Cyclometalation of 2,6-Di-*tert*-butylphenoxide Ligands by Tantalum Aryl Groups: Aliphatic Carbon-Hydrogen Bond Activation and Aryl Isomerization via Benzyne (*o*-Phenylene) Intermediates

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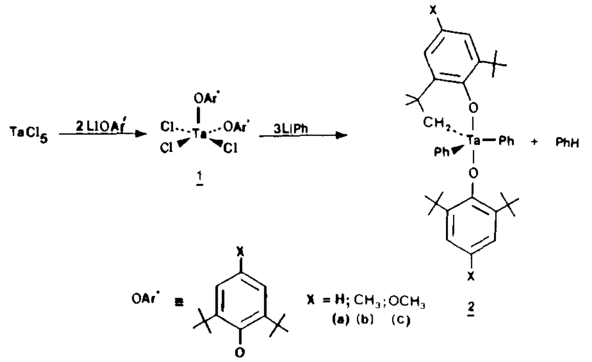
Abstract: Alkylation of the halides $Ta(OAr')_2Cl_3$, $Ta(OAr'\text{-}4\text{-}Me)_2Cl_3$, and $Ta(OAr'\text{-}4\text{-}OMe)_2Cl_3$ containing the bulky aryl oxide ligands 2,6-di-*tert*-butylphenoxide (OAr′), 2,6-di-*tert*-butyl-4-methylphenoxide (OAr′-4-Me), and 2,6-di-*tert*-butyl-4-methoxyphenoxide (OAr′-4-OMe) with LiPh (3 equiv) leads to the formation of benzene (1 equiv) and a diphenyl compound in which one of the aryl oxide ligands has undergone cyclometalation through one of its *tert*-butyl groups. Studies show that the cyclometalation step occurs from a monophenyl intermediate, $Ta(OAr')_2(Ph)Cl_2$, followed by formation of the other monocyclometalated, isolated derivatives $Ta(OC_6H_3Bu^tCMe_2CH_2)(OAr')Cl_2$ and $Ta(OC_6H_3Bu^tCMe_2CH_2)(OAr')(Ph)Cl$. Further thermolysis of the diphenyl compound results in the elimination of 1 equiv of benzene and formation of the biscyclometalated compound $Ta(OC_6H_3Bu^tCMe_2CH_2)_2(Ph)$. A combination of kinetic measurements and deuterium labeling studies shows that the second cyclometalation proceeds through two competing pathways. The first involves a direct combination of the hydrogen of the aliphatic CH bond with the phenyl leaving group while the second proceeds via a benzyne (*o*-phenylene) intermediate. Deuteriation of the aryl oxide *tert*-butyl and Ta-Ph groups indicates kinetic isotope effects for each pathway of 2.3 (5) and 4.1 (8), respectively, at 118.0 (5) °C. The use of substituted aryl leaving groups (3-methyl, 4-methyl, 3-fluoro, and 4-fluoro) shows the cyclometalations to exhibit a negligible substituent dependence. However, further studies show that at elevated temperatures the biscyclometalated compounds are in equilibrium with the benzyne complex $Ta(OC_6H_3Bu^tCMe_2CH_2)(OAr')(C_6H_4)$ formed by opening one of the metallacycle rings. This results in the facile isomerization of either the 3-tolyl or 4-tolyl derivatives to a 50/50 mixture of the two isomers, as well as the scrambling of deuterium atoms throughout the aliphatic and Ta-Ph positions in the labeled compounds. In the case of the fluoro-substituted phenyl compounds, the benzyne intermediate appears to be less accessible with little if any isomerization observed prior to thermal decomposition. The mechanistic implications of these results are discussed. A single-crystal X-ray diffraction study of $Ta(OC_6H_3Bu^tCMe_2CH_2)(OAr')Ph_2$ shows an approximately trigonal-bipyramidal geometry about the tantalum atom with trans-axial oxygen atoms. The trigonal plane consists of the two ipso carbons of the Ta-Ph groups as well as the carbon atom of the metallacycle formed by the cyclometalation. The six-membered ring maintains a bite of $\simeq$80° at the metal with little distortion due to the large, 144°, Ta-O-C angle. Crystal data for $TaC_{40}H_{57}O_2$ at -162 °C: space group $P\bar{1}$, $a = 15.438$ (6) Å, $b = 12.329$ (4) Å, $c = 10.639$ (3) Å, $\alpha = 73.70$ (2)°, $\beta = 67.38$ (2)°, $\gamma = 69.07$ (2)°, $Z = 2$, $d_{calcd} = 1.437$ g cm^{-3}. Using the 4089 unique intensities with $F > 2.33\sigma(F)$ yielded final residuals $R(F) = 0.0322$ and $R_w(F) = 0.0318$.

The past few years have seen a dramatic increase in the study of the chemistry associated with high-valent, early-d-block lanthanide and actinide alkyl compounds.[2,3] A sizeable portion of this work has been prompted by the recently reorganized ability of the metal-alkyl bonds in these systems to activate, either inter- or intramolecularly, normally inert carbon-hydrogen bonds.[4] Detailed mechanistic studies of this reactivity have exposed in some cases the presence of an indirect pathway for CH bond activation via alkylidene intermediates.[5-7] The potency for alkylidene functional groups to intramolecularly activate aliphatic carbon-hydrogen bonds has been quantified in one case.[7]

In the case of early-transition-metal aryl compounds, the literature now contains numerous examples where the reactivity proceeds via a benzyne (*o*-phenylene) intermediate formed by abstraction of an ortho hydrogen from the initial phenyl substituent.[8,9] In a few cases benzyne compounds have actually been isolated and structurally characterized.[10-13] Reactivity studies have demonstrated a rich chemistry for the functional group, ranging from the trapping of dinitrogen to the intermolecular activation of aromatic CH bonds.[8,9]

As part of our synthetic and mechanistic studies of the intramolecular activation of the aliphatic CH bonds of aryl oxide ligation in high-valent, early-transition-metal systems,[6,7,14] we have implicated benzyne intermediates as being responsible for CH bond activation as well as a pathway for facile aryl isomerization processes.[15] We report here a more detailed synthetic and mechanistic study of this reactivity.

Scheme I



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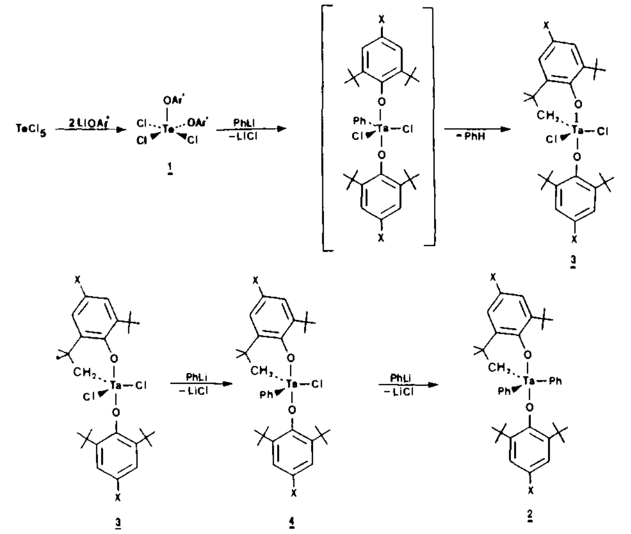
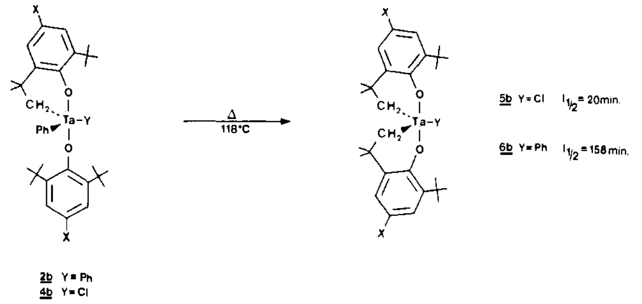
Scheme II



