Organometallics **1997,** *16,* 3421−3430

Synthetic, Structural, and Redox Studies of Arene Alkyl Complexes of Tantalum(III) Supported by Aryloxide and Arenethiolate Ligands

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Received March 10, 1997[⊗]

A series of η^6-hexamethylbenzene alkyl and aryl complexes of tantalum(III) supported by aryloxide and arenethiolate ligands have been prepared, characterized, and compared to their halide analogues. Thus, $(\eta^6\text{-}C_6Me_6)Ta(OAr)_2Cl$ (**1**, Ar = 2,6-$C_6H_3{}^iPr_2$) reacts with MeMgBr at low temperature to afford $(\eta^6\text{-}C_6Me_6)Ta(OAr)_2Me$ (**3**). Low-temperature alkylation of $(\eta^6\text{-}C_6Me_6)Ta(OAr)Cl_2$ (**2**) with 2 equiv of RMgBr forms $(\eta^6\text{-}C_6Me_6)Ta(OAr)R_2$ (**4**, R = Me; **5**, R = Et) and with 2 equiv of RLi affords $(\eta^6\text{-}C_6Me_6)Ta(OAr)R_2$ (**6**, R = CH_2SiMe_3; **7**, R = Ph). Complexes **3**−**7** are more stable than their halide precursors; no products arising from α- or β-H elimination processes were identified upon thermolysis. In addition to NMR studies of these compounds, cyclic voltammetry experiments show two oxidation processes; the $Ta(III) \rightleftarrows Ta(IV)$ couple is quasi-reversible, and the $Ta(IV) \rightarrow Ta(V)$ process is irreversible. Molecules of **5** exhibit a folded arene ligand with π-electron localization (diene−diyl structure) and normal ethyl ligands (no evidence for agostic interactions). Under the appropriate conditions, $(\eta^6\text{-}C_6Me_6)Ta(OAr)Cl_2$ (**2**) can be monoalkylated using 1 equiv of $LiCH_2SiMe_3$ or LiPh to afford $(\eta^6\text{-}C_6Me_6)Ta(OAr)(CH_2SiMe_3)Cl$ (**8**) and $(\eta^6\text{-}C_6Me_6)Ta(OAr)(Ph)Cl$ (**9**). However, attempts to monoalkylate $(\eta^6\text{-}C_6Me_6)Ta(OAr)Cl_2$ with 1 equiv of either MeMgBr or EtMgBr provide the "double-exchange" products $(\eta^6\text{-}C_6Me_6)Ta(OAr)(Me)Br$ (**10**) and $(\eta^6\text{-}C_6Me_6)Ta(OAr)(Et)Br$ (**11**), respectively. The metathesis product $(\eta^6\text{-}C_6Me_6)Ta(OAr)(Et)Cl$ (**12**) is isolated in good yield upon attempts to alkylate $(\eta^6\text{-}C_6Me_6)Ta(OAr)(CH_2SiMe_3)Cl$ (**8**) with $ZnEt_2$. However, $(\eta^6\text{-}C_6Me_6)Ta(OAr)(CH_2SiMe_3)Cl$ (**8**) reacts with PhLi to afford $(\eta^6\text{-}C_6Me_6)Ta(OAr)(CH_2SiMe_3)Ph$ (**13**). The halide alkyl complexes $(\eta^6\text{-}C_6Me_6)Ta(OAr)(Et)Br$ (**11**) and $(\eta^6\text{-}C_6Me_6)Ta(OAr)(CH_2SiMe_3)Cl$ (**8**) react with $LiBEt_3H$ to provide the hydrido complexes $(\eta^6\text{-}C_6Me_6)Ta(OAr)(Et)H$ (**14**) and $(\eta^6\text{-}C_6Me_6)Ta(OAr)(CH_2SiMe_3)H$ (**15**), respectively. The arenethiolate complexes $(\eta^6\text{-}C_6Me_6)Ta(OAr)(SAr')Cl$ (**16**) (Ar′ = 2,4,6-$C_6H_2{}^iPr_3$) and $(\eta^6\text{-}C_6Me_6)Ta(OAr)(S(mes))Cl$ (**17**) (mes = 2,4,6-$C_6H_2Me_3$) are formed upon reacting $(\eta^6\text{-}C_6Me_6)Ta(OAr)Cl_2$ (**2**) with the appropriate lithium arenethiolate reagent, and the characterization of these species is discussed.

Introduction

Several successful forays have been made into niobium and tantalum arene chemistry in recent years as a result of improved methods for introducing an arene ligand to these metals.[1] The initial coordination of an η^6-arene is typically accomplished by one of the following approaches: (1) by reduction of a metal halide in the presence of the arene,[2−4] including Al/AlX_3 reduction under Fischer−Hafner conditions;[5] (2) by substitution reactions using a halide acceptor, in which reduction of the metal does not occur;[6−8] (3) by metal vapor synthesis procedures;[9−12] (4) by alkyne cyclotrimerization chemistry;[13−19] or more recently, (5) by arene exchange reactions.[8] These synthetic strategies have permitted access

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

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S0276-7333(97)00197-0 CCC: $14.00

to a range of oxidation states in niobium and tantalum arenes, from d^6 M(−I) to d^1 M(IV).[1]

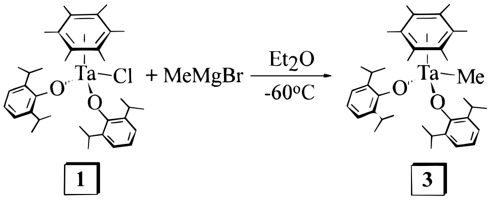
In contrast to complexes of niobium, the majority of d^2 Ta(III) arene species have been prepared by alkyne cycloaddition methods and contain a metal supported by aryloxide ligation.[1] These complexes have proven especially valuable since rare Ta(II) and Ta(IV) arenes are both accessible from redox reactions of their Ta(III) counterparts. Thus, stable Ta(II) complexes (η^6-C_6R_6)Ta(OAr)$_2$ (R = Me, Et; Ar = 2,6-$C_6H_3{}^iPr_2$) are prepared from the one-electron reduction of (η^6-C_6R_6)Ta(OAr)$_2$Cl,[15,18] and electrochemical evidence has been presented for the existence of labile [(η^6-C_6Me_6)Ta(OAr)R_2]$^+$ complexes,[17] thereby affording the first evidence for d^1 arene species.

Arene complexes of Ta(III) are also of interest for the unusual structural properties they may exhibit. For example, Wolczanski and co-workers have prepared {μ-η^2(1,2):η^2(4,5)-C_6H_6}[Ta(silox)$_3$]$_2$ (silox = OSi^{t}Bu$_3$) in which two d^2 tantalum species bind opposite faces of benzene in an η^2-fashion.[20] More relevant to this study are the structural distortions that often occur when an arene coordinates η^6 to Ta(III), *viz.* significant ligand folding and π-electron localization are typically observed.[16]

Finally, the hexamethylbenzene complex (η^6-C_6Me_6)Ta(OAr)$_2$Cl (**1**, Ar = 2,6-$C_6H_3{}^iPr_2$) has been shown to engage in an intramolecular C−H bond activation to provide an unstable, transient "tuck-in" complex (η^6,η^1-$C_6Me_5CH_2$)Ta(OAr)$_2$(H)Cl.[14] This oxidation reaction generates a d^0 metal center that labilizes the η^6 portion of a nascent η^6,η^1-$C_6Me_5CH_2$ ligand and results in the isolation of a d^0 η^1-$C_6Me_5CH_2$ complex.[16] This process is related to the intramolecular metalation in pentamethylcyclopentadienyl ligands (η^5-C_5Me_5) that provide stable complexes containing the η^5,η^1-$C_5Me_4CH_2$ moiety.[21] The prospect of preparing *isolable* η^6,η^1-C_6Me_5-CH_2 complexes led us to identify η^6-C_6Me_6 Ta(III) species containing alkyl or hydride ligands as synthetic targets, in an effort to induce C−H addition of the η^6-C_6Me_6 moiety to a Ta−R or Ta−H bond. In this report, the preparation and properties of a series of arene alkyl complexes of Ta(III) are described in which the metal is supported by aryloxide or arenethiolate ligands. Niobium and tantalum η^6-arenes have recently been reviewed,[1,7] and a portion of these results have been communicated.[17]

Results

Alkylation Studies of Tantalum(III) Arene Species: Dialkyl and Alkyl Halide Complexes. Blue crystals of (η^6-C_6Me_6)Ta(OAr)$_2$Cl (**1**, Ar = 2,6-$C_6H_3{}^iPr_2$) are prepared by reducing Ta(OAr)$_2$Cl$_3$(OEt$_2$) by two electrons in the presence of MeC≡CMe as previously described.[13,14] Turquoise (η^6-C_6Me_6)Ta(OAr)Cl$_2$ (**2**) is subsequently available in near quantitative yield from the metathesis of (η^6-C_6Me_6)Ta(OAr)$_2$Cl (**1**) with Ta(OAr)$_2$Cl$_3$(OEt$_2$), a reaction that is driven by the stability of byproduct Ta(OAr)$_3$Cl$_2$(OEt$_2$).[16] Alkylation studies of both **1** and **2** have been carried out. (η^6-C_6Me_6)Ta(OAr)$_2$Cl (**1**) can be smoothly alkylated with 1 equiv of MeMgBr (Et$_2$O, −60 °C) to afford (η^6-C_6Me_6)Ta(OAr)$_2$Me (**3**) as purple crystals in moderate yield, eq 1. Attempts to alkylate **1** with larger alkyls (Et, CH$_2$SiMe$_3$, or Ph), using either Grignards or alkyllithium reagents, yielded only intractable oils from which no organometallic products could be isolated.

