A Cationic Imido Complex of Permethyltantalocene: H_2 and Carbon−Hydrogen Bond Activation, [2 + 2] Cycloaddition Reactions, and an Unusual Reaction with Carbon Dioxide That Affords Coordinated Isocyanate

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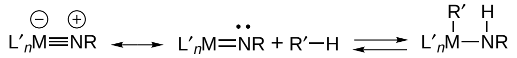
Treatment of the imido hydride complex $Cp^*_2Ta({=}NCMe_3)H$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$) with $[Ph_3C][B(C_6F_5)_4]$ in tetrahydrofuran solution yields the cationic imido complex $[Cp^*_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$ (**1**). Cation **1** reacts cleanly with H_2 to yield $[Cp^*_2Ta(NHCMe_3)H][B(C_6F_5)_4]$. Carbon−hydrogen bond-activation reactions are observed with propyne or phenylacetylene to afford $[Cp^*_2Ta(NHCMe_3)(C{\equiv}CR)][B(C_6F_5)_4]$ ($R = CH_3$, C_6H_5). In the reaction with propyne, an initial mixture of the [2 + 2] cycloaddition product and C−H activation product is thermally driven to the C−H activation product. The heterolytic cleavage reactions for **1** may be rationalized in terms of the presence of both electrophilic and nucleophilic sites of reactivity in the same molecule. Intramolecular activation of a carbon−hydrogen bond of a Cp* methyl group to ultimately yield $[Cp^*Ta(\eta^5\text{-}C_5Me_4CH_2NCMe_3)H][B(C_6F_5)_4]$ precludes C−H activation of the carbon−hydrogen bonds of methane. An unusual reaction occurs with carbon dioxide: dealkylation of the imido group is observed, liberating isobutylene and yielding the isocyanate complex $[Cp^*_2Ta(OH)(NCO)][B(C_6F_5)_4]$. Complex **1** reacts with HCl to afford $[Cp^*_2Ta(NHCMe_3)Cl][B(C_6F_5)_4]$ and decomposes cleanly in methylene chloride solution to give $[Cp^*_2Ta(NHCMe_3)Cl][B(C_6F_5)_4]$ by formal HCl abstraction. X-ray crystal structure determinations for $[Cp^*Ta(\eta^5\text{-}C_5Me_4CH_2NCMe_3)H][B(C_6F_5)_4]$, $[Cp^*_2Ta(NHCMe_3)Cl][B(C_6F_5)_4]$, $[Cp^*_2Ta(NHCMe_3)H][B(C_6F_5)_4]$, $[Cp^*_2Ta(NHCMe_3)(C{\equiv}CC_6H_5)][B(C_6F_5)_4]$ and $[Cp^*_2Ta(OH)(NCO)][B(C_6F_5)_4]$ are reported.

Introduction

Complexes containing metal−ligand multiple bonds constitute extremely interesting subjects of research in organometallic chemistry. Many of these complexes have been shown to be effective reagents or catalysts for oxidations, metathesis reactions, and ammoxidations.[1] Transition-metal−imido complexes have been studied as molecular precursors to thin films,[2] models of hydrodenitrogenation,[3] and probes of electronic structure *via* their luminescent properties.[4] For related alkylidene systems, which are effective metathesis and polymerization catalysts, imido ligands serve as tunable ancillary ligands.[5] Recent work with electrophilic imido complexes has revealed that they are capable of activating the carbon−hydrogen bonds of hydrocarbons (eq 1).[6] There is still great interest in the factors which control the extreme reactivity or (nearly) total inertness of metal−ligand multiple bonds.[7]



$$L'_n\overset{\ominus}{M}{\equiv}\overset{\oplus}{N}R \longleftrightarrow L'_nM{=}\ddot{N}R + R'{-}H \rightleftharpoons L'_n\overset{R'}{M}{-}\overset{H}{N}R \qquad (1)$$

We have described an imido complex of permethyltantalocene $Cp^*_2Ta({=}NCMe_3)H$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$) obtained by the reaction of *in-situ*-prepared tetrahydrofuran solutions of $Cp^*_2TaCl(THF)$ with $Li(NHCMe_3)$.[8]

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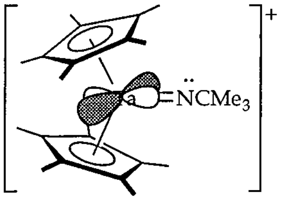
This reaction likely proceeds by an initial displacement of chloride by *tert*-butylamide, followed by an α-hydrogen elimination. $Cp^*_2Ta({=}NCMe_3)H$ serves as a convenient synthetic precursor to a cationic imido complex with the formula $[Cp^*_2Ta({=}NCMe_3)]X$, where X is a noncoordinating (or weakly coordinating) anion. The frontier orbitals of the bent metallocene are oriented such that a vacant orbital remains in the equatorial plane of the tantalocene moiety, giving rise to an interesting combination: an electrophilic tantalum center in close proximity to a nucleophilic nitrogen of the imido ligand.[9]

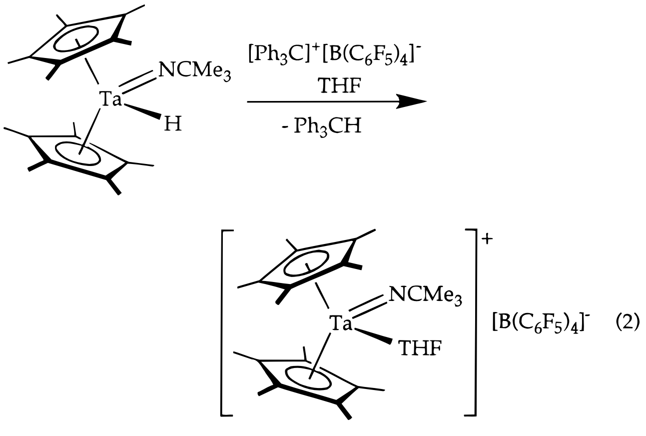


16 electron
LUMO = $1a_1$

Since the electrophilic nature of early transition metal centers is undoubtedly important to the high reactivity for their metal−imido groups, we reasoned that a cationic group 5 complex would exhibit greater reactivity than its isoelectronic neutral zirconium analogs, which have already been shown to activate the C−H bonds of benzene. In this article, we report the successful synthesis of $[Cp^*_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$ and our investigations of the reactivity of this complex toward methylene chloride, H_2, the C−H bonds of acetylenes, and unsaturated C−C and C−O bonds.

Results and Discussion

Preparation and Characterization of $[Cp^*_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$. The reaction between $[Ph_3C][B(C_6F_5)_4]$ and $Cp^*_2Ta({=}NCMe_3)H$ at low temperature in THF gives an orange solution of $[Cp^*_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$ (**1**), triphenylmethane, and a small amount of polytetrahydrofuran (eq 2).



