# A Sterically Demanding Enolate Ligand: Tantalum Ligation and Pyridine Coupling

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Enolate ligands of formula $[OC(Ad)Ar]^-$ (Ad = 2-adamantylidene; Ar = 3,5-$C_6H_3Me_2$ **1a**, Ar = 2,4,6-$C_6H_2Me_3$ **1b**) were designed and prepared as potassium salts to mimic the topology of related *N-tert*-hydrocarbyl and ketimide ligands. Subsequently, trimethyltantalum bis-enolate complexes $TaMe_3(O\text{-}C[Ad]Ar)_2$ (Ar = 3,5-$C_6H_3Me_2$ **2a**, Ar = 2,4,6-$C_6H_2Me_3$ **2b**) were prepared in good yields from a salt metathesis reaction between $TaMe_3Cl_2$ and 2 equiv of the corresponding potassium enolate. Complex **2a** was structurally characterized and found to be monomeric in the solid state and to exhibit an inner coordination sphere of approximate $D_{3h}$ symmetry. Reaction between **2a** and pyridine in the presence of dihydrogen resulted in an unanticipated pyridine coupling with formation of the bipyridine complex $TaMe(O\text{-}C[Ad](3,5\text{-}C_6H_3Me_2))_2(py)(bpy)$, **3a** (py = pyridyl, bpy = 2,2′-bipyridyl), which was structurally characterized to confirm its formulation. Labeling experiments using pyridine-$d_5$ and $D_2$ suggest that formation of the tantalum(III) complex **3a** occurred via C−H activation involving a putative tantalum(III) intermediate, $TaMe(O\text{-}C[Ad](3,5\text{-}C_6H_3Me_2))_2(py)_3$, **4a**.

## Introduction

Early transition metal compounds have been extensively studied owing to their ability to mediate a wide range of processes. In particular, mononuclear tantalum complexes supported by sterically demanding alkoxide, siloxide, or aryloxide ligands are active in coupling reactions,[1,2] C−O activation,[1,2] C−N activation,[3−7] and C−H activation.[8−15] It is especially attractive when two or more of these processes can be sequentially mediated by the same metal complex. For instance, the coupling of pyridine with organic functionalities using cationic zirconocene methyl complexes is known, involving *ortho* C−H activation.[16,17] A few other methods using late transition metals have been described for the coupling of unactivated pyridine molecules, but extant protocols typically require harsh conditions.[18−21]

While related to alkoxide, siloxide, and aryloxide supporting ligands, oxygen-bound enolates constitute an ancillary ligand class not utilized previously in the context of stabilizing low-coordinate early-metal complexes.[22] We suspected that enolate ligation would impart certain benefits to early transition metal complexes, particularly minimizing unwanted side-reactions stemming from ancillary ligand vulnerability.[22−28] Ac-

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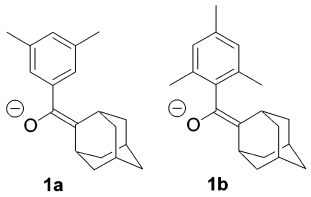
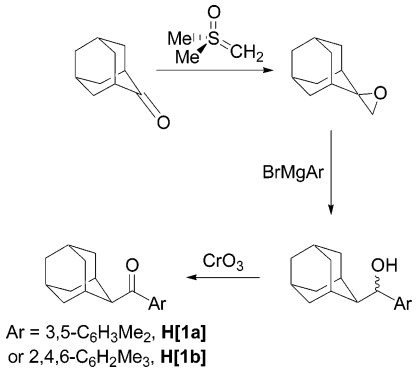



**Figure 1.** Enolate ligands designed to support electrophilic early transition metals.

**Scheme 1. Ligand Synthesis Pathway**




cordingly, we designed an enolate ligand intended to be particularly robust. The design elements included (i) an enolate essentially incapable (for steric reasons) of coordination to a metal through the enolate carbon, and (ii) one round adamantylidene cage and one flat aryl substituent. The latter requirement produces a class of enolate ligands "O-C[Ad]Ar" (Ad = 2-adamantylidene; Ar = 3,5-$C_6H_3Me_2$ **1a**, Ar = 2,4,6-$C_6H_2Me_3$ **1b**), as illustrated in Figure 1, that is reminiscent topologically of the *N-tert*-hydrocarbyl anilide ligands, which have been demonstrated to be versatile ligands for a variety of metals.[29−31]

This work involves the synthesis of a trimethyltantalum complex supported by the new robust enolate ligands. We further describe a new method for dehydrogenative pyridine *C*−*C* coupling at the *ortho* position, mediated by the trimethyltantalum bis-enolate complex. The resulting 2,2′-bipyridyl complex of tantalum(III) is characterized in detail, and the mechanism of its formation is considered with insight gleaned from deuterium labeling studies.

