

# Cross-Coupling Reactions of $d^2$ Tantalum Alkyne Complexes: Selective 1,3-Diene Syntheses and Their Relevance to Alkyne Cyclization Chemistry

Jamie R. Strickler, Pamela A. Wexler, and David E. Wigley\*

Carl S. Marvel Laboratories of Chemistry, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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$\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  (DIPP = 2,6-diisopropylphenoxide) can be reduced by two electrons in the presence of the bulky alkynes  $\text{PhC}\equiv\text{CPh}$  and  $\text{Me}_3\text{SiC}\equiv\text{CMe}$  to provide the pale yellow adducts  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  (1) and  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (2). The reduction of  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  in the presence of smaller internal alkynes (viz.  $\text{EtC}\equiv\text{CEt}$ ) or the terminal alkynes  $\text{Me}_3\text{SiC}\equiv\text{CH}$  or  $\text{Me}_3\text{CC}\equiv\text{CH}$  affords the metallacyclopentadienes  $(\text{DIPP})_3\text{Ta}(\text{C}(\text{Et})=\text{CEtC}(\text{Et})=\text{CEt})$  (3) or  $(\text{DIPP})_3\text{Ta}(\text{CR}=\text{CHCR}=\text{CH})$  (4, R =  $\text{SiMe}_3$ ; 5, R =  $\text{CMe}_3$ ) directly. The molecular structure of the  $\text{PhC}\equiv\text{CPh}$  adduct 1 is approximately tetrahedral (L-Ta-L angles average  $109.4^\circ$ ) and features very short Ta-C<sub>alkyne</sub> distances (2.070 (3) and 2.076 (3) Å, respectively) and an elongated "C=C" bond (1.346 (5) Å), which indicate a strongly bound and substantially reduced alkyne ligand. The molecular structure of metallacycle 3 reveals a trigonal bipyramidal geometry ( $\text{L}_{\text{ax}}-\text{Ta}-\text{L}_{\text{ax}} = 164.9 (3)^\circ$ ) with the metallacyclic  $\alpha$  carbons occupying one axial and one equatorial site. The alkyne complex  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  (1) reacts with  $\text{MeC}\equiv\text{CMe}$ ,  $\text{EtC}\equiv\text{CEt}$ ,  $\text{Me}_3\text{CC}\equiv\text{CH}$ ,  $\text{Me}_3\text{SiC}\equiv\text{CH}$ , or  $\text{PhC}\equiv\text{CH}$  to afford high yields of the metallacyclization products  $(\text{DIPP})_3\text{Ta}(\text{CPh}=\text{CPhCMe}=\text{CMe})$  (6),  $(\text{DIPP})_3\text{Ta}(\text{CPh}=\text{CPhC}(\text{Et})=\text{CEt})$  (7),  $(\text{DIPP})_3\text{Ta}(\text{CPh}=\text{CPhCH}=\text{CCMe}_3)$  (8),  $(\text{DIPP})_3\text{Ta}(\text{CPh}=\text{CPhCH}=\text{CSiMe}_3)$  (9), and  $(\text{DIPP})_3\text{Ta}(\text{CPh}=\text{CPhCH}=\text{CPh})$  (10), respectively, while 1,7-octadiyne  $\text{HC}\equiv\text{C}(\text{CH}_2)_4\text{C}\equiv\text{CH}$  reacts with 2 equiv of  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  to provide the unusual bimetallic complex  $(\text{DIPP})_3\text{Ta}(\text{CPh}=\text{CPhCH}=\text{C}(\text{CH}_2)_4\text{C}=\text{CHCPh}=\text{PhC})\text{Ta}(\text{DIPP})_3$  (11). The alkyne adduct  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (2) also engages in metallacyclization chemistry as it reacts with  $\text{MeC}\equiv\text{CMe}$  to afford  $(\text{DIPP})_3\text{Ta}(\text{CMe}=\text{CSiMe}_3\text{CMe}=\text{CMe})$  (12), with  $\text{PhC}\equiv\text{CH}$  to provide  $(\text{DIPP})_3\text{Ta}(\text{CSiMe}_3=\text{CMeCPh}=\text{CH})$  (13), and with  $\text{Me}_3\text{CC}\equiv\text{CH}$  to afford  $(\text{DIPP})_3\text{Ta}(\text{CCMe}_3=\text{CHCSiMe}_3=\text{CMe})$  (14). All of the metallacyclopentadiene complexes can be hydrolyzed with  $\text{H}_2\text{O}$ /acetone solutions to afford the corresponding 1,3-dienes in essentially quantitative yields. However, iodination of metallacycles 6, 7, and 13 does not yield the expected 1,4-diiodo-1,3-dienes, but rather the ring-opened moniodinated butadienyl compounds  $(\text{DIPP})_3(\text{I})\text{TaCPh}=\text{CPhCMe}=\text{CMe}(\text{I})$  (15),  $(\text{DIPP})_3(\text{I})\text{TaCPh}=\text{CPhC}(\text{Et})=\text{CEt}(\text{I})$  (16), and  $(\text{DIPP})_3(\text{I})\text{TaCSiMe}_3=\text{CMeCPh}=\text{CH}(\text{I})$  (17), respectively. The subsequent hydrolysis of compounds 15-17 provides the corresponding 1-iodo-1,3-dienes.

## Introduction

Several examples of 1,3-diene syntheses have been developed in which a late transition metal, particularly palladium, is employed to promote a carbon-carbon bond-forming step.<sup>1</sup> This preparative method relies upon vinyl nucleophiles and electrophiles which themselves are often prepared by a sequence requiring the hydrometalation of an appropriate alkyne.<sup>2</sup> More recently, strategies for selective carbon-carbon bond formations have been developed in which a mid-to-low-valent early transition metal effects the reductive coupling of unsaturated organic substrates.<sup>3-10</sup> Thus, highly selective 1,3-diene syntheses

may be achieved by the cross-coupling of two different alkynes using group 4 metallocene-based reagents.<sup>8</sup> Furthermore, similar coupling reactions using heteroatom substrates (ketones, aldehydes, imines, nitriles, etc.) can provide convenient routes to vicinal diamines,<sup>10a</sup> 2-amino alcohols,<sup>10b</sup> 1,2-diols,<sup>11</sup> polyfunctionalized aromatic com-

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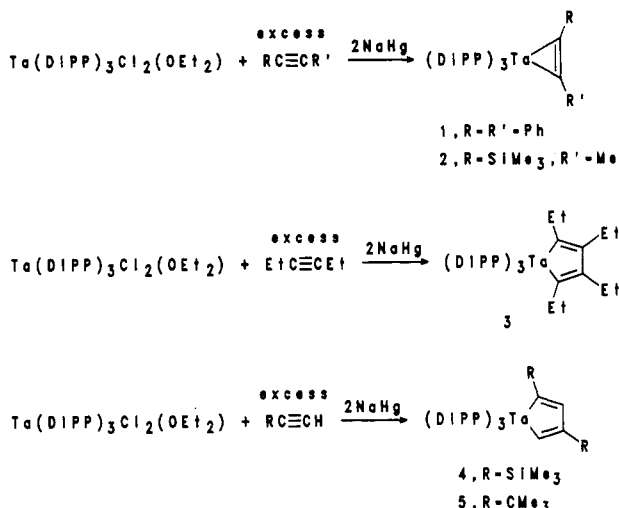
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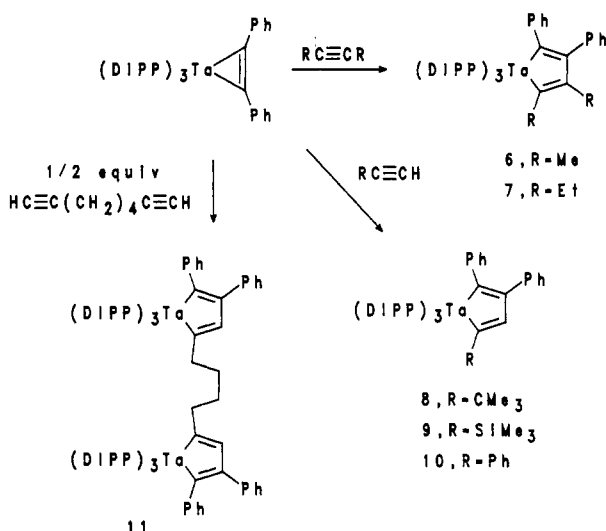
## Scheme I

DIPP = 2,6-diisopropylphenoxide



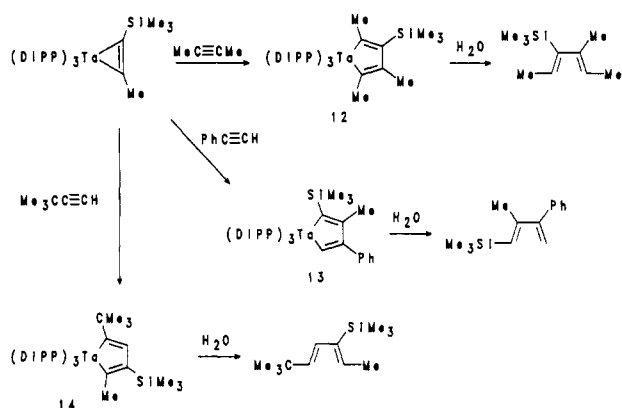
## Scheme II

DIPP = 2,6-diisopropylphenoxide



## Scheme III

DIPP = 2,6-diisopropylphenoxide



pounds (from nascent benzyne),<sup>12</sup> allylic amines,<sup>13</sup> and other products derived from metallacyclic intermediates.<sup>4-7</sup> The versatility and selectivity of these reductive couplings leave little doubt that they represent an emerging synthetic strategy of singular importance.<sup>3</sup>

In a preliminary communication,<sup>14</sup> we reported the cross-coupling chemistry of (DIPP)<sub>3</sub>Ta(PhC≡CPh) (1) and (DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) (2) with terminal and small internal alkynes. This group 5 system may be of a particular interest in cross-coupling methodology since the reactions of 1 and 2 with heteroatom substrates (e.g., aldehydes,<sup>15</sup> ketones,<sup>15</sup> and nitriles<sup>16</sup>) exhibit considerable mechanistic differences from the related reactions using group 4 metallocenes.<sup>9</sup> In addition, tantalum(III) alkyne adducts<sup>17,18</sup> are relevant to catalytic [2 + 2 + 2] cycloaddition chemistry,<sup>19,20</sup> since  $d^2$  Ta(OR)<sub>x</sub>Cl<sub>3-x</sub> fragments can bind to and stabilize successively higher alkyne cyclooligomers.<sup>19c,21</sup> Herein, we present a complete study

of these alkyne adducts and their metallacyclization reactions with other alkynes.

## Results and Discussion

Schemes I-III summarize the reactions developed in this study. The spectroscopic and analytical data for the compounds are reported in the Experimental Section. Throughout this paper, DIPP = 2,6-diisopropylphenoxide.

**Preparation and Properties of Tantalum Alkyne Adducts and Metallacyclopentadienes.** Ta-(DIPP)<sub>3</sub>Cl<sub>2</sub>(OEt<sub>2</sub>) can be reduced by two electrons in the presence of the bulky alkynes PhC≡CPh and Me<sub>3</sub>SiC≡CMe to provide the pale yellow adducts (DIPP)<sub>3</sub>Ta(PhC≡CPh) (1) and (DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) (2) in moderate yields (Scheme I). The isolation of higher alkyne cyclooligomers in this system seems to be quite susceptible to steric effects. Thus, the reduction of Ta(DIPP)<sub>3</sub>Cl<sub>2</sub>(OEt<sub>2</sub>) in the presence of either smaller internal alkynes (viz. EtC≡CEt) or terminal alkynes (viz. Me<sub>3</sub>SiC≡CH or Me<sub>3</sub>CC≡CH) affords the metallacyclopentadienes (DIPP)<sub>3</sub>Ta(CEt=CETCET=CET) (3) or (DIPP)<sub>3</sub>Ta(CR=CHCR=CH) (4, R = SiMe<sub>3</sub>; 5, R = CMe<sub>3</sub>) directly (Scheme I). The regioselectivity of metallacycle formation from terminal alkynes is very high as determined by NMR (>98%; no other regioisomers are detected) and by identification of the butadienes obtained upon protonolysis of

