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**Synthesis and reactivity of tantalum and tungsten alkyne  
complexes: Models for alkyne cyclization**

Wexler, Pamela Andrea, Ph.D.

The University of Arizona, 1990

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**SYNTHESIS AND REACTIVITY OF TANTALUM AND TUNGSTEN  
ALKYNE COMPLEXES: MODELS FOR ALKYNE CYCLIZATION**

by

Pamela Andrea Wexler

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A Dissertation Submitted to the Faculty of the

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In Partial Fulfillment of the Requirements  
For the Degree of

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In the Graduate College

**THE UNIVERSITY OF ARIZONA**

1990

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2

As members of the Final Examination Committee, we certify that we have read  
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entitled Synthesis and Reactivity of Tantalum and Tungsten Alkyne  
Complexes: Models for Alkyne Cyclization

and recommend that it be accepted as fulfilling the dissertation requirement  
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## ABSTRACT

Intermediates in the cyclization reaction of alkynes have been isolated using the group 5 tantalum phenoxide reagents,  $\text{Ta}(\text{DIPP})_2\text{Cl}_3(\text{OEt}_2)$  and  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  (DIPP = O-2,6- $\text{C}_6\text{H}_3$ -i-Pr<sub>2</sub>). The extent of cyclization has been effected by controlling the sterics at the metal center or the alkyne itself. Reducing the less congested bis phenoxide complex,  $\text{Ta}(\text{DIPP})_2\text{Cl}_3(\text{OEt}_2)$ , by two electrons in the presence of 2-butyne or 3-hexyne allowed the isolation of an arene complex,  $(\text{C}_6\text{R}_6)\text{Ta}(\text{DIPP})_2\text{Cl}$  (R = Me, Et), which is formally classified as a 7-metallanorbornadiene. This complex can also be reduced by one more electron to produce a tantalum (II) species that readily undergoes a one-electron addition reaction with halogenated reagents. This complex also underwent an intramolecular C-H activation of one of the alkyl groups on the arene ring. Attempts were made to try and generalize this cyclization and C-H activation chemistry to the group 6 metals.

Tungsten phenoxide and mixed phenylimido-phenoxide reagents were synthesized for use in subsequent cyclization reactions. Reducing the bis phenoxide complex,  $\text{W}(\text{DIPP})_2\text{Cl}_4$ , by two electrons in the presence of a variety of alkynes afforded the alkyne complexes  $\text{W}(\text{DIPP})_2\text{Cl}_2(\text{RC}\equiv\text{CR}')$  (R = R' = Me, Et, Ph; R =  $\text{CMe}_3$ , R' = H). The mixed phenylimido-phenoxide complexes,  $\text{W}(\text{NAr})(\text{DMP})_x\text{Cl}_{3-x}$  (x = 1 or 2; NAr = N-2,6- $\text{C}_6\text{H}_3$ -i-Pr<sub>2</sub>; DMP = O-2,6- $\text{C}_6\text{H}_3\text{Me}_2$ ), were also reduced by two electrons in the presence of alkynes to afford adducts (i.e.  $\text{W}(\text{NAr})(\text{DMP})_2(\text{EtC}\equiv\text{CEt})$ ). These alkyne adduct complexes failed to undergo any cycloaddition reactions.

Reduction of the tantalum tris phenoxide complex,  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$ , by two electrons in the presence of the bulky alkynes diphenylacetylene or trimethylsilyl-1-propyne afforded the isolation of the alkyne adducts  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  and

$(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  respectively. The alkyne adduct  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  undergoes regioselective cross-coupling reactions with smaller alkynes to afford metallacyclopentadienes. Metallacyclopentadienes can be formed directly from the reduction of the tris phenoxide complex in the presence of smaller alkynes (i.e.  $(\text{DIPP})_3\text{Ta}(\text{CEt}=\text{CEtCEt}=\text{CEt})$ ). The alkyne adduct undergoes cyclization reactions with nitriles that contain  $\alpha$ -hydrogens to yield metallacycloenamine complexes  $(\text{DIPP})_3\text{Ta}(\text{CSiMe}_3=\text{CMeC}(=\text{CHR})\text{NH})$ . The adduct also reacts with ketones to produce metallacyclic complexes with the formulation  $(\text{DIPP})_3\text{Ta}(\text{CSiMe}_3=\text{CMeC}(\text{RR}')\text{O})$ .

## CHAPTER 1

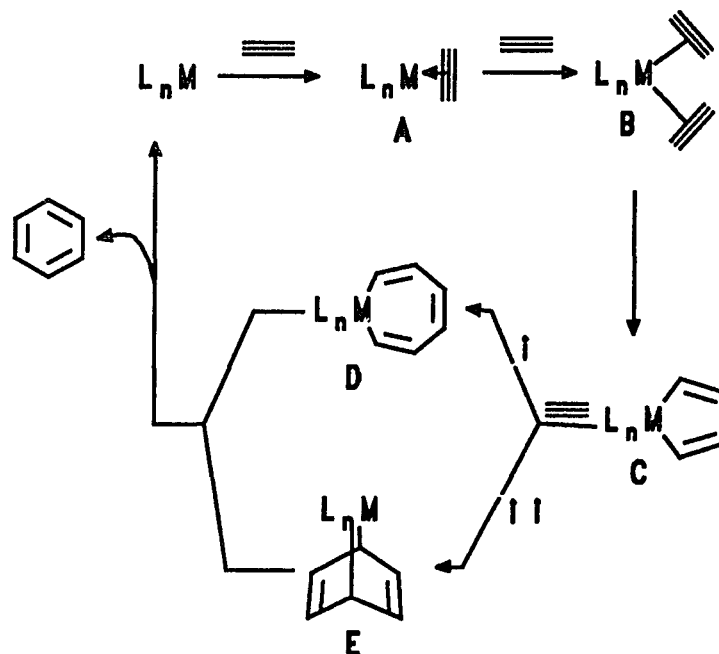
### INTRODUCTION

#### Background

Among the most important reactions in organic synthesis are those in which carbon-carbon bonds are formed. Two major types of carbon-carbon bond forming reactions are polymerization and cycloaddition reactions of unsaturated species. A variety of metal systems have been developed that catalyze and control the formation of the new carbon-carbon bonds. For example, metal catalysts that cyclotrimerize alkynes to arenes span the whole d-transition series.<sup>1-24</sup> Most of the systems used to explore the mechanism of the reaction that cyclotrimerizes alkynes employ late transition metals, chiefly cobalt,<sup>24</sup> iridium, rhodium,<sup>15</sup> palladium, and platinum.<sup>17,18</sup>

The most commonly proposed mechanism (Scheme 1.1) for low-to-mid valent metals involves the oxidative (with respect to the metal) coupling of two alkynes to yield a metallacyclopentadiene (C). This step is believed to be preceded by the sequential coordination of two alkyne molecules to yield a mono alkyne adduct (A), followed by a bis alkyne adduct (B). The proposed intermediates (A) and (C) are often observed and therefore generally accepted as intermediates. Complex (B) has been observed by several workers, particularly by Japanese workers studying cobalt systems.<sup>22</sup> The reaction of the third equivalent of alkyne with the metallacyclopentadiene (C) is the most elusive step in the mechanism. At least two possible reaction pathways exist for this next step in the cycle. It has been suggested<sup>15,16</sup> that either i) the third alkyne inserts directly into a metal carbon bond of the metallacyclopentadiene (C) to form a metallacycloheptatriene (D), or ii) the alkyne can undergo a Diels-Alder addition to produce a

Scheme 1.1



**M - metal catalyst**

7-metallanorbornadiene (**E**). Regardless of which path is correct, the final step in the process is probably the simple reductive elimination of the arene to regenerate the metal catalyst. Recent observations have implicated a metallacycloheptatriene intermediate in the catalytic trimerization of 2-butyne using a  $[Co(py)_6]^+$  system.<sup>13</sup> An example of an intermolecular Diels-Alder addition was obtained from the reaction of a coordinatively saturated cobaltacyclopentadiene complex with dimethylacetylene dicarboxylate,  $MeO_2CC\equiv CCO_2Me$ .<sup>19,20</sup> These two examples indicate that both pathways are plausible. The mechanism proposed in Scheme 1.1 requires the metal to have a d electron count of at least two in order for the oxidative coupling of the alkynes to occur. Most of the known catalyst systems fulfill this requirement.

A number of Nb and Ta complexes catalytically cyclotrimerize alkynes, but no reactive alkyne-containing intermediates have been reported.<sup>5-11</sup> Numerous alkyne adducts of these metals as well as group 6 metals have been isolated but are unreactive toward additional alkyne and do not form metallacyclopentadienes.<sup>25-43</sup> For example, Schrock found that the complex  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{RC}\equiv\text{CR}')\text{Cl}_2$  was unreactive towards additional alkyne even under forcing conditions.<sup>35</sup> However, in  $(\eta^5\text{C}_5\text{H}_5)\text{M}(\text{CO})_4$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) one of the two carbonyls could be replaced with diphenylacetylene upon photolysis to yield a mono or bis alkyne adduct  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{PhC}\equiv\text{CPh})$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})(\text{PhC}\equiv\text{CPh})_2$  respectively.<sup>40-43</sup> Metallacyclopentadienes were not observed in this system but the free butadiene  $\text{PhCH}=\text{CPhCPh}=\text{CHPh}$  was formed upon thermal degradation of the compounds. Refluxing a benzene solution of  $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})(\text{PhC}\equiv\text{CPh})_2$  with excess diphenylacetylene produces the cyclobutadiene complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\eta^4\text{-C}_4\text{Ph}_4)(\text{PhC}\equiv\text{CPh})(\text{CO})$  which liberates free hexaphenylbenzene upon thermolysis.<sup>43</sup>

The lack of reactivity in these complexes may be attributed to the use of cyclopentadienyls as ancillary ligands. These ligands can both sterically and electronically saturate the metal centers making them unreactive towards additional alkyne. The Cp ligand is considered to occupy three coordination sites on the metal and to donate five electrons (neutral sense). This saturation at the metal center may explain why Curtis<sup>36</sup> and Schrock's<sup>35</sup>  $\text{Cp}^*\text{Ta}(\text{RC}\equiv\text{CR}')\text{Cl}_2$  complexes are unreactive towards additional alkyne even under forcing conditions.

