Organometallics **2002,** *21,* 5549−5563 5549

Tantalum Alkyl and Silyl Complexes of the Bulky (Terphenyl)imido Ligand $[2,6\text{-}(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3N{=}]^{2-}$ ($[Ar^*N{=}]^{2-}$). Generation and Reactivity of $[(Ar^*N{=})(Ar^*NH)Ta(H)(OSO_2CF_3)]$, Which Reversibly Transfers Hydride to an Aromatic Ring of the Arylamide Ligand

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Received June 26, 2002

Tantalum complexes containing the sterically demanding imido ligand $[2,6\text{-}(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3N{=}]^{2-}$ ($[Ar^*N{=}]^{2-}$) are reported. The dimethyl complex $(Ar^*N{=})(Ar^*NH)TaMe_2$ (**4**), prepared by the reaction of 2 equiv of Ar*NHLi (**3**) with $TaMe_3Cl_2$, was structurally characterized. Compound **4** forms adducts with donor ligands such as trimethylphosphine and pyridine and readily reacts with CO to give a monoinsertion product, the η^2-acyl complex **5**. The dichloride complex $(Ar^*N{=})(Ar^*NH)TaCl_2$ (**7**), formed by the reaction of 2 equiv of Ar^*NH_2 (**2**) with $TaMe_3Cl_2$, reacted cleanly with NpLi ($Np = Me_3CCH_2$) to give the dineopentyl species $(Ar^*N{=})(Ar^*NH)TaNp_2$ (**8**), which was structurally characterized. Unlike **4**, complex **8** does not form adducts with donor ligands. The cationic complex $[(Ar^*N{=})(Ar^*NH)TaMe][MeB(C_6F_5)_3]$ (**9**), prepared by the reaction of **4** with $B(C_6F_5)_3$, slowly converted to $[(Ar^*N{=})(Ar^*NH)TaMe][HBC_6F_5)_3]$ in the presence of $PhSiH_3$. Treatment of **4** with AgOTf ($OTf = OSO_2CF_3$) provided the methyl triflate complex $(Ar^*N{=})(Ar^*NH)TaMeOTf$ (**10**), which reacts cleanly with H_2 in bromobenzene to provide red-orange crystals of the η^5-cyclohexadienyl complex $(Ar^*N{=})[2\text{-}(\eta^5\text{-}2,4,6\text{-}Me_3C_6H_3)\text{-}6\text{-}MesC_6H_3NH]Ta(OTf)$ (**11**, Mes = $2,4,6\text{-}Me_3C_6H_2$). Complex **11**, which was structurally characterized, represents a previously unobserved arene hydrogenation intermediate formed by *endo* transfer of a single hydride from the metal center to an arene ring. The hydride intermediate $[(Ar^*N{=})(Ar^*NH)Ta(H)\text{-}OTf]$ (**A**) was not observed spectroscopically, but was trapped by exposure of **10** to H_2 in the presence of excess 1-hexene to give $(Ar^*N{=})(Ar^*NH)Ta(Hex)OTf$ (**12**). Complex **11** is in equilibrium with **A**, which is the more reactive isomer, as indicated by its ability to catalyze olefin hydrogenation, diene cyclization, and silane deuteration. Complex **7** reacts cleanly with $(THF)_3LiSi(SiMe_3)_3$, $(THF)_2LiSi(^tBu)Ph_2$, and $(THF)_2LiSiHMes_2$ to provide the silyl chloride complexes $(Ar^*N{=})(Ar^*NH)Ta(SiR_3)Cl$ ($SiR_3 = Si(SiMe_3)_3$, $(^tBu)Ph_2$, $SiHMes_2$; **13a**−**c**). Hydrogenolysis of **13a**−**c** yields silane and a species with spectroscopic features similar to those of **11**.

Introduction

In recent years, early transition metal complexes have received increased attention, as such species have been found to mediate a number of stoichiometric and catalytic processes including olefin polymerization,[1−3] dehydropolymerizations,[4−6] hydrosilylation,[7−11] arene hydrogenation,[12,13] and alkane activation.[14−20] Because much of the previous research in this area is based on metallocene derivatives, recent efforts have sought to expand the utility of this chemistry with the develop-

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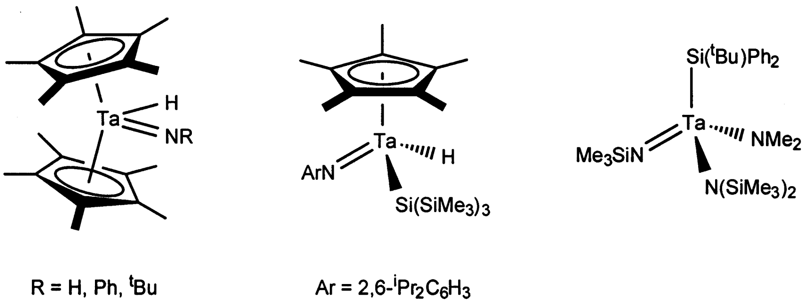
10.1021/om020509y CCC: $22.00
Publication on Web 11/06/2002

Chart 1. Examples of Imido Complexes Containing Silyl and/or Hydride Ligands



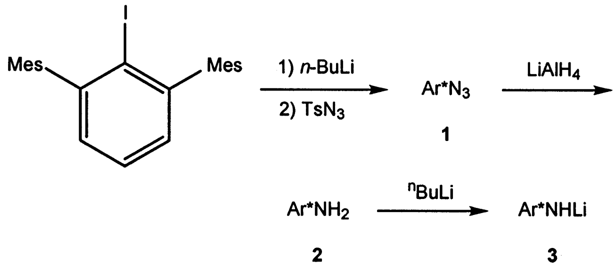
ment of new ancillary (non-cyclopentadienyl) ligand sets.[5,21,22] One strategy for ligand design targets sterically demanding ligands that enforce a low coordination number at the metal center for enhancement of metal-centered electrophilicity.

Recent efforts in our laboratory have focused on reactive early metal centers containing imido ancillary ligands. This work resulted in the isolation of molybdenum and tungsten complexes of the type $(2,6\text{-}{}^iPr_2C_6H_3N{=})_2M[Si(SiMe_3)_3]CH_2CMe_3$, which possess highly reactive M$-$C and M$-$Si σ-bonds.[23] In addition, we have prepared the stable silyl hydride complex $Cp^*(2,6\text{-}{}^iPr_2C_6H_3N{=})Ta[Si(SiMe_3)_3](H)$,[24] which reacts with $PhSiH_3$ by way of Si$-$N coupling to form two dimeric products with bridging silanimine ligands[25,26] and thermally rearranges via an interesting series of Si$-$Si and Si$-$C bond-breaking/bond-making and C$-$H bond activation steps.[24] Generally, however, d^0 tantalum imido complexes have not featured prominently in σ-bond metathesis reactivity, and complexes containing both imido ligands and reactive σ-bonds (M$-$H, M$-$Si) are exceedingly rare.[27-32] Of the few examples known (Chart 1), most are supported by cyclopentadienyl ligands. Replacing the cyclopentadienyl substituents with less electron-rich ligands may lead to a more electrophilic metal center capable of enhanced reactivity.

In this report, we describe the preparation of non-cyclopentadienyl tantalum complexes containing the new terphenyl imido ligand $[2,6\text{-}(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3\text{-}N{=}]^{2-}$ ($[Ar^*N{=}]^{2-}$). Terphenyl ligands have been employed extensively for the stabilization of highly reactive main group species,[33] and Rothwell and co-workers have developed aryl oxide analogues as ancillary ligands for early metal hydrides.[13,34-37] Sterically encumbering terphenyl imido ligands can potentially prevent hydride dimerization while enforcing coordinative unsaturation at a highly electron-deficient metal center. Recently, we have reported preliminary results describing a "masked hydride" complex based upon this imido-amido ligand set.[38] Here, we describe our further investigations into this system which have resulted in the isolation of alkyl, hydride, and silyl derivatives.

Results and Discussion

Ligand Synthesis. The terphenyl aniline **2** was prepared according to the literature procedure reported by Yoshifuji and co-workers for a similar compound.[39] 2,6-Dimesitylphenyliodide reacted with ${}^nBuLi$ at 0 °C in hexanes,[40,41] and the resulting lithium salt was treated with *p*-toluenesulfonyl azide to provide $2,6\text{-}Mes_2C_6H_3N_3$ (**1**, Mes = $2,4,6\text{-}Me_3C_6H_2$) as red-orange crystals in 96% yield (eq 1). Reduction of compound **1** using $LiAlH_4$ in diethyl ether afforded clear, diamond-shaped crystals of aniline **2** in 86% yield. Lithium anilide **3** was obtained as a yellow powder in 99% yield by warming a chilled pentane solution of compound **2** to room temperature in the presence of ${}^nBuLi$ and removing the solvent and volatile byproducts in vacuo (eq 1).



(1)

Synthesis and Reactivity of Imido-Amido Dialkyl Tantalum Complexes. Lithium anilide **3** (1 or

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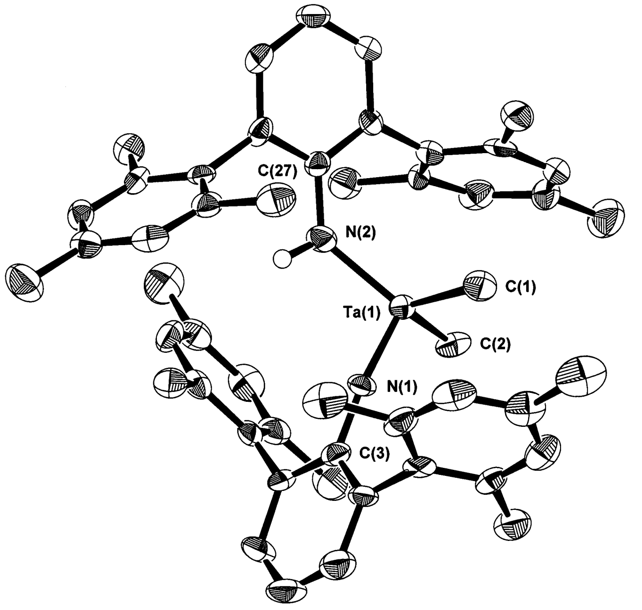
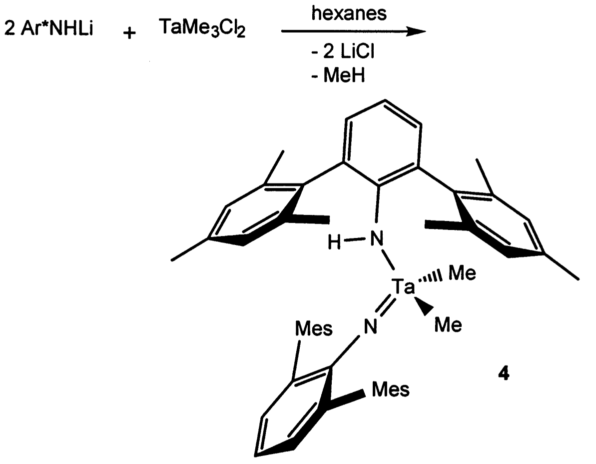


Figure 1. ORTEP diagram of (Ar*N=)(Ar*NH)TaMe$_2$ (**4**).

2 equiv) reacted with TaMe$_3$Cl$_2$ in hexanes to provide (Ar*N=)(Ar*NH)TaMe$_2$ (**4**, Ar* = 2,6-Mes$_2$C$_6$H$_3$) as a yellow, crystalline solid in 71% yield (eq 2). No complexes containing only one nitrogen-donor ligand were isolated or observed. Compound **4** displays distinct imido and amido ligand environments and C_s symmetry by NMR spectroscopy (22 °C). The TaMe$_2$ group was identified by a ^{1}H NMR resonance at −0.41 ppm and a ^{13}C NMR resonance at 57.5 ppm, while the amido NH group was observed as a ^{1}H NMR resonance at 7.34 ppm and a ν_{NH} infrared stretch at 3303 cm^{-1}. The observed spectroscopic data are consistent with those reported for the only other known imido-amido dialkyl tantalum compound, (^{t}Bu$_3$SiN=)(^{t}Bu$_3$NH)TaMe$_2$.[42]



(2)

X-ray quality crystals were obtained by cooling a concentrated pentane solution of complex **4** to −35 °C over several days. The molecular structure is shown in Figure 1, and important bond distances and angles are listed in Table 1. The structure reveals a pseudotetrahedral geometry with bond lengths and angles well within the expected ranges, including a Ta=N bond length of 1.743(6) Å and a Ta−N bond length of 1.994(6) Å.[43−46]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (Ar*N=)(Ar*NH)TaMe$_2$ (4)

	Bond Lengths		
Ta(1)−N(1)	1.743(6)	Ta(1)−C(1)	2.136(7)
Ta(1)−N(2)	1.994(6)	Ta(1)−C(2)	2.132(7)
N(1)−C(3)	1.405(9)	N(2)−C(27)	1.418(9)
	Bond Angles		
Ta(1)−N(1)−C(3)	169.2(5)	Ta(1)−N(2)−C(27)	132.8(5)
N(1)−Ta(1)−N(2)	102.4(3)	C(1)−Ta(1)−C(2)	109.7(3)
N(1)−Ta(1)−C(1)	104.2(3)	N(2)−Ta(1)−C(1)	115.0(3)
N(1)−Ta(1)−C(2)	99.7(3)	N(2)−Ta(1)−C(2)	122.5(3)

Initial experiments with **4** focused on replacing the amido ligand to obtain other (Ar*N=)TaMe$_2$X complexes as possible precursors to a trihydride derivative. However, complex **4** did not react with Me$_3$SiCl or MeI (benzene-d_6, 85 °C, 2 days), and treatment with PCl$_5$ (toluene, room temperature, 21 h) provided an intractable mixture of products. Since the amido ligand could not be substituted, several attempts were made to prepare imido-amido dihydride derivatives. Treatment of benzene-d_6 solutions of **4** with H$_2$ under a variety of temperatures and pressures resulted in complex reaction mixtures, which contained free amine. Heating **4** in the presence of excess PhSiH$_3$ (6 equiv) to 120 °C (benzene-d_6) over 2 days resulted in the formation of methane and Ph$_2$SiH$_2$ (1 equiv), as well as several unidentified products.[47−51] Analysis of the reaction mixture by GC/MS revealed a trace amount of PhMeSiH$_2$, which is consistent with σ-bond metathesis reactivity.[48,52]

Although compound **4** could not be converted to a hydride derivative, other reactivity modes (insertion chemistry and adduct formation) were observed (Scheme 1). Placing a benzene-d_6 solution of **4** under an atmosphere of CO led to the monoinsertion product (Ar*N=)(Ar*NH)Ta(η^2-COMe)Me (**5**), which was characterized by a CO*Me* ^{1}H NMR resonance at 2.26 ppm, a *C*OMe ^{13}C NMR resonance at 317.1 ppm, and a ν_{CO} infrared stretch at 1421 cm^{-1}. The downfield ^{13}C NMR acyl resonance and low-energy IR absorbance are indicative of an η^2-acyl bonding mode.[53,54] Complex **5** was characterized in solution and could not be obtained on a preparative scale since exposing solutions of **5** to vacuum led to decarbonylation and the subsequent isolation of **4**.