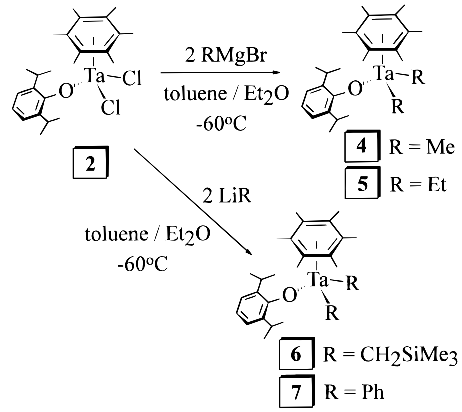


(1)

(η^6-C_6Me_6)Ta(OAr)Cl$_2$ (**2**) reacts rapidly with 2 equiv of MeMgBr at low temperature to provide, after appropriate workup, blue-violet crystals of (η^6-C_6Me_6)Ta(OAr)Me$_2$ (**4**) in ca. 75% yield, Scheme 1. The analogous reactions using 2 equiv of EtMgBr, Me$_3$SiCH$_2$Li, or PhLi afford blue-violet (η^6-C_6Me_6)Ta(OAr)Et$_2$ (**5**), dark violet (η^6-C_6Me_6)Ta(OAr)(CH$_2$SiMe$_3$)$_2$ (**6**), and purple (η^6-C_6Me_6)Ta(OAr)Ph$_2$ (**7**) in high yield. Molecular ion peaks were obtained for (η^6-C_6Me_6)Ta(OAr)Me$_2$ (**4**, $m/z = 550$) and (η^6-C_6Me_6)Ta(OAr)Et$_2$ (**5**, $m/z = 578$) in low resolution CI mass spectrometry studies. In contrast to the precursor dichloride **2** and monochloride **1**, complexes **3**−**7** are more stable thermally (qualitatively, **7** > **3** ≈ **4** > **6** > **5**). For example, while (η^6-C_6Me_6)Ta(OAr)$_n$Cl$_{3-n}$ (n = 1, 2) are completely decomposed in <1 min in refluxing toluene-d_8,[16] (η^6-C_6Me_6)Ta(OAr)Me$_2$ (**4**) and (η^6-C_6Me_6)Ta(OAr)Ph$_2$ (**7**) are only ca. 40−50% decomposed after 5 days under these conditions. The only identifiable product formed upon thermolyzing **3**−**7** is C_6Me_6; the metal-containing species reduce to an intractable, insoluble material. Even the β-H-containing complex (η^6-C_6Me_6)Ta(OAr)Et$_2$ (**5**) thermally decomposes more slowly than the chloride complexes, and the expected elimination products (e.g., C_2H_6 or C_2H_4) were not observed spectroscopically. Exhaustive photolysis of these compounds achieved the same results over a shorter period; for example, solutions of **5** and **7** were completely decomposed over a period of 2−3 h, and all the Ta(III) arene complexes were decomposed in <48 h under photolytic conditions (^{1}H NMR, C_6D_6).

Because facile elimination or tuck-in reactions were not observed in the dialkyl complexes,[22] we sought to prepare monoalkyl halide species from which we might access the corresponding alkyl hydrides. However,

Scheme 1



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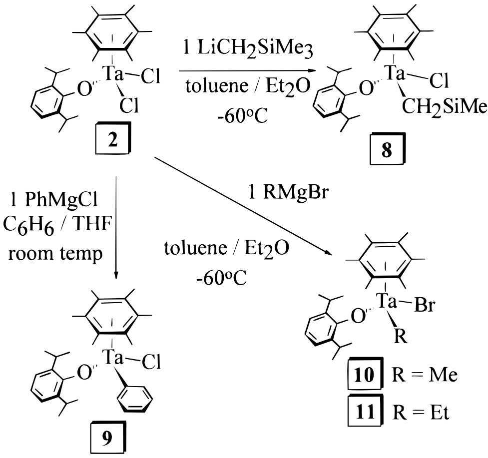
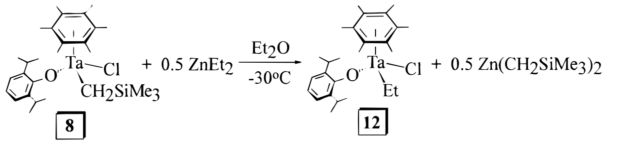
Scheme 2



attempts to prepare pure (η^6-C$_6$Me$_6$)Ta(OAr)(Me)Cl by the reaction of (η^6-C$_6$Me$_6$)Ta(OAr)Cl$_2$ with 1 equiv of MeMgCl or MeLi under the conditions outlined above provides a low yield of (η^6-C$_6$Me$_6$)Ta(OAr)Me$_2$, along with intractable decomposition products. However, the mono(alkyl) complex (η^6-C$_6$Me$_6$)Ta(OAr)(CH$_2$SiMe$_3$)Cl (**8**) is readily prepared from reacting (η^6-C$_6$Me$_6$)Ta(OAr)Cl$_2$ (**2**) with 1 equiv of LiCH$_2$SiMe$_3$ under these conditions (toluene/Et$_2$O, −60 °C), Scheme 2. Our attempts to prepare (η^6-C$_6$Me$_6$)Ta(OAr)(Ph)Cl from (η^6-C$_6$Me$_6$)Ta(OAr)Cl$_2$ and 1 equiv of LiPh under similar conditions were also problematic. However, we have found that this reaction proceeds smoothly using PhMgCl in benzene/THF, even at room temperature, to afford blue (η^6-C$_6$Me$_6$)Ta(OAr)(Ph)Cl (**9**) in moderate to high yields, Scheme 2. Therefore, the mixed alkyl halide complexes such as **8** and **9** are clearly stable, but the synthetic approaches to these species are critical to ensure that further reaction or degradation is halted.

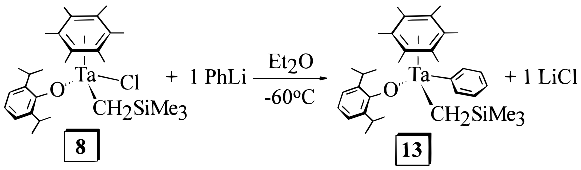
Quite different results were obtained when alkylating (η^6-C$_6$Me$_6$)Ta(OAr)Cl$_2$ with the bromide Grignards. (η^6-C$_6$Me$_6$)Ta(OAr)Cl$_2$ (**2**) reacts with 1 equiv of MeMgBr or EtMgBr to provide the "double-exchange" products (η^6-C$_6$Me$_6$)Ta(OAr)(Me)Br (**10**) and (η^6-C$_6$Me$_6$)Ta(OAr)(Et)Br (**11**), respectively, in >95% yield (^{1}H NMR), Scheme 2. The complexes were identified by, *inter alia*, their CI mass spectra in which bromine isotopes were obvious: (η^6-C$_6$Me$_6$)Ta(OAr)(Me)Br (**10**) m/z = 614 (^{79}Br), 616 (^{81}Br); (η^6-C$_6$Me$_6$)Ta(OAr)(Et)Br (**11**) m/z = 628 (^{79}Br), 630 (^{81}Br). These reactions are no doubt driven by the lattice energy of MgCl$_2$, as the expected product in the reaction **2** and EtMgBr, (η^6-C$_6$Me$_6$)Ta(OAr)(Et)Cl (*vide infra*), is observed in <5% yield. This species is presumed to be a kinetic product that reacts further with byproduct "MgClBr" to form **11** and MgCl$_2$.

(η^6-C$_6$Me$_6$)Ta(OAr)(Et)Cl (**12**) can be prepared by an independent and equally interesting metathesis reaction. Thus, (η^6-C$_6$Me$_6$)Ta(OAr)(CH$_2$SiMe$_3$)Cl reacts with 0.5 equiv of ZnEt$_2$ (Et$_2$O, −30 °C) in an unusual exchange reaction to form the unexpected product (η^6-C$_6$Me$_6$)Ta(OAr)(Et)Cl (**12**) in moderate yield, along with Zn(CH$_2$SiMe$_3$)$_2$, identified by ^{1}H NMR, eq 2. This reaction may provide some insight into the relative bond energetics of early transition metal verses zinc alkyl since qualitatively the bond energies follow [(Ta^{III}−Et) + (Zn−CH$_2$SiMe$_3$)] > [(Ta^{III}−CH$_2$SiMe$_3$) + (Zn−Et)].



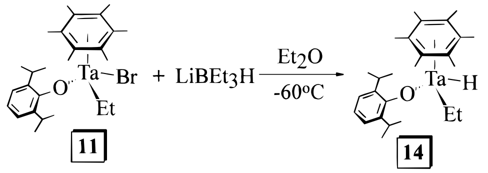
(2)

The utility of the monohalide compounds as precursors to mixed ligand dialkyl species was examined using (η^6-C$_6$Me$_6$)Ta(OAr)(CH$_2$SiMe$_3$)Cl (**8**). The reaction of (η^6-C$_6$Me$_6$)Ta(OAr)(CH$_2$SiMe$_3$)Cl (**8**) with 1 equiv of PhLi gives (η^6-C$_6$Me$_6$)Ta(OAr)(CH$_2$SiMe$_3$)Ph (**13**) in high yield as a purple solid, eq 3. Compound **13** is formed in near quantitative yield but isolated in ca. 70% yield due to its high solubility. This species exhibits a thermal stability that is intermediate between the diphenyl derivative **7** and the bis(CH$_2$SiMe$_3$) complex **6**.



(3)

Tantalum(III) Arene Alkyl Hydride Complexes. With the required alkyl halide species in hand, we set out to prepare alkyl hydride complexes. (η^6-C$_6$Me$_6$)Ta(OAr)EtBr (**11**) reacts with LiBEt$_3$H (Et$_2$O, −60 °C) to provide (η^6-C$_6$Me$_6$)Ta(OAr)Et(H) (**14**) as an extremely soluble, magenta solid in high yield, eq 4. Similarly, (η^6-C$_6$Me$_6$)Ta(OAr)(CH$_2$SiMe$_3$)Cl (**8**) reacts smoothly with LiBEt$_3$H under identical conditions to afford (η^6-C$_6$Me$_6$)Ta(OAr)(CH$_2$SiMe$_3$)(H) (**15**) as a violet solid, eq 5. Both **14** and **15** exhibit a Ta*H* hydride resonance at ca. δ 5.87 (C$_6$D$_6$) and a ν(Ta−H) stretch between 1760 and 1780 cm^{-1}. While **15** is stable for months at room temperature in Et$_2$O (and for days in THF), **14** decomposes slowly (to C$_6$Me$_6$ and unidentified products) over a period of hours.