### Research Description

The research in this dissertation was aimed at accomplishing four goals. First, most of the mechanistic studies on the metal-promoted cyclizations of alkynes that have been undertaken involve the late transition metals, namely  $\text{CpCoL}_2$  complexes. Would

early transition metals react by a similar pathway or one completely different from that seen in the late transition metals? A second question to address was whether or not the difference in reactivity expected for an early metal would allow the isolation of intermediates in the proposed mechanistic pathway and whether these isolated intermediates would be reactive enough to afford the next step in the proposed pathway. Third, could these cyclization intermediates, through steric control, be used to selectively form organic substrates? And finally, could successful studies using group 5 metals be generalized to encompass group 6 complexes as well?

This dissertation will focus on the use of tantalum and tungsten phenoxide or tungsten imido-phenoxide reagents to address the above questions. Phenoxide ligands or imido ligands were chosen for the following reasons. Early transition metals prefer to attain their highest oxidation state, thus making it feasible to isolate intermediates in the cyclization pathway upon the two-electron reduction of these metal centers. Unlike the cyclopentadienyl ligand which is considered to be a five-electron donor (neutral sense) and occupy three of the metal's coordination sites, phenoxide ligands have the ability to be either one- or three-electron donors while occupying only one coordination site. Similarly, imido ligands also have the ability to be variable electron donors, donating either two or four electrons while occupying a single coordination site. Cyclopentadienyl ligands are normally chosen for their steric bulk which should help in the isolation of the desired compounds. Different degrees of steric bulk using phenoxide ligands can be achieved by changing the size and number of substituent groups on the phenoxide ring. The phenoxide ligands should provide a more electrophilic metal center which should increase the reactivity and potential utility of these reagents. Chapter 2 explores the question of whether or not tungsten phenoxide systems would undergo the cyclization<sup>7</sup> and C-H activation<sup>44</sup> reactions that were successfully carried out on the tantalum analogues.

Chapters 3 and 4 present the use of phenoxide reagents as successful models of the tantalum-promoted alkyne cyclization pathway. A tantalum alkyne adduct undergoes successful coupling reactions with other alkynes as well as aldehydes, ketones, and nitriles. Chapter 5 demonstrates that by reducing the steric congestion around the metal center which allowed the isolation of the intermediates in Chapters 3 and 4, an arene could be formed from the coupling of three equivalents of alkyne. This chapter also explores the one-electron reduction and oxidative addition reactions that these arene complexes undergo.

## CHAPTER 2

### PREPARATION AND REACTIVITY OF SOME TUNGSTEN PHENOXIDE, PHENYLIMIDO, AND PHENYLIMIDO-PHENOXIDE COMPLEXES

#### INTRODUCTION

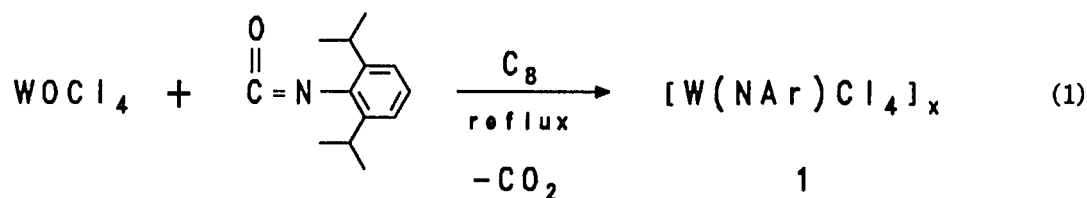
Most of the early transition metals seem to have their greatest stability in their highest oxidation state. This stability has made molybdenum and tungsten two of the most widely used metals as metathesis catalysts or catalyst precursors.<sup>45-47</sup> Early transition metals also have the ability to form multiple bonds with themselves and with C, N, and O. For example, organoimido complexes (containing NR ligands) may bond to the metal with a double or formal triple bond in either a linear or bent fashion. If the ligand is bent, it is considered a two-electron donor, whereas if the ligand is linear, it is considered a four-electron donor.<sup>48</sup> These complexes have been used in synthetic procedures ranging from amination,<sup>49</sup> aziridination,<sup>50,51</sup> olefin metathesis,<sup>52</sup> and the ammoxidation of propylene.<sup>53</sup> Use of metal-ligand multiple bonding can reduce the coordination number of the metal while maintaining the same formal oxidation state.<sup>48b</sup>

Alkyne cyclization by reduced tantalum compounds provides Ta(III) arene species that have been shown to engage in intramolecular C-H activations,<sup>44</sup> although these complexes are extremely susceptible to steric effects.<sup>54</sup> These results prompted a study to see the extent to which the principles that appear to govern the group 5 chemistry could be applied to group 6 chemistry. A series of phenoxide and mixed phenylimido phenoxide compounds was prepared to see if they too might undergo alkyne cyclization reactions and arene C-H activations like their group 5 analogues. With the successful activation of one of the methyl groups of  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{DIPP})_2\text{Cl}$  ( $\text{DIPP} = 2,6\text{-OC}_6\text{H}_3\text{-i-Pr}_2$ ), I set out to prepare the analogous compound  $(\eta^6\text{-C}_6\text{Me}_6)\text{W}(\text{NAr})(\text{DIPP})\text{Cl}$  ( $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-i-Pr}_2$ ) to see

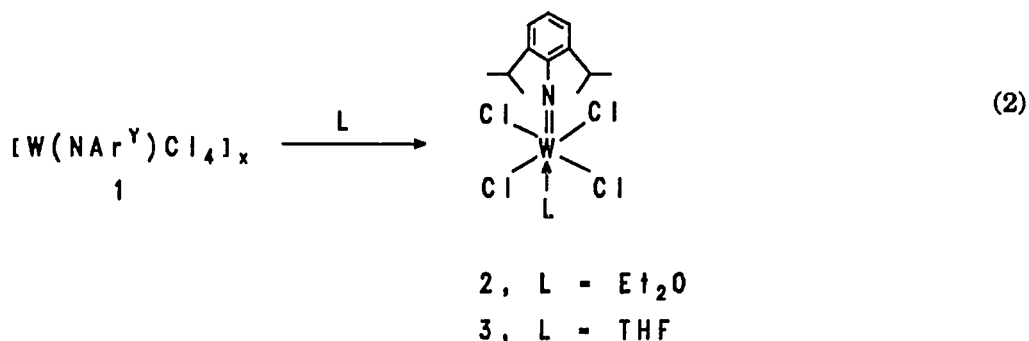
if the W=NAr linkage could induce *intramolecular* C-H activation of the hexamethylbenzene ligand in a manner analogous to the activation Bergman has seen with  $[\text{Cp}_2\text{Zr}=\text{NCMe}_3]$  which is capable of activating the C-H bonds of benzene producing an amide ligand from the imide ligand.<sup>55</sup>

## RESULTS AND DISCUSSION

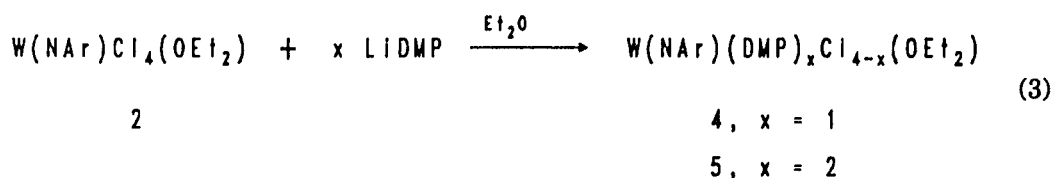
**Preparation of Tungsten Imido Complexes.** Imido complexes of groups 4 - 8 have been prepared. There are about a dozen different ways to prepare imido complexes, but the most common methods employed are: i) deprotonation of primary amines, ii) replacement of an oxo ligand using silylamines, iii) oxo/imido exchange using phosphinimines, isocyanates, or sulfinylamines, or iv) addition of organic azides.<sup>48</sup> I used the oxo/imido exchange reaction with an isocyanate to prepare my imido complexes.  $\text{WOCl}_4$  was prepared from  $\text{WCl}_6$  using either the method described by Handy et al.<sup>56</sup> or Gibson et al.,<sup>57</sup> but can also be prepared from tungstic acid and thionyl chloride.<sup>58</sup> When an octane slurry of  $\text{WOCl}_4$  is refluxed with 1 equivalent of 2,6-diisopropylphenyl isocyanate for 24 h, the monoimido complex  $[\text{W}(\text{NAr})\text{Cl}_4]_x$  (**1**) (Ar = 2,6-diisopropylphenyl) can be prepared in high yield (equation 1).<sup>59</sup> The use of lower or higher boiling solvents results in much



lower yields of the imido complex. Dissolving complex **1** in donor solvents such as diethyl ether or tetrahydrofuran results in the formation of a monomeric imido complex with one coordinated solvent ligand  $\text{W}(\text{NAr})\text{Cl}_4(\text{L})$  (**2**, L = OEt<sub>2</sub>; **3**, L = THF) (equation 2). Only one chloride stretch ( $\nu$  M-Cl) at  $337\text{ cm}^{-1}$  is observed in the IR spectrum of **2**, which can be

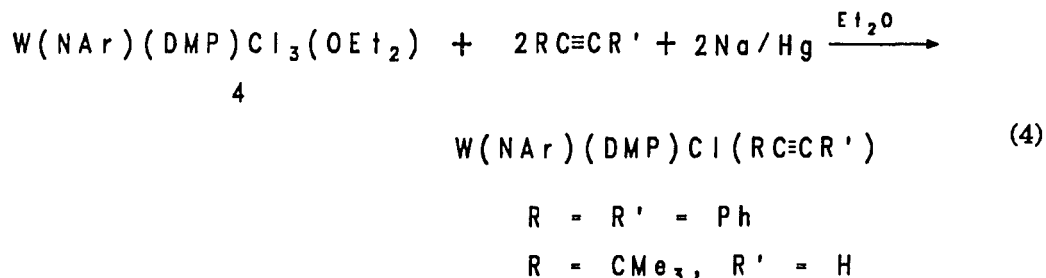


accounted for if the monoimide is trans to the coordinated ether. Reacting these complexes with either lithium alkoxide salts or trimethylsilyl alkoxide reagents led to the formation of the mixed imido alkoxide complexes  $W(NAr)(DMP)Cl_3(OEt_2)$  (4) and  $W(NAr)(DMP)_2Cl_2(OEt_2)$  (5) (DMP = 2,6-dimethylphenoxide) (equation 3). Since alkoxide

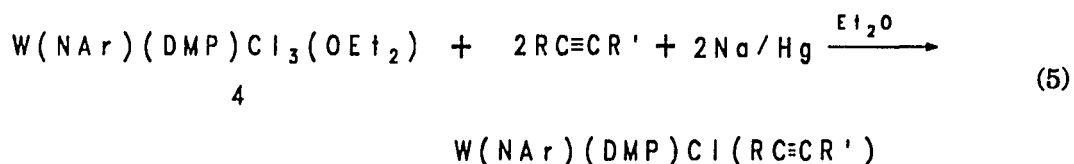


ligands are considered to be  $\pi$ -donors than chlorides, the DMP ligands should be oriented cis to the strong  $\pi$ -donating imido ligand.