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**Table I. Details of the X-ray Diffraction Study for (DIPP)<sub>3</sub>Ta(PhC≡CPh) (1) and (DIPP)<sub>3</sub>Ta(CEt=CEtCEt=CEt) (3)**

molec formula	C <sub>50</sub> H <sub>61</sub> TaO <sub>3</sub> (1)	C <sub>48</sub> H <sub>71</sub> TaO <sub>3</sub> (3)
molec wt	890.99	877.05
space group	P1 (No. 2)	P2 <sub>1</sub> /n (No. 14)
unit cell vol, Å <sup>3</sup>	2810.5	4655.9
a, Å	11.339 (3)	14.340 (15)
b, Å	12.308 (2)	16.332 (22)
c, Å	17.989 (4)	19.929 (11)
α, deg	84.02 (2)	90.0
β, deg	88.42 (2)	94.05 (7)
γ, deg	65.55 (2)	90.0
Z	2	4
calcd density, g cm <sup>-3</sup>	1.30	1.25
cryst dimens, mm	0.70 × 0.40 × 0.25	0.50 × 0.30 × 0.50
data collectn temp, °C	23 ± 1	23 ± 1
Mo Kα radiation, λ, Å	0.71073	0.71073
monochromator	graphite	graphite
abs coeff, cm <sup>-1</sup>	24.3	23.7
2θ range, deg	2–50	2–50
total no. of rflns measd	8528, 8068 unique	9088, 8245 unique
no. of rflns measd with I > 3σ(I)	6746	3191
scan type	θ–2θ	θ–2θ
scan speed, deg min <sup>-1</sup>	4–12	2–8
parameters refined	487	469
R	0.023	0.046
R <sub>w</sub>	0.027	0.045

**Table II. Selected Bond Distances (Å) and Bond Angles (deg) in (DIPP)<sub>3</sub>Ta(PhC≡CPh) (1)<sup>a</sup>**

Bond Distances			
Ta–O(1)	1.869 (2)	Ta–O(5)	2.076 (3)
Ta–O(2)	1.912 (2)	Ta–Acet <sup>b</sup>	1.961
Ta–O(3)	1.889 (2)	O(1)–C(11)	1.384 (4)
Ta–C(4)	2.070 (3)	O(2)–C(21)	1.383 (4)
		O(3)–C(31)	1.371 (4)
		C(4)–C(5)	1.346 (5)
		C(4)–C(41)	1.472 (5)
		C(5)–C(51)	1.463 (5)
Bond Angles			
O(1)–Ta–O(2)	103.7 (1)	O(3)–Ta–Acet <sup>b</sup>	113.6
O(1)–Ta–O(3)	117.0 (1)	C(4)–Ta–C(5)	37.9 (1)
O(1)–Ta–C(4)	114.0 (1)	Ta–O(1)–C(11)	158.8 (2)
O(1)–Ta–C(5)	101.1 (1)	Ta–O(2)–C(21)	148.1 (2)
O(1)–Ta–Acet <sup>b</sup>	108.5	Ta–O(3)–C(31)	156.7 (2)
O(2)–Ta–O(3)	100.0 (1)	Ta–C(4)–C(5)	71.3 (2)
O(2)–Ta–C(4)	94.6 (1)	Ta–C(4)–C(41)	151.9 (3)
O(2)–Ta–C(5)	132.3 (1)	C(5)–C(4)–C(41)	136.8 (3)
O(2)–Ta–Acet <sup>b</sup>	113.5	Ta–C(5)–C(4)	70.8 (2)
O(3)–Ta–C(4)	121.1 (1)	Ta–C(5)–C(51)	153.6 (3)
O(3)–Ta–C(5)	104.0 (1)	C(4)–C(5)–C(51)	135.1 (3)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits. <sup>b</sup> Acet represents the C(4)–C(5) midpoint.

compounds 3–5 (vide infra). This head-to-tail coupling represents presumably the most sterically feasible way to alleviate congestion at the metal as well as to minimize steric interactions within the metallacyclic ring. No alkyne adducts have been detected or isolated in the reactions with these substrates, even when a deficiency of alkyne is used; thus, the metallacyclization step is apparently quite rapid.

**X-ray Structural Determinations of (DIPP)<sub>3</sub>Ta(PhC≡CPh) (1) and (DIPP)<sub>3</sub>Ta(CEt=CEtCEt=CEt) (3).** An X-ray crystal structure determination of (DIPP)<sub>3</sub>Ta(CEt=CEtCEt=CEt) (3) (vide infra) revealed a severely crowded coordination sphere about the tantalum atom, as suggested by the large Ta–O–C<sub>ipso</sub> angles in the phenoxide ligands. Thus, the steric constraints which allow the isolation of this metallacycle are sufficient to prevent any further reaction with 3-hexyne and the formation of higher alkyne cyclooligomers.<sup>19c</sup> Therefore, the adduct (DIPP)<sub>3</sub>Ta(PhC≡CPh) (1) reflects the slight advantage that steric congestion (which will not allow an additional

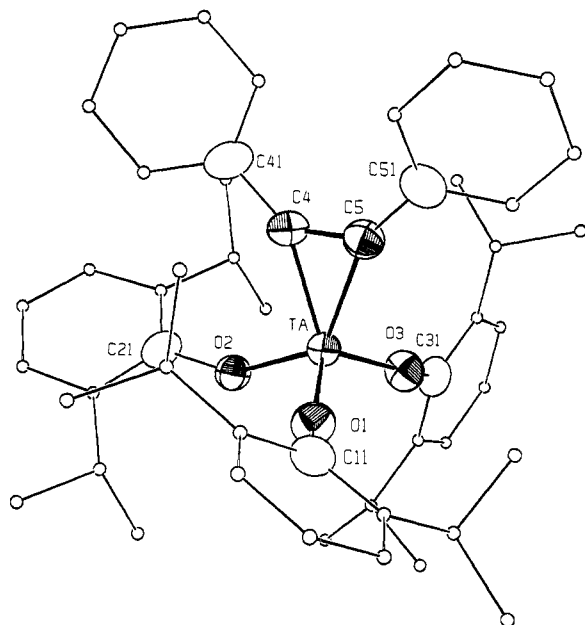
**Table III. Positional Parameters and Their Estimated Standard Deviations for (DIPP)<sub>3</sub>Ta(PhC≡CPh) (1)<sup>a</sup>**

atom	x	y	z	B, Å <sup>2</sup>
Ta	0.23876 (1)	0.26405 (1)	0.22655 (1)	2.328 (2)
O1	0.2689 (2)	0.2545 (2)	0.1243 (1)	3.43 (5)
O2	0.0617 (2)	0.3760 (2)	0.2304 (1)	2.96 (5)
O3	0.3191 (2)	0.3436 (2)	0.2766 (1)	3.35 (5)
C4	0.2078 (3)	0.1213 (3)	0.2804 (2)	3.15 (7)
C5	0.3354 (3)	0.0853 (3)	0.2684 (2)	3.17 (7)
C11	0.3119 (3)	0.2031 (3)	0.0583 (2)	3.00 (7)
C12	0.2471 (3)	0.1426 (3)	0.0278 (2)	3.84 (8)
C12B	0.1823 (4)	-0.0039 (4)	0.1046 (3)	6.0 (1)
C12A	0.1363 (4)	0.1235 (3)	0.0675 (3)	5.0 (1)
C12C	0.0208 (5)	0.1514 (4)	0.0151 (4)	8.4 (2)
C13	0.2914 (4)	0.0978 (3)	-0.0400 (2)	5.2 (1)
C14	0.3925 (5)	0.1118 (4)	-0.0751 (2)	5.5 (1)
C15	0.4559 (4)	0.1710 (4)	-0.0442 (2)	4.9 (1)
C16A	0.4817 (3)	0.2847 (3)	0.0609 (3)	4.65 (9)
C16B	0.5616 (4)	0.3298 (4)	0.0061 (4)	7.5 (1)
C16	0.4167 (3)	0.2183 (3)	0.0241 (2)	3.64 (8)
C16C	0.5656 (4)	0.2087 (4)	0.1275 (3)	6.3 (1)
C21	-0.0651 (3)	0.3959 (3)	0.2468 (2)	3.30 (7)
C22B	-0.0963 (4)	0.5771 (4)	0.1041 (3)	6.3 (1)
C22	-0.1526 (3)	0.4311 (3)	0.1860 (2)	3.70 (8)
C22A	-0.1103 (3)	0.4585 (3)	0.1090 (2)	4.53 (9)
C22C	-0.1992 (4)	0.4617 (5)	0.0453 (3)	7.6 (2)
C23	-0.2787 (3)	0.4454 (4)	0.2025 (3)	5.4 (1)
C24	-0.3156 (4)	0.4299 (4)	0.2742 (3)	6.1 (1)
C25	-0.2293 (4)	0.4009 (4)	0.3333 (3)	5.6 (1)
C26B	0.0031 (5)	0.4799 (4)	0.3970 (3)	6.2 (1)
C26	-0.1000 (3)	0.3845 (3)	0.3210 (2)	4.02 (8)
C26A	-0.0045 (4)	0.3626 (3)	0.3835 (2)	4.8 (1)
C26C	-0.0304 (5)	0.3001 (5)	0.4565 (3)	7.7 (2)
C31	0.3294 (3)	0.4168 (3)	0.3262 (2)	3.12 (7)
C32A	0.2125 (4)	0.5926 (3)	0.2291 (3)	5.0 (1)
C32C	0.3113 (6)	0.5951 (6)	0.1719 (3)	8.9 (2)
C32B	0.0995 (6)	0.7152 (5)	0.2305 (4)	8.9 (2)
C32	0.2770 (3)	0.5399 (3)	0.3049 (2)	3.70 (8)
C33	0.2866 (4)	0.6140 (3)	0.3560 (3)	5.3 (1)
C34	0.3438 (4)	0.5668 (4)	0.4250 (3)	6.2 (1)
C35	0.3949 (4)	0.4447 (4)	0.4445 (2)	5.8 (1)
C36	0.3902 (3)	0.3660 (3)	0.3960 (2)	4.14 (8)
C36A	0.4459 (4)	0.2324 (4)	0.4172 (2)	5.4 (1)
C36C	0.3740 (7)	0.1975 (6)	0.4776 (5)	13.3 (3)
C36B	0.5872 (5)	0.1804 (5)	0.4368 (5)	10.1 (2)
C41	0.1225 (3)	0.0676 (3)	0.3149 (2)	3.75 (8)
C42	0.1630 (4)	-0.0106 (3)	0.3811 (3)	5.4 (1)
C43	0.0832 (5)	-0.0607 (4)	0.4140 (3)	7.3 (1)
C44	-0.0357 (4)	-0.0343 (4)	0.3830 (3)	8.0 (1)
C45	-0.0768 (4)	0.0417 (4)	0.3187 (3)	7.0 (1)
C46	0.0021 (4)	0.0944 (3)	0.2851 (3)	5.0 (1)
C51	0.4494 (3)	-0.0292 (3)	0.2788 (2)	3.76 (8)
C52	0.5732 (4)	-0.0318 (4)	0.2846 (3)	5.0 (1)
C53	0.6812 (4)	-0.1411 (4)	0.2917 (3)	6.6 (1)
C54	0.6684 (5)	-0.2476 (4)	0.2921 (3)	7.1 (1)
C55	0.5477 (5)	-0.2457 (4)	0.2856 (3)	7.1 (2)
C56	0.4393 (4)	-0.1382 (3)	0.2799 (3)	5.4 (1)

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

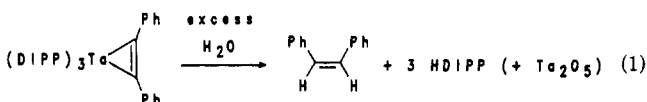
molecule of PhC≡CPh to approach and couple) has over the electronic driving force to metallacyclize (which would allow the metal to attain its highest oxidation state).

Pale yellow, single crystals of (DIPP)<sub>3</sub>Ta(PhC≡CPh) (1) suitable for an X-ray analysis were grown from a pentane solution at -40 °C. The molecular structure of 1 is presented in Figure 1 while crystal data and details of the structural analysis are reported in Table I. Representing the C(4)–C(5) midpoint as "Acet", relevant bond distances and bond angles in (DIPP)<sub>3</sub>Ta(PhC≡CPh) are presented in Table II and atomic coordinates in Table III. In the simplest possible description, the geometry about the metal is distorted tetrahedral. Thus, the L–Ta–L (L = O(1), O(2), O(3), and Acet) angles span the range 100.0

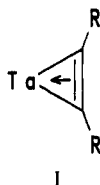


**Figure 1.** ORTEP drawing of  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  (**1**, DIPP = 2,6-diisopropylphenoxide) with local coordination atoms shown as 50% probability ellipsoids.