Scheme III



Results and Discussion

Synthesis and Characterization of Compounds. Treatment of the monomeric bis(aryl oxide) compounds $Ta(OAr')_2Cl_3$ (**1a**), $Ta(OAr'\text{-}4\text{-}Me)_2Cl_3$ (**1b**), and $Ta(OAr'\text{-}4\text{-}OMe)_2Cl_3$ (**1c**) (OAr' = 2,6-di-*tert*-butylphenoxide, OAr'-4-Me = 4-methyl-2,6-di-*tert*-butylphenoxide, OAr'-4-OMe=4-methoxy-2,6-di-*tert*-butylphenoxide) with ≥3 equiv of phenyllithium in diethyl ether or aromatic hydrocarbon solvents at room temperature leads to the monocyclometalated diphenyl compounds **2a**, **2b**, and **2c** directly along with 1 equiv of benzene (Scheme I). The addition of only 1 equiv of LiPh to **1** at low temperatures was found to lead to the monocyclometalated dichloride **3**. Hence it appears that the intramolecular activation of the aliphatic CH bonds of the *tert*-butyl groups occurs in an undetected intermediate compound $Ta(OAr')_2(Ph)Cl_2$ (Scheme II). Subsequent reaction of **3** with LiPh then leads to the mixed phenyl chloride **4** and eventually the diphenyl **2** (Scheme II). Treatment of the trichloride **1** with only 2 equiv of LiPh at low temperature leads directly to compound **4**. Even in the reaction of **1** with a large excess of LiPh or ClMgPh we have no evidence for the formation of a triphenyl compound, although with the less cyclometalatable 2,6-diisopropylphenoxide ($OAr\text{-}2,6\text{-}Pr^i_2$) ligand, the derivative $Ta(OAr\text{-}2,6\text{-}Pr^i_2)_2(Ph)_3$ is readily synthesized.[17] The thermolysis of the mono- and diphenyl compounds **4** and **2** in hydrocarbon solvents at temperatures >80 °C leads to the clean formation of 1 more equiv of benzene and the biscyclometalated derivatives **5** and **6**, respectively (Scheme III). Monitoring the thermolysis of **4** or **2** in toluene-d_8 solutions by ^1H NMR showed the second ring closure to be essentially quantitative.

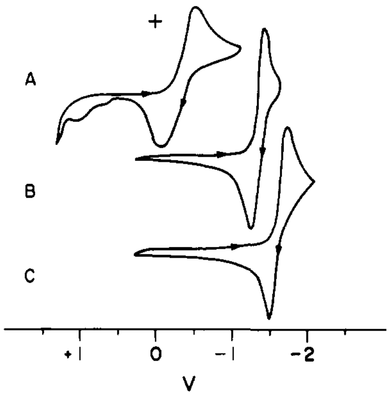


Figure 1. Cyclic voltammograms of (A) $Ta(OC_6H_2\text{-}4\text{-}Me\text{-}Bu^tCMe_2CH_2)(OAr'\text{-}4\text{-}Me)Cl_2$ (**3b**), (B) $Ta(OC_6H_2\text{-}4\text{-}Me\text{-}Bu^tCMe_2CH_2)(OAr'\text{-}4\text{-}Me)(Ph)(Cl)$ (**4b**), and (C) $Ta(OC_6H_2\text{-}4\text{-}Me\text{-}Bu^tCMe_2CH_2)(OAr'\text{-}4\text{-}Me)(Ph)_2$ (**2b**). Potentials are in volts versus a Ag quasi-reference electrode, against which $Cp_2Fe^{0/+} = +0.47$ V.

These cyclometalated complexes can be readily characterized by NMR techniques. In particular, the six-membered metallacycle formed by the intramolecular activation of the OAr'-*tert*-butyl groups has a number of distinct signatures in both the ^1H and ^{13}C NMR spectra. In the ^{13}C NMR spectrum the $Ta\text{-}CH_2CMe_2$ carbon is found to resonate in the region δ 90–105, a similar region in which this group appears in the related, metalated tantalum-methyl derivatives.[7] In the bismetalated compounds **5** and **6** as well as the asymmetric monometalated **4**, the diastereotopic protons of this methylene group appear as a well-resolved AX pattern. Similarly, the methyl groups $Ta\text{-}CH_2CMe_2$ give rise to two singlets in the ^1H and $\{^1H\}^{13}C$ NMR spectra. Example ^1H NMR spectra of **2a** and **6a** are available as Supplementary Material. The Ta-Ph groups also give rise to characteristic signals, e.g., the ipso Ta-C(Ph) carbons at ≃δ 200 in the ^{13}C NMR and the ortho protons as well-resolved multiplets downfield of the normal aromatic hydrogens in the ^1H NMR spectrum.

All of the compounds are sufficiently volatile to allow ready characterization by mass spectrometric methods. The use of a combination of electron impact and chemical ionization techniques resulted in large parent molecular ions as well as diagnostic fragment ions. This technique proved particularly valuable in our labeling studies (vide infra).

Although not a technique routinely applied to characterize organometallic compounds of this type, the cyclic voltammograms of these derivatives proved distinctive. In tetrahydrofuran (THF) solvent with $(Bu^n_4N)(PF_6)$ as supporting electrolyte a reasonably accessible one-electron reduction wave is observable for these

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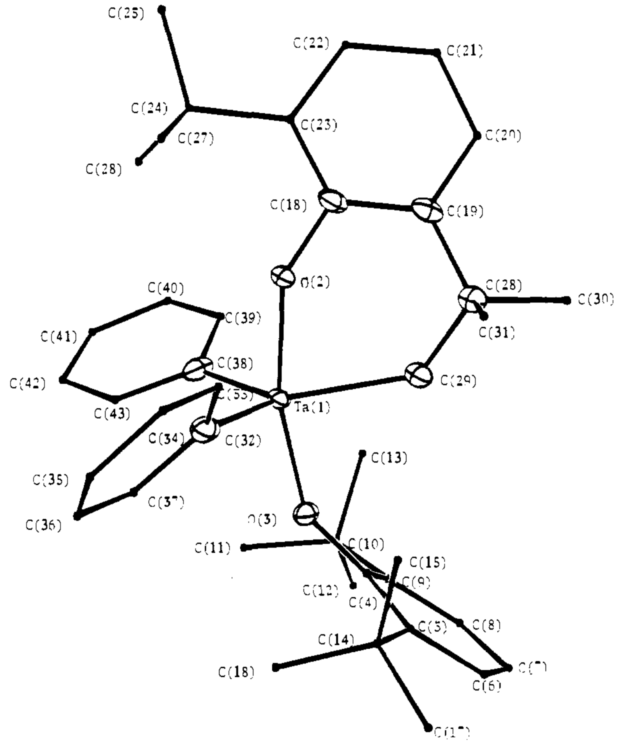

Figure 2. ORTEP view of $Ta(OC_6H_3Bu^tCMe_2CH_2)(OAr')(Ph)_2$ (**2a**), emphasizing the central coordination sphere and metallacycle ring.

d^0-metal compounds.[18] Figure 1 shows sample voltammograms for some selected derivatives. The monocyclometalated dichloride **3b** has a very accessible one-electron reduction wave at −0.30 V. However, the difference in the cathodic and anodic waves is very large, an indication that some chemical change, possibly solvation or chloride dissociation occurs on reduction. The mixed phenyl chloride **4** and diphenyl **2** are more difficult to reduce, and yet again the redox waves in the cyclic voltammograms have values of $(E_{p_c} - E_{p_a})$ greater than observed for the $Cp_2Fe^{0/+}$ couple under identical conditions.[18]

In order to more fully characterize the geometry of these compounds as well as the structural features of the six-membered metallacycle they contain, an X-ray diffraction study of **2a** was undertaken. An ORTEP view of **2a** is given in Figure 2, while Tables I and II contain fractional coordinates and selected bond distances and angles, respectively. It can be seen that the coordination geometry about the tantalum atom can best be described as trigonal bipyramidal with trans-axial oxygen atoms. The three carbon atoms of the two phenyl groups and metalated *tert*-butyl group then form the trigonal plane. The molecular structure of **2a** can be compared to that of $Ta(OAr')_2(CH_3)_3$,[7] while the Ta–O and Ta–C distances appear normal for these groups bound to Ta(V).[19] The six-membered metallacyclic ring manages to maintain an 81° bite at the metal with little puckering due to the large Ta–O–C angle. An almost identical conformation was seen (and discussed) in the monocyclometalated compound $Ti(OC_6H_3Bu^tCMe_2CH_2)(OAr')(CH_2SiMe_3)(py)$.[14]

Mechanistic Studies. Having characterized the cyclometalated compounds, we turned our attention to gaining insight into the pathways and mechanisms whereby the d^0-Ta(V) metal intramolecularly activates these aliphatic carbon–hydrogen bonds using aryl substituents. A combination of kinetics and labeling studies was used as well as the use of various substituted aryl leaving groups. These studies have been aided greatly by the use of the parent phenol HOAr′-4-Me specifically deuteriated only in the aromatic *tert*-butyl and protic positions (vide infra).