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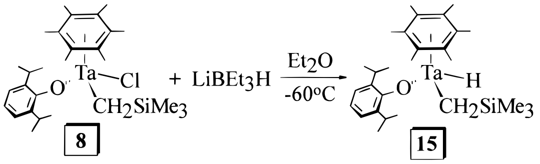


(5)

Thermolytic decomposition studies of **14** and **15** provided no evidence for the generation of a tuck-in complex (see Discussion section). However, preliminary evidence was uncovered for the occurrence of a hydride exchange process. Thus, the reaction of (η^6-C$_6$Me$_6$)Ta(OAr)(CH$_2$SiMe$_3$)Cl (**10**) with LiBEt$_3$D (Et$_2$O, −60 °C) provides a violet solid in high yield. A ^{1}H NMR study of this complex reveals a spectrum identical to that of (η^6-C$_6$Me$_6$)Ta(OAr)(CH$_2$SiMe$_3$)(H) (**15**) with the hydride resonance at δ 5.87 (C$_6$D$_6$) integrating to ca. 0.67 protons. Although evidence as to the nature of this supposed exchange process has not been obtained,

Table 1. Details of the X-ray Diffraction Study of (η^6-C_6Me_6)Ta(OAr)Et_2 (5)

Crystal Parameters	
molecular formula	$C_{28}H_{45}OTa$
mol wt	578.62
F(000)	1176
cryst color	red
space group	orthorhombic, *Pnma* (No. 62)
unit cell volume, Å^3	2671.8(11)
a, Å	18.717(4)
b, Å	12.487(4)
c, Å	11.431(3)
Z	4
D(calcd), g cm^{-3}	1.44
cryst dimens, mm	0.50 × 0.30 × 0.62
ω width, deg	0.25
abs coeff, cm^{-1}	40.8
data collection temp, °C	23 ± 1
Data Collection	
diffractometer	Enraf-Nonius CAD4
monochromator	graphite crystal, incident beam
Mo Kα radiation, λ, Å	0.710 73
2θ range, deg	2−50
octants collected	$+h,+k,\pm l$
scan type	ω−2θ
scan speed, deg min^{-1}	1−7
scan width, deg	2.0 + (2θKα_2-2θKα_1)
total no. of reflns measd	2811 (2456 unique)
corrections	Lorentz-polarization; ψ-scan absorption (min 0.585, max 0.999, avg 0.789)
Solution and Refinement	
solution	direct methods
refinement	full-matrix least-squares
minimization function	$\Sigma w(\|F_o\| - \|F_c\|)^2$
no. of reflns used in refinement; $I > 3\sigma(I)$	2005
no. of params refined	228
R ($\Sigma\|\|F_o\| - \|F_c\|/\Sigma\|F_o\|$)	0.020
*R*w ($[\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w(F_o)^2]^{1/2}$)	0.027
esd of obs of unit weight	1.18
convergence, largest shift	0.02σ
Δ/σ(max), e^{-1}/Å^3	0.42 (6)
Δ/σ(min), e^{-1}/Å^3	-0.58 (0)
computer hardware	VAX
computer software	SDP/VAX (Enraf-Nonius)

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) in (η^6-C_6Me_6)Ta(OAr)Et_2 (5)[a,b]

Bond Distances			
Ta−C(1)	2.302(5)	Ta−C(10)	2.207(4)
Ta−C(2)	2.513(3)	C(10)−C(11)	1.510(7)
Ta−C(3)	2.448(4)	Ta−O(20)	1.912(3)
Ta−C(4)	2.187(5)	O(20)−C(21)	1.363(6)
C(1)−C(2)	1.457(4)	C(3)−C(4)	1.469(5)
C(2)−C(3)	1.372(5)		
Bond Angles			
Bz*−Ta−C(10)	109.38(9)	C(1)−Ta−O(20)	170.9(2)
Bz*−Ta−O(20)	151.0(1)	C(1)−Ta−C(10)	86.4(1)
C(10)−Ta−C(10′)	103.1(1)	C(1)−Ta−C(4)	78.2(2)
O(20)−Ta−C(10)	88.0(1)	C(4)−Ta-O(20)	110.9 (2)
Ta-O(20)-C(21)	177.4(3)	C(4)-Ta−C(10)	126.3(1)
Ta−C(10)−C(11)	113.1(3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Bz* = C_6Me_6 centroid.

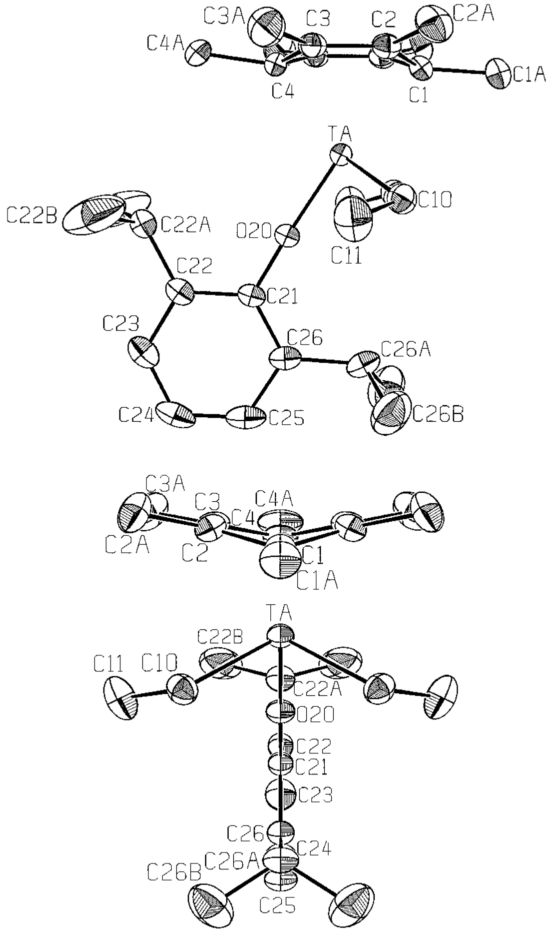


Figure 1. ORTEP drawings of (η^6-C_6Me_6)Ta(OAr)Et_2 (**5**), with atoms shown as 50% probability ellipsoids.

experiments to determine whether this is an exchange process into the ring or other ancillary ligand are being examined.

X-ray Structural Study of (η^6-C_6Me_6)Ta(OAr)Et_2 (5). Dark blue-violet, single crystals of (η^6-C_6Me_6)Ta(OAr)Et_2 (**5**) suitable for an X-ray structural study were grown from pentane at −35 °C. A summary of the crystal data and structural analysis are given in Table 1, and relevant bond distances and bond angles are provided in Table 2. Figure 1 presents two views of (η^6-C_6Me_6)Ta(OAr)Et_2 in which the crystallographic mirror symmetry is evident. Altogether, 14 of the 30 non-hydrogen atoms lie along this crystallographically imposed mirror plane. The plane is *perpendicular* to the C_6Me_6 ligand and *contains* the OAr phenyl ring and the Ta atom, as well as C(1), C(1a), C(4), and C(4a) of the C_6Me_6 ligand.

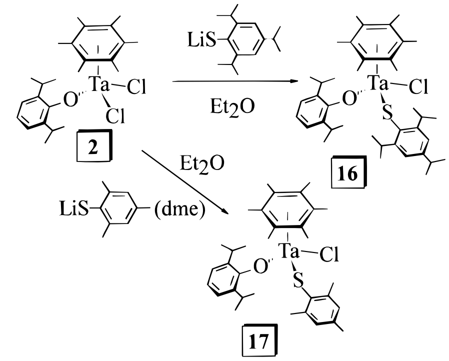
The molecular structure of (η^6-C_6Me_6)Ta(OAr)Et_2 (**5**) reveals an interesting comparison to the parent dichloride complex **2**.[16] As seen in Figure 1, the η^6-C_6Me_6 ligand in (η^6-C_6Me_6)Ta(OAr)Et_2 displays the following structural features: (1) substantial folding; the dihedral angle between the C(1)−C(2)−C(3)−C(4) and C(1)−C(2′)−C(3′)−C(4) planes in **5** is 27.3(0.2)°, which compares with 26.8(0.3)° for (η^6-C_6Me_6)Ta(OAr)Cl_2 (**2**); (2) an interruption of aromaticity within the C_6Me_6 ring, *viz.* a diene−diyl (or 1,4-diene) type π localization; and (3) the close approach of C(1) and C(4) to the metal, *viz.* 2.302(5) and 2.187(5) Å, respectively, compared to an average 2.481(4) Å for the other arene carbons. These structural features are duplicated in all other structurally characterized Ta(III) arene compounds and may be attributed to a selective interaction between a filled metal δ function ($d_{x^2-y^2}$, where the mirror plane constitutes the *xz* plane) with *one* arene π* LUMO of the E_{2u} set (B_2 symmetry), as previously described.[16,18] In addition, the longer Ta−C(1) vs Ta−C(4) metal−carbon distances may reflect a structural *trans* effect since C(1) is *trans* to the strong π donor aryloxide ligand. The rotational conformation of the arene ring in **5** is such that the ethyl Ta−C$_\alpha$ bonds and alkoxide Ta−O−C$_{ipso}$ linkage perfectly eclipse the arene carbon atoms rather than stagger them as the Ta−ligand bonds do in (η^6-C_6Me_6)Ta(OAr)Cl_2 (**2**).[16] Finally, the plane of the OAr ligand in **5** is oriented perpendicular to the arene ligand and 90° from the analogous OAr plane in **2**. The orientation of the ethyl ligands about the metal center can be rationalized by a space-filling model of the molecule in which the ethyl ligands are shown to fit nicely into a steric pocket formed by the hexamethylbenzene ring and the isopropyl groups on the OAr ligand. No evidence for agostic interactions in the structure of **5** are evident.