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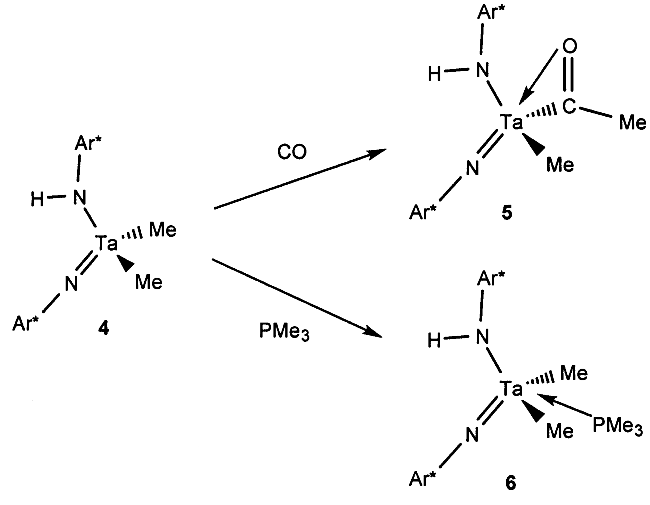
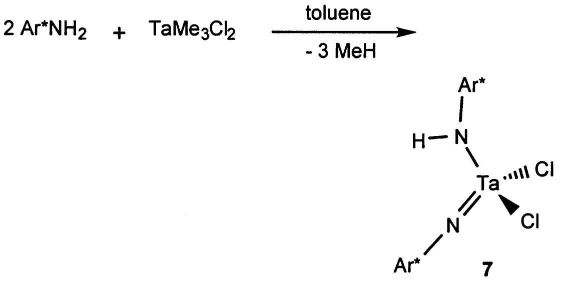
Scheme 1



Adduct formation was observed upon treating compound **4** with donor ligands such as trimethylphosphine and pyridine. Compound **4** reacted cleanly with PMe_3 (1 equiv) in benzene-d_6 at room temperature to provide (Ar*N=)(Ar*NH)$TaMe_2(PMe_3)$ (**6**) in 99% yield (relative to internal standard, Scheme 1). Complex **6** was spectroscopically characterized in solution. The ^1H NMR spectrum of **6** contained two sets of resonances for the mesityl methyl groups, indicating that the complex has C_s symmetry. The PMe_3 group appeared in the ^1H NMR spectrum as a sharp doublet at 0.56 ppm ($^2J_{PH} = 5$ Hz), but a very broad resonance was observed in the $^{31}P\{^1H\}$ NMR spectrum at -19.1 ppm, suggesting that rapid exchange between free and bound PMe_3 occurs at room temperature. Upon treatment of **4** with excess PMe_3 (3 equiv, toluene-d_8), all of the resulting ^1H NMR resonances are identical to those of **6**, with the exception of the PMe_3 signal, which appears as a broad singlet at 0.70 ppm (the chemical shift for free PMe_3). No resonance was observed for the bound phosphine. However, cooling the toluene-d_8 solution to -40 °C revealed a sharp doublet at 0.44 ppm ($^2J_{PH} = 10$ Hz) in the ^1H NMR spectrum and a singlet at -12.59 ppm in the $^{31}P\{^1H\}$ NMR spectrum, along with separate signals due to free PMe_3. Unlike Wolczanski's ($^tBu_3SiN$=)($^tBu_3NH$)-$TaMe_2$, which reacts cleanly with Lewis bases to liberate methane and form a bis(imido) complex,[42] compound **4** decomposes to a mixture of products when heated (120 °C) in benzene-d_6 in the presence of excess PMe_3 or pyridine. Furthermore, heating a benzene-d_6 solution of **6** to 85 °C in the presence of H_2 (1 atm) provided a complex reaction mixture.

Aniline **2** (2 equiv) reacts cleanly with $TaMe_3Cl_2$ in toluene at 75 °C over 21 h to yield (Ar*N=)(Ar*NH)-$TaCl_2$ (**7**) as light brown crystals in 68% yield (eq 3).



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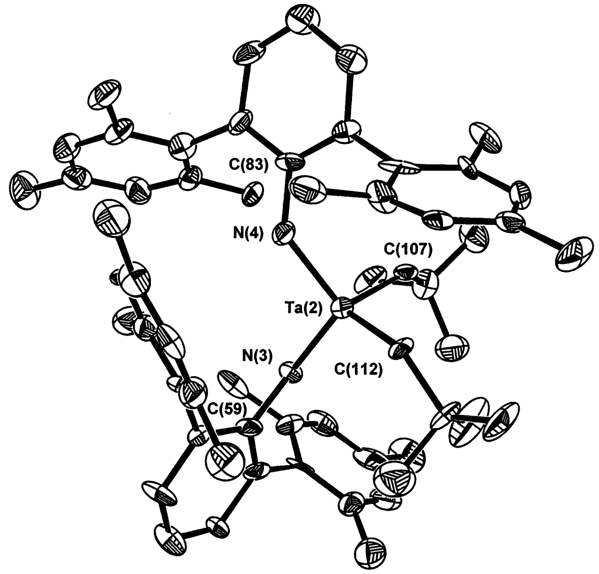
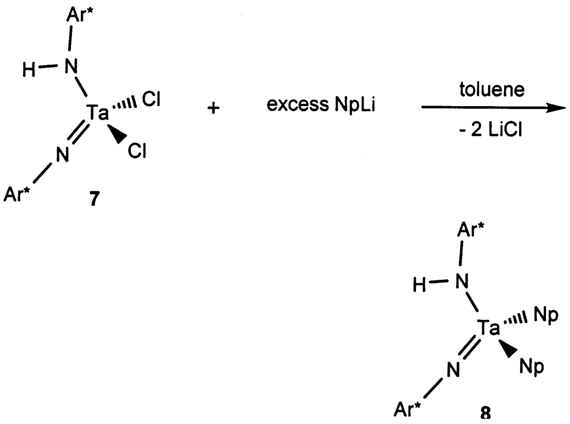


Figure 2. ORTEP diagram of (Ar*N=)(Ar*NH)$TaNp_2$ (**8**).

Complex **7** contains distinct imido and amido ligand environments by NMR spectroscopy, which also indicates C_s symmetry for **7** (22 °C). On an NMR tube scale, 1 equiv of aniline **2** was observed to react with $TaMe_3Cl_2$ to give complex **7** along with unreacted $TaMe_3Cl_2$ (in benzene-d_6, 80 °C).

Complex **7** reacted cleanly with excess NpLi (3 equiv, Np = Me_3CCH_2) in toluene over 5.5 h to provide yellow crystals of (Ar*N=)(Ar*NH)$TaNp_2$ (**8**) in 72% yield (eq 4). Diastereotopic methylene resonances were observed in the ^1H NMR spectrum (dichloromethane-d_2) at -0.02 and -0.36 ppm ($J = 15$ Hz), but one of the mesityl methyl resonances was not observed. A VT NMR study revealed that the missing signal appears as a sharp singlet (integrating to 12 H) upon heating a toluene-d_8 sample to 90 °C. The broad mesityl resonance observed at room temperature is likely due to restricted rotation resulting from introduction of the bulky neopentyl ligands.



(4)

An X-ray crystallographic study revealed a pseudotetrahedral geometry about the tantalum metal center of **8**. The molecular structure is shown in Figure 2, and important bond lengths and angles are listed in Table 2. The data were collected for a twinned crystal which contained two molecules of **8** and one pentane molecule per unit cell. The complex has Ta=N and Ta−N bond lengths of 1.777(9) and 1.998(9) Å for Ta(1) and 1.774-

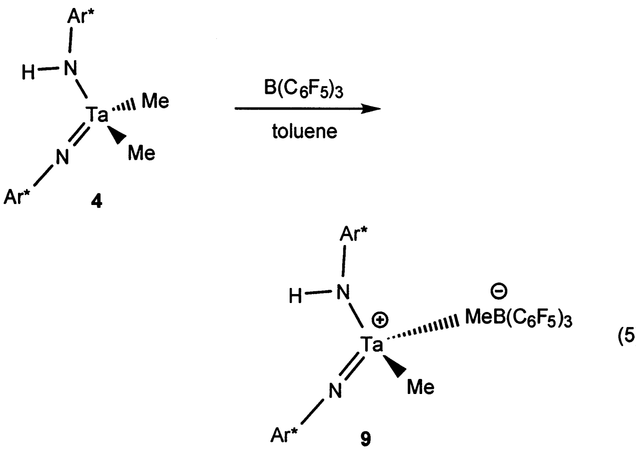
Table 2. Selected Bond Lengths (Å) and Angles (deg) for (Ar*N=)(Ar*NH)TaNp$_2$ (8)

Bond Lengths			
Ta(2)−N(3)	1.774(9)	Ta(2)−C(107)	2.12(1)
Ta(2)−N(4)	1.986(8)	Ta(2)−C(112)	2.13(1)
N(3)−C(59)	1.42(1)	N(4)−C(83)	1.42(1)
Bond Angles			
Ta(2)−N(3)−C(59)	162.9(8)	Ta(2)−N(4)−C(83)	135.1(8)
N(3)−Ta(2)−N(4)	106.6(4)	C(107)−Ta(2)−C(112)	108.0(5)
N(3)−Ta(2)−C(107)	116.9(4)	N(4)−Ta(2)−C(107)	108.0(5)
N(3)−Ta(2)−C(112)	104.4(4)	N(4)−Ta(2)−C(112)	112.9(4)

(9) Å and 1.986(8) Å for Ta(2). The structure does not differ significantly from that of complex **4**, although the neopentyl ligands provide much more steric crowding about the metal center.

Attempts to observe clean σ-bond metathesis reactions of the Ta−C bonds of **8** were not successful. No reaction was observed with H_2 (1 atm) in benzene-d_6 at room temperature, and heating the reaction mixture to 50 °C over 4 days resulted in conversion to an intractable mixture of products (which contained neopentane). Similarly, treating a benzene-d_6 solution of **8** with $PhSiH_3$ (2 equiv) resulted in no reaction at room temperature, and a complex reaction mixture after heating to 80 °C for 8 days. In addition, **8** does not form observable adducts with PMe_3 or pyridine (benzene-d_6, room temperature), presumably due to the increased steric bulk of the neopentyl ligands (relative to **4**).

Synthesis and Reactivity of [(Ar*N=)(Ar*NH)-TaMe][MeB(C$_6$F$_5$)$_3$] (9). Since the dialkyl complexes **4**, **6**, and **8** could not be converted to hydride derivatives by reactions with H_2 or $PhSiH_3$, investigations focused on the preparation of cationic derivatives which might feature enhanced electrophilicity and higher reactivities. Complex **4** was found to react rapidly with $B(C_6F_5)_3$ at room temperature in toluene to yield the cationic complex [(Ar*N=)(Ar*NH)TaMe][MeB(C$_6$F$_5$)$_3$] (**9**) as a red-orange solid in 81% yield (eq 5). The terminal TaMe group in complex **9** was identified by a ^{1}H NMR resonance at −0.19 ppm and a ^{13}C NMR signal at 29.8 ppm, which was confirmed by a ^{1}H,^{13}C-HMQC experiment. The ^{11}B NMR spectrum contained a singlet at −14.93 ppm, suggesting a tetrahedral environment about the boron atom, while ^{1}H,^{11}B-HMQC spectroscopy confirmed that a singlet at 1.16 ppm in the ^{1}H NMR spectrum is due to [MeB(C$_6$F$_5$)$_3$]$^-$. The ^{1}H,^{13}C-HMQC experiment also indicated that the [MeB(C$_6$F$_5$)$_3$]$^-$ methyl group is associated with a ^{13}C NMR resonance at ~10 ppm, even though no signal was observed in the ^{13}C-{^{1}H} NMR spectrum at room temperature.