Table I. Fractional Coordinates and Isotropic Thermal Parameters for $Ta(OC_6H_2Bu^tCMe_2CH_2)(OAr')(Ph)_2$ (**2a**)

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Ta(1)	2813.1 (2)	3081.0 (2)	1158.9 (2)	10
O(2)	2389 (3)	4434 (3)	−99 (4)	12
O(3)	3126 (3)	2006 (3)	2732 (4)	12
C(4)	3125 (4)	1806 (5)	4080 (6)	14
C(5)	2286 (5)	1566 (5)	5179 (6)	15
C(6)	2227 (5)	1624 (6)	6509 (7)	20
C(7)	2934 (5)	1840 (6)	6765 (7)	25
C(8)	3783 (5)	1934 (6)	5721 (7)	23
C(9)	3932 (5)	1874 (5)	4363 (6)	15
C(10)	4949 (5)	1859 (5)	3296 (6)	16
C(11)	5256 (5)	1010 (6)	2283 (7)	21
C(12)	5739 (5)	1420 (6)	4022 (8)	25
C(13)	4972 (5)	3116 (6)	2520 (7)	24
C(14)	1494 (4)	1217 (6)	4975 (7)	17
C(15)	843 (5)	2276 (6)	4291 (7)	21
C(16)	1971 (5)	188 (6)	4172 (7)	21
C(17)	798 (5)	761 (6)	6380 (7)	22
C(18)	2187 (4)	5638 (5)	−401 (6)	13
C(19)	1853 (4)	6249 (5)	710 (6)	12
C(20)	1727 (5)	7456 (5)	397 (7)	16
C(21)	1882 (5)	8039 (5)	−957 (7)	18
C(22)	2163 (5)	7423 (6)	−2016 (6)	16
C(23)	2320 (4)	6206 (5)	−1784 (6)	13
C(24)	2589 (5)	5552 (5)	−2983 (6)	16
C(25)	2667 (5)	6405 (6)	−4360 (7)	22
C(26)	3593 (5)	4642 (6)	−3151 (7)	24
C(27)	1797 (5)	4965 (6)	−2709 (7)	21
C(28)	1584 (4)	5613 (5)	2204 (6)	15
C(29)	2343 (5)	4417 (5)	2413 (6)	15
C(30)	1517 (5)	6343 (5)	3215 (6)	16
C(31)	570 (4)	5430 (5)	2577 (7)	16
C(32)	1940 (4)	2215 (5)	846 (6)	14
C(33)	1022 (5)	2783 (6)	652 (7)	18
C(34)	509 (5)	2167 (6)	445 (7)	19
C(35)	893 (5)	978 (6)	395 (7)	23
C(36)	1820 (5)	408 (6)	537 (7)	20
C(37)	2323 (4)	1008 (5)	767 (6)	15
C(38)	4272 (4)	2765 (5)	−266 (6)	14
C(39)	4837 (5)	3556 (6)	−743 (6)	17
C(40)	5764 (5)	3320 (6)	−1683 (7)	23
C(41)	6133 (5)	2291 (6)	−2223 (7)	22
C(42)	5591 (5)	1510 (6)	−1850 (7)	20
C(43)	4671 (5)	1742 (6)	−861 (6)	17

Table II. Selected Bond Distances and Angles for **2a**

	Distances, Å		
Ta(1)–O(2)	1.909 (4)	Ta(1)–C(32)	2.154 (6)
Ta(1)–O(3)	1.926 (4)	Ta(1)–C(38)	2.145 (6)
Ta(1)–C(29)	2.158 (6)		
	Angles, Deg		
O(2)–Ta(1)–O(3)	165.4 (2)	C(39)–Ta(1)–C(32)	128.5 (2)
O(2)–Ta(1)–C(29)	80.7 (2)	C(39)–Ta(1)–C(38)	117.6 (2)
O(2)–Ta(1)–C(32)	89.8 (2)	C(32)–Ta(1)–C(38)	112.9 (2)
O(2)–Ta(1)–C(38)	90.1 (2)	Ta(1)–O(2)–C(18)	143.7 (4)
O(3)–Ta(1)–C(29)	84.7 (2)	Ta(1)–O(3)–C(4)	149.6 (4)
O(3)–Ta(1)–C(32)	98.9 (2)		
O(3)–Ta(1)–C(38)	97.2 (2)		

An initially unexpected result concerns the fact that the first intramolecular CH bond activation takes place immediately after the introduction of one phenyl group into the tantalum coordination sphere. This contrasts with the behavior observed for the alkylating agents $LiCH_3$, $LiCH_2SiMe_3$, and $Mg(CH_2Ph)_2$ where the products of substitutions were $Ta(OAr')_2(CH_3)_3$ and $Ta(OAr')_2({=}CHX)(CH_2X)$ (X = $SiMe_3$, Ph).[19] A comparison of the rates of the second cyclometalation in the two compounds **4** and **2** at 118 °C shows that the monochloride metalates approximately 8 times faster than the diphenyl derivative (Table III, Scheme III). Both the intermolecular activation and intramolecular activation of carbon–hydrogen bonds by metal–alkyl bonds in these and related systems are accommodated into a mechanistic pathway involving a four-center, four-electron tran-

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Table III. Kinetic Data for the Formation of Biscyclometalated Derivatives at 118 °C

reaction	$10^5k/s^{-1}$
4b → **5b**[a]	52 (4)
2b → **6b**[a]	7.3 (4)
$\mathbf{2b}^{d_{10}}$ → [0.92($\mathbf{6b}^{d_5}$) + 0.08($\mathbf{6b}^{d_4}$)][b]	5.8 (3)
$\mathbf{2b}^{d_{10}}$ → $\mathbf{6b}^{d_5}$	5.3 (4)
$\mathbf{2b}^{d_{10}}$ → $\mathbf{6b}^{d_4}$	0.5 (2)
2b* → [0.55($\mathbf{6b}^{*d_0}$) + 0.45($\mathbf{6b}^{*d_1}$)][c]	4.2 (8)
2b* → $\mathbf{6b}^{*d_0}$	2.3 (5)
2b* → $\mathbf{6b}^{*d_1}$	1.9 (4)
$k(\mathbf{2b}^{d_{10}} \rightarrow \mathbf{6b}^{d_5}) + k(\mathbf{2b}^{*} \rightarrow \mathbf{6b}^{*d_1})$	7.2 (8)
k_H/k_D (direct path) = $[k(\mathbf{2b}^{d_{10}} \rightarrow \mathbf{6b}^{d_5})]/[k(\mathbf{2b}^{*} \rightarrow \mathbf{6b}^{*d_{10}})]$	2.3 (5)
k_H/k_D (benzyne path) = $[k(\mathbf{2b}^{*} \rightarrow \mathbf{6b}^{*d_1})]/[k(\mathbf{2b}^{d_{10}} \rightarrow \mathbf{6b}^{d_4})]$	4.1 (8)

[a] Scheme III. [b] Scheme IV. [c] Scheme V.

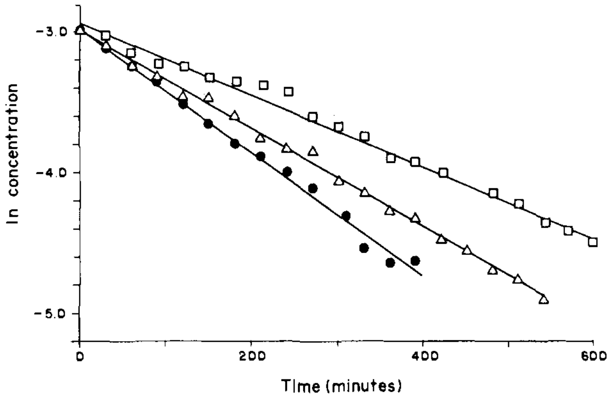
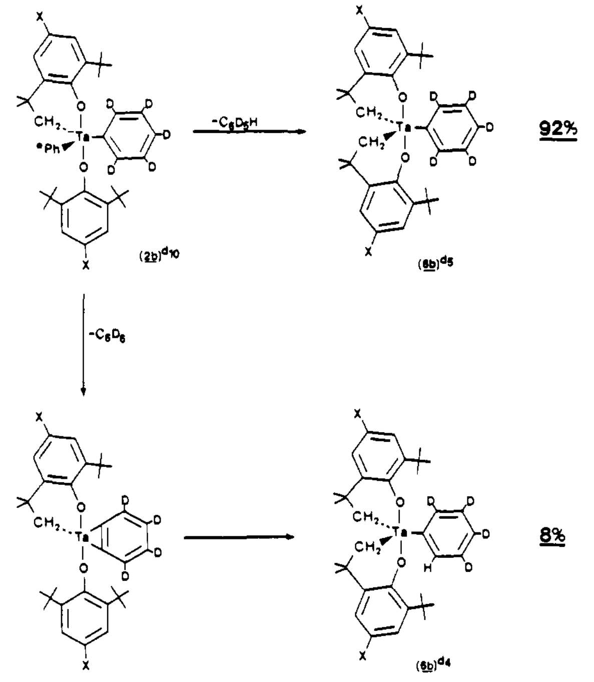
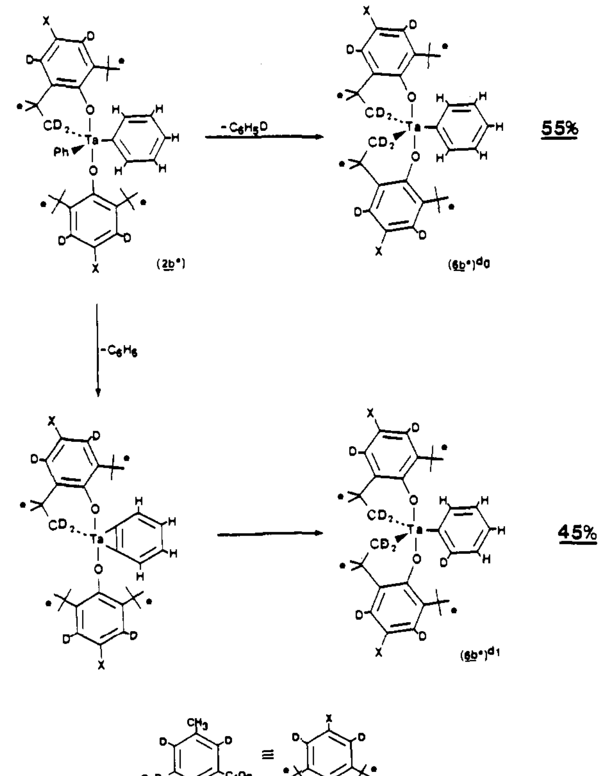