## Results and Discussion

Ketones corresponding to the desired enolate ligands were synthesized as white microcrystalline powders in three steps from commercially available 2-adamantanone (Scheme 1). Smooth methylene transfer from $Me_2S(CH_2)(O)$ (generated in situ by dehydrohalogenation of trimethylsulfoxonium iodide using sodium hydride) to 2-adamantanone provides 2-adamantyl epoxide,[32] which can be converted to the secondary carbinol $^2$AdCH(OH)Ar ($^2$Ad = 2-adamantyl; Ar = 3,5-$C_6H_3Me_2$ or 2,4,6-$C_6H_2Me_3$) upon addition of the corresponding aryl Grignard reagent.[33] Oxidation of crude carbinol samples with Jones' reagent delivered ketones $^2$AdC(O)Ar in moderate yields (53% for Ar = 3,5-$C_6H_3Me_2$, 65% for Ar = 2,4,6-$C_6H_2Me_3$ from adamantyl epoxide). Ketone purification consisted simply of recrystallization from cold methanol. Ligand deprotonation was efficiently accomplished by KH in THF, the resulting salts $[K(O\text{-}C[Ad]Ar)]_x$ (Ad = 2-adamantylidene rather than adamantyl; Ar = 3,5-$C_6H_3Me_2$ **K[1a]**, Ar = 2,4,6-$C_6H_2Me_3$ **K[1b]**) being obtained as white powders convenient for delivery of the enolate ligand to metal halides via transmetalation.

Trimethyltantalum bis-enolate complexes $TaMe_3(O\text{-}C[Ad]Ar)_2$ (Ar = 3,5-$C_6H_3Me_2$ **2a**, Ar = 2,4,6-$C_6H_2Me_2$ **2b**) were prepared quantitatively as white crystalline solids by treatment of 2 equiv of [K(O-C[Ad]Ar)] with $TaMe_3Cl_2$.[34] Associated with the single enolate ligand environment in the tantalum complexes is a diagnostic pair of broad $^1$H NMR signals at 3.58 and 2.88 ppm for **2a** and 3.58 and 2.22 ppm for **2b**, attributable to the two different allylic protons. The anticipated $^3J$ coupling of each allylic proton with the four neighboring adamantyl protons cannot be resolved in the NMR spectrum, resulting in the observed broadening. Besides these pairs of allylic protons, the remaining adamantyl signals are unremarkable multiplets due to overlapping peaks. The signals corresponding to the tantalum-bound methyls are located at 0.69 and 0.43 ppm for these complexes, respectively.

Single crystals of **2a**, grown from a saturated *n*-pentane solution at −40 °C, were examined by X-ray crystallography to confirm the monomeric nature and preferred coordination geometry of the trimethyltantalum(V) bis-enolate motif (Figure 2). As has been encountered previously for trimethyltantalum bis-alkoxide systems,[22,23,26] a regular trigonal bipyramidal geometry sporting exclusively equatorial methyl ligands is observed, and thus is realized an inner coordination sphere of approximate $D_{3h}$ symmetry. The three C−Ta−C angles are 120.1(3)°, 119.3(3)°, and 120.5(2)°, while the O(1)−Ta−O(2) angle is 175.76(10)°. The near-linear Ta−O(1)−C(11) (178.5(2)°) and Ta−O(2)−C(21) (161.7(2)°) angles taken together with relatively short Ta−O(1) (1.874(2) Å) and Ta−O(2) (1.883(2) Å) interatomic distances indicate significant Ta−O multiple-bond character, as has been invoked for related tantalum complexes supported by siloxide[1,2,6,35,36] and aryloxide[3−5,22−28,37,38] ligands.

Symmetry analysis of the molecular orbitals of **2a** reveals that the nine tantalum valence orbitals can interact favorably with all possible symmetry-adapted linear combinations of ligand donor functions. These

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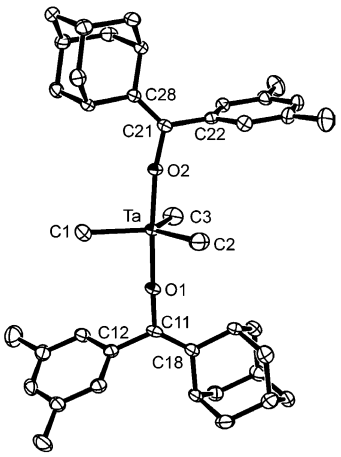



**Figure 2.** ORTEP diagram of $TaMe_3(O\text{-}C[Ad](3,5\text{-}C_6H_3Me_2))_2$ (**2a**) with thermal ellipsoids at the 35% probability level. Selected bond distances (Å): Ta−O(1), 1.874(2); Ta−O(2), 1.883(2); Ta−C(1), 2.137(5); Ta−C(2), 2.139(4); Ta−C(3), 2.150(5). Selected bond angles (deg): O(1)−Ta−O(2), 175.76(10); C(1)−Ta−C(2), 120.1(3); C(1)−Ta−C(3), 119.3(3); C(2)−Ta−C(3), 120.5(2); Ta−O(1)−C(11), 178.5(2); Ta−O(2)−C(21), 161.7(2).

interactions give rise to five $\sigma$ bonds transforming as $2A_1' + A_2'' + E'$ and four $\pi$ interactions transforming as $E' + E''$. Thus, **2a** may be considered an 18e complex. In accord with this analysis, it was found that the complex underwent no reaction in toluene (0.22 M) upon heating at 85 °C for 24 h. Complex **2a** also resisted adduct formation in the presence of up to 3 equiv of trimethylphosphine under the same reaction conditions. Furthermore, the robust trimethyltantalum complex was found not to react with stoichiometric amounts of protic reagents including 3,5-dimethylaniline and phenylphosphine in toluene solution at elevated temperatures, although free ketone ligand was formed upon hydrolysis with water.