(5)

An unusual spectroscopic feature of complex **9** is a small, slightly broad peak integrating to 1 H at 5.19 ppm in the ^{1}H NMR spectrum. This resonance does not exhibit coupling to other nuclei over the temperature range of −80 to 100 °C in toluene-d_8 solution (by ^{1}H NMR spectroscopy). However, the ^{1}H,^{1}H-TOCSY spectrum revealed that this resonance is coupled to another one integrating to 1 H at 6.68 ppm, and a ^{1}H,^{13}C-HMQC experiment indicated that the signals at 5.19 and 6.68 ppm are due to hydrogens bonded to aromatic carbons which give rise to ^{13}C NMR shifts at 119.6 and 136.1 ppm, respectively. These data suggest that the resonance at 5.19 ppm is actually due to an upfield-shifted proton bonded to an aromatic ring. A possible explanation for this unusual chemical shift is the presence of an agostic C···H···Ta interaction. However, the $^1J_{CH}$ coupling constant associated with this resonance is 180 Hz, whereas the other aromatic carbons exhibit $^1J_{CH}$ values ranging from 160 to 165 Hz. Typically, for agostic interactions, $^1J_{CH}$ values are significantly lower relative to those of other C−H bonds in the molecule.[55,56] A more likely explanation for this unusual chemical shift is that steric restrictions lead to an interaction between this aromatic hydrogen and the π-system of another aromatic ring (see below).

According to Horton and co-workers, the chemical shift difference between the *meta* and *para* fluorines in the ^{19}F{^{1}H} NMR spectrum indicates the degree of [MeB(C$_6$F$_5$)$_3$]$^-$ coordination to a cationic metal center.[57] Differences of fewer than 3 ppm appear to indicate a noncoordinated [MeB(C$_6$F$_5$)$_3$]$^-$ anion, whereas values of 3−6 ppm suggest coordination. In the case of complex **9**, $\Delta(m,p\text{-F}) = 2.6$ ppm, indicating noncoordination. Further insight into the degree of anion coordination can be obtained from the chemical shift change of the [MeB(C$_6$F$_5$)$_3$]$^-$ ^{1}H NMR resonance upon addition of a Lewis base. Significant changes suggest a more coordinated anion. Treating a bright orange benzene-d_6 solution of **9** with pyridine (2 equiv) instantaneously gave rise to a bright yellow solution. The [MeB(C$_6$F$_5$)$_3$]$^-$ ^{1}H NMR resonance (determined by ^{1}H,^{11}B-HMQC spectroscopy) shifted only slightly, from 1.16 to 1.25 ppm, suggesting a noncoordinated anion.

Attempts to prepare hydride derivatives of compound **9** were unsuccessful. Complex **9** did not react with H_2 (1 atm), even upon heating a benzene-d_6 solution as high as 120 °C for 3 days, or a bromobenzene-d_5 solution as high as 105 °C for 3 days. Treating complex **9** with $PhSiH_3$ (1 equiv) in benzene-d_6 at room temperature resulted in the slow formation (>1 week) of $PhMeSiH_2$ and a new tantalum-containing product. However, ^{1}H,^{11}B-HMQC spectroscopy and labeling experiments with $PhSiD_3$ (1 equiv) revealed that a hydride was transferred to boron to give a hydridoborate functionality.[48] Complex **9** was found to slowly polymerize ethylene (1 atm) at room temperature in

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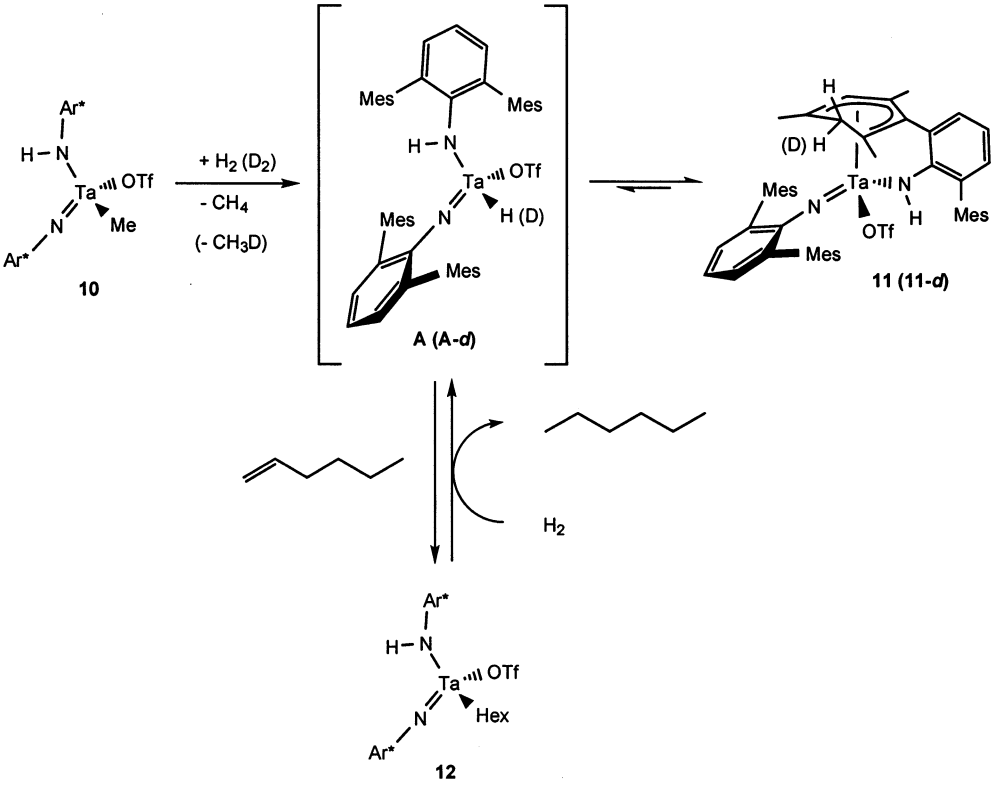
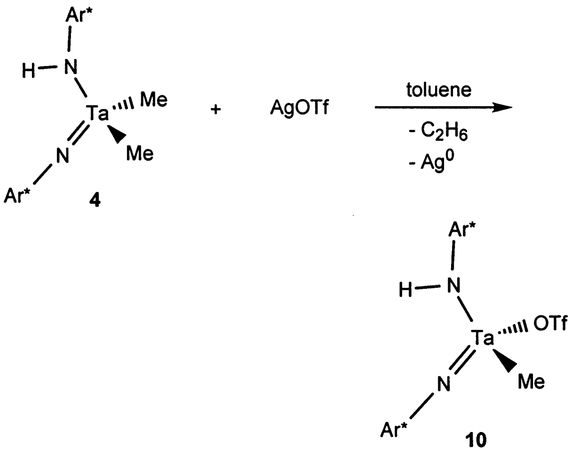
Scheme 2



benzene-d_6, but it did not react with excess 1-hexene under identical conditions.

The Masked Hydride [(Ar*N=)(Ar*NH)Ta(H)-(OSO$_2$CF$_3$)] (A). Complex **4** reacted cleanly with AgOTf (1 equiv, OTf = OSO$_2$CF$_3$) in toluene at room temperature over 27 h to provide (Ar*N=)(Ar*NH)TaMeOTf (**10**) as yellow-orange crystals in 78% yield (eq 6). Resonances were observed for the TaMe group at 0.22 ppm in the ^{1}H NMR spectrum and at 45.0 ppm in the ^{13}C{^{1}H} NMR spectrum. 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 **10** along with ethane formation, consistent with the oxidative cleavage reactions reported by Jordan and co-workers[58−61] and Tilley and co-workers.[62]



(6)

Complex **10** did not react with PhSiH$_3$ (5 equiv) in benzene-d_6 at temperatures up to 100 °C, but upon heating to 120 °C for 4 days, the PhSiH$_3$ was completely converted to 0.5 equiv of Ph$_2$SiH$_2$ as complex **10** gave rise to several unidentified products. Trace quantities of PhMeSiH$_2$, (Ph$_2$SiH)$_2$, and Ph$_3$SiH were also observed in the reaction mixture (by GC/MS). The observed silicon-containing products are consistent with σ-bond metathesis reactivity leading to redistribution of substituents at silicon.[47−51] Similar results were observed for the reaction at 95 °C in bromobenzene-d_5.

As described above, attempts to prepare a hydride derivative by the reactions of **4**, **6**, **8**, and **9** with H$_2$ or PhSiH$_3$ failed due to the formation of complex product mixtures. However, heating a bromobenzene solution of complex **10** to 95 °C over 2 days in the presence of H$_2$ (1 atm) provided a red-orange crystalline solid (**11**), which was purified by recrystallization from toluene at −35 °C (Scheme 2). The ^{1}H NMR spectrum of **11** contains two coupled doublets at 3.53 and 4.54 ppm (J = 16 Hz), consistent with the presence of a methylene group with diastereotopic protons. A small broad singlet at 4.26 ppm is correlated to a ^{13}C NMR resonance at 118.8 ppm according to ^{1}H,^{13}C-HMQC spectroscopy. Thus, this complex also appears to possess an aromatic hydrogen atom that exhibits an unusual upfield shift due to interaction with an aromatic ring. In addition, this spectrum appears to be devoid of a resonance attributable to a Ta hydride ligand.

The identity of **11** was established by X-ray crystallography, which revealed a structure containing an η^5-

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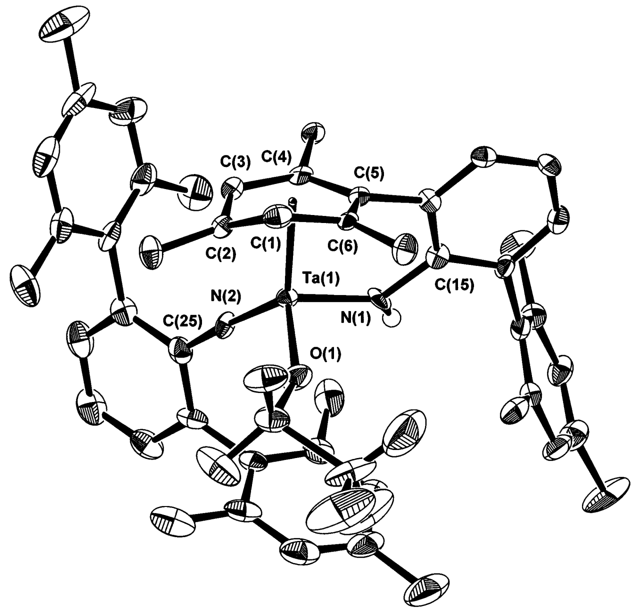


Figure 3. ORTEP diagram of (Ar*N=)[2-(η^5-2,4,6-$Me_3C_6H_3$)-6-$MesC_6H_3NH$]TaOTf (**11**).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for (Ar*N=)[2-(η^5-2,4,6-$Me_3C_6H_3$)-6-$MesC_6H_3NH$]Ta(OTf) (11)[a]

Bond Lengths			
Ta(1)−N(1)	1.990(6)	Ta(1)−O(1)	2.060(4)
Ta(1)−N(2)	1.788(5)	Ta(1)−C(100)	2.0990(3)
Ta(1)···C(1)	3.141(7)	C(1)−C(2)	1.526(9)
Ta(1)−C(2)	2.466(6)	C(2)−C(3)	1.409(9)
Ta(1)−C(3)	2.369(6)	C(3)−C(4)	1.404(9)
Ta(1)−C(4)	2.349(6)	C(4)−C(5)	1.475(9)
Ta(1)−C(5)	2.530(6)	C(5)−C(6)	1.352(9)
Ta(1)−C(6)	2.830(6)	C(1)−C(6)	1.484(9)

Bond Angles			
Ta(1)−N(1)−C(15)	129.0(4)	Ta(1)−N(2)−C(25)	175.6(5)
N(1)−Ta(1)−C(100)	100.9(1)	C(6)−C(1)−C(2)	109.6(6)
N(2)−Ta(1)−C(100)	128.5(2)	C(1)−C(2)−C(3)	116.2(6)
O(1)−Ta(1)−C(100)	108.5(1)	C(2)−C(3)−C(4)	119.3(6)
N(1)−Ta(1)−N(2)	105.6(2)	C(3)−C(4)−C(5)	118.4(6)
N(1)−Ta(1)−O(1)	102.9(2)	C(4)−C(5)−C(6)	121.0(6)
N(2)−Ta(1)−O(1)	107.4(2)	C(5)−C(6)−C(1)	120.1(6)

[a] C(100) represents the average of the *x*, *y*, and *z* coordinates of the η^5-cyclohexadienyl ring carbons C(2)−C(6).

cyclohexadienyl ligand (Figure 3). Important bond lengths and angles are listed in Table 3. This complex contains a normal imido ligand, as indicated by the Ta(1)−N(2)−C(25) bond angle of 175.6(5)° and the Ta=N bond length of 1.788(5) Å. The amido ligand in **11** is metalated via the transfer of a hydrogen atom to one mesityl group, to give rise to an η^5-cyclohexadienyl ligand. The reduced mesityl ring is puckered at C(1), such that the Ta(1)···C(1) distance is 3.141(7) Å, while the bond lengths from Ta(1) to C(2)−C(6) range from 2.349(6) to 2.830(6) Å. The internal angles of the cyclohexadienyl ligand involving C(2)−C(6) range from 116.2(6)° to 121.0(6)°, suggesting sp^2 hybridization, whereas the C(6)−C(1)−C(2) angle (109.6(6)°) is consistent with sp^3 hybridization. In addition, the remaining aromatic hydrogen on the η^5-cyclohexadienyl ring is sterically positioned near the π-system of one of the imido mesityl substituents, likely causing the unusual upfield aromatic ^1H NMR resonance observed for both complexes **9** and **11**.