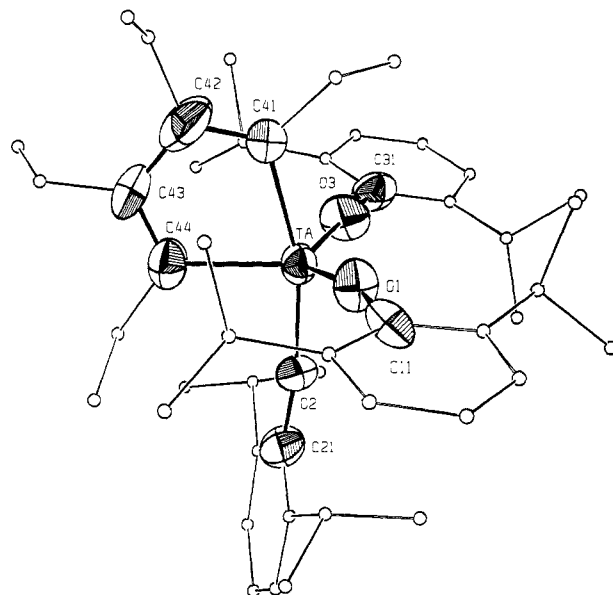
(1)–117.0 (1) $^\circ$  and average 109.4 $^\circ$ . The Ta–O–C<sub>ipso</sub> angles fall in the range 148.1 (2)–158.8 (2) $^\circ$  and average 154.5 $^\circ$ , which seems to indicate that the coordination sphere in **1** is considerably less congested than that in the metallacyclic complex **3**, where the Ta–O–C<sub>ipso</sub> angles average 170.2 $^\circ$ . The very short Ta–C(4) and Ta–C(5) distances (2.070 (3) and 2.076 (3) Å, respectively) and the distended C(4)–C(5) bond (1.346 (5) Å) are clearly indicative of a strongly bound and substantially reduced alkyne ligand.<sup>17,18,22</sup> These structural data, in conjunction with the downfield <sup>13</sup>C NMR resonances for C<sub>alkyne</sub> ( $\delta$  216 for **1**, CDCl<sub>3</sub>;  $\delta$  226.0 and 224.4 for **2**, C<sub>6</sub>D<sub>6</sub>) and the *cis*-olefin obtained upon hydrolysis of **1** (eq 1), all suggest a formal



four-electron interaction<sup>23,24</sup> involving both alkyne  $\pi_{\parallel}$  and  $\pi_{\perp}$  bonding orbitals with the metal. Therefore, a formal tantalum(V) metallacyclopene description of these adducts in which additional donation from the alkyne  $\pi_{\perp}$  orbital to the metal (structure I) seems to be the dominant contributor to the structure. Related group 5<sup>17,18,22</sup> and



group 6<sup>24</sup> alkyne adducts have been characterized by similar structures. Note, however, that this structural form does not prevent the metallacyclization reaction (vide in-



**Figure 2.** ORTEP drawing of  $(\text{DIPP})_3\text{Ta}(\text{CEt}=\text{CtCt}=\text{Ct})$  (**3**, DIPP = 2,6-diisopropylphenoxide) with local coordination atoms shown as 50% probability ellipsoids.

**Table IV.** Selected Bond Distances (Å) and Bond Angles (deg) in  $(\text{DIPP})_3\text{Ta}(\text{CEt}=\text{CtCt}=\text{Ct})$  (**3**)<sup>a</sup>

Bond Distances					
Ta–O(1)	1.858 (4)	Ta–C(44)	2.147 (8)	C(41)–C(42)	1.32 (1)
Ta–O(2)	1.920 (5)	O(1)–C(11)	1.392 (9)	C(42)–C(43)	1.49 (1)
Ta–O(3)	1.845 (5)	O(2)–C(21)	1.364 (9)	C(43)–C(44)	1.35 (1)
Ta–C(41)	2.166 (9)	O(3)–C(31)	1.38 (1)	C(44)–C(54)	1.53 (1)
Bond Angles					
O(1)–Ta–O(2)	96.9 (2)	C(41)–Ta–C(44)	75.7 (4)		
O(1)–Ta–O(3)	124.3 (2)	Ta–O(1)–C(11)	165.2 (5)		
O(1)–Ta–C(41)	89.8 (3)	Ta–O(2)–C(21)	170.8 (5)		
O(1)–Ta–C(44)	118.5 (3)	Ta–O(3)–C(31)	174.6 (5)		
O(2)–Ta–O(3)	98.4 (2)	Ta–C(41)–C(42)	117.0 (8)		
O(2)–Ta–C(41)	164.9 (3)	C(41)–C(42)–C(43)	115.1 (9)		
O(2)–Ta–C(44)	89.2 (3)	C(42)–C(43)–C(44)	116.3 (8)		
O(3)–Ta–C(41)	88.9 (4)	Ta–C(44)–C(43)	115.7 (7)		
O(3)–Ta–C(44)	115.0 (3)				

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

fra),<sup>18b</sup> although the metal center *lowers* its valence electron count in order to attain a higher oxidation state. Compared to the group 4 complex  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{1-hexyne})(\text{PMe}_3)$ ,<sup>9a</sup> the alkyne ligand in **1** appears to be more highly reduced as judged from the longer “C≡C” bond in **1** (1.346 (5) Å) than in  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{1-hexyne})(\text{PMe}_3)$  (1.286 (5) Å), even though the metal center in the zirconium complex might be considered more “electron rich”.

Given the metallacyclic nature of the structure, an alternative description of the structure about tantalum is that of a *highly* distorted trigonal bipyramid with the axial positions occupied by O(2) and C(5) (although O(2)–Ta–C(5) = 132.3 (1) Å) and the equatorial positions occupied by O(1), O(3), and C(4) (average  $L_{\text{eq}}\text{-Ta-}L_{\text{eq}}$  angle = 117.4 $^\circ$ ; average  $L_{\text{eq}}\text{-Ta-}L_{\text{ax}}$  angle = 90.2 $^\circ$ ). The distortion from a TBP structure arises from the severe constraints imposed by the alkyne ligand in that one  $L_{\text{eq}}\text{-Ta-}L_{\text{ax}}$  angle (C(4)–Ta–C(5) = 37.9 $^\circ$ ) is much less than 90 $^\circ$ .

The molecular structure of the metallacycle  $(\text{DIPP})_3\text{Ta}(\text{CEt}=\text{CtCt}=\text{Ct})$  (**3**) is presented in Figure 2. Crystal data and structural analysis details for **3** are reported in Table I, relevant bond distances and bond angles in Table IV, and atomic coordinates in Table V. In the solid state, this compound assumes a trigonal bipyramidal geometry (O(2)–Ta–C(41) = 164.9 (3) $^\circ$ ) with the

(22) Curtis has performed extended Hückel MO calculations on related  $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{alkyne})\text{X}_2$  (M = Nb, Ta) complexes, which provide results consistent with this notion; see: Curtis, M. D.; Real, J.; Kwon, D. *Organometallics* **1989**, *8*, 1644.

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Table V. Positional Parameters and Their Estimated Standard Deviations for (DIPP)<sub>3</sub>Ta(CEt≡CEtCEt≡CEt)<sub>(3)<sup>a</sup></sub>

atom	x	y	z	B, Å <sup>2</sup>
Ta	0.22854 (4)	0.21520 (3)	0.02187 (3)	3.270 (8)
O1	0.2296 (5)	0.2318 (5)	-0.0703 (3)	4.1 (2)
O2	0.3601 (4)	0.2305 (5)	0.0429 (4)	3.7 (2)
O3	0.2161 (6)	0.1142 (5)	0.0616 (4)	5.0 (2)
C11	0.2493 (8)	0.2578 (7)	-0.1343 (6)	3.9 (3)
C12	0.2706 (8)	0.1982 (7)	-0.1819 (5)	3.8 (3)
C12A	0.2626 (9)	0.1092 (8)	-0.1663 (7)	5.5 (4)
C12B	0.172 (1)	0.0757 (9)	-0.1969 (9)	8.4 (5)
C12C	0.344 (1)	0.059 (1)	-0.1905 (9)	8.6 (5)
C13	0.2950 (9)	0.2288 (9)	-0.2433 (6)	5.1 (3)
C14	0.2971 (9)	0.3087 (9)	-0.2587 (7)	6.0 (4)
C15	0.271 (1)	0.3646 (9)	-0.2116 (7)	6.4 (4)
C16A	0.214 (1)	0.4021 (8)	-0.0975 (7)	6.3 (4)
C16	0.2456 (9)	0.3423 (8)	-0.1476 (6)	4.6 (3)
C16B	0.259 (2)	0.487 (1)	-0.1006 (9)	11.8 (7)
C16C	0.110 (1)	0.408 (1)	-0.1022 (9)	10.5 (6)
C21	0.4495 (8)	0.2508 (8)	0.0648 (6)	4.6 (3)
C22B	0.437 (1)	0.217 (1)	0.2517 (8)	10.2 (6)
C22	0.4839 (9)	0.2306 (8)	0.1326 (6)	5.5 (4)
C22C	0.449 (1)	0.094 (1)	0.1778 (9)	9.3 (6)
C22A	0.425 (1)	0.1832 (8)	0.1777 (7)	6.2 (4)
C23	0.576 (1)	0.253 (1)	0.1483 (7)	8.1 (5)
C24	0.6296 (9)	0.294 (1)	0.1076 (8)	9.5 (5)
C25	0.594 (1)	0.313 (1)	0.0442 (8)	7.9 (5)
C26	0.5029 (8)	0.2943 (9)	0.0213 (6)	5.0 (3)
C26A	0.4698 (9)	0.3088 (8)	-0.0509 (6)	5.5 (4)
C26B	0.492 (1)	0.239 (1)	-0.0958 (8)	8.6 (5)
C26C	0.506 (1)	0.391 (1)	-0.0779 (9)	9.6 (6)
C31	0.2142 (8)	0.0406 (8)	0.0951 (6)	4.4 (3)
C32A	0.136 (1)	0.117 (1)	0.1874 (7)	8.2 (5)
C32B	0.032 (1)	0.110 (1)	0.186 (1)	14.0 (8)
C32C	0.173 (2)	0.131 (1)	0.258 (1)	13.5 (8)
C32	0.179 (1)	0.0411 (8)	0.1566 (7)	5.7 (4)
C33	0.179 (1)	-0.036 (1)	0.1914 (8)	8.2 (5)
C34	0.210 (1)	-0.103 (1)	0.1656 (8)	9.6 (5)
C35	0.242 (1)	-0.1009 (9)	0.1030 (8)	6.7 (4)
C36B	0.382 (1)	-0.021 (2)	-0.003 (1)	14.7 (9)
C36C	0.245 (2)	-0.093 (1)	-0.048 (1)	14.2 (8)
C36	0.2474 (8)	-0.0296 (8)	0.0654 (6)	4.4 (3)
C36A	0.2825 (9)	-0.0277 (8)	-0.0041 (7)	5.9 (4)
C41	0.0777 (8)	0.2266 (9)	0.0142 (7)	5.9 (3)
C42	0.0416 (9)	0.286 (1)	0.0484 (8)	7.8 (4)
C43	0.1104 (9)	0.3357 (9)	0.0905 (7)	5.9 (4)
C44	0.2014 (9)	0.3180 (7)	0.0847 (6)	4.6 (3)
C51	0.015 (1)	0.179 (1)	-0.043 (1)	13.0 (7)
C52	-0.061 (1)	0.303 (1)	0.052 (1)	14.4 (6)
C53	0.080 (1)	0.404 (1)	0.1332 (9)	9.6 (5)
C54	0.2769 (9)	0.3651 (8)	0.1266 (6)	5.5 (4)
C61	0.022 (1)	0.101 (2)	-0.038 (1)	18 (1)
C62	-0.101 (1)	0.355 (1)	0.003 (1)	20.8 (9)
C63	0.057 (1)	0.377 (1)	0.201 (1)	14.6 (7)
C64	0.319 (1)	0.434 (1)	0.0874 (8)	7.6 (5)

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

small C(41)-Ta-C(44) angle (75.7 (4)°) constraining the metallacyclic  $\alpha$  carbons to occupy one axial and one equatorial site. Bond length alternation in the carbon ring is evident (Table IV), and the metallacyclic ring is quite planar. Perhaps the most revealing structural feature is the severe crowding of the coordination sphere which is manifested in the linear Ta-O-C<sub>ipso</sub> angles (from 165.2 (5)° to 174.6 (5)°). Such crowding suggests that the "extent" of alkyne cyclotrimerization is susceptible to steric effects in these phenoxide compounds<sup>7</sup> and is consistent with the fact that cyclotrimerization with 3-hexyne does not proceed further in compound 3.<sup>19</sup> The crystal structure of a related tantalum(V) ene-diamide (formally diazabutadiene dianion) metallacycle has been reported which likewise is characterized by the metallacycle occupying axial and

equatorial positions of a trigonal bipyramid.<sup>7b,c</sup>

**Cross-Coupling Reactions of Tantalum Alkyne Complexes.** The slight advantage that steric constraints in (DIPP)<sub>3</sub>Ta(RC≡CR') (1 and 2) (which will not allow an additional molecule of RC≡CR' to coordinate) have over the electronic driving force to metallacyclize (vide supra) may be overcome by simply using a smaller alkyne that can approach the metal. This is also the case with aldehydes, ketones, and nitriles, which can  $\eta^1$ -coordinate the electrophilic metal center prior to coupling with the alkyne.<sup>15,16</sup> The fact that compounds 1 and (presumably) 2 exhibit a metallacyclopentene structure does not seem to be a factor in this coupling reaction, although group 5 alkyne complexes characterized by similar metallacyclopentene bonding have been described<sup>17,18</sup> which do not react with additional alkyne to form metallacycles.<sup>25</sup>