Figure 3. First-order plots for the disappearance of **2b** (●), $\mathbf{2b}^{d_{10}}$ (△), and **2b*** (□).

Scheme IV



Scheme V



sition state.[4] A mechanistically related reaction is the sometimes synthetically valuable hydrogenolysis of high-valent, early-transition-metal–alkyl bonds.[4a,20–23] Again a four-center, four-electron transition state has been proposed. A study by Schwartz et al. on the hydrogenolysis of a series of compounds $Cp_2Zr(X)(R)$ showed little difference in the rate of the reaction on going from X = R to X = Cl.[22] Similarly, no difference in reactivity was mentioned by Bercaw and Mayer for the hydrogenolysis of the compounds Cp^*TaMe_4 and Cp^*TaMe_3Cl.[21] The acceleration in the rate of cyclometalation of the aryl oxide ligands in the present work on going from **2** to **4** may, therefore, indicate a significant difference between heterolytic pathways involving H–H and C–H bonds. Certainly the trend helps explain the instability of the proposed intermediate $Ta(OAr')_2Cl_2(Ph)$ toward intramolecular CH bond activation.

However, in the case of the conversion of the diphenyl **2** to **6** one has to consider the possibility of a pathway involving a benzyne intermediate. There is considerable precedence for such intermediates in early-transition-metal organometallic chemistry, including the structural characterization of two derivatives of this functionality.[8–13] The reaction of trichloride **1b** with 3 equiv of LiC_6D_5 allows the isolation of the monocyclometalated compound $Ta(OC_6H_3Bu^tCMe_2CH_2)(OAr')(C_6D_5)_2$ ($\mathbf{2b}^{d_{10}}$). The formation of this complex as essentially pure d_{10} (by mass spectroscopy) and the absence of any Ta–Ph resonances in the ^1H NMR spectrum are consistent with the reaction sequence proposed for converting **1** to **2** (Scheme II). However, comparing the rates of cyclometalation of **2b** and $\mathbf{2b}^{d_{10}}$ shows a definite, although rather slight, retardation of the rate of the cyclometalation of the second aryl oxide ligand (Figure 3). Mass spectrometric analysis of the product of thermolysis of $\mathbf{2b}^{d_{10}}$ at 118 °C showed a mixture of $\mathbf{6b}^{d_5}$ (92%) and $\mathbf{6b}^{d_4}$ (8%). We interpret this result as indicating two pathways to the biscyclometalated, monophenyl compound **6b** (Scheme IV). One involves direct combination of the *tert*-butyl CH bond hydrogen atom with the Ta–Ph leaving group, while the other involves the formation of an intermediate benzyne (*o*-phenylene) functionality. The latter reaction pathway then involves the activation of the aliphatic CH bond by a metal–carbon bond in the strained metallacyclopropane ring. Confirmation of this

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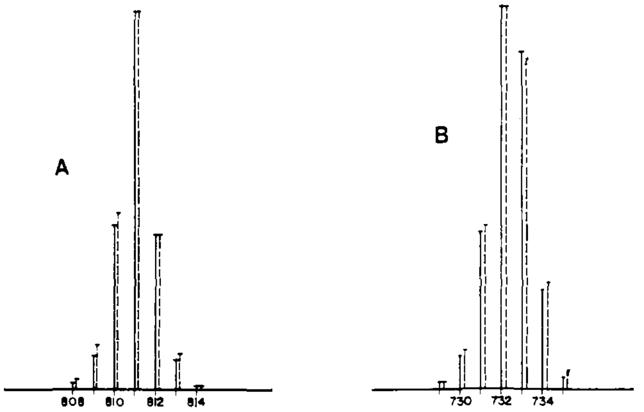


Figure 4. Observed (solid) and simulated (dashed) mass spectral patterns (A) for the parent molecular ion of $\mathbf{2b}^*$, simulated by using 98.5% deuteriation in the 39 aryl oxide aliphatic and aromatic positions, and (B) for the parent molecular ions of the products from thermolysis of $\mathbf{2b}^*$ at 118 °C, simulated by using (55% $\mathbf{6b}^{*d_0}$ + 45% $\mathbf{6b}^{*d_1}$) (Scheme V).

hypothesis comes from the thermolysis of the deuteriated aryl oxide compound $Ta[OC_6D_2Bu^t(CD_3)_2CD_2\text{-}4\text{-}CH_3](OAr^*\text{-}4\text{-}CH_3)(C_6H_5)_2$ ($\mathbf{2b}^*$) formed by treatment of $Ta(OAr^*\text{-}4\text{-}Me)_2Cl_3$ ($\mathbf{1b}^*$) with LiC_6H_5 (Scheme V). The deuteriation of the aryl oxide *tert*-butyl groups causes a more pronounced retardation of the rate of cyclometalation (Figure 3). The two pathways are again confirmed by mass spectrometric analysis of the product (Figure 4), showing both $\mathbf{6b}^{*d_0}$ (55%) and $\mathbf{6b}^{*d_1}$ (45%) (Scheme V). By combining the kinetic measurements with the mass spectrometric data, one can determine the relative importance of the two pathways as well as the kinetic isotope effects associated with each one. This treatment assumes the observed rate constants are the linear sum of the rates for each of the two pathways. Furthermore, it is also assumes that deuteriation of the Ta-Ph and OAr′-4-Me carbon-hydrogen bonds will only affect the rates of the benzyne intermediate and direct pathways, respectively. The kinetic data and results of this treatment are collected in Table III. The internal consistency of these results can be seen by comparing the observed rate of ring closure of the unlabeled compound **2b** with that predicted from the data obtained from the thermolysis of $\mathbf{2b}^{d_{10}}$ and $\mathbf{2b}^*$.

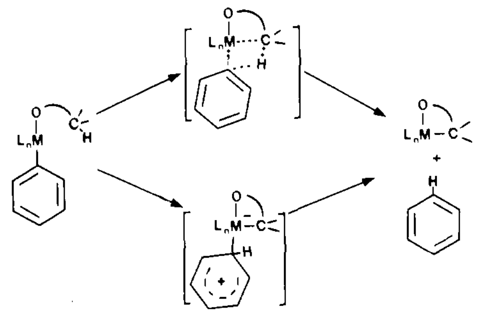
The primary kinetic isotope effect obtained for the formation of the benzyne intermediate, 4.1 (8) at 118 °C, compares favorably with the value of 6.5 (10) reported by Marks et. al for the formation of an intermediate benzyne from $Cp^*_2Zr(Ph)_2$.[8a] The formation of benzyne ligands bound to this and other d^0-metal centers presumably proceeds via a multicenter transition state.[4] The value of 2.3 (5) for the primary kinetic isotope effect associated with the direct pathway is smaller than values reported by other workers for mechanistically related cyclometalation reactions.[4b] However, it can be compared with the value of 1.9 (5) found for the directly related ring-closure reaction of $Ta(OC_6H_2\text{-}4\text{-}Me\text{-}Bu^tCMe_2CH_2)(OAr'\text{-}4\text{-}Me)(CH_3)_2$ at 135 °C.[24] The mechanistic significance of the magnitude of k_H/k_D values in these types of reactions is presently unclear.

