

(THF)₄]⁺.⁵² Related structures had been previously reported by Bau for the [Cu₅Ph₆]⁻⁵³ and later for the [LiCu₄Ph₆]⁻⁵⁴ ions. When 12-crown-4 is added to a solution of LiCuPh₂ or LiCuMe₂, the lithium is abstracted from the aggregate, and the first mononuclear anions of the type [CuPh₂]⁻ or [CuMe₂]⁻⁵⁵ (Figure 16) are formed. Other species can also be trapped from the reaction mixtures as illustrated by the structure of the intermediate [Cu(Br)CH(SiMe₃)₂]⁻ ion⁵³ (Figure 17).

Conclusion

It is clear that 12-crown-4 is an effective agent for the removal of Li⁺ ions from many lithium compounds that are aggregated in solution. The main limitation to its effectiveness arises where lithium is strongly bound to its counteranion as in the case of NR₂⁻ and OR⁻ species. However, with the proper substituents, such as in [N-(SiPh₃)₂]⁻, separation can be achieved in certain cases. It may be that suitable modification of the OR⁻ ligand,

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as in [-OBMe₂]⁻⁵⁶ will also allow separation of a free [OR]⁻ anion. However, stronger Li⁺ coordinating agents such as the cryptand [211]⁵⁷ or spherand ligands⁵⁸ will be required to separate the more common NR₂⁻ and OR⁻ ions. There is also further scope for development in the choice of solvent. For example, use of amine solvents⁵ may permit the isolation of carbanions that are far too reactive to isolate in the presence of ethers. Thus, the characterization of a far wider range of reactive ions than is at present known is highly probable in the future.

The author gratefully acknowledges the many collaborators cited in the references who have contributed to this work and in particular the three redoubtable crystallographers Ruth Bartlett, Hakon Hope, and Marilyn Olmstead. Without them this work would have been impossible. Generous financial support from the National Science Foundation, the A. P. Sloan Foundation, the Petroleum Research Fund, and the Research Corp. is also acknowledged.

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Cyclometalation Chemistry of Aryl Oxide Ligation

IAN P. ROTHWELL

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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The search for homogeneous transition-metal systems that have the ability to activate normally inert carbon-hydrogen bonds under mild conditions has been the focus of endeavor by many research groups over the past two decades.¹ The significant successes achieved over the past few years have identified two general categories of compound that exhibit this type of reactivity. The first, more thoroughly studied, set involves the activation of carbon-hydrogen bonds by an oxidative-addition pathway to low-valent transition-metal centers.¹⁻⁴ This reactivity was initially extensively characterized for the intramolecular activation of the carbon-hydrogen bonds contained in various ligands already coordinated to the metal centers via a heteroatom site.⁵⁻⁷ However, more recently metal systems able to intermolecularly activate even the most difficult hydrocarbon substrate, methane, have been developed.⁸⁻¹² The second, still rapidly developing, area of metal-mediated carbon-hydrogen bond activation involves the use of high-valent, electron-deficient early-d-block,¹³ lanthanide,¹⁴ and actinide¹⁵ metal com-

pounds. Again, systems able to activate methane under mild conditions have been devised.^{16,17} The absence of an accessible oxidative-addition pathway for these electron-deficient systems has led to the proposal of mechanisms that are electrophilic in nature to account for the observed reactivity.^{18,19}

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Ian Rothwell was born in Manchester, England, in 1955. After receiving his B.Sc. (1976) and Ph.D. (1979) from University College, London, under the supervision of A. J. Deeming, he moved to Indiana University to carry out postdoctoral research with Malcolm H. Chisholm and then to Purdue University, where he is currently Associate Professor. Professor Rothwell's interests presently lie in the area of early-transition-metal inorganic and organometallic chemistry.

Table I
Activation Parameters for the Cyclometalation of Aryl Oxide Ligands at d⁰-Metal Centers

