Early-Transition-Metal-Mediated [2 + 2 + 2] Cycloadditions: Formation and Fragmentation of a Reactive Metallacyclopentadiene and Its Direct Conversion to η^6-Arene and η^2-Pyridine Complexes of Tantalum

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The kinetic product from reducing $\mathrm{Ta(DIPP)_2Cl_3(OEt_2)}$ (where DIPP = $\mathrm{O\text{-}2,6\text{-}C_6H_3{}^iPr_2}$) in the presence of $\mathrm{HC{\equiv}CCMe_3}$ is the α,α' metallacyclopentadiene complex $\mathrm{(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)}$ (**1**). Thermolysis of **1** provides the α,β' isomer $\mathrm{(DIPP)_2ClTa(CCMe_3{=}CHCCMe_3{=}CH)}$ (**2**). Kinetic and mechanistic studies of the **1** → **2** isomerization are presented which lead to the proposal that the rearrangement proceeds by the disruption of the metallacycle and the formation of an intermediate Ta(V) metallacyclopropene $\mathrm{(DIPP)_2ClTa(HC{=}CCMe_3)}$ adduct, followed by its reaction with free $\mathrm{HC{\equiv}CCMe_3}$ to reform the metallacycle. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with a = 12.130 (2) Å, b = 18.541 (3) Å, c = 15.844 (3) Å, β = 95.48 (1)°, and V = 3547.1 Å^3 with Z = 4 and ρ_{calcd} = 1.38 g cm^{-3}. The final R = 0.029 and R_w = 0.033 for 6835 reflections (6456 unique). Complex **1** assumes a TBP structure in the solid state with metallacyclic C_α carbons occupying equatorial sites. Complex **2** (but not **1**) engages in cycloaddition chemistry with $\mathrm{HC{\equiv}CCMe_3}$ to afford the η^6-arene complex $(\eta^6\text{-}1,3,5\text{-}\mathrm{C_6H_3{}^tBu_3})\mathrm{Ta(DIPP)_2Cl}$ (**6**). **6** can be alkylated with MeMgBr to afford purple crystals of $(\eta^6\text{-}1,3,5\text{-}\mathrm{C_6H_3{}^tBu_3})\mathrm{Ta(DIPP)_2(CH_3)}$ (**7**). Compound **7** crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with a = 13.555 (1) Å, b = 20.607 (1) Å, c = 14.595 (1) Å, β = 97.91 (6)°, V = 4037.8 Å^3 with Z = 4 and ρ_{calcd} = 1.31 g cm^{-3}. The final R = 0.024 and R_w = 0.026 for 7686 reflections (6769 unique). The arene ligand in **7** exhibits a diene–diyl distortion and thus resembles a purported intermediate in the [2 + 2 + 2] cycloaddition of alkynes, the 7-metallanorbornadiene. Complex **2** (but not **1**) forms adducts with THF and $\mathrm{N{\equiv}CCMe_3}$, viz. $\mathrm{(DIPP)_2Cl(THF)Ta(CCMe_3{=}CHCCMe_3{=}CH)}$ (**5**) and $\mathrm{(DIPP)_2Cl(Me_3CC{\equiv}N)Ta(CCMe_3{=}CHCCMe_3{=}CH)}$ (**8**). Compound **8** undergoes a cycloaddition reaction upon warming to room temperature to afford $(\eta^2(N,C)\text{-}2,4,6\text{-}\mathrm{NC_5H_2{}^tBu_3})\mathrm{Ta(DIPP)_2Cl}$ (**9**). Compound **9** crystallizes in the orthorhombic space group $Pca2_1$ (No. 29) with a = 20.674 (2) Å, b = 10.087 (5) Å, c = 19.908 (5) Å, and V = 4151.6 Å^3 with Z = 4 and ρ_{calcd} = 1.31 g cm^{-3}. The final R = 0.037 and R_w = 0.041 for 4153 reflections (3799 unique). The η^2-pyridine ligand in **9** is severely distorted, and spectroscopic and electrochemical studies on **9** reveal that the metal is in a higher effective oxidation state than the metal in the η^6-arene complex **6**.

Introduction

Metallacyclic complexes of the transition metals have come to occupy a singular role in the catalytic and stoichiometric conversions of organic molecules.[1] Their intermediacy has been demonstrated, for example, in the oligomerization[2,3] and metathesis[4] of olefins and acetylenes, as well as implicated in their polymerization.[5] More recently, highly selective carbon–carbon bond-forming reactions have been developed[6] in which a low-valent transition metal effects the metallacyclization of unsaturated organic substrates. Therefore, understanding the formation and fragmentation of metallacycles may be regarded as central to fully utilizing these processes.

Metallacyclo*pentadienes*, generated from the oxidative coupling of two acetylene molecules, constitute viable intermediates in [2 + 2 + 2] cycloaddition chemistry.[3] While their participation in the catalytic chemistry is apparent,[3,7] their *direct* conversion into a higher, complexed cyclooligomer is rarely observed.[8,9] Such interconversions may be relevant to understanding the interactions between aromatic hydrocarbons and metal surfaces,[10] atoms,[11] and complexes.[12] Herein, we report the formation and fragmentation of a reactive metallacyclopentadiene and examine the mechanistic details of its isomerization to a more

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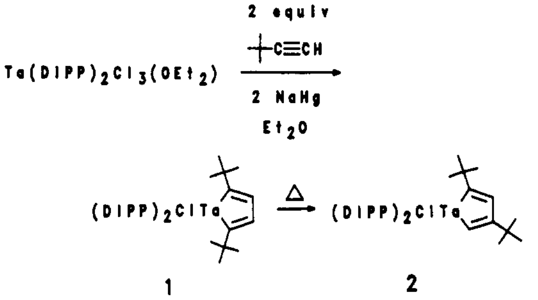
stable regioisomer. In addition, we demonstrate the direct conversion of a metallacyclopentadiene to η^6-arene and η^2-pyridine ligands. These latter reactions are of special significance since interconversions among the various arene–metal structural forms (e.g. $\eta^6 \rightleftarrows \eta^4 \rightleftarrows \eta^2$)[12b,13,14] may be of considerable importance to aromatic C–H bond activation,[15] arene hydrogenation,[16] and alkyne cyclotrimerization.[3] A portion of these results have been communicated.[8]

Results

Preparation and Properties of Tantallacyclopentadienes. Upon reaction of $Ta(DIPP)_2Cl_3(OEt_2)$[17] (DIPP = O-2,6-$C_6H_3{}^iPr_2$), 2 equiv of $HC{\equiv}CCMe_3$, and 2 equiv of NaHg in diethyl ether solution, the metallacyclopentadiene complex $(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)$ (1) can be isolated in 55% yield (eq 1). Examining the reaction solution reveals that



(1)

1 *forms* in near quantitative yield, along with some 1,3,5-$C_6H_3{}^tBu_3$, implicating the transient occurrence of the other regioisomer, $(DIPP)_2ClTa(CCMe_3{=}CHCCMe_3{=}CH)$, in

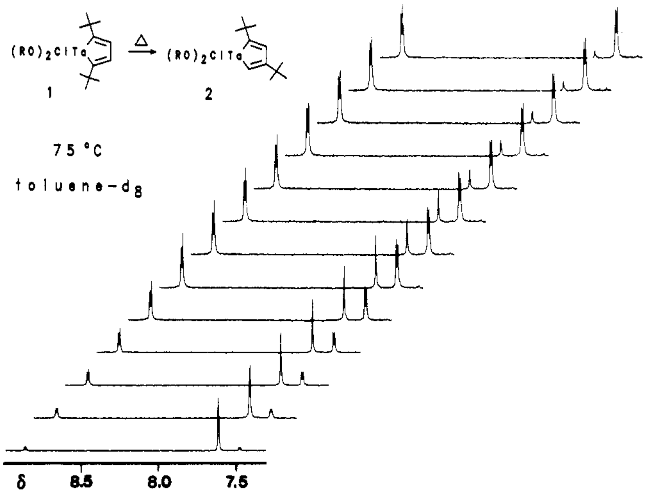
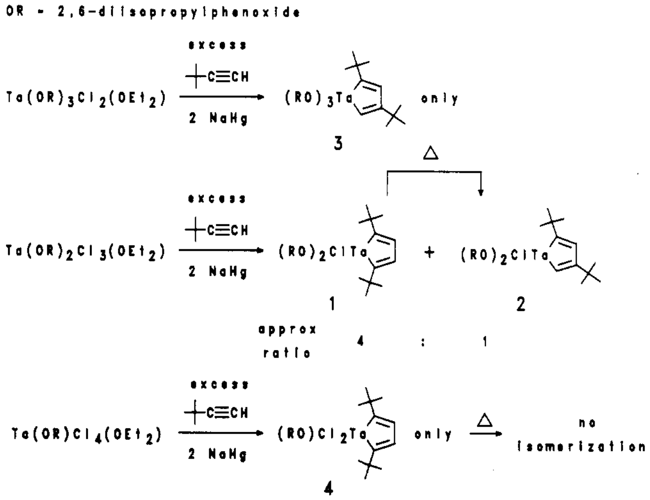


Figure 1. Partial ^1H NMR spectra of the metallacyclic $=CH-$ resonances (toluene-d_8, 75 °C) demonstrating the isomerization of the α,α' metallacycle $(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)$ (1, δ 7.61 singlet) to the α,β' isomer $(DIPP)_2ClTa(CCMe_3{=}CHCCMe_3{=}CH)$ (3, δ 8.86 and 7.47 doublets; DIPP = O-2,6-$C_6H_3{}^iPr_2$).

Scheme I



this reaction. The fluxional behavior of 1 in solution results in broad resonances in its room-temperature NMR spectra. However, at −40 °C, the α,α' substitution is verified from the δ 7.45 (s) chemical shift of the metallacyclic $C_\beta H$ protons[18] (toluene-d_8), by examining the hydrolysis reaction of 1 (which forms only (*E,E*)-$Me_3CCH{=}CHCH{=}CHCMe_3$[18] and HO-2,6-$C_6H_3{}^iPr_2$ as the Et_2O-soluble products), and finally from its X-ray structural determination (vide infra).

The low-temperature ^1H and ^{13}C NMR spectra of 1 allow the assignment of a ground-state structure. The structure of a tantallacyclopentadiene closely related to 1, viz. $(DIPP)_3Ta(CEt{=}CEtCEt{=}CEt)$, has been shown[19] to conform to a TBP structure, with the C_α–Ta–$C_{\alpha'}$ angle of 75.7 (4)° restricting the metallacyclic α carbons to occupy one axial and one equatorial site. However, the −40 °C NMR spectra of 1 require *equivalent* metallacyclic α carbons which therefore must be situated either in two

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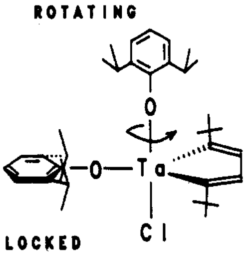
Table I. Details of the X-ray Diffraction Study for $(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)$ (1), $(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^tBu_3)Ta(DIPP)_2(CH_3)$ (7), and $(\eta^2(N,C)\text{-}2,4,6\text{-}NC_5H_2{}^tBu_3)Ta(DIPP)_2Cl$ (9)

molecular formula	$C_{36}H_{54}ClO_2Ta$ (1)	$C_{43}H_{67}O_2Ta$ (7)	$C_{41}H_{63}ClTaNO_2$ (9)
mol wt	735.23	796.95	818.37
cryst color	yellow	purple red	dark red
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$Pca2_1$ (No. 29)
unit cell vol, Å^3	3547.1	4037.8	4151.6
a, Å	12.130 (2)	13.555 (1)	20.674 (2)
b, Å	18.541 (3)	20.607 (1)	10.087 (5)
c, Å	15.844 (3)	14.595 (1)	19.908 (5)
α, deg	90.0	90.0	90.0
β, deg	95.48 (1)	97.91 (6)	90.0
γ, deg	90.0	90.0	90.0
Z	4	4	4
calcd dens, g cm^{-3}	1.38	1.31	1.31
cryst dimens, mm	0.40 × 0.50 × 0.20	0.33 × 0.53 × 0.13	0.30 × 0.30 × 0.30
data colln temp, °C	23 ± 1	20 ± 1	23 ± 1
Mo Kα radiation, λ, Å	0.71073	0.71073	0.71073
monochromator	graphite	graphite	graphite
abs coeff, cm^{-1}	31.6	27.2	27.1
2θ range, deg	2-50	2-50	2-50
total no. of reflns measd	6835 (6456 unique)	7686 (6769 unique)	4153 (3799 unique)
no. of reflns measd with $I > 3\sigma(I)$	4181	4184	2536
scan type	θ-2θ	θ-2θ	θ-2θ
scan speed, deg min^{-1}	2-8	3	2-8
no. of params refined	361	433	204
R	0.029	0.024	0.037
R_w	0.033	0.026	0.041

equatorial sites of a TBP or two basal sites of a SP. The DIPP ^1H NMR resonances provide the necessary information to unambiguously assign the structure at −40 °C as that shown in I, and then only if one DIPP is freely



I

rotating about $Ta{-}O{-}C_{ipso}$ and the other (viz. the one which lies *perpendicular* to the molecular plane of symmetry) is locked in place on the NMR time scale. The solid-state structure of 1 (vide infra) is consistent with this orientation.

Metallacycle 1 represents the kinetic product of the cyclization reaction shown in eq 1 since it can be thermolyzed (≥50 °C) to provide its more stable α,β' isomer $(DIPP)_2ClTa(CCMe_3{=}CHCCMe_3{=}CH)$ (2). This thermodynamic product is formed in near-quantitative yield but is isolated in moderate yield due to its high solubility in hydrocarbon solvents. The rearrangement is quite clean when effected at higher temperatures (ca. 90 °C), as no other organometallic species are observed throughout the process (^1H NMR analysis) (Figure 1).

