)), 143.9 (s, C_o (*C*$_6$Me$_5$)), 140.7 (s, C_{ipso} (*C*$_6$Me$_5$)), 139.5 (s, C_o (OR)), 135.6 (s, C_m (*C*$_6$Me$_5$)), 124.1 (d, C_m (OR)), 123.5 (d, C_p (OR)), 114.5 (s, C_p (*C*$_6$Me$_5$)), 68.5 (t, *C*H$_2$C$_6$Me$_5$), 36.1 (s, *C*Me$_3$), 29.6 (q, C*Me*$_3$), 27.4 (d, *C*HMe$_2$), 25.7, 23.8 (q, CH*Me*$_2$), 19.1, 16.8 (q, *o*- and *m*-C$_6$*Me*$_5$), 17.6 (q, *p*-C$_6$*Me*$_5$). Anal. Calcd for $C_{42}H_{62}ClO_2Ta$: C, 61.87; H, 7.66; Cl, 4.35. Found: C, 61.87; H, 7.83; Cl, 4.28.

(η^1-$C_6Me_5CH_2$)Ta($CH_2CH_2CH_2Cl$)(OR)$_2$Cl (5). To a solution of 1.0 g (1.36 mmol) of **1** in 20 mL of diethyl ether was added 0.67 mL (8.16 mmol) of 3-chloropropene. The solution was stirred for 48 h over which time it gradually became yellow. The solvent was removed under reduced pressure to yield a yellow oil. The hexamethylbenzene formed during the reaction was removed by sublimation at 50 °C, 10^{-3} Torr. The resulting solid was washed with a small amount of cold (−20 °C) pentane and dried in vacuo, yielding 0.55 g (0.68 mmol, 50%) of pale yellow **5**. Analytically pure samples can be obtained by recrystallization from Et_2O/pentane at −40 °C: ^1H NMR δ 7.16–6.97 (A_2B multiplet, 6 H, H_{aryl}), 3.43 (spt, 4 H, C*H*Me$_2$), 3.38 (s, 2 H, C*H*$_2$C$_6$Me$_5$), 3.03 (t, 2 H, $^3J_{HH}$ = 5.9 Hz, CH$_2$CH$_2$C*H*$_2$Cl), 2.29 (s, 3 H, *p*-CH$_3$), 2.25 (m, 2 H, CH$_2$C*H*$_2$CH$_2$Cl), 1.98 and 1.86 (s, 6 H each, *o*- and *m*-CH$_3$), 1.38 and 1.30 (d, 12 H each, CH*Me*$_2$), 0.57 (m, 2 H, C*H*$_2$CH$_2$CH$_2$Cl); ^{13}C NMR δ 155.6 (s, C_{ipso} (OR)), 143.8 (s, C_o (*C*$_6$Me$_5$)), 141.3 (s, C_{ipso} (*C*$_6$Me$_5$)), 139.3 (s, C_o (OR)), 135.6 (s, C_m (*C*$_6$Me$_5$)), 124.2 (d, C_m (OR)), 123.7 (d, C_p (OR)), 114.4 (s, C_p (*C*$_6$Me$_5$)), 67.8, 65.8 (t, *C*H$_2$C$_6$Me$_5$ and *C*H$_2$CH$_2$CH$_2$Cl), 51.3 (t, CH$_2$CH$_2$*C*H$_2$Cl), 33.1 (t, CH$_2$*C*H$_2$CH$_2$Cl), 27.7 (d, *C*HMe$_2$), 25.9, 23.9 (q, CH*Me*$_2$), 19.0, 16.6 (*o*- and *m*-C$_6$*Me*$_5$), 17.3 (*p*-C$_6$*Me*$_5$). Anal. Calcd for $C_{39}H_{57}Cl_2O_2Ta$: C, 57.85; H, 7.10; Cl, 8.76. Found: C, 57.85; H, 7.26; Cl, 8.06.

$CD_3C{\equiv}CCD_3$. A solution of 0.184 mol of *n*-BuLi in 75 mL of diethyl ether was prepared from 115 mL of a 1.6 M solution of *n*-BuLi in hexanes by solvent removal under reduced pressure, followed by reconstitution of the *n*-BuLi in diethyl ether. Acetylene (freed from acetone by passing through two cold traps at −78 °C) was bubbled through the solution for 30 min, whereupon a thick, white precipitate formed. This mixture was stirred for an additional hour, and the solvent was removed under reduced pressure. The resulting white solid was redissolved in 50 mL of THF, and the solution was refluxed for 30 min to ensure complete disproportionation to Li_2C_2. CD_3I (25 g, 0.172 mol) was transferred into the reaction mixture, and stirring was continued for 2 days. This solution was then filtered, and the product was distilled from the solution; all fractions were collected up to 60 °C. These fractions were added to 20 mL of di-*n*-butyl ether, and the product was redistilled. Pure $CD_3C{\equiv}CCD_3$ was collected between 26–28 °C. The yield of $CD_3C{\equiv}CCD_3$ was 3.15 g (0.112 mol) or 61% based upon *n*-BuLi. The product was dried over activated alumina prior to use.