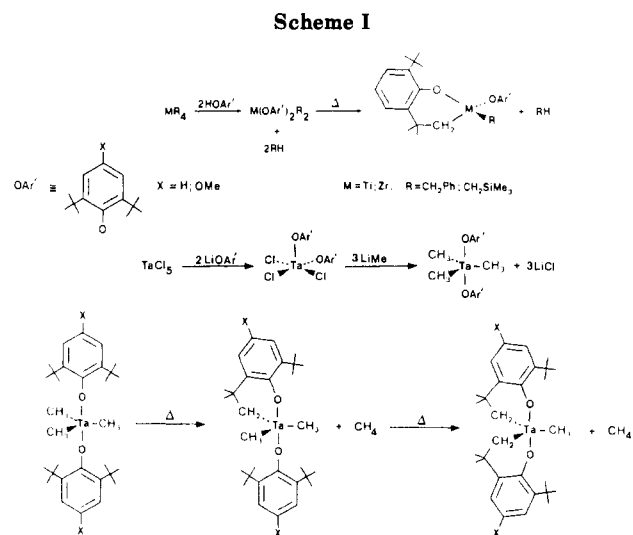
reaction ^a	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , eu
Ti(OAr') ₂ (CH ₂ Ph) ₂ → Ti(OC ₆ H ₃ Bu ^t CM ₂ CH ₂)(OAr')(CH ₂ Ph) + CH ₃ Ph	23.0 (10)	-13 (3)
Zr(OAr') ₂ (CH ₂ Ph) ₂ → Zr(OC ₆ H ₃ Bu ^t CM ₂ CH ₂)(OAr')(CH ₂ Ph) + CH ₃ Ph ^b	21.6 (10)	-19 (3)
Ta(OAr') ₂ (CH ₃) ₃ → Ta(OC ₆ H ₃ Bu ^t CM ₂ CH ₂)(OAr')(CH ₃) ₂ + CH ₄ ^c	26.4 (10)	-7 (3)
Ta(OC ₆ H ₃ Bu ^t CM ₂ CH ₂)(OAr')(CH ₃) ₂ → Ta(OC ₆ H ₃ Bu ^t CM ₂ CH ₂) ₂ (CH ₃) + CH ₄ ^d	29.5 (10)	-6 (4)
Ta(OAr') ₂ (=CH ₂)(CH ₃) → Ta(OC ₆ H ₃ Bu ^t CM ₂ CH ₂)(OAr')(CH ₃) ₂	14.3 (12)	-31 (6)
Ta(OAr'-4OMe) ₂ (=CH ₂)(CH ₃) → Ta(OC ₆ H ₂ Bu ^t -4OMe-CM ₂ CH ₂)(OAr'-4OMe)(CH ₃) ₂	15.4 (11)	-28 (6)
Ta(OAr'') ₃ (CH ₃) ₂ → Ta(OC ₆ H ₃ PhC ₆ H ₄)(OAr'')(CH ₃) + CH ₄	25.3 (10)	-15 (3)

^a OAr' = 2,6-di-*tert*-butylphenoxide; OAr'' = 2,6-diphenylphenoxide. ^b $k_H/k_D(114^\circ\text{C}) = 4.8$ (4). ^c $k_H/k_D(180^\circ\text{C}) = 5.2$ (4). ^d $k_H/k_D(135^\circ\text{C}) = 1.9$ (5).

In 1981 after having witnessed part of the "Renaissance" in transition-metal alkoxide chemistry in the laboratories of Prof. Malcolm H. Chisholm at Indiana University, I began a study of the inorganic and organometallic transition-metal chemistry associated with sterically demanding aryl oxide ligation.²⁰ Our use of the bulky 2,6-di-*tert*-butylphenoxide (OAr') group as a hopefully innocent ancillary ligand on high-valent, early-transition-metal centers was soon complicated by reactivity involving the ligands themselves. In particular, we managed to characterize a number of cyclometalation reactions involving the mild, intramolecular activation of the aliphatic carbon-hydrogen bonds of the alkyl side chain.¹⁸ Although this particular ligand reactivity was initially unforeseen, we decided to study it in detail.²¹ This was prompted by the current interest in CH bond activation at these and related metal centers as well as by the need to better understand this potentially frustrating side reaction, which may interfere with other reactivity studies. The products of these reactions, containing a six-membered metallacycle, are stable and typically formed quantitatively, making detailed mechanistic studies possible. This Account is an overview of our mechanistic studies into these cyclometalation reactions.

Activation by Metal-Alkyl Bonds

Because of steric pressure, the number of 2,6-di-*tert*-butylphenoxide (OAr') ligands that can be introduced into a metal coordination sphere is limited to a maximum of three in compounds such as M(OAr')₃ (M = Ti,²² Sc²³) and M(OAr')₃X (M = Ti, Zr, Hf; X = halide).^{22,24} However, alkyl derivatives containing only two of these groups are readily synthesized via alkylation of the corresponding mixed chloro,aryl oxide substrate²⁶ or protonolysis reactions involving the parent phenol with homoleptic alkyls (Scheme I).²⁵ Although



these alkyl compounds prove to be valuable substrates for investigating a range of organometallic reactivity,²⁷ they all demonstrate thermal instability. At temperatures ranging from 25 (M = Ti) to 140 °C (M = Ta) the compounds undergo loss of 1 equiv of alkane with the clean, high-yield formation of a series of derivatives containing a six-membered metallacycle ring (Scheme I).^{28,29} In the case of the tantalum compound, two sequential ring-closure reactions can take place, leading to a bis-cyclometalated derivative (Scheme I). The use of 4-substituted 2,6-di-*tert*-butylphenoxide ligands OAr'-4Me and OAr'-4OMe generates identical chemistry with no noticeable change in cyclometalation rates. This reactivity contrasts markedly with the thermal stability found for similar alkyl derivatives containing 2,6-dimethyl- or 2,6-diisopropylphenoxide ligands, which possess much more activated, benzylic carbon-hydrogen bonds in their alkyl side chains.²⁵ Furthermore, the apparent preference for the formation of a six-membered, and not five-membered, metallacycle seems to "violate" one of the early rules of cyclometalation chemistry.⁵ However, one important characteristic of high-valent, early-transition-metal alkoxide and aryl oxide chemistry is the presence of significant

