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Cyclometalated Tantalum Diphenolate Pincer Complexes: Intramolecular C−H/M−CH_3 σ-Bond Metathesis May Be Faster than O−H/M−CH_3 Protonolysis

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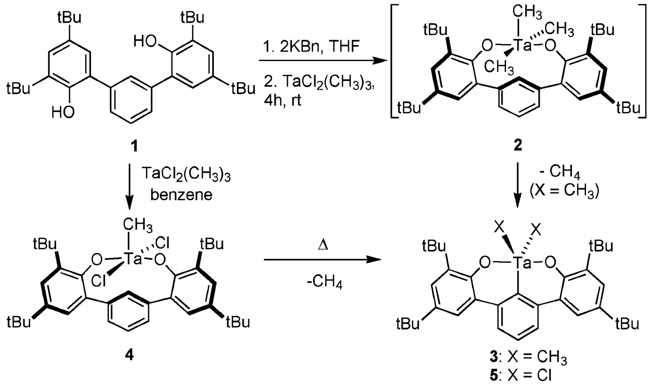
Summary: A diphenol linked at the ortho positions to a benzene ring was metalated with $TaCl_2(CH_3)_3$. Deuterium labeling of the phenol hydrogens and of the linking 1,3-benzenediyl ring reveals an unexpected mechanism involving protonolysis of a methyl group, followed by C−H/Ta−CH_3 σ-bond metathesis, leading to cyclometalation of the linking ring and finally protonation of the cyclometalated group by the pendant phenol.

The activation of C−H bonds is a topic of broad current interest.[1] The development of a useful synthetic methodology for selectively functionalizing C−H bonds with metal catalysts could be expedited through the fundamental reactivity of C−H bonds with metal species.[1] In this context, it is important to establish the factors that control the tolerance of the metal center to functionality while preserving the C−H activation ability. The activation of C−H bonds is well established to occur via five basic transformations: oxidative addition, σ-bond metathesis, 1,2-addition, electrophilic displacement of H^+, and four-center cleavage by two metalloradicals.[1a,2] While some of the late-metal systems show tolerance to heteroatoms and protic groups (in fact, selectivity is commonly derived from precoordination of the transition metal to a heteroatom), early-transition-metal organometallic species capable of C−H bond activation are generally irreversibly deactivated. Herein we report a tantalum system capable of C−H/Ta−CH_3 σ-bond metathesis under mild conditions. Importantly, this process dominates, even when a more direct route to the same final product by protonolysis of the Ta−CH_3 bond by a pendant phenol is an alternative.

As part of our continuing interest in developing systems for olefin polymerization and other organometallic transformations, we have recently investigated a series of a pincer bisphenolate frameworks.[3] The 1,3-benzenebis(phenol) **1** provides an interesting precursor, given the possibility of cyclometalation to generate currently unexplored trianionic pincer systems.[4] A salt metathesis route using $TaCl_2(CH_3)_3$ indeed provided the cyclometalated product **3** within hours at room temperature (Scheme 1). Formation of **3** presumably occurs via intermediate generation of a simple salt metathesis product, complex **2**, which then undergoes σ-bond metathesis, with loss of methane. Whereas the C−H (or C−C) activation route for accessing cyclometalated pincer frameworks is common for late-transition-metal systems,[6] cyclometalation with early metals normally relies on using starting materials for which the phenyl carbon has been previously functionalized with [MgX] or Li.[5] The strategy used in preparing **3** is reminiscent of cyclometalations via σ-bond metathesis observed for tantalum systems with phenolate ligands ortho-substituted with *tert*-butyl, isopropyl, or phenyl groups.[2e,7] On the other hand, the previously characterized $Ta(CH_3)_3(OC_6H_3\text{-}2,6\text{-}Ph_2)_2$ and $Ta(CH_2Ph)_3(OC_6H_3\text{-}2,6\text{-}Ph_2)_2$ lose CH_4 only above 200 °C and toluene above 175 °C, respectively.[7b] In contrast, the related proposed tantalum trialkyl intermediate **2** proceeds readily to cyclometalated product **3** at room temper-

Scheme 1



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(3) Group 4 and 5 chemistry supported by tridentate bis(phenolate) ligands related to **1** will be reported in subsequent full papers.