DC≡CCMe$_3$. A solution of 44.8 mmol of *n*-BuLi in 15 mL of di-*n*-butyl ether was prepared from 28 mL of a 1.6 M *n*-BuLi solution in hexanes by solvent removal under reduced pressure, followed by reconstitution of the *n*-BuLi in di-*n*-butyl ether. This *n*-BuLi solution was added slowly to a solution of 5 mL (3.34 g, 40.7 mmol) of HC≡CCMe$_3$ in 35 mL of di-*n*-butyl ether which had been cooled to 0 °C. When the addition was complete, the solution was allowed to warm to room temperature and stirred overnight (ca. 16 h). After this time, the solution of LiC≡CCMe$_3$ was cooled to 0 °C, and 1.5 mL of D_2O (1.66 g, 82.9 mmol) were added slowly with vigorous stirring. This mixture was allowed to warm to room temperature and stirred for 6 h, over which time a white precipitate formed. The product was collected from the solution at −20 °C, in vacuo, in a trap-to-trap distillation. Yield of DC≡CCMe$_3$ was 2.94 g (35.4 mmol) or 87% based upon HC≡CCMe$_3$. The product was dried over activated alumina prior to use.

(η^6-$C_6(CD_3)_6$)Ta(OR)$_2$Cl (1-d_{18}). This compound was prepared in a manner analogous to **1**, and in comparable yield, by substituting $CD_3C{\equiv}CCD_3$ for 2-butyne.

(*E*)-(η^1-$C_6(CD_3)_5CD_2$)Ta(CH=CD(CMe$_3$))(OR)$_2$Cl (3-d_{18}). This compound was prepared in a manner analogous to **3**, and in comparable yield, by substituting **1**-d_{18} for **1** [^1H NMR δ 5.41 (br s, C*H*=CD-(CMe$_3$), $^3J_{HD}$ is not resolved at 250 MHz); ^{13}C NMR δ 182.0 (*C*H=CD(CMe$_3$)) observed, δ 159.3 resonance (CH=*C*D(CMe$_3$)) is sufficiently broadened to not be observed]. Proton assignments are confirmed by irradiation of the proton at δ 5.41 in the heteronuclear decoupled spectrum of (all-protio) **3**, which causes collapse of the δ 182.0 doublet (*C*H=CH(CMe$_3$)) to a nuclear Overhauser enhanced singlet. Protonolysis of **3**-d_{18} (excess H_2O, 1:9 v/v in acetone) yields C*H*$_2$=CD(CMe$_3$) cleanly: ^1H NMR δ 4.80 (sxt, $^3J_{HD}$ (trans to D) = 3 Hz, $^2J_{HH}$ (gem) = 1.5 Hz), 4.74 (q, $^3J_{HD}$ (cis to D) $\approx$ $^2J_{HH}$ (gem) = 1.5 Hz).

(*E*)-(η^1-$C_6Me_5CH_2$)Ta(CD=CH(CMe$_3$))(OR)$_2$Cl (3-d_1). This compound was prepared in a manner analogous to **3**, and in comparable yield, by substituting DC≡CCMe$_3$ for HC≡CCMe$_3$ [^1H NMR **3**-d_1 δ 6.83 (br s, CD=C*H*(CMe$_3$), $^3J_{HD}$ is not resolved at 250 MHz)]. Other resonances are identical with those of **3**.

Iodination of (*E*)-(η^1-$C_6Me_5CH_2$)Ta(CH=CH(CMe$_3$))(OR)$_2$Cl (3). A solution of 0.5 g (0.6 mmol) of **3** in 10 mL of diethyl ether was treated with 0.31 g (1.2 mmol) of iodine. The resulting yellow-orange solution was pumped to dryness and 0.15 g of white, crystalline $C_6Me_5CH_2I$ was sublimed out of the reaction mixture at 55 °C, 10^{-3} Torr (85%). In a

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separate NMR tube experiment, 30 mg of **3** was treated with 18.6 mg of iodine. The reaction was seen to proceed cleanly with quantitative formation of $C_6(CH_3)_5CH_2I$ and (*E*)-CHI=CH(CMe_3) and Ta-$(OR)_2I_2Cl$: ^1H NMR spectrum $C_6(CH_3)_5CH_2I$ ($CDCl_3$) δ 4.41 (s, 2 H, CH_2I), 2.14 (s, 3 H, *p*-CH_3), 2.11 and 2.10 (s, 6 H each, *o*- and *m*-CH_3); (*E*)-CHI=CH(CMe_3) (C_6D_6) δ 6.41 (d, 1 H, $^3J_{HH}$ = 15.8 Hz, CHI=CH(CMe_3)), 5.73 (d, 1 H, $^3J_{HH}$ = 15.8 Hz, CHI=C*H*(CMe_3)), 0.68 (s, 9 H, CHI=CH(CMe_3)).