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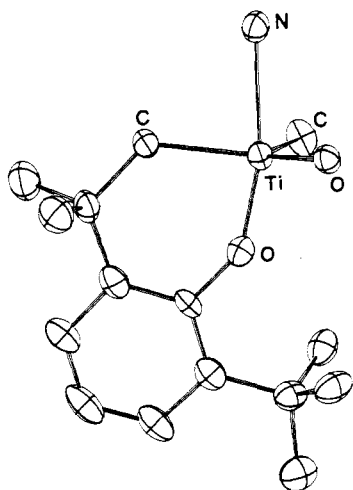


Figure 1. ORTEP view of the cyclometalated compound $\text{Ti}(\text{OC}_6\text{H}_3\text{Bu}^t\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{CH}_2\text{SiMe}_3)(\text{py})$ (ref 28) emphasizing the six-membered metallacycle.

amounts of oxygen-p to metal-d π -bonding,^{30–32} as evidenced structurally by the presence of short metal-oxygen distances and large M–O–R angles.³³ In the case of derivatives of 2,6-di-*tert*-butylphenoxide with these metals, angles for M–O–Ar' close to 180° are common.^{25,26} This feature of aryl oxide bonding has the effect of removing metalatable substituents away from the metal center and probably accounts for the lack of metalation chemistry observed for the other phenoxide ligands. Structural studies also show that the six-membered metallacycle formed by metalation of OAr' ligands is able to maintain a 90° angle at the metal center with little puckering due to the large angles subtended at the oxygen atom of the ring (Figure 1).²⁸

Kinetic studies show that these cyclization reactions are all first order, and structural studies show the reagents and products are monomeric. Activation parameters have also been obtained for some of the reactions in hydrocarbon solution (Table I). Mechanistically, there are a number of viable pathways by which these reactions could proceed. A number of these are shown in Scheme II. The direct, oxidative-addition pathway (A) is inaccessible for these d^0 compounds, the resulting Ti^{6+} - or Ta^{7+} -containing intermediates being totally unprecedented. The radical pathway^{18,28} (B) involving initiation by thermal homolysis of the M–R bond has little experimental support. The high yield of these reactions, with no evidence for hydrogen atom abstraction by the postulated alkyl radical either from solvents or from added hydrogen donor reagents, and the values of the activation parameters argue strongly against pathway B.^{18,28} In fact, the photochemical reactivity of these and other group 4 and group 5 metal mixed alkyl, aryl oxides has been shown to be dominated by initial homolysis of the metal–carbon σ -bonds, but no cyclometalated products are produced.³⁴ An

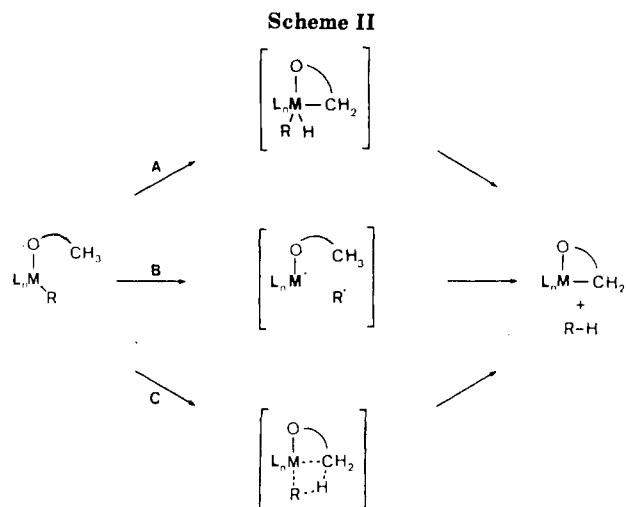
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indirect pathway proceeding via an alkylidene intermediate has considerable literature precedence^{35,36} (vide infra). However, careful labeling studies clearly show that the alkane molecule lost during the reaction arises exclusively from the combination of the alkyl leaving group with a hydrogen atom of the aryl oxide Bu' group.