Accordingly, compounds 1 and 2 react rapidly with a variety of smaller alkynes, including terminal alkynes, to afford metallacyclopentadiene complexes in good yields (Schemes II and III). Thus, (DIPP)<sub>3</sub>Ta(PhC≡CPh) (1) reacts immediately with MeC≡CMe, EtC≡CEt, Me<sub>3</sub>CC≡CH, Me<sub>3</sub>SiC≡CH, or PhC≡CH in diethyl ether to form red solutions containing metallacycles 6-10, Scheme II. The red-orange products are crystallized from -40 °C pentane solutions. Similarly, the 1,7-octadiyne HC≡C(CH<sub>2</sub>)<sub>4</sub>C≡CH reacts with 2 equiv of (DIPP)<sub>3</sub>Ta(PhC≡CPh) to provide the unusual bimetallic complex 11 shown in Scheme II. The high regioselectivity of these cross-coupling reactions using terminal alkynes is notable, as only one isomer is observed in every case. Again, steric effects appear to play an important role in these reactions, as the bulkier substituents usually take  $\alpha$  rather than  $\beta$  metallacycle positions in Scheme II, perhaps to avoid an unfavorable  $\beta, \beta'$  interaction within the metallacycle itself.<sup>4a</sup> It seems likely that the observed regiochemistry is *principally* sterically driven, since the various  $\alpha$ -substituents have opposite inductive effects (relative to hydrogen).<sup>26</sup> A study of the regiochemistry exhibited in cobaltacyclopentadiene formation has provided a similar argument.<sup>27</sup>

Scheme III presents similar cross-coupling reactions using (DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) (2). The regiochemistry observed presumably reflects the balance between minimizing congestion about the metal and preventing unfavorable  $\beta, \beta'$ -substituent interactions.<sup>4a</sup> Thus, (DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) (2) reacts with MeC≡CMe to afford (DIPP)<sub>3</sub>Ta(CMe=CSiMe<sub>3</sub>CMe=CMe) (12) and with PhC≡CH to provide (DIPP)<sub>3</sub>Ta(CSiMe<sub>3</sub>=CMeCPh=CH) (13), both isolated as the sole regioisomer. However, 2 also reacts with Me<sub>3</sub>CC≡CH to afford (DIPP)<sub>3</sub>Ta(CCMe<sub>3</sub>=CHCSiMe<sub>3</sub>=CMe) (14). Thus, when comparing the regioisomerism in the formation of 8-10 (Scheme II) with that of 12-14 (Scheme III), we can suggest the following. Firstly, the avoidance of a  $\beta, \beta'$ -substituent interaction seems to dictate the regioisomerism in the formation of 8-10. Secondly, the Me<sub>3</sub>Si group appears to exhibit a somewhat greater steric demand (expected from a larger Si vs C atom and therefore longer

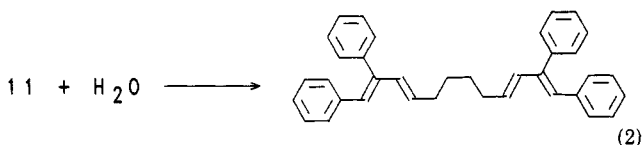
(25) The compounds ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)M(CO)<sub>2</sub>(PhC≡CPh) (M = Nb, Ta) react with PhC≡CPh to give only ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)M(CO)(PhC≡CPh)<sub>2</sub> and not metallacyclopentadienes. The free butadiene PhCH=CPhCPh=CHPh is formed only upon thermal degradation of the complexes; see: (a) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Pasynskii, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1969, 100. (b) Aleksandrov, G. G.; Gusev, A. I.; Struchkov, Y. T. *Zh. Strukt. Khim.* 1968, 9, 333.

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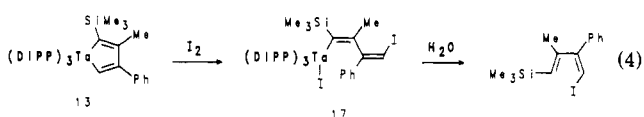
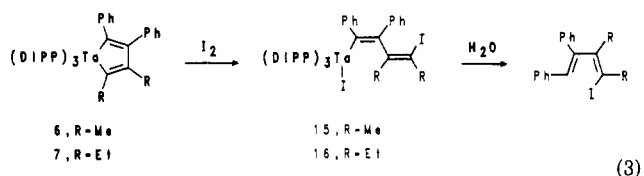
Si-C vs C-C bond lengths) as the  $\beta,\beta'$ -(Me,Ph) interaction in 13 is preferred over having both SiMe<sub>3</sub> and Ph groups in  $\alpha,\alpha'$  positions, which would be highly unfavorable with the large DIPP ligands. Finally, complex 14 represents both the avoidance of a  $\beta,\beta'$ -substituent interaction and the positioning of a CMe<sub>3</sub> group, rather than slightly larger SiMe<sub>3</sub>, in a position  $\alpha$  to the metal.

**Protonolysis and Iodination Reactions of Metallacyclopentadienes.** All of the metallacyclic carbon atoms in compounds 6–13 were not observed by <sup>13</sup>C NMR spectroscopy (see Experimental Section); therefore, the regioselectivity assignments were unambiguously determined by examining the 1,3-dienes that formed quantitatively upon hydrolyzing the metallacycles. The diagnostic <sup>1</sup>H NMR data are reported at the end of each experimental preparation for the corresponding metallacycles. For example, the very low solubility of dinuclear complex 11 made it difficult to formulate. However, the hydrolysis of complex 11 yielded (*Z,E*)-CHPh=CHCH=CH(CH<sub>2</sub>)<sub>4</sub>-(*E,Z*)-CH=CHCPh=CHPh (eq 2) as



identified by <sup>1</sup>H NMR, which assisted the formulation of 11 as the dinuclear complex shown in Scheme II. The protonolysis reactions of the metallacycles formed from 2, shown in Scheme III, proved essential in assigning the regiochemistry of the coupling reactions and demonstrated the preferred method of quantitatively releasing the 1,3-diene after assembly at the metal.

Another question to be addressed in this study was whether the metallacycle could be removed through iodination to afford 1,4-diiodo-1,3-dienes of potential synthetic utility.<sup>8</sup> Iodination of metallacycles 6, 7, and 13 did not yield the diiodide products but instead yielded the ring-opened monoiodinated butadienyl compounds shown in eqs 3 and 4. Thus, the addition of  $\geq 1$  equiv of I<sub>2</sub> to



6 or 7 affords solutions containing the ring-opened butadienyl complexes 15 and 16, respectively, eq 3. Complex 13 also reacted with I<sub>2</sub> to yield a similar ring-opened complex 17, eq 4. Thus, the iodine appears to only attack the less hindered side of the metallacycle. These results are to be compared to the iodination of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CR}=\text{CRCR}=\text{CR})$  complexes in which diiodo products formed in high yield.<sup>8</sup> Upon hydrolysis of the butadienyl derivatives 15–17, the 1-iodo-1,3-dienes are generated essentially quantitatively, eqs 3 and 4.

### Concluding Remarks

The alkyne adducts described here are relevant models for alkyne cyclotrimerization by tantalum and niobium<sup>19</sup> since (i) they represent the first tantalum alkyne complexes that metallacycle another equivalent of alkyne and (ii)

by use of the appropriate precursor, the reaction can proceed to the next higher cyclooligomer, thereby providing  $\eta^6$ -arene and  $\eta^2$ -pyridine complexes.<sup>19c,21,28</sup> These reactions exhibit considerable steric sensitivity, an observation that carries over to the use of Ta(DIPP)<sub>2</sub>Cl<sub>3</sub>-(OEt<sub>2</sub>) and Ta(DIPP)Cl<sub>4</sub>(OEt<sub>2</sub>) (instead of Ta(DIPP)<sub>3</sub>Cl<sub>2</sub>(OEt<sub>2</sub>)) to afford  $(\eta^6\text{-C}_6\text{R}_6)\text{Ta}(\text{DIPP})_2\text{Cl}$  (R = Me, Et)<sup>19c</sup> and  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})\text{Cl}_2$ <sup>21</sup> through cycloaddition chemistry. The reactivity of the alkyne adducts can, in part, be attributed to their enhanced electrophilicity, as compared to their cyclopentadienyl-supported analogues, through the use of phenoxide ligands. The coupling reactions that produce metallacyclopentadienes exhibit a high degree of regioselectivity as a result of two important factors: (i) larger substituents prefer the  $\alpha$ -metallacycle positions if the metal center will not become too crowded; (ii) The  $\beta,\beta'$ -substituent interactions must be minimal for coupling to occur. The regioselectivity in coupling and the iodination reactions presented here make this a potentially viable synthetic approach to substituted 1,3-dienes and functionalizable iodobutadienes.

### Experimental Section

**General Details.** All experiments were performed under a nitrogen atmosphere by either standard Schlenk techniques<sup>29</sup> or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were purified under N<sub>2</sub> by standard techniques<sup>30</sup> and transferred to the drybox or reaction vessel without exposure to air. The "cold" solvents used to wash isolated solids were cooled to ca. -30 °C before use. In all preparations, DIPP = 2,6-diisopropylphenoxide.

**Starting Materials.** 2-Butyne, 3-hexyne, phenylacetylene, (trimethylsilyl)acetylene, 3,3-dimethyl-1-butyne, and 1,7-octadiyne were obtained from Farchan Laboratories and were dried by passing them down a short (ca. 5–6-cm) column of activated alumina. Deuterated NMR solvents were also passed down a short column of activated alumina prior to use. Ta(DIPP)<sub>3</sub>Cl<sub>2</sub>(OEt<sub>2</sub>), (DIPP)<sub>3</sub>Ta(PhC≡CPh), and (DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) were prepared as reported previously.<sup>15</sup>

**Physical Measurements.** <sup>1</sup>H (250-MHz) and <sup>13</sup>C (62.9-MHz) NMR spectra were recorded at probe temperature (unless otherwise specified) on a Bruker WM-250 or AM-250 spectrometer in C<sub>6</sub>D<sub>6</sub>, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, or CDCl<sub>3</sub> solvent. Chemical shifts are referenced to protio solvent impurities ( $\delta$  7.15, C<sub>6</sub>D<sub>6</sub>; 2.09, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 7.24, CDCl<sub>3</sub>) or solvent <sup>13</sup>C shifts ( $\delta$  128.0, C<sub>6</sub>D<sub>6</sub>; 20.4, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>; 77.0, CDCl<sub>3</sub>) and are reported in parts per million (ppm) downfield of Me<sub>4</sub>Si; routine coupling constants are not reported. Assignments of <sup>13</sup>C NMR resonances were assisted by attached proton tests or by off-resonance-decoupled spectra. All <sup>13</sup>C resonances for the metallacyclic and ring-opened compounds have not been located, due in part to more than one dynamic intramolecular process occurring over a wide temperature range, which effectively precluded uncoupled spectra in the regioselectivity assignments. In these cases, only partial <sup>13</sup>C NMR data are reported. Infrared spectra (reported in cm<sup>-1</sup>) were recorded as Nujol mulls (NaCl plates) between 4000 and 600 cm<sup>-1</sup> with a Perkin-Elmer 1310 spectrometer and were not assigned but were used as fingerprints (w = weak, m = medium, s = strong intensities; sh = shoulder, br = broad, v = very). Elemental analyses were performed by Desert Analytics of Tucson, AZ. All samples were handled under nitrogen and were combusted with tungstic anhydride.

**Protonolysis Reactions.** Assistance in characterizing many of these new metallacyclic compounds was obtained through hydrolyzing the complex and examining spectroscopically the 1,3-diene formed. A typical hydrolysis was performed by the following method. A slight excess of a water/acetone solution

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(30) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.



(ca. 10% v/v) was added to a diethyl ether solution of the compound until a white precipitate formed and the color faded. After the mixture was stirred for 1 h, the sample was dried by allowing it to stand over  $\text{MgSO}_4$  overnight. The resulting mixture was filtered through Celite, and the solvent was removed from the filtrate in vacuo to provide a colorless or pale yellow oil. Purification of the resulting butadiene was not undertaken since the diagnostic  $^1\text{H}$  NMR data (reported at the end of each experimental preparation) could be obtained by examining the NMR spectrum of the entire oil. Therefore, aryl  $^1\text{H}$  NMR data are not included due to the overlapping 2,6-diisopropylphenol resonances.