In order to understand the greater *thermodynamic* stability of isomer 2 over 1, we have examined the reduction of two other tantalum(V) complexes in the presence of $HC{\equiv}CCMe_3$ (Scheme I). These compounds differ *most* significantly in their steric features. Thus, when $Ta(DIPP)_3Cl_2(OEt_2)$ is reduced with 2 equiv of NaHg and 4 equiv of $HC{\equiv}CCMe_3$ (Et_2O soln), the α,β' metallacycle $(DIPP)_3Ta(CCMe_3{=}CHCCMe_3{=}CH)$ (9) *only* is formed in high yield (Scheme I).[19] Upon examination of the entire reaction mixture as described above, no other regioisomers nor any $1,3,5\text{-}C_6H_3{}^tBu_3$ was detected by ^1H NMR spectroscopy. When the sterically less demanding monokis(phenoxide) complex $Ta(DIPP)Cl_4(OEt_2)$ is reduced under similar conditions, the α,α' product $(DIPP)Cl_2Ta(CCMe_3{=}CHCH{=}CCMe_3)$ (4) *only* is isolated. Again, no $1,3,5\text{-}C_6H_3{}^tBu_3$ was found in this reaction. Metallacycle 4 has not been induced to thermally rearrange like metallacycle 1. Upon heating of 4 in toluene-d_8 solution (ca. 90 °C), thermal degradation occurs with the formation of, inter alia, the butadiene $(E,E)\text{-}Me_3CCH{=}CHCH{=}CHCMe_3$ and products possibly arising from C–H activation of the DIPP ligands,[20] but *no* rearrangement to another regioisomer was detected. Therefore, it appears that α,α' substitution products (like 4) are thermodynamically stable if steric interactions at the metal are not severe. As steric congestion at the metal increases, the *thermodynamic* stability of α,α' substitution products is lost first (as in complex 1), followed by their kinetic accessibility (as in complex 3) such that their formation is never observed.

Table II. Selected Bond Distances (Å) and Bond Angles (deg) in $(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)$ (1)[a]

	Bond Distances		
Ta–Cl	2.412 (1)	C(1)–C(2)	1.510 (7)
Ta–O(1)	1.890 (3)	C(2)–C(3)	1.340 (6)
Ta–O(2)	1.890 (3)	C(3)–C(4)	1.500 (7)
Ta–C(2)	2.123 (4)	C(4)–C(5)	1.336 (7)
Ta–C(3)	2.577 (5)	C(5)–C(6)	1.495 (7)
Ta–C(4)	2.556 (5)	O(1)–C(11)	1.358 (5)
Ta–C(5)	2.085 (5)	O(2)–C(21)	1.374 (5)
	Bond Angles		
Cl–Ta–O(1)	84.1 (1)	O(2)–Ta–C(5)	96.7 (2)
Cl–Ta–O(2)	170.5 (1)	C(2)–Ta–C(5)	96.6 (2)
Cl–Ta–C(2)	85.5 (1)	Ta–O(1)–C(11)	157.6 (3)
Cl–Ta–C(5)	92.7 (1)	Ta–O(2)–C(21)	173.2 (3)
O(1)–Ta–O(2)	92.5 (1)	Ta–C(2)–C(3)	93.4 (3)
O(1)–Ta–C(2)	142.7 (2)	C(2)–C(3)–C(4)	127.5 (4)
O(1)–Ta–C(5)	119.5 (2)	C(3)–C(4)–C(5)	128.1 (5)
O(2)–Ta–C(2)	92.0 (2)	Ta–C(5)–C(4)	94.1 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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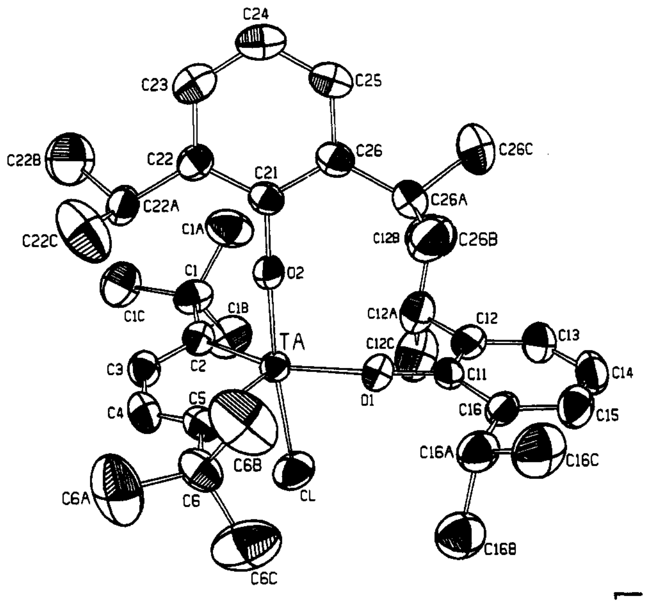


Figure 2. Molecular structure of (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (1, DIPP = O-2,6-C$_6$H$_3$^{i}Pr$_2$) with atoms shown as 50% probability ellipsoids.

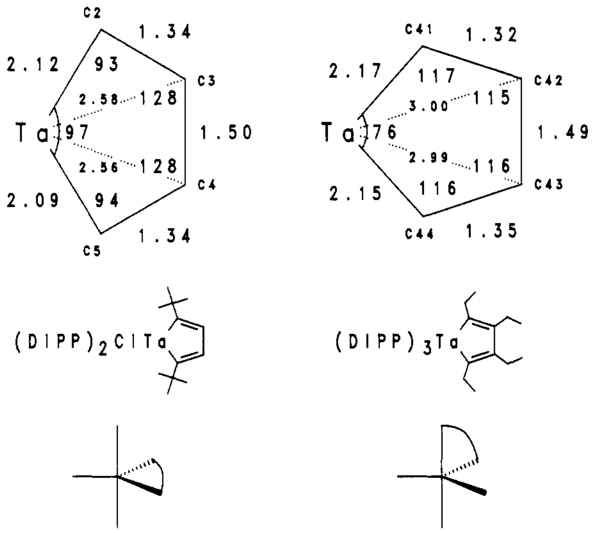
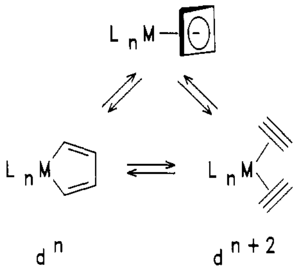


Figure 3. Structural comparison of the "equatorial–equatorial" metallacycle in (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (1, DIPP = O-2,6-C$_6$H$_3$^{i}Pr$_2$) with the "axial–equatorial" metallacycle in (DIPP)$_3$Ta(CEt=CEtCEt=CEt).

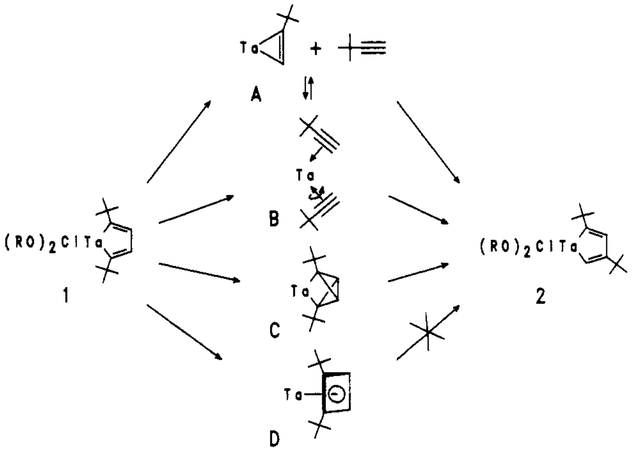
Structural Studies of an Unstable (α,α′-Substituted) Metallacyclopentadiene. Single crystals of (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (1) were obtained from a toluene/pentane solution at −40 °C; the molecular structure of 1 is presented in Figure 2, and Tables I and II summarize relevant data. The approximate TBP geometry (O(2)–Ta–Cl = 170.5 (1)°) displays one axial and one equatorial phenoxide ligand and, as predicted from the NMR data, an equatorial metallacycle. Carbon–carbon bond length alternation around the metallacyclic ring is evident,[21] but the most notable features include the obtuse C_α–Ta–$C_{\alpha'}$ angle (96.6 (2)°) and unusually small Ta–C_α–C_β angles (93.4 (3) and 94.1 (4)°). These features, perhaps arising from the orbital overlap requirements of the TBP structure, result in the close approach of the β carbons (C(3) and C(4)) to the metal (2.577 (5) and 2.556 (5) Å, respectively).[22] Thus, in order to accommodate the metallacycle of (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (1) within the equatorial plane, the C_α–Ta–$C_{\alpha'}$ angle increases relative to an "axial–equatorial" metallacycle, which induces a decrease in the Ta–C_α–C_β angles and an increase in C_α–C_β–$C_{\beta'}$ angles. These features contrast sharply to the metallacycle (DIPP)$_3$Ta(CEt=CEtCEt=CEt) which exhibits a "normal" metallacyclic geometry, as shown in Figure 3.[19] Thus, the C_α–Ta–$C_{\alpha'}$ angle (75.7 (4)°) and the Ta–C_α–C_β angles (116.4° on average) in (DIPP)$_3$Ta(CEt=CEtCEt=CEt) are more consistent with known d^0 metallacyclopentadiene structures.[21,23] The molecular structure of metallacycle 2 was also of interest in view of the reactivity differences between these compounds. However, despite numerous efforts we have been unable to obtain crystals of 2 that are of acceptable quality for X-ray work.

Scheme II



Scheme III

OR = 2,6-diisopropylphenoxide



Isomerization of a d^0 Metallacyclopentadiene: Mechanistic Considerations. The isomerizations of metallacyclopent*anes*[2c,23,24] and metallacyclopent*enes*[25] have been studied in detail in several systems, but mech-

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[21] Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

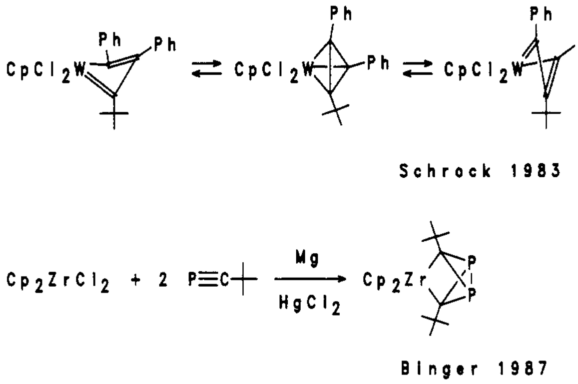
[22] These values are only ca. 0.12 Å longer than mean tantalum-carbon bond distances in many η^5-C$_5$H$_5$ and η^6-C$_6$H$_6$ complexes. See: Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1986**, *303*, 39.

[23] Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952.

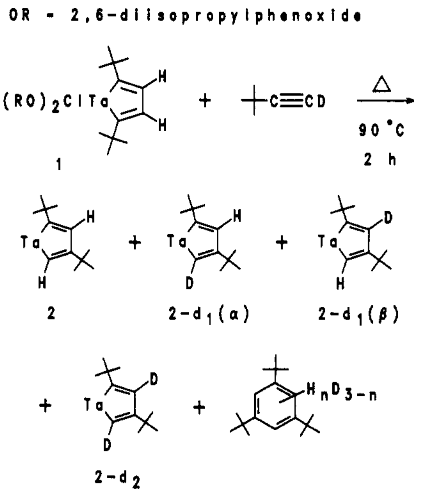
[24] (a) Takahashi, T.; Fujimori, T.; Seki, T.; Saburi, M.; Uchida, Y.; Rousset, C. J.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1990**, 182. (b) Cohen, S. A.; Auburn, P. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136. (c) Grubbs, R. H.; Miyashita, A. *Ibid.* **1978**, *100*, 1300. (d) McLain, S. J.; Wood, C. D.; Schrock, R. R. *Ibid.* **1979**, *101*, 4558. (e) Erker, G.; Dorf, U.; Rheingold, A. L. *Organometallics* **1988**, *7*, 138. (f) Grubbs, R. H.; Miyashita, A. *J. Organomet. Chem.* **1978**, *161*, 371 and references therein. (g) Fellmann, J. D.; Schrock, R. R.; Rupprecht, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5752.

[25] (a) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. (b) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281.

Scheme IV



Scheme V



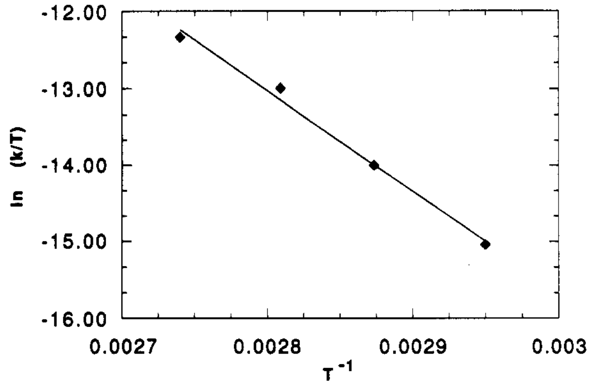
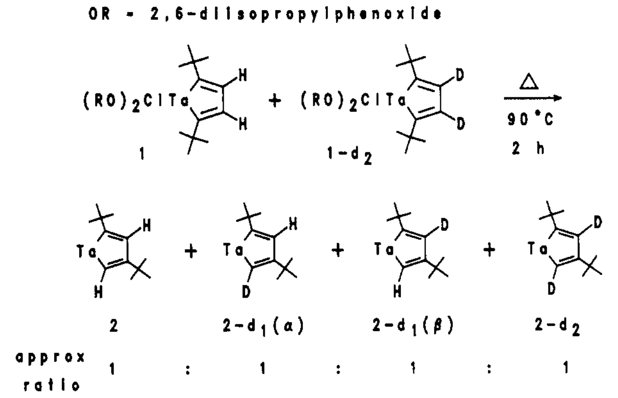


Figure 4. Plot of ln (k/T) vs T^{-1} (activated complex theory plot) for the disappearance of $(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)$ (1, DIPP = $O\text{-}2,6\text{-}C_6H_3{}^iPr_2$).

Table III. First-Order Kinetic Data for the Isomerization of $(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)$ (1) to $(DIPP)_2ClTa(CCMe_3{=}CHCCMe_3{=}CH)$ (2)

temp, °C	10^4k, s^{-1}	corr coeff
66	1.0	0.996
75	2.9	0.999
84	8.0	0.998
92	16	0.997

Scheme VI



anistic information regarding metallacyclopenta*diene* rearrangements is available only in the late metals.[26-29] This is particularly true for low-valent cobalt, where there is evidence for the direct interconversions among all three tautomers shown in Scheme II, including the reversibility of two of these conversions.[26,28] Few metallacyclopentadiene isomerizations in the early transition metals have been reported,[29] and mechanistic information is lacking.