All of the mechanistic data we have obtained to date concerning these reactions are best accommodated by pathway C, proceeding via a 4-center, 4-electron transition state. This pathway allows for concerted metal–carbon bond making and breaking with no formal change in the oxidation state of the metal.^{18,37} Experimentally, the moderately large, negative entropies of activation are a consistent characteristic of these and related intramolecular CH bond activation processes.^{18,38} The adoption of the proposed transition state would be anticipated to lead to a significant loss of rotational entropy from the ground state, and this idea can be used to rationalize the negative ΔS^\ddagger values. The importance of entropy factors for cyclometalation reactions at later transition-metal centers was first recognized and elegantly demonstrated by Shaw and co-workers.³⁹ Presumably for this reason the less sterically demanding ligands such as 2-methyl-6-*tert*-butylphenoxide do not undergo facile cyclometalation reactions. This concept can be related to the classical Thorpe–Ingold or “gem-dimethyl” effect well documented for organic cyclization reactions.⁴⁰

A critical parameter in the mechanistic assessment of carbon–hydrogen bond activation reactions is the presence and magnitude of a deuterium kinetic isotope effect. Recent work by our group using the selectively labeled phenoxide derived from 4-methyl-2,6-di(*tert*-butyl- d_9)phenol- d_2 -*O-d* [DOC_6D_2 -2,6(C_4D_9)-4(CH_3)] demonstrates that these cyclometalation reactions indeed possess significantly large values of k_H/k_D at Zr-

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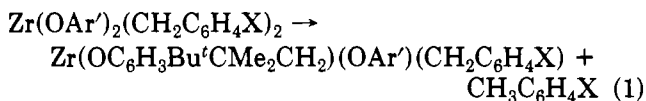
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(IV) and Ta(V) metal centers (Table I),⁴¹ consistent with a primary kinetic isotope effect as expected for pathway C.

A detailed analysis of the proposed, but so far ill-defined, transition state shows the mechanistic pathway to have some similarity to electrophilic substitution at a saturated carbon center. The favored transition-state structure in which a proton is transferred intramolecularly to the alkyl leaving group can be compared to four-center, closed transition states proposed for concerted electrophilic substitution processes at mercury and related metal centers.⁴² This type of S_E2 pathway has sometimes been referred to as a "no-mechanism" reaction.⁴² The concerted pathway C would be predicted to retain the configuration at carbon. An alternate pathway in which the hydrogen atom is lost as a free proton *exo* to the coordination sphere prior to attacking the M-R leaving group bond is not consistent with the high yields typical for these reactions. This latter S_E2 path would also be predicted to lead to an inversion of configuration at the metalated carbon. Although it is unlikely, there have been no studies reported so far which monitor the stereochemistry at carbon during these and related transition-metal-mediated reactions.

Further attempts to gain some insight into the electronic nature of these transition states by our group have focused on the impact of substituents attached to the leaving group on the rate of ring closure. In one specific study using a somewhat limited number of 3- and 4-substituted benzyl leaving groups, we found the cyclometalation at Zr(IV) metal centers to be very insensitive to the substituents (eq 1).²⁸ This result implies little charge separation is present in the transition state and is consistent with results obtained by other groups on related reactions.⁴³



$10^5 k$ at 114 °C: X = H, 32.3; 4-Me, 39.2; 4-F, 45.8; 3-F, 18.4

An important question that is raised concerning the ability of these high-valent, electron-deficient metal centers to activate CH bonds involves the possible importance and intermediacy of direct electronic interactions (bonding) between the metal center and the CH bonds that are eventually activated.⁴⁴ These high-valent, early-transition-metal derivatives of sterically bulky aryl oxide ligands are a class of compound that one might predict would be prone to forming agostic⁴⁴ interactions of this type with any available proximal CH bonds. The bulky substituents restrain the electron-deficient (Lewis acid) metal centers from seeking out electron density from more classical sources, e.g., neutral donor ligands and oligomerization via formation of aryl oxide or halide bridges. Structural studies of compounds containing OAr' ligation have indicated unexpected ground-state conformations of Bu^t groups in

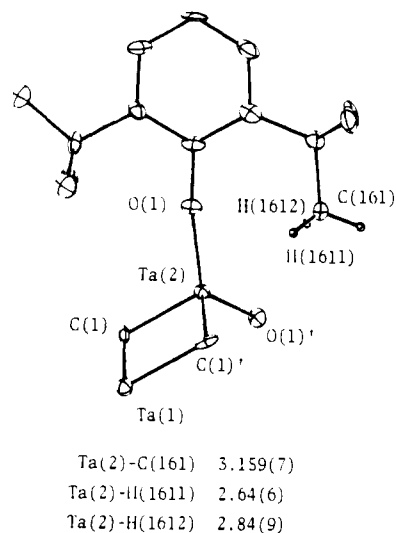
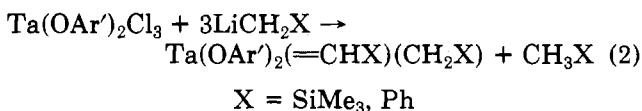