Substituent Effects. We have examined the effect that certain substituents introduced into the Ta-Ar leaving group have on the rates of these cyclometalation reactions. Treatment of the halide $Ta(OAr'\text{-}4\text{-}CH_3)_2Cl_3$ (**1b**) with 3 equiv of the reagent LiC_6H_4X (X = 2-Me, 3-Me, 4-Me) or $BrMgC_6H_4X$ (X = 3-F, 4-F) allows the isolation of the corresponding monocyclometalated derivatives $\mathbf{2b}^{2Me} \rightarrow \mathbf{2b}^{4F}$. Analysis of these compounds by 470-MHz ^1H NMR indicates that the products are isomerically pure, containing the substituents in both aryl groups in the same position as initially contained in the original alkylating reagents. The yield of the *o*-tolyl compound $\mathbf{2b}^{2Me}$ was found to be much lower than for the other derivatives.

Table IV. Rates of Cyclometalation of Substituted Aryl Derivatives at 118 °C

substrate	$10^5k/s^{-1}$	substrate	$10^5k/s^{-1}$
2b	7.3 (4)	$\mathbf{2b}^{3F}$	14.3 (9)
$\mathbf{2b}^{3Me}$	10.4 (7)	$\mathbf{2b}^{4F}$	9.6 (5)
$\mathbf{2b}^{4Me}$	8.9 (4)		

Scheme VI



Thermolysis of these compounds at 118 °C in toluene solution resulted in the formation of 1 equiv of toluene or fluorobenzene and a series of biscyclometalated derivatives. The rates of cyclometalation are contained in Table IV. In the case of $\mathbf{2b}^{2Me}$ considerable amounts of decomposition on thermolysis were observed, making useful kinetic measurements impossible. Temporarily ignoring the added complexity (vide infra) that there are two demonstrated possible pathways for these reactions, it can be seen that there is only a small effect on the rate of the reaction for this rather limited range of substituents. Only a small substituent effect was also observed for the cyclometalation of the aryl oxide ligands in the substituted benzyl compounds $Zr(OAr')_2(CH_2C_6H_4X)_2$ (X = H, 3-Me, 4-Me, 3-F).[14] Recent elegant work by Bercaw et al. on the intermolecular activation of arene CH bonds by scandium systems, $Cp^*_2Sc(R)$ (Cp^* = C_5Me_5), has shown not only small substituent effects on the rate of reaction but also negligible directing effects.[25] These data were used to argue against a reaction pathway involving direct electrophilic attack of the electron-deficient metal center on the aromatic ring to produce a "Wheland" type intermediate. Instead a multicenter transition state pathway was favored in which the aromatic π-system was not perturbed.[25] The "direct" pathway identified in the present study in which the aliphatic CH bond transfers a hydrogen to an aryl leaving group can be mechanistically related (by microscopic reversibility) to the intermolecular activation of aromatic CH bonds by metal-alkyl bonds. Again two mechanistic pathways can be proposed (Scheme VI). The data in this study, indicating a small substituent effect, again do not support the idea for the pathway in which the hydrogen atom of the activated CH bond transfers to the aryl ipso carbon as an incipient proton to generate a "metallo-Wheland" intermediate.

Aryl Isomerization via Reversible Benzyne Formation.[26] As noted above, this system is complicated by the demonstrated presence of a second pathway involving a benzyne intermediate. An even more complicating factor is our observation that the product biscyclometalated derivatives can reversibly regenerate this benzyne intermediate on thermolysis. The most conclusive evidence for this reactivity comes from a study of the effect of thermolysis on the labeled product formed by heating $\mathbf{2b}^{d_{10}}$. This product was shown to contain 92% $\mathbf{6b}^{d_5}$ and 8% $\mathbf{6b}^{d_4}$. Analysis of the high-field ^1H NMR spectrum of this initial mixture does indeed show a small singlet at δ 8.15 ppm due to the fraction of protons incorporated selectively into the ortho positions of the Ta-Ph group via the benzyne intermediate pathway (Scheme IV). However, on extended thermolysis the intensity of this proton

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Scheme VII

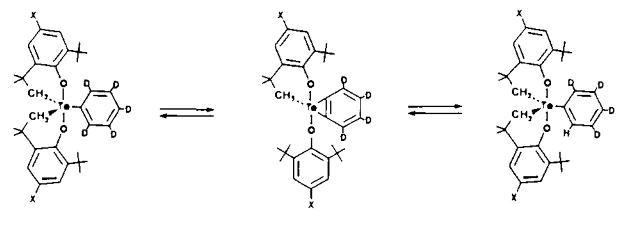


Table V. Product Distribution from Thermolysis of Substituted Aryl Derivatives at 118 °C

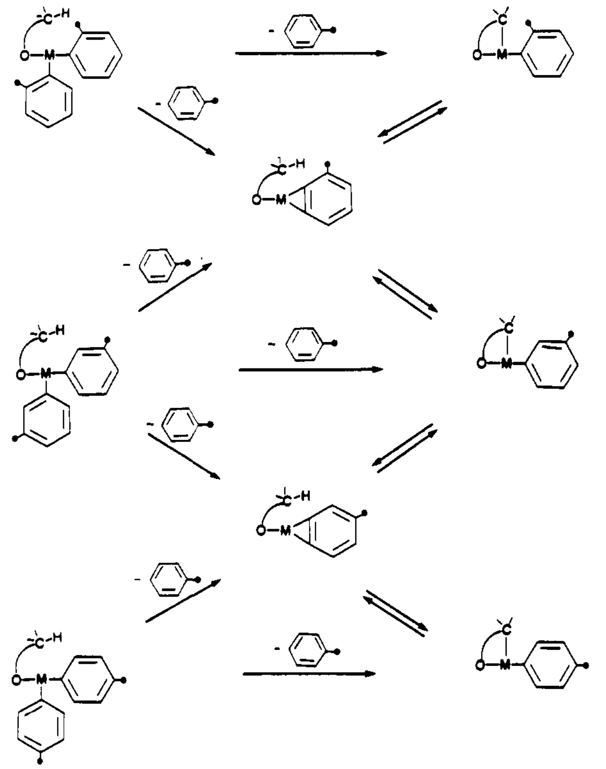
substrate	products, %		
	6b^{2X}	**6b**^{3X}	**6b**^{4X}
2b^{2Me}	0	70	30[a]
2b^{3Me}	0	60	40[a]
2b^{4Me}	0	25	75[a]
2b3F	0	>95	<5[b]
2b^{4F}	0	<5	>95[b]

[a] Extended thermolysis leads to a 50:50 mixture of **6b**^{3Me} and **6b**^{4Me}. [b] Extended thermolysis results in no change in product ratios but eventually leads to decomposition.

signal was found to increase dramatically. Signals due to the incorporation of protons into the meta and eventually the para positions of this ring were also noticed. Extended heating in toluene-d_8 resulted in a ^{1}H NMR spectrum that was essentially indistinguishable in the aromatic region from that of unlabeled **6b**. Complementary studies of the ^{2}H NMR spectra during this process proved informative. Initially all of the deuterium label was observed to be contained in the aromatic region at δ 8.1 and 7.0 due to the ortho and meta/para CD bonds in the Ta–Ph group. However, on thermolysis intensity begins to build up in the aliphatic region at chemical shifts similar to those of both the metalated and unmetalated *tert*-butyl groups of the aryl oxide ligand in unlabeled **6b**. This intramolecular scrambling of the deuterium label is consistent with a reaction in which the alkyl carbon of one of the metallacycle rings in **6b**^{d_5} abstracts an ortho deuterium from the Ta–Ph group to generate the monocyclometalated benzyne intermediate previously proposed in the formation of **6** from **2** (Scheme VII). Intramolecular ring closure in which one of the CH bonds of the generated 2,6-di-*tert*-butylphenoxide ligand inserts into one side of the metallocyclopropane ring regenerates the biscyclometalated product with a proton selectively incorporated into the ortho positions of the Ta–Ph function (Scheme VII). Repeating this process can be seen to lead to scrambling of the label throughout all metalated and nonmetalated *tert*-butyl and Ta–Ph groups.

