acyl carbon atom more closely resemble those of the five-membered ring of $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2C}}\mathrm{O)}$ than those of $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CF_2C}}\mathrm{O)}$, from which this compound came.

The metallacyclobutane complex $\overline{\mathrm{Fe(CO)_4(CF_2CF_2C}}\mathrm{F_2)}$ has a crystallographically imposed mirror plane passing through the axial CO ligands and the β-CF_2 group. The four-membered ring displays a slight pucker to relieve the eclipsed fluorine interactions indicated by the dihedral angles F(1)–C(1)–C(2)–F(4) = 133.7°, F(1)–C(1)–C(2)–F(3) = 12.9°, F(2)–C(1)–C(2)–F(4) = 19.2°, and F(2)–C(1)–C(2)–F(3) = 101.6°. These eclipsed interactions are reduced by the acute nature of the angles at each of the corners of the ring. The pucker in the ring is indicated by the interplane angle between the planes defined by C(1)–Fe–C(1′) and C(1)–C(2)–C(1′), which is 18.8°. For comparison, this angle is 2° in a 3,3-dimethyltitanacyclobutane complex[19] and 22° in a 3,3-dimethylplatinacyclobutane complex.[20] The F–C distance across the ring is 2.613 (5) Å, too long for a bonding interaction.

Conclusions

The goal of this research program was to develop organometallic-based synthetic methods for fluorocarbon chemistry. The construction of four-carbon fragments on an organometallic center followed by insertion of small molecules was the initial goal. It became clear that insertion of CO into preformed M–R_F bonds was not a viable approach. Our investigation of the reverse reaction indicates, under all circumstances, the preferred reaction is decarbonylation of the fluoroacyl, though the kinetic barriers to decarbonylation can be substantial compared to those for the analogous hydrocarbon analogues.

Acknowledgment. We wish to acknowledge the skilled technical assistance of Donald Soring and Lou Lardear. Drs. Joseph Calabrese and Richard Harlow were particularly helpful in preparing the crystallographic portions of this work for publication.

Supplementary Material Available: Listings of anisotropic thermal parameters and additional bond distances and angles (9 pages); listings of structure factors (36 pages). Ordering information is given on any current masthead page. Inquiries for copies of these materials can also be directed to K.J.K.

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Arene Complexes of Tantalum(III) Prepared by Alkyne Cyclization and Alkoxide-Exchange Reactions. Arene Folding and π Localization upon Coordination

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$Ta(DIPP)Cl_4$ (**1**, DIPP = 2,6-diisopropylphenoxide) has been prepared from the reaction of $TaCl_5$ with 1 equiv of $Me_3SiDIPP$ in CH_2Cl_2 and is shown to be dimeric. While $Ta(DIPP)Cl_4$ reacts with Et_2O to form *trans*-$Ta(DIPP)Cl_4(OEt_2)$ (**2**), $TaCl_5$ and Me_3SiDMP (DMP = 2,6-dimethylphenoxide) react in CH_2Cl_2/Et_2O solution to provide *trans*-$Ta(DMP)Cl_4(OEt_2)$ (**3**). Me_3SiDMP (2 equiv) reacts with $TaCl_5$ in CH_2Cl_2/Et_2O solution to form the bisphenoxide complex $Ta(DMP)_2Cl_3{\cdot}OEt_2$ (**6**). All of these compounds cyclize 3-hexyne upon their two-electron reduction to form $(\eta^6\text{-}C_6Et_6)Ta(OR)_xCl_{3-x}$ (**4**, OR = DIPP, $x = 1$; **5**, OR = DMP, $x = 1$; **7**, OR = DMP, $x = 2$) but do not readily undergo the analogous reaction with 2-butyne. However, $(\eta^6\text{-}C_6Me_6)Ta(DIPP)Cl_2$ (**10**) can be prepared in essentially quantitative yield from the reaction of $(\eta^6\text{-}C_6Me_6)Ta(DIPP)_2Cl$ (**9**) with $Ta(DIPP)_2Cl_3{\cdot}OEt_2$, which also provides $Ta(DIPP)_3Cl_2{\cdot}OEt_2$ as the byproduct. Likewise, $(\eta^6\text{-}C_6Et_6)Ta(DMP)_2Cl$ (**7**) is completely converted to $(\eta^6\text{-}C_6Et_6)Ta(DMP)Cl_2$ (**5**) upon its reaction with $Ta(DMP)_2Cl_3{\cdot}OEt_2$ (**6**). $(\eta^6\text{-}C_6Me_6)Ta(DIPP)Cl_2$ (**10**) crystallizes in the orthorhombic space group *Pnma* (No. 62) with $a = 16.506$ (3) Å, $b = 17.237$ (3) Å, $c = 8.911$ (1) Å, and $V = 2535.3$ Å^3 with $Z = 4$ and $\rho_{calcd} = 1.55$ g cm^{-3}. The arene ligand in **10** is characterized by a folded structure and considerable localization of the π-electron density in a 1,4-diene fashion. The thermolysis of **10** produces free C_6Me_6 as the only identifiable product, while the thermal decomposition of **9** produces free C_6Me_6 along with the "tucked in" complex $(\eta^1\text{-}C_6Me_5CH_2)Ta(DIPP)_2Cl_2$ (**11**). Compound **11** can be prepared in higher yields from **9** by its thermal decomposition in the presence of Me_3SiCl.

Introduction

Although most transition metals form stable complexes with arenes,[1] the only ones that have found significant applications in organic synthesis are those of chromium, particularly $(\eta^6\text{-arene})Cr(CO)_3$.[2,3] Coordination to the electron-withdrawing $Cr(CO)_3$ fragment renders the arene susceptible to nucleophilic attack, deactivates the ring with respect to electrophilic substitution, and results in both the arene and benzylic protons becoming more acidic.[4] We

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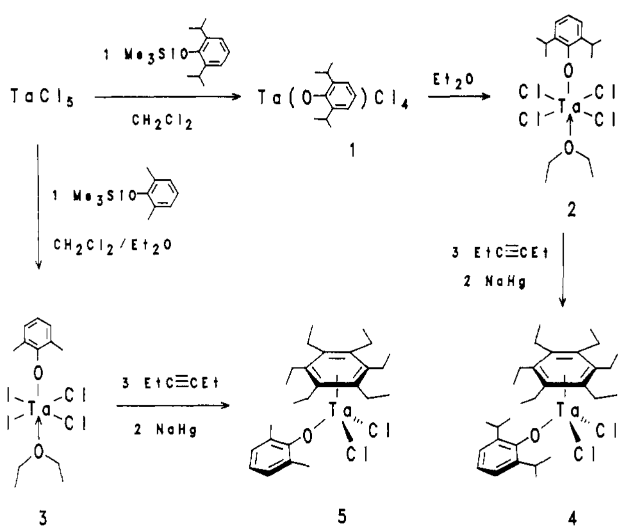
Scheme I



have recently synthesized a tantalum(III) complex of hexamethylbenzene[5] that engages in intramolecular C–H activation chemistry and thereby has permitted the selective functionalization of the resulting "tucked in" η^1-$C_6Me_5CH_2$ ligand.[6] The possibility that such reactions may eventually extend the synthetic utility of arene complexes and complement the existing chromium-based methodologies has prompted us to examine other arene compounds of tantalum.

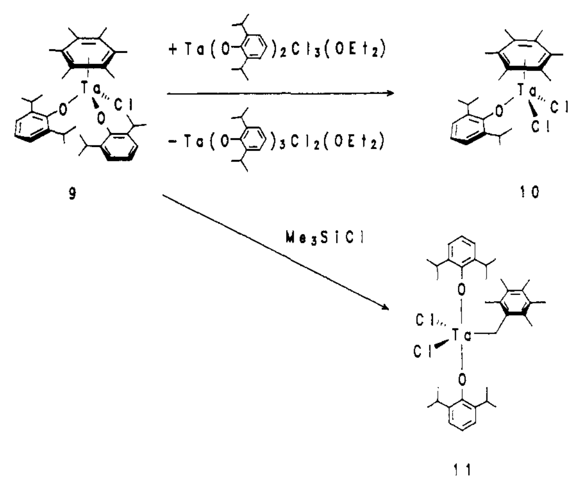
Group 5 arene chemistry is considerably less developed than that of group 6.[1] Most niobium and tantalum arene complexes are either trinuclear clusters derived from the Fischer–Hafner synthesis,[7] bis(arene) compounds and their derivatives originating from metal vapor syntheses,[8] or the tetracarbonyl cations.[9] Herein we report the preparation of new arene complexes of tantalum(III) synthesized by alkyne cyclization chemistry and, in some cases, by a transition-metal-based alkoxide-exchange reaction. As a part of this effort, we have synthesized new monokisalkoxide derivatives of tantalum(V) and also report these results.