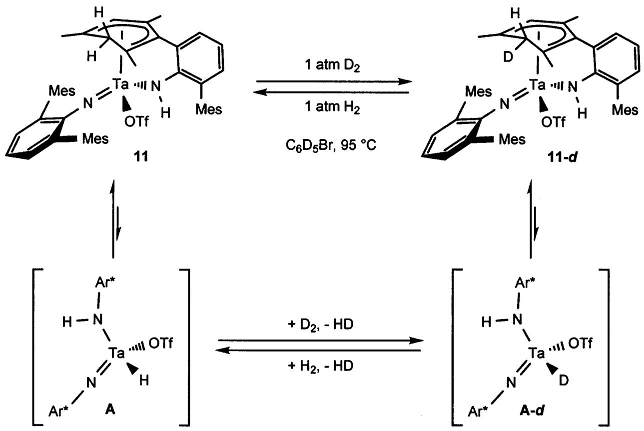
Complex **11** presumably forms via the tantalum hydride intermediate species [(Ar*N=)(Ar*NH)Ta(H)-OTf] (**A**, Scheme 2), and evidence for the existence of this species was obtained by trapping experiments. Heating a bromobenzene-d_5 solution of complex **10** to 95 °C under H_2 (1 atm) in the presence of MeCCMe, ^tBuCCMe, or PhCCPh resulted in complicated reaction mixtures containing complex **11**. When **10** was treated with H_2 in the presence of $Me_3SiCCSiMe_3$ under similar conditions, complete conversion of **10** to **11** was observed, while the alkyne remained unchanged. However, when a bromobenzene-d_5 solution of **10** was treated with H_2 in the presence of 1-hexene (1 equiv), methane was produced along with quantitative amounts of *n*-hexane and complex **11**. This observation suggests that **A** reacted with 1-hexene to give a hexyl triflate complex (**12**), which then reacted with H_2 to give *n*-hexane and complex **11** (Scheme 2). In fact, the reaction of **10** with H_2 (1 atm) in the presence of 10 equiv of 1-hexene (bromobenzene, 95 °C, 2 days) produced the hexyl derivative (Ar*N=)(Ar*NH)Ta(Hex)OTf (**12**) as yellow crystals in 66% yield. The diastereotopic $TaCH_2$ hydrogens are clearly identified by two triplets of doublets appearing at 0.58 and 1.00 ppm. The ^{13}C NMR signal for this methylene group occurs at 66.9 ppm, in approximately the same region as those for the related carbon atoms in **4** and **10**.

Experimental data suggest that in solution complexes **11** and **A** exist in equilibrium. Thus, **11** reacts with 1-hexene (1 equiv, in the absence of H_2) in bromobenzene-d_5 at 95 °C to form the *n*-hexyl derivative **12** (Scheme 2). However, attempts to observe **A** by monitoring the reaction of complex **10** with H_2 (1 atm) by ^1H NMR spectroscopy in bromobenzene-d_5 at 95 °C were unsuccessful; only resonances due to complexes **10** and **11** were observed. Thus, **11** is highly favored in its equilibrium with **A**.

Further insight into the mechanism of formation of **11** was gained by a deuterium-labeling experiment. Treatment of **10** with D_2 (1 atm) in bromobenzene at 95 °C over 3 days provided (Ar*N=)[2-(η^5-2,4,6-$Me_3C_6H_2D$)-6-$MesC_6H_3NH$]TaOTf (**11-*d***) as red-orange crystals from toluene (Scheme 2). The ^1H NMR spectrum of **11-*d*** has no signal at ~3.5 ppm (unlike **11**), but contains a broad singlet at 4.52 ppm integrating to 1 H. The ^2H NMR spectrum, as expected, contains a single, broad resonance at 3.48 ppm, consistent with deuterium incorporation into only one position of the molecule. The $^{13}C\{^1H\}$ NMR spectrum contains a 1:1:1 triplet at 34.5 ppm due to C−D coupling ($^1J_{CD} = 20$ Hz). No further deuterium incorporation was observed after heating a bromobenzene-d_5 solution of complex **11-*d*** with D_2 (1 atm) to 95 °C for 3 days. Furthermore, complex **11-*d*** was found to undergo H/D exchange to yield **11** upon exposure to H_2 (1 atm) in bromobenzene-d_5 at 95 °C (24 h, Scheme 3). This is believed to proceed via a σ-bond metathesis pathway involving the postulated intermediate **A** (or **A-*d***).

To determine the fate of the hydrogen atom that is introduced in the formation of **11**, the through-space couplings involving the reduced mesityl ring in **11** were determined. A ^1H-ROESY NMR experiment (mixing time = 1 s) was used to observe an ROE (rotating frame Overhauser effect) between the singlet at 4.26 ppm

Scheme 3



(H_{Mes}, Figure 4) and the doublet at 4.54 ppm (H_{exo}). However, no ROE was observed between H_{Mes} and H_{endo}. In the structure of complex **11**, the η^5-cyclohexadienyl ring places H_{Mes} closer to H_{exo} than H_{endo} (3.53 vs 4.06 Å). Therefore, the doublet at 4.54 ppm is due to H_{exo}, and the doublet at 3.53 ppm is due to H_{endo}. Furthermore, since the deuterium labeling experiment incorporates deuterium into only one position of the molecule (the H_{endo} position), the hydride transfer proceeds in an *endo* fashion.

Complex **11** results from the insertion of an arene ring into a M−H bond to give a stable η^5-cyclohexadienyl complex. Complexes of this type have been postulated by Rothwell and co-workers as intermediates in the intramolecular hydrogenation of aryl oxide phenyl substituents to cyclohexyl groups.[36] Previous work aimed at the characterization of potential arene hydrogenation intermediates resulted in the isolation of a niobium species in which two hydrogens were transferred to an aromatic ring to give an η^4-cyclohexadiene ligand,[35,63] and a tungsten complex resulting from transfer of four hydrogens to an aromatic ring to yield an η^2-cyclohexene ligand.[37] Complex **11** appears to represent the first example of the product of intramolecular transfer of a single hydride to an aromatic ring to give a stable, η^5-cyclohexadienyl complex.[13] Chromium and manganese complexes containing η^5-cyclohexadienyl ligands resulting from intermolecular hydride transfer to a coordinated arene are known,[64,65] but to the best of our knowledge, no examples of intermolecular or intramolecular hydride transfer to give a stable, η^5-cyclohexadienyl ligand exist among group V arene complexes.[66,67] Green and co-workers have reported low-valent niobium complexes containing both η^6-arenes and hydride ligands,[68,69] and Wigley and co-workers have described similar tantalum species,[70,71] but in neither case has any evidence been observed for transfer of the hydride ligand to the coordinated arene. However, Wigley and co-workers have prepared tantalum chlorides containing η^2-pyridine ligands, which react with $LiBEt_3H$ to give an intermediate tantalum hydride, which then transfers the hydride to the coordinated pyridine.[72,73] In this instance, though, the product is a metallacycle resulting from the cleavage of a C−N bond. Thus, the isolation and structural characterization of complex **11** appears to be the first example of an intramolecular transfer of a single hydride to give a stable, η^5-cyclohexadienyl complex and lends support to one of the mechanisms postulated by Rothwell and co-workers for arene hydrogenation by early metal catalysts.[36]

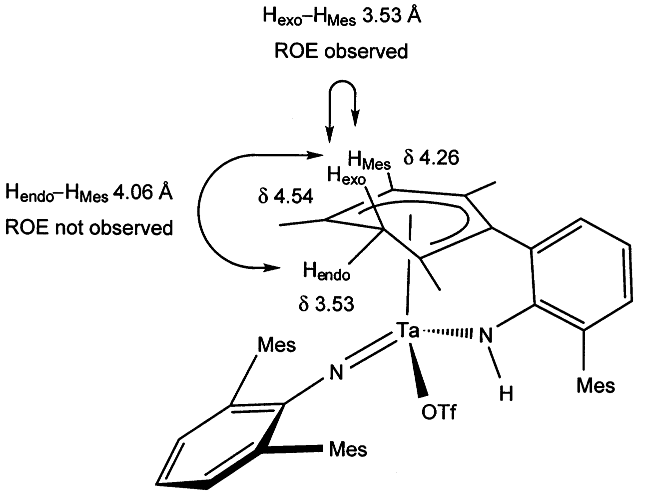


Figure 4. ^1H NMR assignments of **11** based upon ^1H-ROESY data.

A pronounced solvent effect was observed for the hydrogenolysis of complex **10** to **11**. With benzene-d_6 as the solvent, complete conversion of complex **10** to **11** requires heating at 95 °C for 5 days in the presence of H_2 (1 atm). However, with the more polar solvent bromobenzene-d_5, the reaction proceeds significantly faster such that complete conversion is observed after heating at 95 °C for 18 h. The source of this solvent effect is not understood. Triflate dissociation from **10** to produce the transient, cationic species $[(Ar^*N{=})(Ar^*NH)TaMe]^+[OTf]^-$ seems unlikely, since the cationic complex **9** is unreactive toward H_2.

Hydrogenation Catalysis with the Masked Hydride 11. The observed stoichiometric hydrogenation of 1-hexene with **11** suggested the use of this complex as a hydrogenation catalyst. Such catalytic hydrogenations were observed for a number of substrates as shown in Table 4. In a typical reaction, complex **10** was treated with the olefin (or silane) substrate and H_2 (or D_2, 1 atm) in bromobenzene-d_5 at 95 °C. In all cases, the hydrogenation reactions were extremely slow, as might be expected for a sterically encumbered hydride catalyst. More sterically crowded substrates such as cyclohexene and α-methylstyrene reacted much more slowly than

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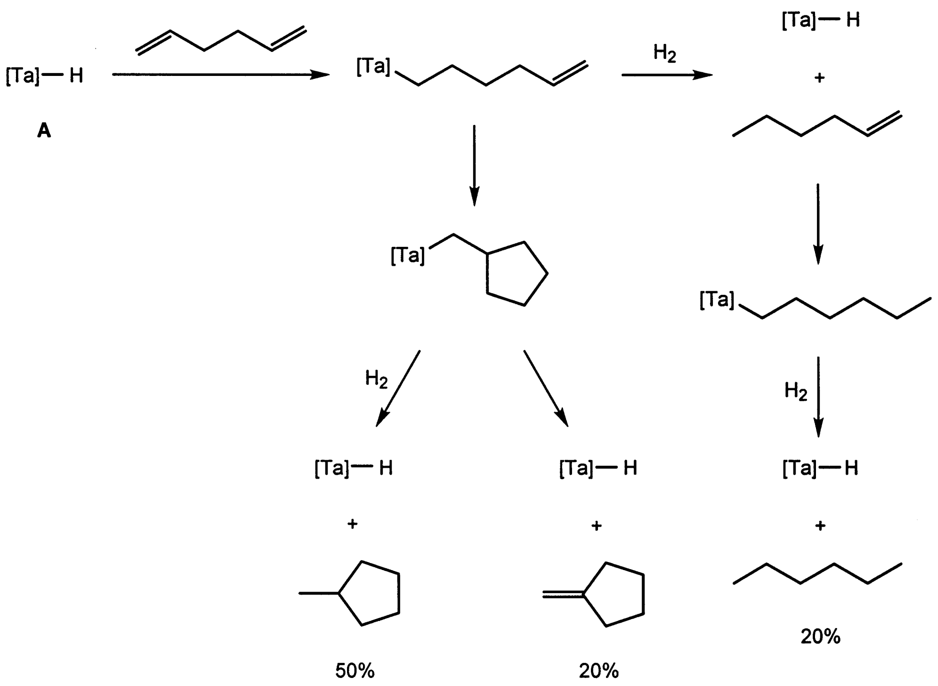
Table 4. Results for Reactions of the Catalytic Precursor 10

substrate	equiv	conversion (%)	product(s)	yield (%)	time (days)
1-hexene	10	100	*n*-hexane	90	7
			2-hexene, 3-hexene	10	
cyclohexene	5	80	cyclohexane	97	12
1,5-hexadiene	14	100	methylcyclopentane	50	9
			methylenecyclopentane	20	
			n-hexane	20	
α-methylstyrene	1	60	cumene	90	4
phenylsilane	5	100	phenylsilane-d_3	99	2

Scheme 4



less substituted alkenes (e.g., 1-hexene and 1,5-hexadiene). Attempts to hydrogenate ethylene were unsuccessful since complex **10** was found to slowly polymerize ethylene (1 atm) at room temperature to yield polyethylene (melting point 132 °C by differential scanning calorimetry). No hydrogenation was observed when benzene was used as the substrate (bromobenzene-d_5, 120 °C, 2 days).