**Reactions of Imido Complexes with Alkynes.** Reduction of  $W(NAr)Cl_4(OEt_2)$  with 2 equivalents of Na/Hg in the presence of alkynes results in the formation of brown oils with no tractable products. In the reduction of  $W(NAr)(DMP)Cl_3(OEt_2)$  (4) with 2 equivalents of Na/Hg in the presence of 1 equivalent of  $RC\equiv CR'$  ( $R = R' = Ph$ ;  $R = CMe_3$ ,  $R' = H$ ), orange oils formulated as  $(RC\equiv CR')W(NAr)(DMP)Cl$  are obtained (equation 4). Reduction of  $W(NAr)(DMP)_2Cl_2(OEt_2)$  (5) with 2 equivalents of Na/Hg in the presence of 2-3 equivalents of 3-hexyne produces a golden-brown oil that has not been induced to

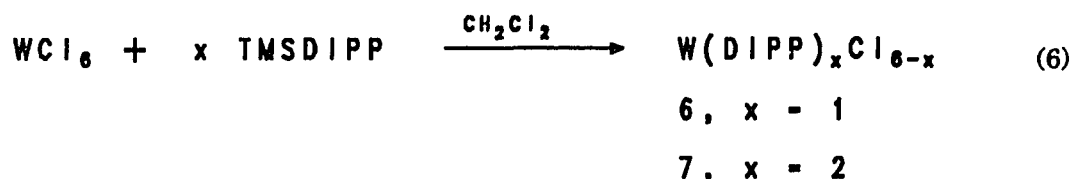


crystallize. The product of the reaction is an alkyne adduct that is the only compound formed on the basis of the "clean"  $^1\text{H}$  NMR spectrum of the entire oil (equation 5).<sup>60</sup> From the room temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the complex, the DMP ligands are equivalent, the ends of the coordinated 3-hexyne are equivalent, the protons of the NAr ligand are all equivalent, and only one resonance is observed for each different type of carbon atom. These data suggest that either the complex may be formulated as having a pseudotetrahedral geometry with a plane of symmetry passing through the molecule or the complex is fluxional at room temperature.

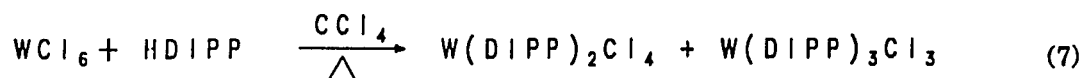


**Tungsten Alkoxide Complexes.** In attempts to prepare imido-alkoxide complexes, some new routes to tungsten alkoxide complexes were developed. A monoalkoxide complex was prepared by reacting  $\text{WCl}_6$  with 1 equivalent of  $\text{Me}_3\text{SiDIPP}$  (DIPP = 2,6-diisopropylphenoxide) in  $\text{CH}_2\text{Cl}_2$  to give  $\text{W}(\text{DIPP})\text{Cl}_5$  (6) with a slight contamination of bis phenoxide product (equation 6). Reaction of 2 equivalents of  $\text{Me}_3\text{SiDIPP}$  produced the bis phenoxide complex,  $\text{W}(\text{DIPP})_2\text{Cl}_4$  (7) (equation 6). Inverse

addition of the  $WCl_6$  to the  $Me_3SiDIPP/CH_2Cl_2$  solution forms only the bis phenoxide

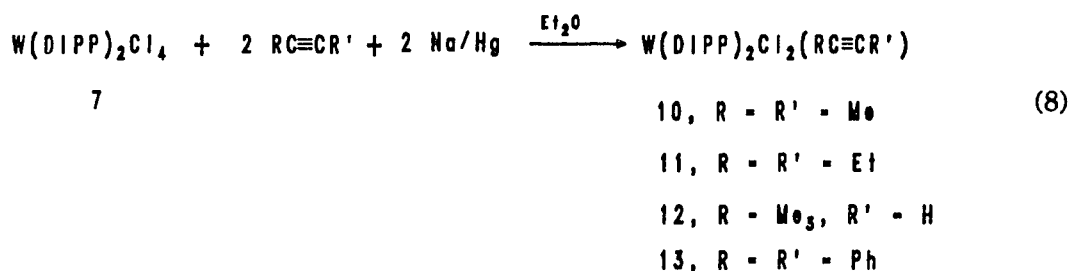


compound with no contamination of the mono phenoxide product. This method produces no tris phenoxide contamination which Shore reports from the reaction of  $WCl_6$  with 2,6-diisopropylphenol (equation 7).<sup>61</sup> The analogous reaction between  $WCl_6$  and < 1 equiv of



$Me_3SiDMP$  (DMP = 2,6-dimethylphenoxide) in  $CCl_4$  produces  $W(DMP)Cl_5$  (8) (DMP = 2,6-dimethylphenoxide).  $W(DMP)_2Cl_4$  (9) is prepared by reacting tungsten hexachloride with two equivalents of  $Me_3SiDMP$  in a manner analogous to equation 4. The use of between one and two equivalents of the  $Me_3SiDMP$  reagent results in a mixture of 8 and 9 which could not be separated.

**Reaction of Alkoxide Complexes with Alkynes.** By reducing  $W(DIPP)_2Cl_4$  (7) with 2 equivalents of Na/Hg in the presence of excess alkyne, the orange complexes,  $W(DIPP)_2(RC\equiv CR')Cl_2$  (10, R = R' = Me; 11, R = R' = Et; 12, R = t-Bu, R' = H; 13, R = R' = Ph) were obtained (equation 8). Reducing  $W(DIPP)Cl_5$  with 2 equivalents of Na/Hg in the presence of excess acetylenes produced only brown oils with no tractable products. Reduction of  $W(DMP)Cl_5$  (8) with 2 equivalents of Na/Hg in the presence of excess acetylenes also produced brown oils with no tractable products. Reduction of  $W(DMP)_2Cl_4$



(9) with 2 equivalents of Na/Hg in the presence of 3-hexyne or diphenylacetylene produced poor yields of brown-orange solids formulated as  $\text{W(DMP)}_2\text{Cl}_2(\text{RC}\equiv\text{CR})$  solely on the basis of proton NMR spectra.

Attempts were made to see if the acetylene adducts **10** - **13** would react with an additional equivalent of acetylene. Reaction of **13** with 3-hexyne even under the forcing condition of heating the solution to 60 °C produced no reaction. Thus, these tungsten (IV) acetylene adducts did not engage in the first step of cycloaddition. Reacting **11** with nitriles and ketones also resulted only in the isolation of starting material **11**. The lack of reactivity of these alkyne adducts compared to the Ta adducts described in Chapters 3 and 4 may be attributed to the alkyne ligand itself. A correlation between electron donation from the alkyne ligand and the  $^{13}\text{C}$  NMR chemical shifts of some tungsten (II) complexes has been established. Typically, those alkyne ligands with chemical shifts greater than  $\delta$  200 ppm are considered to be "four-electron" donors to the metal.<sup>70</sup> When the alkyne acts as a four-electron donor, the ligand is considered to be substantially reduced with the behavior of a dianion. The alkyne adducts **11** - **13** have  $^{13}\text{C}$  NMR resonances for the alkyne carbons around  $\delta$  180 ppm. In comparison, the alkyne adducts

(DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) (**14**) and (DIPP)<sub>3</sub>Ta(PhC≡CPh) (**16**) have C<sub>alkyne</sub> resonances of δ 226.0 and 224.4 and 216.0 respectively. Adducts **14** and **16** do react with additional equivalents of alkynes as well as with aldehydes, ketones, and nitriles. On the basis of this comparison, the alkyne ligands in **11** - **13** are most probably acting as less than four-electron donors. Also, the change in oxidation state from W(IV) to W(VI) is not as facile as going from Ta(III) to Ta(V).

### SUMMARY AND CONCLUSIONS

Attempts to extend the C-H activation chemistry of the tantalum arenes to tungsten could not be achieved through this route since cyclization beyond the alkyne adduct was not possible. However, this study did provide some new routes to tungsten phenoxide complexes that can be prepared under mild conditions. Most of the tungsten alkyne adducts prepared to date are W(II) complexes. Of those that are W(IV), except for a few examples such as Schrock's W(DMP)<sub>4</sub>(EtC≡CEt) complex,<sup>62</sup> the adducts are supported by phosphine ligands.<sup>63</sup> Compounds **11** - **13** are further examples of W(IV) alkyne adduct complexes that do not contain phosphines. The fact that there are still two chloride ligands bound to the metal may allow further substitution reactions to take place at the metal center. The complex W(NAr)(DMP)<sub>2</sub>(EtC≡CEt) is a rare example of a mixed imido-alkoxide acetylene adduct.

### EXPERIMENTAL

General experimental conditions and details for physical measurements can be found in Appendix A.