Deuteriolysis of $(\eta^1$-$C_6Me_5CH_2)Ta(CH_2CH_2CH_2Cl)(OR)_2Cl$ (5). To a solution of 0.5 g (0.62 mmol) of **5** in 1.0 mL of acetonitrile-d_3 was added 0.3 mL (16.6 mmol) of D_2O. After stirring for 2 h all of the reaction volatiles were distilled into a small ampoule cooled to −196 °C which contained a small amount of activated alumina. The reaction volatiles were allowed to reach room temperature and filtered into an NMR tube. ^1H NMR spectroscopy revealed the presence of $DCH_2CH_2CH_2Cl$. The solid remaining from the original reaction mixture was extracted with diethyl ether. The resulting solution was filtered and dried over activated alumina, and the solvent was removed under reduced pressure to yield a white, oily solid. A white crystalline solid was sublimed out at 50 °C and 10^{-3} Torr and shown by ^1H NMR spectroscopy to be $C_6(CH_3)_5(CH_2D)$: partial ^1H NMR spectrum $DCH_2CH_2CH_2Cl$ (in CD_3CN) δ 0.96 (1:2:1 triplet ($^3J_{HH}$ = 7.3 Hz) of 1:1:1 triplets ($^2J_{HD}$ = 2.2 Hz), 2 H, CH_2D); $C_6(CH_3)_5(CH_2D)$ (in $CDCl_3$) δ 2.124 (s, 15 H, CH_3), 2.106 (1:1:1 t, 2 H, $^2J_{HD}$ = 2.2 Hz, CH_2D).

Kinetics of Reaction of $(\eta^6$-$C_6Me_6)Ta(OR)_2Cl$ (1) with 3,3-Dimethyl-1-butyne. A solution of 0.5 g (0.68 mmol) of **1** in 20 mL of diethyl ether was treated with a large excess (4 mL, 34 mmol, 50 equiv) of 3,3-dimethyl-1-butyne at 25 °C. The reaction was sampled at hourly intervals by withdrawing 0.5 mL of the reaction mixture, removing the solvent under reduced pressure, and dissolving the resulting solid in C_6D_6. The relative concentration of **1** in each sample was determined from monitoring the η^6-C_6Me_6 resonances by ^1H NMR spectroscopy. The first-order rate law $\ln [\mathbf{1}] = -kt + \ln [\mathbf{1}]_{t=0}$ is obeyed over at least 3 half-lives as a plot of $-\ln \{[\mathbf{1}]/[\mathbf{1}]_{t=0}\}$ vs t is linear (correlation = 0.9991) with k_{obsd} = 0.174 h^{-1} and $t_{1/2}$ = 3.98 h.

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Synthesis and Reactions of 5-Methylenebicyclo[2.2.0]hex-2-ene Derivatives from Hexamethyl(Dewar benzene)

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Abstract: Treatment of hexamethyl(Dewar benzene) (HMDB) with *tert*-butyl hypochlorite provides a rearranged chlorinated derivative, *exo*-6-chloro-1,2,3,4,6-pentamethyl-5-methylenebicyclo[2.2.0]hex-2-ene (**1**). Thermal rearrangement of **1** gives pentamethylbenzyl chloride (**4**); the activation energy decreases in more polar solvents, suggesting an ionic intermediate during the chloride migration and/or ring opening. The intermediate is postulated to be a delocalized carbocation that can be intercepted by nucleophiles to give substitution products. Treatment of **1** with $NaOCH_3$ in methanol gives two isomeric methoxide substitution products, **2** and **3**, in a 60:40 ratio. The structure of **2** involves the same skeletal structure and retention of stereochemistry relative to **1**; the structure of **3** indicates neighboring group participation of the transannular π bond. The rate law for the formation of **2** and **3** is first order in **1** and independent of $NaOCH_3$ concentration. A common ion rate depression is observed, added chloride ion causing a decreased rate of formation of both **2** and **3** equally, indicating reversible ionization to a common delocalized carbocation. Thermolysis of **2** gives hexamethylbenzene plus formaldehyde; NMR spectra provide evidence for a methylenecyclohexadiene intermediate, indicating that ring opening precedes loss of formaldehyde. Inclusion of basic alumina in the thermolysis of **2** diverts the reaction to formation of pentamethylbenzyl methyl ether (**5**). Thermolysis of **3** gives a complex mixture of products, including **5**.

Hexamethyl(Dewar benzene) (HMDB; 1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2,5-diene) has been a compound of both synthetic and theoretical interest. It is readily synthesized from 2-butyne,[1] making it the most accessible of the Dewar benzenes. The Dewar benzenes are a class of compounds that have an available reaction (aromatization) which is highly favorable thermodynamically (ΔH = −60 to −56 kcal/mol for HMDB)[2] yet relatively unfavorable kinetically, due to orbital symmetry constraints[3] (E_a = 31-37 kcal/mol for HMDB,[2,4] 23 kcal/mol for the parent Dewar benzene[5]).

Our original intention was to study substituted Dewar benzenes to determine the effect of substituents on the kinetics and thermodynamics of the Dewar benzene aromatization and conversely to determine the effect of the Dewar benzene system on neighboring functional group reactions. However, rearrangements are among the most common reactions of the Dewar benzene skeleton, particularly induced by electrophilic reagents.[6] Although we sought to avoid electrophilic conditions, each of the derivatives

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