Results and Discussion

Schemes I and II summarize the reactions developed in this study. Spectroscopic and analytical data for the compounds are given in the Experimental Section. Throughout this paper, DIPP = 2,6-diisopropylphenoxide and DMP = 2,6-dimethylphenoxide.

Monoalkoxy Chloride Complexes of Tantalum(V). $Ta(DIPP)_2Cl_3{\cdot}OEt_2$ can be reduced by two electrons in the presence of excess RC≡CR (R = Me, Et) to provide the arene complexes $(\eta^6\text{-}C_6R_6)Ta(DIPP)_2Cl$.[6] One major question to be addressed in this study was whether the monokisalkoxides $Ta(OR)Cl_4$ could participate in alkyne cyclization chemistry to provide $(\eta^6\text{-arene})Ta(OR)Cl_2$ species that may be more useful synthetically than the corresponding bisalkoxides. Monokisalkoxide or -siloxide derivatives of tantalum are rare; known examples include $Ta(OPh)Cl_4$[10] and the siloxides $Ta\{OSiMe_2[C(SiMe_3)_3]\}Cl_4$[11] and $Ta(OSi[2\text{-}MeC_6H_4]_3)Cl_4{\cdot}1.5OEt_2$.[12] With the preparation of $Nb(OR)Cl_4$ (R = Me, Et, Me_3Si) using Me_3SiOR reagents providing the precedence,[13] we have found that $TaCl_5$ reacts smoothly with $Me_3SiDIPP$ in dichloromethane solution to afford high yields of red-orange $Ta(DIPP)Cl_4$ (**1**). Accurate molecular weight measurements of **1** in solution have been precluded by its thermal degradation. However, like the niobium compounds $Nb(OR)Cl_4$,[13] $Ta(DIPP)Cl_4$ is formulated as a dimer on the basis of low-resolution CI mass spectrometry measurements.

Scheme II



Diethyl ether reacts rapidly with a dichloromethane solution of $Ta(DIPP)Cl_4$ to form the adduct, $Ta(DIPP)Cl_4(OEt_2)$ (**2**). On the basis of molecular weight measurements and the single ν(Ta–Cl) mode in the far IR, **2** is assigned a monomeric structure with a trans geometry. Trans isomerism is seen in the structurally characterized $Ta(OSi[2\text{-}MeC_6H_4]_3)Cl_4(OEt_2)$[12] and the phenoxides $Ta(OPh)Cl_4L$ (L = pyridine or α-picoline) are formulated as trans from their IR spectra.[14] It has proved more convenient to isolate the diethyl ether adducts of the DMP derivatives directly. Thus, $TaCl_5$ and 1 equiv of Me_3SiDMP react in CH_2Cl_2 to form a curdy precipitate that dissolves readily upon the addition of Et_2O, and high yields of the yellow, crystalline etherate $Ta(DMP)Cl_4(OEt_2)$ (**3**) are isolated (Scheme I).

(Arene)tantalum(III) Complexes. Since the alkyne cyclizations are best performed in diethyl ether (Scheme I), it is the monomeric etherate derivatives **2** and **3** that are the reactive alkoxide species in these preparations. Scheme I depicts the cyclotrimerization of EtC≡CEt by $Ta(DIPP)Cl_4(OEt_2)$ and $Ta(DMP)Cl_4(OEt_2)$, upon their two-electron reduction, to provide turquoise crystals of $(\eta^6\text{-}C_6Et_6)Ta(DIPP)Cl_2$ (**4**) and $(\eta^6\text{-}C_6Et_6)Ta(DMP)Cl_2$ (**5**),

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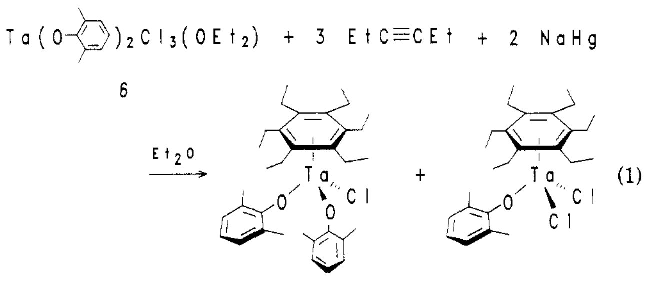
respectively. Although **4** and **5** are formed in moderate to low yield, no other organometallic products from these reactions have been isolated. It is essential that these reactions be initiated at low temperature to favor cyclotrimerization over polymerization of EtC≡CEt.[15] Attempts to cyclotrimerize alkynes at temperatures above −20 °C resulted in the formation of polymers and brown oils from which no organometallic products were tractable. In addition, a quantity of free hexaethylbenzene is invariably produced in these reactions. On the basis of the structural characterization of (η^6-C_6Me_6)Ta(DIPP)Cl_2 (vide infra), **4** and **5** are formulated as monomeric.

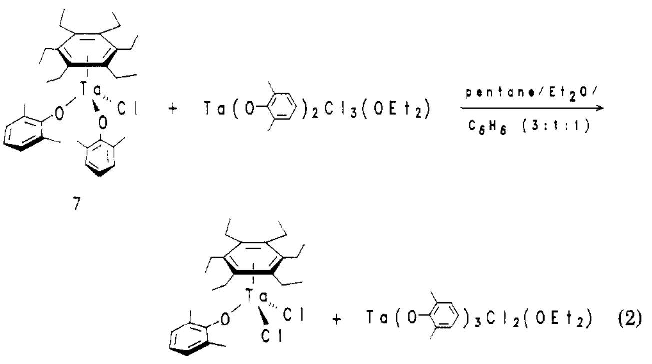
Pure Ta(DMP)$_2Cl_3$·OEt_2 (**6**) is available in high yield by the addition of 2 equiv of Me_3SiDMP to a CH_2Cl_2/Et_2O solution of $TaCl_5$. This complex also cyclizes EtC≡CEt, and the η^6-C_6Et_6 complex, (η^6-C_6Et_6)Ta(DMP)$_2$Cl (**7**), is isolated in ca. 15% yield. However, samples of **7** prepared in this fashion invariably contain an almost equimolar amount of the monoalkoxide (η^6-C_6Et_6)Ta(DMP)Cl_2 (**5**), eq 1. One can envisage two routes by which **5** might arise from this reaction. The reduction of Ta(DMP)$_2Cl_3$·OEt_2 could produce incipient "Ta(DMP)Cl_2" along with "Ta(DMP)$_2$Cl", both of which cyclize EtC≡CEt to their respective arene complexes. Second, it is also possible that some (η^6-C_6Et_6)Ta(DMP)$_2$Cl (**7**) formed early on in reaction 1 can itself react with starting complex Ta(DMP)$_2Cl_3$·OEt_2 (**6**) in a metathesis reaction to form (η^6-C_6Et_6)Ta(DMP)Cl_2 (**5**) and Ta(DMP)$_3Cl_2$·OEt_2 (**8**). This latter possibility was tested independently. When a typical **5**/**7** mixture (55% **5**, 45% **7**) isolated from eq 1 is reacted with Ta(DMP)$_2Cl_3$·OEt_2 (**6**) (pentane/Et_2O/C_6H_6 = 3:1:1; **7**/**6** mole ratio = 1:1), the portion of **7** in the mixture is completely converted to **5** (^{1}H NMR) after a 10-min reaction period, eq 2. The trisphenoxide complex Ta(DMP)$_3Cl_2$·OEt_2 (**8**) formed in this reaction was verified by comparing it spectroscopically with an authentic sample (prepared from the reaction of $TaCl_5$ with 3 equiv of LiDMP in benzene/Et_2O).



6

(1)

7 5



7

(2)

5

A striking difference between the cyclotrimerization chemistry of 3-hexyne and 2-butyne is observed in this tantalum system. (η^6-C_6Me_6)Ta(DIPP)$_2$Cl seems to be the only hexamethylbenzene compound readily available by reducing Ta(OR)$_x$Cl$_{5-x}$/MeC≡CMe solutions (OR = DMP or DIPP, x = 1 or 2).[5] Although (η^6-C_6Me_6)Ta(DIPP)Cl_2 is inaccessible through cyclization chemistry, reaction 2 provided the precedent for an alternate route that affords this compound in high yield.