Complex **2a** exhibited no reaction with dihydrogen in toluene (1 atm, 90−100 °C, 24 h). In contrast, a solution of the complex in pyridine under a dihydrogen atmosphere turned from pale yellow to red within 15 min when heated at 70 °C in a sealed vessel. The color change suggests that **2a** was reduced, possibly to a tantalum(III) intermediate (vide infra). By monitoring the reaction in an NMR tube sealed with a Teflon stopcock, it was revealed that **2a** was fully consumed only after 5 days. Workup of the reaction mixture after 5 days of heating led to the isolation (in 29−45% yield depending on the reaction scale, see below for formulation) of a red-brown solid that was only sparingly soluble in aliphatic solvents. The $^1$H NMR spectrum of the *n*-pentane filtrate after removal of the red-brown solid and concentration indicated the presence of multiple compounds, from which no clean product was further isolated. On the other hand, a $^1$H NMR spectroscopic study of the red-brown solid in $C_6D_6$ revealed a single enolate ligand environment and a singlet for one remaining $TaCH_3$ group with respect to two enolate residues. Furthermore, the aromatic region was comprised of well-resolved multiplets (7 distinct signals in a 2:2:2:2:2:2:1 ratio), consistent with one of two possible isomers **3a** or **3a′** (Figure 3). A 2D $^1$H−$^1$H correlation spectroscopic (COSY) study of the intriguing new product in $C_6D_6$ is consistent with these two formulations but does not distinguish the tantalum(V) bis-pyridyl complex, **3a′**, from the tantalum(III) 2,2′-bipyridine complex, **3a**.

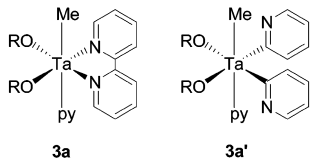



**Figure 3.** Tantalum(V) bis-pyridyl and tantalum(III) 2,2′-bipyridine formulations consistent with NMR data for the product obtained by hydrogenolysis of **2a** in pyridine solution.

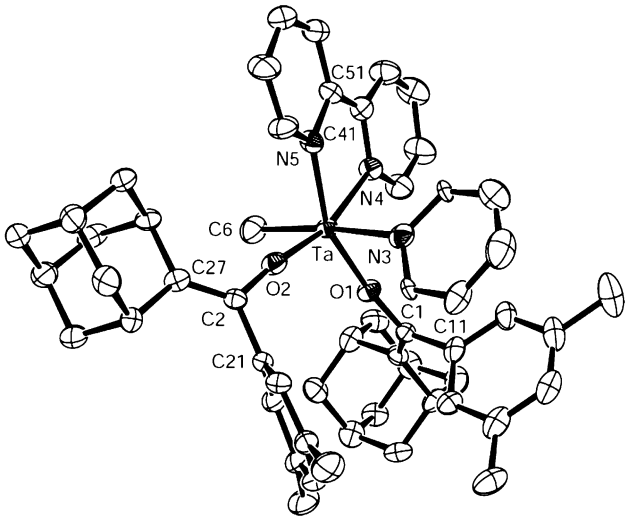
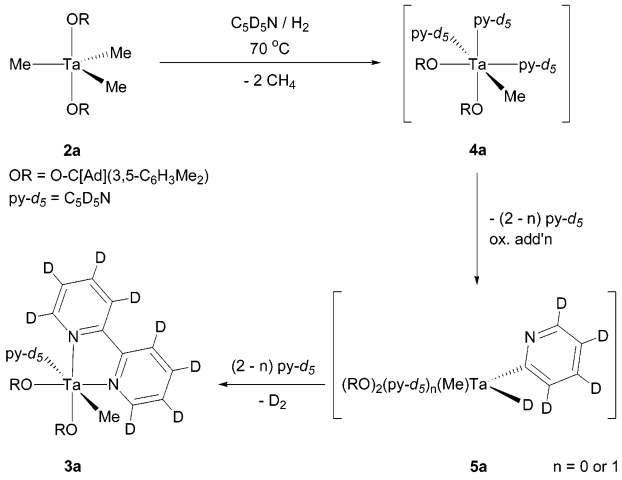



**Figure 4.** ORTEP diagram of $TaMe(O\text{-}C[Ad](3,5\text{-}C_6H_3Me_2))_2(py)(bpy)$ (**3a**) with thermal ellipsoids at the 35% probability level. Selected bond distances (Å): Ta−O(1), 1.903(6); Ta−O(2), 1.903(7); Ta−C(6), 2.184(11); Ta−N(3), 2.370(9); Ta−N(4), 2.110(7); Ta−N(5), 2.093(8); C(41)−C(51), 1.386(15). Selected bond angles (deg): Ta−O(1)−C(1), 170.5(6); Ta−O(2)−C(2), 170.3(6); O(1)−Ta−N(5), 158.1(3); O(2)−Ta−N(4), 163.6(3); C(6)−Ta−N(3), 170.5(4).