**Preparations.  $(\text{DIPP})_3\text{Ta}(\text{CET}=\text{CETCET}=\text{CET})$  (3).** To a  $-40^\circ\text{C}$  solution of 0.99 g (1.15 mmol) of  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  in 20 mL of diethyl ether were added 0.53 mL (4.7 mmol) of 3-hexyne and 0.76 mL (2.3 mmol) of 0.52% NaHg amalgam. The solution was stirred at room temperature for 18 h. After this time, the mixture was filtered through Celite and the solvent was removed in vacuo to provide an orange oil. The oil was reconstituted in ca. 5 mL of diethyl ether, and upon adding 5 mL of acetonitrile, an orange precipitate began to form. This sample was stored at  $-40^\circ\text{C}$  overnight to afford orange crystals (0.79 g, 0.90 mmol, 78% yield), which were filtered off, washed with cold acetonitrile, and dried in vacuo. Recrystallization of this compound from  $\text{Et}_2\text{O}/\text{MeCN}$  solution at  $-40^\circ\text{C}$  provided analytically pure samples.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 323 K):  $\delta$  7.08–6.90 (m, 9 H,  $\text{H}_{\text{aryl}}$ ), 3.65 (spt, 6 H,  $\text{CHMe}_2$ ), 2.80 (q, 4 H,  $\text{C}_\alpha\text{CH}_2\text{CH}_3$ ), 2.17 (q, 4 H,  $\text{C}_\beta\text{CH}_2\text{CH}_3$ ), 1.19 (d, 36 H,  $\text{CHMe}_2$ ), 1.11 (t, 3 H,  $\text{C}_\alpha\text{CH}_2\text{CH}_3$ ), 0.92 (t, 3 H,  $\text{C}_\beta\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$ , 323 K):  $\delta$  205.1 (s,  $\text{C}_\alpha$ ), 163.1 (s,  $\text{C}_\beta$ ), 157.5 (s,  $\text{C}_{\text{ipso}}$ ), 138.7 (s,  $\text{C}_o$ ), 123.8 (d,  $\text{C}_p$ ), 123.7 (d,  $\text{C}_m$ ), 29.2 (t,  $\text{C}_\alpha\text{CH}_2\text{CH}_3$ ), 27.6 (d,  $\text{CHMe}_2$ ), 24.4 (q,  $\text{CHMe}_2$ ), 22.0 (t,  $\text{C}_\beta\text{CH}_2\text{CH}_3$ ), 15.5 (q, coincident  $\text{C}_\alpha\text{CH}_2\text{CH}_3$  and  $\text{C}_\beta\text{CH}_2\text{CH}_3$ ). IR: 1580 w, 1430 s, 1375 s, 1360 m, 1322 s, 1250 s, 1192 s, 1110 m, 1095 sh, 1040 m, 910 s, 896 s, 878 m, 790 m, 748 s, 710 m, 702 m. Anal. Calcd for  $\text{C}_{48}\text{H}_{71}\text{O}_3\text{Ta}$ : C, 65.74; H, 8.16. Found: C, 65.95; H, 8.27.

**$(\text{DIPP})_3\text{Ta}(\text{CSiMe}_3=\text{CHCSiMe}_3=\text{CH})$  (4).** To a  $-40^\circ\text{C}$  solution of 0.51 g (0.59 mmol) of  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  were added 0.16 mL (1.13 mmol) of (trimethylsilyl)acetylene and 0.33 mL (1.13 mmol) of 0.59% NaHg amalgam. The reaction was stirred at room temperature for 24 h over which time a yellow color developed. The mixture was then filtered through Celite, and the solvent was removed in vacuo to afford a yellow oil. The oil was dissolved in pentane and cooled to  $-40^\circ\text{C}$  for 24 h to provide yellow crystals (0.29 g, 0.32 mmol, 54% yield), which were filtered off, washed with minimal cold pentane, and dried in vacuo. This sample was sufficiently pure for elemental analysis, but the compound can be recrystallized from pentane at  $-40^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 318 K):  $\delta$  8.56, 8.35 (d,  $^4J_{\text{HH}} = 1.5$  Hz, 1 H each,  $\text{C}_\beta\text{H}$  and  $\text{C}_\alpha\text{H}$ ), 7.08–6.89 (m, 9 H,  $\text{H}_{\text{aryl}}$ ), 3.58 (spt, 6 H,  $\text{CHMe}_2$ ), 1.20 (d, 36 H,  $\text{CHMe}_2$ ), 0.12, 0.10 (s, 9 H each,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 318 K):  $\delta$  212.6 ( $\text{C}_\alpha\text{SiMe}_3$ ), 202.6 ( $\text{C}_\beta\text{H}$ ), 180.8 ( $\text{C}_\beta\text{SiMe}_3$ ), 157.8 ( $\text{C}_{\text{ipso}}$ ), 153.3 ( $\text{C}_\beta\text{H}$ ), 138.4 ( $\text{C}_\alpha$ ), 124.0 ( $\text{C}_p$ ), 123.7 ( $\text{C}_m$ ), 27.8 ( $\text{CHMe}_2$ ), 24.2 ( $\text{CHMe}_2$ ), 0.25 and  $-1.4$  ( $\text{SiMe}_3$ ). IR: 1558 w, 1516 w, 1321 m, 1248 br s, 1175 s, 1092 br m, 1052 vw, 1038 w, 1023 vw, 906 br s, 890 sh, 870 w, 843 m, 823 m, 787 m, 742 s, 710 w, 695 w. Anal. Calcd for  $\text{C}_{46}\text{H}_{70}\text{O}_3\text{Si}_2\text{Ta}$ : C, 60.84; H, 7.77. Found: C, 60.95; H, 8.07.

**$(\text{DIPP})_3\text{Ta}(\text{CCMe}_3=\text{CHCCMe}_3=\text{CH})$  (5).** A solution of 1.02 g (1.19 mmol) of  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  in 20 mL of diethyl ether was prepared and cooled to  $-40^\circ\text{C}$ , after which 0.57 mL (4.6 mmol) of 3,3-dimethyl-1-butyne and 0.66 mL (2.4 mmol) of 0.59% NaHg amalgam were added. The solution was stirred at room temperature for 48 h over which time a golden brown color developed. After this time, the mixture was filtered through Celite and the solvent was removed in vacuo to afford a golden, frothy oil. Upon reconstituting this oil in pentane and cooling the solution to  $-40^\circ\text{C}$  (for 48 h), golden brown crystals (0.47 g, 0.54 mmol, 45% yield, 2 crops) formed, were collected, washed with minimal cold pentane, and dried in vacuo. Recrystallization of this compound from pentane at  $-40^\circ\text{C}$  provided analytically pure samples.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.68, 7.56 (d,  $^4J_{\text{HH}} = 2.1$  Hz, 1 H each,  $\text{C}_\beta\text{H}$  and  $\text{C}_\alpha\text{H}$ ), 7.11–6.86 (m, 9 H,  $\text{H}_{\text{aryl}}$ ), 3.95, 3.68, 3.26 (spt, 2 H each,  $\text{CHMe}_2$ ), 1.34, 1.28 (d, 12 H each,  $\text{CHMe}_2$ ), 1.19, 1.08 (s, 9 H each,  $\text{CMe}_3$ ), 0.97 (d, 12 H,  $\text{CHMe}_2$ ). Partial  $^{13}\text{C}$  NMR

( $\text{C}_6\text{D}_6$ ):  $\delta$  218.0 ( $\text{C}_\alpha\text{CMe}_3$ ), 183.9 ( $\text{C}_\beta\text{CMe}_3$ ), 180.2 ( $\text{C}_\alpha\text{H}$ ), 135.5 ( $\text{C}_\beta\text{H}$ ), 41.1, 37.0 ( $\text{CMe}_3$ ), 31.5, 29.1 ( $\text{CMe}_3$ ). IR: 1582 w, 1553 w, 1503 w, 1326 m, 1270 sh, 1258 s, 1188 s, 1142 w, 1110 sh, 1098 m, 1058 w, 1042 m, 1014 w, 968 sh, 932 w, 910 m, 898 m, 877 m, 807 w, 791 m, 750 s, 716 m, 708 m, 672 m, 660 sh. Anal. Calcd for  $\text{C}_{48}\text{H}_{71}\text{O}_3\text{Ta}$ : C, 65.74; H, 8.16. Found: C, 66.01; H, 8.28.

**$(\text{DIPP})_3\text{Ta}(\text{CHPh}=\text{CPhCMe}=\text{CMe})$  (6).** To a  $-40^\circ\text{C}$  solution of 1.0 g (1.1 mmol) of  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  (1) in 20 mL of diethyl ether was added 0.18 mL (2.3 mmol) of 2-butyne. The solution color immediately changed from pale yellow to light orange. After the solution was stirred for 24 h (over which time a dark red–orange color developed), the reaction volatiles were removed in vacuo to afford an orange oil. The oil was reconstituted in pentane and cooled to  $-40^\circ\text{C}$  whereupon 0.62 g (0.66 mmol; 60%) of orange solid precipitated and was collected, washed with minimal cold pentane, and dried in vacuo. Analytically pure samples were obtained by recrystallization from  $\text{Et}_2\text{O}/\text{pentane}$  solution at  $-40^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.19–6.49 (m, 19 H,  $\text{H}_{\text{aryl}}$  and  $\text{C}_6\text{H}_5$ ), 3.68 (br, 6 H,  $\text{CHMe}_2$ ), 2.38 (q, 3 H,  $^5J_{\text{HH}} = 1.3$  Hz,  $\text{C}_\alpha\text{CH}_3$ ), 1.80 (q, 3 H,  $^5J_{\text{HH}} = 1.3$  Hz,  $\text{C}_\beta\text{CH}_3$ ), 1.20 (d, 36 H,  $\text{CHMe}_2$ ). The  $\delta$  2.38 and 1.80 quartets were completely resolved only by resolution enhancement.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  203.3, 196.2 ( $\text{C}_\alpha$  and  $\text{C}_\beta$ ), 166.4 and 153.2 ( $\text{C}_\beta$  and  $\text{C}_\alpha$ ), 157.4 ( $\text{C}_{\text{ipso}}$ , DIPP), 146.2, 141.0 ( $\text{C}_{\text{ipso}}$ ,  $\text{C}_6\text{H}_5$ ), 138.5, 131.9, 129.8, 127.8, 127.6, 126.3, 124.5, 124.0, 123.6 ( $\text{C}_o$ ,  $\text{C}_m$ ,  $\text{C}_p$ , DIPP and  $\text{C}_6\text{H}_5$ ), 27.7 ( $\text{CHMe}_2$ ), 24.2 ( $\text{CHMe}_2$ ), 23.8, 17.7 ( $\text{C}_\alpha\text{Me}$  and  $\text{C}_\beta\text{Me}$ ). IR: 1585 br w, 1432 s, 1325 m, 1250 s, 1192 s, 1110 m, 1095 m, 1040 m, 912 s, 900 s, 880 m, 790 m, 748 m, 712 w, 701 m, 695 m. Anal. Calcd for  $\text{C}_{54}\text{H}_{67}\text{O}_3\text{Ta}$ : C, 68.63; H, 7.14. Found: C, 69.15; H, 7.08. Hydrolysis of 6 yielded (*Z,E*)- $\text{CHPh}=\text{CPhCMe}=\text{CHMe}$ . Partial  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.72 (s, 1 H,  $\text{CHPh}$ ), 5.49 (q,  $^3J_{\text{HH}} = 7.0$  Hz, 1 H,  $\text{CHMe}$ ), 1.85 (s, 3 H,  $\text{CMe}$ ), 1.52 (d,  $^3J_{\text{HH}} = 7.0$  Hz, 3 H,  $\text{CHMe}$ ).

**$(\text{DIPP})_3\text{Ta}(\text{CPh}=\text{CPhCET}=\text{CET})$  (7).** A 0.96-g sample (1.1 mmol) of  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  (1) was dissolved in 20 mL of diethyl ether, and the solution was cooled to  $-40^\circ\text{C}$ . Upon addition of 0.25 mL (2.2 mmol) of 3-hexyne (with stirring), the solution color immediately changed from pale yellow to light orange and slowly became dark red–orange overnight. After stirring for 24 h, the solvent was removed in vacuo to yield an orange oil. The oil was dissolved in pentane, and upon cooling to  $-40^\circ\text{C}$ , an orange solid was obtained. This solid was collected, washed with minimal cold pentane, and dried in vacuo; yield 0.62 g (0.64 mmol, 60%). Analytically pure samples were obtained by recrystallization from  $\text{Et}_2\text{O}/\text{pentane}$  solution at  $-40^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$ , 233 K):  $\delta$  7.23–6.48 (m, 19 H,  $\text{H}_{\text{aryl}}$  and  $\text{C}_6\text{H}_5$ ), 4.35, 3.43, 3.23 (spt, 2 H each,  $\text{CHMe}_2$ ), 3.03 (q, 2 H,  $\text{C}_\alpha\text{CH}_2\text{CH}_3$ ), 2.35 (q, 2 H,  $\text{C}_\beta\text{CH}_2\text{CH}_3$ ), 1.70, 1.48, 1.23, 1.19, 0.91, 0.72 (d, 6 H each,  $\text{CHMe}_2$ ), 0.94, 0.92 (t, 3 H each,  $\text{C}_\alpha\text{CH}_2\text{CH}_3$  and  $\text{C}_\beta\text{CH}_2\text{CH}_3$ ). No temperature could be identified at which all intramolecular dynamic processes were sufficiently fast or slow to observe all carbon nuclei of this compound. Partial  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_5\text{CD}_3$ , 233 K):  $\delta$  204.4, 199.9 ( $\text{C}_\alpha$  and  $\text{C}_\beta$ ), 174.4, 169.6 ( $\text{C}_\beta$  and  $\text{C}_\alpha$ ). IR: 1585 br w, 1435 s, 1325 m, 1250 s, 1190 s, 1109 m, 1095 m, 1070 w, 1053 w, 1040 m, 980 w, 905 s, 898 s, 888 sh, 877 sh, 790 m, 750 m, 715 sh, 703 m, 696 m. Anal. Calcd for  $\text{C}_{56}\text{H}_{71}\text{O}_3\text{Ta}$ : C, 69.12; H, 7.35. Found: C, 69.30; H, 7.44. Hydrolysis of 7 yielded (*Z,E*)- $\text{CHPh}=\text{CPhCET}=\text{CHET}$ . Partial  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.79 (s, 1 H,  $\text{CHPh}$ ), 5.47 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 1 H,  $\text{CHET}$ ), 2.28 (q,  $^3J_{\text{HH}} = 7.3$  Hz, 2 H,  $\text{CCH}_2\text{CH}_3$ ), 2.01 (pseudopentet,  $^3J_{\text{HH}} = 7.3$  Hz  $\approx$   $^3J_{\text{HH}} = 7.5$  Hz, 2 H,  $\text{CHCH}_2\text{CH}_3$ ), 1.07 (t,  $^3J_{\text{HH}} = 7.3$  Hz, 3 H,  $\text{CCH}_2\text{CH}_3$ ), 0.86 (t,  $^3J_{\text{H}} = 7.5$  Hz, 3 H,  $\text{CHCH}_2\text{CH}_3$ ).