Figure 2. ORTEP view of one of the aryl oxide ligands in $(\text{Ar}'\text{O})_2\text{Ta}(\mu\text{-CSiMe}_3)_2\text{Ta}(\text{CH}_2\text{SiMe}_3)_2$ (ref 46) emphasizing the proximity of one of the *tert*-butyl methyl groups to the metal center.

three cases.^{26,45,46} One example is shown in Figure 2.⁴⁶ It can be seen that instead of adopting the expected conformation which maximizes the distance between the metal center and the Bu^t methyl groups, in these cases the Bu^t group rotates so that one of its methyl groups is pointing directly toward the metal and its coordination sphere. The refined distances to these methyl groups are short, but on the outer fringes of the values one would expect based on other literature data to represent a significant M...H...C bond.⁴⁴ These structural studies need to be complemented by both solution and solid-state spectroscopic studies in order to better characterize the nature of these interactions. However, these observations do demonstrate that it is not difficult for the methyl groups of these aryl oxide ligands to approach close to the metal centers for interaction with both vacant metal orbitals and alkyl leaving groups, leading to the formation of the product metallacycle ring.

Activation by Metal-Alkylidene and -Alkylidyne Bonds

Given the reactivity patterns that have been delineated for early-transition-metal alkyl compounds over the past few years,^{35,47} it is not surprising that the use of bulky aryl oxide ligation in conjunction with early-transition-metal-alkyl bonds sometimes leads to the thermal formation of alkylidene ($\text{M}=\text{CHX}$) functional groups via sterically induced α -hydrogen abstraction processes. Hence alkylation of $\text{Ta}(\text{OAr}')_2\text{Cl}_3$ with $\text{LiCH}_2\text{SiMe}_3$ or $\text{Mg}(\text{CH}_2\text{Ph})_2$ does not lead to the corresponding trisalkyls but instead leads to the mixed alkyl,alkylidene compounds as shown in eq 2.^{25,48}



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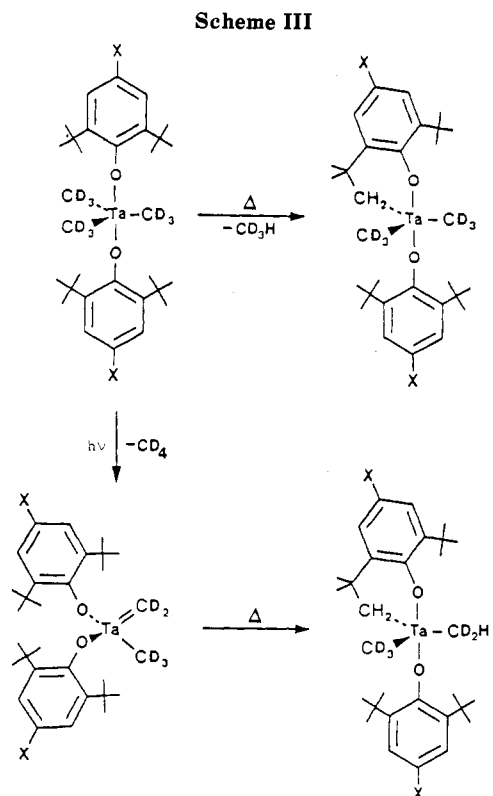
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(44) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* 1983, 250, 395.

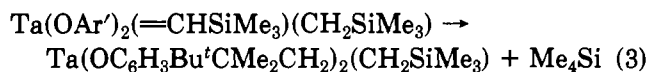
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(47) Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 3.

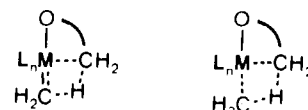


However, these compounds exhibit low thermal stability and in the case of the (trimethylsilyl)methylidene compound, mild thermolysis leads to the bis-cyclometalated compound and 1 equiv of Me_4Si (eq 3).⁴⁸ This reaction



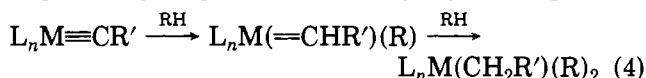
demonstrates that it is possible for alkylidene functional groups to activate aliphatic carbon-hydrogen bonds, the reaction here involving the intramolecular addition of the CH bond across the tantalum carbon double bond. In fact, the reaction represents an intramolecular reverse of the α -hydrogen abstraction process itself.^{35a} Reassessment of the reactivity of the trimethyl complex $\text{Ta}(\text{OAr}')_2\text{Me}_3$ (Scheme I) using deuteriated methyl groups shows that no methylidene intermediate is involved in the thermal cyclometalation chemistry.²⁹ However, on photolysis the trimethyl compound is found to yield the methyl methylidene $\text{Ta}(\text{OAr}')_2(=\text{CH}_2)(\text{CH}_3)$ essentially quantitatively along with 1 equiv of methane.^{29,49} On standing at room temperature for a few hours the methylidene then goes on to produce the monocyclusmetalated compound that can also be obtained directly from the trimethyl complex on thermolysis.⁴⁹ A simple labeling study allows one to clearly demonstrate the two distinct pathways, one thermal and the other photochemical, leading to the mono-metallated derivative (Scheme III).^{29,49}