The observed products for the reaction with 1,5-hexadiene are methylcyclopentane (50%), methylenecyclopentane (20%), and *n*-hexane (20%). Methylcyclopentane could arise via olefin insertion into the tantalum hydride, followed by intramolecular olefin insertion into the resulting Ta−C bond, and hydrogenolysis of the resulting tantalum alkyl to yield the alkane and regenerate the catalyst (Scheme 4). However, β-hydride elimination appears to be a competing process in this reaction, given the formation of methylenecyclopentane (and the formation of 2-hexene and 3-hexene observed during the hydrogenation of 1-hexene). The reductive cyclization of 1,5-hexadiene to methylcyclopentane has previously been observed by Bercaw and co-workers for scandocene hydride catalysts,[74,75] and Marks has reported efficient catalysts for this transformation based on yttrium and lutetium.[76] The decreased reactivity of [(Ar*N═)(Ar*NH)Ta(H)OTf] (**A**) relative to the Bercaw and Marks systems can be attributed to the steric bulk of the terphenyl ligands, which should decrease the rates of insertion and hydrogenolysis.

In addition to olefin hydrogenation and diene cyclization, this system was found to effect the catalytic deuteration of the Si−H positions of $PhSiH_3$ by D_2 (Table 4). This process may proceed in a concerted fashion through a σ-bond metathesis mechanism which places silicon in the β-position of a four-center transition state.[5] An alternative pathway involves possible silyl intermediates of the form [(Ar*N═)(Ar*NH)Ta($SiH_xD_{(2-x)}Ph$)OTf], though attempts to observe such species by ^1H NMR spectroscopy were unsuccessful. No reaction was observed upon treating complex **11** with $PhSiH_3$ (1 equiv) in bromobenzene-d_5 at room temperature, and an intractable mixture of products was observed upon heating the reaction mixture to 105 °C for 5 days. Similarly, no reaction was observed between complex **11** and CH_4 under identical conditions.

Synthesis of Tantalum Silyl Complexes. To determine if this system would support reactive Ta−Si σ-bonds, we sought the preparation of silyl derivatives of **7** via salt-metathesis reactions. Complex **7** reacts cleanly with the lithium silyl reagents $(THF)_3LiSi(SiMe_3)_3$, $(THF)_2LiSi(^tBu)Ph_2$, and $(THF)_2LiSiHMes_2$ to provide the corresponding silyl chloride complexes (Ar*N═)(Ar*NH)Ta(SiR_3)Cl (SiR_3 = $Si(SiMe_3)_3$ (**13a**),

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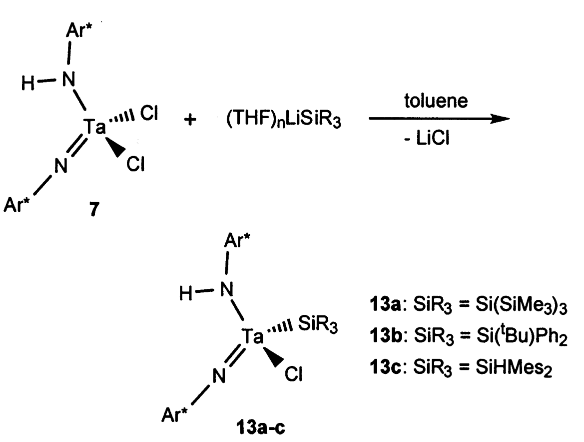
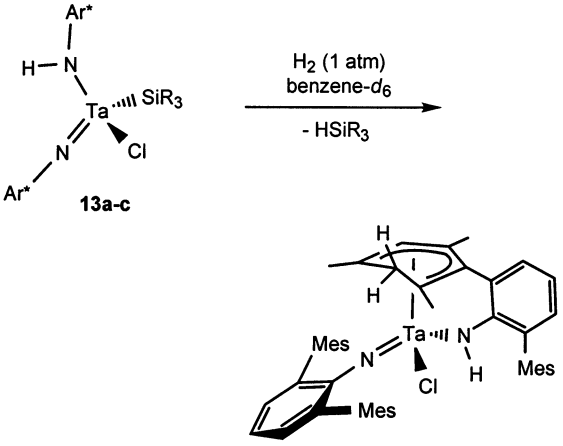
$Si(^tBu)Ph_2$ (**13b**), $SiHMes_2$ (**13c**)) in 42%, 69%, and 80% yields, respectively (eq 7). The only other examples of imido silyl complexes of tantalum are $(Me_3SiN{=})[(Me_3Si)_2N]Ta[Si(^tBu)Ph_2]_2$,[29] $(Me_3SiN{=})[(Me_3Si)_2N](Me_2N)Ta[Si(^tBu)Ph_2]$,[29] $Cp(2,6\text{-}^iPr_2C_6H_3N{=})Ta(H)(SiMe_2Cl)(PMe_3)$,[28] and $Cp^*(2,6\text{-}^iPr_2C_6H_3N{=})Ta(SiR_3)X$ (SiR_3 = $Si(SiMe_3)_3$, $SiPh_3$, $SiHMes_2$; X = Cl, alkyl, hydride).[25,26] Silyl complexes **13a**−**c** are extremely light sensitive, necessitating their preparation and storage under conditions of low ambient lighting. Monitoring a benzene-d_6 solution of complex **13a** exposed to ambient lab light over 2 days by ^1H NMR spectroscopy revealed the formation of $HSi(SiMe_3)_3$, but no tantalum-containing products could be identified.



(7)

All three silyl complexes contain broad mesityl resonances in their ^1H NMR spectra, presumably due to restricted rotation caused by introduction of the sterically bulky silyl ligands. Although the structure and connectivity of complex **13a** were confirmed by X-ray crystallography, the refinement of accurate metric parameters was not possible due to severe positional disorder of the tantalum and nitrogen atoms and rotational disorder of the $-Si(SiMe_3)_3$ group.

Complexes **13a**−**c** were found to react cleanly with H_2 (1 atm) in benzene-d_6 at room temperature over 3 days in the dark to yield $HSiR_3$ and a complex that exhibits spectroscopic features similar to those of **11**, including a pair of doublets at 3.12 and 4.53 ppm (J = 15 Hz) and a broad, aromatic singlet integrating to 1 H at 4.01 ppm (eq 8). The formation of $HSiR_3$ (1 equiv) suggests that this reaction proceeds through a σ-bond metathesis pathway to give an intermediate hydride, which is then transferred to one of the mesityl rings to produce the η^5-cyclohexadienyl complex $(Ar^*N{=})[2\text{-}(\eta^5\text{-}2,4,6\text{-}Me_3C_6H_3)\text{-}6\text{-}MesC_6H_3NH]TaCl$. Attempts to isolate this complex were complicated by persistent quantities of unidentified impurities.



(8)

Treating complex **13a** with silanes such as $PhSiH_3$ or Ph_2SiH_2 (1 equiv) in benzene-d_6 at 85 °C over several days in the dark led to the formation of $HSi(SiMe_3)_3$, but no metal-containing products could be identified and most of the silane remained unchanged (70% $PhSiH_3$ remained after 6 days; 90% Ph_2SiH_2 remained after 3 days). Heating complex **13a** in the absence of silanes also yields $(Me_3Si)_3SiH$, which appears to be a kinetic product of the thermal decomposition of **13a**.

Conclusions

The results described here provide further evidence that imido hydride complexes are accessible, potentially reactive species that can give rise to novel chemistry. Complex **11**, with an imido-amido ligand set featuring the sterically demanding $2,6\text{-}Mes_2C_6H_3$ aryl group, represents an arene hydrogenation intermediate resulting from the transfer of hydride from tantalum to one of the mesityl rings. In previous work by Rothwell and co-workers, intramolecular transfers of two and four hydrides to aryl oxide phenyl substituents were observed.[35,37,63] Complex **11** reacts with small molecules via its more reactive isomer **A**, with which it is in equilibrium, and exhibits many of the reactions expected for a d^0 metal hydride. Thus, it is a catalyst for olefin hydrogenation, diene cyclization, and H/D exchange at silicon, although the sterically encumbering nature of the terphenyl ligands leads to relatively low turnover rates.

Complexes **13a**−**c** represent rare examples of imido silyl tantalum species and confirm that the $(Ar^*N{=})(Ar^*NH)$ ligand set can be used to support reactive Ta−Si σ-bonds. These silyl species react with H_2 to yield the corresponding silane and a complex that has spectroscopic features similar to those for the η^5-cyclohexadienyl complex **11**. As shown in other d^0 systems, silyl ligands appear to provide facile routes to the corresponding hydride derivative via hydrogenolysis.[24] Continuing studies focus on the development of imido hydrides and silyls that are highly reactive in σ-bond metathesis processes.

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 and toluene-d_8 were purified and dried by vacuum distillation from sodium/potassium alloy.

Bromobenzene-d_5 was degassed and then dried over 4 Å molecular sieves. Dichloromethane-d_2 was purified and dried by vacuum distillation from CaH_2.

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), 99.376 MHz (^{29}Si), 160.462 MHz (^{11}B), or 202.457 MHz (^{31}P) using a Bruker DRX-500 (^{1}H, ^{13}C, ^{29}Si, ^{11}B, ^{31}P) 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{^{1}H} NMR spectra were referenced internally by the ^{13}C NMR signal of the NMR solvent relative to tetramethylsilane. ^{19}F{^{1}H} NMR spectra were referenced relative to an α,α,α-trifluorotoluene external standard. ^{29}Si NMR spectra were referenced using a tetramethylsilane external standard. ^{11}B NMR spectra were referenced using a $BF_3{\cdot}OEt_2$ external standard. ^{31}P{^{1}H} NMR spectra were referenced relative to an 85% aqueous H_3PO_4 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,^{11}B coupling and total correlation spectroscopy (TOCSY) was used to identify some coupled ^{1}H NMR systems. Nuclear Overhauser enhancement spectroscopy (NOESY) was used to identify the η^5-cyclohexadienyl methyl groups in complexes **11** and **11-*d***, and rotating frame Overhauser enhancement spectroscopy (ROESY) was used to identify the H_{endo} and H_{exo} hydrogens in complexes **11** and **11-*d*** (mixing time = 1 s). 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 used without further purification. Lithium aluminum hydride was purified by diethyl ether extraction. Carbon monoxide was purchased from Scott Specialty Gases, hydrogen was purchased from Praxair, and deuterium was purchased from Airgas. The compounds 2,6-$Mes_2C_6H_3I$,[77] *p*-toluenesulfonyl azide,[78] $TaMe_3Cl_2$,[79] NpLi,[80] $B(C_6F_5)_3$,[81] $(THF)_3LiSi(SiMe_3)_3$,[82] $(THF)_2LiSi(^tBu)Ph_2$,[83] and $(THF)_2LiSiHMes_2$[62] were prepared as reported in the literature.

2,6-$Mes_2C_6H_3N_3$ (1). A solution of ^{n}BuLi in hexanes (1.6 M, 40.8 mmol) was added dropwise over 20 min via addition funnel to a stirred slurry of 2,6-$Mes_2C_6H_3I$ (18.00 g, 40.87 mmol) in hexanes (400 mL) at 0 °C. The resulting yellow slurry was warmed to room temperature and stirred for an additional 16 h. The reaction mixture was then cooled to 0 °C, and a solution of *p*-toluenesulfonyl azide (8.26 g, 41.9 mmol) in diethyl ether (125 mL) was added via cannula. After stirring for 2 h at 0 °C, the reaction mixture was quenched with water (250 mL). The aqueous phase was separated and extracted with diethyl ether (3 × 200 mL). The organic phases were combined, washed with water (200 mL), and dried over $MgSO_4$. Filtration followed by solvent removal in vacuo resulted in red-orange crystals of compound **1** (13.8 g, 96%). The analytically pure compound was obtained by recrystallization from diethyl ether at −35 °C. Mp: 144−152 °C. ^{1}H NMR: δ 2.10 (s, 12 H, *o*-Me), 2.17 (s, 6 H, *p*-Me), 6.85 (s, 4 H, Mes-H), 6.88 (d, 2 H, *m*-H), 6.94 (t, 1 H, *p*-H). ^{13}C{^{1}H} NMR: δ 20.9 (*o*-Me), 21.5 (*p*-Me), 126.2, 128.9, 130.6, 135.7, 135.7, 136.7, 136.8, 137.9 (aromatic C's). IR (Nujol, cm^{-1}): 2137 (m), 2098 (s), 2083 (s), 1414 (m), 1313 (m), 847 (w), 802 (w), 757 (w). Anal. Calcd for $C_{24}H_{25}N_3$: C, 81.09; H, 7.09; N, 11.82. Found: C, 81.03; H, 7.30; N, 11.59.

2,6-$Mes_2C_6H_3NH_2$ (2). A solution of compound **1** (5.09 g, 14.3 mmol) in diethyl ether (100 mL) was added dropwise over 30 min via addition funnel to a stirred solution of lithium aluminum hydride (0.561 g, 14.8 mmol) in diethyl ether (100 mL). After the addition was completed, the reaction mixture was heated at reflux for 4.5 h (55 °C bath). The reaction mixture was cooled to room temperature and quenched with reagent grade diethyl ether (50 mL) and water (50 mL). Büchner funnel filtration followed by separation, drying of the organic phase over $MgSO_4$, and solvent reduction in vacuo afforded colorless, diamond-shaped crystals of compound **2** (4.06 g, 86%) from diethyl ether at −35 °C. Mp: 142−143 °C. ^{1}H NMR: δ 2.12 (s, 12 H, *o*-Me), 2.20 (s, 6 H, *p*-Me), 3.02 (br s, 2 H, NH_2), 6.86 (t, 1 H, *p*-H), 6.87 (s, 4 H, Mes-H), 6.90 (d, 2 H, *m*-H). ^{13}C{^{1}H} NMR: δ 20.7 (*o*-Me), 21.5 (*p*-Me), 118.9, 126.6, 129.2, 129.4, 136.3, 137.2, 137.4, 141.6 (aromatic C's). IR (Nujol, cm^{-1}): 3475 (m, ν_{NH2}), 3380 (m, ν_{NH2}). Anal. Calcd for $C_{24}H_{27}N$: C, 87.49; H, 8.26; N, 4.25. Found: C, 87.44; H, 8.48; N, 4.13.