**Preparations.** [W(NAr)Cl<sub>4</sub>]<sub>x</sub> (x ≥ 2) (**1**). 3.82 g (11.2 mmole) of WOCl<sub>4</sub> was suspended in 100 mL of octane. 2.40 mL (11.2 mmole) of 2,6-diisopropylphenyl isocyanate was syringed out and added to the solution. The solution was allowed to reflux 24 h over

which time the solution changed color from orange to brown to forest green. Upon cooling to room temperature, the green solution turned brown and a brown solid precipitated out. The solution was filtered and washed with pentane leaving behind orange brown microcrystals that weighed 2.73 g (5.4 mmole, 71% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.54 (d, 2 H,  $\text{H}_m$ ), 6.73 (t, 1 H,  $\text{H}_p$ ), 4.44 (spt, 2 H,  $\text{CHMe}_2$ ), 1.40 (d, 12 H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  155.7 ( $\text{C}_o$ ), 135.3 ( $\text{C}_p$ ), 121.9 ( $\text{C}_m$ ), 28.0 ( $\text{CHMe}_2$ ), 25.8 ( $\text{CHMe}_2$ ). The  $\text{C}_{\text{ipso}}$  resonance was not observed. IR: 1582 s, 1470 m, 1461 s, 1384 s, 1363 s, 1349 m, 1303 w, 1286 w, 1256 m, 1229 m, 1179 m, 1146 m, 1101 w, 1056 m, 1006 w, 934 m, 798 s, 752 s, 378 s, 359 s, 338 s, 257 w. Anal. Calcd for  $\text{C}_{12}\text{H}_{17}\text{NCl}_4\text{W}$ : C, 28.77; H, 3.42; N, 2.80. Found: C, 28.74; H, 3.51; N, 2.67.

**W(NAr)Cl<sub>4</sub>(OEt<sub>2</sub>) (2).** 4.49 g (9.0 mmole) of **1** was placed in a sintered glass frit. Upon the addition of diethyl ether, **1** dissolved and changed color from brown to kelly green. The solution was filtered to remove any solid that did not dissolve, concentrated to 15 mL, and cooled to  $-40\text{ }^\circ\text{C}$ . 4.34 g (7.3 mmole, 82% yield) of kelly green crystals were filtered off and dried under vacuum. Analytically pure samples can be obtained by recrystallization from  $\text{Et}_2\text{O}/\text{C}_5$  at  $-40\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.18 (d, 2 H,  $\text{H}_m$ ), 6.26 (t, 1 H,  $\text{H}_p$ ), 4.90 (spt, 2 H,  $\text{CHMe}_2$ ), 4.31 (q, 4 H,  $\text{CH}_3\text{CH}_2\text{O}$ ), 1.32 (d, 12 H,  $\text{CHMe}_2$ ), 1.07 (t, 6 H,  $\text{CH}_3\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  156.0 ( $\text{C}_o$ ), 134.2 ( $\text{C}_p$ ), 122.0 ( $\text{C}_m$ ), 73.6 ( $\text{OCH}_2\text{CH}_3$ ), 27.7 ( $\text{CHMe}_2$ ), 26.2 ( $\text{CHMe}_2$ ), 25.3 ( $\text{OCH}_2\text{CH}_3$ ). The  $\text{C}_{\text{ipso}}$  resonance was not observed. IR (CsI): 1584 m, 1470 m, 1454 m, 1384 m, 1361 m, 1256 w, 1230 w, 1179 w, 1147 w-m, 1085 w, 1054 m, 1023 m, 993 w, 934 w, 890 w, 829 w, 803 m, 772m, 757 m, 337 vs. Anal. Calcd. for  $\text{C}_{16}\text{H}_{27}\text{NOCl}_4\text{W}$ : C, 33.42; H, 4.73; N, 2.44. Found: C, 33.47; H, 4.83; N, 2.66.

**W(NAr)Cl<sub>4</sub>(THF) (3).** 2.00 g (4.0 mmole) of **1** was placed in a sintered glass frit. Upon the addition of tetrahydrofuran, **1** dissolved and changed color from brown to green.

The solution was filtered to remove any solid that did not dissolve, concentrated to 15 mL, and cooled to -40 °C. 1.42 g (2.5 mmole, 62% yield) of lime green crystals were filtered off and dried under vacuum. Analytically pure samples can be obtained by recrystallization from pentane at -40 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.20 (d, 2 H,  $\text{H}_m$ ), 6.26 (t, 1 H,  $\text{H}_p$ ), 4.96 (spt, 2 H,  $\text{CHMe}_2$ ), 4.43 (m, 4 H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.35 (d, 12 H,  $\text{CHMe}_2$ ), 1.25 (m, 4 H,  $\text{CH}_2\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  156.0 ( $\text{C}_o$ ), 134.2 ( $\text{C}_p$ ), 122.0 ( $\text{C}_m$ ), 73.6 ( $\text{OCH}_2\text{CH}_2$ ), 27.7 ( $\text{CHMe}_2$ ), 26.2 ( $\text{CHMe}_2$ ), 25.3 ( $\text{OCH}_2\text{CH}_2$ ). IR (CsI): Anal. Calcd. for  $\text{C}_{16}\text{H}_{27}\text{NOCl}_4\text{W}$ : C, 33.42; H, 4.73; N, 2.44. Found: C, 33.69; H, 4.68; N, 2.48.

**W(NAr)(DMP)Cl<sub>3</sub>(OEt<sub>2</sub>) (4).** To a room temperature solution of 1.00 g (1.7 mmole) of **2** dissolved in 15 mL of diethyl ether was added 0.40 g (2.0 mmole) of  $\text{Me}_3\text{SiDMP}$ . After being stirred 24 h at room temperature, the solvent was removed in vacuo producing a red brown oil. The oil was reconstituted in a minimal volume of pentane and cooled to -40 °C. 0.74 g (1.5 mmole, 89% yield) of black microcrystals were filtered off, washed with a minimal volume of cold pentane, and dried in vacuo.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.33-6.79 (m, 6 H,  $\text{H}_{\text{aryl}}$  NAr and DMP), 4.31 (q, 4 H,  $\text{OCH}_2\text{CH}_3$ ), 4.00 (spt, 2 H,  $\text{CHMe}_2$ ), 2.42 (s, 6 H, Me), 1.40 (t, 6 H,  $\text{OCH}_2\text{CH}_3$ ), 1.12 (d, 12 H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  153.1 ( $\text{C}_o$  NAr), 131.6 ( $\text{C}_p$  DMP), 129.0 ( $\text{C}_m$  DMP), 127.9 ( $\text{C}_o$  DMP), 125.6 ( $\text{C}_p$  NAr), 122.3 ( $\text{C}_m$  NAr), 65.0 ( $\text{OCH}_2\text{CH}_3$ ), 27.6 ( $\text{CHMe}_2$ ), 25.5 ( $\text{CHMe}_2$ ), 17.4 (Me), 13.6 ( $\text{OCH}_2\text{CH}_3$ ). The  $\text{C}_{\text{isop}}$  resonances for NAr and DMP were not observed. IR: 1586 m, 1461 m, 1386 m, 1361 m, 1259 m, 1232 w, 1171 s, 1147 m, 1098 s, 1057 m, 1029 m, 995 s, 936 w, 878 s, 828 m, 803 s, 774 s, 759 s, 727 s, 628 w, 584 m, 565 m, 502 m, 460 m, 409 m, 343 s, 330 s. Anal. Calcd. for  $\text{C}_{24}\text{H}_{36}\text{NO}_2\text{Cl}_3\text{W}$ : C, 43.63; H, 5.49; N, 2.12. Found: C, 43.94; H, 5.60; N, 1.96.

**W(NAr)(DMP)<sub>2</sub>Cl<sub>2</sub>(OEt<sub>2</sub>) (5).** To a room temperature solution of 1.58 g (2.7

mmole) of **2** dissolved in 15 mL of diethyl ether was added 0.73 g (5.7 mmole) of LiDMP. After being stirred 24 h at room temperature, the solvent was removed in vacuo affording a red oil. The oil was reconstituted in a minimal volume of pentane and cooled to -40 °C. 1.25 g (1.7 mmole, 63% yield) of maroon microcrystals were filtered off, washed with a minimal volume of cold pentane, and dried in vacuo.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.28-6.93 ( $\text{A}_2\text{B}$  m, 3 H,  $\text{H}_{\text{aryl}}$  NAr), 7.04-6.79 ( $\text{A}_2\text{B}$  m, 6 H  $\text{H}_{\text{aryl}}$  DMP), 3.83 (spt, 2 H,  $\text{CHMe}_2$ ), 3.73 (q, 4 H,  $\text{OCH}_2\text{CH}_3$ ), 2.44 (s, 6 H, Me), 1.27 (t, 6 H,  $\text{OCH}_2\text{CH}_3$ ), 1.12 (d, 12 H,  $\text{CHMe}_2$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  162.6 ( $\text{C}_{\text{ipso}}$  DMP) 148.9 ( $\text{C}_o$  NAr), 129.4 ( $\text{C}_p$  DMP), 128.5 ( $\text{C}_m$  DMP), 128.2 ( $\text{C}_o$  DMP), 124.5 ( $\text{C}_p$  NAr), 122.5 ( $\text{C}_m$  NAr), 65.3 ( $\text{OCH}_2\text{CH}_3$ ), 27.9 ( $\text{CHMe}_2$ ), 24.8 ( $\text{CHMe}_2$ ), 17.3 (Me), 14.6 ( $\text{OCH}_2\text{CH}_3$ ). The  $\text{C}_{\text{ipso}}$  resonance for NAr was unobserved. IR (CsI): 1585 w, 1462 m, 1416 w, 1384 w, 1360 w, 1347 w, 1261 m, 1191 s, 1148 w, 1094 m, 1034 m, 995 m, 885 s, 827 w, 892 m, 767 s, 757 s, 727 s, 561 m, 500 w, 354 m, 305m. Anal. Calcd. for  $\text{C}_{32}\text{H}_{45}\text{NO}_3\text{Cl}_2\text{W}$ : C, 51.49; H, 6.08; N, 1.88 . Found: C, 50.90; H, 6.08; N, 1.91.