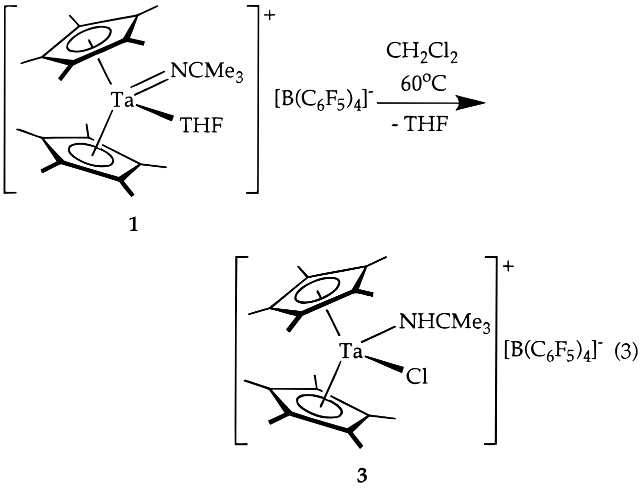
1

Large orange crystals of **1** could be isolated by layering methylene chloride solutions with petroleum ether. If the reaction is warmed too rapidly or $Cp^*_2Ta({=}NCMe_3)H$ is of insufficient purity, large amounts of polytetrahydrofuran are formed, precluding the isolation of the desired product.

If the reaction is carried out in benzene, a product precipitates immediately. Dissolution of this solid in methylene chloride and subsequent recrystallization affords the unusual cyclometalated product that arises from the intramolecular activation of a C−H bond of a Cp* ligand. An X-ray structure determination (Table 1) for $[Cp^*\overline{Ta(\eta^5\text{-}C_5Me_4CH_2N}CMe_3)H][B(C_6F_5)_4]$ (**2**) reveals the connectivity shown in Figure 1.

It is noteworthy that the methylene group ends up attached to nitrogen rather than tantalum, opposite to that expected on the basis of the previously observed regiochemistry given in eq 1. Presumably, the stability of the less strained pseudo-five-membered ring tautomer vis-á-vis the pseudo-four-membered ring alternative is the rationale for the product observed. Since no intermediates are observed during this reaction, it is not known whether the initial activation occurs in the traditional fashion, followed by a ring-expansion, or whether the isolated product is directly formed during the activation step (Scheme 1).

Reactivity of $[Cp^*_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$. The reaction of **1** with methylene chloride proceeds cleanly at 60 °C to give a single product. ^1H NMR spectra reveal a resonance at δ 7.18, the position and broadness of the peak suggesting an N−H. An X-ray structure determination (Figure 2, Table 1) identified the compound as $[Cp^*_2Ta(NHCMe_3)Cl][B(C_6F_5)_4]$ (**3**) (eq 3).



3

The tantalum−nitrogen distance of 1.94 Å is consistent with a single bond[10] and a Ta−N−C1 angle of 155.4°. A relatively weak absorption at 3355 cm^{-1} in the infrared spectrum is attributable to ν(N−H). Interestingly, when this reaction is carried out in methylene chloride-d_2, the N−***H*** resonance of the final product is prominent, suggesting either that the solvent

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(10) See, for example: Allen, F. H.; Davies, J. E. Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187. For 16 examples of Ta=N−R, *d*(Ta−N) from 1.707 to 1.830 Å mean 1.778 Å, angle range from 165.35° to 180°, mean of 173.23°. For 41 examples of Ta−NRR′, *d*(Ta−N) from 1.929 to 2.275 Å, mean of 2.004 Å, angle range from 104.21° to 144.62°, mean of 124.3°.

Table 1. Crystal Data[a]

compd no.	2	3	4	7	8
formula	$C_{48}H_{39}BF_{20}NTa$	$C_{48}H_{40}BClF_{20}NTa$	$C_{48}H_{41}BF_{20}NTa$	$C_{56}H_{45}BF_{20}NTa$	$C_{45}H_{31}BF_{20}NO_2Ta$
mol wt	1201.57	1238.02	1203.58	1303.71	1189.47
color	yellow	orange	yellow	yellow	orange
habit	irregular	prismatic	prismatic	blade	rod
cryst size, mm	0.15 × 0.37 × 0.78	0.04 × 0.15 × 0.37	0.37 × 0.44 × 0.55	0.15 × 0.30 × 0.40	0.30 × 0.36 × 0.45
cryst syst	triclinic	monoclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	15.692(3)	15.200(3)	10.719(2)	12.470(3)	12.626(3)
b, Å	17.045(4)	16.540(3)	15.076(3)	14.748(4)	12.763(3)
c, Å	19.208(4)	18.702(4)	15.275(3)	15.880(4)	15.352(3)
α, deg	94.23(2)	90	80.21(3)	100.32(2)	70.84(3)
β, deg	113.87(2)	92.30(3)	83.08(3)	109.39(2)	69.45(3)
γ, deg	96.90(2)	90	85.50(3)	97.98(2)	77.43(3)
V, $Å^3$	4621(2)	4698(2)	2410.5(8)	2648(1)	2173.4(8)
Z	4	4	2	2	2
d_{calc}, g cm^{-3}	1.727	1.750	1.658	1.635	1.818
μ, cm^{-1}	24.63	25.13	23.92	21.56	26.56
trans coeff	0.69, 1.13	0.09, 1.05	0.94, 1.06	0.83, 1.09	0.76, 1.10
decay, %	1.9		3.3	3.2	1.0
2θ range, deg	2, 40	2, 40	2, 40	3, 40	3, 45
h min, max	−15, 15	−3, 14	−10, 10	−12, 12	−12, 13
k min, max	−16, 16	−15, 15	−14, 14	−14, 14	−12, 13
l min, max	−18, 18	−17, 17	−14, 14	−15, 15	−14, 16
no. of reflns	17 795	9479	9274	9449	11 863
no. of indep reflns	8619	4366	4489	4915	5675
GOF merge (mult)	1.07 (8618)	1.02 (4171)	1.16 (3545)	1.16 (4134)	1.05 (5674)
R(*F*)	0.080[b]	0.089[c]	0.076[c]	0.049[b]	0.058[c]
$R_w(F^2)$[d]	0.084	0.080	0.127	0.020	0.069
GOF[e]	1.55	1.28	2.84	1.41	1.47
data, parameters	8617, 969	4366, 640	4489, 641	4915, 712	5675, 631
$\Delta\rho$ max, min, e $Å^{-3}$	1.46, −1.04	0.68, −1.26	1.75, − 0.64	0.98, −1.00	1.01, − 0.86

[a] Nonius CAD-4 diffractometer, Mo Kα radiation, $\lambda = 0.7107$ Å, graphite monochromator, ω scans, 293 K. [b] $R(F) = \Sigma|F_c - |F_o||/\Sigma F_o$, $F_o > 0$. [c] $R(F) = \Sigma||F_c| - F_o|/\Sigma|F_o|$. [d] $R_w(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$. [e] GOF $= [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$.