2,6-$Mes_2C_6H_3NHLi$ (3). A solution of ^{n}BuLi in hexanes (2.8 M, 22.4 mmol) was added via syringe to a stirred solution of compound **2** (7.19 g, 21.8 mmol) in pentane (200 mL) at 0 °C. After warming the reaction mixture to room temperature over 1.5 h, the solvent and volatile byproducts were removed in vacuo to yield **3** (7.24 g, 99%) as a light yellow powder. ^{1}H NMR: δ 1.41 (br s, 1 H, NH), 1.97 (s, 12 H, *o*-Me), 2.20 (s, 6 H, *p*-Me), 6.66 (t, 1 H, *J* = 7 Hz, *p*-H), 6.77 (s, 4 H, Mes-H), 6.84 (d, 2 H, *J* = 7 Hz, *m*-H). ^{13}C{^{1}H} NMR: δ 20.6 (*o*-Me), 21.5 (*p*-Me), 113.2 (CH), 127.2 (aromatic C), 129.0, 129.8 (CH's), 136.8, 136.8, 140.2, 156.7 (aromatic C's). IR (Nujol, cm^{-1}): 3284 (w, ν_{NH}). Anal. Calcd for $C_{24}H_{26}LiN$: C, 85.94; H, 7.81; N, 4.18. Found: C, 85.92; H, 7.66; N, 4.44.

(2,6-$Mes_2C_6H_3N$=)(2,6-$Mes_2C_6H_3NH$)$TaMe_2$ (4). A solution of $TaMe_3Cl_2$ (0.880 g, 2.96 mmol) in hexanes (20 mL) was added to a stirred slurry of compound **3** (1.985 g, 5.92 mmol) in hexanes (120 mL) at −35 °C. Upon addition, the reaction mixture changed from yellow to orange. After warming to room temperature over 2 h, the reaction mixture was filtered and the remaining solid was extracted with hexanes (4 × 120 mL). Concentrating and cooling the combined extracts to −35 °C afforded several crops of yellow, blocklike crystals of **4** (1.834 g, 71%). Mp: 208−211 °C. ^{1}H NMR: δ −0.41 (s, 6 H, $TaMe_2$), 2.02 (s, 12 H, *o*-Me), 2.06 (s, 12 H, *o*-Me), 2.09 (s, 6 H, *p*-Me), 2.22 (s, 6 H, *p*-Me), 6.74 (m, 3 H, *m*-H, *p*-H), 6.85 (s, 4 H, Mes-H), 6.87 (s, 4 H, Mes-H), 6.88 (t, 1 H, *J* = 10 Hz, *p*-H), 6.99 (d, 2 H, *J* = 5 Hz, *m*-H), 7.34 (br s, 1 H, NH). ^{13}C{^{1}H} NMR (dichloromethane-d_2): δ 20.7 (*o*-Me), 20.9 (*o*-Me), 21.3 (*p*-Me), 21.4 (*p*-Me), 57.5 ($TaMe_2$), 120.9, 122.8, 128.0, 128.2, 129.7, 130.1, 130.2, 136.3, 136.4, 137.0, 137.5, 138.5, 138.8, 139.0, 148.3, 154.0 (aromatic C's). IR (Nujol, cm^{-1}): 3303 (m, ν_{NH}). Anal. Calcd for $C_{50}H_{57}N_2Ta$: C, 69.27; H, 6.63; N, 3.23. Found: C, 68.93; H, 6.87; N, 2.99.

(2,6-$Mes_2C_6H_3N$=)(2,6-$Mes_2C_6H_3NH$)TaMe(η^2-COMe) (5). Compound **4** (25.7 mg, 29.6 μmol) was dissolved in benzene-d_6 (~0.7 mL) and transferred 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 CO (1 atm). Upon exposure to CO (<1 min), the reaction mixture changed from pale yellow to bright yellow. Compound **5** was observed as the only product by ^{1}H NMR spectroscopy (99% relative to internal standard). ^{1}H NMR: δ 0.04 (s, 3 H, TaMe), 1.83 (s, 6

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H, Mes-Me), 2.00 (s, 6 H, Mes-Me), 2.04 (s, 6 H, Mes-Me), 2.07 (s, 6 H, Mes-Me), 2.08 (s, 6 H, Mes-Me), 2.26 (s, 3 H, COMe), 2.29 (s, 6 H, Mes-Me), 6.54 (br s, 2 H, Ar*-H), 6.63 (br d, 2 H, $J = 7$ Hz, Ar*-H), 6.69 (t, 1 H, $J = 8$ Hz, *p*-H), 6.78 (dd, 1 H, $J = 7$ Hz, $J = 8$ Hz, *p*-H), 6.84 (br s, 2 H, Ar*-H), 6.88 (d, 2 H, $J = 8$ Hz, *m*-H), 6.90 (s, 2 H, Ar*-H), 6.94 (s, 2 H, Ar*-H), 7.91 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 20.2, 20.5, 21.4, 21.4, 21.7, 22.2, 31.3, 33.6 (aliphatic C's), 121.2, 123.0, 129.7, 130.0, 130.5, 130.6, 135.9, 136.1, 136.5, 137.2, 137.4, 138.8, 138.8, 139.1, 148.8, 153.7 (aromatic C's), 317.1 (*C*OMe). IR (benzene-d_6, cm^{-1}): 3308 (w, ν_{NH}), 1421 (s, ν_{CO}).

(2,6-Mes$_2$C$_6$H$_3$N=)(2,6-Mes$_2$C$_6$H$_3$NH)TaMe$_2$(PMe$_3$) (6). Compound **4** (31.1 mg, 35.9 μmol) was dissolved in benzene-d_6 (~0.7 mL) and transferred to an NMR tube fitted with a J. Young Teflon stopper. Trimethylphosphine (3.7 μL, 35.7 μmol) was then added to the NMR tube via syringe. Upon addition, the reaction mixture became pale yellow. Compound **6** was observed as the only product by ^{1}H NMR spectroscopy (99% relative to internal standard). ^{1}H NMR: δ −0.61 (s, 6 H, TaMe$_2$), 0.56 (d, 9 H, $J_{PH} = 5$ Hz, PMe$_3$), 2.04 (s, 12 H, *o*-Me), 2.09 (s, 6 H, *p*-Me), 2.21 (s, 12 H, *o*-Me), 2.31 (s, 6 H, *p*-Me), 6.81 (br m, 8 H, Ar*-H), 6.94 (d, 2 H, $J = 8$ Hz, *m*-H), 6.94 (s, 4 H, Mes-H), 7.23 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 14.1 (d, $J_{PC} = 13$ Hz, PMe$_3$), 21.4 (*p*-Me), 21.6 (*p*-Me), 21.7 (*o*-Me), 21.7 (*o*-Me), 41.0 (br s, TaMe$_2$), 121.0, 122.4, 128.8, 129.4, 129.9, 130.7 (CH's), 131.4, 136.1, 137.2, 137.3, 137.3, 137.7, 138.5, 139.2, 150.3, 155.4 (aromatic C's). $^{31}P\{^1H\}$ NMR: δ −19.1 (br s, PMe$_3$). IR (benzene-d_6, cm^{-1}): 3281 (w, ν_{NH}).

(2,6-Mes$_2$C$_6$H$_3$N=)(2,6-Mes$_2$C$_6$H$_3$NH)TaCl$_2$ (7). TaMe$_3$Cl$_2$ (1.157 g, 3.90 mmol) and compound **2** (2.528 g, 7.67 mmol) were dissolved in toluene (80 mL) and heated to 75 °C for 21 h. After cooling the reaction mixture to room temperature, the solvent and volatile byproducts were removed in vacuo to give a brown solid. The solid was extracted with toluene (3 × 30 mL) and filtered to give a red-brown solution. The combined extracts were concentrated to ca. 30 mL, layered with an equal volume of pentane, and cooled to −35 °C to give several crops of light brown crystals. Each crop of crystals was washed with cold pentane (2 × 15 mL) and dried in vacuo to afford analytically pure **7** (2.369 g, 68%). Mp: 177−180 °C. ^{1}H NMR: δ 2.01 (s, 12 H, *o*-Me), 2.05 (s, 12 H, *o*-Me), 2.13 (s, 6 H, *p*-Me), 2.22 (s, 6 H, *p*-Me), 6.70 (m, 3 H, *m*-H, *p*-H), 6.80 (t, 1 H, $J = 7$ Hz, *p*-H), 6.87 (s, 4 H, Mes-H), 6.88 (s, 4 H, Mes-H), 6.91 (d, 2 H, $J = 7$ Hz, *m*-H), 8.93 (br s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 21.1 (*o*-Me), 21.4 (*o*-Me), 21.5 (*p*-Me), 21.6 (*p*-Me), 123.8, 126.1, 128.3, 128.7, 130.5, 130.7, 130.9, 134.8, 136.8, 137.0, 137.2, 139.2, 139.2, 139.8, 146.1, 152.9 (aromatic C's). IR (Nujol, cm^{-1}): 3305 (m, ν_{NH}). Anal. Calcd for $C_{48}H_{51}Cl_2N_2Ta$: C, 63.51; H, 5.66; N, 3.09. Found: C, 63.64; H, 5.52; N, 2.97.

(2,6-Mes$_2$C$_6$H$_3$N=)(2,6-Mes$_2$C$_6$H$_3$NH)Ta(CH$_2$CMe$_3$)$_2$ (8). Compound **7** (0.301 g, 0.331 mmol) and Me$_3$CCH$_2$Li (0.083 g, 1.07 mmol) were dissolved in toluene (25 mL) and stirred at room temperature for 5.5 h. The solvent was removed in vacuo, and the light brown solid was extracted with pentane (3 × 20 mL) and filtered. The combined extracts were concentrated to ca. 50 mL and cooled to −35 °C to afford two crops of yellow crystals of **8** (0.234 g, 72%). ^{1}H NMR (dichloromethane-d_2): δ −0.36 (d, 2 H, $J = 15$ Hz, CH$_2$), −0.02 (d, 2 H, $J = 15$ Hz, CH$_2$), 0.54 (s, 18 H, ^{t}Bu), 1.88 (br s, 12 H, *o*-Me), 2.03 (s, 12 H, *o*-Me), 2.24 (s, 6 H, *p*-Me), 2.27 (s, 6 H, *p*-Me), 6.66 (br s, 1 H, NH), 6.77 (br s, 3 H, Ar*-H), 6.8−6.9 (complex, 7 H, Ar*-H), 6.90 (s, 4 H, Mes-H). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2): δ 21 (br, *o*-Me), 21.4 (*p*-Me), 21.4 (*p*-Me), 21.9 (*o*-Me), 34.9 (C*Me*$_3$), 35.5 (*C*Me$_3$), 105.8 (TaCH$_2$), 121.6, 122.1, 128.8 (br), 129.7, 129.8, 131.4, 131.7, 136.3, 136.8, 137.2, 137.4, 138.0, 138.3, 139.0, 149.0, 155.5 (aromatic C's). IR (Nujol, cm^{-1}): 3264 (w, ν_{NH}). Anal. Calcd for $C_{58}H_{73}N_2Ta$: C, 71.14; H, 7.51; N, 2.86. Found: C, 71.09; H, 7.16; N, 3.10.