Tantalum(III) Arene Complexes Supported by Arenethiolate Ligands. We recently described the η^2-(*N,C*)-pyridine complexes [η^2(*N,C*)-2,4,6-$NC_5{}^tBu_3H_2$]Ta-$(OAr)_2$X (X = Cl,[23,24] alkyl,[24] or aryl[25]) and related [η^2(*N,C*)-quinoline]Ta$(OAr)_n$$Cl_{3-n}$L ($n$ = 2, 3)[26] as models for the catalyst−substrate complex in hydrodenitrogenation (HDN) catalysis.[27,28] The importance of the reducing ability of Ta(III) in binding and disrupting the aromaticity of the nitrogen heterocycle has been demonstrated,[20,29] although the nitrogen heterocycles are π localized in a 1,3-diene fashion rather than the 1,4-diene localization described above for the η^6-C_6Me_6 ligands. Because most hydrotreating catalysts are metal sulfide based,[27,28,30,31] we set out to compare these aryloxide-supported species to more sulfur-rich Ta(III) complexes.[32]

Reacting (η^6-C_6Me_6)Ta(OAr)Cl_2 (**2**) with 1 equiv of LiSAr′ (Ar′ = 2,4,6-$C_6H_2{}^iPr_3$, Et_2O, room temperature) afforded blue (η^6-C_6Me_6)Ta(OAr)(SAr′)Cl (**16**) in high yield, Scheme 3. This compound exhibits improved thermal stability over its aryloxide analogue (η^6-C_6Me_6)Ta$(OAr)_2$Cl (**1**) as well as its precursor **2**. Light blue crystals of (η^6-C_6Me_6)Ta(OAr)(S(mes))Cl (**17**, mes = 2,4,6-$C_6H_2Me_3$) are also available in high yield from **2** and LiS(mes)(dme) under similar conditions, Scheme 3. The greater thermal stability of this complex as compared to **1** or **2** is also noted.

Attempts to alkylate (η^6-C_6Me_6)Ta(OAr)(SAr′)Cl (**16**) using a variety of alkylating agents did not afford the alkyl (η^6-C_6Me_6)Ta(OAr)(SAr′)R species cleanly; considerable decomposition of the starting complex is observed in these reactions. Since (η^6-C_6Me_6)Ta(OAr)Cl_2 (**2**) is prepared from (η^6-C_6Me_6)Ta$(OAr)_2$Cl (**1**) and Ta$(OAr)_2$-$Cl_3(OEt_2)$,[16] we attempted the reaction of (η^6-C_6Me_6)-Ta(OAr)(S(mes))Cl (**17**) with Ta$(OAr)_2Cl_3(OEt_2)$ in an attempt to prepare (η^6-C_6Me_6)Ta(S(mes))Cl_2. However, under a variety of conditions, only starting material was recovered from this reaction. Finally, we note that some of the HDN substrate−catalyst models such as [η^2(*N,C*)-6-methylquinoline]Ta$(OAr)_2$Cl(OEt_2)[26] are best prepared by arene displacement in (η^6-C_6Me_6)Ta$(OAr)_2$Cl (**1**) with the appropriate *N*-heterocycle. In preliminary studies, however, neither **16** nor **17** have, in our hands, reacted smoothly with 6-methylquinoline to afford the corresponding [η^2(*N,C*)-6-methylquinoline]Ta(SR)(OAr)Cl species.

Scheme 3



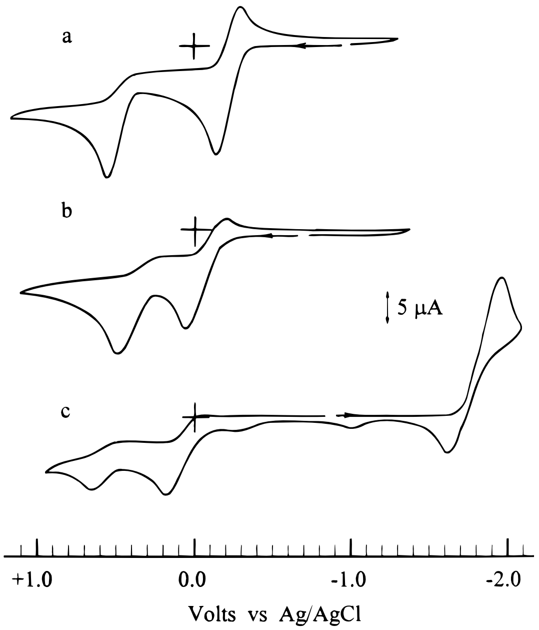


Figure 2. Cyclic voltammograms of (a) (η^6-C_6Me_6)Ta-(OAr)Ph_2 (**7**) in CH_2Cl_2, (b) (η^6-C_6Me_6)Ta(OAr)Me_2 (**4**) in THF, and (c) (η^6-C_6Me_6)Ta(OAr)(CH_2SiMe_3)Cl (**8**) in THF. All solutions are 0.1 M in $^nBu_4NPF_6$ and voltammograms are taken at a Pt disk electrode (vs Ag/AgCl) at a scan rate of 150 mV/s.

Electrochemical Studies of Tantalum(III) Arene Alkyls: Evidence for the Formation of Tantalum(IV) Arene Species. The stability of some of these arene alkyl complexes has permitted their electrochemical characterization. Cyclic voltammetry (CV) experiments on (η^6-C_6Me_6)Ta(OAr)Ph_2 (**7**) (CH_2Cl_2, 0.1 M in $^nBu_4NPF_6$) reveal two, one-electron oxidation processes, Figure 2 and Table 3. A quasi-reversible oxidation (the Ta(III) $\rightleftarrows$ Ta(IV) couple) occurs at $E_{1/2} = -0.22$ V vs Ag/AgCl ($E_{pa} - E_{pc}$ = 120 mV) while a second, irreversible oxidation (Ta(IV) → Ta(V)) comes at E_{pa} = +0.53 V vs

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Table 3. Redox Potentials (V vs Ag/AgCl) for Arene Alkyl Complexes of Tantalum[a]

complex	E^1_{pa}	E^2_{pa}	E_{pc}
THF Solution			
(η^6-C_6Me_6)Ta(OAr)Me_2 (**4**)	+0.07	+0.50	
(η^6-C_6Me_6)Ta(OAr)Et_2 (**5**)[b]	−0.02	+0.39	
(η^6-C_6Me_6)Ta(OAr)$(Ph)_2$ (**7**)	+0.12		
(η^6-C_6Me_6)Ta(OAr)(CH_2SiMe_3)Cl (**8**)	+0.18	+0.64	−1.91
(η^6-C_6Me_6)Ta(OAr)(Et)Br (**11**)	+0.22	+0.70	−2.03
(η^6-C_6Me_6)Ta(OAr)(CH_2SiMe_3)H (**15**)	+0.12		
CH_2Cl_2 Solution			
(η^6-C_6Me_6)Ta(OAr)$(Ph)_2$ (**7**)	$E_{1/2} = -0.22$	+0.53	

[a] All solutions were 0.1 M in $^nBu_4NPF_6$, and all potentials are reported in V vs Ag/AgCl. [b] The redox potentials for (η^6-C_6Me_6)-Ta(OAr)Et_2 (**5**) in THF solution are incorrectly reported in ref 17.

Ag/AgCl. A plot of i_{pa} vs the square root of the sweep rate ($\nu^{1/2}$) is linear ($R = 0.993$) for the −0.22 V oxidation, and i_{pa}/i_{pc} becomes 1.0 at scan rates >300 mV/s, so this process is best described as quasi-reversible on the CV time scale. Bulk electrolysis of a solution of **7** reveals that 1.0 ± 0.1 electron is transferred in the −0.22 V oxidation, although the resulting solution is devoid of electrochemically active species. Dilute samples of **7** may be chemically oxidized in toluene ([Cp_2Fe][BPh_4], −78 °C) to afford *highly* reactive solutions that exhibit an ESR signal (X-band, $\langle g \rangle = 1.933$, peak-to-peak separation = 145 G). However, ^{181}Ta hyperfine is not observed (at room temperature or −196 °C) nor necessarily expected in these spectra.[16,18] Cyclic voltammetry experiments on THF solutions of (η^6-C_6Me_6)Ta(OAr)Ph_2 (**7**) were less informative, since these solutions were less stable than the CH_2Cl_2 solutions described above. An irreversible oxidation of **7** appears at +0.12 V vs Ag/AgCl and is followed by ill-defined, irreversible electrochemical processes.

Cyclic voltammetry experiments on the remaining arene complexes, however, were conducted in THF since their CH_2Cl_2 and N≡CMe solutions are unstable. Compounds **4** and **5** also exhibit two electrochemical oxidations in THF but both are irreversible, Table 3. Consistent with the ease of oxidation of (η^6-C_6Me_6)Ta(OAr)Me_2 (**4**) is the very low energy ionization band (5.91 eV) observed in its He I photoelectron spectrum. Although (η^6-C_6Me_6)Ta$(OAr)_2$Cl (**1**) can be reduced by one electron to afford isolable (η^6-C_6Me_6)-Ta$(OAr)_2$,[18] **4** or **5** do not undergo electrochemical reduction to ca. −2 V vs Ag/AgCl in THF. All of these data support the metal center in these complexes being more electron rich than in their chloride precursor and suggest that their improved thermal stability may arise through enhanced back-bonding to the arene.

The alkyl halide complexes (η^6-C_6Me_6)Ta(OAr)(CH_2SiMe_3)Cl (**8**) and (η^6-C_6Me_6)Ta(OAr)(Et)Br (**11**) were examined in THF solution and, like their dialkyl analogues, exhibit two irreversible electrochemical oxidations. However, unlike **4** and **5**, compounds **8** and **11** now reveal an irreversible electrochemical reduction near −2 V vs Ag/AgCl in THF, Figure 2 and Table 3. This reduction does not constitute a product wave that arises as a result of the oxidations, since this feature is also observed with initial negative potential sweeps. The alkyl hydrides were found to be very unstable in these experiments. Thus, (η^6-C_6Me_6)Ta(OAr)(CH_2SiMe_3)H (**15**) reveals a single, completely irreversible oxidation process that produces a species without electrochemical activity. Finally, we note that the cyclic voltammetry scans shown in Figure 2 represent the best data obtained with these compounds. Most of the complexes reported here (including the arenethiolate species) exhibit limited stability in polar electrochemical solvents, and the irreversible processes that typically follow the initial oxidation suggest an even greater instability of a resulting cation.