**W(DIPP)Cl<sub>5</sub> (6)**. 0.64 g (2.5 mmole) of  $\text{Me}_3\text{SiDIPP}$  was added to a solution of 1.01 g  $\text{WCl}_6$  (2.5 mmole) in 15 mL of  $\text{CH}_2\text{Cl}_2$ . The deep orange red solution immediately changed color to dark purple upon addition of the  $\text{Me}_3\text{SiDIPP}$  reagent. After being stirred 48 h at room temperature, the solvent was removed in vacuo affording a black solid. The black solid was washed with a minimal volume of cold pentane and filtered yielding 1.16 g (2.2 mmole, 88%) of black microcrystals.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.59 (d, 2 H,  $\text{H}_m$ ), 6.45 (t, 1 H,  $\text{H}_p$ ), 4.45 (spt, 2 H,  $\text{CHMe}_2$ ), 1.38 (d, 12 H,  $\text{CHMe}_2$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  154.0 ( $\text{C}_{\text{ipso}}$ ), 150.6 ( $\text{C}_o$ ), 136.2 ( $\text{C}_p$ ), 123.2 ( $\text{C}_m$ ), 26.7 ( $\text{CHMe}_2$ ), 26.5 ( $\text{CHMe}_2$ ). IR: 1577 m, 1392 w, 1361 m, 1105 w, 938 m, 795 m, 746 m, 313 s. Anal. Calcd. for  $\text{C}_{12}\text{H}_{17}\text{OCl}_5\text{W}$ : C, 26.77; H, 3.18. Found: C, 27.29; H, 3.31.

**W(DIPP)<sub>2</sub>Cl<sub>4</sub> (7).** 2.65 g (10.6 mmole) of Me<sub>3</sub>SiDIPP was diluted to 15 mL with CH<sub>2</sub>Cl<sub>2</sub>. 2.01 g (5.0 mmole) of WCl<sub>6</sub> was added to the solution. Addition of reagents in this order minimizes the production of **6** as one of the products. After being stirred 48 h at room temperature, the solvent was removed in vacuo affording a black solid. The solid was washed with a minimal volume of cold pentane, filtered, and dried under vacuum yielding 2.66 g (3.9 mmole, 78%) of black brown microcrystals. Analytically pure samples can be obtained by recrystallization from pentane at -40 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.34 (d, 4 H, H<sub>m</sub>), 6.91 (t, 2 H, H<sub>p</sub>), 3.97 (spt, 4 H, CHMe<sub>2</sub>), 1.20 (d, 24 H, CHMe<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 156.5 (C<sub>ipso</sub>), 145.5 (C<sub>o</sub>), 131.4 (C<sub>m</sub>), 123.8 (C<sub>p</sub>), 26.7 (CHMe<sub>2</sub>), 25.2 (CHMe<sub>2</sub>). IR: 1578 s, 1472 w, 1458 m, 1382 m, 1361 m, 1231 m, 1178 m, 1145 w, 1094 m, 1057 m, 995 w, 916 s, 881 w, 796 s, 747 s, 715 w, 625 w, 605 w, 543 w, 440 w, 367 s, 326 vs, 267 w. Anal. Calcd. for C<sub>24</sub>H<sub>34</sub>O<sub>2</sub>Cl<sub>4</sub>W: C, 42.38; H, 5.04. Found: C, 42.68; H, 5.38.

**W(DMP)Cl<sub>5</sub> (8).** 0.32 g (1.6 mmol) of Me<sub>3</sub>SiDMP was added to 1.003 g (2.5 mmol) of WCl<sub>6</sub> in 15 mL of CCl<sub>4</sub>. The solution was allowed to stir 24 h at room temperature. The purple solution was filtered leaving behind 0.32 g (0.6 mmol) of gray-black solid. The filtrate was removed in vacuo producing 0.72 g (1.5 mmol) of black microcrystals. <sup>1</sup>H NMR indicates both products are identical, therefore, the total yield is 1.04 g (2.1 mmol, 84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.37 (d, 2 H, H<sub>m</sub>), 6.26 (t, 1 H, H<sub>p</sub>), 3.58 (s, 6 H, Me). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 141.0 (C<sub>o</sub>), 137.0 (C<sub>p</sub>), 127.6 (C<sub>m</sub>), 16.7 (Me). The C<sub>ipso</sub> resonance was not observed. IR: 1578 m, 1377 m, 1357 m, 1253 m, 958 m, 939 w, 779 m, 390 w, 340 sh, 301 s. Anal. Calcd for C<sub>8</sub>H<sub>9</sub>OCl<sub>5</sub>W: C, 19.92; H, 1.88; Cl, 36.76. Found: C, 19.81; H, 1.90; Cl, 35.08.

**W(DMP)<sub>2</sub>Cl<sub>4</sub> (9).** 0.55 g (1.4 mmol) of WCl<sub>6</sub> was added to a solution of 0.51 g (2.6 mmol) of Me<sub>3</sub>SiDMP in 20 mL of CCl<sub>4</sub>. After being stirred 24 h at room temperature, the

solution was filtered to remove 0.60 g of black solid. The solvent of the filtrate was removed in vacuo producing an additional 0.09 g of product. The solids were combined (0.68 g, 1.2 mmol, 86% yield), washed with a minimal volume of cold pentane, and dried in vacuo.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.21 (d, 4 H,  $\text{H}_m$ ), 6.75 (t, 2 H,  $\text{H}_p$ ), 2.90 (s, 12 H, Me). The sample was too insoluble to record a  $^{13}\text{C}$  NMR spectrum. IR: 1580 m, 1462 w, 1395 w, 1372 m, 1294 w, 1259 m, 1187 s, 1161 s, 1093 m, 1031 w, 994 w, 915 s, 776 s, 734 m, 709 m, 564 m, 537 w, 498 w, 321 s, 283 m. Anal. Calcd. for  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Cl}_4\text{W}$ : C, 33.84; H, 3.19; Cl, 24.97. Found: C, 34.16; H, 3.34; Cl, 24.21.

**W(DIPP) $_2$ Cl $_2$ (MeC $\equiv$ CMe) (10).** To a  $-40$  °C solution of 0.50 g (0.7 mmole) of **8** in 15 mL of diethyl ether were added 0.27 mL (2.8 mmole) of 2-butyne and 0.40 mL of 0.50 % Na/Hg. The reaction mixture was shaken for 1 min and then allowed to stir at room temperature for 1 h. The resulting orange solution was filtered through Celite. The solvent was removed in vacuo producing a dry orange solid. The solid was dissolved in pentane and cooled to  $-40$  °C. 0.19 g (0.3 mmole, 41% yield) of orange red solid was filtered off, washed with a minimal volume of cold pentane, and dried in vacuo.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.09-6.95 (m, 6 H,  $\text{H}_{\text{aryl}}$ ), 3.47 (s, 6 H,  $\text{MeC}_{\text{acet}}$ ), 2.96 (spt, 4 H,  $\text{CHMe}_2$ ), 1.19 (d, 24 H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  178.9 ( $\text{C}_{\text{acet}}$ ), 159.1 ( $\text{C}_{\text{ipso}}$ ), 138.4 ( $\text{C}_o$ ), 125.2 ( $\text{C}_m$ ), 122.9 ( $\text{C}_p$ ), 27.6 ( $\text{CHMe}_2$ ), 23.5 ( $\text{CHMe}_2$ ), 17.2 ( $\text{MeC}_{\text{acet}}$ ). IR: 1579 w, 1320 s, 1300 w, 1240 s, 1178 br s, 1140 sh, 1092 s, 1035 w, 910 br s, 872 w, 835 vw, 795 sh, 785 m, 738 s, 710 m. Anal. Calcd. for  $\text{C}_{28}\text{H}_{40}\text{O}_2\text{Cl}_2\text{W}$ : C, 50.70; H, 6.08. Found: C, 50.97; H, 6.21.

**W(DIPP) $_2$ Cl $_2$ (EtC $\equiv$ CEt) (11).** To a  $-40$  °C solution of 0.50 g (0.7 mmole) of **8** in 15 mL of diethyl ether were added 0.13 mL (1.4 mmole) of 3-hexyne and 0.40 mL of 0.50% Na/Hg. The reaction mixture was shaken for 1 min and then allowed to stir at room temperature for 1 h. The resulting orange solution was filtered through Celite. The

solvent was removed in vacuo producing a dry orange solid. The solid was dissolved in pentane and cooled to  $-40\text{ }^{\circ}\text{C}$ . 0.29 g (0.4 mmole, 57% yield) of orange needles was filtered off, washed with a minimal volume of cold pentane, and dried in vacuo.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.09-6.96 (m, 6 H,  $\text{H}_{\text{aryl}}$ ), 3.86 (q, 4 H,  $\text{CH}_3\text{CH}_2\text{C}_{\text{acet}}$ ), 2.98 (spt, 4 H,  $\text{CHMe}_2$ ), 1.53 (t, 6 H,  $\text{CH}_3\text{CH}_2\text{C}_{\text{acet}}$ ), 1.20 (d, 24 H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  182.1 ( $\text{C}_{\text{acet}}$ ), 159.0 ( $\text{C}_{\text{ipso}}$ ), 138.6 ( $\text{C}_o$ ), 125.4 ( $\text{C}_p$ ), 123.2 ( $\text{C}_m$ ), 27.7 ( $\text{CHMe}_2$ ), 26.6 ( $\text{CH}_3\text{CH}_2\text{C}_{\text{acet}}$ ), 23.6 ( $\text{CHMe}_2$ ), 14.5 ( $\text{CH}_3\text{CH}_2\text{C}_{\text{acet}}$ ). IR: 1578 vw, 1318 m, 1240 br m, 1179 br s, 1138 w, 1091 m, 1033 w, 914 s, 873 w, 787 m, 739 m, 708 m. Anal. Calcd. for  $\text{C}_{30}\text{H}_{44}\text{O}_2\text{Cl}_2\text{W}$ : C, 52.11; H, 6.41. Found: C, 52.33; H, 6.60.