Further confirmation of this mechanism comes from analysis of the products of thermolysis of the three tolyl derivatives **2b**^{2Me}, **2b**^{3Me}, and **2b**^{4Me}. The use of high-field ^{1}H NMR indicated the presence in the initial products of a mixture of isomers. The amounts of each isomer were quantified by integration of the very distinctive and well-resolved signals due to the ortho protons in each tolyl isomer. Table V contains the results of this analysis. Although the reaction is not clean, thermolysis of the *o*-tolyl compound **2b**^{2Me} definitely results in a mixture of *both* **6b**^{3Me} and **6b**^{4Me}. It is impossible to proceed directly to **6b**^{4Me} from **2b**^{2Me} via a single benzyne intermediate. One has to again propose the benzyne equilibrium previously proposed (Scheme VII). Furthermore, it is found that on extended heating of the three initial mixtures obtained they eventually stabilize as an approximately equimolar mixture of the meta and para derivatives **6**^{3Me} and **6**^{4Me} (Table V). The isomerization pathways via the two common intermediates 2-methyl- and 3-methylbenzyne are shown in (Scheme VIII). The facility of this isomerization makes it difficult to evaluate the two alternate pathways for the cyclometalation of these tolyl derivatives. However, the isomerization process allows the conclusion that in this particular system the thermodynamically favored percentages of *o*-, *m*-, and *p*-tolyl isomers is 0:50:50. The work of Bercaw and co-workers on the Cp*$_2$Sc(tolyl) system showed an equilibrium concentration of the three isomers of approximately 10:60:30.[25] Ignoring the obvious steric destabilization expectedfor *o*-tolyl derivatives, one finds the m:p ratio is close to statistical in this case. The energetically very small difference between this ratio and that observed in this particular study was possibly be due to steric destabilization of the *m*-tolyl isomer by the phenoxide ligation rather than electronic effects.

Scheme VIII



The reactivity found for the tolyl compounds contrasts with that seen for the fluorophenyl derivatives **2b**^{3F} and **2b**^{4F}. The products of thermolysis at 118 °C were found to contain only small amounts of isomerized aryl groups. Furthermore, extended heating of the final products resulted in no dramatic changes in the initial ratios of **6b**^{3F} and **6b**^{4F}. At elevated temperatures (140 °C) only decomposition to dark solutions was observed. It would, therefore, appear that the benzyne intermediates shown in Scheme VIII are less readily accessible with fluoro substituents than for the tolyl or unsubstituted compounds.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere or in vacuo either in a Vacuum Atmospheres Dri-Lab or by standard Schlenck techniques. Hydrocarbon solvents were dried by distillation from sodium benzophenone and stored under nitrogen. Ta(OAr′)$_2$Cl$_3$ (**1a**), Ta(OAr′-4-Me)$_2$Cl$_3$ (**1b**), and Ta(OAr′-4-OMe)$_2$Cl$_3$ (**1c**) were obtained by previously reported procedures.[7] Both of the deuteriated compounds C_6D_5Br and 4-methyl-2,6-di-*tert*-butyl(-d_9-)phenol-d_2-*O*-*d* (vide infra) were purchased from Merck and Co. Although ClMgC$_6$H$_4$-*p*-F was obtained commercially, all other metal aryls were synthesized from the corresponding bromides and either Bu^{n}Li or Mg metal. ^{1}H, ^{2}H, and ^{13}C NMR spectra were recorded on Varian Associates XL-200 and Nicolet (Oxford Magnet) 470-MHz spectrometers and are referenced to Me$_4$Si using the protio impurities of commercial benzene-d_6 or toluene-d_8 as internal standards. Mass spectra were recorded on a Finnigan 4000 spectrometer using perfluorobutylamine for calibration. Microanalyses were obtained in-house at Purdue. Considerable difficulties were encountered in obtaining accurate microanalytical data for some of these compounds. In particular, the values for percentage carbon were consistently found to be low, a fact we ascribe to the possible formation of metal carbides on combustion.

Electrochemical measurements were performed with a BioAnalytical Systems Inc. Model CV-27 instrument. A three-component H-cell was used with 0.2 M TBAH/THF solutions. Cyclic voltammograms were obtained with a Pt disk and Ag quasi-reference electrode against which the Cp$_2$Fe$^{0/+}$ couple lies at +0.47 V. Due to the similarity of some of the synthetic procedures, only representative methods will be presented for each type of compound.

Monocyclometalated Compounds 2, 3, and 4. Ta(OC$_6$H$_3$Bu^{t}CMe$_2$CH$_2$)(OAr′)(C$_6$H$_5$)$_2$ (2a). To an orange solution of Ta(OAr′)$_2$Cl$_3$ (**1a**) (1.0 g) in benzene (25 mL) was slowly added solid LiC$_6$H$_5$ (0.39 g, slight excess). The resulting suspension was stirred for 2 h at room temperature. The solution was filtered and the solvent removed in vacuo to leave the crude product as a pale powder, which was washed with a small amount of hexane. The compound proved difficult to recrystallize. However, crystals suitable for X-ray diffraction analysis were obtained from a saturated hexane solution on cooling to −15 °C. Anal. Calcd for TaC$_{40}$H$_{51}$O$_2$: C, 64.51; H, 6.89. Found: C, 64.30; H, 6.82. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.21 (s, Ta–C*H*$_2$CMe$_2$), 1.42 (s, Ta–CH$_2$C*Me*$_2$), 0.96 (s, OC$_|$H$_3$*Bu*^{t}CMe$_2$CH$_2$), 1.24 (s, *Bu*^{t} of OAr′), 8.10 (m, *o*-H of Ta–C$_6$H$_5$), 6.9–7.2 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 100.8 (Ta–*C*H$_2$CMe$_2$), 39.3 (Ta–CH$_2$*C*Me$_2$), 200.1 (ipso, Ta–C$_6$H$_5$), 35.2 (Ta–CH$_2$C*Me*$_2$), 33.4, 33.6 (*C*Me$_3$), 31.9, 32.5 (C*Me*$_3$).

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)(OAr′-4-Me)(C$_6$H$_5$)$_2$ (2b). This compound was obtained in an identical fashion to **2a**, only using Ta(OAr′-4-Me)$_2$Cl$_3$ (**1b**). Anal. Calcd for TaC$_{42}$H$_{55}$O$_2$: C, 65.30; H, 7.20. Found: C, 63.95; H, 7.58. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.25 (s, Ta–C*H*$_2$CMe$_2$), 1.46 (s, Ta–CH$_2$C*Me*$_2$), 1.04 (s, OC$_6$H$_2$*Bu*^{t}), 1.32 (s, *Bu*^{t} of OAr′-4-Me), 2.21 (s), 2.28 (s, 4-*Me*), 8.05 (m, *o*-H of Ta–C$_6$H$_5$), 7–7.2 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 99.8 (Ta–*C*H$_2$CMe$_2$), 38.0 (Ta–CH$_2$*C*Me)$_2$, 202.9 (ipso, Ta–C$_6$H$_5$), 34.9 (Ta–CH$_2$C*Me*$_2$), 34.3, 35.3 (*C*Me$_3$), 31.0, 32.6 (C*Me*$_3$), 21.1, 21.5 (4-*Me*).

Ta(OC$_6$H$_2$-4-OMe-Bu^{t}CMe$_2$CH$_2$)(OAr′-4-OMe)(C$_6$H$_5$)$_2$ (2c). ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.21 (s, Ta–C*H*$_2$CMe$_2$), 1.43 (s, Ta–CH$_2$C*Me*$_2$), 0.96 (s, OC$_6$H$_2$*Bu*^{t}), 1.28 (s, *Bu*^{t} of OAr′-4-OMe), 3.36 (s), 3.37 (s, 4-O*Me*), 8.30 (m, *o*-H of Ta–C$_6$H$_5$), 6.8–7.1 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 99.1 (Ta–*C*H$_2$CMe$_2$), 39.8 (Ta–CH$_2$*C*Me$_2$), 200.8 (ipso, Ta–C$_6$H$_5$), 35.7 (Ta–CH$_2$C*Me*$_2$), 34.2, 35.3 (*C*Me$_3$), 30.4, 32.1 (C*Me*$_3$), 54.9, 55.7 (4-O*Me*).

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)(OAr′)(C$_6$H$_4$-2-Me)$_2$ (2b^{2Me}). This compond was obtained as above, only using LiC$_6$H$_4$-2-Me. The yield of **2b**^{2Me} was much lower than for the other metalated compounds due to the formation of quantities of dark, insoluble byproducts. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.33 (s, Ta–C*H*$_2$CMe$_2$), 1.64 (s, Ta–CH$_2$C*Me*$_2$), 1.07 (s, OC$_6$H$_2$*Bu*^{t}), 1.32 (s, *Bu*^{t} of OAr′-4-Me) 8.62 (m, *o*-H of Ta–C$_6$H$_4$-2-Me), 2.01 (s, Ta–C$_6$H$_4$-2-*Me*), 6.9–7.3 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 96.5 (Ta–*C*H$_2$CMe$_2$), 39.2 (Ta–CH$_2$*C*Me$_3$), 201.5 (ipso, Ta–C$_6$H$_4$-2-Me), 37.2 (Ta–CH$_2$C*Me*$_2$), 34.9, 35.9 (*C*Me$_3$), 30.8, 32.1 (C*Me*$_3$), 25.7 (C$_6$H$_4$-2-*Me*).