Discussion

The arene alkyl complexes reported here all contain the η^6-C_6Me_6 ligand and were of interest to us for, among other things, their potential ability to tuck-in or C−H activate a C_6Me_6 methyl group to afford an η^6,η^1-$C_6Me_5CH_2$ ligand.[14] Intramolecular metalation of a C−H bond[21] in pentamethylcyclopentadienyl ligands (η^5-C_5Me_5) can provide isolable complexes containing the tucked-in η^5,η^1-$C_5Me_4CH_2$ moiety, and various mechanistic pathways may lead to such compounds. For example, C−H addition to an alkyl,[33,34] hydride,[35] or benzyne[36] ligand, C−H addition across a metal−carbon double bond,[22,37] or C−H oxidative addition to a d^2 or d^4 metal[38,39] are all known to afford tucked-in complexes. The hexamethylbenzene ligand (η^6-C_6Me_6) has also been observed to tuck-in, but only by oxidative addition to a d^2 metal.[14] This process renders the η^6 portion of a nascent η^6,η^1-$C_6Me_5CH_2$ ligand labile and results in the isolation of a d^0 η^1-$C_6Me_5CH_2$ complex.[16] Apparently, when δ symmetry back-bonding between a metal orbital and arene LUMO levels is lost, *i.e.*, upon oxidizing the metal to a *neutral* d^0 complex, simple L → M donation is not sufficient to maintain arene coordination in a neutral complex. (This does not appear to be the case when the metal center is *cationic*, as [(η^6-C_6Me_6)$TiCl_3$]$^+$ is a stable species.[40,41])

Therefore, trapping a neutral η^6,η^1-$C_6Me_5CH_2$ complex will most likely require a d^2 metal, a possibility that prompted us to prepare the η^6-C_6Me_6 complexes of Ta(III) containing alkyl, phenyl, and hydride ligands reported here. However, thermolytic decomposition studies of all these compounds provided no evidence for the generation of a tuck-in complex; only free C_6Me_6 and uncharacterizable, intractable decomposition products were obtained.

The most striking feature of these Ta(III) arene alkyl complexes is their resistance to elimination processes. In contrast to the precursor chloride compounds (η^6-C_6Me_6)Ta$(OAr)_2$Cl (**1**) and (η^6-C_6Me_6)Ta(OAr)Cl_2 (**2**), alkyl and dialkyl complexes are comparatively stable thermally, although they are extremely air sensitive. Also significant is the electrochemical evidence for the for-

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mation and limited stability of a d^1 arene complex, an observation that supports their proposed participation in the deoxygenative coupling of an acyl and a cyclopentadienyl ligand as suggested by Meyer and Messerle.[42]

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[43] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were distilled under N_2 from an appropriate drying agent[44] and were transferred to the drybox without exposure to air. NMR solvents were passed down a short (5−6 cm) column of activated alumina prior to use. The "cold" solvents used to wash isolated products were cooled to ca. −35 °C before use. Because compound colors are quite similar, yet exhibit subtle differences, the reported colors are based upon close comparisons with the nominal crayon colors of the Crayola 64 collection. In all preparations, Ar = 2,6-$C_6H_3{}^iPr_2$, Ar′ = 2,4,6-$C_6H_2{}^iPr_3$, and mes = 2,4,6-$C_6H_2Me_3$.

Physical Measurements. ^{1}H and ^{13}C NMR spectra were recorded at probe temperature (unless otherwise specified) on a Bruker AM-250, Varian Gemini 200, or Varian Unity 300 spectrometer in C_6D_6 or toluene-d_8 solvent. Chemical shifts are referenced to protio impurities (δ 7.15, C_6D_6; 2.09, toluene-d_8) or solvent ^{13}C resonances (δ 128.0, C_6D_6; 20.4, toluene-d_8) and are reported downfield of $SiMe_4$. Routine coupling constants are not reported. NMR assignments were assisted by COSY, APT, or gated $^{13}C\{^1H\}$-decoupled spectra. Routine coupling constants are not reported. Electron ionization mass spectra (70 eV) were recorded to $m/z = 999$ on a Hewlett-Packard 5970 mass selective detector and RTE-6/VM data system. For GC-mass spectra, the sample was introduced into the mass spectrometer by a Hewlett-Packard Model 5890 gas chromatograph equipped with an HP-5 column. Cyclic voltammetry experiments were performed in a drybox under a nitrogen atmosphere using a BioAnalytical Systems CV-27 voltammograph and recorded on a Houston Instruments Model 100 X-Y recorder. Measurements were taken on a Pt disk electrode in CH_2Cl_2 or THF solutions containing 0.1 M $^nBu_4NPF_6$ as supporting electrolyte in a single-chamber cell. Voltammograms were recorded at room temperature and at a sweep rate of 150 mV/s. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) are referenced to Ag/AgCl and are uncorrected for junction potentials. Values of n, where n is the number of equivalents of electrons transferred in an exhaustive electrolysis at a constant potential, were determined by measuring the total area under the current vs time curves for the complete reaction. Redox reactions were considered one-electron processes if $n = 1.0 \pm 0.1$. The n-value determinations were obtained in a three-chamber cell configuration (with solution contact through fritted disks) to separate reference and auxiliary electrodes from the Pt flag working electrode. Reversibility criteria have been stated.[45] Chemical ionization mass spectra were recorded to $m/z = 999$ on a Hewlett-Packard 5988A in both positive ion (isobutane reagent) and negative ion (methane reagent) modes. The He I valence PES spectrum of **4** was measured using a McPherson ESCA 36 spectrometer modified with a temperature-controlled sample cell and conditions previously described.[46] The gas-phase sample was generated at ca. 110 °C and 2×10^{-5} Torr, and the operating resolution for the argon $^2P_{3/2}$ ionization (15.76 eV) was maintained at 0.016−0.020 eV throughout data collection. This argon ionization was used as an internal "lock" during the high-resolution He I signal averaging (7−12 eV collections) to maintain drift from the absolute kinetic energy at <0.005 eV. X-band ESR spectra were recorded on toluene solutions or glasses using a Varian E-3 spectrometer. Microanalytical samples were handled under nitrogen and were combusted with WO_3 (Desert Analytics, Tucson, AZ).

Starting Materials. $TaCl_5$ was obtained from Cerac and used as received. $[Ta(OAr)Cl_4]_2$,[16] $LiOAr{\cdot}OEt_2$,[47] $(\eta^6\text{-}C_6Me_6)Ta(OAr)_2Cl$ (**1**),[14] $(\eta^6\text{-}C_6Me_6)Ta(OAr)Cl_2$ (**2**),[16] $LiCH_2SiMe_3$,[48] 2,4,6-triisopropylthiophenol (HSAr′),[49] and 2,4,6-trimethylthiophenol (HS(mes))[49] were prepared as previously described. The lithium salts LiSAr′ and LiS(mes) were prepared by reacting HSAr′ and HS(mes), respectively, with n-butyllithium in pentane. The more soluble dimethoxyethane (dme) adduct LiS(mes)(dme) was prepared by dissolving LiS(mes) in dme and removing the excess solvent in vacuo. The reagents MeMgBr (3 M in Et_2O), EtMgBr (3 M in Et_2O), $LiBEt_3H$ (1 M in THF), PhLi (1.8 M in Et_2O), PhMgCl (2 M in THF), and n-butyllithium (1.6 M in hexanes) were obtained from Aldrich and were used as received. $ZnMe_2$ (Alfa), $ZnEt_2$ (Aldrich), and $AlMe_3$ (Aldrich) were obtained from commercial sources and prepared as either 1.0 or 2.0 M solutions in heptane.

Compound Preparations. $(\eta^6\text{-}C_6Me_6)Ta(OAr)_2Me$ (3). $(\eta^6\text{-}C_6Me_6)Ta(OAr)_2Cl$ (0.30 g, 0.41 mmol) was dissolved in 30 mL of Et_2O and cooled to −60 °C (CO_2/isopropyl alcohol bath). This navy blue solution was rapidly stirred while 0.13 mL (0.39 mmol) of a MeMgBr solution (3 M in Et_2O) was added dropwise over 15 min. The solution color immediately changed to dark purple with the precipitation of a white solid. The reaction was allowed to warm to room temperature over a period of 4 h, over which it became darker purple in color. After the reaction mixture was stirred for an additional 12 h, the solvent was removed in vacuo yielding a purple cake. The product was extracted from the cake with ca. 50 mL of pentane, the extract was filtered through Celite, and the solvent was removed in vacuo yielding a purple, oily solid. This solid was dissolved in minimal pentane and cooled to −35 °C for 48 h to provide 0.19 g (0.26 mmol, 64%) of dark purple crystals, which were filtered off and dried in vacuo. ^{1}H NMR (C_6D_6): δ 7.09−6.91 (A_2B m, 6 H, H_{aryl}), 3.16 (sept, 4 H, $CHMe_2$), 1.87 (s, 18 H, C_6Me_6), 1.19, 1.15 (d, 12 H each, $J_{HH'} = 6.9$ Hz, $CHMe_2$), 0.22 (s, 3 H, $TaCH_3$). The solution was cooled to 185 K in toluene-d_8 with no observed change in its spectrum other than broadening due to increased solvent viscosity. ^{13}C NMR (C_6D_6): δ 156.9 (C_{ipso}), 136.7 (C_o), 123.6 (C_m), 121.5 (C_p), 113.5 (C_6Me_6), 26.1 ($CHMe_2$), 25.0, 24.5 ($CHMe_2$), 24.00 ($TaCH_3$), 15.9 (C_6Me_6). Anal. Calcd for $C_{37}H_{55}O_2Ta$: C, 62.35; H, 7.72. Found: C, 62.07; H, 8.00.