Various intermediates which might be invoked in the 1 → 2 rearrangement are presented in Scheme III. Either pathway via A or B requires the disruption of the metallacycle and the formation of two alkyne molecules, either with both coordinated (B) or with only one coordinated (A). Specifically, pathway 1 → A → 2 does not *require* a bis(alkyne) intermediate; however, the A ⇄ B equilibrium is possibly operative as indicated. (Metallacyclo*pentane* rearrangements, e.g. via disruption to proposed bis(olefin) adducts[24a-c] have been presented.) The intermediacy of cyclobutadiene complex D can be eliminated, as the *tert*-butyl groups would always remain adjacent in such a process. Intermediate C could arise through a 4-electron rearrangement from 1 and then requires a 6-electron electrocyclic process to form 2. Furthermore, a *structural* precedent for C exists, as seen in the reduction of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in the presence of the phosphaalkyne $P{\equiv}CCMe_3$[30] (Scheme IV). Perhaps more relevant to pathway 1 → C → 2 is that certain metallacyclo*butadienes* have been shown to rearrange via a metallatetrahedrane intermediate,[31,32] one example of which is shown in Scheme IV. Since formal analogies between metallacyclobutadienes and metallacyclopentadienes are known (e.g.

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[26] For examples of metallacyclopentadiene ⇄ η^4-cyclobutadiene interconversions, see: (a) Chin, H.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 5068. (b) Brandt, L.; Green, M.; Parkins, A. W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1046. (c) King, M.; Holt, E. M.; Radnia, P.; McKennis, J. S. *Organometallics* **1982**, *1*, 1718 and references therein.

[27] Although the bis(alkyne) → metallacyclopentadiene rearrangement is no doubt operative in low-valent, late-transition-metal complexes, bis(alkyne) intermediates appear very short-lived in the $L_nCo(RC{\equiv}CR)$ + $RC{\equiv}CR$ → $L_nCo(CR{=}CRCR{=}CR)$ conversion; thus their isolation is difficult in the cobalt systems (ref 3a). See also: (a) Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 1907. (b) McDonnell-Bushnell, L. P.; Evitt, E. R.; Bergman, R. G. *J. Organomet. Chem.* **1978**, *157*, 445.

[28] For examples of direct bis(alkyne) adduct ⇄ η^4-cyclobutadiene reaction pathways, without the intermediacy of metallacyclopentadienes, see: (a) Ville, G. A.; Vollhardt, K. P. C.; Winter, M. J. *Organometallics* **1984**, *3*, 1177. (b) Davidson, J. L. *J. Chem. Soc., Chem. Commun.* **1980**, 113. (c) Fritch, J. R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 409.

[29] For previously reported metallacyclopentadiene rearrangements in the early transition metals, see: (a) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870. (b) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211. (c) Buchwald, S. L.; Lucas, E. A.; Lum, R. T. Unpublished results, reported in ref 6b.

[30] Binger, P.; Biedenbach, B.; Krüger, C.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 764.

[31] Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046.

[32] Weinstock, I. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1991**, *113*, 135.

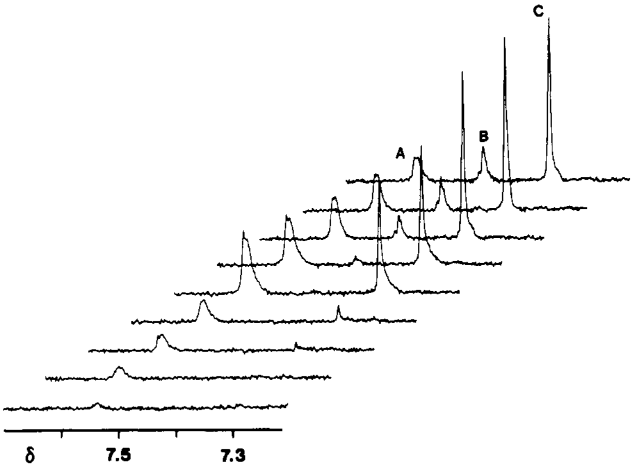


Figure 5. Partial ^{1}H NMR spectra of the isomerization of the α,α' metallacycle $(DIPP)_2ClTa(CCMe_3{=}CDCD{=}CCMe_3)$ (1-d_2) at 50 °C (toluene-d_8) in the presence of $HC{\equiv}CCMe_3$: A = $(DIPP)_2ClTa(CCMe_3{=}CHCD{=}CCMe_3)$ (1-d_1); B = $(DIPP)_2ClTa(CCMe_3{=}CHCCMe_3{=}CD)$ [2-$d_1(\alpha)$]; C = 1,3,5-$C_6H_nD_{3-n}{}^tBu_3$ (DIPP = O-2,6-$C_6H_3{}^iPr_2$).

in their reactions with alkynes to afford η^5-cyclopentadienyl[33] and η^6-arene[8] complexes, respectively), such a process must be considered.

To more firmly establish the details of the 1 → 2 rearrangement, the following experiments have been performed.

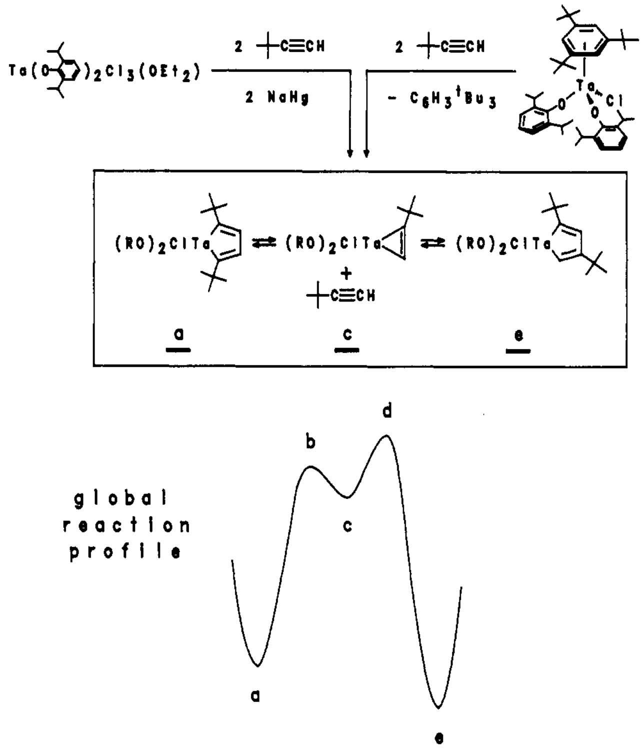
(i) When $(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)$ (1) is thermolyzed (90 °C, 2 h) in the presence of 0.6 equiv of $DC{\equiv}CCMe_3$, the resulting metallacycles showed significant deuterium incorporation, i.e. this reaction afforded 2, 2-$d_1(\alpha)$, 2-$d_1(\beta)$, and small amounts of 2-d_2 (Scheme V). The inverse labeled experiment, viz. the thermolysis of $(DIPP)_2ClTa(CCMe_3{=}CDCD{=}CCMe_3)$ (1-d_2) with <1 equiv of $HC{\equiv}CCMe_3$ revealed the formation of all possible compounds 2-$d_1(\alpha)$, 2-$d_1(\beta)$, and 2-d_2, along with the small amounts of all-protio 2.

(ii) The disappearance of 1 follows clean first-order kinetics over a range of temperatures (Table III). An activated complex plot (Figure 4) provides activation parameters of $\Delta H^\ddagger = 26 \pm 3$ kcal mol^{-1} and $\Delta S^\ddagger = -0.2 \pm 0.3$ eu for a $\Delta G^\ddagger = 26 \pm 3$ kcal mol^{-1}.

(iii) A crossover experiment was undertaken by thermolyzing equimolar 1 ($(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)$) and 1-$d_2$ ($(DIPP)_2ClTa(CCMe_3{=}CDCD{=}CCMe_3)$) at 90 °C for 2 h (Scheme VI). The resulting α,β' metallacycles showed *statistical* crossover. Thus, the approximate ratio of 2:2-$d_1(\alpha)$:2-$d_1(\beta)$:2-d_2 was 1:1:1:1 in the resulting solution. As a control experiment, equimolar 1-d_2 ($(DIPP)_2ClTa(CCMe_3{=}CDCD{=}CCMe_3)$) and 2 ($(DIPP)_2ClTa(CCMe_3{=}CHCCMe_3{=}CH)$) were thermolyzed under identical conditions and no crossover was observed; i.e. the final solution contained only 2 and 2-d_2. Thus, under these conditions, no crossover occurs *after* isomerization.

(iv) When a solution of $(DIPP)_2ClTa(CCMe_3{=}CDCD{=}CCMe_3)$ (1-d_2) and 1.2 equiv of $HC{\equiv}CCMe_3$ is gently thermolyzed (50 °C, C_6D_6), the protio label is incorporated into the starting complex *faster* than it appears in the thermodynamic product (Figure 5). Thus, $(DIPP)_2ClTa(CCMe_3{=}CHCD{=}CCMe_3)$ (1-d_1) forms at a faster rate than 2-$d_1(\alpha)$ and 2-$d_1(\beta)$.

Scheme VII



From these experiments, we can conclude the following concerning the 1 → 2 rearrangement. Experiment i shown in Scheme V ($DC{\equiv}CCMe_3$ incorporation) requires some means of deuterium scrambling, implicating at some point the presence of "$(DIPP)_2ClTa(HC{\equiv}CCMe_3)$" plus free $HC{\equiv}CCMe_3$ in solution during the isomerization. (*Intermolecular scrambling mechanisms are eliminated by the* first-order disappearence of 1.) Scheme V also argues strongly against intermediate C and against intermediate B *only*, i.e. against 1 → B → 2. Perhaps the most significant result is the *statistical* crossover as presented in Scheme VI. These data show that when metallacycle 1 disrupts into "$(DIPP)_2ClTa(HC{\equiv}CCMe_3)$" plus $HC{\equiv}CCMe_3$, *the formation of 2 by recoupling that same alkyne is no more favored than coupling a different alkyne which originated from a neighboring metallacycle's disruption.* These experiments are *most* consistent with the 1 → 2 rearrangement proceeding via 1 → A → 2. If intermediate B (viz. a complex with equivalent, coordinated alkynes) is involved at all, i.e. if the rearrangement occurs via 1 → B → A → 2, then the B → A step must be significantly faster than B → 2, otherwise metallacycle 2 would retain some "memory" of B and *nonstatistical* crossover would have resulted. It is more difficult to comment on the $\Delta S^\ddagger \approx 0$, except that this value does *not* support an activated complex with free rotation about a Ta–alkyne axis as one might expect in a bis(alkyne) complex.

Reaction Profile for the 1 → 2 Isomerization. If $(DIPP)_2ClTa(HC{\equiv}CCMe_3)$ (A) is also an intermediate in the *synthesis* of 1, then eq 1 may hold relevant information about the 1 → 2 isomerization since microscopic reversibility will require that metallacycle 1 forms in the same fashion as it disrupts. Therefore, it may be possible to access the reaction profile for the 1 → 2 isomerization via the synthesis of 1 (Scheme VII). The fact that isomer 1

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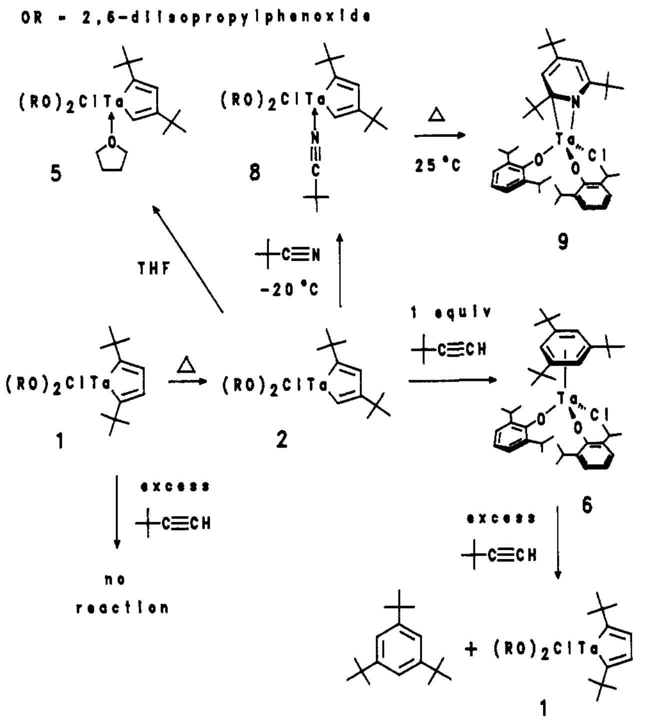
[33] Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* 1982, *104*, 6808.

Scheme VIII



is the predominant product in eq 1 simply reflects the activation barrier to coupling (DIPP)$_2$ClTa(HC≡CCMe$_3$) + HC≡CCMe$_3$ with α,α' regiochemistry is lower than coupling α,β', although the α,β' metallacycle is overall more stable, as depicted in Scheme VII. A closer examination of eq 1 allows us to quantify the kinetic preference for coupling α,α' over α,β' in this system.

Upon reacting Ta(DIPP)$_2$Cl$_3$(OEt$_2$), *4 equiv* of HC≡CCMe$_3$, and 2 equiv of NaHg in Et$_2$O (room temperature) and examining the entire reaction mixture, we find both (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (1) and 1,3,5-C$_6$H$_3{}^t$Bu$_3$ present in a 4:1 molar ratio. Therefore, the ratio of 1:2 formed in this reaction must also be 4:1. This iterative calculation is based accurately upon the fact that at room temperature, any 1 which forms does not isomerize to 2 and any 1,3,5-C$_6$H$_3{}^t$Bu$_3$ which is observed arises only from 2 (vide infra). From this ratio of 1:2, the difference in energy between levels b and d in Scheme VII is calculated to be $\Delta\Delta G^* \approx 0.8$ kcal mol^{-1}, which emphasizes the very slight kinetic preference for coupling α,α' over α,β' in this system.

The assumption that (DIPP)$_2$ClTa(HC≡CCMe$_3$) (A) is also an intermediate in the synthesis of 1 is supported by entering the reaction profile of Scheme VII via yet another route, viz. by reacting (η^6-1,3,5-C$_6$H$_3{}^t$Bu$_3$)Ta(DIPP)$_2$Cl (6, vide infra) with 4 equiv of HC≡CCMe$_3$. Thus, 6 serves as a convenient source of d^2 "Ta(DIPP)$_2$Cl" upon releasing its η^6-1,3,5-C$_6$H$_3{}^t$Bu$_3$ ligand. Examining the entire reaction mixture again reveals that (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (1) and 1,3,5-C$_6$H$_3{}^t$Bu$_3$, *arising from 2 only*, are present in a 4:1 molar ratio (i.e. not including the 1,3,5-C$_6$H$_3{}^t$Bu$_3$ which was released from the original 6).