**$(\text{DIPP})_3\text{Ta}(\text{CPh}=\text{CPhCH}=\text{CCMe}_3)$  (8).** To a  $-40^\circ\text{C}$  solution of 0.49 g (0.55 mmol) of  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  (1) in 15 mL of diethyl ether was added 0.15 mL (1.2 mmol) of 3,3-dimethyl-1-butyne. After the solution was stirred at room temperature overnight (ca. 18 h), the solvent was removed in vacuo to provide a red–orange oil. This oil was dissolved in a minimum volume of diethyl ether, several milliliters of acetonitrile were added, and upon cooling the solution to  $-40^\circ\text{C}$ , orange crystals formed. The crystals were collected, washed with cold acetonitrile, and dried in vacuo; yield 0.37 g (0.38 mmol, 70%). Analytically pure samples were obtained by recrystallization from  $\text{Et}_2\text{O}/\text{MeCN}$

solution at  $-40^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.57 (s, 1 H,  $\text{C}_\beta\text{H}$ ), 7.27–7.06, 6.76–6.50 (m, 19 H total,  $\text{H}_{\text{aryl}}$  and  $\text{C}_\beta\text{H}_5$ ), 3.94 (br, 4 H,  $\text{CHMe}_2$ ), 2.98 (spt, 2 H,  $\text{CHMe}_2$ ), 1.46, 1.36 (d, 12 H each,  $\text{CHMe}_2$ ), 1.13 (s, 9 H,  $\text{C}_\alpha\text{CMe}_3$ ), 0.76 (br d, 12 H,  $\text{CHMe}_2$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  221.3, 196.6 ( $\text{C}_\alpha\text{CMe}_3$  and  $\text{C}_\alpha\text{-Ph}$ ), 158.2, 154.7 ( $\text{C}_{\text{ipso}}$ , DIPP), 146.3 ( $\text{C}_\beta\text{Ph}$ ), 142.1 ( $\text{C}_{\text{ipso}}$ ,  $\text{C}_\beta\text{H}_5$ ), 139.8, 137.6 ( $\text{C}_\alpha$ , DIPP), 137.0 ( $\text{C}_\beta\text{H}$ ), 128.7, 128.6, 127.6, 126.8, 126.4, 123.9 ( $\text{C}_\alpha$ ,  $\text{C}_\beta$ ,  $\text{C}_\beta\text{H}_5$ ), 123.8, 123.6 ( $\text{C}_\beta$ , DIPP), 122.5, 122.1 ( $\text{C}_\beta$ , DIPP), 41.7 ( $\text{CMe}_3$ ), 31.7 ( $\text{CMe}_3$ ), 27.6, 27.0 ( $\text{CHMe}_2$ ), 25.1, 24.2 ( $\text{CHMe}_2$ ). One  $\text{CHMe}_2$  resonance was not observed or is coincident with another signal. IR: 1570 v br, 1495 w, 1430 s, 1360 m, 1317 m, 1243 s, 1181 s, 1100 m, 1076 sh, 1055 w, 1036 m, 1022 w, 905 s, 895 s, 872 m, 800 w, 787 m, 765 w, 750 m, 740 m, 710 m, 700 w, 690 m. Anal. Calcd for  $\text{C}_{56}\text{H}_{71}\text{O}_3\text{Ta}$ : C, 69.12; H, 7.35. Found: C, 69.12; H, 7.29. Hydrolysis of 8 yielded ( $Z,E$ )- $\text{CHPh}=\text{CPhCH}=\text{CHCMe}_3$ . Partial  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.56 (s, 1 H,  $\text{CHPh}$ ), 6.45 (d,  $^3J_{\text{HH}} = 16$  Hz, 1 H,  $\text{CH}$ ), 5.56 (d,  $^3J_{\text{HH}} = 16$  Hz, 1 H,  $\text{CHCMe}_3$ ), 0.96 (s, 9 H,  $\text{CHCMe}_3$ ).

(DIPP) $_3$ Ta( $\text{CPh}=\text{CPhCH}=\text{CSiMe}_3$ ) (9). To a  $-40^\circ\text{C}$  solution of 0.75 g (0.84 mmol) of (DIPP) $_3$ Ta( $\text{PhC}\equiv\text{CPh}$ ) (1) in 15 mL of diethyl ether was added 0.18 mL (1.5 mmol) of (trimethylsilyl)acetylene. After the solution was stirred at room temperature overnight (ca. 18 h), the solvent was removed in vacuo to provide a red-orange oil. Upon dissolving the oil in pentane, the orange solid product began to precipitate. Precipitation was completed by cooling this mixture to  $-40^\circ\text{C}$  overnight. The resulting solid was collected, washed with cold pentane, and dried in vacuo; yield 0.65 g (0.66 mmol, 79%). Analytically pure samples were obtained by recrystallization from  $\text{Et}_2\text{O}$ /pentane solutions at  $-40^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.68 (s, 1 H,  $\text{C}_\beta\text{H}$ ), 7.23–6.45 (m, 19 H,  $\text{H}_{\text{aryl}}$  and  $\text{C}_\beta\text{H}_5$ ), 3.97 (br, 4 H,  $\text{CHMe}_2$ ), 3.14 (br, 2 H,  $\text{CHMe}_2$ ), 1.43, 1.33 (d, 12 H each,  $\text{CHMe}_2$ ), 0.87 (br, 12 H,  $\text{CHMe}_2$ ), 0.074 (s, 9 H,  $\text{SiMe}_3$ ). At no temperature between 213 and 358 K were all intramolecular dynamic processes sufficiently fast or slow to observe all carbon nuclei of this compound. Partial  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta$  210.7, 203.8 (br,  $\text{C}_\alpha$  and  $\text{C}_\beta$ ). IR: 1585 br w, 1432 s, 1360 m, 1322 s, 1305 sh, 1288 w, 1255 sh, 1245 s, 1185 s, 1105 m, 1094 m, 1073 w, 1053 w, 1040 m, 1026 w, 938 m, 910 s, 897 s, 869 s, 830 m, 790 m, 755 w, 745 s, 731 m, 709 m, 695 s, 666 w, 640 w. Anal. Calcd for  $\text{C}_{55}\text{H}_{71}\text{O}_3\text{SiTa}$ : C, 66.78; H, 7.23. Found: C, 67.20; H, 7.35. Hydrolysis of 9 yielded ( $Z,E$ )- $\text{CHPh}=\text{CPhCH}=\text{CHSiMe}_3$ . Partial  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.63 (s, 1 H,  $\text{CHPh}$ ), 5.83 (d,  $^3J_{\text{HH}} = 19$  Hz, 1 H,  $\text{CHSiMe}_3$ ), 0.08 (s, 9 H,  $\text{CHSiMe}_3$ ). The  $\text{CH}=\text{CHSiMe}_3$  resonance was obscured by the aryl proton signals.

(DIPP) $_3$ Ta( $\text{CPh}=\text{CPhCH}=\text{CPh}$ ) (10). A 0.54-g sample (0.60 mmol) of (DIPP) $_3$ Ta( $\text{PhC}\equiv\text{CPh}$ ) (1) was dissolved in 15 mL of diethyl ether, the solution was cooled to  $-40^\circ\text{C}$ , and 0.12 mL (1.1 mmol) of phenylacetylene was added. The reaction color quickly changed from pale yellow to red orange upon acetylene addition. After stirring the solution at room temperature overnight (ca. 18 h), the solvent was removed in vacuo to provide a red-orange oil. The oil was dissolved in pentane, and upon cooling the solution to  $-40^\circ\text{C}$ , orange solid formed. This solid was collected, washed with minimal cold pentane, and dried in vacuo; yield 0.45 g (0.45 mmol, 75%). Analytically pure samples were obtained by recrystallization from  $\text{Et}_2\text{O}$ /pentane solution at  $-40^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_5\text{CD}_3$ , 338 K):  $\delta$  7.99 (s,  $\text{C}_\beta\text{H}$ ), 7.17–6.53 (m, 24 H,  $\text{H}_{\text{aryl}}$  and  $\text{C}_\beta\text{H}_5$ ), 3.62 (spt, 6 H,  $\text{CHMe}_2$ ), 1.13 (d, 36 H,  $\text{CHMe}_2$ ). All carbon resonances in this molecule were not observed. Partial  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_5\text{CD}_3$ , 338 K):  $\delta$  203.7, 200.4 ( $\text{C}_\alpha$  and  $\text{C}_\beta$ ). IR: 1585 br w, 1430 s, 1320 m, 1245 s, 1185 s, 1105 m, 1092 m, 1039 w, 1022 w, 939 w, 905 sh, 898 s, 878 w, 869 m, 786 m, 760 w, 750 m, 741 m, 709 w, 692 m. Anal. Calcd for  $\text{C}_{58}\text{H}_{67}\text{O}_3\text{Ta}$ : C, 70.15; H, 6.80. Found: C, 70.18; H, 7.06. Hydrolysis of 10 yielded ( $Z,E$ )- $\text{CHPh}=\text{CPhCH}=\text{CHPh}$ . Partial  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.64 (s, 1 H,  $\text{CHPh}$ ), 6.34 (d,  $^3J_{\text{HH}} = 16$  Hz, 1 H,  $\text{CHPh}$ ). The  $\text{CH}=\text{CHPh}$  signal was obscured by the aryl proton resonances.

(DIPP) $_3$ Ta( $\text{CPh}=\text{CPhCH}=\text{C}(\text{CH}_2)_4\text{C}=\text{CHCPh}=\text{PhC}$ ) $_2$ Ta(DIPP) $_3$  (11). To a  $-40^\circ\text{C}$  solution of 0.52 g (0.58 mmol) of (DIPP) $_3$ Ta( $\text{PhC}\equiv\text{CPh}$ ) (1) in 15 mL of diethyl ether was added 0.045 mL (0.35 mmol) of 1,7-octadiyne. The reaction color changed from pale yellow to red-orange within minutes. After the solution was stirred overnight (ca. 18 h) at room temperature, an orange

solid had deposited. The solid was collected, washed with cold diethyl ether, and dried in vacuo; yield 0.45 g (0.24 mmol, 83%). An NMR sample of 11 could not be prepared due to its low solubility in all solvents; however, the compound obtained in this fashion was analytically pure. IR: 1580 br w, 1320 s, 1282 s, 1178 s, 1100 m, 1090 m, 1050 w, 1035 m, 1020 w, 916 m, 901 s, 890 s, 870 m, 783 m, 760 m, 738 s, 689 s. Anal. Calcd for  $\text{C}_{108}\text{H}_{132}\text{O}_6\text{Ta}_2$ : C, 68.70; H, 7.05. Found: C, 68.83; H, 7.41. Hydrolysis of 11, followed by trituration of the oil with pentane, yielded the pale yellow solid ( $Z,E$ )- $\text{CHPh}=\text{CPhCH}=\text{CH}(\text{CH}_2)_4\text{-}(E,Z)\text{-CH}=\text{CHCPh}=\text{CHPh}$  in 80% yield. Analytically pure samples were obtained by recrystallization from toluene/pentane solution at  $-40^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.22–6.83 (m, 20 H,  $\text{C}_\beta\text{H}_5$ ), 6.53 (s, 2 H,  $\text{CHPh}=\text{CPhCH}=\text{CH}$ ), 6.42 (d,  $^3J_{\text{HH}} = 15$  Hz, 2 H,  $\text{CHPh}=\text{CPhCH}=\text{CH}$ ), 5.43 (d of t,  $^3J_{\text{HH}} = 15$  and 7 Hz, 2 H,  $\text{CHPh}=\text{CPhCH}=\text{CH}$ ), 1.97 (br q, 4 H,  $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$ ), 1.24 (m, 4 H,  $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$ ). Anal. Calcd for  $\text{C}_{36}\text{H}_{34}$ : C, 92.66; H, 7.34. Found: C, 92.47; H, 7.22.