[(2,6-Mes$_2$C$_6$H$_3$N=)(2,6-Mes$_2$C$_6$H$_3$NH)TaMe][MeB(C$_6$F$_5$)$_3$] (9). Compound **4** (0.215 g, 0.248 mmol) and B(C$_6$F$_5$)$_3$ (0.140 g, 0.274 mmol) were dissolved in toluene (40 mL) to give a bright orange solution. After stirring at room temperature for 1.5 h, the solution was filtered. The filtrate was concentrated to ca. 10 mL, layered with an equal volume of pentane, and cooled to −35 °C to afford two crops of a red-orange oil. Decanting the solvent and drying the oil in vacuo provided compound **9** (0.277 g, 81%) as a red-orange foam. ^{1}H NMR: δ −0.19 (s, 3 H, TaMe), 1.16 (br s, 3 H, $[MeB(C_6F_5)_3]^-$), 1.61 (br s, 6 H, Mes-Me), 1.67 (s, 3 H, Mes-Me), 1.68 (s, 3 H, Mes-Me), 1.76 (s, 3 H, Mes-Me), 1.80 (s, 3 H, Mes-Me), 1.82 (s, 3 H, Mes-Me), 1.89 (br s, 6 H, Mes-Me), 2.20 (s, 3 H, Mes-Me), 2.26 (s, 6 H, Mes-Me), 5.19 (s, 1 H, Ar*-H), 6.60 (br s, 2 H, Ar*-H), 6.68 (s, 1 H, Ar*-H), 6.71 (m, 3 H, Ar*-H), 6.78 (s, 2 H, Ar*-H), 6.83 (s, 2 H, Ar*-H), 6.92 (t, 1 H, $J = 8$ Hz, Mes-H), 6.96 (s, 1 H, Ar*-H), 6.99 (d, 1 H, $J = 8$ Hz, Mes-H). $^{13}C\{^1H\}$ NMR: δ 19.6, 19.8, 20.2, 20.3, 20.5, 20.5, 20.7, 21.2, 21.3, 21.8 (Mes-Me's), 29.8 (TaMe), 119.6 (CH), 125.0 (aromatic C), 126.0, 126.1, 126.2, 128.9, 128.9, 129.0, 129.7, 129.7, 130.1 (CH's), 131.8, 132.5 (aromatic C's), 132.8, 136.1 (CH's), 136.4 (C$_6$F$_5$), 136.5, 136.8, 137.1, 137.6, 137.9, 138.2 (aromatic C's), 138.6 (C$_6$F$_5$), 139.3, 140.3 (aromatic C's), 148.6 (C$_6$F$_5$), 149.8, 150.0 (aromatic C's), 150.5 (C$_6$F$_5$), 151.7, 152.0, 155.1 (aromatic C's). ^{11}B NMR: δ −14.93. $^{19}F\{^1H\}$ NMR: δ −132.3 (d, $J = 19$ Hz), −164.4 (t, $J = 19$ Hz), −167.0 (t, $J = 19$ Hz). IR (Nujol, cm^{-1}): 3304 (m, ν_{NH}). Anal. Calcd for $C_{68}H_{57}BF_{15}N_2Ta$: C, 59.23; H, 4.17; N, 2.03. Found: C, 59.61; H, 4.08; N, 1.94.

(2,6-Mes$_2$C$_6$H$_3$N=)(2,6-Mes$_2$C$_6$H$_3$NH)TaMe(OSO$_2$CF$_3$) (10). Compound **4** (0.566 g, 0.653 mmol) and AgOSO$_2$CF$_3$ (0.169 g, 0.659 mmol) were dissolved in toluene (50 mL) to give a dark brown reaction mixture. After stirring the reaction mixture for 27 h at room temperature, the solvent and volatile byproducts were removed in vacuo to leave behind a yellow-brown oily solid. The solid was extracted with pentane (3 × 30 mL), and the combined extracts were filtered to give a gold-colored solution. The solution was concentrated to ca. 15 mL and cooled to −35 °C overnight to afford two crops of yellow-orange crystals of compound **10** (0.508 g, 78%). ^{1}H NMR: δ 0.22 (s, 3 H, TaMe), 1.88 (s, 6 H, Mes-Me), 2.02 (s, 6 H, Mes-Me), 2.04 (s, 6 H, Mes-Me), 2.15 (s, 6 H, Mes-Me), 2.21 (s, 6 H, Mes-Me), 2.25 (s, 6 H, Mes-Me), 6.62 (d, 2 H, $J = 7$ Hz, *p*-H), 6.73 (t, 3 H, $J = 7$ Hz, *m*-H), 6.79 (dd, 1 H, $J = 7$ Hz, $J = 8$ Hz, *p*-H), 6.84 (s, 2 H, Ar*-H), 6.88 (s, 2 H, Ar*-H), 6.90 (s, 2 H, Ar*-H), 6.93 (s, 4 H, Mes-H), 8.69 (br s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 20.2, 20.7, 21.0, 21.3, 21.6, 21.7, 21.8, 23.1 (Mes-Me's), 45.0 (TaMe), 119.4, 122.0 (aromatic C's), 123.2, 125.5, 128.7, 128.8 (CH's), 129.2 (aromatic C), 130.3, 132.0 (CH's), 134.9, 136.5, 137.3, 137.4, 137.8, 137.9, 139.2, 139.7, 141.8, 147.5, 152.6 (aromatic C's). $^{19}F\{^1H\}$ NMR: δ −75.3. IR (Nujol, cm^{-1}): 3321 (w, ν_{NH}). Anal. Calcd for $(C_{50}H_{54}F_3N_2O_3STa)\cdot(C_5H_{12})_{0.5}$: C, 60.80; H, 5.83; N, 2.70. Found: C, 60.50; H, 6.09; N, 2.68.

(2,6-Mes$_2$C$_6$H$_3$N=)[2-(η^5-2,4,6-Me$_3$C$_6$H$_3$)-6-MesC$_6$H$_3$NH]Ta(OSO$_2$CF$_3$) (11). Compound **10** (0.252 g, 0.252 mmol) was dissolved in bromobenzene (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 95 °C. After 2 days, the 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 solid, which was extracted with toluene (2 × 15 mL). The combined extracts were concentrated to ca. 1 mL and cooled to −35 °C to afford two crops of red-orange crystals of compound **11** (0.187 g, 75%). ^{1}H NMR: δ 1.60 (s, 3 H, η^5-cyclohexadienyl Me), 1.89 (s, 3 H, η^5-cyclohexadienyl Me), 1.92 (s, 3 H, Mes-Me), 1.94 (s, 6 H, Mes-Me), 1.97 (s, 3 H, Mes-Me), 2.07 (s, 3 H, η^5-cyclohexadienyl Me), 2.20 (s, 6 H, Mes-Me), 2.26 (s, 6 H, Mes-Me), 2.27 (s, 3 H, Mes-Me), 3.53 (d, 1 H, $J = 16$ Hz, H$_{endo}$), 4.26 (s, 1 H, Ar*-H), 4.54 (d, 1 H, $J = 16$ Hz, H$_{exo}$), 6.46 (s, 2 H, Ar*-H), 6.69 (m, 1 H, Ar*-H), 6.74 (d, 1 H, Ar*-H), 6.75 (s, 1 H, Ar*-H), 6.80 (m, 1 H, Ar*-H), 6.82 (s, 1 H, Ar*-H), 6.83 (d, 1 H, Ar*-H), 6.89 (br s, 1 H, Ar*-H), 7.00 (br s, 2 H, Ar*-H), 7.06 (br s, 1 H, Ar*-H), 7.34 (br s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 17.2, 19.8, 19.8, 19.9, 20.9, 21.1, 21.5, 21.6, 22.8 (Mes-Me's), 34.9 (CH_2), 118.8 (CH), 119.0, 121.6 (aromatic C's), 122.4, 124.3, 127.3, 128.4 (CH's), 128.9 (aromatic C), 129.0, 129.3, 129.4, 129.4 (CH's), 129.7 (aromatic C), 129.9, 130.3 (CH's), 130.5 (aromatic C), 130.7 (CH), 133.1, 135.0, 135.3, 136.2, 136.9, 137.2, 137.3, 137.4, 138.2, 138.5, 138.8, 138.9, 151.6, 152.7 (aromatic C's). $^{19}F\{^1H\}$ NMR: δ −75.5. IR (KBr, cm^{-1}): 3308 (m, ν_{NH}). Anal. Calcd for $C_{49}H_{52}F_3N_2O_3STa$: C, 59.63; H, 5.31; N, 2.84; S, 3.25. Found: C, 59.73; H, 5.08; N, 2.81, S, 3.49.

(2,6-$Mes_2C_6H_3N$=)[2-(η^5-2,4,6-$Me_3C_6H_2D$)-6-$MesC_6H_3NH$]-Ta(OSO_2CF_3) (11-*d*). An essentially identical procedure to that used to prepare **11** (substituting D_2 for H_2, heating for 3 days) yielded red-orange crystals of compound **11-*d*** (0.187 g, 79%). Selected data: ^1H NMR: δ 4.52 (br s, 1 H, C*H*D). ^2H NMR: δ 3.48 (br s, CH*D*). $^{13}C\{^1H\}$ NMR: δ 34.5 (1:1:1 t, $^1J_{CD}$ = 20 Hz, CHD). Anal. Calcd for $C_{49}H_{51}DF_3N_2O_3STa$: C, 59.57; H, 5.20; N, 2.84; S, 3.25. Found: C, 59.67; H, 5.41; N, 2.87; S, 3.40.

(2,6-$Mes_2C_6H_3N$=)(2,6-$Mes_2C_6H_3NH$)Ta(Hex)-(OSO_2CF_3) (12). 1-Hexene (0.32 mL, 2.6 mmol) was added via syringe to a 50 mL reaction vessel containing compound **10** (0.254 g, 0.254 mmol) dissolved in bromobenzene (10 mL). The reaction mixture was degassed via three freeze−pump−thaw cycles, sealed under H_2 (1 atm), and then heated to 95 °C. After 2 days, the reaction mixture was cooled to room temperature and diluted with toluene (10 mL). The solvent and excess 1-hexene were removed in vacuo to leave behind a yellow-brown crystalline solid. The solid was extracted into toluene (2 × 10 mL), and the combined extracts were concentrated to ca. 2 mL and cooled to −35 °C to afford two crops of yellow crystals of compound **12** (0.179 g, 66%). Analytically pure material was obtained by recrystallization from pentane at −35 °C. ^1H NMR: δ 0.58 (td, 1 H, J = 13 Hz, J = 3 Hz, $TaCH_2$), 0.91 (t, 3 H, J = 7 Hz, $Ta(CH_2)_5CH_3$), 1.00 (td, 1 H, J = 13 Hz, J = 4 Hz, $TaCH_2$), 1.01 (m, 4 H, $TaCH_2(CH_2)_3CH_2CH_3$), 1.15 (m, 2 H, $TaCH_2(CH_2)_3CH_2CH_3$), 1.28 (sextet, 2 H, J = 7 Hz, $Ta(CH_2)_4CH_2CH_3$), 1.95 (s, 6 H, Mes-Me), 2.12 (s, 6 H, Mes-Me), 2.27 (s, 6 H, Mes-Me), 2.29 (s, 6 H, Mes-Me), 1.4−2.7 (br s, 12 H, Mes-Me), 6.68 (br s, 2 H, Ar*-H), 6.74 (d, 1 H, J = 7 Hz, Ar*-H), 6.79 (m, 2 H, Ar*-H), 6.83 (br s, 2 H, Ar*-H), 6.85 (s, 1 H, Ar*-H), 6.87 (br m, 3 H, Ar*-H), 6.93 (d, 1 H, J = 7 Hz, Ar*-H), 6.96 (br s, 2 H, Ar*-H), 8.43 (br s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 14.7 ($Ta(CH_2)_5CH_3$), 20.6, 21.2, 21.5, 21.7 (Mes-Me's), 23.6 ($Ta(CH_2)_4CH_2CH_3$), 28.1 ($TaCH_2(CH_2)_3CH_2CH_3$), 32.4 ($TaCH_2(CH_2)_3CH_2CH_3$), 36.0 ($TaCH_2(CH_2)_3CH_2CH_3$), 66.9 ($TaCH_2$), 119.5, 122.1 (aromatic C's), 122.8, 125.3 (CH's), 128.9 (aromatic C), 129.0, 129.3, 130.6 (CH's), 134.9, 136.3, 137.4, 138.5, 139.4, 148.0, 152.8 (aromatic C's). $^{19}F\{^1H\}$ NMR: δ −75.6. IR (KBr, cm^{-1}): 3327 (m, ν_{NH}). Anal. Calcd for $C_{55}H_{64}F_3N_2O_3STa$: C, 61.67; H, 6.02; N, 2.62; S, 2.99. Found: C, 61.39; H, 5.97; N, 2.50; S, 3.19.

Hydrogenation Catalysis with Catalyst Precursor 10. In a typical reaction, compound **10** (~2 mg, ~2 μmol) and Cp_2Fe (~1 mg, ~5.4 μmol) were dissolved in ~0.7 mL of bromobenzene-d_5, and the resulting solution was transferred to an NMR tube fitted with a J. Young Teflon stopper. The olefin or silane substrate (~14 μmol) was added via syringe, and the reaction mixture was degassed via three freeze−pump−thaw cycles. The NMR tube was then closed under H_2 (or D_2, 1 atm) and heated to 95 °C for several days. Reaction progress and yields were determined by ^1H NMR spectroscopy relative to the Cp_2Fe internal standard, and product identities were confirmed by GC/MS analysis and spectroscopic comparison to authentic samples.