The greater potency of the methylidene group for the activation of carbon-hydrogen bonds in these systems compared to its saturated, alkyl counterpart can be rationalized by considering the two proposed transition states (diagram). For an alkylidene compound the formation of the new metal-carbon σ -bond of the me-



tallacycle ring takes place at the expense of only the (presumably weaker) π -component of the tantalum-carbon double bond, whereas an alkyl leaving group involves the concerted sacrifice of the Ta-R σ -bond (σ -bond metathesis). A kinetic study of the ring-closure reaction of the methylidene (Table I)²⁹ does indeed show a much lower value for ΔH^\ddagger for the reaction compared to values found for the cyclometalation of $\text{Ta}(\text{OAr}')_2\text{Me}_3$. However, the ring closure was found to exhibit a very large, negative value for ΔS^\ddagger .²⁹ Whether this entropic inhibition is a characteristic of activation by methylidene groups in general or a quirk of this particular ligand system is as yet unknown.

On the basis of the observed reactivity of alkylidene functional groups one might expect related results for alkylidyne ($\text{M}\equiv\text{CR}$) groups. In fact, these species have the potential for activating two carbon-hydrogen bonds sequentially (eq 4). The alkylidyne-bridged, di-



tantalum compound $(\text{Ar}'\text{O})_2\text{Ta}(\mu\text{-CSiMe}_3)_2\text{Ta}(\text{CH}_2\text{SiMe}_3)_2$ does yield the bis-metallated compound $\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{CMe}_2\text{CH}_2)_2(\text{CH}_2\text{SiMe}_3)$, but only in very low yields and at high temperatures.⁴⁶ Attempts by Schrock et al. to isolate a tungsten alkylidyne compound containing 2,6-di-*tert*-butylphenoxide coligation resulted in the formation of a cyclometalated alkylidene compound,⁵⁰ indicating that terminal alkylidyne functionalities are indeed potent groups for carbon-hydrogen bond activation.

Activation by Metal-Aryl and Metal-Benzyne (*o*-Phenylene) Functional Groups

Just as the chemistry of high-valent, early-transition-metal alkyl compounds can sometimes be complicated by alkylidene intermediates, so mechanistic studies of the chemistry of the metal-aryl bond have been shown to sometimes be complicated by the intermediacy of metal-benzyne (*o*-phenylene) functionalities.⁵¹⁻⁵⁴ When $\text{Ta}(\text{OAr}')_2\text{Cl}_3$ is treated with LiPh (3 equiv) the product obtained at room temperature is the monocyclometalated compound $\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{Ph})_2$ with 1 equiv of benzene.^{55,56} Careful study of the reaction sequence shows that the CH bond activation takes place after the introduction of only one phenyl substituent into the coordination sphere (Scheme IV).⁵⁷ This sequence implies that the presence of the chloride ancillary lig-

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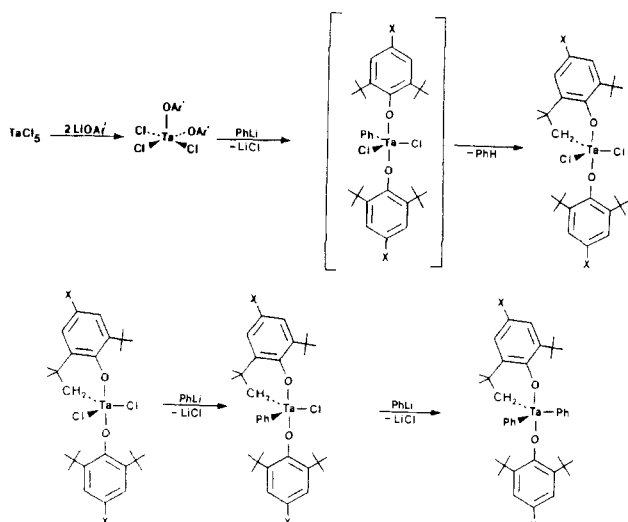
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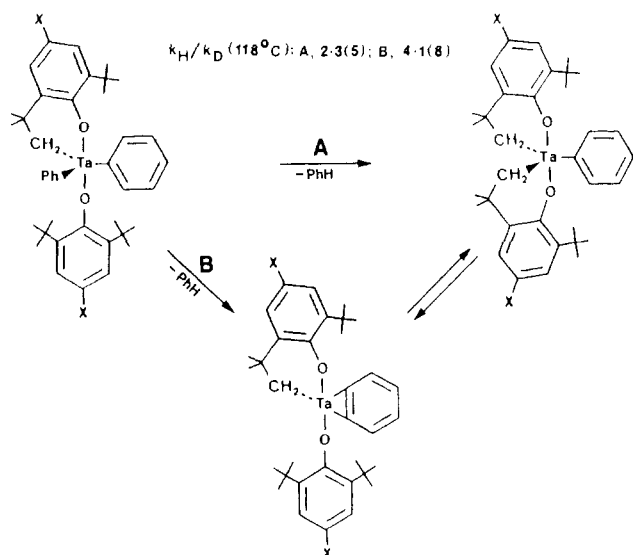
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Scheme IV