(DIPP) $_3$ Ta( $\text{CMe}=\text{CSiMe}_3\text{CMe}=\text{CMe}$ ) (12). To a  $-40^\circ\text{C}$  solution of 0.56 g (0.68 mmol) of (DIPP) $_3$ Ta( $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ) (2) in 10 mL of diethyl ether was added 0.12 mL (1.53 mmol) of 2-butyne. The solution color slowly changed from yellow to orange over 30 min. After being stirred for 6 h at room temperature, the solvent was removed in vacuo to afford an orange oil. The oil was reconstituted in a minimal volume of pentane, and the solution was cooled to  $-40^\circ\text{C}$  for 24 h. The orange crystals that formed (0.084 g, 0.01 mmol, 14% yield) were collected, washed with minimal cold pentane, and dried in vacuo.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.07–6.91 (m, 9 H,  $\text{H}_{\text{aryl}}$ ), 3.61 (spt, 6 H,  $\text{CHMe}_2$ ), 2.33, 2.19, 1.92 (s, 3 H each,  $\text{C}_\alpha\text{Me}$ ,  $\text{C}_\beta\text{Me}$ , and  $\text{C}_\gamma\text{Me}$ ), 1.18 (d, 36 H,  $\text{CHMe}_2$ ), 0.28 (s, 9 H,  $\text{SiMe}_3$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  221.4, 195.4 ( $\text{C}_\alpha\text{Me}$  and  $\text{C}_\beta\text{Me}$ ), 170.1, 149.8 ( $\text{C}_\beta\text{SiMe}_3$  and  $\text{C}_\beta\text{Me}$ ), 157.3 ( $\text{C}_{\text{ipso}}$ ), 138.3 ( $\text{C}_\alpha$ ), 123.7 ( $\text{C}_\gamma$ ), 123.1 ( $\text{C}_\beta$ ), 27.6 ( $\text{CHMe}_2$ ), 24.1 ( $\text{CHMe}_2$ ), 23.7, 23.4, 19.4 ( $\text{C}_\alpha\text{Me}$ ,  $\text{C}_\beta\text{Me}$ , and  $\text{C}_\gamma\text{Me}$ ), 3.3 ( $\text{SiMe}_3$ ). Anal. Calcd for  $\text{C}_{66}\text{H}_{69}\text{O}_3\text{SiTa}$ : C, 62.85; H, 7.91. Found: C, 62.89; H, 8.10. Hydrolysis of 12 yielded ( $Z,E$ )- $\text{CHMe}=\text{CSiMe}_3\text{CMe}=\text{CHMe}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.98, 5.02 (q,  $^3J_{\text{HH}} = 7.0$  Hz, 1 H each,  $\text{CHMe}$ ), 1.76, 1.59 (d,  $^3J_{\text{HH}} = 7.0$  Hz, 3 H each,  $\text{CHMe}$ ), 1.63 (s, 3 H,  $\text{CMe}$ ), 0.15 (s, 9 H,  $\text{SiMe}_3$ ).

(DIPP) $_3$ Ta( $\text{CSiMe}_3=\text{CMeCPh}=\text{CH}$ ) (13). To a room-temperature solution of 0.77 g (0.93 mmol) of (DIPP) $_3$ Ta( $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ) (2) in 10 mL of diethyl ether was added 0.15 mL (1.4 mmol) of phenylacetylene. The solution color immediately changed from yellow to red-orange upon acetylene addition. After being stirred for 24 h at room temperature, the solution was filtered through Celite, and removing the solvent in vacuo afforded an orange oil. The oil was reconstituted in pentane and cooled to  $-40^\circ\text{C}$  for 24 h. The orange-brown cubes that formed (0.36 g, 0.38 mmol, 41% yield) were collected, washed with minimal cold pentane, and dried in vacuo. Recrystallization of this compound from pentane at  $-40^\circ\text{C}$  provided analytically pure samples.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.89 (s, 1 H,  $\text{C}_\alpha\text{H}$ ), 7.26–6.85 (m, 14 H,  $\text{H}_{\text{aryl}}$  and  $\text{C}_\beta\text{H}_5$ ), 3.98, 3.77, 3.14 (br, 2 H each,  $\text{CHMe}_2$ ), 1.92 (s, 3 H,  $\text{C}_\beta\text{Me}$ ), 1.36 (br d, 24 H,  $\text{CHMe}_2$ ), 0.92 (br, 12 H,  $\text{CHMe}_2$ ), 0.26 (s, 9 H,  $\text{SiMe}_3$ ). Partial  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  203.8 ( $\text{C}_\alpha\text{SiMe}_3$ ), 192.7 ( $\text{C}_\alpha\text{H}$ ), 180.1, 163.1 ( $\text{C}_\beta\text{Me}$  and  $\text{C}_\beta\text{Ph}$ ). IR: 1575 w, 1320 m, 1245 s, 1182 s, 1095 m, 1034 w, 990 w, 930 m, 904 s, 890 m, 872 w, 840 m, 826 sh, 785 m, 760 w, 741 s, 708 w, 691 m, 653 w. Anal. Calcd for  $\text{C}_{50}\text{H}_{69}\text{O}_3\text{SiTa}$ : C, 64.78; H, 7.50. Found: C, 64.87; H, 7.68. Hydrolysis of 13 yielded ( $E$ )- $\text{CHSiMe}_3=\text{CMeCPh}=\text{CH}_2$ . Partial  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.50, 5.30, 5.15 (br s, 1 H each,  $\text{CH}_2=\text{CPh}$  and  $\text{CHSiMe}_3$ ), 2.03 (s, 3 H,  $\text{CMe}$ ), 0.13 (s, 9 H,  $\text{CHSiMe}_3$ ). The broad singlets between  $\delta$  5 and 6 preclude a proton occupying a  $\beta$  ring position in metallacycle 13. The fact that coupling is not observed between  $=\text{CHMe}$  protons (as in ( $Z,E$ )- $\text{CHPh}=\text{CPhCMe}=\text{CHMe}$ , vide supra or in ( $Z,E$ )- $\text{CHMe}=\text{CSiMe}_3\text{CH}=\text{CHCMe}_3$ , vide infra) indicates that 13 is not the alternate regioisomer (DIPP) $_3$ Ta( $\text{CMe}=\text{CSiMe}_3\text{CPh}=\text{CH}$ ).

(DIPP) $_3$ Ta( $\text{CCMe}_3=\text{CHCSiMe}_3=\text{CMe}$ ) (14). To a room-temperature solution of 0.87 g (1.05 mmol) of (DIPP) $_3$ Ta( $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ) (2) in 10 mL of diethyl ether was added 0.30 mL (2.44 mmol) of 3,3-dimethyl-1-butyne. The solution changed color from yellow to orange over several minutes. After being stirred at room temperature for 24 h, the solution was filtered through



Celite, and the solvent was removed in vacuo to provide a frothy, orange oil. This oil was dissolved in pentane and cooled to  $-40^{\circ}\text{C}$  for 24 h whereupon yellow orange needles of product formed (0.44 g, 0.49 mmol, 47% yield, 2 crops). The product was filtered off, washed with minimal cold pentane, and dried in vacuo. This sample was sufficiently pure for elemental analysis but could be recrystallized from pentane at  $-40^{\circ}\text{C}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.69 (s, 1 H,  $\text{C}_\beta\text{H}$ ), 7.03–6.88 (m, 9 H,  $\text{H}_{\text{aryl}}$ ), 3.62 (spt, 4 H,  $\text{CHMe}_2$ ), 3.54 (spt, 2 H,  $\text{CHMe}_2$ ), 2.75 (s, 3 H,  $\text{C}_\alpha\text{Me}$ ), 1.23 (s, 9 H,  $\text{CMe}_3$ ), 1.17, 1.15, 1.12 (d, 6 H each,  $\text{CHMe}_2$ ), 0.11 (s, 9 H,  $\text{SiMe}_3$ ). IR: 1580 w, 1375 m, 1355 m, 1320 br s, 1293 w, 1250 br s, 1100 br s, 1050 w, 1036 m, 1015 w, 990 w, 915 w, 908 m, 886 s, 865 m, 830 s, 787 m, 740 s, 695 s, 665 w, 618 m. Anal. Calcd for  $\text{C}_{48}\text{H}_{69}\text{O}_3\text{SiTa}$ : C, 63.56; H, 8.11. Found: C, 63.64; H, 8.29. Hydrolysis of 14 yielded (*Z,E*)- $\text{CHMe}=\text{CSiMe}_3\text{CH}=\text{CHCMe}_3$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.23 (q, 1 H,  $^3J_{\text{HH}} = 7.1$  Hz,  $\text{CHMe}$ ), 5.92, 5.52 (d,  $^3J_{\text{HH}} = 16$  Hz, 1 H each,  $\text{CHCMe}_3=\text{CH}$ ), 1.82 (d, 3 H,  $\text{CHMe}$ ), 1.02 (s, 9 H,  $\text{CMe}_3$ ), 0.19 (s, 9 H,  $\text{SiMe}_3$ ).

(DIPP)<sub>3</sub>(I)TaCPh=CPhCMe=CMe(I) (15). To a  $-40^{\circ}\text{C}$  solution of 0.75 g (0.79 mmol) of (DIPP)<sub>3</sub>Ta(CPh=CPhCMe=CMe) (6) in 15 mL of diethyl ether was added 0.24 g (0.95 mmol) of iodine. The reaction was allowed to stir overnight (ca. 18 h) at room temperature, over which time a yellow powder had precipitated. The solids were collected, washed with cold ether, and dried in vacuo; yield 0.68 g (0.57 mmol, 72%). Analytically pure samples were obtained by recrystallization from toluene/pentane at  $-40^{\circ}\text{C}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_5\text{CD}_3$ , 353 K):  $\delta$  7.66–7.63, 7.21–6.79 (m, 19 H,  $\text{H}_{\text{aryl}}$  and  $\text{C}_6\text{H}_5$ ), 3.59 (br, 6 H,  $\text{CHMe}_2$ ), 2.57, 2.00 (s, 3 H each,  $\text{C}_\alpha\text{Me}$  and  $\text{C}_\beta\text{MeI}$ ), 1.02 (d, 36 H,  $\text{CHMe}_2$ ). All carbon resonances in this molecule have not been observed. Partial  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_5\text{CD}_3$ , 353 K):  $\delta$  202.8 ( $\text{C}_\alpha\text{Ph}$ ). IR: 1585 w, 1427 s, 1316 s, 1238 s, 1169 br s, 1098 s, 1093 s, 1048 w, 1035 m, 926 m, 907 m, 885 s, 865 s, 790 m, 774 m, 762 m, 742 s, 727 m, 704 m, 694 s. Anal. Calcd for  $\text{C}_{54}\text{H}_{69}\text{I}_2\text{O}_3\text{Ta}$ : C, 54.10; H, 5.63. Found: C, 54.49; H, 5.86. Hydrolysis of 15 yielded (*Z,Z*)- $\text{CHPh}=\text{CPhCMe}=\text{CMeI}$ . Partial  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.47 (s, 1 H,  $\text{CHPh}$ ), 2.63 (q, 3 H,  $^5J_{\text{HH}} = 1.0$  Hz,  $\text{CMe}$ ), 1.82 (q, 3 H,  $^5J_{\text{HH}} = 1.0$  Hz,  $\text{CMeI}$ ).