**$\text{W}(\text{DIPP})_2\text{Cl}_2(\text{Me}_3\text{CC}\equiv\text{CH})$  (12).** To a  $-40\text{ }^{\circ}\text{C}$  solution of 0.50 g (0.7 mmole) of **8** in 15 mL of diethyl ether were added 0.18 mL (1.4 mmole) of 3,3-dimethyl-1-butyne and 0.40 mL of 0.50% Na/Hg. The reaction mixture was shaken for 1 min and then allowed to stir at room temperature for 1 h. The resulting orange solution was filtered through Celite. The solvent was removed in vacuo producing a dry orange solid. The solid was dissolved in pentane and cooled to  $-40\text{ }^{\circ}\text{C}$ . 0.27 g (0.4 mmole, 57% yield) of orange powder was filtered off, washed with a minimal volume of cold pentane, and dried in vacuo.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.44 (s, 1 H,  $\text{HC}_{\text{acet}}$ ), 7.11-6.97 (m, 6 H,  $\text{H}_{\text{aryl}}$ ), 3.00 (spt, 4 H,  $\text{CHMe}_2$ ), 1.70 (s, 9 H,  $\text{Me}_3\text{CC}_{\text{acet}}$ ), 1.22, 1.18 (d, 12 H each,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  194.2, 170.0 ( $\text{C}_{\text{acet}}$ ), 159.1 ( $\text{C}_{\text{ipso}}$ ), 139.0 ( $\text{C}_o$ ), 125.8 ( $\text{C}_p$ ), 123.3 ( $\text{C}_m$ ), 40.5 ( $\text{CMe}_3$ ), 30.8 ( $\text{CMe}_3$ ), 27.6 ( $\text{CHMe}_2$ ), 24.3, 22.8 ( $\text{CHMe}_2$ ). IR: 1579 vw, 1320 m, 1270 vw, 1240 m, 1133 br s, 1139 w, 942 w, 913 br s, 874 w, 788 m, 744 m, 739 m, 710m. Anal. Calcd. for  $\text{C}_{30}\text{H}_{44}\text{O}_2\text{Cl}_2\text{W}$ : C, 52.11; H, 6.41. Found: C, 51.89; H, 6.57.

**$\text{W}(\text{DIPP})_2\text{Cl}_2(\text{PhC}\equiv\text{CPh})$  (13).** To a  $-40\text{ }^{\circ}\text{C}$  solution of 0.50 g (0.7 mmole) of **8** in 15 mL of diethyl ether were added 0.27 g (1.4 mmole) of diphenylacetylene and 0.40 mL of

0.50 % Na/Hg. The reaction mixture was shaken for 1 min and then allowed to stir at room temperature for 1 h. The resulting orange solution was filtered through Celite. The solvent was removed in vacuo producing a dry orange solid. The solid was dissolved in pentane and cooled to -40 °C. 0.34 g (0.4 mmole, 61% yield) of orange brown solid was filtered off, washed with a minimal volume of cold pentane, and dried in vacuo.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.20 (d, 4 H,  $\text{H}_o$   $\text{C}_6\text{H}_5$ ), 7.21-6.84 (m, 12 H,  $\text{H}_{\text{aryl}}$ ,  $\text{H}_m$   $\text{H}_p$   $\text{C}_6\text{H}_5$ ), 3.45 (br m, 4 H,  $\text{CHMe}_2$ ), 1.16 (d, 24 H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  182.0 ( $\text{C}_{\text{acet}}$ ), 160.2 ( $\text{C}_{\text{ipso}}$  DIPP), 139.6 ( $\text{C}_o$  DIPP), 135.0 ( $\text{C}_{\text{ipso}}$   $\text{C}_6\text{H}_5$ ), 132.0 ( $\text{C}_m$   $\text{C}_6\text{H}_5$ ), 131.3 ( $\text{C}_p$   $\text{C}_6\text{H}_5$ ), 128.8 ( $\text{C}_o$   $\text{C}_6\text{H}_5$ ), 126.3  $\text{C}_p$  DIPP), 123.7 ( $\text{C}_m$  DIPP), 28.2 ( $\text{CHMe}_2$ ), 23.8 ( $\text{CHMe}_2$ ). IR: 1678 m, 1584 w, 1319 w, 1268 m, 1240 w, 1178 br s, 1091 m, 1079 sh, 1050 vw, 1034 vw, 1018 w, 983 br, 912 s, 875 w, 818 vw, 786 w, 769 w, 754 m, 739 m, 719 sh, 710 w, 673 w. Anal. Calcd. for  $\text{C}_{38}\text{H}_{44}\text{O}_2\text{Cl}_2\text{W}$ : C, 57.96; H, 5.63. Found: C, 56.84; H, 5.84.

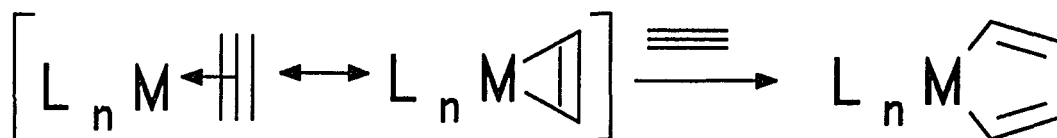
## CHAPTER 3

TANTALUM PHENOXIDE ALKYNE COMPLEXES AND THEIR  
METALLACYCLIZATION CHEMISTRY

## INTRODUCTION

A number of both early and late transition metals are known to catalytically polymerize and cyclotrimerize alkynes.<sup>1-22</sup> Most cyclotrimerization studies have focused on the late transition metals and only recently has interest been shown in the early metals. Several niobium and tantalum compounds catalytically cyclotrimerize<sup>5-8</sup> and polymerize<sup>64</sup> alkynes. Since metallacyclopentadienes are most often implicated as intermediates,<sup>7,18,19</sup> one might expect these metallacycles to form by reacting isolable alkyne complexes with more alkyne (Scheme 3.1). However, known alkyne adducts of

Scheme 3.1



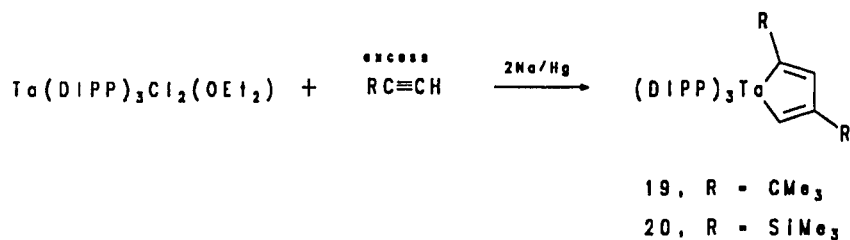
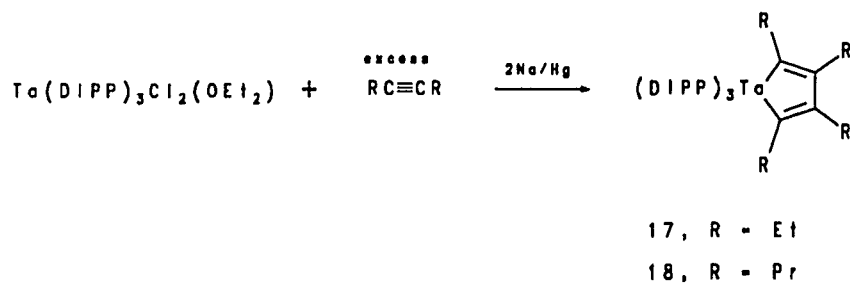
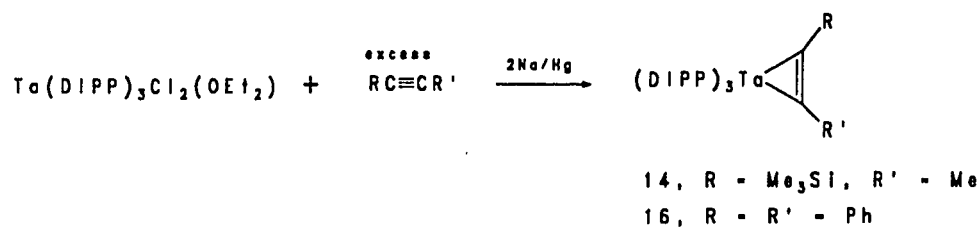
these metals, such as  $(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_2(\text{RC} \equiv \text{CR})$  ( $\text{M} = \text{Nb}^{35}, \text{Ta}^{34}$ ) and  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})(\text{PhC} \equiv \text{CPh})$  ( $\text{M} = \text{Nb}^{40}, \text{Ta}^{41}$ ), are unreactive toward other alkynes.<sup>22,25,26,40,41,65-67</sup> Phenoxide ligands in the place of cyclopentadienyl ligands make the metal center more electrophilic;<sup>7</sup> therefore, I set out to prepare some tantalum alkyne and metallacyclopentadiene complexes containing phenoxide ligands.

## RESULTS AND DISCUSSION

**Preparation and Properties of Tantalum Alkyne Adducts and Metallacyclopentadienes.** Reducing the sterically congested complex,  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$ , by two electrons in the presence of the bulky alkynes  $\text{Me}_3\text{SiC} \equiv \text{CMe}$

and  $\text{PhC}\equiv\text{CPh}$  produces the pale yellow adducts  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (**14**) and  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  (**16**) in moderate yields (Scheme 3.2). Unlike compound **16** which forms yellow crystals, compound **14** was isolated and used as an oil. Complex **14**

Scheme 3.2



could only be induced to crystallize upon coordination of one equivalent of THF to make the adduct  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})(\text{THF})$  (**15**). The isolation of higher cyclooligomers using the tris phenoxide complex is quite susceptible to steric effects. Thus, the reduction of  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  in the presence of both smaller internal alkynes (viz.  $\text{EtC}\equiv\text{CEt}$  or  $\text{PrC}\equiv\text{CPr}$ ) or terminal alkynes (viz.  $\text{Me}_3\text{CC}\equiv\text{CH}$  or  $\text{Me}_3\text{SiC}\equiv\text{CH}$ ) affords the metallacyclopentadienes  $(\text{DIPP})_3\overline{\text{Ta}(\text{CR}=\text{CRCR}=\text{CR})}$  (**17**, R = Et; **18**, R = Pr) or

