Synthesis and Reactivity of Alkyl, Hydride, and Silyl Derivatives of the (Terphenyl)imido Fragments Cp*(Ar^{Mes}N═)Ta (Cp* = η^5-C_5Me_5; Ar^{Mes} = 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$) and Cp*(Ar^{Trip}N═)Ta (Ar^{Trip} = 2,6-(2,4,6-$^iPr_3C_6H_2)_2C_6H_3$)

John Gavenonis and T. Don Tilley*

Department of Chemistry, University of California, Berkeley, Berkeley, California 94720-1460

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The syntheses and reactivities of tantalum alkyl, hydride, and silyl complexes containing a sterically demanding, mixed Cp*-(terphenyl)imido (Cp* = η^5-C_5Me_5) ligand set are reported. The dichloride complex Cp*(Ar^{Mes}N═)$TaCl_2$ (**1**), prepared by the reaction of Ar^{Mes}NHLi (Ar^{Mes} = 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$) with Cp*$TaCl_4$ in the presence of a large excess of NEt_3, was structurally characterized. Complex **1** reacted readily with $KSi(SiMe_3)_3$ to give the silyl chloride compound Cp*(Ar^{Mes}N═)Ta[$Si(SiMe_3)_3$]Cl (**2**), and with MeLi (2 equiv) to yield the dimethyl complex Cp*(Ar^{Mes}N═)$TaMe_2$ (**4**). Compound **2** reacted with $PhSiH_3$ via the intermediate complex Cp*(Ar^{Mes}N═)Ta(SiH_2Ph)Cl to give the hydrido chloride complex Cp*(Ar^{Mes}N═)Ta(H)Cl (**3**). While the analogous compound of the [DippN═]$^{2-}$ (Dipp = 2,6-$^iPr_2C_6H_3$) ligand is a dimer with bridging hydrides, compound **3** contains a terminal hydride, as indicated by the downfield ^{1}H NMR resonance of the hydride ligand (15.28 ppm). Treatment of **4** with AgOTf (OTf = OSO_2CF_3) provided the methyl triflate compound Cp*(Ar^{Mes}N═)Ta(Me)OTf (**6**), which reacted cleanly with H_2 in bromobenzene to yield pale yellow crystals of the hydrido triflate complex Cp*(Ar^{Mes}N═)Ta(H)OTf (**7**). Complexes **4**, **6**, and **7** reacted with $PhSiH_3$ at high temperatures (85−100 °C) to give silane products arising from σ-bond metathesis and redistribution of the substituents at silicon. The neopentyl hydride complex Cp*(Ar^{Mes}N═)Ta(CH_2CMe_3)H (**8**), prepared by treating **7** with $LiCH_2CMe_3$, reacted with $PhSiH_3$ at room temperature via the silyl hydride intermediate species Cp*(Ar^{Mes}N═)Ta(SiH_2Ph)H to yield the dihydride dimer [Cp*(Ar^{Mes}N═)TaH(μ-H)]$_2$ (**5**). In an effort to stabilize a monomeric dihydride complex, the more sterically demanding [Ar^{Trip}N═]$^{2-}$ (Ar^{Trip} = 2,6-(2,4,6-$^iPr_3C_6H_2)_2C_6H_3$) ligand was employed. The dichloride complex Cp*(Ar^{Trip}N═)$TaCl_2$ (**12**) and the dimethyl complex Cp*(Ar^{Trip}N═)$TaMe_2$ (**13**) were prepared using procedures analogous to those used for the syntheses of **1** and **4**. Treatment of **13** with H_2 in bromobenzene yielded the hydrido bromide complex Cp*(Ar^{Trip}N═)Ta(H)Br (**14**), which formed via solvent activation by the intermediate dihydride species Cp*(Ar^{Trip}N═)-TaH_2. When D_2 was used in place of H_2, Cp*(2-[2-(^{i}Pr-d_6)-4,6-$^iPr_2C_6H_2$]-6-Trip-C_6H_3N═)-Ta(D)Br (**14-d_7**, Trip = 2,4,6-$^iPr_3C_6H_2$) was obtained. Compound **14-d_7** arises from the intramolecular C−H bond activation of the methyl groups of one of the isopropyl substituents of the [Ar^{Trip}N═]$^{2-}$ ligand. Hydrogenolysis of the neopentyl hydride complex Cp*-(Ar^{Trip}N═)Ta(CH_2CMe_3)H (**15**) in bromobenzene-d_5 allowed observation of the corresponding dihydride complex, which was observed to slowly convert to the hydrido bromide species **14**.

Introduction

Early transition metal complexes have received increased attention in recent years, as such species have been found to mediate a number of stoichiometric and catalytic transformations. Examples of such processes include olefin polymerization,[1−3] dehydropolymerizations,[4−6] hydrosilylation,[7−11] arene hydrogenation,[12,13] alkane activation,[14−19] alkane hydrogenolysis,[20] and alkane functionalization.[21,22] Our investigations of the

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catalytic transformations of silanes,[6,23] stannanes,[24−26] and hydrocarbons[21,22] have centered on the development of early metal (d^0) catalysts which are highly reactive in σ-bond metathesis processes. Much of this chemistry is derived from reactions of active hydride ligands, as d^0 metal−hydrogen bonds are capable of activating a wide range of molecular substrates.[19,27,28] Thus, it is of interest to develop strategies for the stabilization of coordinatively unsaturated, *monomeric* hydride complexes, since d^0 hydrides have a marked tendency to dimerize or oligomerize via the formation of strong bridging hydride interactions.[6,23,27] Species of the latter type tend to be less soluble, and less reactive, than complexes possessing terminal metal−hydrogen bonds.[27] For example, we have observed that zirconocene complexes with the CpCp* (Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5) ligand set are more active than Cp_2Zr derivatives as catalysts for the dehydropolymerization of hydrosilanes.[6,23] This is presumably due to the ability of the more sterically demanding ligand set to stabilize monomeric hydrides.

The development of new chemistry based on reactive hydrides of the d^0 metals should benefit greatly from identification of non-cyclopentadienyl ancillary ligands that stabilize monomeric complexes.[2,6,23,27,29] Ideally, such ligands will possess sterically directed bulk that will destabilize hydride-bridged dimers, while providing sufficient space at the metal center for binding small molecules. Of course, a good ancillary ligand will also be inert to reactions with the hydride functionality.

With these considerations in mind, we have examined the utility of imido ligands in supporting reactive M−H and M−Si σ-bonds.[30−37] For example, tantalum complexes of the mixed pentamethylcyclopentadienyl-imido fragment Cp*(DippN═)Ta (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$), e.g. Cp*(DippN═)Ta[Si(SiMe$_3$)$_3$]H, are stable yet reactive toward hydrosilanes.[31,32] However, the corresponding dihydride forms a dimer, [Cp*(DippN═)TaH(μ-H)]$_2$, which is unreactive toward $PhSiH_3$ in refluxing benzene.[31] In a study of more sterically demanding imido ligands, we have synthesized imido-amido complexes possessing the terphenyl imido ligand [2,6-Mes$_2$C$_6$H$_3$N═]$^{2-}$ ([Ar^{Mes}N═]$^{2-}$, Mes = 2,4,6-Me$_3$C$_6$H$_2$).[35,36] In this system, the hydrido triflate complex [(Ar^{Mes}N═)(Ar^{Mes}NH)Ta(H)OTf] may be obtained, but it reversibly transfers hydride from tantalum to one of the mesityl rings to give the η^5-cyclohexadienyl complex (Ar^{Mes}N═)[2-(η^5-2,4,6-Me$_3$C$_6$H$_3$)-6-MesC$_6$H$_3$NH]TaOTf as the more stable isomer. This complex reacts with small molecules via the more reactive, hydride isomer.

Herein we describe further efforts to develop isolable, coordinatively unsaturated, monomeric tantalum hydride complexes capable of enhanced reactivity in σ-bond metathesis processes. Our investigations have focused on complexes of the Cp*(Ar^{Mes}N═)Ta and Cp*(Ar^{Trip}N═)Ta (Ar^{Trip} = 2,6-Trip$_2$C$_6$H$_3$, Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$) fragments. As discussed below, these fragments stabilize complexes with hydride, silyl, and alkyl ligands, which are highly reactive in Si−H, Si−C, and C−H bond activations.

Results and Discussion

Preparation of Cp*(Ar^{Mes}N═)TaCl$_2$ (1). A dichloride complex of the Cp*(Ar^{Mes}N═)Ta fragment was desired as a convenient starting point for the synthesis of tantalum(V) silyl, hydride, and alkyl complexes. Generally, dichloride complexes of this type can be prepared by a variety of methods,[38−44] although few employ the readily available starting material Cp*TaCl$_4$.[38,39] In 1992, Gibson and co-workers reported the synthesis of Cp*(DippN═)TaCl$_2$ via reaction of Cp*TaCl$_4$ with DippNH(SiMe$_3$) (2 equiv, Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) in 1,2-dichloroethane.[38] Also, Wigley and co-workers described the synthesis of this compound by treating Cp*TaCl$_4$ with DippNHLi (2 equiv) in diethyl ether.[39]

An initial attempt to prepare Cp*(Ar^{Mes}N═)TaCl$_2$ (**1**) was based upon the published methods involving 2 equiv of a lithium amide reagent (with the second equiv acting as a base to deprotonate the putative Cp*(RNH)TaCl$_3$ intermediate). A bright red reaction mixture was observed upon treatment of Cp*TaCl$_4$ with Ar^{Mes}NHLi (2 equiv)[35,36] in benzene-d_6 at room temperature (likely reflecting the formation of an intermediate Cp*(Ar^{Mes}NH)TaCl$_3$ species), and the solution turned to bright orange over the course of 12 h. A ^{1}H NMR spectrum of the reaction mixture revealed the formation of Cp*(Ar^{Mes}N═)TaCl$_2$ (**1**) and Ar^{Mes}NH$_2$ (1 equiv). While

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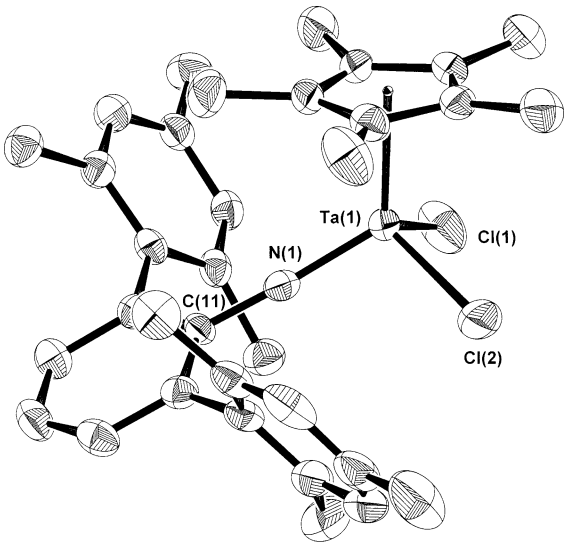
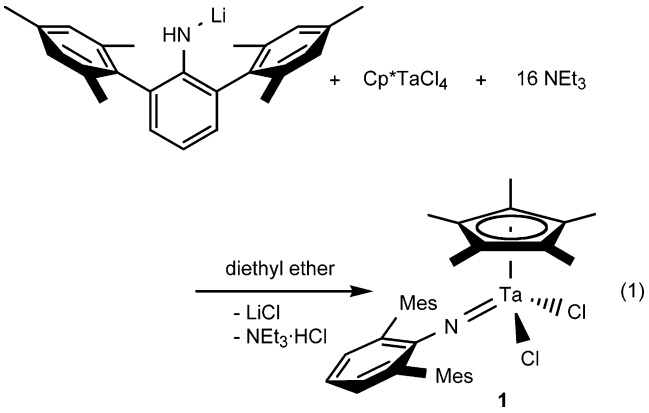


Figure 1. ORTEP diagram of Cp*(Ar^{Mes}N═)TaCl$_2$ (**1**).

this method provides a reasonable synthesis of compound **1**, it is complicated by the similar solubility properties of **1** and Ar^{Mes}NH$_2$, which makes it difficult to purify the desired product. In addition, Ar^{Mes}NHLi is relatively valuable, in that it is prepared via a four-step synthesis starting from 1,3-dichlorobenzene.[35,36] Thus, we sought an alternative synthesis of **1** involving a more convenient deprotonation of the putative intermediate Cp*(Ar^{Mes}NH)TaCl$_3$. Fortunately, treatment of a diethyl ether suspension of Cp*TaCl$_4$ and NEt$_3$ (16 equiv) with a diethyl ether solution of Ar^{Mes}NHLi (room temperature, 2 days) afforded compound **1** as an orange crystalline solid in 85% yield (eq 1). The ^{1}H NMR



spectrum of **1** contains two resonances for the methyl protons of the terphenyl ligand, indicating a mirror plane of symmetry for the molecule. The *o*-Me and *p*-Me resonances appear at 2.38 and 2.25 ppm, respectively.