An X-ray structural analysis was undertaken on single crystals grown from a diethyl ether solution of the red-brown material layered with *n*-pentane. The study revealed the tantalum(III) 2,2′-bipyridine formulation, **3a**, to be correct (Figure 4). The six-coordinate pseudo-octahedral tantalum(III) complex exhibits near-linear Ta−O(1)−C(1) (170.5(6)°) and Ta−O(2)−C(2) (170.3(6)°) angles, as seen for its synthetic precursor, and the C(41)−C(51) bond length in the bipyridine ligand is 1.386(15) Å. However, the Ta−O(1) (1.903(6) Å) and Ta−O(2) (1.903(7) Å) bond lengths of $TaMe(O\text{-}C[Ad](3,5\text{-}C_6H_3Me_2))_2(py)(bpy)$, **3a**, are slightly longer (by ca. 0.02 Å) than the corresponding tantalum−oxygen bond lengths in **2a**.

To better understand this multistep reaction, three deuterium-labeling studies were conducted: (i) a reaction was carried out using $C_5D_5N$ under $H_2$; (ii) a reaction was carried out using $C_6H_5N$ under $D_2$; and (iii) a reaction was carried out using $C_5D_5N$ under $D_2$. In each case, the gases evolved upon complete reaction were vacuum-transferred simultaneously for $^1$H NMR and infrared (IR) spectroscopic analysis. The following is a summary of observations that bear on the mecha-

**Scheme 2. Mechanistic Skeleton Consistent with the Data Involving *β*-Elimination from the Tantalum(III) Intermediate 4a and Subsequent Reductive *C*−*C* Coupling of Two Coordinated Pyridines at the *ortho* Position to Give 3a**




nism of $TaMe_3(O\text{-}C[Ad](3,5\text{-}C_6H_3Me_2))_2$ hydrogenolysis and pyridine C−C coupling:

1. The sole gaseous product of the reaction was methane ($C_6D_6$, 0.16 ppm, singlet); no ethane was formed.

2. Use of $C_5D_5N$ as solvent in conjunction with $H_2$ produced $CH_4$ as the sole methane isotopomer.

3. Use of $D_2$ gas with either $C_5D_5N$ or $C_6H_5N$ as solvent produced 60% $CH_3D$ ($C_6D_6$, 0.15 ppm, triplet, $J_{HD} = 2.0$ Hz) and 40% $CH_4$.

4. In none of the deuterium labeling studies was observed either of the following: (i) incorporation of D into the Ta−C$H_3$ group of the isolated and purified product or (ii) formation of HD gas.

Taken collectively, and bearing in mind that the isolated $TaMe(O\text{-}C[Ad](3,5\text{-}C_6H_3Me_2))_2(py)(bpy)$ product is not formed quantitatively, the above observations place some limits on the possible reaction mechanisms. Clearly, the lack of $CH_3D$ formation using a $H_2/C_5D_5N$ combination rules out pyridine as the source of H for the two departing methyl groups, implying that both departing Ta−Me groups have reacted *prior* to pyridine *ortho* C−D bond activation. A minimalist mechanistic skeleton consistent with the data is presented in Scheme 2. The first step is reductive hydrogenolysis (by any of several possible mechanisms) of both Ta−Me groups to produce a tantalum(III) intermediate (not observed) where coordination of pyridine seems likely since no reaction is observed in toluene. As illustrated in Scheme 2 for the reaction between **2a** and $C_5D_5N$ under $H_2$, the postulated six-coordinate intermediate, $TaMe(O\text{-}C[Ad]\text{-}(3,5\text{-}C_6H_3Me_2))_2(py)_3$ (**4a**), exhibits a *fac* arrangement of the three pyridine ligands reminiscent of the py/bpy arrangement in the structurally characterized final product. Pyridine dissociation leads to the formation of $TaMe(O\text{-}C[Ad](3,5\text{-}C_6H_3Me_2))_2(py)_n$ ($n = 1$ or 2), from which C−H activation occurs to give a pyridyl-hydride/deuteride complex.[39] Conversion of this logical tantalum(V) intermediate to the observed and isolated final product is not mechanistically well-defined. The carbon−carbon bond forming step might involve either C−C reductive elimination from a bis-pyridyl species or, alternatively, intramolecular pyridyl nucleophilic attack on coordinated pyridine.

## Conclusions and Future Work

A new class of original enolate ligands has been conceived and synthesized to explore their applications as ancillary ligands for stabilizing low-coordinate early transition metals. The outcome of the design was a pair of enolate ligands that are topologically reminiscent of related anilide and ketimide ligands.[29−31,40] Trimethyltantalum bis-enolate complexes were subsequently prepared in high yield, and then converted in the presence of both dihydrogen and pyridine to an interesting complex, **3a**, containing both a coordinated pyridine and bipyridine. Preliminary mechanistic investigations suggest the intermediacy of monomethyl tantalum bis-enolate complexes in a complex multistep pathway. Further investigations of interest include attempts to access isolable tantalum(III) species by reduction of halogenated tantalum(V) bis- and tris-enolates (since the $d^2$ tantalum moiety portends fascinating and promising small molecule activation properties), as well as synthetic routes to prepare other early transition metal complexes supported by the enolate ligand system.