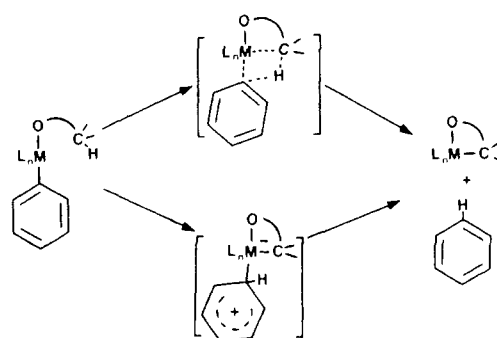
Scheme V



ands can accelerate the rate of carbon-hydrogen bond activation, possibly by increasing the Lewis acidity of the metal center. This argument appears to be supported by the more rapid, second cyclometalation of $\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{CMe}_2\text{CH}_2)(\text{OAr}')(\text{Ph})(\text{X})$ with $\text{X} = \text{Cl}$ compared to $\text{X} = \text{Ph}$ ⁵⁷ although this conclusion is somewhat clouded by the differing steric requirements of these two groups.

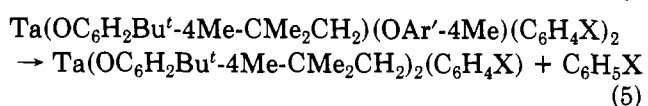
However, the second cyclometalation step of the monocyclusmetallated diphenyl compound is complicated by the fact that there are two, competing pathways operative (Scheme V).⁵⁷ The more direct pathway involves the loss of a phenyl leaving group with the hydrogen atom of the metalated Bu^t group, while the second indeed involves the intermediacy of a metal-benzene complex. The latter pathway involves two carbon-hydrogen bond activation steps. Initially the benzyne intermediate is generated by abstraction of an ortho hydrogen of a $\text{Ta}-\text{C}_6\text{H}_5$ function by an adjacent phenyl leaving group, liberating benzene. Then the metallacycle ring is formed by the insertion of an aliphatic carbon-hydrogen bond of a Bu^t group into one side of the strained metalocyclopropane ring of the benzyne (*o*-phenylene) function. The use of deuterium labels either in the phenyl or in the phenoxide groups

Scheme VI



clearly demonstrates the presence of both pathways.⁵⁷ Furthermore, by using a combination of kinetics and mass spectrometric data, it is possible to calculate how much of the reaction proceeds via which path as well as the deuterium kinetic isotope effects for both carbon-hydrogen bond activation steps (Scheme V).⁵⁷

The use of a limited range of substituents in the aryl leaving group shows little dramatic change in the rate of these reactions (eq 5).⁵⁶ This is a particularly sig-



10^5k at 118 °C: $\text{X} = \text{H}$, 7.3; 3-Me, 10.4; 4-Me, 8.9; 3-F, 14.3; 4-F, 9.6

nificant mechanistic observation. The shift from a saturated alkyl leaving group to the unsaturated aryl group introduces further mechanistic pathways. Transfer of the hydrogen of the activated carbon-hydrogen bond to the aryl group may take place directly to the sp^2 σ -lobe involved in the $\text{Ta}-\text{Ph}$ bond, leading to a transition state similar to that for simple alkyl leaving groups. A second possibility, however, involves transfer to the aryl ring to produce a "metallo-Wheland" intermediate complex which then eliminates benzene. In this latter path either step may be rate determining (Scheme VI). The lack of a dramatic substituent effect for the loss of aryl leaving groups appears to rule out the pathway involving breakdown of the aryl aromaticity.⁵⁸ The direct pathway (Scheme V) is related by microscopic reversibility to the intermolecular activation of benzene by metal-alkyl bonds. Work by Bercaw et al. on the metalation of aromatics by Cp^*ScR compounds also shows negligible substituent effects.⁵⁹ Aromatic mercuration shows a strong dependence on the nature of substituents in the aromatic ring, with a ρ -parameter of ~ 4 for the reaction rates when plotted against σ^+ values.⁶⁰ The possibility of a mechanism shift in systems of this type with more dramatic substituents, however, should not be discounted.

A further complication with these particular aryl systems is presented by the fact that the product bis-cyclometallated derivatives are in equilibrium at higher temperatures with the monometallated benzyne complex (Scheme V).^{56,57} This is demonstrated by the thermal

(58) Electrophilic cyclopalladation may also take place without formation of an arenium ion. See: Deeming, A. J.; Rothwell, I. P. *Pure Appl. Chem.* 1980, 52, 649.