X-ray quality crystals were obtained by cooling a concentrated pentane solution of **1** to −35 °C. The molecular structure is shown in Figure 1, and important bond distances and angles are listed in Table 1. The structure reveals a three-legged piano stool geometry with bond lengths and angles well within the expected ranges.[40,45−47] The Ta═N bond length of 1.788(4) Å and

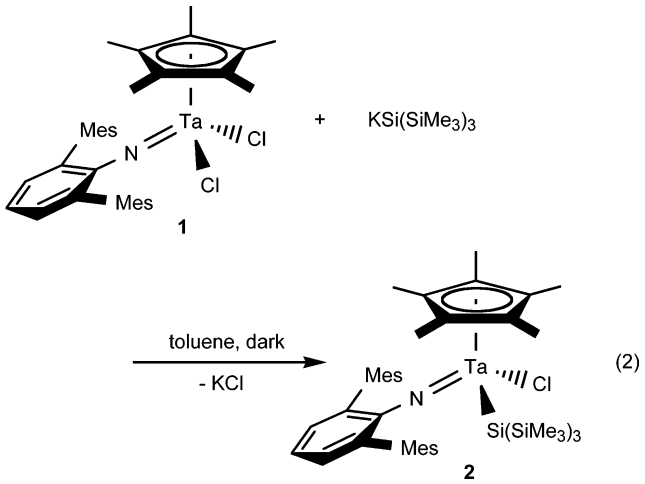
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Cp*(ArMesN═)TaCl$_2$ (1)[a]

Bond Lengths			
Ta(1)−N(1)	1.788(4)	Ta(1)−Cl(1)	2.331(1)
Ta(1)−C(100)	2.1189(2)	Ta(1)−Cl(2)	2.327(1)
N(1)−C(11)	1.385(5)		
Bond Angles			
Ta(1)−N(1)−C(11)	174.7(3)	Cl(1)−Ta(1)−Cl(2)	103.40(7)
N(1)−Ta(1)−C(100)	121.7(1)	Cl(1)−Ta(1)−C(100)	110.17(4)
N(1)−Ta(1)−Cl(1)	104.0(1)	Cl(2)−Ta(1)−C(100)	111.34(4)
N(1)−Ta(1)−Cl(2)	104.5(1)		

[a] C(100) represents the average of the *x*, *y*, and *z* coordinates of the Cp* ring carbons C(1)−C(5).

the imido bond angle of 174.7(3)° are similar to those reported for Cp*(DippN═)TaCl$_2$ (1.780(5) Å and 171.4(5)°)[38] and Cp*(2,6-Me$_2$C$_6$H$_3$)TaCl$_2$ (1.774(5) Å and 169.9(5)°).[48]

Synthesis and *σ*-Bond Metathesis Reactivity of Cp*(Ar^{Mes}N═)Ta[Si(SiMe$_3$)$_3$]Cl (2). Initial attempts to obtain derivatives of Cp*(Ar^{Mes}N═)Ta with reactive *σ*-bonds involved introduction of silyl ligands via salt metathesis reactions. Complex **1** reacted cleanly with the potassium silyl reagent KSi(SiMe$_3$)$_3$ to provide the corresponding silyl chloride complex Cp*(Ar^{Mes}N═)-Ta[Si(SiMe$_3$)$_3$]Cl (**2**) as a red-orange solid in 71% yield (eq 2). The ^{1}H NMR spectrum of compound **2** contains



a resonance for the −Si(SiMe$_3$)$_3$ group at 0.44 ppm and five resonances for the six nonequivalent methyl groups of the [Ar^{Mes}N═]$^{2-}$ ligand. The ^{29}Si NMR signal observed for the tantalum-bound silicon atom (−44.7 ppm) is similar to those reported for the related compounds Cp*(DippN═)Ta[Si(SiMe$_3$)$_3$]Cl (−47.8 ppm)[32] and (Ar^{Mes}N═)(Ar^{Mes}NH)Ta[Si(SiMe$_3$)$_3$]Cl (−37.09 ppm).[36] Much like (Ar^{Mes}N═)(Ar^{Mes}NH)Ta[Si(SiMe$_3$)$_3$]Cl, and in contrast to Cp*(DippN═)Ta[Si(SiMe$_3$)$_3$]Cl, compound **2** is light sensitive, necessitating its preparation and storage in conditions of low ambient lighting. Exposure of benzene-*d*$_6$ solutions of **2** to ambient room light (room temperature, 6 days) led to decomposition to a complex mixture of unidentified products.

Previously, silyl compounds of the form Cp*(DippN═)Ta(SiR$_3$)Cl (SiR$_3$ = Si(SiMe$_3$)$_3$, SiPh$_3$, SiHMes$_2$) were readily prepared by treatment of Cp*(DippN═)-

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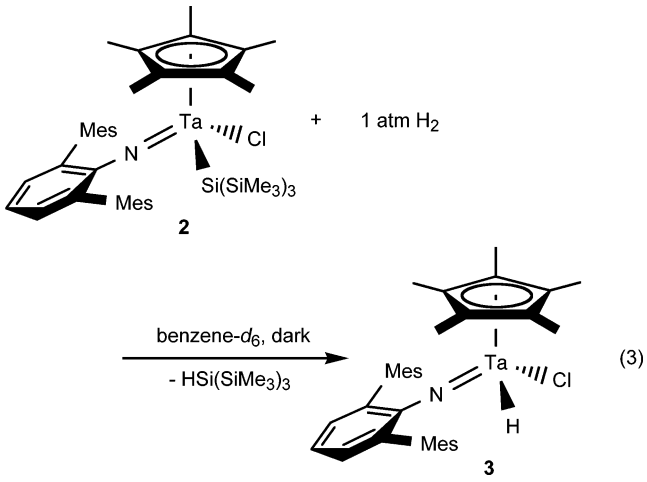
$TaCl_2$ with the corresponding lithium silyl reagents $(THF)_nLiSiR_3$.[32] However, only complex reaction mixtures containing free silane were observed for the reactions of **1** with $(THF)_3LiSi(SiMe_3)_3$ (13 h), $(THF)_2LiSi(^tBu)Ph_2$ (15 min), $(THF)_2LiSiHMes_2$ (5 h), and $(THF)_3LiSiPh_3$ (36 h) in benzene-d_6 at room temperature. Furthermore, **2** was not observed as a product in the reaction of **1** with $(THF)_3LiSi(SiMe_3)_3$ in diethyl ether after warming the reaction mixture from −78 °C to room temperature in the absence of light. Since **2** is sensitive to ambient light, the reaction of **1** with $(THF)_2LiSi(^tBu)Ph_2$ was repeated in the dark (benzene-d_6, room temperature, 15 min), but a complex reaction mixture was observed nonetheless.

Compound **2** reacted rapidly with H_2 (1 atm, benzene-d_6) at room temperature in the dark to give a yellow-orange solution of $Cp^*(Ar^{Mes}N{=})Ta(H)Cl$ (**3**, eq 3). Due



(3)

to the similar solubility properties for **3** and $HSi(SiMe_3)_3$, the hydride complex could not be isolated free of silane impurities and was characterized spectroscopically in solution. Compound **3** features a downfield ^1H NMR resonance at 15.28 ppm and an IR stretch at 1818 cm^{-1}, indicating the presence of a terminal tantalum hydride ligand.[49,50] In contrast, the analogous compound of the $[DippN{=}]^{2-}$ ligand is a dimer with bridging hydride ligands, $[Cp^*(DippN{=})TaCl(\mu\text{-}H)]_2$, and features a $Ta(\mu\text{-}H)Ta$ ^1H NMR resonance at 7.91 ppm.[32] No reaction was observed between **3** and $PhSiH_3$ (1 equiv) in benzene-d_6 up to 70 °C, but further heating to 95 °C for 2 days resulted in consumption of most of the $PhSiH_3$ (82%). Trace Ph_2SiH_2 (0.04 equiv) was the only new silane product found, and no new tantalum-containing products were observed.

Compound **3** was also obtained in 77% yield from the reaction of **2** with $PhSiH_3$ (1 equiv, benzene-d_6) at 70 °C over 43 h in the dark. Monitoring the reaction progress by ^1H NMR spectroscopy indicated the formation of the silyl chloride complex $Cp^*(Ar^{Mes}N{=})Ta(SiH_2Ph)Cl$, which is consumed as **3** is formed. This complex could not be isolated from the reaction mixture, but after 25 h it had formed in 44% yield from the reaction of **2** with $PhSiH_3$ and was characterized by ^1H NMR spectroscopy in solution. The compound contains a Cp* resonance at 1.59 ppm and two coupled doublets (J = 1.4 Hz, TOCSY) at 4.80 and 5.76 ppm due to the diastereotopic hydrogens of the SiH_2Ph group.[51] In addition, a ^1H,^{29}Si-HMQC experiment revealed that these two doublets are coupled to a ^{29}Si NMR signal at 16.0 ppm (J_{SiH} = 176 Hz).

The phenylsilyl complex $Cp^*(Ar^{Mes}N{=})Ta(SiH_2Ph)Cl$ apparently forms via the σ-bond metathesis reaction of **2** with $PhSiH_3$ and then decomposes to hydride **3** and a mixture of unidentified silane products.[51−53] A labeling study with $PhSiD_3$ (1 equiv) revealed the formation of $Cp^*(Ar^{Mes}N{=})Ta(D)Cl$ (identified by ^1H and ^2H NMR spectroscopy) and $DSi(SiMe_3)_3$ (GC−MS), indicating that phenylsilane is the hydride source in this reaction. Notably, no $(PhSiH_2)_2$ was observed by ^1H NMR spectroscopy or GC−MS. However, when **2** was treated with excess $PhSiH_3$ (13 equiv), a 98% conversion to **3** was observed along with the formation of $(PhSiH_2)_2$ (0.25 equiv; 3.3 equiv of $PhSiH_3$ consumed). The observed lack of $(PhSiH_2)_2$ in the reaction with 1 equiv of $PhSiH_3$ might be due to the increased reactivity of $(PhSiH_2)_2$ relative to $PhSiH_3$ in σ-bond metathesis processes.[54] However, the possibility exists that another mechanism may be operative in this reaction.

Several attempts were made to increase the amount of the observed silyl intermediate by replacing $PhSiH_3$ with sterically bulkier silanes ($MesSiH_3$, $DippSiH_3$, Ph_3SiSiH_3, and $PhMeSiH_2$) and silanes containing donor substituents capable of coordinating to early transition metals ($C_6F_5SiH_3$ and $o\text{-}MeOC_6H_4SiH_3$).[55,56] However, reactions with bulkier silanes simply led to the slower formation of **3**, without significant buildup of the intermediate silyl complex. In addition, whereas the reaction of **2** with $C_6F_5SiH_3$ was rapid relative to the corresponding reaction with $PhSiH_3$, the reaction with $o\text{-}MeOC_6H_4SiH_3$ proceeded more slowly. In neither case was the intermediate silyl species observed as the major component of the reaction mixture (by ^1H NMR spectroscopy).