Direct Conversion of a Metallacyclopentadiene to an η^6-Arene Complex. No reaction is observed between complex 1 and HC≡CCMe$_3$, presumably due to the steric protection that α,α' substitution of the metallacycle affords the metal center. Consistent with this notion is the fact that no THF or N≡CMe adduct of 1 has been observed.

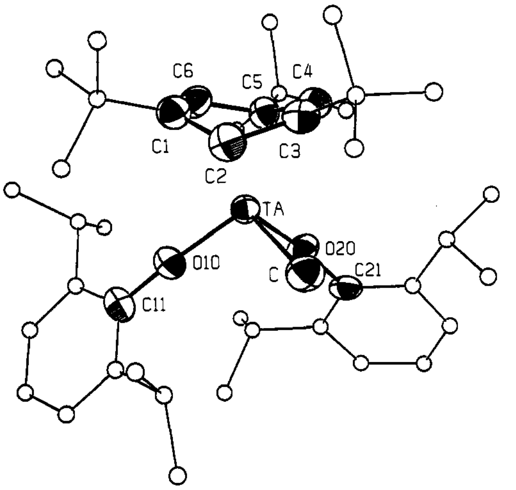
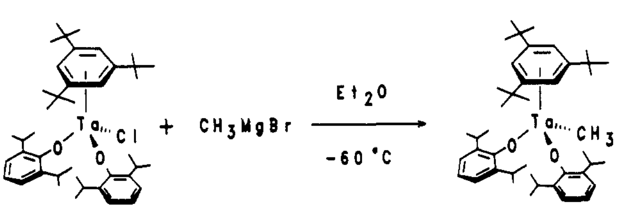


Figure 6. Molecular structure of (η^6-1,3,5-C$_6$H$_3{}^t$Bu$_3$)Ta(DIPP)$_2$(CH$_3$) (7) emphasizing the folding of the arene ligand. Atoms are shown in 50% probability (DIPP = O-2,6-C$_6$H$_3{}^i$Pr$_2$).

However, an α,β' metallacycle is considerably less congested (e.g. THF adduct 5 forms readily, Scheme VIII); thus 2 appears ideal to "reenter" the cycloaddition sequence. Cold (≤-40 °C) solutions of metallacycle 2 react rapidly with 1 equiv of HC≡CCMe$_3$ to provide solutions from which blue crystals of (η^6-1,3,5-C$_6$H$_3{}^t$Bu$_3$)Ta(DIPP)$_2$Cl (6) are obtained in up to 70% yield (Scheme VIII). Although η^6-arene formation by alkyne cycloaddition chemistry is well-known,[3] this reaction represents a rare observation of the *direct* conversion of a metallacyclopentadiene to an η^6-arene complex, a key step in [2 + 2 + 2] cycloaddition chemistry.[3] Upon reaction of 2 with 3 equiv of HC≡CCMe$_3$ or upon reaction of 6 with 2 equiv of HC≡CCMe$_3$, 1 equiv of 1,3,5-C$_6$H$_3{}^t$Bu$_3$ is formed and (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (1) can be regenerated, thus completing the cycloaddition sequence (Scheme VIII).

If the reaction of 2 or 6 with HC≡CCMe$_3$ is run at a temperature high enough to isomerize the resulting metallacycle 1 to 2 (typically ≥70 °C), then the cyclotrimerization of HC≡CCMe$_3$ to tri-*tert*-butylbenzene becomes catalytic in tantalum. Thus, the reaction of 1 with a large excess of HC≡CCMe$_3$ at 75 °C (toluene-d_8) provides ca. 0.7 turnovers/h for the production of 1,3,5-C$_6$H$_3{}^t$Bu$_3$ and a total of ca. 20 turnovers before the catalyst deactivates.

Solid-State and Solution Structure of η^6-Arene Complexes. Despite numerous attempts, crystals of 6 suitable for X-ray structural analysis could not be obtained. Therefore a derivative of 6 was prepared by alkylation as presented in eq 2 which provided excellent



6 7 (2)

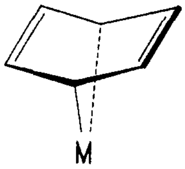
crystals for X-ray structural analysis. The molecular structure of (η^6-1,3,5-C$_6$H$_3{}^t$Bu$_3$)Ta(DIPP)$_2$(CH$_3$) (7) is presented in Figure 6, and Tables I and IV summarize crystal and structural data. The salient structural feature is the *highly* distorted arene ligand which is characterized

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) in (η^6-1,3,5-$C_6H_3{}^tBu_3$)Ta(DIPP)$_2$(CH_3) (7)[a]

	Bond Distances		
Ta–C(1)	2.513 (4)	Ta–O(20)	1.934 (2)
Ta–C(2)	2.223 (4)	O(10)–C(11)	1.362 (4)
Ta–C(3)	2.560 (4)	O(20)–C(21)	1.367 (4)
Ta–C(4)	2.507 (3)	C(1)–C(2)	1.464 (5)
Ta–C(5)	2.183 (4)	C(2)–C(3)	1.486 (5)
Ta–C(6)	2.411 (4)	C(3)–C(4)	1.355 (5)
Ta–arene$_{cent}$	1.942 (2)	C(4)–C(5)	1.466 (5)
Ta–C	2.201 (4)	C(5)–C(6)	1.479 (5)
Ta–O(10)	1.894 (2)	C(6)–C(1)	1.371 (5)
	Bond Angles		
C–Ta–O(10)	101.0 (1)	Ta–O(20)–C(21)	162.0 (2)
C–Ta–O(20)	83.9 (1)	C(1)–C(2)–C(3)	114.7 (3)
O(10)–Ta–O(20)	97.6 (1)	C(2)–C(3)–C(4)	117.3 (3)
arene$_{cent}$–Ta–C	109.9 (2)	C(3)–C(4)–C(5)	121.6 (3)
arene$_{cent}$–Ta–O(10)	126.7 (1)	C(4)–C(5)–C(6)	111.9 (3)
arene$_{cent}$–Ta–O(20)	127.2 (1)	C(5)–C(6)–C(1)	122.2 (3)
Ta–O(10)–C(11)	174.7 (3)	C(2)–C(1)–C(6)	116.1 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

by (i) substantial folding[34] (the dihedral angle between the C(1)–C(2)–C(3)–C(4) and C(1)–C(2′)–C(3′)–C(4) planes in 7 is 33.1 ± 0.5°, which is near the top of the range of ca. 26–34° for related (η^6-C_6Me_6)TaX_3 complexes of Ta(III)), (ii) an interruption of aromaticity within the $C_6H_3{}^tBu_3$ ring (viz. a 1,4-diene or "diene–diyl" type π localization as depicted in II), and (iii) the close approach

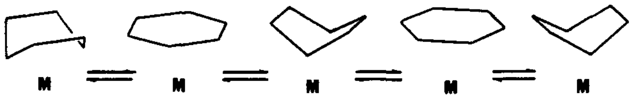


II

of C(2) and C(5) to the metal (2.223 (4) and 2.183 (4) Å, respectively, compared to an average 2.498 (4) Å for the other arene carbons). Thus, 7 (and no doubt 6) possesses one of the most distorted and π-localized arene ligands ever observed in η^6 coordination. These structural features (arene π localization and folding, etc.) have been attributed to a back-bonding interaction between filled metal δ functions and the arene LUMO as previously described.[17]

Low-temperature NMR studies, however, cannot unambiguously freeze out a folded structure in solution. At 40 °C, the three arene ^{13}CH atoms of the η^6-1,3,5-$C_6H_3{}^tBu_3$ ligand in 6 resonate at δ 105.3 ($^1J_{CH}$ = 169 Hz), while their attached protons appear at δ 5.02 (toluene-d_8). Rapid ring rotation *alone* cannot account for the equivalence of these groups in a static, folded structure,[3d] thus interconversion *among* folded structures is proposed, perhaps as suggested in Scheme IX. This rapid flip-flop motion, *combined with* rapid ring rotation, is consistent with the 40 °C data. Upon cooling, the δ 5.02 signal (η^6-1,3,5-$C_6\mathit{H}_3{}^tBu_3$) broadens into the baseline and reappears at δ 4.94 (s, 2 H) and 5.19 (s, 1 H) at –50 °C. Although a folded structure might be frozen out in this experiment, *slow rotation* of the arene about the metal–arene vector is the more likely cause of this inequivalence.[35] Thus, while there can be little doubt that the arene ligand in 6 is folded as in 7, such a structure cannot be unambiguously observed in solution.

Scheme IX



Compound 7 and no doubt 6 show a strong structural resemblance to a purported intermediate in [2 + 2 + 2] cycloaddition chemistry, the 7-metallanorbornadiene.[3,7] Such a species represents the Diels–Alder adduct between the metallacyclopentadiene and an incoming alkyne, although there is no direct evidence that 6 has arisen through this mechanism.

Direct Conversion of a Metallacyclopentadiene to an η^2-Pyridine Complex. The [2 + 2 + 2] reaction leading to η^6-arene complex 6 prompted the search for other such reactions, especially those using nitriles with a view to forming free or coordinated pyridines.[36] The –40 °C reaction of 2 (either isolated or formed in situ from 1) with *tert*-butyl cyanide results in the high-yield formation of the yellow orange adduct $(DIPP)_2Cl(Me_3CC{\equiv}N)\overline{Ta(CCMe_3{=}CHCCMe_3{=}CH)}$ (8) ($\nu_{C\equiv N}$ = 2278 cm^{-1}) (Scheme VIII). The η^1 nitrile complex 8 is thermally unstable in solution and can only be isolated below ca. –20 °C. Upon dissolving in room-temperature C_6D_6, 8 begins to rearrange to maroon complex 9 within minutes (Scheme VIII). The NMR spectra of 9 reveal that *all three tert*-butyl groups are inequivalent, even to 90 °C, and *five* inequivalent aromatic pyridine carbons are observed. These data *eliminate* a simple η^6-pyridine complex[37] which contrasts sharply with η^6-arene coordination as in 6.

Further physical characterization of 9 provides informative contrasts between 9 and 6. Samples of 9 can be sublimed at 110 °C with little decomposition (2 × 10^{-5} Torr), while 6 releases its arene slowly at room temperature. The He I valence photoelectron spectrum of 9 reveals its lowest energy ionization (at ca. 6.75 eV) is characterized by a band shape reminiscent of the lowest energy ionization from tantalum(III) olefin complexes which show a d^0 metallacyclopropane electronic structure.[38] Thus, this 6.75-eV ionization has much less metal character than expected if 9 were a d^2 Ta(III) complex.[38] The cyclic voltammogram of 9 displays an irreversible oxidation at $E_{p,a}$ = +0.63 V vs Ag/AgCl (CH_2Cl_2 solution, 0.1 M in $^nBu_4NPF_6$) which is ca. *0.5 V more positive* than the oxidation of the related arene complex (η^6-C_6Me_6)Ta(DIPP)$_2$Cl.[39] This oxidation is followed by several ill-defined electrochemical processes, no doubt arising from the instability of the resulting cation. Accordingly, the chemical oxidation of 9 (e.g. with pyridine *N*-oxide) provides free 2,4,6-$NC_5H_2{}^tBu_3$,[40] which is readily isolated by

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[34] A summary of structurally folded arenes appears in ref 17.

[35] At –50 °C only *one* ^{13}CH carbon of the $C_6H_3{}^tBu_3$ ligand is observed at δ 99.4 ($^1J_{CH}$ = 172 Hz), which places an upper limit of δ 117.1 on the other ring carbon (which would be buried under broad DIPP signals), suggesting that the folded, π localized structure shown above has in fact not been frozen out.

[36] For pyridine syntheses via [2 + 2 + 2] cycloaddition chemistry, see: (a) Wakatsuki, Y.; Yamazaki, H. *Synthesis* **1976**, 26. (b) Wakatsuki, Y.; Yamazaki, H. *Tetrahedron Lett.* **1973**, 3383. (c) Vollhardt, K. P. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4996. (d) Bönnemann, H.; Brinkmann, R. *Synthesis* **1975**, 600. (e) Parnell, C. A.; Vollhardt, K. P. C. *Tetrahedron* **1985**, 5791.

[37] For examples of η^6 pyridines, see: (a) Davies, S. G.; Shipton, M. R. *J. Chem. Soc., Chem. Commun.* **1989**, 995. (b) Morris, R. H.; Ressner, J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 909. (c) Timms, P. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 273. (d) Simons, L. H.; Riley, P. E.; Davis, R. E.; Lagowski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 1044. (e) Wucherer, E. J.; Muetterties, E. L. *Organometallics* **1987**, *6*, 1691 and 1696.

[38] Lichtenberger, D. L.; Darsey, G. P.; Kellogg, G. E.; Sanner, R. D.; Young, V. G., Jr.; Clark, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 5019.

[39] (a) The $E_{p,a}$ for (η^6-C_6Me_6)Ta(DIPP)$_2$Cl occurs at ca. +0.10 V vs Ag/AgCl. Unfortunately, (η^6-1,3,5-$C_6H_3{}^tBu_3$)Ta(DIPP)$_2$Cl (**5**) reacts with MeC≡N, CH_2Cl_2, and other electrochemical solvents so that a direct comparison between **5** and **7** is not yet possible. See ref 3d. (b) Arney, D. J.; Bruck, M. A.; Wigley, D. E. *Organometallics* **1991**, *10*, 3947.

[40] Dimroth, K.; Mach, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 460.

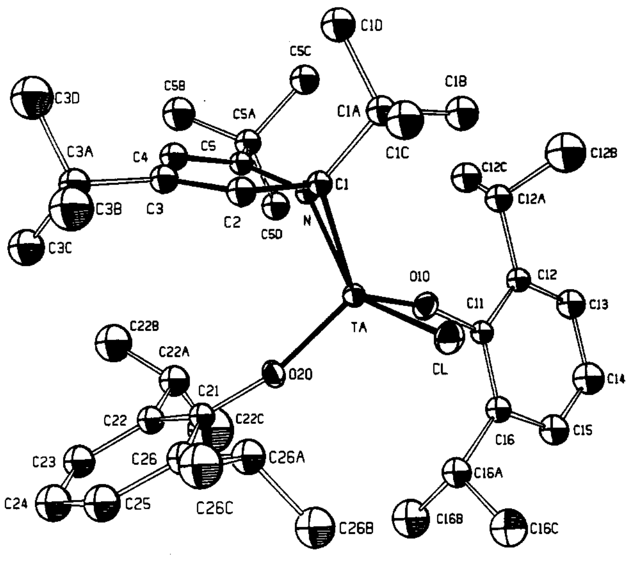


Figure 7. Molecular structure of (η^2(*N*,*C*)-2,4,6-$NC_5H_2{}^tBu_3$)-Ta(DIPP)$_2$Cl (7, DIPP = O-2,6-$C_6H_3{}^iPr_2$) with atoms shown in 50% probability.