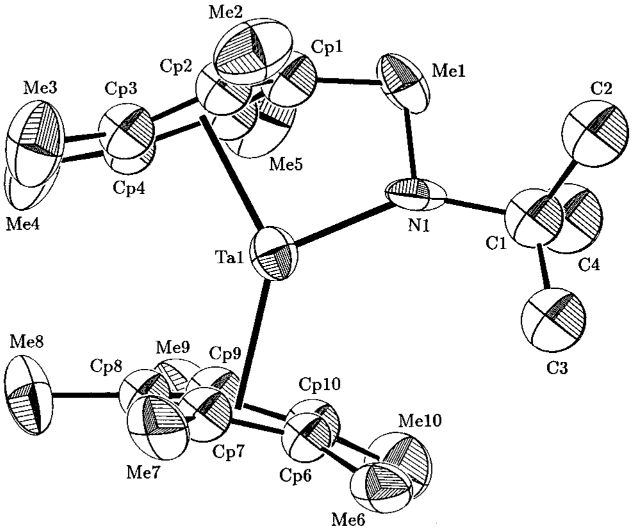


Figure 1. Drawing of the cation of $[Cp^*Ta(\eta^5\text{-}C_5Me_4CH_2\text{-}NCMe_3)H][B(C_6F_5)_4]$ (**2**) (50% ellipsoids). Ta1−Cp*(1) = 2.081 Å, Ta1−Cp*(2) = 2.131 Å, Ta1−N1 = 1.976(10) Å, N1−C1 = 1.555(17) Å, N1−Me1 = 1.441(16) Å, Cp1−Me1 = 1.479(19) Å; Cp*1−Ta1−Cp*2 = 137.8°, Ta1−N1−C1 = 146.1(8)°, Ta1−N1−C1 = 108.4(9)°.

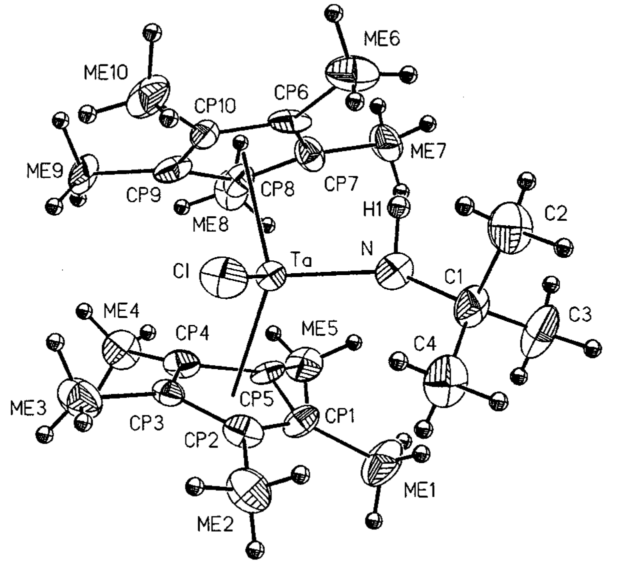
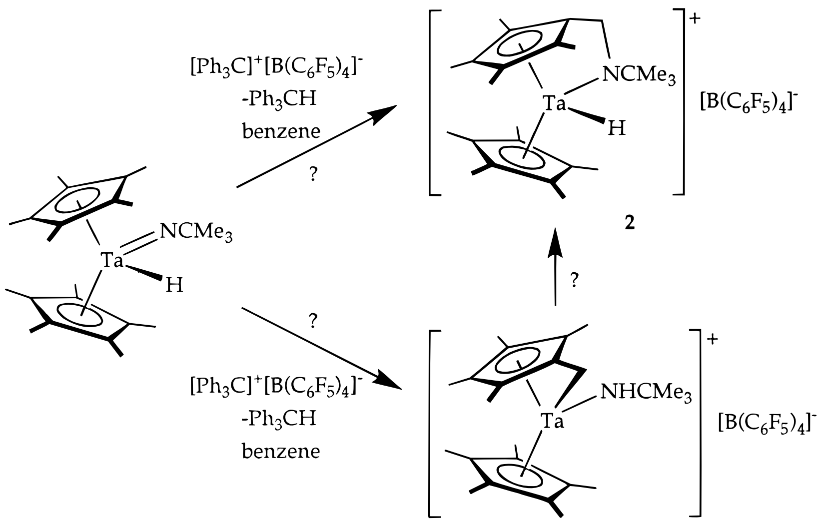


Figure 2. Drawing of the cation of $[Cp^*_2Ta(NHCMe_3)Cl]$-$[B(C_6F_5)_4]$ (**3**) (50% ellipsoids). Ta−Cp*(1) = 2.158 Å, Ta−Cp*(2) = 2.173 Å, Ta−N = 1.940(11) Å, Ta−Cl = 2.372(3) Å, N−C(1) = 1.511(14) Å, N−H(1) = 1.180(11) Å, Ta−H(1) = 2.31 Å; Cp*1−Ta−Cp*2 = 132.5°, N−Ta−Cl = 94.1(3)°, Ta−N−C1 = 155.4(9)°.

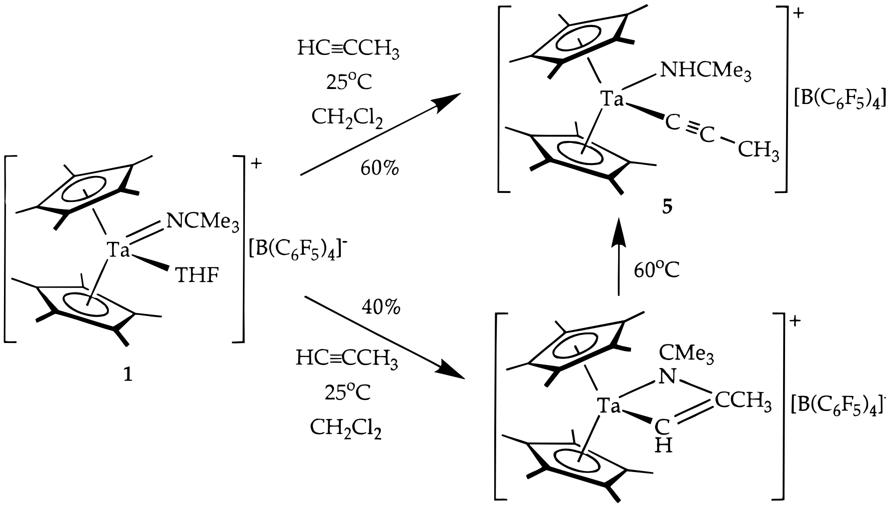
is not the source of the hydrogen or that [N−H] is readily exchanged with residual protons of the glass. No experiments have been conducted to attempt to resolve this issue, however.

Since the reaction between $[Cp^*_2Ta({=}NCMe_3)(THF)]$-$[B(C_6F_5)_4]$ and methylene chloride is formally abstraction of HCl from the solvent, the direct reaction of **1** with 1 equiv of HCl was carried out on an NMR-tube scale in methylene chloride-d_2. The reaction affords principally **3**, but also another Cp*-containing product and a white precipitate are formed. The minor product does not contain a tertiary butyl group and is tentatively postulated to be $[Cp^*_2TaCl_2][B(C_6F_5)_4]$. It is likely that to a small extent HCl reacts further with the initial amido-chloro product **3** to cleave the *tert*-butylamido group from the metal, which precipitates as Me_3CNH_3-Cl.