Synthesis and Reactivity of Tantalum Alkyl and Hydride Complexes. The reaction of complex **1** with MeLi (2 equiv) in diethyl ether provided $Cp^*(Ar^{Mes}N{=})TaMe_2$ (**4**) as a bright yellow crystalline solid in 88% yield. Complex **4** displays C_s symmetry by ^1H NMR spectroscopy (22 °C). The $TaMe_2$ group was identified by a ^1H NMR resonance at −0.27 ppm and a ^{13}C NMR resonance at 50.6 ppm. The observed spectroscopic data are consistent with those reported in the literature for the related species $Cp^*(RN{=})TaMe_2$ (R = Me, ^{t}Bu, CH_2CMe_3, $Si(^tBu)_3$, 2,6-$Me_2C_6H_3$, Dipp),[32,41,44,57,58] although the $TaMe_2$ ^1H NMR resonance of **4** is shifted slightly upfield relative to the values reported in the literature (which range from 0.13 to 0.31 ppm). However, the $TaMe_2$ ^1H NMR resonance of $(Ar^{Mes}N{=})(Ar^{Mes}NH)TaMe_2$ also appears upfield of the values listed above (−0.41 ppm).[36]

The Ta−Me bonds of **4** were evaluated for σ-bond metathesis reactivity by the exposure of this compound to H_2 and $PhSiH_3$. Compound **4** reacted slowly with H_2

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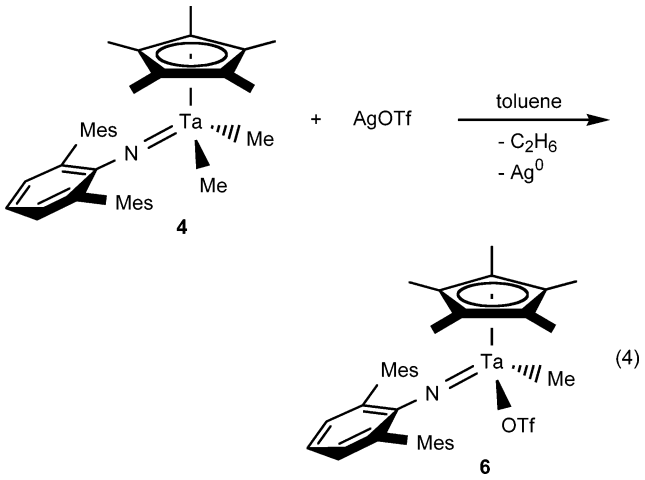
(1 atm) in toluene at 85 °C over 18 days to give a 90% yield of the dihydride dimer $[Cp^*(Ar^{Mes}N{=})TaH(\mu\text{-}H)]_2$ (**5**). Complex **5** was readily identified by its ^{1}H NMR resonances, including a Cp* resonance at 1.77 ppm and two triplets corresponding to the terminal and bridging hydride ligands at 15.52 and 5.32 ppm (J = 7 Hz), respectively.[31,32] In addition, **4** reacted slowly with $PhSiH_3$ (1 equiv) at 85 °C over 4 days (benzene-d_6) to give trace amounts of **5** (6%) and Ph_2SiH_2 (0.06 equiv, relative to an internal Cp_2Fe standard). However, when **4** was treated with excess $PhSiH_3$ (6 equiv) under the same conditions, after 9 days only 19% of **4** remained and a 46% yield of **5** was observed. In addition, Ph_2SiH_2 (1 equiv), $PhMeSiH_2$ (0.20 equiv), CH_4 (0.13 equiv in solution), and Ph_3SiH (trace, by GC−MS), as well as several unidentified products, were observed in the reaction mixture. These results are consistent with σ-bond metathesis reactivity and redistribution of the substituents at silicon.[33,36,55,56,59−61] When **4** was treated with H_2 (1 atm) in bromobenzene-d_5 at 95 °C (7 days), the hydrido-bromide complex $Cp^*(Ar^{Mes}N{=})Ta(H)Br$ was formed. The identification of this compound was based upon comparisons of its ^{1}H NMR data (Ta−H: 16.14 ppm) to those of compound **14** (vide infra).

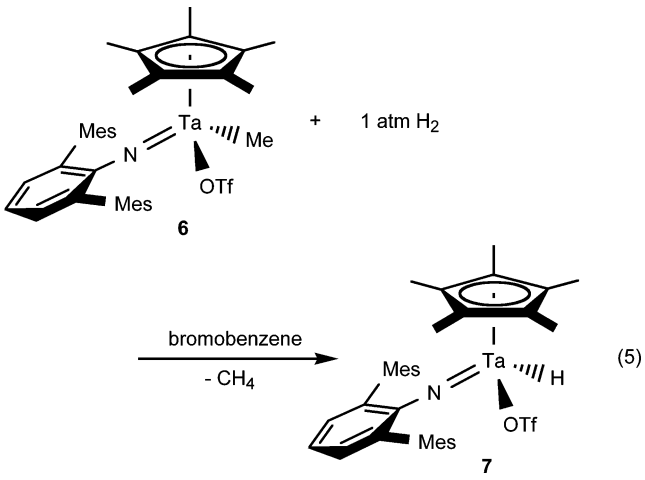
As σ-bond metathesis reactions are sometimes cleaner for compounds containing only one reactive σ-bond,[23,52] synthetic efforts were focused on the preparation of a mono(alkyl) derivative of the $Cp^*(Ar^{Mes}N{=})Ta$ fragment. Literature methods describe the synthesis of tantalum methyl chloride complexes of the form $Cp^*(RN{=})TaMeCl$ (R = 2,6-$Me_2C_6H_3$) by treatment of the dichloride complex with $ZnMe_2$ and by redistribution of the methyl ligands between $Cp^*(RN{=})TaCl_2$ and $Cp^*(RN{=})TaMe_2$.[62] However, when complex **1** was treated with $ZnMe_2$, MeMgCl, and MeLi under a variety of conditions, mixtures containing **1**, **4**, and the desired $Cp^*(Ar^{Mes}N{=})TaMeCl$ complex were obtained. The methyl chloride species could not be separated from the reaction mixture. In addition, no reaction was observed between **1** and **4** at 100 °C (benzene-d_6, 3 days).

Complex **4** reacted cleanly with AgOTf (OTf = OSO_2CF_3) at room temperature in toluene to provide the corresponding methyl triflate compound $Cp^*(Ar^{Mes}N{=})Ta(Me)OTf$ (**6**) in 89% yield (eq 4). Complex **6** is a yellow-orange crystalline solid that features a Ta−Me ^{1}H NMR resonance at 0.56 ppm and a ^{13}C NMR resonance at 48.1 ppm. These values are similar to those reported for the related compound $(Ar^{Mes}N{=})(Ar^{Mes}NH)Ta(Me)OTf$.[35,36] Monitoring an NMR tube scale reaction of complex **4** with AgOTf (benzene-d_6, room temperature, 22 h) by ^{1}H NMR spectroscopy revealed complete conversion to **6** along with ethane formation, consistent with previously reported oxidative cleavage reactions.[36,63]



(4)

The methyl triflate complex **6** reacted cleanly with H_2 (1 atm) in bromobenzene at 100 °C over 3 days to give the hydrido triflate complex $Cp^*(Ar^{Mes}N{=})Ta(H)OTf$ (**7**) as pale yellow crystals in 85% yield (eq 5). No



(5)

evidence for bromobenzene solvent activation by the tantalum hydride was observed as in the hydrogenolysis of **4** and **13** (vide infra). Complex **7** contains a Ta−H resonance in its ^{1}H NMR spectrum at 15.20 ppm (**7-*d***: ^{2}H NMR 15.06 ppm), and a weak Ta−H stretch is observed in the IR spectrum at 1845 cm^{-1} (**7-*d***: ν_{TaD} = 1320 cm^{-1}). The downfield ^{1}H NMR resonance indicates the presence of a terminal hydride.[49,50] For comparison, the imido-amido complex $(Ar^{Mes}N{=})(Ar^{Mes}NH)Ta(Me)OTf$ reacts with H_2 via the intermediate hydride $[(Ar^{Mes}N{=})(Ar^{Mes}NH)Ta(H)OTf]$ to yield the η^5-cyclohexadienyl complex $(Ar^{Mes}N{=})[2\text{-}(\eta^5\text{-}2,4,6\text{-}Me_3C_6H_3)\text{-}6\text{-}MesC_6H_3NH]TaOTf$. Thus, substitution of the amido ligand of $(Ar^{Mes}N{=})(Ar^{Mes}NH)Ta(Me)OTf$ with Cp* (as in **6**) suppresses the arene activation pathway and allows isolation of the terminal hydride (**7**). As for the analogous imido-amido reaction, a pronounced solvent effect was observed for the hydrogenolysis of **6** to **7**. In benzene-d_6, the reaction did not go to completion (30−35% conversion) after heating to 70 °C for 3 days, and prolonged heating at 95−110 °C for 5 days gave no additional conversion. However, the reaction proceeded to completion at 95 °C in bromobenzene-d_5 over 2 days. As in the case of the solvent effect observed for the imido-amido hydrogenolysis reaction,[36] the source of this solvent effect is not completely understood.

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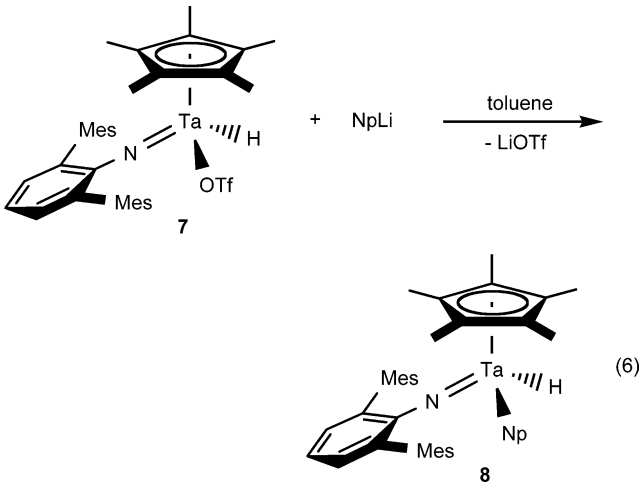
No reaction was observed between complex **6** and $PhSiH_3$ in benzene-d_6 at temperatures up to 70 °C, but further heating to 110 °C for several days led to the formation of **7** and silanes arising from σ-bond metathesis and redistribution of substituents at silicon.[33,36,55,56,59−61] When **6** was treated with a stoichiometric amount of $PhSiH_3$, **7** formed in low yield (7% relative to an internal Cp_2Fe standard) along with trace amounts of $PhMeSiH_2$, Ph_2SiH_2, H_2, and CH_4 (by ^{1}H NMR and GC−MS). However, in the presence of excess $PhSiH_3$ (5 equiv), **6** was completely consumed and **7** was formed in 77% yield. In addition, some $PhSiH_3$ (1 equiv) remained unreacted, and $PhMeSiH_2$ (0.20 equiv), Ph_2SiH_2 (0.13 equiv), H_2 (0.15 equiv in solution), and CH_4 (0.10 equiv in solution), along with a number of unidentified trace silane products, were observed in the reaction mixture. Treatment of complex **7** with $PhSiH_3$ (8 equiv) at 110 °C in benzene-d_6 led to the slow (over 3 days) consumption of 50% of the $PhSiH_3$ along with 21% of **7**. At least four tantalum-containing products were formed in low yields (by ^{1}H NMR), along with H_2 (0.43 equiv in solution), trace Ph_2SiH_2 (0.08 equiv), and other unidentified silanes. Silane resonances observed in the 4.4−5.0 and 5.0−5.5 ppm regions of the ^{1}H NMR spectrum (for reactions of **6** and **7**) were likely due to small amounts of linear and cyclic silane oligomers.[6,55,64−69]

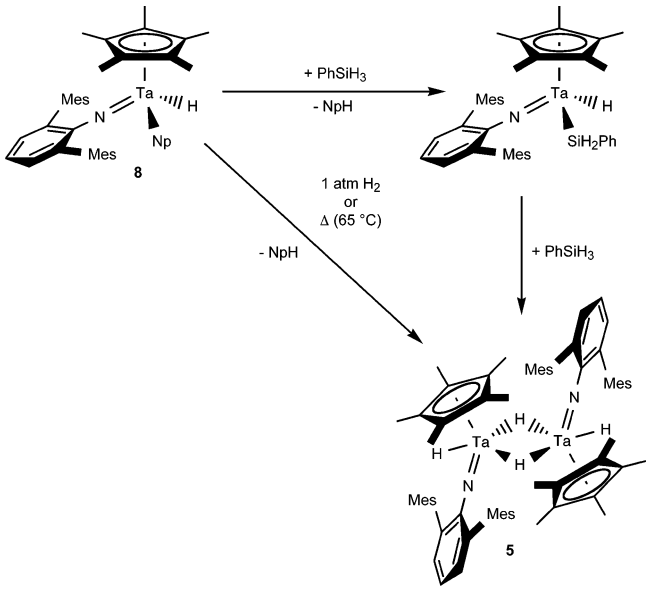
The reaction of **7** with NpLi (Np = Me_3CCH_2) in toluene at room temperature allowed isolation of the neopentyl hydride complex $Cp^*(Ar^{Mes}N{=})Ta(CH_2CMe_3)H$ (**8**) as a yellow crystalline solid in 50% yield (eq 6). The



(6)

^{1}H NMR spectrum of **8** contains a sharp singlet for the hydride resonance at 18.42 ppm, indicative of a terminal tantalum hydride (ν_{TaH} = 1775 cm^{-1}),[49,50] along with a pair of coupled doublets at −0.26 and 1.04 ppm (J = 10 Hz) for the diastereotopic methylene resonances. No coupling was observed between the Ta−H and methylene protons (TOCSY), and the ^{1}H NMR chemical shifts and J_{CH} values for the methylene group indicate that no α-agostic interaction is present in the molecule. In contrast, the related compound $Cp^*(DippN{=})Ta(CH_2CMe_3)H$ contains an α-agostic interaction, and its ^{1}H NMR spectrum indicates coupling between the hydride ligand and the nonagostic methylene hydrogen.[32] Compound **8** was thermally unstable in solution and in the solid state at room temperature, necessitating its storage at −35 °C. Heating a benzene-d_6 solution of **8** to

Scheme 1



65 °C gave rise to a complex reaction mixture which included $[Cp^*(Ar^{Mes}N{=})TaH(\mu\text{-}H)]_2$ (**5**), NpH, and several unidentified products (Scheme 1).