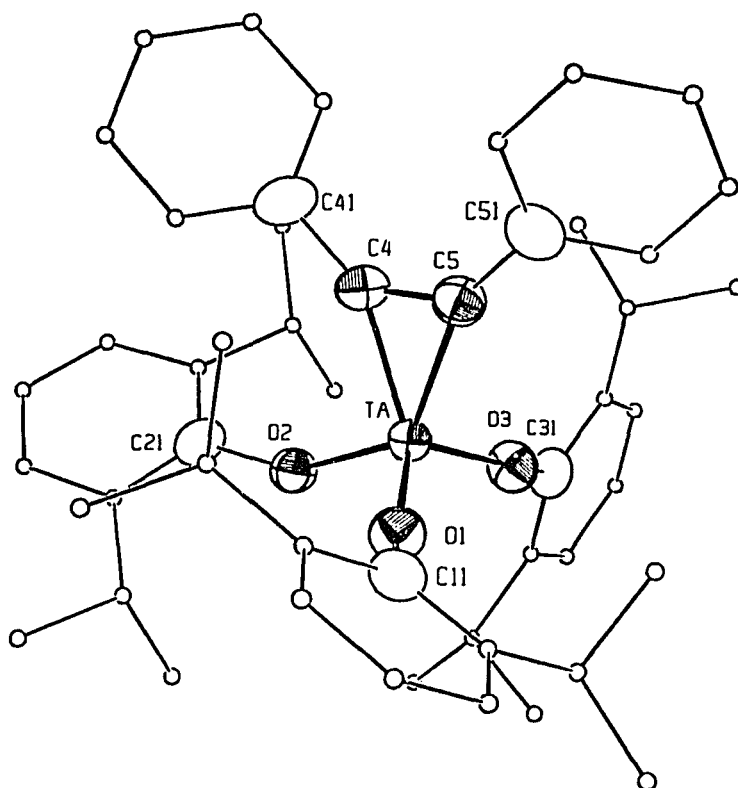
(DIPP)<sub>3</sub>Ta( $\overline{\text{CR}=\text{CHCR}=\text{CH}}$ ) (**19**, R = CMe<sub>3</sub>; **20**, R = SiMe<sub>3</sub>) directly (Scheme 3.2). The regioselectivity of metallacycle formation from terminal alkynes is very high as determined by NMR (>98%; no other regioisomers are detected) and by identification of the butadienes obtained upon the protonolysis of compounds **17** - **20** (vide infra). This head-to-tail coupling presumably represents the most sterically feasible way to alleviate congestion at the metal center as well as to minimize steric interactions within the metallacyclic ring. In contrast, reduction of the bis phenoxide starting material in the presence of Me<sub>3</sub>CC≡CH initially produces a metallacycle with an α,α' arrangement of the t-butyl groups which upon thermolysis is converted to the less sterically demanding α,β arrangement of the t-butyl groups.<sup>68</sup> No alkyne adducts have been detected or isolated in the reactions using these substrates, even when a deficiency of alkyne is used; thus, the metallacyclization step is apparently quite rapid.

Efforts to convert the metallacyclopentadienes into arenes or pyridines have proven unsuccessful. Heating **17** in MeC≡N in an attempt to make a pyridine, produced an oil that could not be induced to crystallize. The <sup>1</sup>H NMR spectrum of the oil showed a mixture of products. Heating **17** in the presence of additional equivalents of 3-hexyne to form the arene, resulted only in the isolation of the starting material **17**. The reaction of **20** with Me<sub>3</sub>CC≡N or MeEtCO failed to produce any insertion products and resulted only in the isolation of the starting material.

**X-ray Structural Determinations of (DIPP)<sub>3</sub>Ta(PhC≡CPh) (16) and (DIPP)<sub>3</sub>Ta( $\overline{\text{CEt}=\text{CEtCEt}=\text{CEt}}$ ) (17).** An X-ray crystal structure determination of (DIPP)<sub>3</sub>Ta( $\overline{\text{CEt}=\text{CEtCEt}=\text{CEt}}$ ) (**17**) (vide infra) revealed a severely crowded coordination sphere about the tantalum atom, as suggested by the large, nearly linear, 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 cyclooligomers.<sup>7</sup> Therefore the acetylene adduct  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  (**16**) reflects the slight advantage that steric congestion (which does not allow another molecule of  $\text{PhC}\equiv\text{CPh}$  to 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  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  (**16**) were grown from a pentane solution at  $-40\text{ }^\circ\text{C}$ . The molecular structure of **16** is presented in Figure 3.1. A



**Figure 3.1** ORTEP drawing of  $(\text{DIPP})_3\text{Ta}(\text{PhC}\equiv\text{CPh})$  (**16**) with local coordination atoms shown as 50% probability ellipsoids.

summary of the crystal data and a complete listing of bond lengths and angles are reported in Appendix B. Representing the C(4)-C(5) midpoint as "Acet", relevant bond

lengths and angles are provided in Tables 3.1 and 3.2 respectively. 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 (1)° - 117 (1)° and average 109.4°. The Ta-O-C<sub>ipso</sub> angles are between 148.1 (2)° and 158.8 (2)° with an average value of 154.5° which seems to indicate a less sterically congested environment around the metal center than in the metallacyclic complex **17**, where the Ta-O-C<sub>ipso</sub> angles average 170.2°. The very short Ta-C(4) and Ta-C(5) distances (2.070 (3) Å and 2.076 (3)

**Table 3.1** Selected Bond Distances (Å) in (DIPP)<sub>3</sub>Ta(PhC≡CPh) (**16**)<sup>a</sup>

Ta-O(1)	1.869(2)	Ta-O(2)	1.912(2)	Ta-O(3)	1.889(2)
Ta-C(4)	2.070(3)	Ta-C(5)	2.076(3)	Ta-acet <sup>b</sup>	1.961
O(1)-C(11)	1.384(4)	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)

**Table 3.2** Selected Bond Angles (deg) in (DIPP)<sub>3</sub>Ta(PhC≡CPh) (**16**)

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)

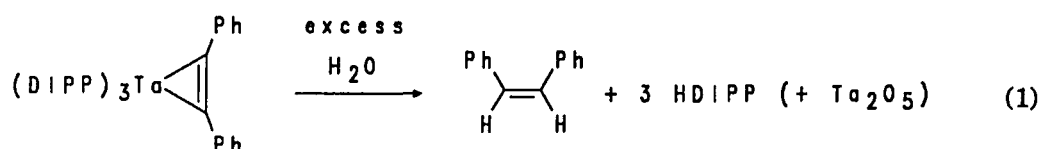
<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digit.

<sup>b</sup>Acet represents the C(4)-C(5) midpoint.

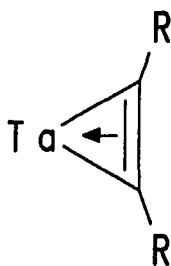
Å, respectively) and the distended C(4)-C(5) bond (1.346 (5) Å) are clearly indicative of a strongly bound and substantially reduced alkyne ligand.<sup>5,6,10,27,28,30,31,34,36,38,89</sup>

These structural data, in conjunction with the downfield <sup>13</sup>C NMR resonance for C<sub>alkyne</sub> (δ 216 for **16**; 226.0 and 224.4 for **14**, C<sub>6</sub>D<sub>6</sub>) and the *cis*-olefin obtained upon the hydrolysis of

**16** (equation 1), all suggest a formal 4-electron interaction<sup>69,70</sup> involving both alkyne



$\pi_{\parallel}$  and  $\pi_{\perp}$  bonding orbitals with the metal. Therefore, a formal Ta(V) metallacyclopropene 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>10,25-28,30,31,34,36,38,39</sup> and group 6<sup>69</sup> alkyne adducts have been



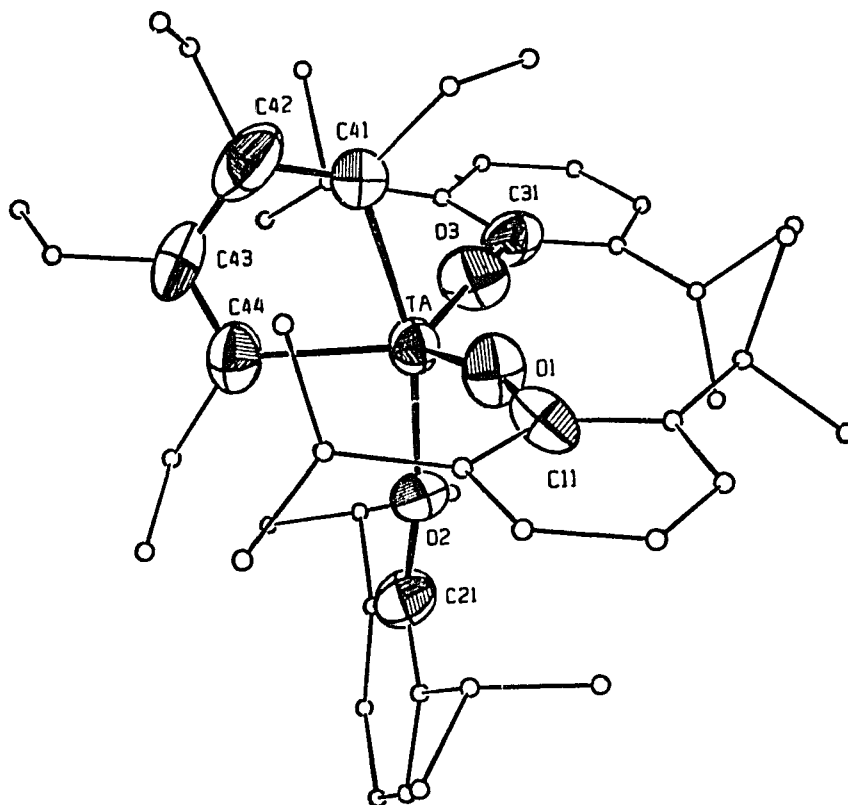
**I**

characterized with similar structures. However, this structural form does not prevent the metallacyclization reaction (vide infra),<sup>34</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>71</sup> the alkyne ligand in **16** appears to be more highly reduced as judged from the longer "C≡C" bond in **16** (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 alkyne, an alternative description of the geometry 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) °) and the equatorial positions occupied by O(1), O(3), and C(4) (average L<sub>eq</sub>-Ta-L<sub>eq</sub> angle = 117.4°; average L<sub>eq</sub>-Ta-L<sub>ax</sub> angle = 90.2°). The distortion from a TBP structure arises from the severe constraints imposed by the alkyne ligand in that one L<sub>eq</sub>-Ta-L<sub>ax</sub> angle (C(4)-Ta-C(5) = 37.9 °) is much less than 90°.