Binuclear Exchange Reactions. Upon reacting (η^6-C_6Me_6)Ta(DIPP)$_2$Cl (**9**) with Ta(DIPP)$_2Cl_3$·OEt_2, an alkoxide/chloride ligand exchange ensues and turquoise (η^6-C_6Me_6)Ta(DIPP)Cl_2 (**10**) and pale yellow Ta(DIPP)$_3Cl_2$·OEt_2[16] are formed in near quantitative yields (Scheme II). This result, like eq 2, is consistent with the well-documented scrambling of alkoxide ligands in redistribution reactions involving binuclear intermediates with μ-OR groups.[17,18] The driving force for this exchange is apparently the marked stability of trisalkoxide tantalum(V) complexes as compared to their bisalkoxide analogues. This feature has been noted by Sullivan in the attempted preparation of (trisilox)$_2TaCl_3$ (trisilox = OSiMe_2[C(SiMe_3)$_3$]), which instead provided primarily (trisilox)$_3TaCl_2$ (along with $TaCl_5$) in a redistribution reaction.[11]

Accurate solution molecular weight measurements of **10**, like those of **1**, are precluded by the compound's thermal instability. When a solution of **10** (ca. 0.07 M in C_6D_6) is maintained at room temperature, its turquoise color is slowly replaced by green brown as thermolysis occurs. After 5 days, the decomposition of **10** is complete and hexamethylbenzene, formed quantitatively, is the only identifiable product (^{1}H NMR, $(Me_3Si)_2O$ internal standard). No organometallic products could be isolated or identified from this reaction. Although the metal center in (η^6-C_6Me_6)Ta(DIPP)Cl_2 (**10**) is less congested than that of its precursor (η^6-C_6Me_6)Ta(DIPP)$_2$Cl (**9**), *it is* **9** that shows the more rapid thermal decomposition. After standing at room temperature for 48 h, a less concentrated solution of **9** (0.007 M in Et_2O) was stripped to dryness, and the residue dissolved in C_6D_6. By ^{1}H NMR, no **9** remained, but two major products were identified. Thus, this decomposition affords ca. a 30% yield of free C_6Me_6 ($(Me_3Si)_2O$ internal standard), along with ca. a 30% yield of another compound that we have subsequently isolated and identified as (η^1-$C_6Me_5CH_2$)Ta(DIPP)$_2Cl_2$ (**11**). The remainder of **9** had decomposed to an intractable, brown oil characterized only by the broad, ill-defined resonances in its ^{1}H NMR spectrum.

The formation of (η^1-$C_6Me_5CH_2$)Ta(DIPP)$_2Cl_2$ (**11**) is *apparently* the result of two processes: (i) a binuclear chloride exchange reaction; (ii) the activation of a C–H bond of the C_6Me_6 ligand by the d^2 metal. The hexamethylbenzene ligand of (η^6-C_6Me_6)Ta(DIPP)$_2$Cl (**9**) has been observed to undergo intramolecular C–H activation in its reaction with *tert*-butylacetylene to form, presumably via incipient (η^6,η^1-$C_6Me_5CH_2$)Ta(H)(DIPP)$_2$Cl, the η^1-pentamethylbenzyl complex (*E*)-(η^1-$C_6Me_5CH_2$)Ta(CH=

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(18) Because mild thermal conditions are sufficient to labilize the arene ligand of (η^6-C_6Me_6)Ta(DIPP)$_2$Cl, we were attempting to use this feature in the reaction of (η^6-C_6Me_6)Ta(DIPP)$_2$Cl with Ta(DIPP)$_2Cl_3$·OEt_2 to form binuclear tantalum(IV) phenoxides. Thus, while binuclear μ-OR species are implicated, under these conditions an alkoxide/chloride exchange results and the arene is not labilized.

Table I. Summary of Crystal Data and Data Collection Parameters for (η^6-C_6Me_6)Ta(O-2,6-C_6H_3-*i*-Pr_2)Cl_2

mol formula	$C_{24}H_{35}Cl_2TaO$
mol wt	591.40
space group	*Pnma* (No. 62)
unit cell volume, Å^3	2535.3
a, Å	16.506 (3)
b, Å	17.237 (3)
c, Å	8.911 (1)
Z	4
calcd density, g cm^{-3}	1.55
cryst dimens, mm	0.20 × 0.25 × 0.45
data coll temp, °C	23 ± 1
Mo Kα radiation, λ, Å	0.71073
monochromator	graphite
abs coeff, cm^{-1}	45.1
transm coeff	0.707–0.999
2θ range, deg	2–50
total no. of reflns measd	2592 total, 2333 unique
no. of reflns measd with $I > 3\sigma(I)$	1754
scan type	θ–2θ
scan speed, deg min^{-1}	2–8
parameters refined	132
R	0.024
R_w	0.030

CHCMe$_3$)(DIPP)$_2$Cl.[6] Evidence has been presented for the intramolecular nature of this "tuck-in" reaction,[6] but at some point in the formation of **11**, a bimolecular, *formally* hydride–chloride ligand exchange must occur. Higher yields of **11** were in fact formed when the thermolysis of **9** was carried out in the presence of 2–3 mol equiv of Me_3SiCl (Scheme II). Thus, the reaction of (η^6-C_6Me_6)-Ta(DIPP)$_2$Cl (0.070 mmol) with 2.5 equiv of Me_3SiCl (Et_2O solution) provides a 45% yield (0.032 mmol) of (η^1-$C_6Me_5CH_2$)Ta(DIPP)$_2Cl_2$ (^{1}H NMR, $(Me_3Si)_2O$ internal standard; isolated yields of **11** are ca. 25%). Since the reaction appears quite complex, we have not searched for any Me_3SiH that might be formed in an exchange reaction of Me_3SiCl with (η^x,η^1-$C_6Me_5CH_2$)Ta(H)(DIPP)$_2$Cl, nor have we attempted to unravel any mechanistic details. We note that the energetics of hydride–chloride exchange reactions between silicon and early transition metals typically drives a purported reaction of this type in the opposite direction, for example, in d^2 tungsten halides.[19] Furthermore, this does not appear to be a general reaction, since the thermolysis of **9** in the presence of other organic halides (e.g., CH_2Cl_2) does not appear to afford higher yields of **11**. The structure of **11** depicted in Scheme II is based upon the equivalence of the phenoxide ligands (^{1}H and ^{13}C NMR) and upon the structurally characterized compound Ta(O-2,6-C_6H_3-*t*-Bu_2)$_2Me_3$, in which the phenoxide ligands occupy the axial sites of a trigonal bipyramid.[20,21]

Structural Study of (η^6-C_6Me_6)Ta(O-2,6-C_6H_3-*i*-Pr_2)Cl_2. Turquoise, single crystals of (η^6-C_6Me_6)Ta-(DIPP)Cl_2 (**10**) suitable for an X-ray structural determination were grown from toluene solution at −30 °C. A summary of the crystal data and the structural analysis are given in Table I, positional parameters in Table II, and important bond distances and angles in Table III. Figures 1 and 2 present views of **10**. The Ta, O(11), and C(11)

Table II. Positional Parameters and Their Estimated Standard Deviations for (η^6-C_6Me_6)Ta(O-2,6-C_6H_3-*i*-Pr_2)Cl_2[a]

atom	*x*	*y*	*z*	*B*, Å^2
Ta	0.46560 (2)	0.250	0.33389 (3)	2.765 (5)
Cl	0.56586 (9)	0.1571 (1)	0.4130 (2)	5.75 (3)
O(11)	0.3968 (3)	0.250	0.500	3.31 (9)
C(11)	0.3359 (4)	0.250	0.6033 (8)	3.1 (1)
C(12)	0.3065 (3)	0.3216 (3)	0.6529 (6)	3.9 (1)
C(12A)	0.3436 (4)	0.3964 (3)	0.5988 (8)	5.2 (1)
C(12B)	0.4131 (6)	0.4202 (5)	0.698 (1)	10.1 (3)
C(12C)	0.2818 (5)	0.4609 (4)	0.580 (1)	9.3 (3)
C(13)	0.2447 (4)	0.3187 (4)	0.7596 (7)	5.4 (1)
C(14)	0.2152 (6)	0.250	0.8104 (9)	5.9 (2)
C(21)	0.3637 (3)	0.2904 (3)	0.1603 (6)	3.7 (1)
C(22)	0.4397 (3)	0.3326 (3)	0.1507 (6)	4.2 (1)
C(23)	0.5060 (4)	0.2895 (4)	0.0779 (7)	5.2 (1)
C(31)	0.2856 (3)	0.3345 (4)	0.1904 (8)	5.7 (1)
C(32)	0.4395 (5)	0.4206 (4)	0.1538 (8)	6.9 (2)
C(33)	0.5754 (4)	0.3368 (5)	0.0140 (9)	8.9 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Relevant Bond Distances (Å) and Angles (deg) for (η^6-C_6Me_6)Ta(O-2,6-C_6H_3-*i*-Pr_2)Cl_2[a]