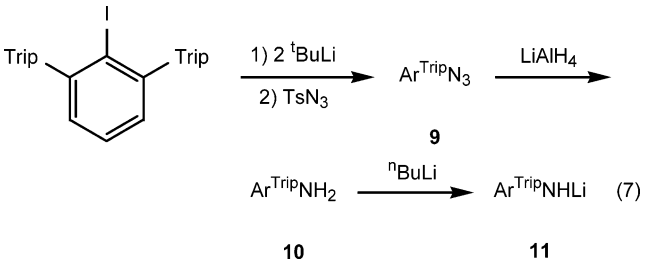
Whereas **2**, **6**, and **7** reacted very slowly with $PhSiH_3$ at elevated temperatures, complex **8** was completely converted to **5** and NpH upon treatment with $PhSiH_3$ (1 equiv) at room temperature (8 h, benzene-d_6, Scheme 1). Monitoring the reaction by ^{1}H NMR spectroscopy revealed that after 15 min a species characterized by a Cp* resonance at 1.62 ppm, a Ta−H resonance at 15.30 ppm, and coupled SiH_2 doublets at 4.48 and 5.06 ppm (TOCSY) had formed in 18% yield. These data are consistent with a transient silyl hydride complex of the form $Cp^*(Ar^{Mes}N{=})Ta(SiH_2Ph)H$.[51−53] Complex **8** also reacted rapidly with H_2 (1 atm) at room temperature (<15 min, benzene-d_6) to form the dihyride dimer **5** and NpH (Scheme 1).

Since $Cp^*(DippN{=})Ta[Si(SiMe_3)_3]H$ is highly reactive in bond activation chemistry,[31,32] attempts were made to prepare an isolable silyl hydride complex of the $Cp^*(Ar^{Mes}N{=})Ta$ fragment. However, a complex reaction mixture was observed upon treating **7** with $(THF)_3LiSi(SiMe_3)_3$ at room temperature (benzene-d_6, dark). After 20 min, a compound with spectroscopic properties consistent with the desired silyl hydride complex (^{1}H NMR: δ 0.39 ($TaSi(SiMe_3)_3$), 1.80 (Cp*), 22.24 (Ta−H)) was observed in 19% yield. The ^{1}H NMR resonances assigned to this species disappeared completely within 1 h. While at least seven products were present in the reaction mixture after 23 h (according to the Cp* region of the spectrum), some of the compounds were identified. The dihydride dimer **5** was observed in 14% yield, and $HSi(SiMe_3)_3$ was formed in 24% yield (relative to an internal Cp_2Fe standard). Similar results were obtained for the reaction of **7** with $KSi(SiMe_3)_3$ (benzene-d_6, dark, room temperature).

Preparation of a More Sterically Demanding Ligand Precursor. Since the $Cp^*(Ar^{Mes}N{=})Ta$ fragment does not stabilize a monomeric dihydride complex, other imido ligands containing more sterically demanding substituents were sought. Given the ease of preparation of ligands of the terphenyl framework, and the

literature precedent for tailoring their steric properties,[70−73] synthetic efforts were focused on alternative (terphenyl)imido ligands. Power and co-workers have successfully employed the [2,6-(2,4,6-$^{i}Pr_3C_6H_2$)C_6H_3]$^-$ aryl group to stabilize the monomeric indium complex [2,6-(2,4,6-$^{i}Pr_3C_6H_2$)C_6H_3]In,[70,74−76] while less bulky terphenyl ligands led to the formation of indium dimers. It was therefore of interest to investigate the potential of the Cp*(Ar^{Trip}N═)Ta fragment (Ar^{Trip} = 2,6-$Trip_2C_6H_3$, Trip = 2,4,6-$^{i}Pr_3C_6H_2$) for stabilizing monomeric dihydride complexes.

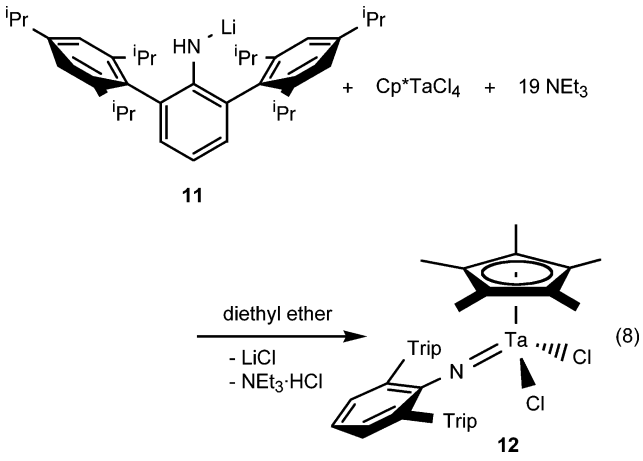
The aniline $Ar^{Trip}NH_2$ (**10**) was readily prepared according to the recently reported procedure for the analogous compound $Ar^{Mes}NH_2$.[35] 2,6-(2,4,6-Triisopropylphenyl)phenyliodide reacted with ^{t}BuLi (2 equiv) in 5:1 hexanes−diethyl ether upon warming of the reaction solution from −78 °C to room temperature,[71,76] and the resulting lithium salt was treated with *p*-toluenesulfonyl azide to provide 2,6-$Trip_2C_6H_3N_3$ (**9**) as pale yellow crystals in 95% yield (eq 7). Reduction of compound **9**



(7)

with $LiAlH_4$ in diethyl ether followed by hydrolysis afforded white crystals of aniline **10** in 85% yield. Lithium anilide **11** was obtained as an off-white powder in 98% yield by warming a chilled hexanes solution of compound **10** to room temperature in the presence of ^{n}BuLi and removing the solvent and volatile byproducts in vacuo (eq 7). While compounds **9**, **10**, and **11** have been previously reported by Power and co-workers,[77] the modified method described above provides improved yields for these compounds.

Synthesis and Reactivity of Complexes Containing the [Ar^{Trip}N═]$^{2-}$ Ligand. Treatment of a diethyl ether suspension of Cp*$TaCl_4$ and NEt_3 (20 equiv) with a diethyl ether solution of Ar^{Trip}NHLi (**11**, room temperature, 3 days) afforded Cp*(Ar^{Trip}N═)$TaCl_2$ (**12**) as an orange crystalline solid in 75% yield (eq 8). The ^{1}H NMR spectrum of **12** contains three doublets (integrating to 12 H each) for the ^{i}Pr-Me groups and two septets (integrating to 4 H and 2 H, respectively) for the ^{i}Pr-H groups.



(8)

Compound **12** reacted rapidly with MeLi (2 equiv) in diethyl ether to provide Cp*(Ar^{Trip}N═)$TaMe_2$ (**13**) as a yellow crystalline solid in 81% yield. The $TaMe_2$ group of compound **12** was identified by a ^{1}H NMR resonance at −0.31 ppm and a ^{13}C NMR resonance at 50.5 ppm. While the ^{1}H NMR chemical shift of **12** is slightly upfield of those for related compounds Cp*(RN═)$TaMe_2$ (R = Me, ^{t}Bu, CH_2CMe_3, Si(^{t}Bu)$_3$, 2,6-$Me_2C_6H_3$, Dipp),[32,41,44,57,58] it is similar to the chemical shifts reported for compound **4** (−0.27 ppm) and (Ar^{Mes}N═)-(Ar^{Mes}NH)$TaMe_2$ (−0.41 ppm).[36]

Observation and Trapping of the Reactive Hydride Cp*(Ar^{Trip}N═)TaH_2. Compound **13** reacted cleanly with H_2 (1 atm) in bromobenzene at 110 °C (4 days) to yield the hydrido bromide species Cp*(Ar^{Trip}-N═)Ta(H)Br (**14**) as a crystalline orange solid in 80% yield (Scheme 2). The hydride ligand of complex **14** was clearly identified by a ^{1}H NMR resonance at 17.00 ppm and an IR stretch at 1838 cm^{-1} (**14-*d***: ν_{TaD} = 1300 cm^{-1}), which are consistent with a terminal tantalum hydride.[49,50] Compound **14** appears to form via the dihydride intermediate species Cp*(Ar^{Trip}N═)TaH_2, although this compound was not observed while monitoring an NMR tube scale reaction of **13** and H_2 (1 atm) by ^{1}H NMR spectroscopy (bromobenzene-d_5, 110 °C). However, this intermediate was observed in the reaction of **15** with H_2 (1 atm) in bromobenzene-d_5 (room temperature, vide infra). The proposed intermediate species Cp*(Ar^{Trip}N═)TaH_2 then reacted with bromobenzene solvent to yield **14** and benzene (Scheme 2). As bromobenzene-d_5 does not react with the alkyl hydride complex **15** (vide infra), the formation of the dihydride complex appears to precede the reaction with bromobenzene. Attempts to prepare the dihydride complex by treating **13** with H_2 (1 atm) in benzene-d_6 (85 °C) gave complex reaction mixtures that did not contain any resonances that could be clearly attributed to the dihydride product. While the conversion of a metal hydride to a metal halide using a halocarbon reagent is a well-precedented transformation,[28,49,50,78,79] bromobenzene is not commonly used as the halide source. However, in 1990, Jones, Eisenberg, and co-workers reported the reaction of Cp_2TaH_3 with C_6H_5Br and

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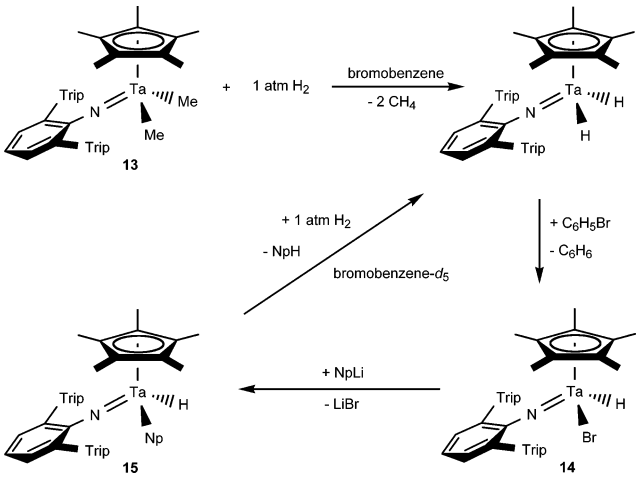
Scheme 2



$C_3H_7C{\equiv}CC_3H_7$ (4-octyne) to yield $Cp_2TaBr(\eta^2\text{-}C_3H_7C{\equiv}CC_3H_7)$ in low yield.[80]

When **13** was treated with D_2 (1 atm) instead of H_2 in bromobenzene (110 °C, 8 days), orange crystals of Cp*(2-[2-(^{i}Pr-d_6)-4,6-^{i}Pr$_2$C$_6$H$_2$]-6-Trip-C$_6$H$_3$N═)Ta(D)-Br (**14-*d*$_7$**) were obtained in 68% yield. The ^{1}H NMR spectrum of **14-*d*$_7$** is identical to the spectrum of **14**, except that the doublets at 1.49 and 1.52 ppm integrate to 3 H (instead of 6 H) each and the resonance at 17.00 ppm is not observed. The ^{2}H{^{1}H} NMR spectrum contains broad signals at 1.46 and 16.84 ppm, integrating to 6 D and 1 D, respectively. Furthermore, the IR spectrum contains broad, weak stretches attributed to CD_3 groups at 2170 and 2208 cm^{-1}. The Ta−D infrared stretch was not located, but is likely the shoulder observed on a strong absorbance at 1312 cm^{-1} (ν_{TaD} = 1300 cm^{-1}, calculated). The NMR data indicate that the methyl groups of one of the isopropyl substituents of the [Ar^{Trip}N═]$^{2-}$ ligand were deuterated during the course of the reaction. Compound **14-*d*$_7$** likely forms via intramolecular C−H bond activation of an isopropyl group positioned near the Ta−D ligand. Furthermore, the deuteration of only one isopropyl group implies that the Trip group is unable to rotate relative to the central phenyl ring of the terphenyl ligand framework. No substrate activation was observed upon heating **14** with benzene-d_6 solvent (135 °C, 41 h) or with CH_4 (1 atm, benzene-d_6, 135 °C, 41 h).