Scheme 1



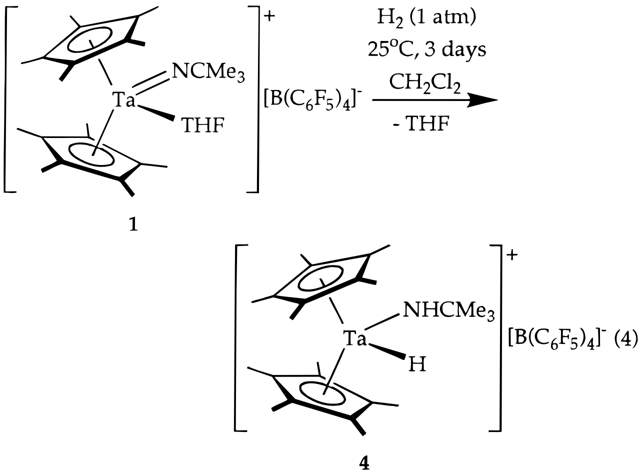
Scheme 2



Reaction of methane with **1** was attempted in methylene chloride solution, but even under a several atmospheres of methane pressure, the only product observed was complex **3**. In the less-reactive solvent chlorobenzene, the attempted reaction with methane yielded only the "tuck-in" product **2**. Thus, the intramolecular C−H bond-activation process for **1** appears to preclude reactions with methane.

The availability of $[Cp^*{}_2Ta(NHCMe_3)Cl][B(C_6F_5)_4]$ (**3**) prompted the attempted synthesis of $[Cp^*{}_2Ta(NHCMe_3)(CH_3)][B(C_6F_5)_4]$, the expected product from the activation of a carbon−hydrogen bond of methane by **1**. Should this compound exhibit sufficient thermal stability, one could conclude that the lack of reactivity of **1** with methane is likely kinetic not thermodynamic in nature. Unfortunately, we have been unable to cleanly convert **3** to $[Cp^*{}_2Ta(NHCMe_3)(CH_3)][B(C_6F_5)_4]$. ^1H NMR experiments indicated that the alkylating agent dimethylmercury (as well as diethylzinc) undergoes no reaction with **3**. Whereas addition of methyllithium to **3** does lead to rapid evolution of methane, simple deprotonation occurs in preference to metathesis of the Ta−Cl bond with $LiCH_3$, as evidenced by the formation of $Cp^*{}_2Ta({=}NCMe_3)Cl$ rather than $[Cp^*{}_2Ta(NHCMe_3)(CH_3)][B(C_6F_5)_4]$ and LiCl.

$[Cp^*{}_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$ (**1**) does, however, react cleanly with dihydrogen (eq 4).



The NMR spectrum of the recrystallized product (**4**) shows two broad downfield peaks at δ 7.74 and 8.52,

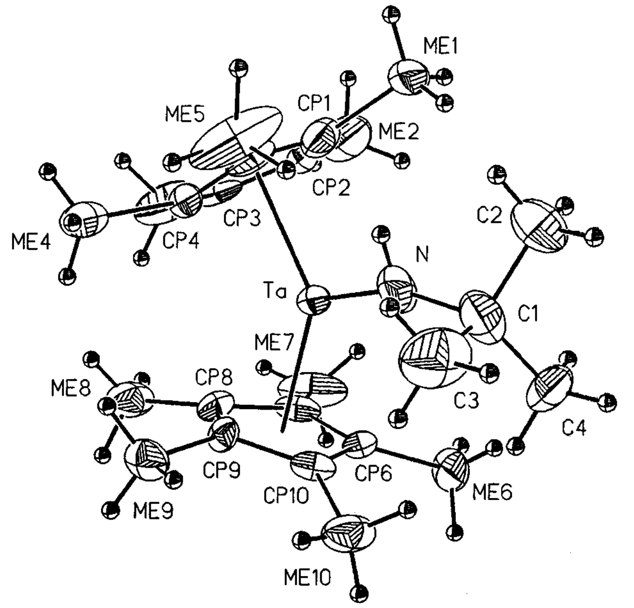
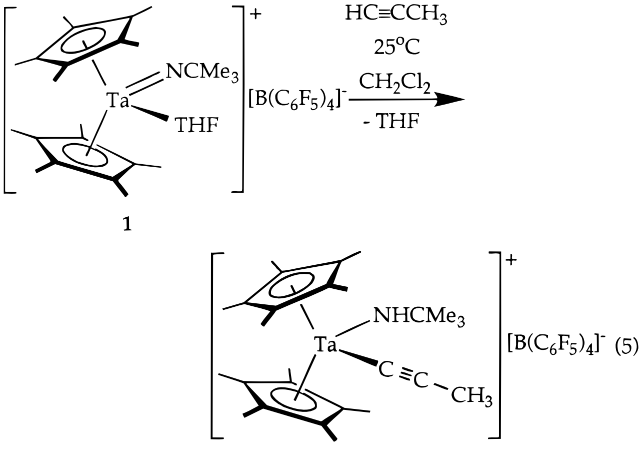


Figure 3. Drawing of the cation of [Cp*$_2$Ta(NHCMe$_3$)H][B(C$_6$F$_5$)$_4$] (**4**) (50% ellipsoids). Ta−Cp*(1) = 2.14 Å, Ta−Cp*(2) = 2.12 Å, Ta−N = 1.93(2) Å, N−C1 = 1.59(3) Å; Cp*1−Ta−Cp*2 = 137°, Ta−N−C1 = 159(2)°.

consistent with the expected amido−hydride product [Cp*$_2$Ta(NHCMe$_3$)H][B(C$_6$F$_5$)$_4$]. An infrared resonance is observed at 3336 cm^{-1} attributable to ν(N−H), and another is observed at 1862 cm^{-1} attributable to ν(Ta−H). An X-ray structural determination (Table 1) confirmed the structure of **4** (Figure 3). When solutions of **4** in methylene chloride are allowed to stand for prolonged periods at room temperature, **3** is slowly formed.

Given the relative ease with which **1** reacts with H$_2$, we then examined acetylenes in the hopes that their C−H bonds, with a relatively large amount of s character, might prove more reactive than the sp^3-hybridized C−H bonds of methane. Thus, reaction of **1** and propyne was examined. After a few hours at room temperature, the ^{1}H NMR signals for **1** are replaced by two sets of new Cp* and *tert*-butyl resonances. The presence of a broad peak at δ 7.02 suggested that the expected C−H activation had taken place to form [Cp*$_2$Ta(NHCMe$_3$)(C≡CCH$_3$)][B(C$_6$F$_5$)$_4$] (**5**) (eq 5).



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The observation of a resonance in the infrared spectrum at 3338 cm^{-1} attributable to ν(N−H) further supports this hypothesis. The other product has been identified as the [2 + 2] addition product, azametallacyclobutene, tentatively assigned to have the following isomeric structure: [Cp*$_2$TaN(CMe$_3$)C(CH$_3$)=CH][B(C$_6$F$_5$)$_4$] (**6**). Heating the initially formed *ca.* 60:40 mixture of **5** and **6** to 60 °C for several hours results in conversion entirely to the C−H activation product **5** (Scheme 2).