(4) Experimental procedures for **1** and **3**−**5**, single-crystal X-ray diffraction studies, and a discussion of kinetic deuterium isotope effects are presented in the Supporting Information.

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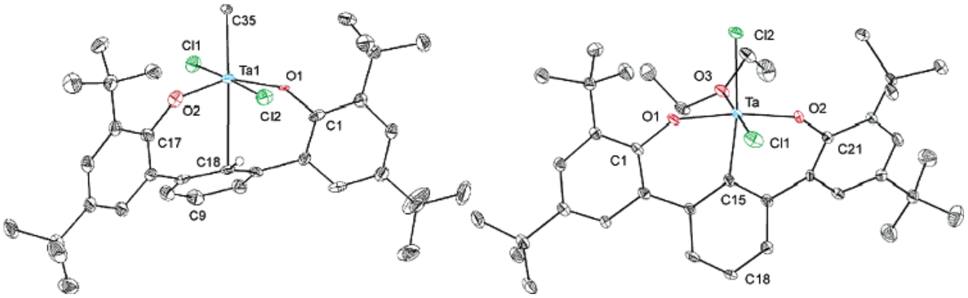
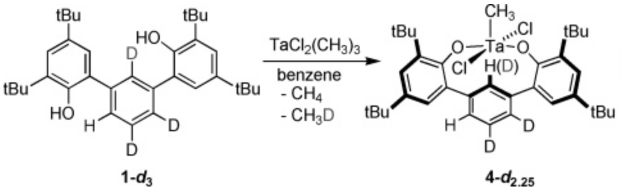


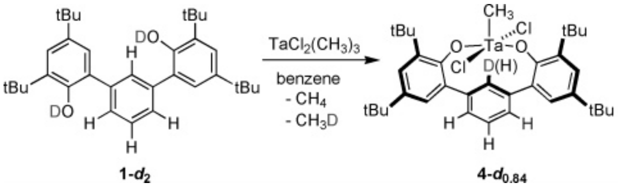
Figure 1. Structural drawings of **4** (left) and **5-OEt$_2$** (right) with thermal ellipsoids at the 50% probability level.[4]

ature. This suggests that the pincer nature of the ligand, with initial chelation of the two phenolates, facilitates the cyclometalation, possibly by locking the aryl group close to the orientation for σ-bond metathesis of [Ta−CH$_3$] with [C(ipso)−H].

An alkane elimination route was explored for the metalation of **1** with TaCl$_2$(CH$_3$)$_3$, leading at room temperature to a species that still displays signals for a Ta*CH$_3$* group and the C(ipso)−*H* in the ^{1}H and ^{13}C NMR spectra (**4**; Scheme 1). A single-crystal X-ray diffraction study supported the spectroscopic assignment as **4** as that shown (Figure 1). The tantalum center is six-coordinated, taking into account the weak interaction with the arene ipso carbon (Ta−C bond length of 2.791(5) Å). The methyl group is located trans to the arene system, the position with the smallest trans influence. Isolation of **4** lends support to the proposed route for the formation of **3** (vide supra), and indeed compound **4** is also found to undergo σ-bond metathesis to generate cyclometalated product **5** upon heating to 90 °C. Conversion of **4** to **5** is first order. An Eyring analysis afforded activation parameters for this transformation ($\Delta H^{\ddagger} = 27.1 \pm 0.9$ kcal/mol; $\Delta S^{\ddagger} = -2 \pm 2$ cal/(mol K)) consistent with intramolecular σ-bond metathesis. The isotope effect of 1.6 ± 0.2 at 125 °C suggests a sequence involving fast preequilibrium to generate a species with the Ta−CH$_3$ group from trans to cis followed by rate-determining σ-bond metathesis.