	Bond Distances		
Ta–Cl	2.408 (1)	C(12)–C(13)	1.395 (8)
Ta–O(11)	1.866 (3)	C(13)–C(14)	1.359 (8)
Ta–C(21)	2.389 (5)	C(21)*–C(21)	1.39 (1)
Ta–C(22)	2.207 (5)	C(21)–C(22)	1.452 (7)
Ta–C(23)	2.472 (6)	C(22)–C(23)	1.472 (8)
O(11)–C(11)	1.363 (7)	C(23)*–C(23)	1.36 (1)
C(11)–C(12)	1.397 (6)	C(21)–C(31)	1.520 (7)
C(12)–C(12A)	1.507 (8)	C(22)–C(32)	1.518 (8)
C(12A)–C(12B)	1.50 (1)	C(23)–C(33)	1.518 (8)
C(12A)–C(12C)	1.519 (9)		
	Bond Angles		
Cl–Ta–centroid (C_6Me_6)	117.28 (5)	C(22)–C(23)–C(23)*	120.3 (3)
O(11)–Ta–centroid (C_6Me_6)	127.7 (1)	C(21)*–C(21)–C(31)	120.0 (3)
Cl–Ta–Cl*	83.34 (8)	C(22)–C(21)–C(31)	119.6 (5)
Cl–Ta–O(11)	100.72 (9)	C(21)–C(22)–C(32)	119.8 (5)
Ta–O(11)–C(11)	170.0 (4)	C(23)–C(22)–C(32)	120.9 (6)
C(21)*–C(21)–C(22)	120.0 (3)	C(22)–C(23)–C(33)	117.1 (6)
C(21)–C(22)–C(23)	114.6 (5)	C(23)*–C(23)–C(33)	122.5 (5)

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

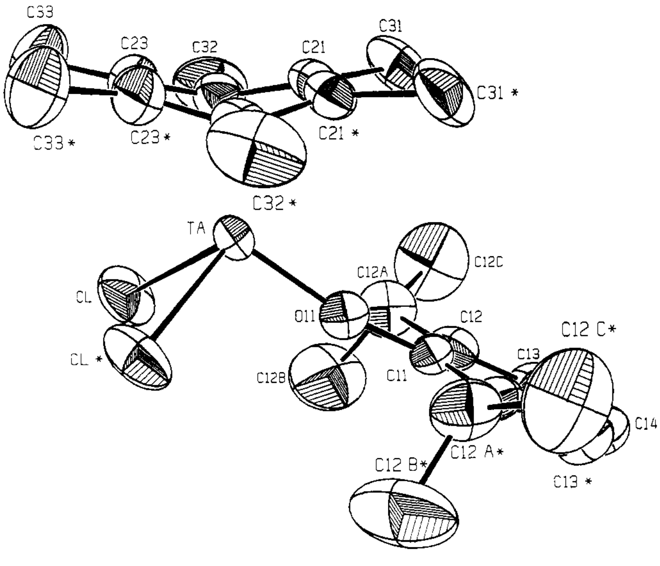

Figure 1. ORTEP drawing of (η^6-C_6Me_6)Ta(O-2,6-C_6H_3-*i*-Pr_2)Cl_2 (**10**), emphasizing the folding of the hexamethylbenzene ligand. Atoms are shown as 50% probability ellipsoids.

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(19) (a) The reaction of $WCl_4(SMe_2)_2$ with Et_3SiH is reported to generate $WCl_3H(SMe_2)_2$ and Et_3SiCl.[19b] (b) Boorman, P. M.; Moynihan, K. J.; Patel, V. D.; Richardson, J. F. *Inorg. Chem.* **1985**, *24*, 2989.

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(21) (a) Although related tantalum(V) compounds, e.g., the bis-alkylidene complex Ta(=CHCMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$[21b], are characterized by the π-bonding ligands in the equatorial plane of the TBP structure, we prefer the structural assignment presented in Scheme II since **11** is more closely related to the bisalkoxide derivatives in ref 20. (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930.

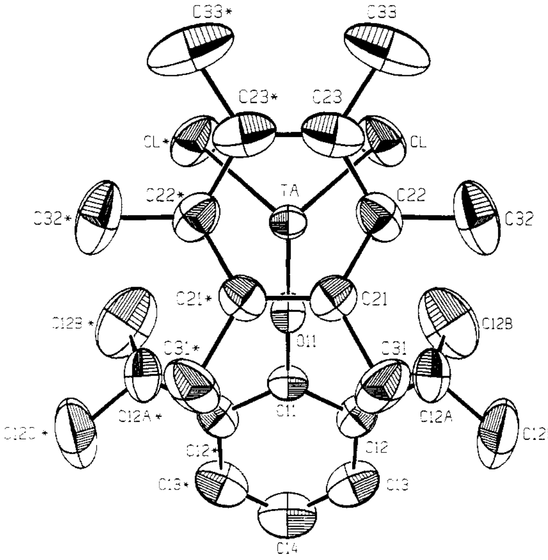


Figure 2. ORTEP drawing of (η^6-C_6Me_6)Ta(O-2,6-C_6H_3-*i*-Pr_2)Cl_2 (**10**), emphasizing the crystallographically imposed mirror plane along which the Ta, O(11), and C(11) lie.

atoms lie along a crystallographically imposed mirror plane.

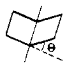
One salient feature of this molecular structure is the substantial bending of the coordinated C_6Me_6 ligand (Figure 1). Arene folding is severe as the dihedral angle between the C(22)-C(23)-C(23)*-C(22)* plane and the C(22)*-C(21)*-C(21)-C(22) plane is 26.8 ± 0.3°. This folding results in a "boat" structure characterized by two carbon atoms (C(22) and C(22)*) making a close approach to the metal (Ta-C(22) = Ta-C(22)* = 2.207 (5) Å) and can be compared to other structurally characterized "bent arenes" as summerized in Table IV. Both the "boat" structure, as seen in complex **10**, and the "inverted boat", in which two carbon atoms are *further* away from the metal than the other four ring carbons, have been characterized structurally. The dihedral angle or "fold angle" of selected bent arenes is also reported in Table IV.[22]

Carbon-carbon bond lengths around the ring (Table III) manifest another effect of coordinating an arene to a d^2 early-transition-metal center: considerable localization of the arene π-electron density has occurred such that its aromaticity has been disrupted. The coordinated arene exhibits a 1,4-diene type π localization within the ring as the "double" bonds C(21)-C(21)* and C(23)-C(23)* average 1.375 Å, while the "single" bonds C(21)-C(22), C(22)-C(23), C(21)*-C(22)*, and C(22)*-C(23)* average 1.462 Å. The numerical difference in these average "single" and "double" bond lengths can be used as a measure of the degree of π localization, and values for compound **10** and other distorted arenes are presented in Table IV for comparison. Thus **10**, along with (η^6-C_6Me_6)Ta$(DIPP)_2$Cl[5] and (η^6-C_6Et_6)Ta$(DIPP)_2$[24] contain some of the most distorted and π-localized arene ligands observed in η^6 coordination environments. Although the inverted boat structures may exhibit significantly different carbon-carbon bond lengths within the arene ring, only a portion of the boat structure complexes display *significant* 1,4-diene π localization (Table IV). The model compound norbornadiene,[23] in which π-electron localization is complete, is a useful comparison. Thus, these data suggest a 7-metallanorbornadiene (i.e., dienediyl) contribution to the