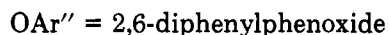
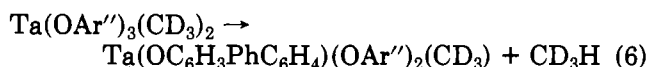
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isomerization of 3-methylphenyl or 4-methylphenyl compounds into an approximately equimolar mixture of the two isomers. Furthermore, thermolysis of the deuteriated compound $\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{CMe}_2\text{CH}_2)_2(\text{C}_6\text{D}_5)$ results in scrambling of the deuterium label over all aliphatic and Ta-Ph sites in the molecule, consistent with a reversible opening and closing of the metallacycle rings by abstraction of an ortho deuterium from the Ta-C₆D₅ group.^{56,57}

Intramolecular Activation of Aromatic Carbon-Hydrogen Bonds

The electrophilic (Lewis acid) nature of the metal centers involved in the intramolecular activation of the aliphatic carbon-hydrogen bonds of these aryl oxide ligands has led us to investigate related ligation which presents the opportunity for intramolecular activation of aromatic carbon-hydrogen bonds. In particular, the ligand 2,6-diphenylphenoxide (OAr'') offers the possibility for six-membered metallacycle formation, only this time chelation occurs via activation of a side-chain aromatic CH bond. Although this reactivity would stoichiometrically be identical with that seen for 2,6-di-*tert*-butylphenoxides, the aromatic substrate offers the potential for activation pathways directly related to classical electrophilic substitution mechanisms.⁴³ Our initial studies of this ligand indicate that it is slightly less sterically demanding than 2,6-di-*tert*-butylphenoxide, and organometallic derivatives of group 4 and group 5 metals containing this group can be readily synthesized.^{27,61} These compounds are thermally more robust than those of its aliphatic (OAr') counterpart, but with extended heating at high temperatures they will undergo loss of alkane and formation of the expected metallacycle ring.⁶² In the case of tantalum the bis-, and trisalkyls of stoichiometry $\text{Ta}(\text{OAr}'')_3\text{R}_2$ and $\text{Ta}(\text{OAr}'')_2\text{R}_3$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{Ph}$) have been isolated⁶¹ and shown to undergo ring closure in hydrocarbon solvents with first-order kinetics.⁶² A mechanistic study of $\text{Ta}(\text{OAr}'')_3\text{Me}_2$ shows that the monocyclometalated product is formed directly, with no methylidene intermediate.⁶²



Activation parameters for the reaction again show moderately large, negative entropies of activation for the ring-closure reaction (Table I). One of the meta-

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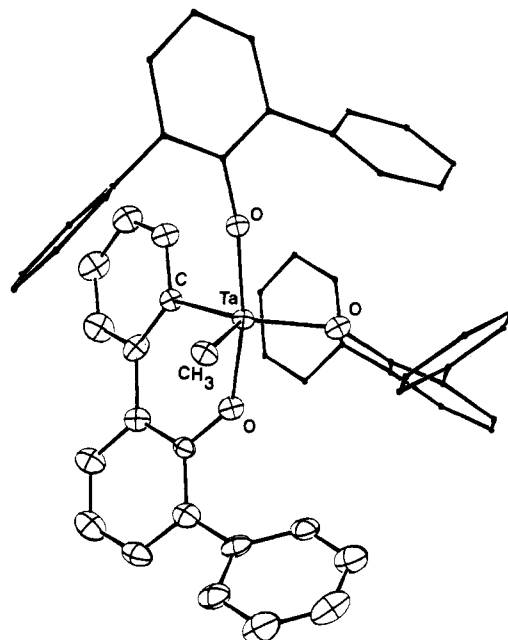


Figure 3. ORTEP view of the cyclometalated compound $\text{Ta}(\text{OC}_6\text{H}_3\text{PhC}_6\text{H}_4)(\text{OAr}'')_2(\text{CH}_3)$ emphasizing the central coordination sphere.

lated products has been structurally characterized (Figure 3), and the six-membered metallacycle ring is only slightly puckered, the characteristically Ta-O-C angle allowing the chelate to comfortably maintain a -90° angle at the metal center.⁶² Further mechanistic studies of cyclometalation reactions involving 2,6-diphenylphenoxide ligands are to be focused on the impact of various substituents in the aryl side rings.⁴³

Concluding Remarks

The use of 2,6-di-*tert*-butylphenoxide ligation attached to high-valent, early-transition-metal centers has demonstrated the ability of these metals to activate normally inert CH bonds under mild conditions. Furthermore, the systems developed have proved valuable in that they have allowed us not only to identify various functional groups that are capable of inducing CH bond activation but also in some cases to evaluate their potency for this reactivity.

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