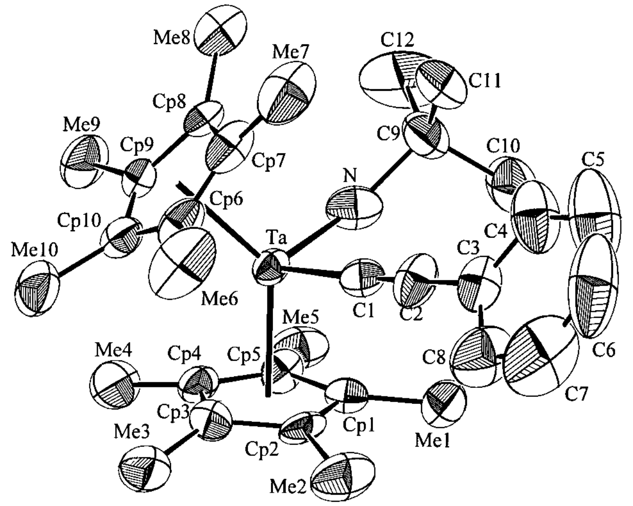
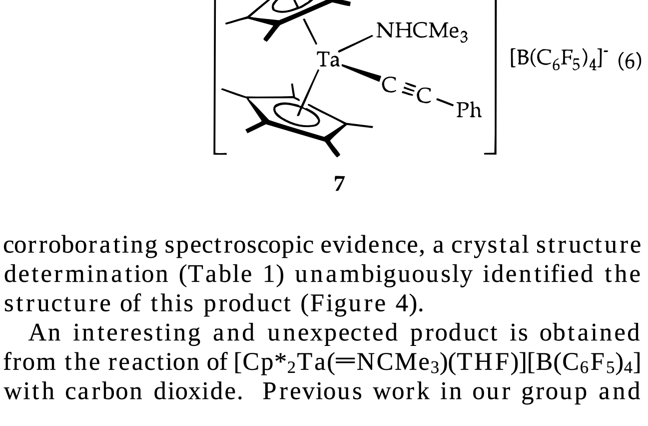


Figure 4. Drawing of the cation of [Cp*$_2$Ta(NHCMe$_3$)(C≡CC$_6$H$_5$)][B(C$_6$F$_5$)$_4$] (**7**) (50% ellipsoids). Ta−Cp(A) = 2.157 Å, Ta−Cp(B) = 2.172 Å, Ta−N = 1.928(7) Å, Ta−C1 = 2.097(9) Å, N−C9 = 1.570(12) Å, C1−C2 = 1.202(13) Å, C2−C3 = 1.459(14) Å; Cp(A)−Ta−Cp(B) = 134.7°, N−Ta−Cl = 92.5(3)°, Ta−N−C9 = 151.8(6)°.

On the basis of the hypothesis that the C−H activation is essentially a heterolysis reaction, a more acidic substrate was chosen in the hopes that the C−H activation product would predominate. Indeed, phenylacetylene reacts rapidly and cleanly with [Cp*$_2$Ta(=NCMe$_3$)(THF)][B(C$_6$F$_5$)$_4$] at room temperature to give the expected C−H addition product [Cp*$_2$Ta(NHCMe$_3$)(C≡CC$_6$H$_5$)][B(C$_6$F$_5$)$_4$] (**7**) (eq 6). In addition to the corroborating spectroscopic evidence, a crystal structure determination (Table 1) unambiguously identified the structure of this product (Figure 4).



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An interesting and unexpected product is obtained from the reaction of [Cp*$_2$Ta(=NCMe$_3$)(THF)][B(C$_6$F$_5$)$_4$] with carbon dioxide. Previous work in our group and

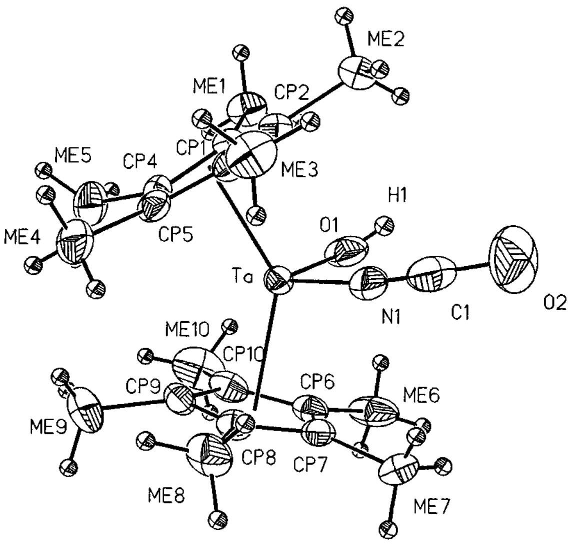


Figure 5. Drawing of the cation of $[Cp^*_2Ta(OH)(NCO)][B(C_6F_5)_4]$ (**7**) (50% ellipsoids). Ta−Cp*(1) = 2.131 Å, Ta−Cp*(2) = 2.142 Å, Ta−O1 = 1.926(5) Å, Ta−N1 = 1.944(7) Å, N1−C1 = 1.076(11) Å, C1−O2 = 1.320(12) Å, O1−H1 = 0.77 Å; Cp*(1)−Ta−Cp*(2) = 138.9°, O1−Ta−N1 = 99.4(3)°, Ta−N−C1 = 163.8(10)°, Ta−O1−H1 = 114.5(2)°.

others gave precedent for a formal [2 + 2] addition to form an η^2-carbamate complex. Instead, a rapid reaction gave a product that is lacking the *tert*-butyl group, according to elemental analysis and ^{1}H NMR. An X-ray structure determination (Figure 5, Table 1) was required to finally establish the structure as $[Cp^*_2Ta(OH)(NCO)][B(C_6F_5)_4]$ (**8**) (Scheme 3).

Although rather speculative, we propose that the initially formed [2 + 2] product likely undergoes a productive retro-[2 + 2] to generate an oxo intermediate that subsequently abstracts a proton from *tert*-butyl with the release of isobutylene. (Scheme 4).

Re-examination of the data from the original sealed-tube NMR experiment confirmed the presence of isobutylene in the product mixture. No other ^{1}H NMR signals, in particular those for isobutane, were observed, arguing against the intermediacy of $^•CMe_3$ radicals during the formation of **8**. Reaction of **1** with $^{13}CO_2$ allowed unambiguous assignment of ν(C−O) at 2252 cm^{-1} for the isocyanato complex, which shifts by 62 cm^{-1} upon isotopic substitution. This unusual transformation represents an interesting new carbon−nitrogen bond-cleavage reaction promoted by carbon dioxide, albeit with simultaneous formation of a (CO_2-derived) carbon−nitrogen bond.

Conclusions

The hoped-for reactivity of $[Cp^*_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$ with methane was not observed due to a facile intramolecular C−H activation reaction. The noninnocence of the ancillary Cp* ligand has proven to be problematic for this extremely reactive compound. Even so, many reactions were found to be competitive with the intramolecular reaction, permitting the synthesis and characterization of a number of new cationic complexes of permethyltantalocene. The anticipated C−H activation is observed for the fairly reactive and unhindered sp C−H bonds. Particularly interesting was the reaction of $[Cp^*_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$ with carbon dioxide, which results in dealkylation of the imido ligand.

The importance of unreactive ancillary ligands once again is underscored by the observed reactivity of $[Cp^*_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$. In this regard, the parent tantalocene analog $[(\eta^5{-}C_5H_5)_2Ta({=}NR)(L)]^+$ might prove reactive toward a wider range of C−H bonds and unsaturated substrates. The original proposal that more electrophilic metal imido complexes would be more reactive toward hydrocarbon C−H bonds is supported by these studies. In reactions with acetylenes, the C−H activation products proved to be more stable than the [2 + 2] addition products. While C−H activation undoubtedly is encouraged by the polar Ta=N bond, the key feature is likely the highly electrophilic, cationic tantalum center.