## Experimental Section

**General Procedures.** Unless otherwise stated, all manipulations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen or using Schlenk techniques under an argon atmosphere. Adamantyl epoxide[32] and $TaMe_3Cl_2$[34] were prepared according to published procedures. 2-Admantanone, 5-bromo-*m*-xylene, and bromomesitylene were obtained from Aldrich and used as received. Diethyl ether, *n*-pentane, *n*-hexane, and toluene were dried and deoxygenated by the method of Grubbs.[41] Pyridine was distilled from calcium hydride and collected under vacuum. $C_6D_6$ and $C_5D_5N$ were degassed and dried over 4 Å molecular sieves. Celite, alumina, and 4 Å molecular sieves were dried in vacuo overnight above 200 °C. $^1$H NMR (300 or 500 MHz) and $^{13}$C NMR (75 MHz) spectra were recorded on Varian Unity 300, Mercury 300, and Inova-501 spectrometers at room temperature unless otherwise stated. $^1$H and $^{13}$C NMR chemical shifts are reported with respect to internal solvent (7.16 ppm for $C_6D_5H$ and 128.39 (t) ppm for $C_6D_6$). IR spectra were recorded on a Bio-Rad FT-IR spectrometer using a solution KBr cell. C, H, and N elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

**Synthesis. OC($^2$Ad)Ar (1-H) ($^2$Ad = 2-adamantyl; Ar = 3,5-$C_6H_3Me_2$, Ar = 2,4,6-$C_6H_2Me_3$).** Since the preparations of both ligands were carried out in essentially the same way, only the synthesis of OC($^2$Ad)Ar ($^2$Ad = 2-adamantyl; Ar = 2,4,6-$C_6H_2Me_3$, **H[1b]**) is given in detail.

**Preparation of the Grignard Reagent.** A 2 L, two-neck, round-bottom flask was charged with 5.5 g (0.23 mol) of Mg powder and 600 mL of diethyl ether and capped with a reflux condenser and a septum. After the Mg was activated with 2.0 mL (10 mol %) of 1,2-dibromoethane, as observed by the decolorization of a grain of $I_2$, 34.4 g (0.17 mol) of bromomesi-

(39) Another possibility suggested by a reviewer involves direct coupling of two coordinated pyridines followed by subsequent loss of dihydrogen, obviating the requirement for C−H activation at Ta occurring and an intermediate such as **5a** being formed.

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tylene was syringed slowly into the vigorously stirring slurry containing Mg over a period of 0.5 h. A greenish-gray slurry developed within 12 h, after which the Grignard reagent was cooled in an ice-bath.

**Preparation of 2-Adamantyl(2,4,6-$C_6H_2Me_3$)methanol.** A 2 L, two-neck, round-bottom flask, charged with 25.1 g (0.15 mol) of adamantyl epoxide dissolved in 800 mL of diethyl ether, was sealed with two septa and cooled to −78 °C. The cooled Grignard reagent was then transferred via cannula to the epoxide solution, and the reaction mixture warmed and maintained at −42 °C in a liquid $N_2$/acetonitrile bath for 2 h, after which it was stirred at ambient temperature for 22 h. The white slurry was quenched with 500 mL of 1 M HCl, and the two colorless phases separated. After extracting the aqueous phase with hexanes, the combined organic phases were neutralized with several portions of dilute sodium bicarbonate solution and dried over anhydrous $MgSO_4$. After removal of the solvent, 41.6 g (0.14 mol, 93%) of white solid was collected (90% pure by $^1$H NMR spectroscopy). The product is readily recrystallized from cold *n*-pentane but can be used without purification in the next step. $^1$H NMR ($C_6D_6$): $\delta$ 1.07 (s, 1 H), 1.42 (s, 2 H), 1.58−2.09 (m, 12 H), 2.14 (s, 3 H, Me), 2.27 (s, 3 H, Me), 2.46−2.66 (m, 4 H), 5.18 (d, $J$ = 9.9 Hz, 1 H, C*H*(OH)), 6.72 (s, 1 H, *meta*-H), 6.78 (s, 1 H, *meta*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 21.19 (*meta*-Me), 21.60 (*para*-Me), 28.56, 28.97, 29.14, 30.01, 32.62, 33.57, 38.80, 39.91, 40.07, 49.50, 70.96 (C−O), 129.70, 132.22, 136.50, 136.63 (*meta*-C), 137.46 (*meta*-C), 138.31. IR ($C_6D_6$, cm$^{-1}$): 3582 (O−H, m), 2903 (C−H, s), 2848 (C−H, m). Anal. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92. Found: C, 84.40; H, 9.80.

**OC($^2$Ad)(2,4,6-$C_6H_2Me_3$) ($^2$Ad = 2-adamantyl, H[1b]).** A 14.70 g (0.147 mol, 1.5 equiv) sample of $CrO_3$ dissolved in 50 mL of 6 M $H_2SO_4$ was slowly added to a vigorously stirring acetone solution of 41.55 g (0.146 mol) of the alcohol obtained above. The reaction is highly exothermic, with the acetone refluxing occasionally during the addition; however, the exothermicity is well-controlled if the acid is added slowly. After the dark green solution had cooled to ambient temperature, the two phases were separated, and the aqueous phase extracted with petroleum ether. The organic phases were combined, neutralized with dilute KOH, dried over anhydrous $MgSO_4$, and concentrated to give 36.55 g (0.129 mol, 88%) of white solid (95% pure by $^1$H NMR spectroscopy). The product was purified by recrystallization from cold methanol (28.18 g, 0.100 mol, 65% from adamantyl epoxide). $^1$H NMR ($C_6D_6$): $\delta$ 1.52−1.88 (m, 10 H), 2.07 (s, 3 H, *para*-Me), 2.18 (s, 6 H, *ortho*-Me), 2.29−2.40 (m, 4 H), 2.98 (s, 1 H, OCC*H*), 6.63 (s, 2 H, *meta*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 20.56 (*meta*-Me), 21.31 (*para*-Me), 28.25 (C−H), 28.62 (C−H), 30.00 (C−H), 33.70 ($CH_2$), 38.01 ($CH_2$), 39.53 ($CH_2$), 58.29 (OC*C*H), 129.60 (*meta*-C), 134.32 (*ortho*-C), 138.36 (*para*-C), 139.88 (*ipso*-C), 211.43 (O═C). IR ($C_6D_6$, cm$^{-1}$): 2908 (C−H, s), 2851 (C−H, m), 1719 (m), 1690 (C═O, s). Anal. Calcd for $C_{20}H_{26}O$: C, 84.99; H, 9.28. Found: C, 84.76; H, 9.44.