Table V. Selected Bond Distances (Å) and Bond Angles (deg) in (η^2(*N*,*C*)-2,4,6-$NC_5H_2{}^tBu_3$)Ta(DIPP)$_2$Cl (7)[a]

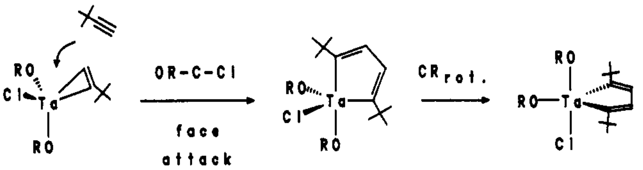
	Bond Distances		
Ta–Cl	2.344 (3)	N–C(5)	1.394 (9)
Ta–N	1.963 (6)	C(1)–C(2)	1.45 (1)
Ta–C(1)	2.133 (9)	C(2)–C(3)	1.43 (1)
Ta–O(10)	1.877 (6)	C(3)–C(4)	1.46 (1)
Ta–O(20)	1.860 (6)	C(4)–C(5)	1.35 (2)
N–C(1)	1.47 (2)		
	Bond Angles		
Cl–Ta–N	131.1 (4)	Ta–N–C(5)	140.4 (5)
Cl–Ta–C(1)	92.5 (3)	C(1)–N–C(5)	121 (1)
Cl–Ta–O(10)	95.6 (2)	Ta–C(1)–N	62.9 (4)
Cl–Ta–O(20)	102.2 (2)	Ta–C(1)–C(2)	111.7 (6)
N–Ta–C(1)	41.9 (6)	N–C(1)–C(2)	112.6 (8)
N–Ta–O(10)	101.1 (6)	C(1)–C(2)–C(3)	120.6 (9)
N–Ta–O(20)	109.9 (3)	C(2)–C(3)–C(4)	116 (1)
C(1)–Ta–O(10)	127.5 (3)	C(3)–C(4)–C(5)	124 (1)
C(1)–Ta–O(20)	111.5 (3)	N–C(5)–C(4)	117 (1)
O(10)–Ta–O(20)	117.1 (3)	Ta–O(10)–C(11)	161.5 (6)
Ta–N–C(1)	75.2 (5)	Ta–O(20)–C(21)	164.9 (6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

sublimation. All of the above data require the formulation of **9** as the pyridine complex (2,4,6-$NC_5H_2{}^tBu_3$)Ta-(DIPP)$_2$Cl; however, the striking differences between **6** and **9** implicate a structural formulation other than an η^6 complex. Specifically, the pyridine ligand in **9** must be bound in a fashion which allows the metal center to attain a higher effective oxidation state that is accessible in **6** and which renders all carbons inequivalent. Proposed upon the precedence provided by the structurally characterized (silox)$_3$Ta(η^2(*N*,*C*)NC_5H_5)[41,42] (silox = $^tBu_3SiO$) and confirmed by X-ray crystallography, **9** is characterized by an η^2 coordination of the pyridine ligand.

Structural Characterization of an η^2-Pyridine Complex Prepared by [2 + 2 + 2] Cycloaddition Chemistry. Figure 7 presents the molecular structure of (η^2(*N*,*C*)-2,4,6-$NC_5H_2{}^tBu_3$)Ta(DIPP)$_2$Cl (**9**), and Tables I and V summarize important crystal and structural data. The η^2 coordination mode of the pyridine ligand is evident from the Ta–C(1) bond of 2.126 (9) Å and Ta–N bond of 1.966 (6) Å, while C(2) and C(5) are clearly out of bonding range from Ta (2.99 (1) and 3.159 (8) Å, respectively). A clear 1,3-diene π localization is not as evident in this ligand (Table V) as it is in Wolczanski's related (silox)$_3$Ta(η^2-(*N*,*C*)-NC_5H_5) complex.[42] However, these structural data and the redox and PES data for **9** are clearly indicative of a tantalum(V) "metallaaziridine" structure,[43] rather than a tantalum(III) formulation. The pyridine ligand is severely distorted toward a twist-boat conformation, in contrast to the planar pyridine in (silox)$_3$Ta(η^2(*N*,*C*)-NC_5H_5). The dihedral angle between the best pyridine plane and the Ta–(*N*,*C*) plane is 117.6 (5)° while Ta–N–C(5) = 140.3 (5)° and Ta–C(1)–C(2) = 111.5 (6)°. A short Ta–N bond in conjunction with the NMR data (see Experimental Section) fully supports the η^2-(*N*,*C*) mode of bonding as in (silox)$_3$Ta(η^2(*N*,*C*)-NC_5H_5), rather than an η^2-(*C*,*C*) mode reported in the lutidine complex [(η^2-lutidene)Os$(NH_3)_5$]$^{2+}$.[44]

Scheme X



A series of (silox)$_3$Ta(η^2(*N*,*C*)-substituted pyridine) complexes have been prepared by Wolczanski, and EHMO calculations on the model compound (HO)$_3$Ta(η^2(*N*,*C*)-NC_5H_5) revealed the origins of η^2 stability over η^6 or η^1 coordination.[42] First, the η^2 mode is favored since it can engage in π-back-bonding interactions with the reducing Ta$(OH)_3$ moiety (rather than the less-efficient δ back-bonding of the η^6 mode[17,45]), thereby allowing the metal to achieve its highest oxidation state. Also, η^2 bonding avoids the strong, 4-electron, two-orbital destabilization between the Ta$(OH)_3$ dz^2 orbital and the pyridine N-donor orbital which would arise from the σ-only interactions of an η^1 mode. Distorting the pyridine α hydrogen out of the pyridine plane, i.e. pyramidalization about the α carbon, is important in stabilizing the η^2 structure in (HO)$_3$Ta-(η^2(*N*,*C*)-NC_5H_5).[42] The C_α position in (η^2(*N*,*C*)-2,4,6-$NC_5H_2{}^tBu_3$)Ta(DIPP)$_2$Cl (**9**) is *tert*-butyl substituted and pyramidalization about this C_α is observed (average angle about C_α = 107.7°) as this *tert*-butyl substituent is displaced well out of the best pyridine plane. While this distortion must be sterically enhanced, it is consistent with the most electronically favored structure.

Discussion

Metallacyclopentadiene Formation and Fragmentation. Perhaps the most puzzling feature of this chemistry is why the kinetic α,α' metallacycle **1** forms at all. Steric factors have been proposed to explain the α,α' regioselectivity in cobaltacyclopentadienes,[27a] and electronic factors seem to indicate that β,β' regioselectivity is favored in the metallacyclization of Fe(olefin)$_2$(CO)$_3$.[23] Most observations of metallacyclizations[1,23] are in accord with this

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[41] Neithamer, D. R.; Párkányi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421.

[42] Covert, K. J.; Neithamer, D. R.; Zonnevylle, M. C.; LaPointe, R. E.; Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1991**, *30*, 2494.

[43] (a) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720. (b) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *Ibid.* **1983**, *105*, 2651. (c) Durfee, L. D.; Hill, J. E.; Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1989**, *28*, 3095. (d) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 2088.

[44] (a) Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101. (b) For related η^2-pyridinium complexes, see: Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 2896.

[45] Brown, P. R.; Cloke, F. G. N.; Green, M. L. H.; Hazel, N. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1075.

β,β' prediction, although there is an obvious steric constraint to this in **1** or **2**.

The kinetic regioselectivity may be rationalized if we consider that the incoming acetylene approaches the metal toward one face of pseudotetrahedral $(DIPP)_2ClTa(HC{\equiv}CCMe_3)$ (the most sterically accessible approach) and that the first formed metallacycle will be an approximate TBP with one of the incoming C_{acet} atoms in an axial position (Scheme X). Such a proposal has been made for the reaction between pseudotetrahedral d^0 alkylidynes (viz. $Re({\equiv}CCMe_3)({=}NAr)(OR)_2$) and acetylenes to afford metallacyclo*buta*dienes.[32] Thus, adding $HC{\equiv}CCMe_3$ to one of the two $OR\text{–}C_{acet}\text{–}Cl$ faces will be more facile than to the $OR\text{–}C_{acet}\text{–}OR$ face (addition to the OR–OR–Cl face is nonproductive), and in adding, the *tert*-butyl groups of each alkyne avoid each other. The first formed TBP is an axial–equatorial metallacycle which then rapidly pseudorotates about the equatorial $C_\alpha R$ to afford the observed kinetic product. A coglike packing efficiency of the ligands in equatorial–equatorial metallacycle **1**, evident from examining molecular models (see Figure 3), probably affords an overall lower energy than the first formed axial–equatorial metallacycle. While the metallacycle **1** appears strained, preliminary molecular orbital studies indicate that **1** breaks apart from an equatorial–axial TBP structure, *just as we have proposed it forms*.[46]

We[19] and others[47] have observed that formal d^2 tantalum(III) alkyne adducts (e.g. $(DIPP)_3Ta(PhC{\equiv}CPh)$[19]) are much more accurately described as d^0 tantallacyclopropenes.[48] In the absence of available d electrons, these metal centers cannot effectively stabilize an approaching acetylene via π back-donation. Attempts to calculate optimized geometries for the d^2 bis(alkyne) complex $Cl_3Ta(HC{\equiv}CH)_2$ by ab initio and extended Hückel methods resulted in either the two alkynes collapsing to the metallacyclopentadiene with no activation barrier or one of the alkynes being released by the metal center and the other being substantially reduced to a metallacyclopropene structure.[46] Thus, the formation of **1** and **2** is best described as the reaction of one molecule of $HC{\equiv}CCMe_3$ and $(DIPP)_2Cl\overline{Ta(HC{=}C}CMe_3)$, a reaction which the available data suggest is a more accurate description of their formation than a metallacyclization reaction of "$(DIPP)_2ClTa(HC{\equiv}CCMe_3)_2$". In this way, compounds like purported $(DIPP)_2Cl\overline{Ta(HC{=}C}CMe_3)$ are similar to the highly reactive d^0 group 4 metals in olefin polymerization in which olefin adducts are implicated as transient species but usually not stable, which supports the relevance of such metal centers in the polymerization sequence.[49,50]

Formation of η^6-Arene and η^2-Pyridine Complexes. The formations of η^6-arene complex **6** and η^2-pyridine complex **9** directly from a metallacyclopentadiene represent a key step in the cycloaddition chemistry of alkynes. Compound **9** is particularly relevant to [2 + 2 + 2] cycloaddition chemistry. While a "metallanorcaradiene" (η^2-benzene) has been considered as a possible intermediate which forms from the collapse of a metallacycloheptatriene in the cycloaddition preparation of benzocyclobutanes,[51] complex **9** may generally represent a heretofore *unrecognized* intermediate in metal catalyzed [2 + 2 + 2] cycloaddition chemistry. No intermediates are observed in the rearrangement of **8** to **9** (^1H NMR, room temperature); thus whether a transient η^6-pyridine or *N*-metallacycloimine $(\overline{TaN{=}CCMe_3CH{=}CCMe_3CH{=}C}CMe_3)$ is involved is unknown. Since the tri-*tert*-butylbenzene ligand coordinates η^6 in complexes **6** and **7**, it is unlikely that *steric* constraints are inducing an incipient η^6-tri-*tert*-butylpyridine ligand to slip to the observed η^2 form in **9**. The structure of **9** suggests that a metal–ligand π interaction ($d\pi \Rightarrow p\pi^*$) is preferred over the rather inefficient δ back-bonding ($d\delta \Rightarrow$ arene δ^* (arene π^* LUMO) as in **7**) to allow the metal to attain its highest oxidation state. This conclusion was obtained by Wolczanski's theoretical study of related $(HO)_3Ta(\eta^2(N,C)\text{-}NC_5H_5)$.[42] The η^2 coordination and the misshapen pyridine ligand resulting from an obvious disruption of its aromaticity both extract a high energetic price,[52] but one which apparently can be afforded from the gains made in π back-bonding.[42] The difference in the thermal stabilities of **6** and **9** reflects this strong interaction. Additionally, compounds related to **9** may be relevant to C–H bond activation: intermediate η^2-(*N,C*) pyridine species may be implicated prior to pyridyl ($\eta^2(N,C)\text{-}NC_5H_4$) formation[49c,53] and related pyridine C_α functionalizations.[54]

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[55] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were distilled under N_2 from an appropriate drying agent[56] and were transferred to the drybox without exposure to air. The "cold" solvents used to wash isolated solid products were cooled to ca. −30 °C before use. All NMR solvents were passed down a short (5–6-cm) column of activated alumina prior to use. In all preparations, DIPP = $0\text{-}2,6\text{-}C_6H_3{}^iPr_2$.

Starting Materials and Reagents. 3,3-Dimethyl-1-butyne (*tert*-butylacetylene) was obtained from Farchan Laboratories and was passed down a short (6–8-cm) column of activated alumina at ca. −10 °C prior to use. *tert*-Butyl cyanide was purchased from Aldrich and dried by passing down a short activated alumina column at room temperature. Pyridine *N*-oxide (Aldrich) was sublimed (45 °C, 10^{-5} Torr) prior to use. $Ta(DIPP)_2Cl_3(OEt_2)$,[17] $[Ta(DIPP)Cl_4]_2$,[17] and $(DIPP)_3\overline{Ta(CCMe_3{=}CHCCMe_3{=}C}H)$[19] (**3**) were prepared as described previously. The deuterated acetylene $DC{\equiv}CCMe_3$ was prepared by the reaction of ^nBuLi (hexane solution) with a pentane solution of $HC{\equiv}CCMe_3$, isolating the $LiC{\equiv}CCMe_3$, suspending it in $^nBu_2O$, and quenching it with D_2O. The product was isolated by distillation (collected at −78 °C), after having been passed through a −78 °C condenser, and dried over activated alumina prior to use.

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[46] Albright, T. A. Personal communication.