$(\eta^6\text{-}C_6Me_6)Ta(OAr)Me_2$ (4). $(\eta^6\text{-}C_6Me_6)Ta(OAr)Cl_2$ (1.00 g, 1.69 mmol) was dissolved in 30 mL of toluene and cooled to −60 °C (CO_2/isopropyl alcohol bath). This turquoise solution was stirred rapidly while a MeMgBr solution (1.07 mL, 3.21 mmol, 3 M in Et_2O) was added dropwise over 15 min. The reaction color quickly changed to blue violet with the formation of a white precipitate. This solution was slowly warmed to room temperature (over 4 h), during which time it became a darker blue violet. After an additional 12 h, the solvent was removed in vacuo yielding a blue violet cake. The product was extracted from the cake with pentane (ca. 50 mL), the extract

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was filtered through Celite, and the solvent was removed in vacuo yielding an oily, blue violet solid. This solid was dissolved in minimal pentane and cooled to −35 °C for 48 h to afford 0.74 g (1.34 mmol, 79%) of dark blue violet crystals, which were filtered off and dried in vacuo. ^{1}H NMR (C_6D_6): δ 7.04−6.91 (A_2B m, 3 H, H_{aryl}), 3.33 (sept, 2 H, C*H*Me$_2$), 1.69 (s, 18 H, C_6Me_6), 1.24 (d, 12 H, CH*Me*$_2$), 0.82 (s, 6 H, $TaCH_3$). ^{13}C NMR (C_6D_6): δ 157.1 (C_{ipso}), 136.2 (C_o), 123.4 (C_m), 122.5 (C_p), 107.2 (*C*$_6$Me$_6$), 27.2 (*C*HMe$_2$), 23.7 (CH*Me*$_2$), 22.7 (TaCH_3), 15.7 (C$_6$*Me*$_6$). MS: [CI$^-$], *m/z* 550, [(η^6-C_6Me_6)Ta(OAr)(CH_3)$_2$]$^-$; [CI$^+$], *m/z* 535, [(η^6-C_6Me_6)Ta(OAr)(CH_3)]$^+$ ([M − CH_3]$^+$). Anal. Calcd for $C_{26}H_{41}OTa$: C, 56.72; H, 7.51. Found: C, 56.74; H, 7.72.

(η^6-C_6Me_6)Ta(OAr)Et_2 (5). The reaction of 0.30 g (0.51 mmol) of (η^6-C_6Me_6)Ta(OAr)Cl_2 in 30 mL of toluene and 0.32 mL (0.963 mmol) of a EtMgBr solution (3 M in Et_2O) at −60 °C was carried out in the manner described above for preparing (η^6-C_6Me_6)Ta(OAr)Me_2 (**4**). Workup of the reaction by an identical procedure afforded 0.24 g (0.65 mmol, 82%) of product as dark blue violet crystals. ^{1}H NMR (C_6D_6): δ 7.11−6.96 (A_2B m, 3 H, H_{aryl}), 3.48 (sept, 2 H, C*H*Me$_2$), 1.79 (s, 18 H, C_6Me_6), 1.65 (m, 4 H, C*H*$_2$CH$_3$), 1.50 (t, 6 H, CH$_2$C*H*$_3$), 1.27 (d, 6 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 157.2 (C_{ipso}), 137.0 (C_o), 123.8 (C_m), 122.4 (C_p), 107.9 (*C*$_6$Me$_6$), 34.8 (*C*H$_2$CH$_3$), 26.5 (*C*HMe$_2$), 24.4 (CH*Me*$_2$), 15.8 (C$_6$*Me*$_6$), 15.4 (CH$_2$*C*H$_3$). MS: [CI$^-$], *m/z* 578, [(η^6-C_6Me_6)Ta(OAr)(CH_2CH_3)$_2$]$^-$; [CI$^+$], *m/z* 549, [(η^6-C_6Me_6)Ta(OAr)(CH_2CH_3)]$^+$([M − Et]$^+$). Anal. Calcd for $C_{28}H_{45}OTa$: C, 58.12; H, 7.84. Found: C, 58.37; H, 8.09.

(η^6-C_6Me_6)Ta(OAr)(CH_2SiMe_3)$_2$ (6). The reaction of 0.50 g (0.85 mmol) of (η^6-C_6Me_6)Ta(OAr)Cl_2 in 30 mL of toluene and 0.16 g (1.68 mmol) of $LiCH_2SiMe_3$ in ca. 10 mL of Et_2O was carried out at −60 °C in the manner described above for preparing (η^6-C_6Me_6)Ta(OAr)Me_2 (**4**). Workup by an analogous procedure provided 0.40 g (0.57 mmol, 69%) of product as dark violet crystals. ^{1}H NMR (C_6D_6): δ 6.97−6.83 (A_2B m, 3 H, H_{aryl}), 3.27 (sept, 2 H, C*H*Me$_2$), 1.78 (s, 18 H, C_6Me_6), 1.37 (d, $J_{HH'}$ = 11.5 Hz, 2 H, C*H*$_2$SiMe$_3$), 1.21 (d, 12 H, CH*Me*$_2$), 0.35 (s, 18 H, CH$_2$Si*Me*$_3$), 0.28 (d, $J_{HH'}$ = 11.5 Hz, 2 H, C*H*$_2$SiMe$_3$). The sample was cooled to 185 K in toluene-d_8 with no observed change its ^{1}H in spectrum other than broadening due to increased solvent viscosity. ^{13}C NMR (C_6D_6): δ 156.59 (C_{ipso}), 136.47 (C_o), 123.78 (C_m), 122.64 (C_p), 109.27 (*C*$_6$Me$_6$), 34.34 (*C*H$_2$SiMe$_3$), 26.68 (*C*HMe$_2$), 24.82 (CH*Me*$_2$), 16.49 (C$_6$*Me*$_6$), 4.43 (CH$_2$Si*Me*$_3$). Anal. Calcd for $C_{32}H_{57}OSi_2Ta$: C, 55.31; H, 8.27. Found: C, 55.58; H, 8.34.

(η^6-C_6Me_6)Ta(OAr)Ph_2 (7). (η^6-C_6Me_6)Ta(OAr)Cl_2 (1.00 g, 1.69 mmol) was dissolved in 30 mL of toluene and cooled to −60 °C (CO_2/isopropyl alcohol bath). This turquoise solution was rapidly stirred while a PhLi solution (1.83 mL, 3.29 mmol, 1.8 M in Et_2O) was added dropwise over 15 min. The solution color changed to dark purple with the formation of a white precipitate. This solution was allowed to warm to room temperature slowly (over 4 h), during which time it became a darker purple. The reaction was stirred for an additional 12 h, the mixture was filtered through Celite, and the solvent was removed in vacuo to yield the product as a purple powder. Washing this powder with minimal cold pentane yielded 1.00 g (1.48 mmol, 88%) of product as a brilliant purple powder suitable for further reactions. Analytically pure samples were obtained by recrystallization from Et_2O at −35 °C. ^{1}H NMR (C_6D_6): δ 7.51−6.87 (m, 13 H, H_{aryl} (OAr and C_6H_5)), 3.47 (sept, 2 H, C*H*Me$_2$), 1.68 (s, 18 H, C_6Me_6), 0.91 (d, 12 H, CH*Me*$_2$). The solution was cooled to 185 K in toluene-d_8 with no observed change in its ^{1}NMR other than broadening due to increased solvent viscosity. ^{13}C NMR (C_6D_6): δ 173.3 (C_{ipso}, C_6H_5), 157.8 (C_{ipso}, OAr), 138.0 (C_o, OAr), 135.2 (C_o, C_6H_5), 126.8 (C_m, C_6H_5), 125.8 (C_p, C_6H_5), 123.5 (C_m, OAr), 122.9 (C_p, OAr), 111.1 (*C*$_6$Me$_6$), 27.0 (*C*HMe$_2$), 23.9 (CH*Me*$_2$), 16.2 (C$_6$*Me*$_6$). Anal. Calcd for $C_{36}H_{45}OTa$: C, 64.09; H, 6.72. Found: C, 63.88; H, 6.77.

(η^6-C_6Me_6)Ta(OAr)(CH_2SiMe_3)Cl (8). The reaction of 1.00 g (1.69 mmol) of (η^6-C_6Me_6)Ta(OAr)Cl_2 in 30 mL of toluene with 0.16 g (1.68 mmol) of $LiCH_2SiMe_3$ in ca. 10 mL of Et_2O was carried out at −60 °C in the manner described above for preparing (η^6-C_6Me_6)Ta(OAr)Me_2 (**4**). The resulting navy blue reaction solution was filtered through Celite, and the solvent was removed in vacuo yielding a dark blue oily crust. Trituration with cold pentane yielded 0.50 g (0.78 mmol, 92%) of product as a dark blue powder sufficiently pure for further reactions. Analytically pure samples were obtained by recrystallization at −35 °C from concentrated solutions of Et_2O/pentane (ca. 50:50 v/v). ^{1}H NMR (C_6D_6): δ 6.98−6.83 (A_2B m, 3 H, H_{aryl}), 3.28 (sept, 2 H, C*H*Me$_2$), 1.75 (s, 18 H, C_6Me_6), 1.29 and 1.27 (overlapping d, 12 H total, CH*Me*$_2$), 1.12 (d, 1 H, $J_{HH'}$ = 12 Hz, C*H*H′SiMe$_3$), 0.51 (s, 9 H, CHH′Si*Me*$_3$), 0.32 (d, 1 H, $J_{HH'}$ = 12 Hz, CH*H*′SiMe$_3$). ^{13}C NMR (C_6D_6): δ 156.4 (C_{ipso}), 136.2 (C_o), 123.6 (C_m), 123.5 (C_p), 114.7 (*C*$_6$Me$_6$), 29.5 (*C*H$_2$SiMe$_3$), 26.9 (*C*HMe$_2$), 24.4 and 23.9 (CH*Me*$_2$), 16.0 (C$_6$*Me*$_6$), 4.5 (CH$_2$Si*Me*$_3$). Anal. Calcd for $C_{28}H_{46}OClSiTa$: C, 52.29; H, 7.21. Found: C, 52.52; H, 7.52.