**OC($^2$Ad)(3,5-$C_6H_3Me_2$) ($^2$Ad = 2-adamantyl, H[1a]).** A total of 25.85 g (0.096 mol, 53% from 30.0 g of adamantyl epoxide) was obtained. $^1$H NMR ($C_6D_6$): $\delta$ 1.49−1.58 (d, 2 H), 1.64 (s, 2 H), 1.73−1.86 (m, 6 H), 2.08 (s, 6 H, Me), 2.30−2.42 (m, 4 H), 3.25 (s, 1 H, OCC*H*), 6.83 (s, 1 H, *para*-H), 7.53 (s, 2 H, *ortho*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 21.73 (Me), 28.59 (C−H), 28.92 (C−H), 31.22 (C−H), 33.62 (C−$H_2$), 38.25 (C−$H_2$), 39.47 (C−$H_2$), 52.75 (OC*C*H), 126.70 (*ortho*-C), 134.09 (*para*-C), 138.38 (*meta*-C), 138.50 (*ipso*-C), 203.47 (O═C). IR ($C_6D_6$, cm$^{-1}$): 2906 (C−H, s), 2851 (C−H, m), 1723 (w), 1679 (C═O, s). Anal. Calcd for $C_{20}H_{24}O$: C, 85.03; H, 9.01. Found: C, 84.93; H, 8.92.

**K(O-C[Ad](3,5-$C_6H_3Me_2$)) (Ad = 2-adamantylidene, K[1a]).** A 2.16 g (0.054 mol) sample of KH was added to a 200 mL THF solution of 13.95 g (0.052 mol) of OC($^2$Ad)($C_6H_3Me_2$) (**H[1a]**) at room temperature. Slow effervescence occurred, the slurry changing from colorless to reddish-brown within 5 min. After 16 h of stirring at room temperature, the reaction mixture was filtered through Celite and the THF was subsequently removed in vacuo from the brown filtrate. The residue was then washed with *n*-pentane and dried to give 14.87 g (93%) of solvent-free **K[1a]** as a white powder. $^1$H NMR ($C_6D_6$): $\delta$ 1.58−2.20 (m, 12 H), 2.28 (s, 6 H, Me), 2.75 (s, 1 H, allylic α-H), 2.93 (s, 1 H, allylic α-H), 6.70 (s, 1 H, *para*-H), 7.06 (s, 2 H, *ortho*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$) could not be obtained due to the poor solubility of the salt. IR ($C_6D_6$, cm$^{-1}$): 2904 (C−H, s), 2849 (C−H, m), 2840 (C−H, m), 1680 (m), 1587 (m), 1300 (m), 1242 (m), 1197 (m). Anal. Calcd for $C_{19}H_{23}OK$: C, 74.46; H, 7.56. Found: C, 74.18; H, 7.68.

**K(O-C[Ad](2,4,6-$C_6H_2Me_3$)) (Ad = 2-adamantylidene, K[1b]).** A 2.71 g (0.068 mol) sample of KH was added to a 200 mL THF solution of 18.18 g (0.068 mol) of OC($^2$Ad)(2,4,6-$C_6H_2Me_3$) (**H[1b]**) at room temperature. Slow effervescence occurred, the slurry changing from colorless to yellow-brown within 5 min. After 10 h of stirring at room temperature, the reaction mixture was filtered through Celite and the THF was subsequently removed in vacuo. The salt was then dissolved in *n*-pentane twice and dried to give 20.69 g (94%) of solvent-free **K[1b]**. $^1$H NMR ($C_6D_6$): $\delta$ 1.65−2.20 (m, 13 H), 2.23 (br s, 9 H, all Me), 2.85 (s, 1 H, allylic α-H), 6.75 (s, 2 H, *meta*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 20.64 (*ortho*-Me), 21.47 (*para*-Me), 30.09 (C−H), 30.41 (C−H), 34.33 (C−H), 38.81 (C−$H_2$), 40.32 (C−$H_2$), 40.58 (C−$H_2$), 107.04, 128.78 (*meta*-C), 134.21 (*ortho*-C), 134.40, 144.06, 149.00. IR ($C_6D_6$, cm$^{-1}$): 2897 (C−H, s), 2840 (C−H, s), 1631 (w), 1605 (w), 1364 (m), 1351 (m), 1299 (C−O, s), 1265 (s), 1202 (m). Anal. Calcd for $C_{20}H_{25}OK$: C, 74.95; H, 7.86. Found: C, 75.08; H, 7.78.