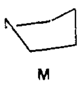
Table IV. Structural Data for Selected η^6-Arene Ligands That Show Folding upon Coordination

complex	fold angle θ,[a] deg: inverted boat[b]	fold angle θ,[a] deg: boat[c]	degree of π-localization[d] $\Delta_{(C-C)avg-(C=C)avg}$, Å	ref
norbornadiene		64.4	0.192 (8)	23
(C_6Me_6)Ta$(DIPP)_2$Cl		34.4	0.075 (20)	5
(C_6Me_6)Ta(DIPP)Cl_2		26.8	0.087 (13)	this work
(C_6Et_6)Ta$(DIPP)_2$		20.8	0.068 (11)	24
$[(C_6Me_6)_3Nb_3Cl_6]^+$		22.6[e]	0.12 (4)[e]	25
$[(C_6Me_6)_3Nb_3Cl_6]^{2+}$		17.8[e]	0.044 (28)[e]	26
($C_{10}H_8$)Ti{^{t}BuSi-(CH_2PMe_2)$_3$}		12.4	0.05 (1)[f]	27
(C_6H_6)Ru(1,5-COD)		5.2	0.044 (16)	28
($C_6Me_3H_3$)Ni$(C_6F_5)_2$	5.5		*d*	29
(C_6H_5Me)Ni$(C_6F_5)_2$	8.2		*d*	30
($C_6H_5BPh_3$)Rh[P-$(OMe)_3]_2$	7.3		*d*	31
$[(C_6H_5Me)Mo\text{-}(SMe)_2]_2^{2+}$	9.6		*d*	32
(C_6H_5Me)MoMe_2-$(PPhMe_2)_2$	10.9		*d*	33

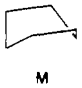
[a] The fold angle or dihedral angle about the C(1)-C(4) ring carbon vector, represented by



[b] Inverted boat structure has two arene carbons further away from the metal than the other four, represented by



[c] Boat distortion has two arene carbons closer to the metal than the other four, as in compound **10**, represented by



[d] Calculated as the difference between average "single" bonds and average "double" bonds only in structures that exhibit unambiguous 1,4-diene type π localization and reported even if this difference $\Delta \leq 3\sigma$. Uncertainties in the differences are calculated as σ(difference) = $[\sigma_1^2 + \sigma_2^2]^{1/2}$. [e] Data from the most π-localized arene ligand of the crystallographically independent ligands in the molecule are reported. (This ligand may not be the most folded ligand in the molecule.) [f] The naphthalene LUMO (B_{2g}), which is populated by the metal $d_{x^2-y^2}$, has contributions from only four of the six carbon atoms that coordinate the metal. Accordingly, only three carbon-carbon bonds are used in this calculation. See refs 27 and 34.

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(22) The data presented in Table IV represent η^6-arene ligands, as clearly judged from metal-carbon bond distances, and not η^4-arene ligands. For η^4-arenes, see: (a) Albright, J. O.; Datta, S.; Dezube, B.; Kouba, J. K.; Marynick, D. S.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1979**, *101*, 611. (b) Boncella, J. M.; Green, M. L. H.; O'Hare, D. *J. Chem. Soc., Chem. Commun.* **1986**, 618. (c) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347. (d) Huttner, G.; Lange, S.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 556. (e) Bowyer, W. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5657.

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(25) These data reported from ref 25a. Another structural determination of this complex has been undertaken in which disorder in the crystal was observed.[25b] (a) Stollmaier, F.; Thewalt, U. *J. Organomet. Chem.* **1981**, *222*, 227. (b) Churchill, M. R.; Chang, S. W.-Y. *J. Chem. Soc., Chem. Commun.* **1974**, 248.

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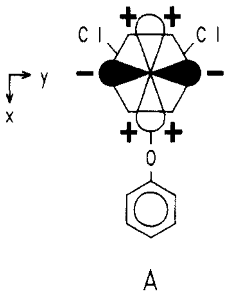
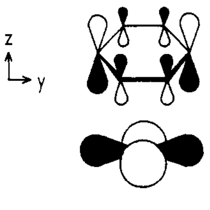
structure of (η^6-C_6Me_6)Ta(DIPP)Cl_2 (**10**), which we have noted in other tantalum arene compounds.[5,24]

The structural effects noted above are no doubt a manifestation of the selective δ overlap of the filled $d_{x^2-y^2}$ orbital with *one* arene π^* LUMO of the E_{2u} set (B_2 symmetry);[34] see A and B. Thus, the carbon–carbon bond distances are readily understood from the nodal properties of this B_2 π^* orbital (structure A). The close approach of C(22) and C(22)* to the metal may be a reflection of the better overlap of the filled $d_{x^2-y^2}$ with the arene B_2 which is possible upon bending, arising from the larger contributions to the B_2 MO from these carbons,[34] as depicted in structure B. Preliminary Fenske–Hall MO calculations provide results that are consistent with this picture of metal–ligand interactions.[35] The HOMO of the model complex (η^6-C_6H_6)Ta(OC_6H_5)Cl_2 is calculated to be 26% Ta $d_{x^2-y^2}$ and a surprising 41% arene B_2 π^* in character. The population analysis of the HOMO constituent orbitals reveals extensive back bonding into the arene as the $d_{x^2-y^2}$ contains 0.50 electron while the arene B_2 π^* is populated by 0.91 electron.[35]



A



B

A comparison of the alkoxide–metal interactions between (η^6-C_6Me_6)Ta(DIPP)Cl_2 (**10**) and the starting complex (η^6-C_6Me_6)Ta$(DIPP)_2$Cl (**9**) reveals that (i) the Ta–O(11)–C(11)$_{ipso}$ angle in **10** (170.0 (4)°) is more linear than either alkoxide linkage in **9** (146.5 (6) and 162.6 (6)°) and (ii) the Ta–O(11) bond length in **10** (1.866 (3) Å) is shorter than either alkoxide bond in **9** (1.935 (5) and 1.887 (5) Å). Since the coordination sphere in **10** is clearly less crowded than in **9**, these effects may be rationalized in terms of increased oxygen p π donation to empty metal d orbitals, and perhaps signalling donation from both perpendicular p π orbitals. However, the oxygen p orbital oriented perpendicular to the phenoxide phenyl ring is conjugated with this ring and will participate less efficiently in π donation than the p orbital that lies *in* the plane of the phenyl ring.[36] Therefore, whether the phenoxide ligand in **10** can be considered as a five-electron donor[37] (neutral sense) is not clear, but it is evident that p π donation to the metal in **10** is greater than in **9**, and that both the d_{xz} and d_{xy} orbitals appear available in this compound.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[38] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were purified under N_2 by standard techniques[39] and transferred to the drybox without exposure to air. The "cold" solvents used to wash isolated solid products were cooled to ca. −20 °C before use. In all preparations DIPP = 2,6-diisopropylphenoxide and DMP = 2,6-dimethylphenoxide.

Starting Materials. Tantalum(V) chloride (resublimed) was purchased from Alfa and used as received. 2-Butyne and 3-hexyne were purchased from Farchan Laboratories and passed down a short (ca. 5–6 cm) column of activated alumina (at ca. −10 °C) prior to use. Chlorotrimethylsilane and hexamethyldisilazane were purchased from Petrarch and used as received. 2,6-Diisopropylphenol and 2,6-dimethylphenol were obtained from Aldrich and were distilled or recrystallized before use. (η^6-C_6Me_6)Ta$(DIPP)_2$Cl (**9**)[5] and the lithium phenoxides[36a] were prepared as described previously.

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 or $C_6D_5CD_3$ solvent. Chemical shifts are referenced to protio impurities (δ 7.15, C_6D_6; δ 2.09, $C_6D_5CD_3$) or solvent ^{13}C resonances (δ 128.0, C_6D_6; δ 20.4, $C_6D_5CD_3$) and are reported downfield of Me_4Si. Infrared spectra in the region of 600–180 cm^{-1} were recorded as CsI pellets on a Perkin-Elmer PE-983 spectrometer. Molecular weight measurements were determined by vapor pressure osmometry using a device similar to one previously described.[40] Chemical ionization mass spectra were recorded to m/z = 999 on a Hewlett-Packard 5988A in both positive ion (isobutane reagent) and negative ion (methane reagent) modes. All microanalytical samples were handled under N_2 and were combusted with WO_3 (Desert Analytics, Tucson, AZ).