(η^6-C_6Me_6)Ta(OAr)(Ph)Cl (9). To a solution of 0.462 g (0.782 mmol) of (η^6-C_6Me_6)Ta(OAr)Cl_2 (**2**) in 20 mL of benzene was added PhMgCl (0.400 mL, 2 M in THF, 0.800 mmol) at room temperature. This mixture was stirred for 20 h and filtered through Celite, and the solvent was removed from the filtrate in vacuo yielding a blue oil. The product was extracted from this oil with pentane (ca. 20 mL), the extract was filtered through Celite, and the filtrate was concentrated to ca. 10 mL in vacuo and cooled to −35 °C. This procedure afforded 0.38 g (0.60 mmol, 77%) of (η^6-C_6Me_6)Ta(OAr)(Ph)Cl as a blue, crystalline solid that was filtered off and dried in vacuo. Analytically pure samples were obtained by recrystallization from pentane at −35 °C. ^{1}H NMR (C_6D_6): δ 7.86 (d, 2 H, H_o, C_6H_5), 7.31 (t, 2 H, H_m, C_6H_5), 7.13 (t, 1 H, H_p, C_6H_5), 7.00−6.80 (A_2B m, 3 H, H_{aryl}, OAr), 3.35 (sept, 2 H, C*H*Me$_2$), 1.72 (s, 18 H, C_6Me_6), 1.23, 1.19 (d, 6 H each, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 174.82 (C_{ipso}, C_6H_5), 157.15 (C_{ipso}, OAr), 141.63 (C_o, C_6H_5), 136.74 (C_o, OAr), 126.85 (C_m, C_6H_5), 126.07 (C_p, Ph), 123.65 (C_m, OAr), 123.52 (C_p, OAr), 114.93 (*C*$_6$Me$_6$), 27.39 (*C*HMe$_2$), 24.46, 24.11 (CH*Me*$_2$), 16.67 (C$_6$*Me*$_6$). Anal. Calcd for $C_{30}H_{40}OClTa$: C, 56.92; H, 6.36. Found: C, 55.91; H, 6.57.

(η^6-C_6Me_6)Ta(OAr)(Me)Br (10). The reaction of 0.50 g (0.85 mmol) of (η^6-C_6Me_6)Ta(OAr)Cl_2 in 30 mL of toluene with MeMgBr (0.25 mL, 3 M in Et_2O, 0.76 mmol) was carried out at −60 °C in the manner described above for preparing (η^6-C_6Me_6)Ta(OAr)Me_2 (**4**). Workup in an analogous manner afforded 0.40 g (0.65 mmol, 77%) of product as dark purple, analytically pure crystals. ^{1}H NMR (C_6D_6): δ 6.97−6.88 (A_2B m, 3 H, H_{aryl}), 3.34 (sept, 2 H, C*H*Me$_2$), 1.78 (s, 18 H, C_6Me_6), 1.28, 1.20 (d, 6 H each, $J_{HH'}$ = 6.8 Hz, CH*Me*$_2$), 1.23 (s, 3 H, C*H*$_3$). ^{13}C NMR (C_6D_6): δ 157.15 (C_{ipso}), 136.18 (C_o), 123.36 (C_m), 122.47 (C_p), 107.24 (*C*$_6$Me$_6$), 27.22 (*C*HMe$_2$), 23.73 (CH*Me*$_2$ coincident), 22.72 (*C*H$_3$), 15.69 (C$_6$*Me*$_6$). MS: [CI$^-$], *m/z* 616, [(η^6-C_6Me_6)Ta(OAr)(CH_3)^{81}Br]$^-$; [CI$^-$], *m/z* 614, [(η^6-C_6Me_6)Ta(OAr)(CH_3)^{79}Br]$^-$; [CI$^-$], *m/z* 572, <3% of total product, [(η^6-C_6Me_6)Ta(OAr)(CH_3)^{37}Cl]$^-$; [CI$^-$], m/z 570, <3% of total product, (η^6-C_6Me_6)Ta(OAr)(CH_3)^{35}Cl]$^-$; [CI$^+$], *m/z* 535, [(η^6-C_6Me_6)Ta(OAr)(CH_3)]$^+$ ([M − X]$^+$). Anal. Calcd for $C_{25}H_{38}BrOTa$: C, 48.79; H, 6.22. Found: C, 49.38; H, 6.47.

(η^6-C_6Me_6)Ta(OAr)(Et)Br (11). The reaction of 0.50 g (0.85 mmol) of (η^6-C_6Me_6)Ta(OAr)Cl_2 in 30 mL of toluene and EtMgBr (0.25 mL, 3 M in Et_2O, 0.76 mmol) was carried out at −60 °C in the manner described above for preparing (η^6-C_6Me_6)Ta(OAr)Me_2 (**4**). Workup in an analogous manner afforded 0.39 g (0.61 mmol, 72%) of product as dark purple crystals that were filtered off and dried in vacuo. ^{1}H NMR (C_6D_6): δ 7.04−6.88 (A_2B m, 3 H, H_{aryl}), 3.36 (sept, 2 H, C*H*Me$_2$), 2.11 (t, 3 H, CH$_2$C*H*$_3$), 1.95 (m, 2 H, C*H*$_2$CH$_3$), 1.80 (s, 18 H, C_6Me_6), 1.28 and 1.21 (d, 6 H each, $J_{HH'}$ = 6.8 Hz, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 157.4 (C_{ipso}), 136.3 (C_o), 123.6 (C_m), 123.3 (C_p), 113.4 (*C*$_6$Me$_6$), 36.5 (*C*H$_2$CH$_3$) 26.9 (*C*HMe$_2$), 24.4 (CH*Me*$_2$ coincident), 19.5 (CH$_2$*C*H$_3$), 16.3 (C$_6$*Me*$_6$). MS: [CI$^-$], *m/z* 630, [(η^6-C_6Me_6)Ta(OAr)(CH_2CH_3)^{81}Br]$^-$; [CI$^-$], *m/z* 628, [(η^6-C_6Me_6)Ta(OAr)(CH_2CH_3)^{79}Br]$^-$; [CI$^+$], *m/z* 601, [(η^6-

$C_6Me_6)Ta(OAr)^{81}Br]^+([M - Et]^+)$; $[CI^+]$, *m/z* 599, $[(\eta^6\text{-}C_6Me_6)Ta(OAr)^{79}Br]^+([M - Et]^+)$. An elemental analysis on this compound was not obtained due to the <5% impurity of $(\eta^6\text{-}C_6Me_6)Ta(OAr)(Et)Cl$.

$(\eta^6\text{-}C_6Me_6)Ta(OAr)(Et)Cl$ (12). A 0.34 g (0.53 mmol) sample of $(\eta^6\text{-}C_6Me_6)Ta(OAr)(CH_2SiMe_3)Cl$ was dissolved in 20 mL of Et_2O and cooled to −30 °C. To this rapidly stirred, navy blue solution was added dropwise 0.03 g (0.258 mmol) of $ZnEt_2$ in ca. 10 mL of Et_2O over a period of 1 min. The color of the solution did not change over the course of the reaction. This solution was allowed to warm to room temperature over 40 min and stirred an additional 48 h. The resultant navy blue solution was filtered, and the solvent was removed in vacuo yielding a dark blue oil. Dissolving this oil in minimal pentane and cooling the solution to −35 °C for 48 h yielded 0.18 g (0.33 mmol, 62%) of product as dark purple rocks suitable for further reactions. Analytically pure samples were obtained by recrystallization from pentane at −35 °C. ^1H NMR (C_6D_6): δ 7.02−6.87 (A_2B m, 3 H, H_{aryl}), 3.36 (sept, 2 H, $CHMe_2$), 2.04 (t, 3 H, CH_2CH_3), 1.90 (m, 3 H, CH_2CH_3), 1.78 (s, 18 H, C_6Me_6), 1.29, 1.23 (d, 6 H each, $J_{HH'} = 6.7$ Hz, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 156.4 (C_{ipso}), 136.2 (C_o), 123.5 (C_m), 123.1 (C_p), 113.5 (C_6Me_6), 36.3 (CH_2CH_3), 26.9 ($CHMe_2$), 24.2, 23.9 ($CHMe_2$), 18.22 (CH_2CH_3), 15.9 (C_6Me_6). Anal. Calcd for $C_{26}H_{40}OClTa$: C, 53.38; H, 6.89. Found: C, 53.22; H, 7.17.

$(\eta^6\text{-}C_6Me_6)Ta(OAr)(CH_2SiMe_3)Ph$ (13). A 0.19 g (0.29 mmol) sample of $(\eta^6\text{-}C_6Me_6)Ta(OAr)(CH_2SiMe_3)Cl$ was dissolved in 20 mL of Et_2O and cooled to −60 °C (CO_2/isopropyl alcohol bath). To this rapidly stirred, navy blue solution was added 0.16 mL (0.29 mmol) of a PhLi solution dropwise (1.8 M in Et_2O, diluted to ca. 10 mL in Et_2O) over the course of ca. 10 min. The solution developed an inky purple color and formed a white precipitate as the solution was allowed to warm to room temperature over 4 h. After the reaction was stirred for another 18 h, the mixture was filtered through Celite and the solvent was removed in vacuo yielding a dark purple, oily solid. Dissolving this solid in minimal Et_2O and cooling to −35 °C for 48 h yielded 0.14 g (0.21 mmol, 72%) of product as purple rocks. Analytically pure samples were obtained by recrystallization from pentane at −35 °C. ^1H NMR (C_6D_6): δ 7.60−6.87 (A_2B m, 8 H, H_{aryl}), 3.37 (sept, 2 H, $CHMe_2$), 1.67 (s, 18 H, C_6Me_6), 1.34 (d, 1 H, $J_{HH'} = 12.4$ Hz, $CHH'SiMe_3$), 1.31, 1.27 (d, 6 H each, $J_{HH'} = 6.8$ Hz, $CHMe_2$), 0.55 (d, 1 H, $J_{HH'} = 12.4$ Hz, $CHH'SiMe_3$), 0.11 (s, 9 H, CH_2SiMe_3). ^{13}C NMR (C_6D_6): δ 179.5 (C_{ipso}, C_6H_5), 157.2 (C_{ipso}), 140.1 (C_o, C_6H_5), 136.6 (C_o), 126.9 (C_m, C_6H_5), 125.2 (C_p, C_6H_5), 123.7 (C_m), 122.9 (C_p), 110.1 (C_6Me_6), 37.4 (CH_2SiMe_3), 27.1 ($CHMe_2$), 24.7, 24.4 ($CHMe_2$), 16.6 (C_6Me_6), 4.5 (CH_2SiMe_3). Anal. Calcd for $C_{34}H_{51}OSiTa$: C, 59.63; H, 7.51. Found: C, 60.00; H, 7.87.