Experimental Section

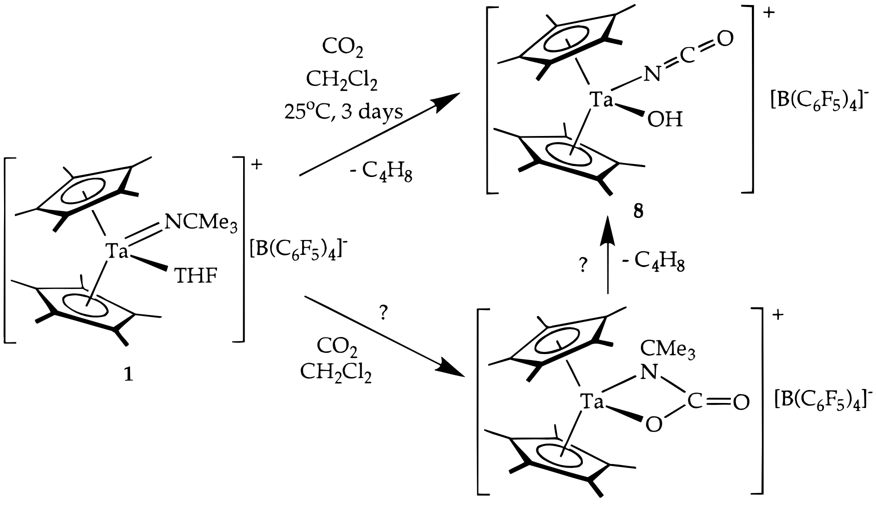
General Considerations. All air- and/or moisture-sensitive compounds were manipulated using standard Schlenk techniques or in a drybox under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a General Electric QE 300 (300.152 MHz for ^{1}H) spectrometer and referenced to residual proton impurities or carbon signals in the NMR solvent. Fluorine spectra were recorded on a Bruker AM500 (500.13 MHz for ^{1}H) spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 series spectrophotometer as Nujol mulls. Elemental analyses were performed by Fenton Harvey at Caltech. Preliminary NMR reactions were all performed using Teflon-valved NMR tubes. ^{1}H NMR and ^{13}C NMR spectra are summarized in Tables 2 and 3, respectively.

Synthesis of $[Cp^*_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$ (1). $Cp^*_2Ta(NHCMe_3)H$ (2.13 g, 4.07 × 10^{-4} mol) was treated with $Ph_3C[B(C_6F_5)_4]$ (3.75 g, 4.07 × 10^{-4} mol) in 75 mL of THF at room temperature. The color changed from deep purple to brown to orange over a period of 1 h. After a total of 2 h of stirring, THF was removed to a volume of 10 mL *in vacuo* and 50 mL of petroleum ether was condensed onto the residue. After initially oiling out, the residue became a solid in about 5 min. The yellow solid was collected by filtration and washed with petroleum ether twice. After pumping on the solid overnight, the yellow product (4.21 g, 82%) was collected. Recrystallization by layering a methylene chloride solution with petroleum ether afforded 2.4 g of large orange crystals. Anal. Calcd for $C_{52}H_{37}BF_{20}NO$: C, 49.43; H, 2.95; N, 1.11. Found: C, 48.48, 48.75; H, 3.62, 3.68; N, 0.99, 0.80. IR: 1213 (m), 847 (m) cm^{-1}.

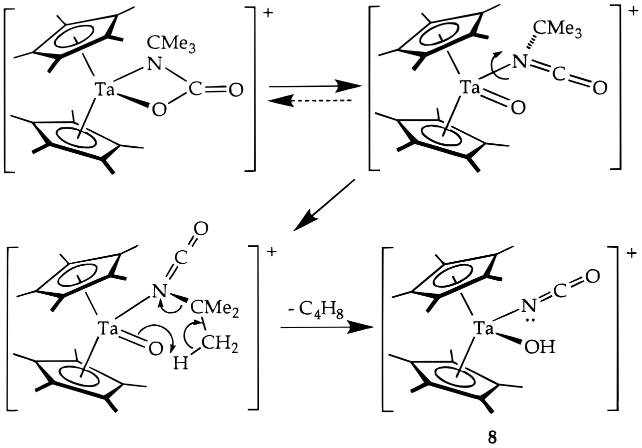
Synthesis of $[Cp^*_2Ta(NHCMe_3)Cl][B(C_6F_5)_4]$ (3). $[Cp^*_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$ (0.5 g, 3.95 × 10^{-4} mol) was placed in a small Teflon-valved flask with 5 mL of methylene chloride in the glovebox. This flask was placed in an oil bath and heated to 55 °C for 12 h. The yellow-brown solution from the reaction was pumped down to a brown oily solid *in vacuo.* The product was purified by recrystallization from a methylene chloride and diethyl ether solution, which was layered with petroleum ether. The orange crystals were isolated by decanting as much solvent as possible and evaporation of the residual *in vacuo* (0.322 g isolated, 69% yield). A suitable crystal for structural analysis by X-ray diffraction was cleaved from a larger orange needle. Anal. Calcd for $C_{48}H_{40}BClF_{20}N$: C, 46.57; H, 3.26; N, 1.13. Found: C, 46.45; H, 3.39; N, 0.98. ^{19}F NMR (methylene chloride-d_2): δ −135.2 (d), −165.9 (t), −169.7 (t). IR: 3355 (w), 1181 (m) cm^{-1}.

Alternate Synthesis of $[Cp^*_2Ta(NHCMe_3)Cl][B(C_6F_5)_4]$ (NMR-tube scale). $[Cp^*_2Ta({=}NCMe_3)(THF)][B(C_6F_5)_4]$ (0.1 g, 8 × 10^{-5} mol) was placed in a small Teflon-valved NMR tube with 0.7 mL of methylene chloride in the glovebox. A 6.9 mL gas bulb was attached to the NMR tube, evacuated,

Scheme 3



Scheme 4



and filled with 220 Torr of HCl at 25 °C. The contents of the tube were frozen at 77 K, and the HCl was opened to the tube. Upon warming to room temperature, a flocculate white precipitate was present in the solution (multiple products by NMR). The tube was warmed to 60 °C for 1 h, during which time the precipitate dissolved. The primary product is [Cp*$_2$-Ta(NHCMe$_3$)Cl][B(C$_6$F$_5$)$_4$]

Synthesis of [Cp*$_2$Ta(NHCMe$_3$)H][B(C$_6$F$_5$)$_4$] (4). [Cp*$_2$-Ta(=NCMe$_3$)(THF)][B(C$_6$F$_5$)$_4$] (0.5 g, 3.95×10^{-4} mol) was placed in a small (15 mL) Teflon-valved flask with 5 mL of methylene chloride in the glovebox. The flask was evacuated, and 1 atm of hydrogen (approximately 6×10^{-4} mol) was added at room temperature. The solution was stirred for 3 days, then the resulting yellow solution was pumped down to a yellow solid *in vacuo*. It was purified by recrystallization by layering a methylene chloride solution of the compound with petroleum ether (yield 0.380 g, 80%). A single crystal for structure determination by X-ray diffraction was grown by layering a methylene chloride solution with petroleum ether. Anal. Calcd for $C_{48}H_{41}BF_{20}N$: C, 47.90; H, 3.43; N, 1.16; Found: C, 47.54; H, 3.45; N, 0.96. ^{19}F NMR (methylene chloride-*d*$_2$): δ −135.2 (d), −165.9 (t), −169.8 (t). IR: 3336 (w), 1862 (w, br), 1182 (m) cm^{-1}.