(DIPP)<sub>3</sub>(I)TaCPh=CPhCtEt=CtEt(I) (16). A solution of 0.31 g (0.31 mmol) of (DIPP)<sub>3</sub>Ta(CPh=CPhCtEt=CtEt) (7) in 15 mL of diethyl ether was prepared and cooled to  $-40^{\circ}\text{C}$ . A 0.16-g sample (0.63 mmol) of  $\text{I}_2$  was added to the solution, and the reaction was stirred overnight (ca. 18 h) at room temperature over which time the product precipitated as a yellow powder. The powder was filtered off, washed with cold diethyl ether, and dried in vacuo; yield 0.30 g (0.25 mmol, 80%). Analytically pure samples were obtained by recrystallization from toluene/pentane solution at  $-40^{\circ}\text{C}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.37–7.34, 7.14–6.81 (m, 19 H,  $\text{H}_{\text{aryl}}$  and  $\text{C}_6\text{H}_5$ ), 4.45 (br, 1 H,  $\text{CHMe}_2$ ), 3.14, 2.53 (second-order m, 2 H,  $\text{CHMe}_2$ ), 2.87 (second-order m, 1 H,  $\text{CHMe}_2$ ), 1.20, 0.49 (t, 3 H each,  $\text{C}_\gamma\text{CH}_2\text{CH}_3$  and  $\text{C}_\beta(\text{CH}_2\text{CH}_3)\text{I}$ ); a broad featureless resonance spanning  $\delta$  1.7–0.3 ( $\text{CHMe}_2$ ,  $\text{C}_\gamma\text{CH}_2\text{CH}_3$ , and  $\text{C}_\beta(\text{CH}_2\text{CH}_3)\text{I}$ ) was unresolved. No temperature could be identified at which all intramolecular dynamic processes were sufficiently fast or slow to sharpen all the resonances of this compound. Partial  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  201.9 ( $\text{C}_\alpha\text{Ph}$ ). Anal. Calcd for  $\text{C}_{56}\text{H}_{71}\text{I}_2\text{O}_3\text{Ta}$ : C, 54.82; H, 5.83. Found: C, 55.05; H, 6.05. Hydrolysis of 16 yielded (*Z,Z*)- $\text{CHPh}=\text{CPhCtEt}=\text{CtEtI}$ . Partial  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.43 (s, 1 H,  $\text{CHPh}$ ), 2.70, 2.13 (q,  $^3J_{\text{HH}} = 7.3$ , 7.5 Hz, 2 H each,  $\text{C}_\gamma\text{CH}_2\text{CH}_3$  and  $\text{C}_\beta(\text{CH}_2\text{CH}_3)\text{I}$ ), 1.24, 0.99 (t, partially obscured, 3 H each,  $\text{C}_\gamma\text{CH}_2\text{CH}_3$  and  $\text{C}_\beta(\text{CH}_2\text{CH}_3)\text{I}$ ).

(DIPP)<sub>3</sub>(I)TaCSiMe<sub>3</sub>=CMeCPh=CH(I) (17). To a  $-40^{\circ}\text{C}$  solution of 0.24 g (0.26 mmol) of (DIPP)<sub>3</sub>Ta(CSiMe<sub>3</sub>=CMeCPh=CH) (13) in 10 mL of diethyl ether was added 0.06 g (0.23 mmol) of  $\text{I}_2$ . The yellow solution immediately took on an orange color that turned to yellow after several hours. After this solution was stirred for 24 h at room temperature, the solvent was removed in vacuo, leaving behind a frothy, yellow oil. The oil was dissolved in pentane and cooled to  $-40^{\circ}\text{C}$  for 24 h, and the resulting yellow crystals (0.17 g, 0.14 mmol, 54% yield) were collected, washed with minimal cold pentane, and dried in vacuo. The product was sufficiently pure for analysis but could be recrystallized from pentane at  $-40^{\circ}\text{C}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.86

(s, 1 H,  $\text{C}_\beta\text{H}$ ), 7.58–6.85 (m, 14 H,  $\text{H}_{\text{aryl}}$  and  $\text{C}_6\text{H}_5$ ), 3.98 (spt, 6 H,  $\text{CHMe}_2$ ), 1.83 (s, 3 H,  $\text{C}_\beta\text{Me}$ ), 1.15 (d, 36 H,  $\text{CHMe}_2$ ), 0.26 (s, 9 H,  $\text{SiMe}_3$ ).  $^{13}\text{C NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  184.3 ( $\text{C}_\beta\text{H}$ ), 160.9 ( $\text{C}_\alpha\text{SiMe}_3$ ), 157.5 ( $\text{C}_{\text{ipso}}$ , DIPP), 157.1 ( $\text{C}_\beta\text{Me}$ ), 140.5 ( $\text{C}_{\text{ipso}}$ ,  $\text{C}_6\text{H}_5$ ), 139.0 ( $\text{C}_\alpha$ , DIPP), 129.0 ( $\text{C}_\alpha$ ,  $\text{C}_6\text{H}_5$ ), 128.8 ( $\text{C}_\beta$ ,  $\text{C}_6\text{H}_5$ ), 127.3 ( $\text{C}_m$ ,  $\text{C}_6\text{H}_5$ ), 124.1 ( $\text{C}_p$ , DIPP), 124.0 ( $\text{C}_m$ , DIPP), 112.3 ( $\text{C}_\gamma$ ), 27.3 ( $\text{CHMe}_2$ ), 24.6 ( $\text{CHMe}_2$ ), 24.0 ( $\text{C}_\beta\text{Me}$ ), 1.9 ( $\text{SiMe}_3$ ). IR: 1580 w, 1537 w, 1430 s, 1358 m, 1322 s, 1192 s, 1182 s, 1096 m, 1090 sh, 1084 sh, 1035 m, 926 m–s, 904 s, 890 s, 870 m, 835 s, 785 m, 761 w, 740 s, 700 m, 692 sh. Anal. Calcd for  $\text{C}_{50}\text{H}_{69}\text{I}_2\text{O}_3\text{SiTa}$ : C, 50.85; H, 5.89. Found: C, 50.54; H, 6.05. Hydrolysis of 17 yielded (*E,Z*)- $\text{CHSiMe}_3=\text{CMeCPh}=\text{CH(I)}$ . Partial  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  5.49, 4.96 (s, 1 H each,  $\text{CHSiMe}_3$  and  $\text{CPh}=\text{CH(I)}$ ), 1.92 (d,  $^4J_{\text{HH}} = 0.7$  Hz, 3 H,  $\text{CMe}$ ), 0.32 (d,  $^4J_{\text{HH}} = 0.9$  Hz, 9 H,  $\text{SiMe}_3$ ).

**X-ray Structural Determination of (DIPP)<sub>3</sub>Ta(PhC≡CPh) (1).** A yellow irregular crystal of (DIPP)<sub>3</sub>Ta(PhC≡CPh) (1), grown from a pentane solution at  $-40^{\circ}\text{C}$  was mounted in a glass capillary with its long axis roughly parallel to the  $\phi$  axis of the goniometer. Preliminary examination and data collection were performed on a Syntex P2<sub>1</sub> diffractometer using Mo K $\alpha$  radiation monochromatized with graphite ( $\lambda = 0.71037 \text{ \AA}$ ). Table I summarizes the crystal data and structure refinement results. Two check reflections were measured every 98 data reflections; the intensities of these standards had decreased by 11.0% by the end of the data collection. An anisotropic decay correction was applied. The correction factors ranged from 0.984 to 1.118 with an average value of 1.046. Lorentz and polarization corrections were also applied. The linear absorption coefficient is  $24.3 \text{ cm}^{-1}$  for Mo K $\alpha$  radiation. An empirical absorption correction was made by using the method described by Walker and Stuart<sup>31</sup> with the correction factors ranging from 0.903 to 1.109. The structure was solved with the Patterson heavy-atom method and refined in full-matrix least squares. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined. The largest peak in the final difference Fourier map was  $-0.47 \text{ e}^{-1}/\text{Å}^3$ . All calculations were performed on a VAX computer using SDP/VAX.<sup>32</sup>

**X-ray Structural Determination of (DIPP)<sub>3</sub>Ta(CEt=CtEtCtEt=CtEt) (3).** A red-orange irregular crystal of (DIPP)<sub>3</sub>Ta(CEt=CtEtCtEt=CtEt) (3) having approximate dimensions of  $0.50 \times 0.30 \times 0.50 \text{ mm}$  was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed on a Syntex P2<sub>1</sub> diffractometer using Mo K $\alpha$  radiation monochromatized with graphite ( $\lambda = 0.71037 \text{ \AA}$ ). Table I summarizes the crystal data and structure refinement results. As a check on crystal quality, 3 representative reflections were measured every 46 reflections, the intensities of which remained constant within experimental error throughout the data collection. From the systematic absences of  $h0l$ ,  $h+l=2n$  and  $0k0$ ,  $k=2n$  and from subsequent least squares refinement, the space group was determined to be  $P2_1/n$  (No. 14). Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is  $23.7 \text{ cm}^{-1}$  for Mo K $\alpha$  radiation.  $\psi$  scans showed no systematic variation. A differential absorption correction was performed without improvement; therefore, the structure was refined without an absorption correction. The intensities of equivalent reflections were averaged. The agreement factors for the averaging of the 345 observed and accepted reflections was 3.8% based upon intensity and 2.9% based upon  $F_o$ . The structure was solved with the Patterson heavy-atom method and refined in full-matrix least squares. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined. The largest peak in the final difference Fourier map was  $0.71 \text{ e}^{-1}/\text{Å}^3$ . All calculations were performed on a VAX computer using SDP/VAX.<sup>32</sup>

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130220-54-1; (Z,E)-CHPh=CPhCH=CHSiMe<sub>3</sub>, 130220-55-2; (Z,E)-CHPh=CPhCH=CHPh, 87968-73-8; (Z,E),(E,Z)-CHPh=CPhCH=CH(CH<sub>2</sub>)<sub>4</sub>CH=CHCPh=CHPh, 130220-56-3; 3-hexyne, 928-49-4; (trimethylsilyl)acetylene, 1066-54-2; 3,3-dimethyl-1-butyne, 917-92-0; 2-butyne, 503-17-3; phenylacetylene, 536-74-3; 1,7-octadiyne, 871-84-1.

**Supplementary Material Available:** Full details of the structure solution and crystallographic details for (DIPP)<sub>3</sub>Ta(PhC≡CPh) and (DIPP)<sub>3</sub>Ta(CEt=CetCet=Cet) including tables of atomic positional and thermal parameters, bond distances and angles, and dihedral angles and ORTEP figures (26 pages); tables of observed and calculated structure factor amplitudes (48 pages). Ordering information is given on any current masthead page.

## Indirect Cooperative Effects Leading to Synergism in Bimetallic Homogeneous Catalysts Containing Azolates as Bridging Ligands

Miguel A. Esteruelas, Maria P. Garcia, Ana M. López, and Luis A. Oro\*

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain

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The binuclear compounds [H(CO)(PPh<sub>3</sub>)<sub>2</sub>Ru(μ-bim)Ir(COD)] (1) (bim = 2,2'-biimidazolate, COD = 1,5-cyclooctadiene) and [H(CO)(PPh<sub>3</sub>)<sub>2</sub>Ru(μ-pz)<sub>2</sub>Ir(TFB)] (2) (pz = pyrazolate, TFB = tetrafluorobenzobarrelene) are more active catalysts for the hydrogenation of cyclohexene than the mononuclear parent compounds [RuH(Hbim)(CO)(PPh<sub>3</sub>)<sub>2</sub>], [Ir(Hbim)(COD)], [RuH(pz)(CO)(Hpz)(PPh<sub>3</sub>)<sub>2</sub>], and [Ir(TFB)(Hpz)<sub>2</sub>BF<sub>4</sub>]. In the presence of 1, the reaction rate is first order with respect to the concentration of 1 and cyclohexene, second order with respect to hydrogen pressure, and inversely proportional to the concentration of added phosphine. For the reaction catalyzed by 2, the experimental data are in accordance with a rate expression of the form  $-d[\text{cyclohexene}]/dt = k[2][\text{cyclohexene}]P(\text{H}_2)$  [ $P(\text{H}_2)$  = hydrogen pressure]. On the basis of the kinetic results and experimental evidence, the origin of the catalytic synergism is assigned to indirect cooperative effects between the metallic centers of the binuclear complexes. The kinetic investigation of the hydrogenation of cyclohexene catalyzed by [Ir(μ-pz)(TFB)]<sub>2</sub> (3) is also reported, suggesting that the full catalytic cycle involves binuclear species.

### Introduction

Studies of multicomponent metal systems under homogeneous conditions have revealed the existence of catalytic activity enhancement when compared to that of the individual components;<sup>1</sup> this enhancement effect is known collectively as synergism,<sup>2,3</sup> and it has played an important role in the development of homogeneous polymetallic catalysis.<sup>4</sup> From a mechanistic point of view, the concept

of synergism has been applied to metal atoms either operating individually<sup>3</sup> or, more rigorously, in concert<sup>5-8</sup> in reaction sequences. A genuine bimetallic mechanism in which two metal centers act in concert has been postulated by Kalck's group, for the olefin hydroformylation catalyzed by compounds of the type *cis*-[Rh<sub>2</sub>(μ-SBu<sup>t</sup>)<sub>2</sub>(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>], on the basis of theoretical calculations and spectroscopic studies.<sup>5</sup> Bimetallic catalytic pathways involving the concerted action of two metals have been also proposed for processes such as the hydration of acrylonitrile to acrylamide catalyzed by dinuclear palladium complexes,<sup>6</sup> alkene hydroformylation catalyzed by compounds of the type [Ru<sub>2</sub>(μ-OOCR)<sub>2</sub>(CO)<sub>4</sub>(PR<sub>3</sub>)<sub>2</sub>],<sup>7</sup> or hydrogen transfer

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