An alkyl hydride derivative was prepared by treating **14** with NpLi in toluene to afford Cp*(Ar^{Trip}N═)Ta(CH$_2$-CMe$_3$)H (**15**) as an orange solid in 76% yield (Scheme 2). The ^{1}H NMR spectrum of **15** contains a sharp singlet for the hydride resonance at 16.66 ppm, indicating the presence of a terminal tantalum hydride,[49,50] and a pair of coupled doublets at −0.90 and 1.46 ppm (J = 12 Hz) for the diastereotopic methylene resonances. As in complex **8** (and in contrast to Cp*(DippN═)Ta(CH$_2$-CMe$_3$)H[32]), no coupling was observed between the Ta−H and methylene protons (TOCSY), and the ^{1}H NMR chemical shifts and J_{CH} values for the methylene group indicate that no α-agostic interaction is present in the molecule. The IR spectrum of complex **15** contains a Ta−H stretch at 1807 cm^{-1}. Compound **15** was thermally unstable in solution and in the solid state at room temperature, necessitating its storage at −35 °C. Heating a bromobenzene-d_5 solution of **15** to 50 °C (2 days) gave rise to a complex reaction mixture, which included NpH and several unidentified products. Persistent impurities of unidentified compounds prevented satisfactory elemental analysis.

A complex reaction mixture that includes NpH (1 equiv) was obtained when a benzene-d_6 solution of **15** was exposed to H_2 (1 atm, room temperature, <12 min). In contrast, when bromobenzene-d_5 was used as the reaction solvent, the dihydride complex Cp*(Ar^{Trip}N═)-TaH$_2$ was observed (vide infra) in 58% yield after 22 min (Scheme 2). This compound is slowly converted to the hydrido bromide complex **14** over the course of ca. 2.5 h. While Cp*(Ar^{Trip}N═)TaH$_2$ was still present in the reaction mixture, H_2 and the tantalum hydride resonances were not observed, presumably because of fast exchange between the hydride ligands and free H_2 in solution on the NMR time scale. However, after complete conversion of Cp*(Ar^{Trip}N═)TaH$_2$ to **14**, H_2 was evident in the ^{1}H NMR spectrum. If the reaction mixture is degassed to remove H_2 after 7 min, the TaH$_2$ group is observed as a broad singlet (width at half-height = 85 Hz), integrating to 2 H at 10.96 ppm. No other Ta−H signals were observed upon examining the region of +50 to −10 ppm. The Cp* resonance for this compound is located at 1.78 ppm. Whereas dihydride dimers were observed for Cp*-imido complexes containing the [DippN═]$^{2-}$ and [Ar^{Mes}N═]$^{2-}$ ligands,[31,32] a monomeric species is obtained when the more sterically demanding [Ar^{Trip}N═]$^{2-}$ ligand was employed. The increased steric bulk of the [Ar^{Trip}N═]$^{2-}$ ligand prevents dimerization of the reactive dihydride complex Cp*(Ar^{Trip}N═)TaH$_2$, which slowly reacts with bromobenzene-d_5 solvent and rapidly decomposes in benzene-d_6.

Concluding Remarks

In an effort to develop new, highly reactive reagents and catalysts for σ-bond metathesis processes, we have examined a series of early transition metal nonmetallocene complexes containing imido ligands.[31−37] Our previous investigations have indicated that while such complexes are capable of novel bond-activation chemistry, the imido ligand is sometimes involved in reactions with hydrosilanes.[31,37] The results described here provide further evidence that a pentamethylcyclopentadienyl-imido ancillary ligand set can support stable tantalum complexes containing reactive M−R (R = hydride, silyl) σ-bonds. The increased steric bulk of the [Ar^{Mes}N═]$^{2-}$ and [Ar^{Trip}N═]$^{2-}$ ligands relative to the [DippN═]$^{2-}$ ligand permitted the study of monomeric monohydride (Ar^{Mes} and Ar^{Trip} ligands) and dihydride (Ar^{Trip} ligand) complexes and appears to prevent reaction of the Ta═N double bond of the imido ligand with PhSiH$_3$. However, the stable, isolable monohydride complexes containing halide and triflate ligands react with PhSiH$_3$ only under forcing conditions (excess PhSiH$_3$, long reaction times, high temperatures) to give products that arise from the redistribution of substituents at silicon. In contrast, monomeric monohydride metallocene halides of the group 4 transition metals are

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among the most active catalysts for silane[6,23] (and stannane)[25,26] dehydropolymerizations.

The most reactive complexes of these mixed Cp*-imido ligand frameworks are those containing two active σ-bonds. For example, the neopentyl hydride Cp*($Ar^{Mes}N$=)Ta(CH_2CMe_3)H (**8**) rapidly reacts with $PhSiH_3$ to generate the intermediate silyl hydride complex Cp*($Ar^{Mes}N$=)Ta(SiH_2Ph)H, which then converts to the dimeric dihydride product. Attempts to generate a silyl hydride complex via salt metathesis resulted in the highly reactive, transient species Cp*($Ar^{Mes}N$=)Ta[$Si(SiMe_3)_3$]H. In contrast to the CpCp*Hf and Cp*(DippN=)Ta analogues,[31,32,81] silyl hydride derivatives of Cp*($Ar^{Mes}N$=)Ta are neither stable nor isolable.

Taken together, the results presented here indicate that complexes containing sterically demanding imido ligands and two reactive σ-bonds are highly reactive in bond-activation chemistry. The observation of the reactive, monomeric dihydride complex Cp*($Ar^{Trip}N$=)TaH_2 and the intramolecular C−H bond activation of **14** suggest that complexes of the $[Ar^{Trip}N=]^{2-}$ ligand represent promising candidates for future investigations.

Experimental Procedures

General Procedures. All experiments were conducted under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres drybox unless otherwise noted. Dry, oxygen-free solvents were used unless otherwise indicated. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and saturated $NaHCO_3$. Pentane was then dried over $MgSO_4$, stored over activated 4 Å molecular sieves, and distilled from potassium benzophenone ketyl under a nitrogen atmosphere. Thiophene impurities were removed from toluene by treatment with H_2SO_4 and saturated $NaHCO_3$. Toluene was then dried over $MgSO_4$ and distilled from potassium under a nitrogen atmosphere. Diethyl ether and hexanes were distilled from sodium benzophenone ketyl under a nitrogen atmosphere, and bromobenzene was distilled from CaH_2 under a nitrogen atmosphere. Benezene-d_6 was purified and dried by vacuum distillation from sodium/potassium alloy. Bromobenzene-d_5 was degassed and then dried over 4 Å molecular sieves.

NMR spectra were recorded at 500.132 MHz (^{1}H), 61.423 MHz (^{2}H), 125.759 MHz (^{13}C), 376.503 MHz (^{19}F), or 99.376 MHz (^{29}Si) using a Bruker DRX-500 (^{1}H, ^{13}C, ^{29}Si) or AMX-400 (^{2}H, ^{19}F) spectrometer. ^{1}H and ^{2}H NMR spectra were referenced internally by the residual solvent signal relative to tetramethylsilane. $^{13}C\{^1H\}$ NMR spectra were referenced internally by the ^{13}C NMR signal of the NMR solvent relative to tetramethylsilane. $^{19}F\{^1H\}$ NMR spectra were referenced relative to an α,α,α-trifluorotoluene external standard. ^{29}Si NMR spectra were referenced using a tetramethylsilane external standard. In some cases, distortionless enhancement by polarization transfer (DEPT) was used to assign the ^{13}C NMR resonances as CH_3, CH_2, CH, or C, and ^{1}H-coupled and decoupled insensitive nuclei enhanced by polarization transfer (INEPT) were used to identify ^{29}Si resonances, $^1J_{SiH}$ values, and $^1J_{CH}$ values. Heteronuclear multiple quantum coherence (HMQC) was used to identify ^{1}H,^{13}C and ^{1}H,^{29}Si coupling, and total correlation spectroscopy (TOCSY) was used to identify some coupled ^{1}H NMR systems. All spectra were recorded at room temperature (~22 °C) unless otherwise indicated. Infrared spectra were recorded as thin film Nujol mulls on NaCl plates, as KBr pellets, or in solution using a Mattson FTIR spectrometer at a resolution of 4 cm^{-1}. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

All chemicals were purchased from Aldrich or Fluka and were used without further purification. Lithium aluminum hydride was purified by diethyl ether extraction. Triethylamine was distilled from CaH_2 under a nitrogen atmosphere. Hydrogen was purchased from Praxair, and deuterium was purchased from Airgas. The compounds 2,6-$Mes_2C_6H_3NHLi$,[35,36] Cp^*TaCl_4,[82] $KSi(SiMe_3)_3$,[83−85] $LiCH_2CMe_3$,[86] 2,6-$Trip_2C_6H_3I$,[71] and *p*-toluenesulfonyl azide[87] were prepared as reported in the literature.

Cp*(2,6-$Mes_2C_6H_3N$=)$TaCl_2$ (1). A solution of 2,6-$Mes_2C_6H_3$-NHLi (2.01 g, 5.98 mmol) in diethyl ether (150 mL) was added dropwise over 1 h to a stirred slurry of Cp^*TaCl_4 (2.74 g, 5.98 mmol) in NEt_3 (13.0 mL, 93.3 mmol) and diethyl ether (400 mL). Upon addition, the reaction mixture appeared brick-red in color. After stirring at room temperature for 2 days, the reaction mixture became bright orange. The solvent, excess NEt_3, and volatile byproducts were removed in vacuo to leave behind a bright orange solid. The solid was extracted with pentane (5 × 70 mL), and the combined extracts were filtered to give an orange-colored solution. The solution was concentrated to ca. 125 mL and cooled to −35 °C overnight to afford three crops of orange crystals of compound **1** (3.64 g, 85%). ^{1}H NMR (benzene-d_6): δ 1.63 (s, 15 H, C_5Me_5), 2.25 (s, 6 H, *p*-Me), 2.38 (s, 12 H, *o*-Me), 6.79 (t, 1 H, J = 7.5 Hz, *p*-H), 6.95 (s, 4 H, Mes-H), 7.00 (d, 2 H, J = 7.5 Hz, *m*-H). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 11.5 ($C_5\mathit{Me}_5$), 21.5 (*o*-Me), 22.0 (*p*-Me), 122.2 (C_5Me_5), 124.2, 129.0, 130.1, 136.4, 137.5, 137.7, 139.8, 151.3 (aromatic C's). IR (Nujol, cm^{-1}): 739 (w), 761 (s), 780 (m), 803 (w), 845 (s), 982 (m), 1026 (m), 1090 (m), 1249 (vw), 1269 (w), 1287 (w), 1314 (vs), 1407 (vs), 1486 (m), 1567 (vw), 1576 (vw), 1613 (m), 1722 (vw). Anal. Calcd for $C_{34}H_{40}Cl_2NTa$: C, 57.15; H, 5.64; N, 1.96. Found: C, 57.35; H, 5.84; N, 2.15.

Cp*(2,6-$Mes_2C_6H_3N$=)Ta[$Si(SiMe_3)_3$]Cl (2). Compound **1** (0.607 g, 0.784 mmol) and $KSi(SiMe_3)_3$ (0.279 g, 0.974 mmol) were dissolved in toluene (20 mL), and the resulting mixture was stirred at room temperature in the dark. After 1 h, the solvent was removed in vacuo to give an oily, red solid. The solid was extracted with pentane (2 × 20 mL), and the extracts were filtered to give a red solution. Removal of the solvent in vacuo gave **2** (0.515 g, 71%) as a red-orange foam. ^{1}H NMR (benzene-d_6): δ 0.44 (s, 27 H, $Si(SiMe_3)_3$), 1.81 (s, 15 H, C_5Me_5), 2.11 (s, 3 H, Mes-Me), 2.13 (s, 3 H, Mes-Me), 2.22 (s, 6 H, Mes-Me), 2.46 (s, 3 H, Mes-Me), 2.55 (s, 3 H, Mes-Me), 6.79 (s, 1 H, Mes-H), 6.82 (m, 2 H, J = 5 Hz, *m*-H), 6.86 (s, 1 H, Mes-H), 6.88 (s, 1 H, Mes-H), 6.98 (dd, 1 H, J = 5 Hz, J = 3.5 Hz, *p*-H), 7.05 (s, 1 H, Mes-H). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 7.4 ($Si(SiMe_3)_3$), 12.9 ($C_5\mathit{Me}_5$), 21.4, 21.6, 22.5, 22.7, 23.7, 25.1 (Mes-Me's), 121.6 (C_5Me_5), 124.6, 129.0, 129.3, 129.4, 129.9, 131.5 (CH's), 136.2, 136.8, 137.0, 137.6, 138.4, 139.0, 140.1, 140.6, 143.7, 154.3 (aromatic C's). ^{29}Si NMR (benzene-d_6): δ −4.7 ($Si(\mathit{Si}Me_3)_3$), −44.7 ($\mathit{Si}(SiMe_3)_3$). IR (KBr, cm^{-1}): 413 (vw), 445 (vw), 498 (w), 524 (w), 609 (s), 627 (m), 649 (m), 689 (m), 760 (m), 785 (w), 837 (vs), 969 (w), 983 (w), 1030 (w), 1088 (w), 1162 (vw), 1184 (vw), 1244 (s), 1289 (m), 1326 (s), 1378 (m), 1415 (s), 1444 (m), 1486 (w), 1576 (w), 1611 (w), 2730 (w), 2859 (m), 2916 (s), 2950 (s). Anal. Calcd for $C_{43}H_{67}ClNSi_4Ta$: C, 55.73; H, 7.29; N, 1.51. Found: C, 55.68; H, 7.27; N, 1.57.