Reagent Preparations. (i) Ta$(DIPP)_2Cl_3$·OEt_2. The ether-free analogue of this complex has been reported,[41] but we have found the etherate to be more easily purified, more soluble in a range of organic solvents, and available in somewhat higher yields. To a slurry of 10.08 g (28.13 mmol) of $TaCl_5$ in 300 mL of benzene was added 50 mL of diethyl ether, which resulted in the immediate dissolution of the $TaCl_5$. A solution of 14.08 g (54.5 mmol) of LiDIPP·OEt_2 in diethyl ether (approximately 100 mL) was added to the vigorously stirred tantalum solution over about 10 min. A series of color changes (from rusty brown to orange brown to yellow) and the precipitation of LiCl were observed. The solution was allowed to stir at room temperature for 24 h. The mixture was then filtered through Celite, and the filtrate stripped to dryness to provide a bright, lemon yellow oil. Upon adding pentane to the oil, a yellow solid formed immediately. This solid was collected, washed with cold (ca. −20 °C) pentane, and dried in vacuo to yield 18.2 g (25.4 mmol, 92%) of product sufficiently pure for further reactions. Analytically pure compound can be obtained by recrystallization from Et_2O/pentane at −30 °C. ^{1}H NMR (C_6D_6) δ 7.03–6.81 (A_2B multiplet, 6 H, H_{aryl}), 4.25 (br q, 4 H, OCH_2CH_3), 4.03 (br, 4 H, $CHMe_2$), 1.20 (d, 24 H, $CHMe_2$), 0.89 (t, 6 H, OCH_2CH_3). ^{13}C NMR (C_6D_6) δ 140.7 (C_o), 125.8 (C_p), 124.2 (C_m), 69.0 (OCH_2CH_3), 26.4 ($CHMe_2$), 24.8 ($CHMe_2$), 12.0 (OCH_2CH_3). The C_{ipso} resonance was not observed. Anal. Calcd for $C_{28}H_{44}Cl_3O_3Ta$: C, 46.97; H, 6.19. Found: C, 47.26; H, 6.35.

(ii) Me_3SiO-2,6-C_6H_3-*i*-Pr_2. Both Me_3SiDIPP and Me_3SiDMP were prepared from their respective phenols by a procedure analogous to that reported for other trimethylsilyl ethers.[42] A mixture of HO-2,6-C_6H_3-*i*-Pr_2 (36.6 g, 0.205 mol), Me_3SiCl (35.9 g, 0.33 mol), and $(Me_3Si)_2NH$ (16.2 g, 0.10 mol) were combined in a large flask in ca. 100 mL of pyridine (from a freshly opened bottle, but which has *not* been predried). This mixture was refluxed for 3 days over which time white ammonium salts formed and sublimed into the condenser. The solution was allowed to cool and was filtered, and the reaction volatiles were removed in vacuo with gentle heating (at ca. 60 °C) to afford an oil. Heating

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and vacuum were continued for 6–8 h for complete removal of the pyridine, after which time the oil was filtered again to provide 44.5 g (0.178 mol, 87%) of pure product as a pale yellow to pale brown oil. ^{1}H NMR (C_6D_6) δ 7.19–7.04 (A_2B multiplet, 3 H, H_{aryl}), 3.45 (spt, 2 H, C*H*Me$_2$), 1.30 (d, 12 H, CH*Me*$_2$), 0.29 (s, 9 H, Me_3Si). ^{13}C NMR (C_6D_6) δ 150.2 (C_{ipso}), 139.2 (C_o), 123.9 (C_m), 122.7 (C_p), 27.4 (*C*HMe$_2$), 23.6 (CH*Me*$_2$), 0.8 (Me_3Si).

(iii) Me_3SiO-2,6-$C_6H_3Me_2$. This compound was prepared by a procedure analogous to that described above for Me_3SiO-2,6-C_6H_3-*i*-Pr_2 by using HO-2,6-$C_6H_3Me_2$ (50.1 g, 0.41 mol), Me_3SiCl (72.8 g, 0.67 mol), and $(Me_3Si)_2NH$ (32.5 g, 0.20 mol) in 200 mL of pyridine. A workup procedure similar to that described for Me_3SiO-2,6-C_6H_3-*i*-Pr_2 yielded 54 g (0.28 mol, 68%) of pure Me_3SiO-2,6-$C_6H_3Me_2$ as a pale brown oil. ^{1}H NMR (C_6D_6) δ 6.94–6.75 (A_2B multiplet, 3 H, H_{aryl}), 2.16 (s, 6 H, C_6H_3*Me*$_2$), 0.14 (s, 9 H, Me_3Si). ^{13}C NMR (C_6D_6) δ 153.0 (C_{ipso}), 128.9 (C_m), 128.5 (C_o), 121.8 (C_p), 17.9 (C_6H_3*Me*$_2$), 0.9 (Me_3Si).

Preparations. Ta(DIPP)Cl$_4$ (1). Me_3SiDIPP (0.51 g, 2.05 mmol) was added dropwise to a rapidly stirred slurry of 0.75 g (2.09 mmol) of $TaCl_5$ in 25 mL of CH_2Cl_2. The reaction immediately ensued to provide a red orange solution. The best yields were obtained by allowing the reaction to stir at room temperature for 48 h, after which time the cloudy solution was filtered through Celite, yielding a clear red filtrate. The filtrate was concentrated to approximately one-half volume and cooled to −30 °C. Large red orange crystals that formed over 1 week were filtered off, washed with minimal cold pentane, and dried in vacuo. The yield of Ta(DIPP)Cl$_4$ was 0.94 g (1.88 mmol, 90%). Crystals suitable for microanalysis were grown from pentane solution at −30 °C. ^{1}H NMR (C_6D_6) δ 6.97–6.75 (A_2B multiplet, 3 H, H_{aryl}), 4.09 (spt, 2 H, C*H*Me$_2$), 1.15 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6) δ 159.9 (C_{ipso}), 141.9 (C_o), 128.8 (C_p), 124.5 (C_m), 27.0 (*C*HMe$_2$), 24.6 (CH*Me*$_2$). Mass spectrum [CI$^-$], *m/z* = 998, $[Ta_2(DIPP)_2{}^{35}Cl_7{}^{37}Cl]^-$; [CI$^+$], *m/z* = 963, $[Ta_2(DIPP)_2{}^{35}Cl_6{}^{37}Cl]^+$ ([M − Cl]$^+$); 965, $[Ta_2(DIPP)_2{}^{35}Cl_5{}^{37}Cl_2]^+$ ([M − Cl]$^+$). Anal. Calcd for $C_{12}H_{17}Cl_4OTa$: C, 28.82; H, 3.43; Cl, 28.36. Found: C, 29.22; H, 3.53; Cl, 27.89. Samples sufficiently pure for further reactions can be isolated in ca. 75% yield after the reaction has stirred overnight (ca. 12 h) by removing the volatile products in vacuo, washing the resulting powder with a minimal volume of cold pentane, and drying the sample in vacuo.

Ta(DIPP)Cl$_4$(OEt$_2$) (2). A 0.56 g (1.1 mmol) sample of Ta(DIPP)Cl$_4$ was dissolved in 20 mL of CH_2Cl_2 and stirred while ca. 1 mL of diethyl ether was added dropwise. The solution color immediately changed from red orange to yellow. The solution was allowed to stir at room temperature for 2–3 h, after which time the solvent was removed in vacuo to yield the product as a yellow solid. This solid was washed with minimal cold pentane and dried in vacuo to provide 0.36 g (0.63 mmol, 57%) of product. Analytically pure samples were obtained from pentane at −30 °C. ^{1}H NMR (C_6D_6) δ 7.07–6.83 (A_2B multiplet, 3 H, H_{aryl}), 4.50 (spt, 2 H, C*H*Me$_2$), 4.39 (q, 4 H, OC*H*$_2$CH$_3$), 1.30 (d, 12 H, CH*Me*$_2$), 0.96 (t, 6 H, OCH$_2$C*H*$_3$). ^{13}C NMR (C_6D_6) δ 158.9 (C_{ipso}), 142.2 (C_o), 127.7 (C_p), 124.5 (C_m), 71.0 (O*C*H$_2$CH$_3$), 26.3 (*C*HMe$_2$), 25.1 (CH*Me*$_2$), 11.9 (OCH$_2$*C*H$_3$). IR ν(Ta–Cl) = 335 (s) cm^{-1}. Molecular weight (C_6H_6 solution): calcd for monomer 574, found 615 ± 60. Anal. Calcd for $C_{16}H_{27}Cl_4O_2Ta$: C, 33.47; H, 4.74. Found: C, 33.70; H, 4.90.