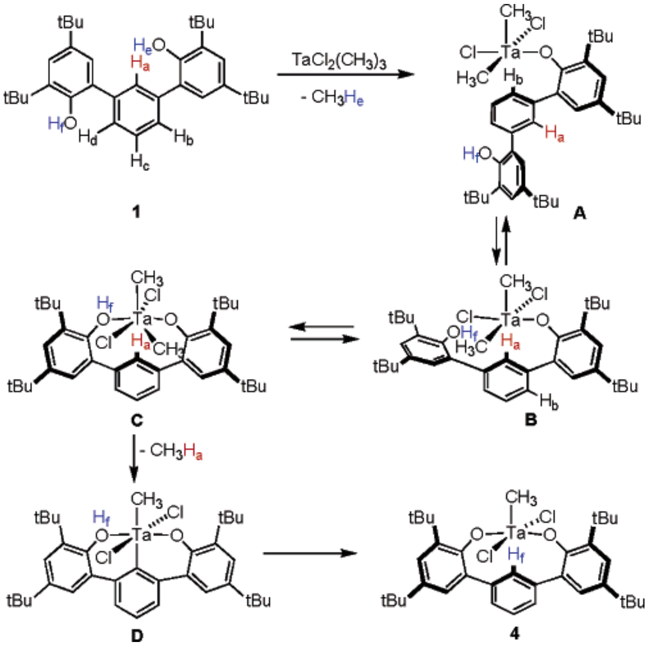
(1)



(2)

Investigation of the outcomes with specifically deuterium-labeled isotopologues of **1** revealed some quite surprising results. The reaction of **1-*d*$_3$** with TaCl$_2$(CH$_3$)$_3$ (eq 1) leads to the formation of **4-*d*$_{2.25}$** in which the *ipso*-C-*D* is (ca. *75%*) replaced with protium. When the formation of methanes was monitored by ^{1}H NMR spectroscopy, *both* CH$_4$ *and* CH$_3$D (2.6(1):1) were observed, suggesting that ca. 36% of the methyl groups leave with a hydrogen from the connecting 1,3-benzenediyl ring.[4] Following the hypothesis that the proton at the ipso carbon originates from the phenol O−H, a derivative labeled at these positions was prepared (eq 2). The reaction of **3-*d*$_2$** with TaCl$_2$(CH$_3$)$_3$ leads to the formation of both CH$_4$ and CH$_3$D (0.9(1):1) (eq 2). Spectroscopic data indicate that position 2 is indeed deuterated (**4-*d*$_{0.84}$**).[4] Formation of both CH$_4$ and CH$_3$D in eqs 1 and 2 indicates that part of the methyls leave with a proton (deuterium) from the phenol O−H(D) and part with a proton (deuterium) from the bridging 1,3-benzenediyl ring. A mechanism that accounts for the observed labeling patterns involves first protonation of a methyl group to form CH$_3$H$_e$ and a tantalum dimethyl dichloride phenolate complex (**A** and its conformer **B**; Scheme 2). Subsequent cyclometalation could occur at the two distinct ortho positions (H$_a$ and H$_b$). Sterically, conformation **A** should be favored over **B**, but cyclometalation at position H$_b$ is not observed. Moreover, because activation of C−H$_b$ resembles previously reported cyclometalation of tantalum *o*-phenylphenolates that require much higher temperatures,[7b] we suggest that σ-bond metathesis probably does not occur from **A** or **B** but rather through **C**. In **C**, coordination of the phenol oxygen brings the CH$_a$ bond into close proximity to Ta in a conformation that may facilitate σ-bond metathesis to lose CH$_3$H$_a$ and give cyclometalated species **D**. Finally, the coordinated phenol protonates the phenyl group to generate the

Scheme 2



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observed product **4**. Thus, the proposed mechanism takes advantage of the double chelation in **C** to facilitate C−H bond activation. It was unexpected that the *σ*-bond metathesis with the aryl C−H bond to give CH_3H_a outcompetes direct protonation by the phenol to give CH_3H_f and **4** directly. While the preference for *σ*-bond metathesis over protonolysis may be due largely to the chelating nature of the ligand in this case, it is nonetheless an encouraging precedent. Carbon−hydrogen bond activation with early metals is thus possible via *σ*-bond metathesis, even in the presence of protic pendant groups on the substrate, suggesting that the development of methods for C−H bond functionalization of such substrates using early-transition-metal complexes might indeed be possible.

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Supporting Information Available: Text giving details of procedures for preparing **1** and **3**−**5** and their isotopologues, tables of bond lengths, angles, etc. for the structures of **4** and **5**, figures giving kinetic and Eyring data for the conversion of **4** to **5**, and CIF files giving crystal data for **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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