[47] Tantalum(III) alkyne adducts are invariably characterized by a highly reduced alkyne, i.e. by a tantalum(V) metallacyclopropene structure. See: (a) Curtis, M. D.; Real, J.; Kwon, D. *Organometallics* **1989**, *8*, 1644. (b) Curtis, M. D.; Real, J.; Hirpo, W.; Butler, W. M. *Ibid.* **1990**, *9*, 66.

[48] A few bis(alkyne) complexes of low-valent tantalum(I) and niobium(I) have been reported, e.g. $(\eta^5\text{-}C_5H_5)M(CO)(PhC{\equiv}CPh)_2$. See: (a) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Pasynskii, A. A. *Izv. Nauk SSSR, Ser. Khim.* **1969**, 100. (b) Aleksandrov, G. G.; Gusev, A. I.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 333.

[49] (a) Jordan, R. F.; Bajgur, C. S.; Willet, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410. (b) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willet, R. *Ibid.* **1987**, *109*, 4111. (c) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *Ibid.* **1987**, *109*, 203.

[50] Occupation of d orbitals in these polymerization systems appears to lead to significant barriers to insertion. See: (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* 1981, *103*, 4308. (b) Eisenstein, O.; Hoffmann, R. *Ibid.* **1980**, *102*, 6148.

[51] Vollhardt, K. P. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4996.

[52] Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884.

[53] (a) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276. (b) Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *214*, 53.

[54] (a) Fanwick, P. E.; Kobriger, L. M.; McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* **1986**, *108*, 8095. (b) Erker, G.; Mühlenbernd, T.; Benn, R.; Rufińska, A. *Organometallics* **1986**, *5*, 402.

[55] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; John Wiley and Sons: New York, 1986.

[56] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd Ed.; Pergamon Press: Oxford, U.K., 1988.

Physical Measurements. ^{1}H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded at probe temperature (unless otherwise specified) on a Bruker WM-250 spectrometer in C_6D_6, toluene-d_8, or $CDCl_3$ solvent. Variable-temperature ^{1}H NMR spectra obtained in kinetic experiments were recorded at 250 MHz on a Bruker AM-250 spectrometer. Chemical shifts are referenced to protio impurities (δ 7.15, C_6D_6; δ 2.09, toluene-d_8; δ 7.24, $CDCl_3$) or solvent ^{13}C resonances (δ 128.0, C_6D_6; δ 20.4, toluene-d_8; δ 77.0, $CDCl_3$) and are reported downfield of Me_4Si. Infrared spectra in the region 4000–600 cm^{-1} were recorded as Nujol mulls (NaCl plates) on a Perkin-Elmer 1310 spectrometer. Cyclic voltammetry experiments were performed in the drybox under N_2 using a BioAnalytical Systems CV-27 voltammograph and recorded on a Houston Instruments Model 100 X-Y recorder. Measurements were taken at a Pt-disk electrode in CH_2Cl_2 solutions containing 0.1 M $^n\mathrm{Bu_4NPF_6}$ as supporting electrolyte. Voltammograms were recorded at room temperature at a sweep rate of 150 mV/s and are referenced to Ag/AgCl (uncorrected for junction potentials). The He I valence PES spectrum of **9** was measured using a McPherson ESCA 36 spectrometer, modified with a temperature-controlled sample cell and conditions previously described.[57] The gas-phase sample was generated at ca. 110 °C and 2×10^{-5} Torr and the operating resolution for the argon $^2P_{3/2}$ ionization (15.76 eV) was maintained at 0.016–0.020 eV throughout the data collection. This argon ionization was used as an internal "lock" during the high-resolution He I signal averaging (7–12-eV collections) to maintain drift from the absolute kinetic energy at <0.005 eV. All microanalytical samples were handled under N_2 and were combusted with WO_3 (Desert Analytics, Tucson, AZ).

Preparations. $\mathrm{(DIPP)_2Cl\overline{Ta(CCMe_3{=}CHCH{=}C}CMe_3)}$ (1). A solution of 2.03 g (2.84 mmol) of $\mathrm{Ta(DIPP)_2Cl_3(OEt_2)}$ in 20 mL of diethyl ether was prepared and cooled to −40 °C. To this vigorously stirred solution were added 0.80 mL (6.5 mmol) of *tert*-butylacetylene and 1.7 mL (5.7 mmol) of a 0.6% NaHg amalgam. After being stirred at room temperature for 18 h, the mixture was filtered through Celite and the solvent was removed from the filtrate in vacuo to afford a maroon red oil. A golden yellow solid formed immediately upon triturating this oil with cold pentane. The solid was collected by filtration and dried in vacuo. When the filtrate was cooled to −40 °C, an additional crop of product formed for a total yield of 1.15 g (1.56 mmol, 55%). Analytically pure samples were obtained by recrystallization from Et_2O/pentane solutions at −40 °C. ^{1}H NMR (toluene-d_8, −40 °C): δ 7.45 (s, 2 H, CH), 7.12–6.82 (m, 6 H, H_{aryl}), 3.76 and 3.44 (spt, 2 H each, C*H*Me$_2$), 1.48 and 1.35 (d, 6 H each, CH*Me*$_2$), 1.23 (s, 18 H, CMe$_3$), 0.99 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (toluene-d_8, −40 °C): δ 221.3 (C_α), 160.0, 156.3 (C_{ipso}), 140.7, 137.6 (C_o), 123.8 (broad, coincident C_m and C_p), 104.9 (C_β), 40.0 (*C*Me$_3$), 30.0 (C*Me*$_3$), 28.9, 26.4 (*C*HMe$_2$), 25.7, 24.5, 23.9 (CH*Me*$_2$). IR: ν 1580 (w), 1550 (br w), 1426 (sh), 1370 (s), 1355 (s), 1318 (s), 1300 (w), 1275 (w), 1260 (m), 1245 (s), 1190 (sh), 1180 (s), 1104 (s), 1092 (m), 1050 (w), 1031 (m), 995 (br), 927 (m), 905 (s), 891 (s), 870 (m), 817 (m), 783 (s), 739 (s), 703 (m) cm^{-1}. Anal. Calcd for $C_{36}H_{54}O_2ClTa$: C, 58.81; H, 7.40. Found: C, 58.99; H, 7.57.

$\mathrm{(DIPP)_2Cl\overline{Ta(CCMe_3{=}CDCD{=}C}CMe_3)}$ (1-*d*$_2$). This deuterated metallacycle was prepared by substituting $DC{\equiv}CCMe_3$ for $HC{\equiv}CCMe_3$ in the preparation described for **1**. This analogous reaction afforded **1**-*d*$_2$ in comparable yields to **1**. ^{1}H NMR (C_6D_6, probe temperature or toluene-d_8, −40 °C): Resonances are identical to those observed for **1**, except the δ 7.45 singlet (toluene-d_8) is not observed.

$\mathrm{(DIPP)_2Cl\overline{Ta(CCMe_3{=}CHCCMe_3{=}C}H)}$ (2). A glass ampule (Teflon stopcock) was charged with 1.76 g (2.33 mmol) of $\mathrm{(DIPP)_2Cl\overline{Ta(CCMe_3{=}CHCH{=}C}CMe_3)}$ (**1**), 30 mL of toluene, and a small stir bar. This solution was heated in an oil bath at 90 °C, with stirring, for 2 h, over which time its color darkened to red-brown. The solution was then allowed to cool, and the solvent was removed in vacuo to provide a deep red oil. This oil was reconstituted in minimal pentane (ca. 5 mL), and upon cooling to −40 °C, a yellow solid formed. The solid was filtered off and dried in vacuo for a yield of 1.00 g (1.35 mmol, 58%, three crops). Recrystallization from pentane (−40 °C) afforded analytically pure samples. ^{1}H NMR (C_6D_6): δ 8.96 (d, $^4J_{HH}$ = 2.6 Hz, 1 H, C_αH), 7.46 (d, $^4J_{HH}$ = 2.6 Hz, 1 H, C_βH), 7.10–6.95 (m, 6 H, H_{aryl}), 3.78 (spt, 4 H, C*H*Me$_2$), 1.34, 1.31 (d, 12 H each, CH*Me*$_2$), 1.12, 1.00 (s, 9 H each, CMe$_3$). ^{13}C NMR (C_6D_6): δ 217.4 (C_αCMe$_3$), 189.4 (C_αH), 181.9 (C_βCMe$_3$), 159.1 (C_{ipso}), 138.5 (C_o), 137.9 (C_βH), 125.7 (C_p), 123.8 (C_m), 41.9, 37.3 (*C*Me$_3$), 31.2, 29.0 (C*Me*$_3$), 28.4 (*C*HMe$_2$), 24.5, 24.1 (CH*Me*$_2$). IR: ν 1545 (m), 1494 (m), 1360 (s), 1322 (s), 1245 (s), 1181 (br s), 1148 (m), 1102 (m), 1093 (m), 1054 (w), 1036 (m), 917 (br s), 870 (m), 788 (s), 744 (s), 711 (s), 670 (m) cm^{-1}. Anal. Calcd for $C_{36}H_{54}O_2ClTa$: C, 58.81; H, 7.40. Found: C, 58.84; H, 7.68.

$\mathrm{(DIPP)_2Cl\overline{Ta(CCMe_3{=}CDCCMe_3{=}C}D)}$ (2-*d*$_2$). This deuterated metallacycle was prepared by substituting $\mathrm{(DIPP)_2Cl\overline{Ta(CCMe_3{=}CDCD{=}C}CMe_3)}$ (1-*d*$_2$) for $\mathrm{(DIPP)_2Cl\overline{Ta(CCMe_3{=}CHCH{=}C}CMe_3)}$ (**1**) in the preparation described for **2**. This analogous reaction afforded **2**-*d*$_2$ in comparable yields to **2**. ^{1}H NMR (C_6D_6): Resonances are identical to those observed for **2**, except the δ 8.96 and 7.46 doublets are not observed.

$\mathrm{(DIPP)Cl_2\overline{Ta(CCMe_3{=}CHCH{=}C}CMe_3)}$ (4). To a −40 °C solution of 2.00 g (4.0 mmol) of $\mathrm{Ta(DIPP)Cl_4}$ in 20 mL of Et_2O (which forms $\mathrm{Ta(DIPP)Cl_4(OEt_2)}$) were added 0.97 mL (17.7 mmol) of *tert*-butylacetylene and 2.40 mL (8.0 mmol) of a 0.56% NaHg amalgam. After being stirred at room temperature for 16 h, the golden brown mixture was filtered through Celite and the solvent was removed in vacuo to provide a brown oil. A yellow-orange solid was obtained upon triturating this oil with 5 mL of pentane. The solid was collected by filtration (1.09 g, 1.84 mmol, 46%) and was obtained analytically pure by recrystallization from Et_2O/pentane solutions at −40 °C. ^{1}H NMR (C_6D_6): δ 7.92 (s, 2 H, C_βH), 7.17–6.92 (m, 3 H, H_{aryl}), 3.85 (spt, 2 H, C*H*Me$_2$), 1.38 (d, 12 H, CH*Me*$_2$), 1.28 (s, 18 H, CMe$_3$). ^{13}C NMR (C_6D_6): δ 236.6 (C_α), 160.0 (C_{ipso}), 137.5 (C_o), 125.0 (C_p), 123.7 (C_m), 109.9 (C_β), 40.3 (*C*Me$_3$), 29.8 (C*Me*$_3$), 29.0 (*C*HMe$_2$), 24.5 (CH*Me*$_2$).

$\mathrm{(DIPP)_2Cl(THF)\overline{Ta(CCMe_3{=}CHCCMe_3{=}C}H)}$ (5). A glass ampule (Teflon stopcock) was charged with 2.03 g (2.76 mmol) of $\mathrm{(DIPP)_2Cl\overline{Ta(CCMe_3{=}CHCH{=}C}CMe_3)}$ (**1**), 30 mL of toluene, 3.0 mL (37 mmol) of THF, and a small stir bar. This solution was heated in an oil bath at 90 °C (with stirring) for 2 h, over which time its color darkened to brown-red. The solution was then allowed to cool, and the solvent was removed in vacuo to provide a yellow-brown solid. This product was washed with minimal cold pentane and dried in vacuo yielding 1.78 g (2.20 mmol, 80%). Analytically pure product was obtained by recrystallization from THF/pentane solutions at −40 °C. ^{1}H NMR (C_6D_6): δ 8.74 (broad d, 1 H, C_αH), 7.55 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, C_βH), 7.09–6.92 (m, 6 H, H_{aryl}), 3.82 (spt, 4 H, C*H*Me$_2$), 3.70 (t (AB), 4 H, OCH$_2$), 1.36 (t (AB), 4 H, OCH$_2$C*H*$_2$), 1.30, 1.29 (d, 12 H each, CH*Me*$_2$), 1.16, 1.13 (s, 9 H each, CMe$_3$). ^{13}C NMR (C_6D_6): δ 220.1 (C_αCMe$_3$), 187.3 ($C_{\alpha'}$H), 179.4 (C_βCMe$_3$), 158.1 (C_{ipso}), 139.0 (C_o), 138.8 (C_βH), 125.2 (C_p), 123.8 (C_m), 70.4 (OCH$_2$), 41.6, 37.1 (*C*Me$_3$), 31.3, 29.2 (C*Me*$_3$), 27.7 (*C*HMe$_2$), 25.7 (OCH$_2$*C*H$_2$), 24.5, 24.3 (CH*Me*$_2$). IR: ν 1579 (w), 1550 (m), 1355 (m), 1327 (s), 1248 (s), 1188 (br s), 1103 (m), 1092 (m), 1035 (m), 1004 (m), 955 (w), 920 (s), 898 (s), 877 (w), 850 (s), 789 (s), 744 (s), 739 (s), 706 (m), 702 (m), 644 (m) cm^{-1}. Anal. Calcd for $C_{40}H_{62}O_3ClTa$: C, 59.51; H, 7.74. Found: C, 58.15; H, 7.83. Consistently low carbon analyses were obtained for this compound which we attribute to the partial loss of coordinated THF upon drying the solid in vacuo.