Cp*(2,6-$Mes_2C_6H_3N$=)Ta(H)Cl (3). Compound **2** (33 mg, 36 μmol) was dissolved in benzene-d_6 (~0.7 mL) and trans-

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ferred to an NMR tube fitted with a J. Young Teflon stopper. The solution was degassed via three cycles of freeze−pump−thaw and closed under H_2 (1 atm). Upon exposure to H_2 (<1 min), the reaction mixture changed from red-orange to yellow-orange in color. Compound **3** was observed as the only metal-containing product (along with $HSi(SiMe_3)_3$) by ^1H NMR spectroscopy (99% relative to internal standard). ^1H NMR (benzene-d_6): δ 1.65 (s, 15 H, C_5Me_5), 2.25 (s, 6 H, Mes-Me), 2.36 (s, 6 H, Mes-Me), 2.37 (s, 6 H, Mes-Me), 6.83 (t, 1 H, J = 7.5 Hz, *p*-H), 6.89 (s, 2 H, Mes-H), 6.94 (s, 2 H, Mes-H), 7.04 (d, 2 H, J = 7.5 Hz, *m*-H), 15.28 (s, 1 H, Ta-H). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 11.5 ($C_5\mathit{Me}_5$), 21.5, 21.8, 21.9 (Mes-Me's), 119.3 (C_5Me_5), 123.4, 128.8, 128.8, 129.2 (CH's), 136.2, 137.2, 137.5, 138.4, 139.0, 152.2 (aromatic C's). IR (KBr, cm^{-1}): 412 (vw), 420 (vw), 444 (vw), 524 (w), 609 (s), 626 (m), 648 (m), 689 (m), 720 (s), 760 (m), 804 (m), 838 (vs), 971 (vw), 983 (w), 1030 (w), 1088 (w), 1245 (s), 1297 (m), 1325 (m), 1414 (s), 1445 (m), 1486 (w), 1577 (w), 1611 (w), 1818 (vw, br, ν_{TaH}), 2729 (w), 2857 (m), 2915 (s), 2949 (s).

Cp*(2,6-Mes$_2$C$_6$H$_3$N=)TaMe$_2$ (4). A solution of MeLi in diethyl ether (1.6 M, 2.3 mmol) was added to a stirred solution of compound **1** (0.804 g, 1.04 mmol) in diethyl ether (50 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 20 min and then warmed to room temperature over 4.5 h. The solvent was removed in vacuo to leave a bright yellow solid, which was extracted with pentane (3 × 25 mL), and the combined extracts were then filtered to give a bright yellow solution. The solution was concentrated to ca. 20 mL and cooled to −35 °C to afford three crops of bright yellow crystals of compound **4** (0.619 g, 88%). ^1H NMR (benzene-d_6): δ −0.27 (s, 6 H, $TaMe_2$), 1.51 (s, 15 H, C_5Me_5), 2.23 (s, 6 H, *p*-Me), 2.39 (s, 12 H, *o*-Me), 6.90 (t, 1 H, J = 10 Hz, *p*-H), 6.91 (s, 4 H, Mes-H), 7.06 (d, 2 H, J = 10 Hz, *m*-H). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 10.9 ($C_5\mathit{Me}_5$), 21.5 (*p*-Me), 21.9 (*o*-Me), 50.6 ($TaMe_2$), 116.9 (C_5Me_5), 122.1, 128.7, 129.7, 135.8, 137.5, 139.2, 139.7, 154.2 (aromatic C's). IR (Nujol, cm^{-1}): 739 (w), 761 (m), 781 (w), 849 (m), 979 (m), 1012 (w), 1028 (w), 1087 (m), 1150 (vw), 1158 (w), 1250 (vw), 1283 (vw), 1324 (s), 1373 (m), 1414 (s), 1487 (m), 1577 (vw), 1610 (w). Anal. Calcd for $C_{36}H_{46}NTa$: C, 64.18; H, 6.88; N, 2.08. Found: C, 64.28; H, 6.67; N, 2.07.

[Cp*(2,6-Mes$_2$C$_6$H$_3$N=)Ta(H)(μ-H)]$_2$ (5). Compound **4** (0.204 g, 0.303 mmol) was dissolved in toluene (10 mL), and the resulting solution was transferred to a 50 mL reaction vessel. The solution was degassed, H_2 (1 atm) was admitted, and the reaction solution was heated to 85 °C. After 18 days, the reaction mixture was cooled to room temperature. The solvent was removed in vacuo to leave behind a red-orange oil, which was extracted with pentane (10 mL). The solvent was removed from the pentane extracts in vacuo to afford **5** (0.176 g, 90%) as a red-orange foam. ^1H NMR (benzene-d_6): δ 1.77 (s, 30 H, C_5Me_5), 2.17 (s, 6 H, Mes-Me), 2.28 (s, 6 H, Mes-Me), 2.32 (s, 6 H, Mes-Me), 2.36 (s, 6 H, Mes-Me), 2.41 (s, 6 H, Mes-Me), 2.42 (s, 6 H, Mes-Me), 5.32 (t, 2 H, J = 7 Hz, Ta(μ-H)Ta), 6.79 (t, 2 H, J = 7.5 Hz, *p*-H), 6.89 (dd, 2 H, J = 8 Hz, J = 2 Hz, *m*-H), 6.91 (s, 2 H, Mes-H), 6.93 (s, 2 H, Mes-H), 7.03 (dd, J = 7 Hz, J = 2 Hz, *m*-H), 7.06 (s, 2 H, Mes-H), 7.07 (s, 2 H, Mes-H), 15.52 (t, 2 H, J = 7 Hz, Ta-H). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 13.1 ($C_5\mathit{Me}_5$), 21.5, 21.8, 23.2, 23.3, 23.3, 23.9 (Mes-Me's), 115.7 (C_5Me_5), 122.0, 128.4, 128.9, 129.1, 129.3, 131.3, 131.6 (CH's), 136.0, 136.4, 137.2, 137.8, 138.2, 138.2, 138.8, 139.5, 140.3, 140.5, 155.8 (aromatic C's). IR (KBr, cm^{-1}): 417 (vw), 498 (w), 522 (w), 576 (w), 604 (w), 627 (w), 699 (w), 741 (s), 755 (s), 776 (s), 849 (m), 924 (vw), 973 (w), 1031 (w), 1071 (vw), 1091 (w), 1261 (w), 1287 (m), 1316 (s), 1378 (s), 1405 (vs), 1447 (s), 1486 (m), 1541 (w), 1559 (w), 1576 (w), 1603 (m), 1816 (w, br, ν_{TaH}), 2729 (w), 2857 (m), 2915 (s), 2947 (s). Anal. Calcd for $C_{68}H_{84}N_2Ta_2$: C, 63.25; H, 6.56; N, 2.17. Found: C, 62.75; H, 6.23; N, 2.76.

Cp*(2,6-Mes$_2$C$_6$H$_3$N=)TaMe(OSO$_2$CF$_3$) (6). Compound **4** (0.636, 0.944 mmol) and $AgOSO_2CF_3$ (0.244 g, 0.948 mmol) were dissolved in toluene (30 mL) to give a yellow-green reaction mixture. After stirring the reaction mixture for 29 h at room temperature, the solvent and volatile byproducts were removed under vacuum to give a yellow-green solid. The solid was extracted with pentane (5 × 30 mL), and the combined extracts were filtered to give a gold-colored solution. The solution was concentrated to ca. 20 mL and cooled to −35 °C overnight to afford yellow-orange crystals of compound **6** (0.676, 89%). ^1H NMR (benzene-d_6): δ 0.56 (s, 3 H, TaMe), 1.54 (s, 15 H, C_5Me_5), 2.24 (s, 6 H, Mes-Me), 2.29 (br s, 6 H, Mes-Me), 2.30 (s, 6 H, Mes-Me), 6.78 (t, 1 H, J = 7.5 Hz, *p*-H), 6.91 (br s, 2 H, Mes-H), 6.93 (d, 2 H, J = 7.5 Hz, *m*-H), 6.98 (br s, 2 H, Mes-H). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 10.8 ($C_5\mathit{Me}_5$), 21.4 (Mes-Me), 21.6 (Mes-Me), 21.8 (Mes-Me), 48.1 (TaMe), 119.2 (aromatic C), 120.7 (C_5Me_5), 124.4, 129.1, 129.3, 129.8 (CH's), 136.8 (aromatic C), 137 (br s, CF_3), 138.2, 139.9, 151.4 (aromatic C's). $^{19}F\{^1H\}$ NMR (benzene-d_6): δ −76.0. IR (Nujol, cm^{-1}): 598 (s), 629 (s), 742 (vw), 760 (m), 778 (vw), 802 (vw), 855 (w), 975 (vs), 1009 (w), 1027 (w), 1093 (w), 1156 (s), 1174 (m), 1196 (vs), 1236 (s), 1324 (s), 1370 (vs), 1414 (s), 1578 (vw), 1612 (w). Anal. Calcd for $C_{36}H_{43}F_3NO_3STa$: C, 53.53; H, 5.37; N, 1.73. Found: C, 53.78; H, 5.39; N, 1.52.

Cp*(2,6-Mes$_2$C$_6$H$_3$N=)Ta(H)(OSO$_2$CF$_3$) (7). Compound **6** (0.560 g, 0.693 mmol) was dissolved in bromobenzene (10 mL), and the resulting solution was transferred to a 50 mL reaction flask sealed with a Teflon stopper. The solution was degassed, H_2 (1 atm) was admitted, and the reaction solution was heated to 100 °C. After 3 days, the red-orange reaction mixture was cooled to room temperature and diluted with toluene (5 mL). The solvent was removed in vacuo to give a red-orange oily solid, which was extracted with toluene (10 mL). The extract was concentrated to ca. 7 mL and cooled to −35 °C to afford pale yellow crystals of compound **7** (0.469 g, 85%). ^1H NMR (benzene-d_6, 20 °C): δ 1.61 (s, 15 H, C_5Me_5), 2.26 (s, 6 H, Mes-Me), 2.3 (br s, 12 H, Mes-Me), 6.80 (t, 1 H, J = 7.5 Hz, *p*-H), 6.94 (s, 4 H, Mes-H), 6.98 (br d, 2 H, J = 12.5 Hz, *m*-H), 15.20 (s, 1 H, TaH). ^1H NMR (benzene-d_6, 80 °C): δ 1.66 (s, 15 H, C_5Me_5), 2.22 (s, 6 H, Mes-Me), 2.25 (s, 6 H, Mes-Me), 2.27 (s, 6 H, Mes-Me), 6.81 (t, 1 H, J = 7.5 Hz, *p*-H), 6.92 (s, 2 H, Mes-H), 6.94 (s, 2 H, Mes-H), 6.98 (d, 2 H, J = 7.5 Hz, *m*-H), 15.34 (s, 1 H, TaH). $^{13}C\{^1H\}$ NMR (benzene-d_6, 80°C): δ 11.3 ($C_5\mathit{Me}_5$), 21.4 (Mes-Me), 21.5 (Mes-Me), 21.6 (Mes-Me), 119.2 (C_5Me_5), 121.7 (aromatic C), 124.0, 128.9, 129.1, 129.6 (CH's), 136.6 (aromatic C), 137.2 (br s, CF_3), 137.4 (br s), 138.5, 139.7, 151.8 (aromatic C's). $^{19}F\{^1H\}$ NMR (benzene-d_6, 20 °C): δ −75.6. IR (KBr, cm^{-1}): 514 (w), 585 (w), 619 (m), 646 (w), 740 (w), 763 (m), 784 (w), 803 (w), 850 (m), 882 (w), 905 (w), 974 (m), 1017 (s), 1090 (m), 1174 (s), 1198 (s), 1224 (vs), 1302 (m), 1326 (s), 1377 (m), 1401 (m), 1456 (m), 1488 (w), 1507 (w), 1520 (w), 1541 (w), 1559 (w), 1576 (w), 1613 (w), 1845 (w, ν_{TaH}), 2730 (w), 2857 (m), 2915 (m), 2953 (m), 2992 (m). Anal. Calcd for $C_{35}H_{41}F_3NO_3STa$: C, 52.96; H, 5.21; N, 1.76; S, 4.04. Found: C, 52.78; H, 5.37; N, 1.65; S, 4.03.