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)(OAr′)(C$_6$H$_4$-3-Me)$_2$ (2b^{3Me}). ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.16 (s, Ta–C*H*$_2$CMe$_2$), 1.38 (s, Ta–CH$_2$C*Me*$_2$), 1.00 (s, OC$_6$H$_2$*Bu*^{t}), 1.26 (s, *Bu*^{t} of OAr′-4-Me), 2.12 (s), 2.18 (s, 4-*Me*), 1.99 (s, C$_6$H$_4$-3-*Me*), 7.87 (d), 7.93 (s, *o*-H's of Ta–C$_6$H$_4$-3-Me), 7–7.2 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 99.6 (Ta–*C*H$_2$CMe$_2$), 38.0 (Ta–CH$_2$*C*Me$_2$), 203.2 (ipso, Ta–C$_6$H$_4$-3-Me), 35.1 (Ta–CH$_2$C*Me*$_2$), 34.4, 35.5 (*C*Me$_3$), 31.1, 32.8 (C*Me*$_3$), 21.6, 21.8 (4-*Me*), 26.5 (C$_6$H$_4$-3-*Me*).

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)(OAr′)(C$_6$H$_4$-4-Me)$_2$ (2b^{4Me}). Anal. Calcd for TaC$_{44}$H$_{59}$O$_2$: C, 65.97; H, 7.43. Found: C, 65.79; H, 7.58. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.15 (s, Ta–C*H*$_2$CMe$_2$), 1.38 (s, Ta–CH$_2$C*Me*$_2$), 1.01 (s, OC$_6$H$_2$*Bu*^{t}), 1.26 (s, *Bu*^{t} of OAr′-4-Me), 2.11 (s), 2.18 (s, 4-*Me*), 1.95 (s, C$_6$H$_4$-4-*Me*), 7.95 (m, *o*-H of Ta–C$_6$H$_4$-4-Me), 7–7.2 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 99.4 (Ta–*C*H$_2$CMe$_2$), 38.7 (Ta–CH$_2$*C*Me$_2$), 200.3 (ipso, Ta–C$_6$H$_4$-4-Me), 35.0 (Ta–CH$_2$C*Me*$_2$), 34.4, 35.4 (*C*Me$_3$), 31.2, 32.8 (C*Me*$_3$), 21.1, 21.7 (4-*Me*), 27.1 (C$_6$H$_4$-4-*Me*).

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)(OAr′-4-Me)(C$_6$H$_4$-3-F)$_2$ (2b^{3F}). This compound was obtained by treating **1b** with BrMgC$_6$H$_4$-3-F. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.16 (s, Ta–C*H*$_2$CMe$_2$), 1.29 (s, Ta–CH$_2$C*Me*$_2$), 0.97 (s, OC$_6$H$_2$*Bu*^{t}), 1.20 (s, *Bu*^{t} of OAr′-4-Me), 2.13 (s), 2.21 (s, 4-*Me*), 7.63 (m), 7.84 (m, *o*-H's of Ta–C$_6$H$_4$-3-F), 7–7.2 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 102.4 (Ta–*C*H$_2$CMe$_2$), 38.8 (Ta–CH$_2$*C*Me$_2$), 203.7 (ipso, Ta–C$_6$H$_4$-3-F), 34.9 (Ta–CH$_2$C*Me*$_2$), 34.2, 35.4 (*C*Me$_3$), 31.0, 32.7 (C*Me*$_3$), 21.2, 21.6 (4-*Me*).

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)(OAr′-4-Me)(C$_6$H$_4$-4-F)$_2$ (2b^{4F}). ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.08 (s, Ta–C*H*$_2$CMe$_2$), 1.31 (s, Ta–CH$_2$C*Me*$_2$), 0.93 (s, OC$_6$H$_2$*Bu*^{t}), 1.17 (s, *Bu*^{t} of OAr′-4-Me), 2.13 (s), 2.20 (s, 4-*Me*), 7.74 (m, *o*-H of Ta–C$_6$H$_4$-4-F), 6.7–7.1 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 101.7 (Ta–*C*H$_2$CMe$_2$), 39.1 (Ta–CH$_2$*C*Me$_2$), 198.0 (ipso, Ta–C$_6$H$_4$-4-F), 35.4 (Ta–CH$_2$C*Me*$_2$), 34.8, 35.9 (*C*Me$_3$), 31.5, 33.1 (C*Me*$_3$), 21.7, 22.0 (4-*Me*).

Ta(OC$_6$H$_3$Bu^{t}CMe$_2$CH$_2$)(OAr′)Cl$_2$ (3a). Addition of only 1 equiv of LiPh to cooled hydrocarbon solutions of **1a** led to a deep yellow solution from which, after filtration, the monometalated dichloride **3a** was obtained as a yellow powder. Anal. Calcd for TaC$_{28}$H$_{40}$O$_2$Cl$_2$: C, 50.83; H, 6.25; Cl, 10.71. Found: C, 49.41; H, 6.52; Cl, 10.57. ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 100.6 (Ta–*C*H$_2$CMe$_2$), 39.1 (Ta–CH$_2$*C*Me$_2$), 35.1 (Ta–CH$_2$C*Me*$_2$), 32.4, 33.0 (*C*Me$_3$), 30.3, 30.5 (C*Me*$_3$).

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)(OAr′-4-Me)(C$_6$H$_5$)Cl (4b). To a solution of Ta(OAr′-4-Me)$_2$Cl$_3$ (**1b**) (30.75 g) in benzene (25 mL) was slowly added solid LiC$_6$H$_5$ (0.154 g, 2 equiv). The resulting mixture was stirred for 1 h and filtered, and the solvent was removed in vacuo to leave the product as a fine yellow powder. Anal. Calcd for TaC$_{36}$H$_{51}$O$_2$Cl: C, 59.10; H, 6.89; Cl, 4.85. Found: C, 58.33; H, 7.12; Cl, 5.65. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.45 (d), 3.48 (d, Ta–C*H*$_2$CMe$_2$), 1.42 (s), 1.44 (s), 1.50 (s, overlapping resonances due to Ta–CH$_2$C*Me*$_2$ and *Bu*^{t} groups), 2.19 (s, 4-*Me*), 8.77 (m, *o*-H of Ta–C$_6$H$_5$), 7–7.25 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 103.6 (Ta–*C*H$_2$CMe$_2$), 39.9 (Ta–CH$_2$*C*Me$_2$), 211.9 (ipso, Ta–C$_6$H$_5$), 35.8, 38.2 (Ta–CH$_2$C*Me*$_2$), 34.9, 35.6 (*C*Me$_3$), 30.9, 32.5 (C*Me*$_3$), 21.8, 22.0 (4-*Me*).

Biscyclometalated Compounds 5 and 6. All of the biscyclometalated compounds were obtained by thermolysis in sealed flasks of the monometalated precursors in toluene at a temperature of 118 °C for various periods of time. Removal of solvent gave the products in essentially quantitative yield except for the *o*-tolyl compound **2b**^{2Me}, which underwent significant decomposition on thermolysis.

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)$_2$Cl (5b). ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.30, 2.68 (d, Ta–C*H*$_2$CMe$_2$), 1.29 (s), 1.33 (s, Ta–CH$_2$C*Me*$_2$), 1.75 (s, *Bu*^{t}), 2.35 (s, 4-*Me*), 7–7.3 (m, aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 101.5 (Ta–*C*H$_2$CMe$_2$), 39.6 (Ta–CH$_2$*C*Me), 35.3, 35.4 (Ta–CH$_2$C*Me*$_2$), 33.9 (*C*Me$_3$), 30.5 (C*Me*$_3$), 21.5 (4-*Me*).

Ta(OC$_6$H$_3$Bu^{t}CMe$_2$CH$_2$)$_2$(C$_6$H$_5$) (6a). ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 1.60 (d), 2.27 (d, Ta–C*H*$_2$CMe$_2$), 1.28 (s), 1.32 (s, Ta–CH$_2$C*Me*$_2$), 1.57 (s, *Bu*^{t}), 8.11 (m, *o*-H of Ta–C$_6$H$_5$), 7–7.2 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 96.5 (Ta–*C*H$_2$CMe$_2$), 39.9 (Ta–CH$_2$*C*Me$_2$), 35.4, 35.5 (Ta–CH$_2$C*Me*$_2$), 33.8 (*C*Me$_3$), 31.5 (C*Me*$_3$), 203.1 (ipso, Ta–C$_6$H$_5$).