$(\eta^6\text{-}1,3,5\text{-}C_6H_3{}^tBu_3)Ta(DIPP)_2Cl$ (6). (i) To a −40 °C solution of 0.49 g (0.67 mmol) of $\mathrm{(DIPP)_2Cl\overline{Ta(CCMe_3{=}CHCCMe_3{=}C}H)}$ (**2**) in 20 mL of pentane was added 1 equiv (0.082 mL) of *tert*-butylacetylene. The solution was shaken vigorously for 3 min, over which time it turned from yellow to forest green in color. This mixture was then stored at −40 °C for 24 h (without stirring), over which time the solution turned deep blue in color and blue crystals of product had formed. These crystals were collected by filtration, washed with cold pentane, and dried in vacuo; yield 0.36 g (0.44 mmol, 66%). (ii) Compound **6** may be prepared in greater overall yield without isolating the

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[57] Calabro, D. C.; Hubbard, J. L.; Blevins, C. H., II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* 1981, *103*, 6839.

α,β' metallacycle **2** as follows: A 2.60-g sample (3.54 mmol) of (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (**1**) was dissolved in minimal toluene (ca. 30 mL) and isomerized to **2** by heating the solution to 90 °C for 2 h. After this time, the solvent was removed in vacuo to afford a red oil. The oil was reconstituted in pentane, and the sample was cooled to −40 °C. To this solution was added 0.44 mL (3.57 mmol, 1 equiv based upon **1**) of *tert*-butylacetylene, the solution was shaken and stored at −40 °C, and the product was collected and handled as described above in (i); yield 1.63 g (1.99 mmol, 56%). ^{1}H NMR (C$_6$D$_6$): δ 7.10–6.90 (m, 6 H, H$_{\mathrm{aryl}}$ (DIPP)), 5.02 (s, 3 H, arene CH), 3.47 (spt, 4 H, C*H*Me$_2$), 1.27, 1.15 (d, 12 H each, CH*Me*$_2$), 1.05 (s, 27 H, C*Me*$_3$). ^{13}C NMR (C$_6$D$_6$): δ 155.9 (C$_{\mathrm{ipso}}$), 137.7 (C$_o$), 123.8 (C$_m$), 122.8 (C$_p$), 105.5 (br, CH, arene), 36.3 (*C*Me$_3$), 30.5 (C*Me*$_3$), 25.8 (*C*HMe$_2$), 25.4, 24.6 (CH*Me*$_2$); *C*CMe$_3$ has not been observed. IR: ν 1580 (w), 1540 (w), 1320 (s), 1258 (s), 1240 (s), 1226 (sh), 1195 (sh), 1179 (s), 1099 (m), 1035 (w), 965 (w), 940 (w), 901 (s), 879 (s), 870 (m), 783 (m), 740 (s), 712 (m) cm^{-1}. Anal. Calcd for C$_{42}$H$_{64}$O$_2$ClTa: C, 61.72; H, 7.89. Found: C, 61.70; H, 8.04.

Isolation of 1,3,5-C$_6$H$_3$^{t}Bu$_3$. An excess (≥3 equiv) of *tert*-butylacetylene was added to a diethyl ether solution of (η^6-1,3,5-C$_6$H$_3$^{t}Bu$_3$)Ta(DIPP)$_2$Cl (**6**) at room temperature which itself was generated in situ in this solution as described above. After being stirred overnight, the reaction volatiles were removed in vacuo to yield an oily, pale yellow solid. Upon sublimation (room temperature, 10^{-5} Torr), the white, crystalline arene product formed on the ice-cooled probe. ^{1}H NMR (C$_6$D$_6$):[58] δ 7.42 (s, 3 H, H$_{\mathrm{aryl}}$), 1.34 (s, 27 H, CMe$_3$). ^{13}C NMR (C$_6$D$_6$): δ 150.3 (*C*CMe$_3$), 119.7 (CH), 35.1 (*C*Me$_3$), 31.8 (C*Me*$_3$).

(η^6-1,3,5-C$_6$H$_3$^{t}Bu$_3$)Ta(DIPP)$_2$(CH$_3$) (7). A solution of 0.25 g (0.30 mmol) of (η^6-1,3,5-C$_6$H$_3$^{t}Bu$_3$)Ta(DIPP)$_2$Cl (**6**) in 25 mL of Et$_2$O was cooled to −60 °C. A solution containing 0.10 mL of MeMgBr (3 M in Et$_2$O, 0.30 mmol), diluted to ca. 15-mL volume with Et$_2$O, was added dropwise to the cold solution of **6**. The reaction was allowed to warm to room temperature and stirred overnight (ca. 12 h), over which time it developed a purple color. The solvent was removed in vacuo, and the residue was extracted with pentane and filtered through Celite. The filtrate was stripped of solvent in vacuo to afford the product as a purple solid; yield 0.17 g (0.21 mmol, 70%). Analytically pure samples were obtained by recrystallizing from toluene at −40 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.10–6.90 (m, 6 H, H$_{\mathrm{aryl}}$ (DIPP)), 4.87 (s, 3 H, arene CH), 3.41 (spt, 4 H, C*H*Me$_2$), 1.24, 1.15 (d, 12 H each, CH*Me*$_2$), 1.07 (s, 27 H, C*Me*$_3$), 0.96 (s, 3 H, TaCH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 156.3 (C$_{\mathrm{ipso}}$), 137.5 (C$_o$), 123.8 (C$_m$), 122.0 (C$_p$), 35.8 (*C*Me$_3$), 30.7 (C*Me*$_3$), 25.7 (*C*HMe$_2$), 25.4, 24.6 (CH*Me*$_2$), 18.6 (TaCH$_3$); Neither arene CH nor *C*CMe$_3$ resonances were observed. Anal. Calcd for C$_{43}$H$_{67}$O$_2$Ta: C, 64.81; H, 8.47. Found: C, 63.70; H, 8.50.

(DIPP)$_2$Cl(Me$_3$CC≡N)Ta(CCMe$_3$=CHCCMe$_3$=CH) (8). A 0.66-g sample (0.90 mmol) of the α,α' metallacycle (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (**1**) was isomerized to the α,β' metallacycle (DIPP)$_2$ClTa(CCMe$_3$=CHCCMe$_3$=CH) (**2**) in toluene as described above. The toluene solvent was then removed in vacuo, and the resulting oil was reconstituted in pentane (ca. 15 mL). The pentane solution was cooled to −40 °C, 0.29 mL (2.62 mmol) of *tert*-butylcyanide was added, and the solution was mixed well. The reaction mixture was maintained at −40 °C overnight (without stirring), over which time the product precipitated as a tan to pale yellow solid which was filtered off, washed with cold pentane, and dried in vacuo; yield 0.31 g (0.38 mmol, 42%). The product obtained in this fashion was analytically pure. ^{1}H NMR (C$_6$D$_6$): δ 8.68 (br, 1 H, C$_\alpha$H), 7.57 (d, $^4J_{\mathrm{HH}}$ = 2.8 Hz, 1 H, C$_{\beta'}$H), 7.10–6.93 (m, 6 H, H$_{\mathrm{aryl}}$), 3.86 (spt, 4 H, C*H*Me$_2$), 1.32, 1.30 (overlapping d, 12 H ea, CH*Me*$_2$), 1.20, 1.14 (s, 9 H ea, CCMe$_3$), 0.75 (s, 9 H, N≡CCMe$_3$). ^{13}C NMR (C$_6$D$_6$): δ 233.7 (*C*$_\alpha$CMe$_3$), 187.1 (C$_{\alpha'}$H), 179.3 (C$_\beta$H), 158.1 (C$_{\mathrm{ipso}}$, DIPP), 139.0 (C$_o$, DIPP), 138.1 (*C*$_{\beta'}$CMe$_3$), 125.1 (C$_p$, DIPP), 123.8 (C$_m$, DIPP), 41.6, 37.1 (C$_{\alpha\text{ and }\beta'}$*C*Me$_3$), 34.4 (N≡C*C*Me$_3$), 31.2, 29.2 (C$_{\alpha\text{ and }\beta'}$C*Me*$_3$), 27.7 (*C*HMe$_2$), 24.4, 24.3 (CH*Me*$_2$), 23.8 (N≡CC*Me*$_3$); N*C* has not yet been located. IR: ν 2278 (m), 1580 (w), 1550 (w), 1355 (m), 1326 (s), 1250 (s), 1190 (s), 1100 (m), 1050 (w), 1038 (m), 920 (s), 892 (s), 870 (m), 787 (m), 747 (m), 740 (s), 715 (m), 700 (m) cm^{-1}. Anal. Calcd for C$_{41}$H$_{63}$ClNO$_2$Ta: C, 60.18; H, 7.76; N, 1.71. Found: C, 59.67; H, 8.04; N, 1.56.

(η^2(*N*,*C*)-2,4,6-NC$_5$H$_2$^{t}Bu$_3$)Ta(DIPP)$_2$Cl (9). This compound is best prepared by isomerizing the α,α' metallacyclopentadiene in situ in the presence of *tert*-butyl cyanide. A glass ampule (Teflon stopcock) was charged with 1.50 g (2.04 mmol) of (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (**1**), 0.44 mL (4.0 mmol) of *tert*-butyl cyanide, ca. 30 mL of toluene, and a small stir bar. This solution was heated in an oil bath at 90 °C (with stirring) for 2 h, over which time its color darkened to maroon. The solution was cooled, and the solvent was removed in vacuo to provide a dark red oil. Reconstituting this oil in minimal pentane (ca. 8 mL) and cooling the solution to −40 °C afforded maroon crystals of product; yield 1.26 g (1.55 mmol, 76%). Analytically pure compound can be obtained by recrystallization from pentane. ^{1}H NMR (toluene-*d*$_8$, 90 °C): δ 7.02–6.84 (A$_2$B mult, 6 H, H$_{\mathrm{aryl}}$), 5.71 (br {fwhm = 40 Hz}, 2 H, NC$_5$*H*$_2$^{t}Bu$_3$), 3.57 (spt, 4 H, C*H*Me$_2$), 1.20 (d, 24 H, CH*Me*$_2$), 1.17, 1.14, 1.03 (s, 9 H ea, NC$_5$H$_2$^{t}*Bu*$_3$). ^{13}C NMR (toluene-*d*$_8$, 90 °C): δ 169.7 (C$_o$, py), 158.1 (C$_{\mathrm{ipso}}$, DIPP), 138.5 (C$_o$, DIPP), 124.2 (C$_m$, DIPP), 124.0 (C$_p$, DIPP), 112.4 (C$_p$, py), 105.1 (br, C$_m$, py), 34.6, 31.0, 30.6 (*C*Me$_3$), 29.8, 29.3 (C*Me*$_3$), 27.6 (*C*HMe$_2$), 24.2, 23.9 (CH*Me*$_2$ or C*Me*$_3$). Partial ^{1}H NMR (C$_6$D$_6$, probe temp): δ 5.93 (br) and 5.55 (s) (1 H ea, NC$_5$*H*$_2$^{t}Bu$_3$), 1.36, 1.12, 1.05 (s, 9 H ea, NC$_5$H$_2$^{t}*Bu*$_3$). Partial ^{13}C NMR (CDCl$_3$, probe temp): 2,4,6-NC$_5$H$_2$^{t}Bu$_3$ ring carbon resonances at δ 171.7, 149.6, 117.4, 106 (br), 100.6. IR: ν 1602 (m), 1580 (sh), 1356 (s), 1320 (s), 1295 (w), 1245 (s), 1177 (s), 1140 (w), 1106 (m), 1090 (s), 1047 (m), 916 (m), 901 (s), 876 (m), 845 (w), 833 (w), 820 (w), 784 (m), 763 (w), 740 (s), 705 (m) cm^{-1}. Anal. Calcd for C$_{41}$H$_{63}$ClNO$_2$Ta: C, 60.18; H, 7.76; N, 1.71. Found: C, 60.50; H, 8.01; N, 1.77.

Isolation of 2,4,6-NC$_5$H$_2$^{t}Bu$_3$. To a room-temperature solution of 0.26 g (0.35 mmol) of (η^2(*N*,*C*)-2,4,6-NC$_5$H$_2$^{t}Bu$_3$)Ta(DIPP)$_2$Cl (**9**) in ca. 15 mL of diethyl ether/THF solution (1:1, v/v) was added 0.030 g (0.32 mmol) of pyridine *N*-oxide. The reaction was stirred for 4 h, over which time the solution color turned from maroon to light orange. The reaction volatiles were removed in vacuo, and the oily solid which remained was dried by the addition and subsequent removal of 5 mL portions of pentane (two or three cycles). The product was separated from this residue be sublimation (room temperature, 5 × 10^{-5} Torr); the white 2,4,6-NC$_5$H$_2$^{t}Bu$_3$ sublimate was collected on a water-cooled probe of which 0.027 g (0.11 mmol, 34%) was isolated. ^{1}H NMR (C$_6$D$_6$):[40] δ 7.21 (s, 2 H, H$_{\mathrm{aryl}}$), 1.48 (s, 18 H, *o*-CMe$_3$), 1.18 (s, 9 H, *p*-CMe$_3$). ^{13}C NMR (C$_6$D$_6$): δ 167.8 (C$_o$), 159.9 (C$_p$), 112.5 (C$_m$), 38.0, (*p*-*C*Me$_3$), 34.9 (*o*-*C*Me$_3$), 30.8 (*p*-C*Me*$_3$), 30.6 (*o*-C*Me*$_3$).

Mechanistic Studies. I. Thermolysis of (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (1) with Me$_3$CC≡CD (Scheme V). A 0.040-g sample (0.10 mmol) of (DIPP)$_2$ClTa(CCMe$_3$=CHCH=CCMe$_3$) (**1**) and 7.5 μL (0.06 mmol) of DC≡CCMe$_3$ were dissolved in ca. 0.5 mL of toluene-*d*$_8$ in an NMR tube and sealed under vacuum. The reaction mixture was thermolyzed in an oil bath at 90 °C for 2 h and then examined by ^{1}H NMR spectroscopy. The two metallacyclic C$_\alpha$H and C$_{\beta'}$H doublets at δ 8.90 and 7.45 in the room-temperature ^{1}H NMR spectrum indicated that (DIPP)$_2$ClTa(CCMe$_3$=CHCCMe$_3$=CH) (**2**) was present. In addition to these resonances were two new resonances, broad singlets, appearing at δ 8.89 and 7.45, of nearly equal intensity, in between each of the doublet resonances in **2**. These singlets were assigned to the metallacycles **2**-*d*$_1$(α) and **2**-*d*$_1$(β) as described above. Integration of the ^{t}*Bu* resonances of 1,3,5-C$_6$H$_3$^{t}Bu$_3$ vs the aryl protons revealed the formation of the mixed labeled compounds 1,3,5-C$_6$H$_n$D$_{3-n}$^{t}Bu$_3$. An accurate measure of the amount of **2**-*d*$_2$ present in the system was not obtained due to the uncertainties associated with the relative amounts of the labeled 1,3,5-C$_6$H$_n$D$_{3-n}$^{t}Bu$_3$ compounds produced under these conditions. The approximate ratio of **2**:**2**-*d*$_1$(α):**2**-*d*$_1$(β) was 1.8:1:1, consistent with the less than stoichiometric amount of DC≡CCMe$_3$ added. The inverse labeled experiment, viz. the thermolysis of (DIPP)$_2$ClTa(CCMe$_3$=CDCD=CCMe$_3$) (**1**-*d*$_2$) with HC≡CCMe$_3$, revealed the formation of all possible compounds

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2-$d_1(\alpha)$, 2-$d_1(\beta)$, and 2-d_2, along with the formation of small amounts of all-protio 2.