Ta(DMP)Cl$_4$(OEt$_2$) (3). A 0.54-g sample (2.78 mmol) of Me_3SiDMP was added dropwise (neat) to a rapidly stirred slurry of 1.00 g (2.79 mmol) of $TaCl_5$ in 15 mL of CH_2Cl_2. The solution quickly turned cloudy, and a curdy, orange precipitate formed. After this mixture was stirred for 30 min, diethyl ether was added dropwise until all of the precipitate had dissolved, yielding a clear orange solution. This solution was allowed to stir at room temperature for 24 h, over which time no further color change was noted. The solvent was removed in vacuo, and the resulting orange oil was dissolved in minimal pentane and cooled to −20 °C. Large yellow crystals formed over 2 days, which were filtered off, washed with a small volume of cold pentane, and dried in vacuo to provide 1.12 g (2.23 mmol, 80%) of product. Analytically pure samples were obtained by recrystallization from pentane at −30 °C. ^{1}H NMR (C_6D_6) δ 6.70–6.52 (A_2B multiplet, 3 H, H_{aryl}), 4.38 (q, 4 H, OC*H*$_2$CH$_3$), 2.77 (s, 6 H, OC$_6$H$_3$*Me*$_2$), 0.94 (t, 6 H, OCH$_2$C*H*$_3$). ^{13}C NMR (C_6D_6) δ 161.3 (C_{ipso}), 131.7 (C_o), 128.9 (C_m), 126.9 (C_p), 71.0 (O*C*H$_2$CH$_3$), 17.4 (OC$_6$H$_3$*Me*$_2$), 11.9 (OCH$_2$*C*H$_3$). Anal. Calcd for $C_{12}H_{19}Cl_4O_2Ta$: C, 27.82; H, 3.70. Found: C, 28.14; H, 3.88.

(η^6-C$_6$Et$_6$)Ta(DIPP)Cl$_2$ (4). A solution of 0.50 g (1.0 mmol) of Ta(DIPP)Cl$_4$ in 20 mL of diethyl ether was cooled to −30 °C. 3-Hexyne (0.34 mL, 3.0 mmol) and 0.5% NaHg amalgam (0.68 mL, 2.0 mmol) were added, and the mixture was shaken vigorously for 8 min. Over this time the color of the solution changed to dark green with the concomitant formation of a small amount of polymer. The solution was then allowed to stir at room temperature for 1 h. The resulting mixture was filtered through Celite, and the filtrate was stripped to dryness to provide a blue green powder. This powder was washed with a minimal amount of cold pentane, yielding 0.10 g of (η^6-C$_6$Et$_6$)Ta(DIPP)Cl$_2$ as a turquoise powder. The filtrate from these washings was cooled to −30 °C for 24 h to yield 0.064 g of additional turquoise product. The total yield of (η^6-C$_6$Et$_6$)Ta(DIPP)Cl$_2$ was 0.164 g (0.24 mmol, 24%). ^{1}H NMR (toluene-d_8) δ 7.07–6.95 (A_2B multiplet, 3 H, H_{aryl}), 3.42 (spt, 2 H, C*H*Me$_2$), 2.13 (q, 12 H, C*H*$_2$CH$_3$), 1.33 (d, 12 H, CH*Me*$_2$), 0.99 (t, 18 H, CH$_2$C*H*$_3$). ^{13}C NMR (toluene-d_8) δ 156.5 (C_{ipso}), 136.7 (C_o), 128.8 (*C*$_6$Et$_6$), 124.5 (C_p), 123.7 (C_m), 26.7 (*C*HMe$_2$), 24.6 (CH*Me*$_2$), 23.4 (*C*H$_2$CH$_3$), 17.6 (CH$_2$*C*H$_3$). Samples suitable for elemental analysis were crystallized from toluene at −30 °C. Anal. Calcd for $C_{30}H_{47}Cl_2OTa$: C, 53.34; H, 7.01. Found: C, 53.59; H, 6.94.

(η^6-C$_6$Et$_6$)Ta(DMP)Cl$_2$ (5). A solution of 0.50 g (1.0 mmol) of Ta(DMP)Cl$_4$(OEt$_2$) in 20 mL of diethyl ether was prepared and cooled to −30 °C. 3-Hexyne (0.34 mL, 3.0 mmol) and 0.5% NaHg amalgam (0.68 mL, 2.0 mmol) were added, and this mixture was shaken vigorously for 8–10 min. Over this time the solution developed a dark green color, and the formation of a small amount of polymer was noted. This mixture was then allowed to stir at room temperature for 1 h. The solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo to provide a blue green solid. Dissolution of this solid in minimal diethyl ether followed by cooling to −30 °C provided 0.060 g (0.097 mmol, 9.7%) of dark blue, crystalline product, which was filtered off and dried in vacuo. Crystals suitable for microanalysis were obtained from further recrystallization from diethyl ether at −30 °C. ^{1}H NMR (C_6D_6) δ 6.89–6.73 (A_2B multiplet, 3 H, H_{aryl}), 2.39 (s, 6 H, OC$_6$H$_3$*Me*$_2$), 2.04 (q, 12 H, C*H*$_2$CH$_3$), 0.90 (t, 18 H, CH$_2$C*H*$_3$). ^{13}C NMR (C_6D_6) δ 159.2 (C_{ipso}), 129.1 (C_m), 128.7 (*C*$_6$Et$_6$), 126.3 (C_o), 123.7 (C_p), 23.4 (*C*H$_2$CH$_3$), 17.6 (coincident OC$_6$H$_3$*Me*$_2$ and CH$_2$*C*H$_3$). Anal. Calcd for $C_{26}H_{39}Cl_2OTa$: C, 50.41; H, 6.35. Found: C, 49.99; H, 6.51.

Ta(DMP)$_2$Cl$_3$·OEt$_2$ (6). To a rapidly stirred slurry of 1.0 g (2.79 mmol) of $TaCl_5$ in 20 mL of CH_2Cl_2 was added ca. 3 mL of diethyl ether, which resulted in the immediate dissolution of $TaCl_5$. A 1.08-g (5.64 mmol) sample of Me_3SiDMP was added dropwise (neat) to this solution, which immediately developed an orange color and which gradually changed to golden yellow over 1 h. The solution was stirred at room temperature for 48 h, after which time it was filtered through Celite, and the solvent removed from the filtrate in vacuo to provide a yellow orange oil. A minimal amount of cold pentane was added to this oil, which resulted in the formation of a bright yellow powder, which was filtered off, washed with a small portion of cold pentane, and dried in vacuo. This procedure provided 1.50 g (2.48 mmol, 89%) of product sufficiently pure for further reactions. The compound was recrystallized from pentane at −30 °C to form analytically pure samples. ^{1}H NMR (C_6D_6, 45 °C) δ 6.81–6.62 (A_2B multiplet, 6 H, H_{aryl}), 4.27 (q, 4 H, OC*H*$_2$CH$_3$), 2.52 (s, 12 H, OC$_6$H$_3$*Me*$_2$), 0.99 (t, 6 H, OCH$_2$C*H*$_3$). ^{13}C NMR (C_6D_6, 45 °C) δ 159.8 (C_{ipso}), 130.3 (C_o), 129.1 (C_m), 125.1 (C_p), 69.5 (O*C*H$_2$CH$_3$), 17.4 (OC$_6$H$_3$*Me*$_2$), 12.2 (OCH$_2$*C*H$_3$). Anal. Calcd for $C_{20}H_{28}Cl_3O_3Ta$: C, 39.79; H, 4.67. Found: C, 40.09; H, 4.91.

(η^6-C$_6$Et$_6$)Ta(DMP)$_2$Cl (7). A solution of 0.25 g (0.41 mmol) of Ta(DMP)$_2$Cl$_3$·OEt$_2$ in 20 mL of diethyl ether was prepared and cooled to −30 °C. 3-Hexyne (0.14 mL, 1.23 mmol) and NaHg amalgam (0.5%, 0.28 mL, 0.82 mmol) were added to this cold solution and the mixture was shaken vigorously for 8–10 min. Over this time a dark blue color developed, and the formation of a small amount of polymer was observed. The solution was then filtered through Celite and the solvent removed from the filtrate in vacuo to provide a blue green powder. This powder was dissolved in a minimum amount of toluene, pentane was layered over the solution, and the mixture was stored at −30 °C for 24 h. The blue crystalline product that formed over this time was filtered off and dried in vacuo yielding 0.064 g of product, which is always contaminated with varying amounts of (η^6-C_6Et_6)Ta(DMP)Cl_2 (5) impurity and which could not be separated. ^{1}H NMR (C_6D_6) δ 7.00–6.76 (A_2B multiplet, 6 H, H_{aryl}), 2.22 (s, 12 H, $OC_6H_3Me_2$), 2.21 (q, 12 H, CH_2CH_3), 1.00 (t, 18 H, CH_2CH_3). ^{13}C NMR (C_6D_6) δ 160.0 (C_{ipso}), 126.8 (C_6Et_6), 126.2 (C_o), 121.3 (C_p), 24.0 (CH_2CH_3), 18.2 (CH_2CH_3), 17.6 ($OC_6H_3Me_2$). The C_{meta} (DMP) resonance was not observed and is most likely obscured by the solvent resonance or coincident with C_{meta} of (η^6-C_6Et_6)Ta(DMP)Cl_2 (5, δ 129.1), which contaminates this sample (see text).