$(\eta^6\text{-}C_6Me_6)Ta(OAr)(Et)H$ (14). A solution of $(\eta^6\text{-}C_6Me_6)Ta(OAr)(Et)Br$ (1.00 g, 1.59 mmol) in 20 mL of Et_2O was prepared, cooled to −60 °C (CO_2/isopropyl alcohol bath), and rapidly stirred while $LiBEt_3H$ (1.90 mL, 1 M in THF, 1.90 mmol) was added dropwise over a period of 15 min. The solution developed an inky violet color and formed a white precipitate as the solution was allowed to warm to room temperature over 4 h. After the reaction was stirred for an additional 1 h, the solvent was removed in vacuo to afford a violet cake. The compound was extracted from the cake with pentane (ca. 50 mL), the extract was filtered through Celite, and the solvent was removed in vacuo to provide a dark violet oil. Dissolving this oil in minimal heptane and cooling to −35 °C for 48 h yielded 0.65 g (1.18 mmol, 76%) of product as violet rocks. Analytically pure samples were obtained by recrystallization from heptane at −35 °C. ^1H NMR (C_6D_6): δ 7.09−6.93 (A_2B m, 3 H, H_{aryl}), 5.87 (s, 1 H, Ta*H*), 3.56 (sept, 2 H, $CHMe_2$), 1.91 (overlapping s and t, 21 H total, C_6Me_6, CH_2CH_3), 1.62 (m, 2 H, CH_2CH_3), 1.29, 1.27 (d, 6 H each, $J_{HH'} = 3.7$ Hz, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 157.4 (C_{ipso}), 136.4 (C_o), 123.3 (C_m), 123.4 (C_p), 105.8 (C_6Me_6), 31.6 (CH_2CH_3), 27.2 ($CHMe_2$), 23.5 ($CHMe_2$ coincident), 18.3 (CH_2CH_3), 16.4 (C_6Me_6). Anal. Calcd for $C_{26}H_{41}OTa$: C, 56.72; H, 7.51. Found: C, 57.12; H, 7.66.

$(\eta^6\text{-}C_6Me_6)Ta(OAr)(CH_2SiMe_3)H$ (15). A solution of 1.00 g (1.55 mmol) of $(\eta^6\text{-}C_6Me_6)Ta(OAr)(CH_2SiMe_3)Cl$ in 20 mL of Et_2O was prepared, cooled to −60 °C (CO_2/isopropyl alcohol bath), and rapidly stirred while $LiBEt_3H$ (1.90 mL, 1 M in THF, 1.90 mmol) was added dropwise over a period of 15 min. The reaction was allowed to warm to room temperature over 4 h and stirred for an additional 48 h, over which time the solution developed an inky violet color and formed a white precipitate. The solution was filtered through Celite, the solvent was removed in vacuo, and the resulting oil was dissolved in minimal pentane and cooled to −35 °C for 48 h. This procedure yielded 0.65 g (1.17 mmol, 75%) of product as purple rocks. Analytically pure samples were obtained by recrystallization from pentane at −35 °C. ^1H NMR (C_6D_6): δ 7.05−6.87 (A_2B m, 3 H, H_{aryl}), 5.87 (s, 1 H, Ta*H*), 3.47 (sept, 2 H, $CHMe_2$), 1.88 (s, 18 H, C_6Me_6), 1.29, 1.26 (overlapping d, 12 H total, $CHMe_2$), 1.01 (d, 1 H, $J_{HH'} = 12$ Hz, $CHH'SiMe_3$), 0.33 (s, 9 H, $CHH'SiMe_3$), −0.27 (d, 1 H, $J_{HH'} = 12$ Hz, $CHH'SiMe_3$). ^{13}C NMR (C_6D_6): δ 157.2 (C_{ipso}), 136.1 (C_o), 123.2 (C_m), 122.5 (C_p), 106.4 (C_6Me_6), 30.0 (CH_2SiMe_3), 27.0 ($CHMe_2$), 23.5 ($CHMeMe'$, coincident), 16.6 (C_6Me_6), 3.3 (CH_2SiMe_3). Anal. Calcd for $C_{28}H_{47}OSiTa$: C, 55.25; H, 7.78. Found: C, 55.12; H, 7.85.

$(\eta^6\text{-}C_6Me_6)Ta(OAr)(SAr')Cl$ (16). A solution of 0.205 g (0.846 mmol) of LiSAr′ (Ar′ = 2,4,6-$C_6H_2{}^iPr_3$) in 15 mL of Et_2O was prepared and added dropwise to a rapidly stirred solution of $(\eta^6\text{-}C_6Me_6)Ta(OAr)Cl_2$ (0.500 g, 0.846 mmol) in 5 mL of Et_2O. This mixture was stirred for 18 h, after which it was filtered through Celite, and the solvent was removed from the filtrate in vacuo to yield a blue oil. This oil dissolved in pentane (ca. 5 mL), whereupon the product precipitated as blue microcrystals. These crystals were filtered off, washed with cold pentane, and dried in vacuo to afford 0.535 g (0.676 mmol, 80%) of $(\eta^6\text{-}C_6Me_6)Ta(OAr)(SAr')Cl$ as an analytically pure, microcrystalline, blue solid. ^1H NMR (C_6D_6): δ 7.68−7.00 (A_2B m, 3 H, H_{aryl}, OAr), 7.21 (s, 2 H, H_m, SAr′), 3.40 (br, 3 H, $CHMe_2$, SAr′), 2.87 (sept, 2 H, $CHMe_2$, OAr), 1.94 (s, 18 H, C_6Me_6), 1.34, 1.25, 1.23 (d, 6 H each, $CHMe_2$), 1.24 (d, 12 H, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 156.1 (C_{ipso}, OAr), 146.2 (C_{ipso}, SAr′), 137.2 (C_o, OAr), 123.8 (C_p, OAr), 123.6 (C_m, OAr), 120.59 (C_p, SAr′), 120.56 (C_m, SAr′), 117.4 (C_6Me_6), 34.5 (*p*-$CHMe_2$, SAr′), 31.4 (*o*-$CHMe_2$, SAr′), 26.6 ($CHMe_2$, OAr), 24.71, 24.68, 24.42, 24.38 ($CHMe_2$), 16.6 (C_6Me_6). One resonance (C_p, SAr′) was not observed and is presumed to be coincident with another signal or the solvent resonance. Anal. Calcd for $C_{39}H_{58}ClOSTa$: C, 59.20; H, 7.38. Found: C, 59.56; H, 7.45.

$(\eta^6\text{-}C_6Me_6)Ta(OAr)(S(mes))Cl$ (17). A solution of 0.105 g (0.423 mmol) of LiS(mes)(dme) (mes = 2,4,6-$C_6H_2Me_3$) in 20 mL of Et_2O was slowly added to a rapidly stirred solution of $(\eta^6\text{-}C_6Me_6)Ta(OAr)Cl_2$ (0.250 g, 0.423 mmol) in 5 mL of Et_2O. This mixture was stirred for 20 h, after which it was filtered through Celite, and the filtrate was stripped of solvent under reduced pressure to afford a blue oil. Upon dissolving this oil in pentane (ca. 2−3 mL), the product precipitated as blue microcrystals. These crystals were filtered off, washed with cold pentane, and dried in vacuo to afford 0.230 g (0.320 mmol, 76%) of $(\eta^6\text{-}C_6Me_6)Ta(OAr)(S(mes))Cl$ as a microcrystalline, blue solid. This compound can be recrystallized from pentane at −35 °C to afford analytically pure samples. ^1H NMR (C_6D_6): δ 7.00−6.94 (m, 4 H, H_m, OAr and S(mes)), 6.91 (dd, 1 H, H_p, OAr), 3.37 (sept, 2 H, $CHMe_2$), 2.45 (br, 6 H, *o*-Me, S(mes)), 1.27 (s, 3 H, *p*-Me, S(mes)), 1.91 (s, 18 H, C_6Me_6), 1.31, 1.26 (d, 6 H each, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 155.6 (C_{ipso}, OAr), 139.9 (C_{ipso}, S(mes)), 136.8 (C_o, OAr), 134.2 (C_o, S(mes)), 128.5 (C_m, S(mes)), 123.8 (C_p, OAr), 123.6 (C_m, OAr), 117.1 (C_6Me_6), 26.6 ($CHMe_2$), 24.8 (*o*-Me, S(mes)), 24.1 ($CHMe_2$), 20.9 (*p*-Me, S(mes)), 16.5 (C_6Me_6). Anal. Calcd for $C_{33}H_{46}ClOSTa$: C, 56.05; H, 6.56. Found: C, 55.61; H, 6.19.

X-ray Structural Determination of $(\eta^6\text{-}C_6Me_6)Ta(OAr)Et_2$ (5). A red, irregular block crystal of $C_{28}H_{45}OTa$ was crystallized from pentane solution (at −35 °C) and mounted in a glass capillary in a random orientation. From the systematic absences of $hk0$, $h = 2n + 1$; $0kl$, $k + l = 2n + 1$ and from subsequent least-squares refinement the space group was determined to be *Pnma* (No. 62). Hydrogen atoms were located and their positions were refined in least-squares; their isotropic thermal parameters were held fixed at 5.0 Å^2. Scattering factors were taken from Cromer and Waber.[50] Anomalous dispersion effects were included in F_c;[51] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[52] All calculations were performed on a VAX computer using SDP/VAX.[53] Details of the structural determination and refinement are reported in Table 1.

Acknowledgement is made to the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (Grant No. DE-FG03-93ER14349) for support of this research. We also thank Dr. Carina Grittini for her assistance.

Supporting Information Available: Text giving complete crystallographic details, tables of atomic positional and thermal parameters, bond distances and angles, least-squares planes, and dihedral angles, and ORTEP diagrams for (η^6-C_6Me_6)Ta(OAr)Et_2 (13 pages). Ordering information is given on any current masthead page.

OM970197C

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