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)$_2$(C$_6$H$_5$) (6b). ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.21 (d), 1.59 (d, Ta–C*H*$_2$CMe$_2$), 1.28 (s), 1.33 (s, Ta–CH$_2$C*Me*$_2$), 1.65 (s, *Bu*^{t}), 2.29 (s, 4-*Me*), 8.15 (m, *o*-H of Ta–C$_6$H$_5$), 7–7.3 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 96.4 (Ta–*C*H$_2$CMe$_2$), 39.8 (Ta–CH$_2$*C*Me$_2$), 35.3, 36.0 (Ta–CH$_2$C*Me*$_2$), 34.2 (*C*Me$_3$), 3.16 (C*Me*$_3$), 21.5 (4-*Me*), 202.7 (ipso, Ta–C$_6$H$_5$).

Ta(OC$_6$H$_2$-4-OMe-Bu^{t}CMe$_2$CH$_2$)$_2$(C$_6$H$_5$) (6c). ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 1.72 (d), 2.32 (d, Ta–C*H*$_2$CMe$_2$), 1.42 (s), 1.46 (s, Ta–CH$_2$C*Me*$_2$), 1.69 (s, *Bu*^{t}), 3.57 (s, 4-OMe), 8.11 (m, *o*-H of Ta–C$_6$H$_5$), 6.9–7.4 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 95.5 (Ta–*C*H$_2$CMe$_2$), 39.7 (Ta–CH$_2$*C*Me$_2$), 35.3, 35.5 (Ta–CH$_2$C*Me*$_2$), 33.5 (*C*Me$_3$), 31.0 (C*Me*$_3$), 54.6 (4-O*Me*), 201.9 (ipso, Ta–C$_6$H$_5$).

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)$_2$(C$_6$H$_4$-3-Me) (6b^{3Me}) and Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)$_2$(C$_6$H$_4$-4-Me) (6b^{4Me}). Thermolysis of the monometalated compounds **2b**^{2Me}, **2b**^{3Me}, and **2b**^{4Me} results in mixtures of **6b**^{3Me} and **6b**^{4Me}. The majority of the signals in the ^{1}H and ^{13}C NMR due to these isomers are unresolvable. However, each isomer can be quantified due to the very characteristic and different resonances due to the ortho protons of the Ta–C$_6$H$_4$-3-Me and Ta–C$_6$H$_4$-4-Me groups.

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)$_2$(C$_6$H$_4$-3-F) (6b^{3F}). ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.71 (d), 1.85 (d, Ta–C*H*$_2$CMe$_2$), 1.38 (s), 1.42 (s, Ta–CH$_2$C*Me*$_2$), 1.67 (s, *Bu*^{t}), 2.31 (4-*Me*), 7.9 (m), 8.1 (m, *o*-H's, Ta–C$_6$H$_4$-3-F), 7–7.3 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 97.6 Ta–*C*H$_2$CMe$_2$), 40.4 (Ta–CH$_2$*C*Me$_2$), 35.7, 36.4 (Ta–CH$_2$C*Me*$_2$), 34.4 (*C*Me$_3$), 32.0 (C*Me*$_3$), 22.0 (4-*Me*), 203.0 (ipso, Ta–C$_6$H$_4$-3-F).

Ta(OC$_6$H$_2$-4-Me-Bu^{t}CMe$_2$CH$_2$)$_2$(C$_6$H$_4$-4-F) (6b^{4F}). ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 2.78 (d), 1.78 (d, Ta–C*H*$_2$CMe$_2$), 1.38 (s), 1.40 (s, Ta–CH$_2$C*Me*$_2$), 1.64 (s, *Bu*^{t}), 2.29 (s, 4-*Me*), 8.05 (m, *o*-H in Ta–C$_6$H$_4$-4-F), 6.8–7.2 (m, other aromatics). ^{13}C NMR (C$_6$D$_6$, 30 °C): δ 96.8 (Ta–*C*H$_2$CMe$_2$), 39.8 (Ta–CH$_2$*C*Me$_2$), 35.3, 36.0 (Ta–CH$_2$C*Me*$_2$), 34.2 (*C*Me$_3$), 31.6 (C*Me*$_3$), 21.5 (4-*Me*), 198.2 (ipso, Ta–C$_6$H$_4$-4-F).

Synthesis and Analysis of Deuterium-Labeled Compounds. Ta(OC$_6$H$_3$-4-Me-Bu^{t}CMe$_2$CH$_2$)(OAr′-4-Me)(C$_6$D$_5$)$_2$ (2b$^{d_{10}}$). This compound was obtained by treatment of Ta(OAr′-4-Me)$_2$Cl$_3$ with LiC$_6$D$_5$ (formed from C$_6$D$_5$Br, 99.5% D) in a fashion identical with that used for the protio compound. Mass spectroscopic analysis of the product showed it to contain <5% of the d_9 compound and the correct pattern expected on the basis of the natural-abundance ^{13}C isotope. The ^{1}H NMR spectrum of **2b**$^{d_{10}}$ was identical with that of unlabeled **2b** except for the total lack of signals due to the Ta–Ph function.

The thermolysis of **2b**$^{d_{10}}$ was carried out at 118 °C in toluene solution in a sealed tube. Analysis of the resulting biscyclometalated compound by mass spectrometry indicated a mixture of **6b**^{d_5} and **6b**^{d_4} (Scheme IV). The pattern obtained from the mass spectrum was fitted to a simulated spectrum that indicated a 92:8 ratio for those two molecules.

Ta[OC$_6$D$_2$-4-CH$_3$-Bu^t-*d*$_9$-C(CD$_3$)$_2$CD$_2$](OAr*-4-Me)(C$_6$H$_5$)$_2$ (2b*). The labeled halide Ta(OAr*-4-Me)$_2$Cl$_3$ was obtained from TaCl$_5$ and LiOAr*-4-Me. Treatment of this with 2 equiv of LiC$_6$H$_5$ allowed the isolation of **2b***. Analysis of **2b*** by mass spectrometry showed a large parent molecular ion. The observed isotope pattern was matched to a

Table VI. Crystal Structure Determination Data for **2a**

formula	$TaC_{40}H_{51}O_2$
fw	744.79
space group	$P\bar{1}$
a, Å	15.438 (6)
b, Å	12.329 (4)
c, Å	10.639 (3)
α, deg	73.70 (2)
β, deg	67.38 (2)
γ, deg	69.07 (2)
Z	2
V, Å^3	1721.61
density (calcd), g/cm^3	1.437
crystal size, mm	*a*
crystal color	colorless
radiation	Mo Kα (λ = 0.71069 cm^{-1})
linear abs coeff, cm^{-1}	31.878
temp, °C	−171
detector aperature	3 mm wide × 4 mm high
takeoff angle, deg	2.0
scan speed, deg/min	4.0
scan width, deg	2.0 + dispersion
bkgd counts, s	3
2θ range, deg	6–45
unique data	4521
unique data with $F_o > 2.33\sigma(F)$	4089
$R(F)$	0.0322
$R_w(F)$	0.0318
goodness of fit	0.929
largest Δ/σ	0.05

simulated spectrum, the best fit being obtained when the amount of deuteriation in the phenoxide groups was set at 98.5% despite the 98% enrichment quoted by the commercial source. Thermolysis of **2b*** at 118 °C in toluene resulted in the biscyclometalated compound. Mass spectrometric analysis indicated a mixture of 55% **6b**^{*d_0} and 45% **6b**^{*d_1} (Scheme V), the amounts again being obtained by use of a simulation program (Figure 4).

Kinetic Measurements. The two thermal cyclometalation reactions were monitored kinetically in sealed, evacuated 5-mm NMR tubes in toluene-d_8 solvent. The sealed tubes were thermolyzed by total immersion in a constant-temperature oil bath. The tubes were removed after various amounts of time and cooled in cold water, and the extent of reaction was determined by ^{1}H NMR. Both the rate constants and activation parameters were determined with the use of a linear least-squares fitting procedure.

Structure Determination of 2a (Table VI). A suitable crystal was obtained and transferred to the goniostat by using standard inert-atmosphere handling techniques employed by the IUMSC.[27] A search of a limited hemisphere of reciprocal space indicated no systematic absenses of symmetry, and the space group was assigned $P\bar{1}$.

The structure was solved by a combination of Patterson techniques and Fourier synthesis, and all atoms, including hydrogen atoms, were located and refined. Final full-matrix refinement included isotropic thermal parameters for the hydrogen atoms and anisotropic thermal parameters for non-hydrogen atoms.

A final difference Fourier synthesis was essentially featureless, with the two largest peaks (1.21 and 1.19 e/Å^3) lying near the Ta.

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Supplementary Material Available: Series of mass spectral simulation patterns for compound **2b*** showing the best fit to be obtained with 98.5% deuteriation in the 39 labeled positions, ^{1}H NMR spectra of **2a** and **6a**, and tables of fractional coordinates of hydrogen atoms, anisotropic thermal parameters, and complete bond distances and angles (14 pages); observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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