Ta(DMP)$_3$Cl$_2$·OEt$_2$ (8). To a rapidly stirred slurry of 1.00 g (2.79 mmol) of $TaCl_5$ in ca. 30 mL of benzene was added sufficient diethyl ether to dissolve the solid (ca. 1 mL). Solid LiDMP (1.07 g, 8.35 mmol) was added directly to this solution, which after a series of color changes gradually changed to light yellow over 30 min. The solution was stirred at room temperature for 48 h, after which time it was filtered through Celite, and the solvent removed from the filtrate in vacuo to provide a light yellow, sticky powder. A minimal amount of pentane was added to this powder, and the product was filtered off, washed with additional pentane, and dried in vacuo to yield 1.53 g (2.22 mmol, 80%) of compound. The compound was recrystallized from toluene/pentane at −30 °C to form analytically pure samples. ^{1}H NMR (C_6D_6, 37 °C) δ 6.89–6.67 (A_2B multiplet, 9 H, H_{aryl}), 4.05 (q, 4 H, OCH_2CH_3), 2.53 (s, 18 H, $OC_6H_3Me_2$), 0.98 (t, 6 H, OCH_2CH_3). ^{13}C NMR (C_6D_6, 37 °C) δ 159.6 (C_{ipso}), 129.6 (C_o), 129.1 (C_m), 123.6 (C_p), 67.9 (OCH_2CH_3), 17.6 ($OC_6H_3Me_2$), 11.9 (OCH_2CH_3). Anal. Calcd for $C_{28}H_{37}Cl_2O_4Ta$: C, 48.78; H, 5.41. Found: C, 48.82; H, 5.43.

(η^6-C$_6$Me$_6$)Ta(DIPP)Cl$_2$ (10). To a room-temperature slurry of (η^6-C_6Me_6)Ta(DIPP)$_2$Cl (0.25 g, 0.341 mmol) in 20 mL of pentane was added 0.24 g (0.34 mmol) of Ta(DIPP)$_2$Cl$_3$·OEt$_2$. The reaction mixture was shaken vigorously for 1 min, over which time a turquoise blue color began to develop. Approximately 1 mL of diethyl ether was added quickly (to completely dissolve any solid reactants that remain) and this mixture was shaken vigorously for an additional 5 min, which resulted in the precipitation of the product as turquoise microcrystals. The product was filtered off, washed with small portions of cold (ca. −20 °C) pentane, and dried in vacuo. The best yield of (η^6-C_6Me_6)Ta(DIPP)Cl_2 obtained by this method was 92% (0.186 g, 0.315 mmol) on the basis of (η^6-C_6Me_6)Ta(DIPP)$_2$Cl, but yields of 75–80% are typical. Analytically pure samples were obtained by recrystallization from toluene/pentane solutions at −30 °C. ^{1}H NMR (C_6D_6) δ 6.98–6.91 (A_2B multiplet, 3 H, H_{aryl}), 3.30 (spt, 2 H, $CHMe_2$), 1.89 (s, 18 H, C_6Me_6), 1.27 (d, 12 H, $CHMe_2$). ^{13}C NMR (C_6D_6) δ 156.1 (C_{ipso}), 136.3 (C_o), 124.4 (C_p), 123.5 (C_m), 121.0 (C_6Me_6), 27.0 ($CHMe_2$), 24.1 ($CHMe_2$), 16.3 (C_6Me_6). Anal. Calcd for $C_{24}H_{35}Cl_2OTa$: C, 48.74; H, 5.97; Cl, 11.99. Found: C, 48.82; H, 6.02; Cl, 11.78. The filtrate from this reaction was stripped to a yellow oil, reconstituted in a minimum volume of pentane, and cooled to −30 °C to provide 0.18 g (0.216 mmol, 63%) of yellow crystals of Ta(DIPP)$_3$Cl$_2$·OEt$_2$. This product was collected, dried in vacuo, and compared spectroscopically with an authentic sample.[17]

(η^1-C$_6$Me$_5$CH$_2$)Ta(DIPP)$_2$Cl$_2$ (11). To a solution of (η^6-C_6Me_6)Ta(DIPP)$_2$Cl (0.25 g, 0.34 mmol) in 20 mL of diethyl ether was added 0.74 g (0.68 mmol) of Me_3SiCl. The solution was stirred for 48 h, over which time a brown color developed. The solvent was removed under reduced pressure to yield a brown, oily solid. The small amount of hexamethylbenzene formed during the reaction was removed by sublimation at 25 °C (10^{-4} Torr). The remaining solid was dissolved in a minimum volume of pentane and cooled to −30 °C, whereupon pale yellow crystals of (η^1-$C_6Me_5CH_2$)Ta(DIPP)$_2$Cl$_2$ formed. The product was filtered off, washed with cold pentane, and dried in vacuo for a yield of 0.065 g (0.085 mmol, 25%). ^{1}H NMR (C_6D_6) δ 7.14–6.94 (A_2B multiplet, 6 H, H_{aryl}), 3.69 (s, 2 H, $CH_2C_6Me_5$), 3.50 (spt, 4 H, $CHMe_2$), 2.45 (s, 3 H, p-CH_3), 2.02 and 1.96 (s, 6 H each, o- and m-CH_3), 1.31 (d, 12 H, $CHMe_2$). ^{13}C NMR (C_6D_6) δ 156.1 (C_{ipso}, DIPP), 143.4 (C_o, $CH_2C_6Me_5$), 143.3 (C_{ipso}, $CH_2C_6Me_5$), 139.8 (C_o, DIPP), 135.8 (C_m, $CH_2C_6Me_5$), 124.4 (C_p, DIPP), 123.9 (C_m, DIPP), 116.4 (C_p, $CH_2C_6Me_5$), 73.9 ($CH_2C_6Me_5$), 27.7 ($CHMe_2$), 24.4 ($CHMe_2$), 18.7 and 16.8 (o- and m-CH_3), 17.1 (p-CH_3). Anal. Calcd for $C_{36}H_{51}Cl_2O_2Ta$: C, 56.33; H, 6.70; Cl, 9.24. Found: C, 56.35; H, 6.71; Cl, 8.84.

Structural Determination of (η^6-C$_6$Me$_6$)Ta(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)Cl$_2$ (10). A turquoise blue, rectangular crystal of (η^6-C_6Me_6)Ta(DIPP)Cl_2 having approximate dimensions 0.20 × 0.25 × 0.45 mm was mounted in a glass capillary with its long axis roughly parallel to the ϕ axis of the goniometer. Preliminary examination and data collection were performed on a Syntex–Nicolet $P2_1$ diffractometer at room temperature with Mo Kα radiation. From the systematic absences of $hk0$, $h = 2n + 1$; $0kl$, $k + l = 2n + 1$, and from the subsequent least-squares refinement, the space group was determined to be *Pnma* (No. 62). Two check reflections were measured every 98 data reflections; the intensities of these standards remained constant within experimental error throughout data collection, and therefore no decay correction was applied. A total of 2592 reflections were collected in the $+h,+k,+l$ octant (2333 unique) in the range $2° \leq 2\theta \leq 50°$, with 1754 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 $R_w = 0.030$. The largest peak in the final difference Fourier map had a height of 0.63 (8) e/Å^3. Lorentz–polarization and empirical absorption corrections were applied. Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and included in the refinement. Calculation of the arene centroid was performed by averaging the x, y, and z coordinates of all carbon atoms in the arene ring (C(21), C(22), C(23), C(21)*, C(22)*, and C(23)*). The bond angle data reported in Table III for this centroid were identical with values derived from centroid calculations using only C(21), C(23), C(21)*, and C(23)*. Refinements were attempted in the acentric space group *Pna*2_1, which has the same extinction conditions as *Pnma*, but the refinement did not converge. The positional and thermal parameters of the atoms that are related by the mirror plane in *Pnma* are highly correlated in the *Pna*2_1 refinement. All calculations were performed on a VAX computer using SDP/VAX.[43]

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Supplementary Material Available: Full details of the structure solution and crystallographic details for (η^6-C_6Me_6)-Ta(O-2,6-C_6H_3-*i*-Pr$_2$)Cl_2, tables of atomic positional and thermal parameters, bond distances and angles, least-squares planes, and dihedral angles, and ORTEP figures (18 pages); tables of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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