Initial Reaction of [Cp*$_2$Ta(=NCMe$_3$)(THF)][B(C$_6$F$_5$)$_4$] with Propyne. [Cp*$_2$Ta(=NCMe$_3$)(THF)][B(C$_6$F$_5$)$_4$] (0.500 g, 3.95×10^{-4} mol) was placed in a Teflon-valved 100 mL flask, and 10 mL of dry methylene chloride was vacuum transferred into the flask. Once the solid was dissolved and the solution warmed to room temperature, approximately 1 atm of propyne (about 3.6×10^{-3} mol) was transferred into the flask. This reaction flask was allowed to stir overnight, during which time the orange solution turned yellow-brown. The solution was then pumped to dryness *in vacuo*. The brownish-yellow product was recrystallized by layering a methylene chloride solution with petroleum ether. Yield: 0.336 g (69%). Anal. Calcd for $C_{51}H_{43}BF_{20}N$: C, 49.66; H, 3.49; N, 1.13. Found: C, 49.59; H, 3.67; N, 1.04. ^{19}F NMR (methylene chloride-*d*$_2$): δ −135.2 (d), −165.9 (t), −169.8 (t).

Table 2. ^{1}H NMR Data[a]

compd	assignment	δ (coupling, Hz)
[Cp*$_2$Ta(=NCMe$_3$)(THF)][B(C$_6$F$_5$)$_4$] (**1**)	C$_5$(C***H***$_3$)$_5$	2.14
	(C***H***$_3$)$_3$C	1.32
	OC***H***$_2$	4.19
	OCH$_2$C***H***$_2$	2.21
[Cp*Ta(η^5-C$_5$Me$_4$CH$_2$NCMe$_3$)H][B(C$_6$F$_5$)$_4$] (**2**)	C$_5$(C***H***$_3$)$_5$	2.19
	(C***H***$_3$)$_3$C	1.18
	Ta***H***	8.58
	NC***H***$_2$	4.59 (d of d)
	C$_5$(C***H***$_3$)$_4$	1.95
		2.06
		2.27
		2.64
[Cp*$_2$Ta(NHCMe$_3$)Cl][B(C$_6$F$_5$)$_4$] (**3**)	C$_5$(C***H***$_3$)$_5$	2.22
	(C***H***$_3$)$_3$C	1.26
	N***H***	7.18
[Cp*$_2$Ta(NHCMe$_3$)H][B(C$_6$F$_5$)$_4$] (**4**)	C$_5$(C***H***$_3$)$_5$	2.22
	(C***H***$_3$)$_3$C	1.30
	N***H***	7.74
	Ta***H***	8.52
[Cp*$_2$Ta(NHCMe$_3$)(C≡CCH$_3$)][B(C$_6$F$_5$)$_4$] (**5**)	C$_5$(C***H***$_3$)$_5$	2.17
	(C***H***$_3$)$_3$C	1.24
	N***H***	7.02
	C***H***$_3$C≡C	1.95[b]
[Cp*$_2$TaN(CMe$_3$)CH=CCH$_3$][B(C$_6$F$_5$)$_4$] (**6**)	C$_5$(C***H***$_3$)$_5$	2.07
	(C***H***$_3$)$_3$C	1.35
	C≡C***H***	4.57 (q, *J* = 2 Hz)
	C***H***$_3$C≡C	2.84 (d, *J* = 2 Hz)
[Cp*$_2$Ta(NHCMe$_3$)(C≡CC$_6$H$_5$)][B(C$_6$F$_5$)$_4$] (**7**)	C$_5$(C***H***$_3$)$_5$	2.24
	(C***H***$_3$)$_3$C	1.29
	N***H***	7.33 (br)
	C$_6$***H***$_5$	7.35 (m)
		7.40 (m)
[Cp*$_2$Ta(OH)(NCO)][B(C$_6$F$_5$)$_4$] (**8**)	C$_5$(C***H***$_3$)$_5$	2.21
	O***H***	8.26 (br)

[a] Spectra were taken in methylene chloride-*d*$_2$ and referenced to residual proton impurities at 5.32 ppm unless indicated otherwise. [b] Chemical shift was not unambiguously resolved.

Synthesis of [Cp*$_2$Ta(NHCMe$_3$)(C≡CCH$_3$)][B(C$_6$F$_5$)$_4$] (5). The solid from the initial reaction of [Cp*$_2$Ta(=NCMe$_3$)-

Table 3. ^{13}C NMR Data[a]

compd	assignment	δ (coupling, Hz)
[Cp*$_2$Ta(=NCMe$_3$)(THF)][B(C$_6$F$_5$)$_4$] (**1**)	$\mathbf{C}_5(\mathrm{CH}_3)_5$	123.4
	$(\mathbf{C}\mathrm{H}_3)_3\mathrm{C}$	34.9
	$\mathrm{C}_5(\mathbf{C}\mathrm{H}_3)_5$	12.7
	$(\mathrm{CH}_3)_3\mathbf{C}$	68.6
	$\mathrm{O}\mathbf{C}\mathrm{H}_2$	88 (br)
	$\mathrm{OCH}_2\mathbf{C}\mathrm{H}_2$	27.4
	$\mathbf{C}_6\mathrm{F}_5$[b]	136.3 (d, J_{CF} =246)
		138.3 (d, J_{CF} = 245)
		148.1 (d, J_{CF} = 242)
[Cp*$_2$Ta(NHCMe$_3$)Cl][B(C$_6$F$_5$)$_4$] (**3**)	$\mathbf{C}_5(\mathrm{CH}_3)_5$	124.5
	$(\mathbf{C}\mathrm{H}_3)_3\mathrm{C}$	31.9
	$\mathrm{C}_5(\mathbf{C}\mathrm{H}_3)_5$	11.9
	$(\mathrm{CH}_3)_3\mathbf{C}$	65.5
[Cp*$_2$Ta(NHCMe$_3$)H][B(C$_6$F$_5$)$_4$] (**4**)	$\mathbf{C}_5(\mathrm{CH}_3)_5$	118.4
	$(\mathbf{C}\mathrm{H}_3)_3\mathrm{C}$	34.0
	$\mathrm{C}_5(\mathbf{C}\mathrm{H}_3)_5$	12.1
	$(\mathrm{CH}_3)_3\mathbf{C}$	64.3
[Cp*$_2$Ta(NHCMe$_3$)(C≡CCH$_3$)][B(C$_6$F$_5$)$_4$] (**5**)	$\mathbf{C}_5(\mathrm{CH}_3)_5$	121.9
	$(\mathbf{C}\mathrm{H}_3)_3\mathrm{C}$	32.6
	$\mathrm{C}_5(\mathbf{C}\mathrm{H}_3)_5$	12.3
	$(\mathrm{CH}_3)_3\mathbf{C}$	64.83
	$\mathbf{C}{\equiv}\mathbf{C}\mathrm{CH}_3$	119.7
		131.8
	$\mathrm{C}{\equiv}\mathrm{C}\mathbf{C}\mathrm{H}_3$	11.35[c]
[Cp*$_2$TaN(CMe$_3$)CH=CCH$_3$][B(C$_6$F$_5$)$_4$] (**6**)	$\mathbf{C}_5(\mathrm{CH}_3)_5$	121.9
	$(\mathbf{C}\mathrm{H}_3)_3\mathrm{C}]$	33.4
	$\mathrm{C}_5(\mathbf{C}\mathrm{H}_3)_5$	11.9
	$(\mathrm{CH}_3)_3\mathbf{C}$	61.1
[Cp*$_2$Ta(NHCMe$_3$)(C≡CC$_6$H$_5$)][B(C$_6$F$_5$)$_4$] (**7**)	$\mathbf{C}_5(\mathrm{CH}_3)_5$	122.0
	$(\mathbf{C}\mathrm{H}_3)_3\mathrm{C}$	32.6
	$\mathrm{C}_5(\mathbf{C}\mathrm{H}_3)_5$	12.4
	$(\mathrm{CH}_3)_3\mathbf{C}$	65.5
	$\mathbf{C}{\equiv}\mathbf{C}\mathrm{Ph}$	133.3
		124.0
	$\mathbf{C}_6\mathrm{H}_5$	128.3
		128.7
		130.4
		146.5
[Cp*$_2$Ta(OH)(NCO)][B(C$_6$F$_5$)$_4$] (**8**)	$\mathbf{C}_5(\mathrm{CH}_3)_5$	126.0
	$\mathrm{C}_5(\mathbf{C}\mathrm{H}_3)_5$	10.9
	$\mathrm{N}\mathbf{C}\mathrm{O}$	140.8