Cp*(2,6-Mes$_2$C$_6$H$_3$N=)Ta(D)(OSO$_2$CF$_3$) (7-*d*). A procedure essentially identical to that used to prepare **7** (substituting D_2 for H_2, heating for 5 days) yielded bright yellow crystals of compound **7-*d*** (0.0979 g, 67%). Selected data: ^2H NMR (benzene, 20 °C): δ 15.06 (br s, 1 D, TaD). IR (KBr, cm^{-1}): 512 (w), 526 (w), 586 (w), 618 (m), 647 (w), 695 (w), 730 (m), 764 (m), 804 (w), 850 (m), 973 (m), 1013 (s), 1093 (w), 1173 (s), 1199 (vs), 1210 (vs), 1226 (vs), 1305 (m), 1320 (m, ν_{TaD}), 1328 (s), 1372 (m), 1402 (m), 1449 (m), 1488 (w), 1507 (w), 1520 (w), 1541 (w), 1559 (w), 1576 (w), 1612 (w), 2730 (w), 2858 (m), 2917 (m), 2946 (m), 2973 (m), 2993 (m). Anal. Calcd for $C_{35}H_{40}DF_3NO_3STa$: C, 52.90; H, 5.33; N, 1.76; S, 4.03. Found: C, 53.12; H, 5.18; N, 1.75; S, 4.18.

Cp*(2,6-Mes$_2$C$_6$H$_3$N=)Ta(CH$_2$CMe$_3$)H (8). Compound **7** (0.224 g, 0.282 mmol) and $LiCH_2CMe_3$ (0.0290 g, 0.371 mmol) were dissolved in toluene (20 mL) and stirred at room temperature for 16 h. The solvent was removed in vacuo, and the yellow-orange oily solid was extracted with pentane (3 × 10 mL) and filtered. The combined extracts were concentrated

to ca. 5 mL and cooled to −78 °C to afford two crops of yellow crystals of compound **8** (0.102 g, 50%). ^{1}H NMR (benzene-d_6): δ −0.26 (d, 1 H, J = 10 Hz, CH_2), 1.04 (d, 1 H, J = 10 Hz, CH_2), 1.05 (s, 9 H, ^{t}Bu), 1.66 (s, 15 H, C_5Me_5), 2.22 (s, 6 H, Mes-Me), 2.39 (br s, 12 H, Mes-Me), 6.88 (s, 2 H, Mes-H), 6.90 (t, 1 H, J = 7 Hz, p-H), 6.93 (s, 2 H, Mes-H), 7.07 (d, 2 H, J = 7 Hz, m-H), 18.42 (s, 1 H, Ta-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 11.5 ($C_5\mathit{Me}_5$), 21.5 (Mes-Me), 22.3 (Mes-Me), 22.5 (Mes-Me), 36.9 ($C\mathit{Me}_3$), 38.4 ($\mathit{C}Me_3$), 87.0 ($TaCH_2$), 117.8 (C_5Me_5), 122.6, 128.8, 129.8 (CH's), 136.1, 139.6, 153.8 (aromatic C's). IR (KBr, cm^{-1}): 418 (vw), 498 (vw), 520 (vw), 551 (vw), 574 (w), 603 (w), 626 (vw), 740 (s), 757 (s), 776 (s), 801 (m), 849 (m), 975 (w), 1029 (w), 1090 (w), 1214 (vw), 1231 (vw), 1250 (w), 1260 (w), 1318 (s), 1377 (m), 1407 (vs), 1447 (s), 1486 (m), 1541 (vw), 1559 (vw), 1577 (w), 1611 (w), 1775 (w, br, ν_{TaH}), 2728 (vw), 2861 (m), 2916 (s), 2949 (s). Anal. Calcd for $C_{39}H_{52}NTa$: C, 65.44; H, 7.32; N, 1.96. Found: C, 64.91; H, 7.39; N, 1.67.

2,6-Trip$_2$C$_6$H$_3$N$_3$ (9). A solution of ^{t}BuLi in pentane (1.7 M, 45.0 mmol) was added dropwise over 10 min via syringe to a stirred slurry of 2,6-Trip$_2$C$_6$H$_3$I (13.34 g, 21.9 mmol) in 5:1 hexanes−diethyl ether (350 mL) at −78 °C.[76] The resulting slurry was warmed to room temperature and then stirred for an additional 11 h. The homogeneous gold reaction mixture was then cooled to 0 °C, and a solution of p-toluenesulfonyl azide (4.53 g, 23.0 mmol) in diethyl ether (20 mL) was added via cannula. After warming to room temperature and stirring for an additional 12 h, the cloudy yellow reaction mixture was quenched with water (300 mL). The aqueous phase was separated and extracted with diethyl ether (3 × 100 mL). The organic phases were combined, washed with water (150 mL), and dried over $MgSO_4$. Filtration followed by solvent removal in vacuo resulted in pale yellow crystals of compound **9** (10.85 g, 95%). The analytically pure compound was obtained by recrystallization from diethyl ether at −35 °C. Mp: 167−168 °C. ^{1}H NMR (benzene-d_6): δ 1.19 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.24 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.33 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 2.85 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 2.92 (septet, 4 H, J = 7 Hz, ^{i}Pr-H), 6.92 (dd, 1 H, J = 7 Hz, J = 8 Hz, p-H), 7.04 (d, 2 H, J = 7 Hz, m-H), 7.20 (s, 4 H, Mes-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 24.3, 24.7, 25.1 (^{i}Pr-Me's), 31.6, 35.2 (^{i}Pr-CH's), 121.4, 124.9, 131.1, 133.7, 134.9, 138.1, 147.8, 150.0 (aromatic C's). IR (Nujol, cm^{-1}): 650 (m), 680 (m), 756 (m), 776 (w), 797 (m), 876 (m), 943 (w), 1053 (w), 1069 (w), 1104 (w), 1170 (w), 1239 (w), 1314 (m), 1337 (w), 1362 (m), 1418 (s), 1569 (w), 1607 (w), 2089 (s), 2111 (s), 2134 (s). Anal. Calcd for $C_{36}H_{49}N_3$: C, 82.55; H, 9.43; N, 8.02. Found: C, 82.44; H, 9.32; N, 7.84.

2,6-Trip$_2$C$_6$H$_3$NH$_2$ (10). A solution of compound **9** (10.85 g, 20.7 mmol) in diethyl ether (200 mL) was added slowly over 5 min via cannula to a stirred solution of lithium aluminum hydride (0.831 g, 21.9 mmol) in diethyl ether (200 mL). After the addition was completed, the yellow reaction mixture was heated at reflux for 4.5 h (50 °C bath). The bright red-orange reaction mixture was cooled to room temperature and slowly quenched with reagent grade diethyl ether (125 mL) and water (200 mL). The organic phase was decanted, and the aqueous phase was extracted with diethyl ether (2 × 200 mL). The organic phases were combined and dried over $MgSO_4$. Filtration followed by solvent removal in vacuo resulted in a white crystalline solid. Recrystallization from diethyl ether at −35 °C afforded two crops of analytically pure **10** (8.74 g, 85%). ^{1}H NMR (benzene-d_6): δ 1.21 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.27 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.28 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 2.86 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 2.96 (s, 2 H, NH_2), 3.02 (septet, 4 H, J = 7 Hz, ^{i}Pr-H), 6.82 (t, 1 H, J = 8 Hz, p-H), 7.03 (d, 2 H, J = 8 Hz, m-H), 7.25 (s, 4 H, Mes-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 24.7, 24.7, 25.1 (^{i}Pr-Me's), 31.3, 35.2 (^{i}Pr-CH's), 118.1, 121.8, 125.7, 130.0, 134.2, 143.3, 148.4, 149.2 (aromatic C's). IR (Nujol, cm^{-1}): 750 (s), 778 (w), 795 (m), 877 (s), 942 (m), 1036 (w), 1057 (m), 1070 (m), 1096 (w), 1104 (w), 1170 (w), 1211 (w), 1240 (w), 1252 (w), 1261 (w), 1301 (m), 1316 (m), 1338 (w), 1361 (s), 1440 (vs), 1567 (m), 1604 (s), 1764 (w), 3383 (m, ν_{NH2}), 3480 (s, ν_{NH2}). Anal. Calcd for $C_{36}H_{51}N$: C, 86.86; H, 10.33; N, 2.81. Found: C, 86.59; H, 10.13; N, 3.00.

2,6-Trip$_2$C$_6$H$_3$NHLi (11). A solution of ^{n}BuLi in hexanes (1.2 M, 3.7 mmol) was added via syringe to a stirred solution of compound **10** (1.79 g, 3.60 mmol) in hexanes (70 mL) at 0 °C. After allowing the reaction mixture to warm to room temperature over 2 h, the solvent and volatile byproducts were removed in vacuo to yield **11** (1.78 g, 98%) as a yellow powder. ^{1}H NMR (benzene-d_6): δ 1.05 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.12 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.33 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.72 (s, 1 H, NH), 2.92 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 2.94 (septet, 4 H, J = 7 Hz, ^{i}Pr-H), 6.60 (t, 1 H, J = 8 Hz, p-H), 6.84 (d, 2 H, J = 8 Hz, m-H), 7.16 (s, 4 H, Mes-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 24.7, 25.0, 25.5 (^{i}Pr-Me's), 30.9, 34.8 (^{i}Pr-CH's), 113.2, 122.4, 127.2, 130.6, 138.6, 147.3, 148.2, 157.9 (aromatic C's). IR (Nujol, cm^{-1}): 630 (m), 653 (m), 746 (s), 778 (w), 798 (vw), 832 (w), 850 (m), 876 (m), 937 (w), 1004 (w), 1073 (m), 1100 (w), 1166 (w), 1186 (vw), 1259 (vs), 1288 (w), 1316 (m), 1361 (s), 1410 (vs), 1566 (w), 1583 (m), 1602 (w), 3676 (w, ν_{NH}). Anal. Calcd for $C_{36}H_{50}LiN$: C, 85.84; H, 10.00; N, 2.78. Found: C, 85.69; H, 9.62; N, 2.93.

Cp*(2,6-Trip$_2$C$_6$H$_3$N=)TaCl$_2$ (12). A solution of compound **11** (2.39 g, 4.74 mmol) in diethyl ether (100 mL) was added dropwise over 1.5 h to a stirred slurry of Cp*$TaCl_4$ (2.17 g, 4.74 mmol) in NEt_3 (13.2 mL, 94.7 mmol) and diethyl ether (150 mL). Upon addition, the reaction mixture became orange and then brick-red in color. After stirring at room temperature for 3 days, the reaction mixture became light orange. The solvent, excess NEt_3, and volatile byproducts were removed under vacuum to give a light orange solid. The solid was extracted with pentane (4 × 75 mL), and the combined extracts were filtered to give an orange-colored solution. The solution was concentrated to ca. 40 mL and cooled to −35 °C overnight to afford two crops of orange crystals of compound **12** (3.13 g, 75%). ^{1}H NMR (benzene-d_6): δ 1.15 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.34 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.54 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.72 (s, 15 H, C_5Me_5), 2.92 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 3.24 (septet, 4 H, J = 7 Hz, ^{i}Pr-H), 6.76 (t, 1H, J = 8 Hz, p-H), 7.19 (d, 2 H, J = 8 Hz, m-H), 7.27 (s, 4 H, Trip-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 11.8 ($C_5\mathit{Me}_5$), 24.2, 24.9, 26.6 (^{i}Pr-Me's), 31.5, 35.4 (^{i}Pr-CH's), 121.7 (C_5Me_5), 122.9, 123.0, 132.6, 137.6, 140.0, 147.7, 148.6, 152.4 (aromatic C's). IR (KBr, cm^{-1}): 434 (w), 577 (w), 651 (w), 765 (m), 803 (m), 849 (w), 873 (m), 922 (vw), 939 (m), 955 (vw), 980 (m), 1027 (w), 1053 (w), 1069 (w), 1093 (m), 1135 (vw), 1153 (vw), 1167 (w), 1193 (vw), 1239 (w), 1251 (w), 1308 (s), 1360 (m), 1382 (s), 1401 (s), 1428 (m), 1460 (s), 1566 (w), 1606 (m), 1756 (vw), 2721 (vw), 2752 (vw), 2866 (s), 2924 (s), 2958 (s), 3046 (w), 3056 (w). Anal. Calcd for $C_{46}H_{64}Cl_2NTa$: C, 62.58; H, 7.31; N, 1.59. Found: C, 62.76; H, 7.42; N, 1.54.