**$TaMe_3$(O-C[Ad](3,5-$C_6H_3Me_2$))$_2$ (Ad = 2-adamantylidene, 2a).** A thawing solution of 2.00 g (6.73 mmol) of $TaMe_3Cl_2$ dissolved in 6 mL of toluene was added to a thawing slurry of 4.131 g (13.48 mmol, 2.00 equiv) of K[OC[2-Ad](3,5-$C_6H_3Me_2$)] (**K[1a]**) in 60 mL of toluene. The slurry turned clear and pale yellow within 1 h with concomitant formation of colorless crystals (KCl), as the reaction mixture warmed to ambient temperature. After removal of toluene from the viscous mixture, the gelatinous residue was extracted with 200 mL of *n*-pentane and filtered. On removal of all volatiles, 4.910 g (6.45 mmol, 96%) of white crystalline plates of pure **2a** remained. The plates were recrystallized from *n*-pentane at −40 °C to give X-ray quality crystals. $^1$H NMR ($C_6D_6$): $\delta$ 0.69 (s, 9 H, Ta−Me), 1.68−1.81 (m, 8 H), 1.88−1.97 (m, 12 H), 2.03−2.12 (m, 4 H), 2.14 (s, 12 H, *meta*-Me), 2.88 (s, 2 H, allylic α-H), 3.58 (s, 2 H, allylic α-H), 6.76 (s, 2 H, *para*-H), 7.22 (s, 2 H, *ortho*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 21.77 (*meta*-Me), 29.25 (C−H), 31.72 (C−H), 33.26 (C−H), 37.87 (C−$H_2$), 39.93 (C−$H_2$), 40.13 (C−$H_2$), 55.86 (Ta−Me), 127.55 (*ortho*-C), 129.01, 129.81 (*para*-C), 137.92 (*meta*-C), 138.26, 147.82. IR ($C_6D_6$, cm$^{-1}$): 2898 (C−H, s), 2848 (C−H, m), 1656 (w), 1598 (m), 1293 (C−O, s), 1247 (m), 1189 (s), 1123 (m). Anal. Calcd for $C_{41}H_{55}O_2Ta$: C, 64.72; H, 7.29. Found: C, 64.90; H, 7.40.

**Synthesis of $TaMe_3$(O-C[Ad](2,4,6-$C_6H_2Me_3$))$_2$ (Ad = 2-adamantylidene, 2b).** A thawing diethyl ether solution containing 0.544 g (1.70 mmol, 2.20 equiv) of K[OC[2-Ad](2,4,6-$C_6H_2Me_3$)] (**K[1b]**) was added to a thawing solution of 0.220 g (0.743 mmol) of $TaMe_3Cl_2$ dissolved in 5 mL of *n*-pentane. Within 10 min, a white precipitate formed in the colorless solution. After 1 h, the precipitate was removed by filtration through a bed of Celite, and the filtrate concentrated in vacuo to give 0.517 g (0.655 mmol, 88%) of spectroscopically pure plates of **2b**. The plates were recrystallized from diethyl ether at −40 °C. $^1$H NMR ($C_6D_6$): $\delta$ 0.43 (s, 9 H, Ta−Me), 1.64−2.02 (m, 24 H), 2.13 (s, 6 H, *para*-Me), 2.22 (s, 2 H, allylic α-H), 2.41 (s, 12 H, *ortho*-Me), 3.58 (s, 2 H, allylic α-H), 6.81 (s, 4 H, *meta*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 20.48 (*ortho*-Me), 21.55 (*para*-Me), 29.30 (C−H), 31.19 (C−H), 33.21 (C−H), 37.82 (C−$H_2$), 39.78 (C−$H_2$), 39.81 (C−$H_2$), 53.71 (Ta−Me), 128.63 (*meta*-C), 128.77, 134.05, 136.97 (*ortho*-C), 137.34, 144.04. IR ($C_6D_6$, cm$^{-1}$): 2909 (C−H, s), 2849 (C−H, m), 1666 (w), 1268 (C−O,

s), 1227 (m), 1208 (s), 1092 (m). Anal. Calcd for $C_{43}H_{59}O_2Ta$: C, 65.47; H, 7.54. Found: C, 65.70; H, 7.72.