[a] All spectra were recorded in methylene chloride-d_2. [b] The chemical shifts of the anion for all compounds in this table were within the experimental error of these values. [c] Peak assignment is ambiguous due to impurities in the sample and/or low signal-to-noise ratio.

(THF)][B(C$_6$F$_5$)$_4$] with propyne was placed in a 25 mL Teflon-valved flask, and 5 mL of dry methylene chloride was added to the flask in the glovebox. This reaction vessel was placed in a 60 °C oil bath for 12 h. After removal of the solvent *in vacuo*, the crude product was recrystallized by layering a methylene chloride solution with petroleum ether. The NMR spectrum confirmed the product identity. IR: 3338 (w), 2115 (w), 1189 (m) cm^{-1}.

Synthesis of [Cp*$_2$Ta(NHCMe$_3$)(C≡CPh)][B(C$_6$F$_5$)$_4$] (7). [Cp*$_2$Ta(=NCMe$_3$)(THF)][B(C$_6$F$_5$)$_4$] (0.500 g, 3.95×10^{-4} mol) was placed in a Teflon-valved 15 mL flask, and 5 mL of dry methylene chloride was pipetted into the flask in the glovebox. Also in the glovebox, 45 μL of phenylacetylene was syringed into the flask. The reaction mixture was stirred overnight. The resulting red solution was reduced in volume to 2 mL *in vacuo*, then 6 mL of petroleum ether was layered onto it. Initially, a viscous oil settled out of the solution, but after vigorous shaking, the product crystallized. X-ray quality crystals were isolated from the crude product and a structure determined. Yield: 0.453 g (88%). Anal. Calcd for $C_{56}H_{45}BF_{20}N$: C, 51.59; H, 3.48; N, 1.07. Found: C, 51.10; H, 3.56; N, 1.10. ^{19}F NMR (methylene chloride-d_2) δ −135.2 (d), −165.9 (t), −169.8 (t). IR: 3342 (w), 2098, 1184 (m) cm^{-1}.

Synthesis of [Cp*$_2$Ta(NCO)(OH)][B(C$_6$F$_5$)$_4$]. [Cp*$_2$Ta(=NCMe$_3$)(THF)][B(C$_6$F$_5$)$_4$] (0.5 g, 3.95×10^{-4} mol) was placed in a Teflon-valved 100 mL flask, and 10 mL of dry methylene chloride was vacuum transferred into the flask. Approximately 1 atm of carbon dioxide (about 3.6×10^{-3} mol) was transferred into the flask. This reaction vessel was allowed to stir for 3 days, during which time the orange solution turned greenish-yellow. The reaction mixture was then pumped to dryness *in vacuo*. The yellow product was recrystallized by layering a methylene chloride solution with petroleum ether. Yield: 0.400 g (85%). Repeated recrystallizations were successful for the isolation of a crystal suitable for an X-ray structure determination. Anal. Calcd for $C_{45}H_{31}BF_{20}NO_2$: C, 45.44; H, 2.63; N, 1.18. Found: C, 45.52; H, 2.61; N, 1.18. ^{19}F NMR (methylene chloride-d_2): δ −135.2 (d), −165.9 (t), −169.7 (t). IR: 3490 (w, br), 3611 (w), 2252 (s), 2190 (s) cm^{-1}.

X-ray Crystal Structure Determinations. For each compound, a suitable crystal was mounted with grease in a capillary tube and optically centered on the diffractometer. The unit cell was determined from setting angles of 25 reflections. Two equivalent sets of data were collected. Table 1 summarizes the crystallographic data. Lorentz and polarization factors were applied, decay (based on 2 or 3 standards) and absorption (based on ψ-scans of 6 reflections) corrections were made, and the data were then merged in the appropriate point group with CRYM[11] programs. Weights w were calculated as $1/\sigma^2(F_o^2)$; variances $(\sigma^2(F_o^2))$ were derived from counting statistics plus an additional term $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014\bar{I})^2$.

Structures **3**, **4**, **7**, and **8** were solved with SHELXS-86[12] by either direct methods or the Patterson technique; **2** was solved using CRYM and a Patterson map. The remaining non-hydrogen atoms were found by successive refinement−difference Fourier syntheses. The hydrogen atoms were included in the refinement as riding atoms, except in **2** where the atoms were fixed but repositioned toward the end of refinement. Most hydrogen-atom coordinates were calculated from the expected chemical positions. For **2**, 14 of the 18 cyclopentadienyl methyl groups (in the two independent cations) showed disordered hydrogen atoms; these were modeled as two sets with 0.5 population each. The hydride on the tantalum was not included. For **3**, the hydrogen on the nitrogen was located in a difference map and included as a riding atom. For **4**, neither the hydrogen bonded to the nitrogen nor the hydride on the tantalum were included. For **7**, the hydrogen on the nitrogen was located in a difference map and included as a riding atom. For **8**, the hydroxyl hydrogen was located in a difference map and included as a riding atom. All non-hydrogen atoms were refined anisotropically. Refinement was full matrix least-squares on F^2 using either CRYM (**2**, **7**) or SHELXL-93[13] (**3**, **4**, **8**). For **4**, extinction coefficient of 0.0011(3) was included.

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OM970815P

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