II. ^{1}H NMR Kinetic Studies of the α,α' (1) to α,β' (2) Metallacyclopentadiene Isomerization (Figure 1). Kinetic experiments were performed on a 0.136 M solution of $\mathrm{(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)}$ (1) (0.50 g dissolved in toluene-d_8 in a 5-mL volumetric flask). In a typical run, a 0.50-mL aliquot of stock solution was added to a 5-mm NMR tube which was then evacuated and sealed. This sample was kept at −15 °C until its use. The sample was placed in the probe and allowed to equilibrate its temperature for 15 min prior to data collection. The probe temperature was verified by a copper–constantan thermocouple set inside a 5-mm NMR tube filled with mineral oil. Data were collected for at least 4 half-lives at each temperature. The temperatures, rate constants, and linear correlation coefficients obtained for first-order plots for each run are recorded in Table III. The kinetic expression for the disappearane of 1[59] is derived from first-order kinetics using the steady-state approximation for the concentrations of $\mathrm{(DIPP)_2ClTa(HC{\equiv}CCMe_3)}$ (A) and $\mathrm{HC{\equiv}CCMe_3}$ in the expression: $1 \rightleftarrows A + \text{alkyne} \rightarrow 2$, where k_1 and k_{-1} describe the forward and reverse reactions $1 \rightleftarrows A + \text{alkyne}$, and k_2 is for $A + \text{alkyne} \rightarrow 2$.[59] As discovered in this reaction, $k_{-1} = 4k_2$.

III. Crossover Experiment: Isomerization of 1 and 1-d_2 (Scheme VI). A solution of 0.026 g of $\mathrm{(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)}$ (1) (0.035 mmol) and $\mathrm{(DIPP)_2ClTa(CCMe_3{=}CDCD{=}CCMe_3)}$ (1-d_2) (0.026 g, 0.035 mmol) in 0.5 mL of toluene-d_8 was prepared and sealed under vacuum. The reaction was thermolyzed in an oil bath at 90 °C for 2 h and then examined by ^{1}H NMR spectroscopy. The two metallacyclic $\mathrm{C_\alpha H}$ and $\mathrm{C_\beta H}$ doublets at δ 8.90 and 7.45 in the room-temperature ^{1}H NMR spectrum indicated that $\mathrm{(DIPP)_2ClTa(CCMe_3{=}CHCCMe_3{=}CH)}$ (2) was present. In addition to these resonances were two new resonances, broad singlets, at δ 8.89 and 7.45 (of nearly equal intensity), appearing between each of the doublet resonances in 2. These singlets were assigned to the metallacycles 2-$d_1(\beta)$ (with the proton in an α metallacycle position) and 2-$d_1(\alpha)$ (with the proton in an β metallacycle position), respectively (Scheme V). The low integration of these resonances relative to that of the DIPP ligands indicated the presence of 2-d_2. The approximate ratio of 2:2-$d_1(\alpha)$:2-$d_1(\beta)$:2-d_2 was 1:1:1:1.

IV. Incorporation of a Label, $\mathrm{HC{\equiv}CCMe_3}$, into the Kinetic Product 1-d_2 (Figure 5). A cold (−40 °C) solution of 0.50 g (0.068 mmol) of $\mathrm{(DIPP)_2ClTa(CCMe_3{=}CDCD{=}CCMe_3)}$ (1-d_2) and 12 μL (0.098 mmol) of $\mathrm{HC{\equiv}CCMe_3}$ in 0.5 mL of toluene-d_8 was prepared and flame-sealed in a 5-mm NMR tube. The sample was placed in the probe adjusted to 50 °C and allowed to equilibrate its temperature for 15 min. The reaction was monitored by ^{1}H NMR spectroscopy over a period of 2 h, over which time $\mathrm{(DIPP)_2ClTa(CCMe_3{=}}\mathit{CH}\mathrm{CD{=}CCMe_3)}$ (1-d_1) was observed in solution before any $1,3,5\text{-}\mathrm{C_6}\mathit{H}_n\mathrm{D}_{3-n}{}^t\mathrm{Bu_3}$ was detected and 1-d_1 reached a maximum concentration before any $\mathrm{(DIPP)_2ClTa(CCMe_3{=}}\mathit{CH}\mathrm{CCMe_3{=}CD)}$ (2-$d_1(\alpha)$) was observed.

Structural Determinations. General Data. Preliminary examinations and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on a Syntex P2$_1$ diffractometer at ambient temperature, with a Crystal Logics control system. Crystal color and dimensions are recorded in Table I. As a check on crystal and electronic stability, two (for 7) or three (for 1 and 9) representative reflections were measured after every 97 reflections. For all three crystals, intensities of these standards remained constant within experimental error throughout data collection; so no decay correction was required. Only those reflections having intensities $I \geq 3\sigma(I)$ were used in the refinements. Hydrogen atoms were placed in calculated positions and included in the refinement. Lorentz–polarization and empirical absorption (Walker and Stuart[60]) corrections were applied to the data for all three compounds. All calculations were performed on a VAX computer using SDP/VAX.[61]

I. $\mathrm{(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)}$ (1). A clear yellow, rectangular block crystal of 1 crystallized from pentane (−40 °C) and was mounted in a glass capillary in a random orientation. From the systematic absences of $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$ and from the subsequent least-squares refinement, the space group was determined to be monoclinic $P2_1/n$ (No. 14). A total of 6835 reflections were collected in the $+h,+k,\pm l$ octants (6456 unique) in the range $2° \leq \theta \leq 50°$, with 4181 reflections having $I \geq 3\sigma(I)$. The structure was solved by the Patterson method and refined by full-matrix least-squares techniques for a final R = 0.029 and R_w = 0.033. The largest peak in the final difference Fourier synthesis was 0.58 (10) e/Å^3. Reflection averaging (agreement on I = 2.0%) corrections were also applied to the data.

II. (η^6-1,3,5-$\mathrm{C_6H_3{}^tBu_3}$)Ta(DIPP)$_2$(CH$_3$) (7). A red block crystal of 7 was mounted in a glass capillary with its long axis roughly parallel to the ϕ axis of the goniometer. From the systematic absences of $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$ and from subsequent least-squares refinement, the space group was determined to be $P2_1/n$ (No. 14). A total of 7686 reflections were collected in the $+h,+k,\pm l$ octants (6769 unique) in the range $2° \leq \theta \leq 50°$, with 4184 reflections having $I \geq 3\sigma(I)$. The structure was solved by the Patterson method and refined by full-matrix least-squares techniques for a final R = 0.024 and R_w = 0.026. The largest peak in the final difference Fourier synthesis was 0.65 (10) e/Å^3. Reflection averaging (agreement on I = 1.6%) corrections were also applied to the data.

III. (η^2(N,C)-2,4,6-$\mathrm{NC_5H_2{}^tBu_3}$)Ta(DIPP)$_2$Cl (9). A dark red irregular crystal of 9 crystallized from pentane (−40 °C) and was mounted in a glass capillary in a random orientation. From the systematic absences of $h0l$, $h = 2n + 1$; $0kl$, $l = 2n + 1$ and from subsequent least-squares refinement, the space group was determined to be $Pca2_1$ (No. 29). As a check on crystal quality, ω scans of several intense reflections were measured; the width at half-height was 0.25°, indicating good crystal quality. A total of 4153 reflections were collected in the $+h,+k,\pm l$ octants (3799 unique) in the range $2° \leq \theta \leq 50°$, with 2536 reflections having intensities $I \geq 3\sigma(I)$. The structure was solved by direct methods in which the tantalum atom was located from an E map. The remaining atoms were located in succeeding difference Fourier syntheses. The final cycle of refinement included 204 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of R = 0.037 and R_w = 0.041. The largest peak in the final difference Fourier synthesis had a height of 0.91 e/Å^3 with an estimated error based on a ΔF of 0.11.

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Registry No. 1, 125950-49-4; 1-d_2, 138753-73-8; 2, 125950-50-7; 2-d_2, 138753-74-9; 2-$d_2(\alpha)$, 138753-76-1; 2-$d_2(\beta)$, 138753-77-2; 3, 130220-40-5; 4, 138753-78-3; 5, 138753-71-6; 6, 125950-51-8; 7, 138753-72-7; 8, 125950-52-9; 9, 125950-53-0; Ta(DIPP)$_2$Cl$_3$(OEt$_2$), 125950-54-1; Ta(DIPP)$_2$Cl$_4$, 138753-75-0; $\mathrm{DC{\equiv}CCMe_3}$, 6833-44-9; 1,3,5-$\mathrm{C_6H_3{}^tBu_3}$, 1460-02-2; 2,4,6-$\mathrm{NC_5H_2{}^tBu_3}$, 20336-15-6; *tert*-butylacetylene, 917-92-0; *tert*-butyl cyanide, 630-18-2.

Supplementary Material Available: Textual presentation of the details of the structure solution and crystallographic details for $\mathrm{(DIPP)_2ClTa(CCMe_3{=}CHCH{=}CCMe_3)}$ (1), (η^6-1,3,5-

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$C_6H_3{}^tBu_3)Ta(DIPP)_2(CH_3)$ (7), and $(\eta^2(N,C)$-2,4,6-$NC_5H_2{}^tBu_3)$-$Ta(DIPP)_2Cl$ (9), tables of experimental details, atomic positional and thermal parameters, bond distances and angles, least-squares planes, and dihedral angles for 1, 7, and 9, tables of torsion angles for 1 and 7, and ORTEP figures for 1, 7, and 9 (56 pages); tables of observed and calculated structure factor amplitudes for 1, 7, and 9 (46 pages). Ordering information is given on any current masthead page.

Syntheses and Mechanistic Studies in the Formation of Endo- and Exo-Cyclometalated Platinum Compounds of *N*-Benzylidenebenzylamines

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The bifunctional ligands 2-$XC_6H_4CH{=}NCH_2$-2′-$X'C_6H_4$, and related ligands with more substituents on the aryl rings, react with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ to give cyclometalated complexes $[PtMe_2X(SMe_2)(C_6H_4CHNCH_2\text{-}2'\text{-}X'C_6H_4)]$ (4) by oxidative addition of C–X bonds (X = Cl, Br), or complexes $[PtMe(SMe_2)(C_6H_4CHNCH_2\text{-}2'\text{-}X'\text{-}C_6H_4)]$ 5 by orthometalation with loss of methane. In both types of compound the iminic functionality is endo to the cycle. Complexes 4 with an exocyclic structure are obtained only for X′ = Br, or for X′ = Cl when the ligand 2,4,6-$C_6H_2(CH_3)_3CH{=}NCH_2$-2′-ClC_6H_4 is used. Compounds 5 with an exocyclic structure are not formed. The following order of reactivity has been deduced: C–Cl endo $\approx$ C–Br exo > C–H endo > C–Cl exo $\gg$ C–H exo. Complexes **4** and **5** and the coordination compounds $[PtMe_2(SMe_2)(2,4,6\text{-}C_6H_2(CH_3)_3CH{=}NCH_2\text{-}2'\text{-}XC_6H_4)]$ (**3**) have been characterized by NMR spectroscopy. Complexes **4** react with PPh_3 to give a displacement reaction of SMe_2 for PPh_3, and the resulting compounds have been characterized by NMR spectroscopy; the compound $[PtMe_2Cl(PPh_3)(C_6H_3ClCHNCH_2C_6H_5)]$ (**6c**) has been characterized crystallographically. Complex **6c** crystallizes in the monoclinic space group $P2_1/a$, with $a = 17.677$ (3) Å, $b = 15.495$ (3) Å, $c = 11.371$ (2) Å, $\beta = 104.59$ (2)°, and $Z = 4$. The kinetics of formation of compounds **4** and **5** has been studied. It is suggested that formation of coordination compounds **3** takes place prior to the oxidative addition, which follows first-order kinetics and occurs by a concerted mechanism.

Introduction

A number of synthetic approaches to cyclometalated complexes have been investigated;[1] the earliest method involves thermal activation of a C–H bond. There has been increasing interest in the cyclometalated platinum compounds of N-donor ligands. van Koten has reported the preparation of platinum(II) complexes containing tridentate NCN ligands, which are useful substrates for the study of the oxidative addition of electrophiles to square-planar d^8 metal complexes.[2] Canty and co-workers have also studied the chemistry of cyclometalated platinum compounds with polydentate nitrogen donor ligands containing one or more pyrazol-1-yl groups.[3] The preparation of platinum(IV) cyclometalated compounds of an azobenzene derivative has been described recently by the reaction of the corresponding platinum(II) cyclometalated compound with chlorine or with *m*-chloroperbenzoic acid.[4]

Recently, platinum(II) and platinum(IV) cyclometalated complexes have been obtained by intramolecular oxidative addition of the Ar–X bonds in the compounds $[PtMe_2(2\text{-}XC_6H_4CHNCH_2CH_2NMe_2)]$ and it has been shown that the reactivity of the Ar–X bond follows the inverse order of Ar–X bond energies.[5] The fact that the intramolecular oxidative addition is much easier than the intermolecular process could be related, among other factors, to the presence of the C=N group, which conjugates with the phenyl group in the cycles formed.

In order to evaluate the importance of this factor, we describe the reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (1) with different *N*-benzylidenebenzylamines in which two different five-membered metallacycles could in principle be obtained, one in which the cycle contains the C=N group (endo) and the other in which it does not (exo).

The oxidative addition of aryl–halogen bonds of *N*-benzylidenebenzylamines to palladium(0) compounds has been reported recently,[6] and for this system, there is a strong tendency to form endocyclic compounds.

Results and Discussion

Syntheses and Characterization of Products. The *N*-benzylidenebenzylamine ligands were prepared by a condensation reaction of the corresponding amine with the

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