**TaMe(O-C[Ad](3,5-$C_6H_3Me_2$))$_2$(py)(bpy) (Ad = 2-adamantylidene, py = N-bound pyridine, bpy = $\kappa^2$-2,2′-bipyridine), 3a.** A 5 mL pyridine solution of **2a** (0.500 g, 0.657 mmol) in a 50 mL reaction vessel was degassed twice before being sealed with a Teflon valve under an $H_2$ atmosphere at −196 °C. After the pale yellow solution had warmed to ambient temperature, the reaction vessel was heated to 70 °C for 5 days. Within 15 min of heating, a red solution formed. After 5 days, all volatiles were removed in vacuo from the dark brown solution. The oily brown residue was then dissolved in diethyl ether, concentrated, and triturated twice with *n*-pentane to yield 0.284 g (0.294 mmol, 45%) of dark brown **3a**. Recrystallization from a diethyl ether solution gave 0.094 g (0.097 mmol, 15%) of brown crystals. $^1$H NMR and COSY ($C_6D_6$, 500 MHz): $\delta$ 1.03 (s, 3 H, Ta−Me), 1.65−2.20 (m, 24 H), 2.06 (s, 12 H, *meta*-Me), 2.73 (s, 2 H, allylic α-H), 3.47 (s, 2 H, allylic α-H), 4.96 (t, $J$ = 5.9 Hz, 2 H, 2,2′-bpy 5,5′-H), 5.56 (dd, $J$ = 6.3 and 8.4 Hz, 2 H, 2,2′-bpy 4,4′-H), 6.29 (t, $J$ = 6.8 Hz, 2 H, py *meta*-H), 6.62 (m, 3 H, enolate *para*-H and py *para*-H), 6.93 (d, $J$ = 9.3 Hz, 2 H, 2,2′-bpy 3,3′-H), 7.00 (s, 4 H, enolate *ortho*-H), 8.11 (d, $J$ = 4.5 Hz, 2 H, py *ortho*-H), 8.31 (d, $J$ = 7.2 Hz, 2 H, 2,2′-bpy 6,6′-H). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 21.79 (*meta*-Me), 29.24 (C−H), 29.27 (C−H), 30.59 (C−H), 33.50 (C−H), 37.89 (C−$H_2$), 39.76 (C−$H_2$), 39.84 (C−$H_2$), 40.11 (C−$H_2$), 40.25 (C−$H_2$), 50.58 (Ta−Me), 111.67 (C−H), 119.37 (C−H), 120.70 (C−H), 124.19 (C−H), 127.41 (enolate *ortho*-C), 127.50, 129.34 (enolate *para*-C), 131.43, 137.19 (py *para*-C), 137.69 (enolate *meta*-C), 137.80 (C−H), 138.78 (enolate *ipso*-C), 146.73, 146.90 (C−H). IR ($C_6D_6$, cm$^{-1}$): 2903 (C−H, s), 2845 (C−H, m), 1646 (w), 1599 (m), 1481 (m), 1293 (s), 1249 (m), 1213 (m), 1191 (s). Anal. Calcd for $C_{54}H_{62}O_2N_3Ta$: C, 67.14; H, 6.47; N, 4.35. Found: C, 66.86; H, 6.34; N, 4.18.

**Isotope-Labeling Studies. (i) Experiment with Pyridine-$d_5$ Only.** The protocol described above for the preparation of **3a** was repeated using 0.276 g (0.363 mmol) of **2a** and 4 mL of pyridine-$d_5$ as the solvent. After 5 days, the gases in the reaction vessel were vacuum-transferred simultaneously into a gas IR cell and a NMR tube containing frozen $C_6D_6$. IR (gas-phase, cm$^{-1}$): 3017 ($CH_4$ $t_2$ stretch), 1306 ($CH_4$ $t_2$ bend). $^1$H NMR ($C_6D_6$): $\delta$ 4.47 (s, $H_2$), trace at 4.43 (t, $J_{HD}$ = 42.5 Hz, HD), 0.16 (s, $CH_4$), trace at 0.15 (t, $J_{HD}$ = 2.0 Hz, $CH_3D$). The brown solution was worked up as above to give 0.104 g (0.106 mmol, 29%) of **3a**-$d_{13}$ as verified by $^1$H NMR.

**(ii) Experiment with Deuterium ($D_2$) Only.** The protocol described above for the preparation of **3a** was repeated using 0.347 g (0.456 mmol) of **2a** and 5 mL of pyridine under an atmosphere of $D_2$. After 5 days, the gases in the reaction bomb flask were vacuum-transferred simultaneously into a gas IR cell and a NMR tube containing frozen $C_6D_6$. IR (gas-phase, cm$^{-1}$, only $CH_3D$ stretches described, see above for $CH_4$ stretches): 2820 (e C−H stretch), 2200 ($a_1$ C−D stretch), 1156 (e C−H bend), 780 ($a_1$ bend). $^1$H NMR ($C_6D_6$): $\delta$ 4.47 (s, $H_2$), 0.15 (t, $J_{HD}$ = 2.0 Hz, $CH_3D$, 61%), 0.16 (s, $CH_4$, 39%). The brown solution was worked up as above to give 0.199 g (0.210 mmol, 45%) of **3a** as verified by comparison of its $^1$H NMR spectrum with that of an independently prepared sample.

**(iii) Experiment with Deuterium ($D_2$) and Pyridine-$d_5$ in NMR Tube Experiment.** The protocol described above for the preparation of **3a** was repeated using 0.035 g (0.046 mmol) of **2a** and approximately 0.7 mL of pyridine-$d_5$ under an atmosphere of $D_2$ in a J-Young NMR tube with a Teflon valve. The reaction was monitored regularly over 5 days. The $^1$H NMR spectrum before heating showed only **2a** and $H_2$ with no indication of any pyridine adducts. Both $CH_3D$ and $CH_4$ were formed in a ratio of ca. 59% to 41%, respectively. The ratio did not change over 5 days, and HD formation was not observed. In addition, more than one tantalum compound was formed, as indicated by the complex $^1$H NMR spectrum. $^1$H NMR ($C_6D_6$, methane species only): $\delta$ 0.11 (t, $J_{HD}$ = 2.0 Hz, $CH_3D$, 59%), 0.12 (s, $CH_4$, 41%).

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**Supporting Information Available:** Full X-ray crystallographic experimental details are provided including tables with data for the X-ray crystallographic studies of **2a** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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