Cp*(2,6-Trip$_2$C$_6$H$_3$N=)TaMe$_2$ (13). A solution of MeLi in diethyl ether (1.6 M, 3.2 mmol) was added to a stirred solution of compound **12** (1.31 g, 1.48 mmol) in diethyl ether (125 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 5 min and then warmed to room temperature over 4 h. The solvent was removed under vacuum to give a bright yellow solid, which was extracted with pentane (3 × 50 mL), and the combined extracts were filtered to give a bright yellow solution. The solution was concentrated to ca. 30 mL and cooled to −35 °C overnight to afford three crops of yellow crystals of compound **13** (1.13 g, 91%). ^{1}H NMR (benzene-d_6): δ −0.31 (s, 6 H, $TaMe_2$), 1.20 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.32 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.44 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.54 (s, 15 H, C_5Me_5), 2.90 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 3.37 (septet, 4 H, J = 7 Hz, ^{i}Pr-H), 6.84 (t, 1 H, J = 8 Hz, p-H), 7.16 (d, 2 H, J = 8 Hz, m-H), 7.23 (s, 4 H, Trip-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 11.1 ($C_5\mathit{Me}_5$), 24.3, 24.9, 26.2 (^{i}Pr-Me's), 31.3, 35.4 (^{i}Pr-CH's), 50.5 ($TaMe_2$), 117.5 (C_5Me_5), 120.5, 121.5, 132.5, 139.0, 139.6, 147.5, 148.1, 155.4 (aromatic C's). IR (KBr, cm^{-1}): 511 (m), 532 (w), 576 (w), 610 (vw), 651 (w), 669 (vw), 712 (vw), 763 (m), 803 (w), 849 (vw), 874 (m), 921 (vw), 940

(w), 957 (vw), 976 (m), 1006 (vw), 1027 (vw), 1053 (w), 1069 (w), 1092 (m), 1150 (w), 1166 (w), 1193 (vw), 1239 (w), 1250 (w), 1313 (s), 1360 (m), 1382 (s), 1405 (vs), 1460 (m), 1566 (w), 1606 (w), 1758 (vw), 2730 (vw), 2755 (vw), 2866 (s), 2925 (s), 2957 (vs), 3023 (w), 3038 (w), 3055 (w). Anal. Calcd for $C_{48}H_{70}$-NTa: C, 68.47; H, 8.38; N, 1.66. Found: C, 68.63; H, 8.57; N, 1.54.

Cp*(2,6-Trip$_2$C$_6$H$_3$N=)Ta(H)Br (14). Compound **13** (0.462 g, 0.549 mmol) was dissolved in bromobenzene (10 mL), and the resulting solution was transferred to a 50 mL reaction flask sealed with a Teflon stopper. The solution was degassed, H_2 (1 atm) was admitted, and the reaction solution was heated to 110 °C. After 4 days, the red-orange reaction mixture was cooled to room temperature and diluted with toluene (10 mL). The solvent was removed in vacuo to leave behind a red-orange crystalline solid, which was extracted with toluene (2 × 10 mL). The extracts were concentrated to ca. 5 mL and cooled to −35 °C to afford three crops of orange crystals of compound **14** (0.392 g, 80%). ^{1}H NMR (benzene-d_6): δ 1.19 (d, 12 H, J = 7 Hz, ^{i}Pr-Me), 1.32 (d, 6 H, J = 7 Hz, ^{i}Pr-Me), 1.33 (d, 6 H, J = 7 Hz, ^{i}Pr-Me), 1.49 (d, 6 H, J = 7 Hz, ^{i}Pr-Me), 1.53 (d, 6 H, J = 7 Hz, ^{i}Pr-Me), 1.75 (s, 15 H, C_5Me_5), 2.90 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 3.19 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 3.28 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 6.83 (t, 1 H, J = 8 Hz, p-H), 7.24 (dd, 4 H, J = 8 Hz, 2 Hz, Trip-H), 7.25 (d, 2 H, J = 8 Hz, m-H), 17.00 (s, 1 H, Ta-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 12.2 ($C_5\mathit{Me}_5$), 24.1, 24.4, 25.0, 25.0, 26.5, 26.6 (^{i}Pr-Me's), 31.3, 31.3, 35.4 (^{i}Pr-CH's), 120.1 (C_5Me_5), 121.4, 121.4, 122.1 (CH's), 123.3, 126.0, 128.9, 129.7 (aromatic C's), 131.6 (CH), 138.0, 139.2, 147.7, 147.7, 148.3, 153.9 (aromatic C's). IR (KBr, cm^{-1}): 429 (vw), 554 (vw), 576 (w), 610 (vw), 651 (m), 729 (vw), 764 (s), 803 (w), 850 (vw), 874 (m), 921 (vw), 940 (m), 956 (vw), 979 (m), 1027 (vw), 1054 (w), 1069 (w), 1090 (m), 1103 (m), 1052 (vw), 1167 (w), 1193 (vw), 1238 (w), 1251 (w), 1314 (s), 1360 (s), 1381 (s), 1407 (vs), 1429 (s), 1460 (s), 1566 (w), 1605 (m), 1838 (w, br, ν_{TaH}), 2717 (vw), 2757 (vw), 2865 (s), 2924 (s), 2958 (vs), 3025 (w), 3040 (w), 3056 (w). Anal. Calcd for $C_{46}H_{65}$BrNTa: C, 61.88; H, 7.34; N, 1.57. Found: C, 62.02; H, 7.48; N, 1.58.

Cp*(2-[2-(^{i}Pr-d_6)-4,6-^{i}Pr$_2$-C$_6$H$_2$]-6-Trip-C$_6$H$_3$N=)Ta(D)-Br (14-d_7). A procedure essentially identical to that used to prepare **14** (substituting D_2 for H_2, heating for 5 days) yielded orange crystals. The ^{1}H NMR spectrum of the crystals indicated incomplete conversion to **14-d_7**, so the crystals (and crystallization filtrate) were treated with D_2 under the conditions described above for an additional 3 days. A workup procedure analogous to that used to isolate **14** provided orange crystals of **14-d_7** (0.296 g, 68%). Selected data: ^{1}H NMR (benzene-d_6): δ 1.49 (d, 6 H, J = 7 Hz, ^{i}Pr-Me), 1.52 (d, 6 H, J = 7 Hz, ^{i}Pr-Me). ^{2}H{^{1}H} NMR (benzene): δ 1.46 (br s, 6 D, CH(CD$_3$)$_2$), 16.84 (br s, 1 D, Ta-D). ^{13}C{^{1}H} NMR (benzene-d_6): δ 26.5 (m, CH(CD$_3$)$_2$), 26.6 (m, CH(CD$_3$)$_2$), 31.2 (m, CH-(CD$_3$)$_2$). IR (KBr, cm^{-1}): 1300 (shoulder of 1312 cm^{-1}, ν_{TaD}), 2170 (w, br, CD$_3$), 2208 (w, br, CD$_3$). Anal. Calcd for $C_{46}H_{58}D_7$-BrNTa: C, 61.39; H, 7.28; N, 1.56. Found: C, 61.61; H, 7.32; N, 1.76.

Cp*(2,6-Trip$_2$C$_6$H$_3$N=)Ta(CH$_2$CMe$_3$)H (15). Compound **14** (25.6 mg, 28.7 μmol) and LiCH$_2$CMe$_3$ (2.2 mg, 28 μmol) were dissolved in benzene-d_6 (~0.7 mL) and kept at room temperature for 3.5 h. The reaction mixture was then filtered, and the solvent was lyophilized to give **15** as an orange powder (14.7 mg, 76%). ^{1}H NMR (benzene-d_6): δ −0.90 (d, 1 H, J = 12 Hz, CH$_2$), 1.04 (s, 9 H, ^{t}Bu), 1.20 (d, 6 H, J = 7 Hz, ^{i}Pr-Me), 1.22 (d, 6 H, J = 7 Hz, ^{i}Pr-Me), 1.32 (d, 6 H, J = 7 Hz, ^{i}Pr-Me), 1.32 (d, 6 H, J = 7 Hz, ^{i}Pr-Me), 1.46 (d, 1 H, J = 12 Hz, CH$_2$), 1.49 (d, 6 H, J = 7 Hz, ^{i}Pr-Me), 1.51 (d, 6 H, J = 7 Hz, ^{i}Pr-Me), 1.71 (s, C_5Me_5), 2.90 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 3.27 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 3.35 (septet, 2 H, J = 7 Hz, ^{i}Pr-H), 6.85 (t, 1 H, J = 7.5 Hz, p-H), 7.23 (s, 2 H, Trip-H), 7.23 (s, 2 H, Trip-H), 7.29 (d, 2 H, J = 7.5 Hz, m-H), 16.66 (s, 1 H, Ta-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 12.2 ($C_5\mathit{Me}_5$), 24.3, 24.4, 24.9, 26.8, 27.4 (^{i}Pr-Me's), 31.2, 31.3, 35.3 (^{i}Pr-CH's), 36.1 (CMe_3), 39.5 (CMe$_3$), 106.8 (TaCH$_2$), 117.9 (C_5Me$_5$), 119.9 (CH), 120.1 (aromatic C), 121.2, 121.3 (CH's), 128.9, 129.7 (aromatic C's), 132.7 (CH), 138.4, 138.9, 147.7, 147.8, 148.0, 155.6 (aromatic C's). IR (KBr, cm^{-1}): 422 (vw), 462 (vw), 498 (w), 575 (w), 650 (m), 686 (w), 710 (vw), 764 (m), 803 (w), 850 (vw), 875 (m), 922 (vw), 940 (w), 978 (m), 1006 (vw), 1029 (vw), 1053 (w), 1070 (w), 1088 (m), 1101 (m), 1168 (w), 1191 (vw), 1238 (w), 1250 (w), 1315 (s), 1361 (s), 1382 (s), 1411 (s), 1461 (s), 1566 (w), 1605 (m), 1807 (m, br, ν_{TaH}), 2724 (vw), 2753 (vw), 2867 (s), 2929 (s), 2958 (vs), 3052 (w).

Table 2. Crystallographic Data for Compound 1

empirical formula	$C_{34}H_{40}Cl_2NTa$
fw	714.55
cryst color, habit	orange block
cryst size (mm)	0.30 × 0.25 × 0.25
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a (Å)	13.8709(2)
b (Å)	12.27320(10)
c (Å)	18.7458(3)
β (deg)	99.857(1)
V (Å^3)	3144.18(7)
orientation reflns (2θ range)	6897 (3.5−45.0°)
Z value	4
D_{calc} (g/cm^3)	1.509
F_{000}	1432.00
μ(Mo Kα) (cm^{-1})	36.83
diffractometer	SMART
radiation	Mo Kα (λ = 0.71069 Å) graphite monochromated
temperature (°C)	−101.0
scan type	ω (0.3° per frame)
scan rate	20.0 s per frame
$2\theta_{max}$ (deg)	51.0
no. of reflns measd	total: 14213 unique: 5617
R_{int}	0.022
transmn factors	T_{max} = 0.33 T_{min} = 0.26
structure solution	direct methods (SIR92)
no. of observations	3802 ($I > 3.00\sigma(I)$)
no. of variables	343
reflns/param ratio	11.08
residuals: R; R_w; R_{all}	0.024; 0.031; 0.039
goodness of fit	1.21
max. shift/error in final cycle	0.00
max. and min. peaks in final diff map (e$^-$/Å^3)	0.46; −0.54

X-ray Structure Determination. Crystals suitable for X-ray diffraction were obtained by cooling a concentrated pentane solution of **1** to −35 °C. An orange, blocklike crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. X-ray diffraction measurements were made on a Siemens SMART diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation. A hemisphere of data was collected using ω scans of 0.3°. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the measured positions of reflections in the range 3.5° < 2θ < 45.0°. The orientation matrix gave a primitive, monoclinic cell with dimensions described in Table 2. Data were collected for 20 s frames. The frame data were integrated using the program SAINT.[88] An empirical absorption correction based on measurements of multiply redundant data was performed using the program XPREP.[89] In addition, XPREP clearly indicated the space group was $P2_1/n$ (#14). Equivalent reflections were merged. The data were corrected for Lorentz and polarization effects. The structure was solved using the teXsan crystallographic

(88) *SAX Area-Detector Integration Program, V4.024*; Siemens Industrial Automation, Inc.: Madison, WI, 1995.
(89) *SHELXTL Crystal Structure Determination Package*; Siemens Industrial Automation, Inc.: Madison, WI, 1995.

software package of the Molecular Structure Corporation, using direct methods (SIR92), and expanded with Fourier techniques.

The structure consists of one molecule of **1** per asymmetric unit. All non-hydrogen atoms were refined anisotropically. C(100) was added as the centroid of the η^5-pentamethylcyclopentadienyl ligand, defined as the average of the *x*, *y*, and *z* coordinates of carbons C(1)−C(5). All hydrogen atoms were refined isotropically in geometrically calculated positions. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics and included a *p*-factor to downweight the intense reflections. Crystallographic data are summarized in Table 2.

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Supporting Information Available: Tables of crystal, data collection, and refinement parameters, atomic coordinates, anisotropic displacement parameters, bond distances, and bond angles for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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