(2,6-$Mes_2C_6H_3N$=)(2,6-$Mes_2C_6H_3NH$)Ta[Si($SiMe_3$)$_3$]Cl (13a). Compound **7** (0.595 g, 0.655 mmol) and $(THF)_3LiSi(SiMe_3)_3$ (0.372 g, 0.790 mmol) were dissolved in toluene (50 mL), and the resulting solution was stirred at room temperature for 23 h in the dark. The solvent was removed in vacuo, and the yellow-brown, oily solid was extracted into pentane (3 × 20 mL) and filtered to give a yellow-brown solution. The combined extracts were concentrated to ca. 10 mL and cooled to −35 °C to afford two crops of yellow crystals of **13a** (0.309 g, 42%). ^1H NMR: δ 0.10 (s, 27 H, $SiMe_3$), 2.13 (s, 6 H, Mes-Me), 2.17 (s, 3 H, Mes-Me), 2.18 (s, 3 H, Mes-Me), 2.27 (br s, 3 H, Mes-Me), 2.29 (s, 3 H, Mes-Me), 2.33 (br s, 3 H, Mes-Me), 2.34 (s, 3 H, Mes-Me), 2.36 (br s, 6 H, Mes-Me), 2.39 (s, 6 H, Mes-Me), 6.65 (dd, 2 H, J = 3 Hz, J = 7 Hz, Ar*-H), 6.68 (s, 1 H, Ar*-H), 6.74−6.85 (complex, 8 H, Ar*-H), 6.89 (s, 1 H, Ar*-H), 6.92 (br s, 1 H, Ar*-H), 6.96 (s, 1 H, Ar*-H), 8.23 (br s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 5.3 ($SiMe_3$), 21.6, 21.8, 22.0 (br), 22.1, 22.1, 22.3 (br), 23.1, 23.3 (br), 23.8 (Mes-Me's), 123.8, 125.0 (CH's), 126.0, 128.9 (aromatic C's), 129.2 (CH), 129.4 (br, CH's), 129.7 (aromatic C), 129.9, 130.3, 130.5 (br), 131.3 (br), 131.8, 131.9, 132.0, 132.9 (CH's), 133.0, 135.9, 136.5 (br), 136.8, 137.0, 137.6, 137.7 (br), 138.5, 138.5, 139.3 (br), 139.5, 139.6 (br), 140.0, 142.8 (br), 150.0, 156.0 (aromatic C's). ^{29}Si NMR: δ −5.68 ($Si(SiMe_3)_3$), −37.09 ($Si(SiMe_3)_3$). IR (Nujol, cm^{-1}): 3254 (w, ν_{NH}). Anal. Calcd for $C_{57}H_{78}ClN_2Si_4Ta\cdot C_5H_{12}$: C, 62.46; H, 7.61; N, 2.35. Found: C, 62.83; H, 7.34; N, 2.17.

(2,6-$Mes_2C_6H_3N$=)(2,6-$Mes_2C_6H_3NH$)Ta[Si(^tBu)Ph_2]Cl (13b). An essentially identical procedure to that used to prepare **13a** (substituting $(THF)_2LiSi(^tBu)Ph_2$ for $(THF)_3LiSi(SiMe_3)_3$) yielded bright, yellow-orange crystals of **13b** (0.428 g, 69%). ^1H NMR: δ 1.07 (s, 9 H, ^tBu), 1.90 (br s, 6 H, Mes-Me), 1.96 (br s, 6 H, Mes-Me), 2.11 (s, 6 H, Mes-Me), 2.32 (s, 6 H, Mes-Me), 2.35 (s, 12 H, Mes-Me), 6.59 (d, 2 H, J = 7 Hz, Ar*-H), 6.70 (br s, 4 H, Ar*-H), 6.73 (t, 2 H, J = 7 Hz, Ar*-H), 6.77 (s, 2 H, Ar*-H), 6.82 (s, 1 H, Ar*-H), 6.83 (s, 1 H, Ar*-H), 6.85 (s, 2 H, Ar*-H), 6.88 (s, 2 H, Ar*-H), 6.99 (d, 2 H, J = 7 Hz, Ar*-H), 7.02 (m, 1 H, Ar*-H), 7.08 (t, 1 H, J = 7.5 Hz, Ar*-H), 7.11 (d, 1 H, J = 7 Hz, Ar*-H), 7.17 (d, 1 H, J = 3 Hz, Ar*-H), 7.31 (br s, 2 H, Ar*-H), 8.90 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 21.1, 21.4, 22.0, 22.1, 22.2 (Mes-Me's), 23.6 ($C(CH_3)_3$), 30.9 ($C(CH_3)_3$), 123.9, 125.0 (CH's), 126.0 (aromatic C), 127.9, 128.0, 128.1, 128.8 (CH's), 128.9, 129.7 (aromatic C's), 129.9 (CH), 130.1 (aromatic C), 130.7, 131.3, 131.8 (CH's), 131.9, 136.2, 136.4, 136.5, 137.3 (aromatic C's), 137.6, 138.4 (CH's), 139.1, 144.2, 149.7, 155.4 (aromatic C's). ^{29}Si NMR: δ 68.86 ($Si(^tBu)Ph_2$). IR (KBr, cm^{-1}): 3270 (w, ν_{NH}). Anal. Calcd for $(C_{64}H_{70}ClN_2SiTa)\cdot(C_5H_{12})_{0.5}$: C, 69.59; H, 6.67; N, 2.44. Found: C, 69.68; H, 6.69; N, 2.43.

(2,6-$Mes_2C_6H_3N$=)(2,6-$Mes_2C_6H_3NH$)Ta($SiHMes_2$)Cl (13c). An essentially identical procedure to that used to prepare **13a** (substituting $(THF)_2LiSiHMes_2$ for $(THF)_3LiSi(SiMe_3)_3$) yielded yellow crystals of **13c** (0.461 g, 80%). ^1H NMR: δ 1.83 (vbr s, 6 H, Mes-Me), 1.95 (vbr s, 6 H, Mes-Me), 2.08 (s, 3 H, Mes-Me), 2.12 (s, 3 H, Mes-Me), 2.14 (br s, 6 H, Mes-Me), 2.22 (s, 6 H, Mes-Me), 2.36 (s, 6 H, Mes-Me), 1.5−2.5 (vbr s, 18 H, Mes-Me), 5.32 (s, 1 H, J_{SiH} = 183 Hz, SiH), 6.59 (s, 2 H, Ar*-H), 6.60 (s, 2 H, Ar*-H), 6.64 (vbr s, 4 H, Ar*-H), 6.76 (br s, 2 H, Ar*-H), 6.77 (d, 1 H, J = 8 Hz, Mes-H), 6.79 (d, 1 H, J = 5 Hz, Mes-H), 6.82 (d, 2 H, J = 8 Hz, Mes-H), 6.84 (br s, 2 H, Ar*-H), 6.94 (d, 2 H, J = 8 Hz, Ar*-H), 9.20 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 20.7, 20.8 (br), 21.2, 21.3, 21.4, 21.5, 21.9 (Mes-Me's), 24.8 (br, Mes-Me), 123.9, 124.4, 128.6, 128.7 (CH's), 128.9 (aromatic C), 129.1, 129.3, 129.7, 131.1 (CH's), 136.2, 136.5, 137.6, 137.8 (br) 138.2, 138.5, 139.0, 143.6, 145.8 (br m), 145.8, 151.1, 154.6 (aromatic C's). ^{29}Si NMR: δ 6.92 (d, J_{SiH} = 181 Hz, $SiHMes_2$). IR (KBr, cm^{-1}): 3274 (m, ν_{NH}), 2120 (w, ν_{SiH}). Anal. Calcd for $C_{66}H_{74}ClN_2SiTa$: C, 69.55; H, 6.54; N, 2.46. Found: C, 69.26; H, 6.84; N, 2.21.

X-ray Structure Determinations. X-ray diffraction measurements were made on a Siemens SMART diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation. The crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. 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 4° (or 3.5°) < 2θ < 45°. The frame data were integrated using the program SAINT (SAX Area-Detector

Table 5. Crystallographic Data for Compounds 4, 8, and 11

	4	**8**	**11**
empirical formula	$C_{50}H_{57}N_2Ta$	$C_{58}H_{73}N_2Ta$	$C_{49}H_{50}F_3N_2O_3STa$
fw	866.96	979.16	984.95
cryst color, habit	yellow plate	yellow plate	red-orange tablet
cryst size (mm)	0.30 × 0.13 × 0.05	0.19 × 0.16 × 0.07	0.32 × 0.19 × 0.05
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)
a (Å)	18.2430(7)	10.9435(9)	10.9651(4)
b (Å)	11.1702(5)	43.319(4)	15.8166(5)
c (Å)	21.552(1)	12.4363(10)	27.5663(9)
β (deg)	104.766(2)	115.977(2)	95.869(1)
V (Å^3)	4246.7(3)	5299.9(8)	4755.8(2)
no. of orientation reflns (2θ range)	2701 (4.0−45.0°)	5338 (3.5−45.0°)	7126 (3.5−45.0°)
Z value	4	4	4
D_{calc} (g/cm^3)	1.356	1.272	1.376
F_{000}	1776.00	2116	1992.00
μ(Mo Kα) (cm^{-1})	26.19	2.11	24.04
diffractometer	SMART	SMART	SMART
radiation	Mo Kα ($\lambda = 0.71069$ Å) graphite monochromated	Mo Kα ($\lambda = 0.71069$ Å) graphite monochromated	Mo Kα ($\lambda = 0.71069$ Å) graphite monochromated
temperature (°C)	−112	−114(2)	−115.0
scan type	ω (0.3° per frame)	ω (0.3° per frame)	ω (0.3° per frame)
scan rate	10.0 s per frame	10.0 s per frame	10.0 s per frame
$2\theta_{max}$ (deg)	51.3	46.5	51.3
no. of reflns measd	total: 19234 unique: 8557	total: 24124 unique: 16564	total: 21548 unique: 8872
R_{int}	0.062	0.0457	0.058
transmn factors	$T_{max} = 0.98$ $T_{min} = 0.69$	$T_{max} = 0.83$ $T_{min} = 0.61$	$T_{max} = 0.89$ $T_{min} = 0.46$
structure solution	direct methods (SIR92)	direct methods (SHELXS-86)	direct methods (SIR92)
no. of observations	3140 ($I > 3.00\sigma(I)$)	13184 ($I > 2.00\sigma(I)$)	5137 ($I > 3.00\sigma(I)$)
no. of variables	481	1117	557
reflns/param ratio	6.53	11.80	9.22
residuals: R; R_w; R_{all}	0.027; 0.024; 0.101	0.0506; 0.0791; 0.0793	0.034; 0.036; 0.071
goodness of fit	0.65	0.942	1.05
max. shift/error in final cycle	0.00	0.018	0.01
max. and min. peaks in final diff map (e$^-$/Å^3)	0.83; −0.51	0.662; −0.542	0.64; −1.58

Integration Program; V4.024; Siemens Industrial Automation, Inc.: Madison, WI, 1995). An empirical absorption correction based on measurements of multiply redundant data was performed using the programs XPREP (part of the SHELXTL Crystal Structure Determination Package; Siemens Industrial Automation, Inc.: Madison, WI, 1995) or SADABS. Equivalent reflections were merged. The data were corrected for Lorentz and polarization effects. A secondary extinction correction was applied if appropriate. The structures were solved using the teXsan crystallographic software package of the Molecular Structure Corp. (compounds **4** and **11**) or the SHELXTL Crystal Structure Determination Package (compound **8**), using direct methods, and expanded with Fourier techniques. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in calculated positions but not refined unless otherwise noted. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_o|)^2$. The weighting scheme was based on counting statistics and included a p-factor to downweight the intense reflections (compounds **4** and **11**). Crystallographic data are summarized in Table 5.

For Compound 4. Crystals were grown by slowly cooling a concentrated pentane solution of compound **4** (68.6 mg, 10 mL) to −35 °C. The structure was found to contain one molecule of complex **4** per asymmetric unit. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined isotropically in geometrically calculated positions except for H(1), the amido NH, which was located from the difference Fourier map and its positional coordinates refined.

For Compound 8. Crystals were grown by cooling a concentrated pentane solution of compound **8** (104 mg, 20 mL) to −35 °C. The structure was found to contain two molecules of complex **8** and one molecule of pentane per asymmetric unit. The crystal was twinned with a twin law given by [−1 0 0 0−1 0 1 0 1], and the batch scale factor refined to 27.16(2)% twin. The enantiomorph was tested by refinement of inversion twin coefficients. The correct enantiomorph is as given with no evidence of inversion twinning in the refinement. All non-hydrogen atoms in the tantalum complexes were refined anisotropically, except for the methyl carbons attached to C(50), which were disordered rotationally over two positions with C(51A), C(51B), C(52A), C(52B), C(53A), and C(53B) refined isotropically in observed positions at 50% occupancy. The pentane appears as a normal aliphatic hydrocarbon with C(117)−C(121) refined isotropically. All hydrogen atoms were refined isotropically in geometrically calculated positions.

For Compound 11. Crystals were grown by vapor diffusion of pentane (∼3 mL) into a concentrated benzene-d_6 solution of compound **11** (30 mg, ∼0.7 mL) at room temperature followed by cooling to −35 °C. The structure was found to contain one molecule of complex **11** and one-half molecule of pentane per asymmetric unit. All non-hydrogen atoms in the tantalum complex were refined anisotropically. C(100) was added as the centroid of the η^5-cyclohexadienyl ligand, defined as the average of the x, y, and z coordinates of carbons C(2)−C(6). All hydrogen atoms for the tantalum complex were refined isotropically in geometrically calculated positions except for H(59), the amido NH, which was located from the difference Fourier map and its positional coordinates refined. The pentane appears as a normal aliphatic hydrocarbon with C(51) located on an inversion center, but is disordered over six positions with the internal carbons (C(51), C(52)) refined anisotropically at full occupancy, and the terminal carbons (C(50)) refined isotropically at 50% occupancy.

Acknowledgment is made to the National Science Foundation for their generous support of this work. We thank Dr. Frederick J. Hollander and Dr. Allen G. Oliver for assistance with the X-ray structure determinations, Dr. Rudi Nunlist for assistance with the ^{1}H-ROESY NMR experiment, and Professor Ian P. Rothwell (Purdue University) for insightful discussions.

Supporting Information Available: Complete IR data and ^{1}H-ROESY NMR spectra; tables of crystal, data collection, and refinement parameters, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for complexes **4**, **8**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020509Y