Orange, single crystals of (DIPP)<sub>3</sub>Ta(CEt=CEtCEt=CEt) (17) were grown from a pentane solution at -40 °C. The molecular structure of the metallacycle (DIPP)<sub>3</sub>Ta(CEt=CEtCEt=CEt) (17) is presented in Figure 3.2. A summary of the



**Figure 3.2** ORTEP drawing of (DIPP)<sub>3</sub>Ta(CEt=CEtCEt=CEt) (17) with local coordination atoms shown as 50% probability ellipsoids.

crystal data and a complete listing of bond lengths and angles are reported in Appendix A. Relevant bond lengths and angles are provided in Tables 3.3 and 3.4 respectively. In the solid state, this compound assumes a trigonal bipyramidal geometry (O(2)-Ta-Cl = 164.9 (3)°) with the small C(41)-Ta-C(44) angle of 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 3.3) 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 nearly 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

**Table 3.3** Selected Bond Distances (Å) in (DIPP)<sub>3</sub>Ta(CEt=CEtCEt=CEt) (17)

Ta-O(1)	1.858(4)	Ta-O(2)	1.920(5)	Ta-O(3)	1.845(5)
Ta-C(41)	2.166(9)	Ta-C(44)	2.147(8)	O(1)-C(11)	1.392(9)
O(2)-C(21)	1.364(9)	O(3)-C(31)	1.38(1)	C(41)-C(42)	1.32(1)
C(42)-C(43)	1.49(1)	C(43)-C(44)	1.35(1)	C(44)-C(54)	1.53(1)

**Table 3.4** Selected Bond Angles (deg) in (DIPP)<sub>3</sub>Ta(CEt=CEtCEt=CEt) (17)

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)	89.9(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)	163.9(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)		

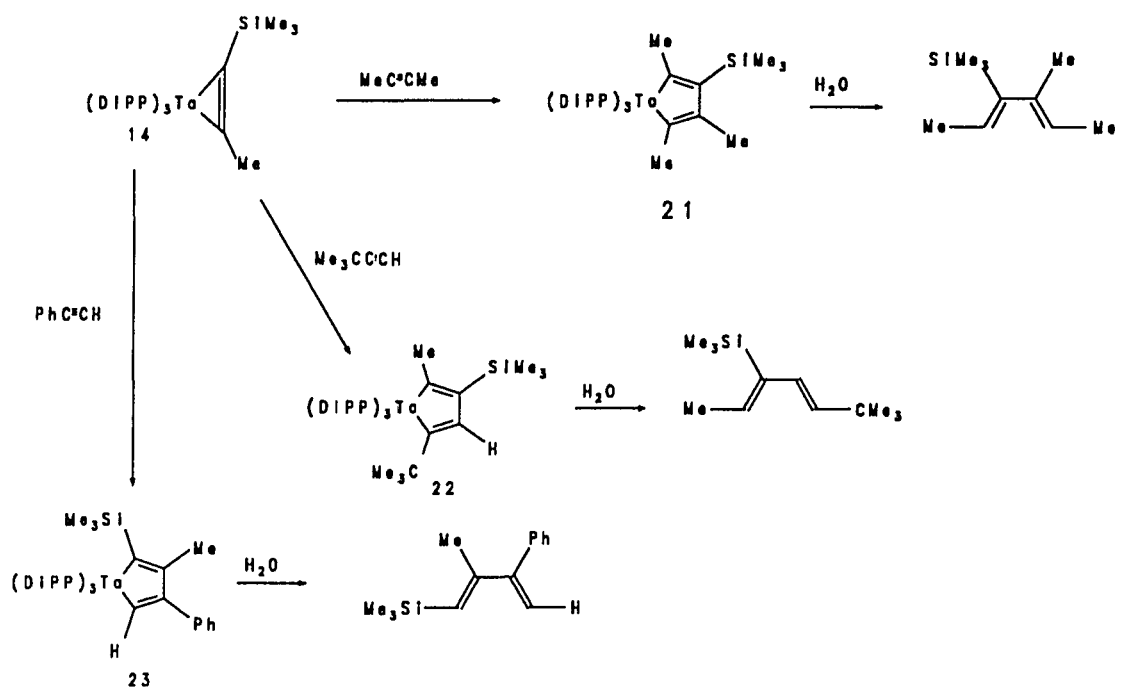
to steric effects in these phenoxide compounds<sup>67,72,73</sup> and is consistent with the fact that cyclotrimerization with 3-hexyne does not proceed further in compound 17.<sup>5-7</sup> The crystal structure of a related tantalum (V) ene-diamide (formally diazabutadiene anion) metallacycle has been reported which likewise is characterized by the metallacycle

occupying axial and equatorial positions of a trigonal bipyramid.<sup>67,73</sup>

**Cross-Coupling Reactions of (DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) (14).** The slight advantage that the steric constraints in (DIPP)<sub>3</sub>Ta(RC≡CR') (14 and 16) have over the electronic driving force to metallacyclize may be overcome by simply reducing the steric congestion at the metal center, and choosing an alkyne with less steric bulk than diphenylacetylene or trimethylsilyl-1-propyne. This approach also works for aldehydes, ketones, and nitriles which can coordinate in an η<sup>1</sup> fashion to the electrophilic metal center prior to coupling with the alkyne already bound to the metal.<sup>74,75</sup> Discussion of these types of reactions is presented in Chapter 4. Although other group 5 alkyne complexes<sup>10,25-28,30,31,34,36,38,39</sup> are characterized by the same type of metallacyclopropene bonding description, they do not react with additional alkyne to form metallacycles.<sup>40,41</sup>

Scheme 3.3 presents some cross-coupling reactions using (DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) (14). The regiochemistry observed presumably reflects the balance between minimizing congestion about the metal and preventing unfavorable β,β'-substituent interactions.<sup>76</sup> Thus, (DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) (14) reacts with MeC≡CMe to afford (DIPP)<sub>3</sub>Ta(MeC=CSiMe<sub>3</sub>CMe=CMe) (21) and with PhC≡CH to provide (DIPP)<sub>3</sub>Ta(CSiMe<sub>3</sub>=CMeCPh=CH) (22), both isolated as the sole regioisomer. However 14 also reacts with Me<sub>3</sub>CC≡CH to afford (DIPP)<sub>3</sub>Ta(CCMe<sub>3</sub>=CHSiMe<sub>3</sub>=CMe) (23). The following reasoning is suggested to explain the observed regioisomers. First, 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 Si-C vs C-C bond lengths) as the β,β'-(Me,Ph) interaction in 22 is preferred over having both the SiMe<sub>3</sub> and Ph groups in the α,α' positions which would be highly unfavorable with the large DIPP ligands. Secondly, complex 23 represents both the avoidance of a β,β'-substituent interaction and the positioning

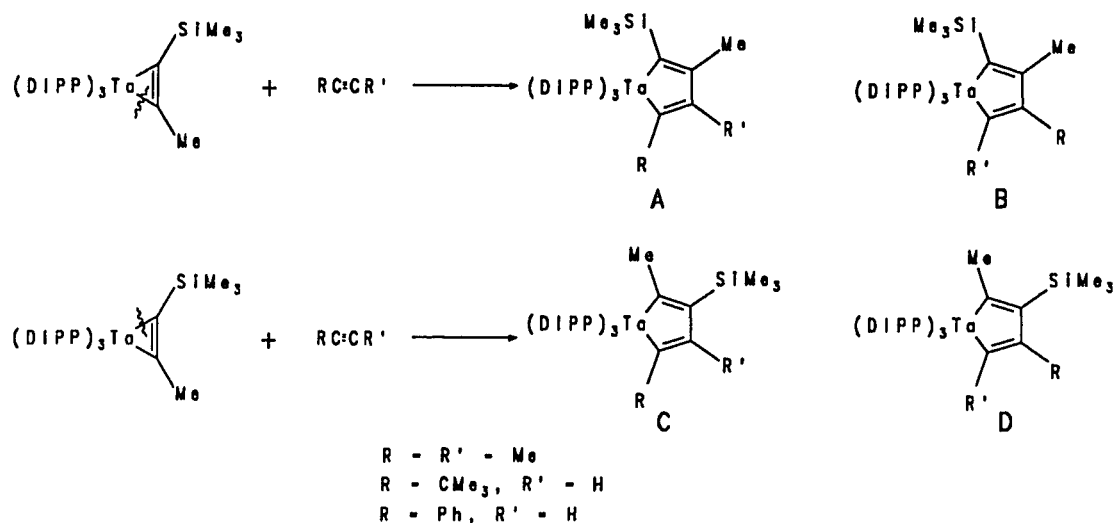
Scheme 3.3



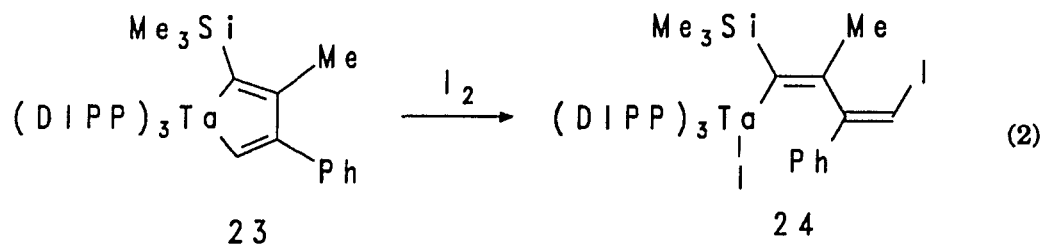
of the CMe<sub>3</sub> group, rather than slightly larger SiMe<sub>3</sub>, in a position  $\alpha$  to the metal.

**Hydrolysis and Iodination Reactions of Coupled Products.** Absolute identification of the metallacyclic products could not be based solely on NMR spectroscopy, since all the ring carbons could not be located - thereby precluding the use of decoupled <sup>13</sup>C NMR spectra. Therefore the protonolysis reactions of the metallacycles formed from 14, shown in Scheme 3.3, proved essential in assigning the regiochemistry of the coupling reactions and demonstrated the preferred method of quantitatively releasing the 1,3-dienes after assembly at the metal. Scheme 3.4 shows the possible regioisomers that could be formed depending on the orientation of the new alkyne with respect to the alkyne complex. The diagnostic <sup>1</sup>H NMR data are reported at the end of each experimental preparation for the corresponding metallacycles.

Scheme 3.4



Another question to be addressed was whether or not the metallacycle could be removed from the metal through iodination to produce 1,4-diiodo-1,3-dienes which are of potential synthetic utility.<sup>77</sup> Iodination of metallacycle **23** did not yield the expected diiodide product, but rather the ring opened mono-iodinated butadienyl compound shown in equation 2. The addition of 1 equivalent of I<sub>2</sub> to **23** affords crystals of the



ring-opened butadienyl product (DIPP)<sub>3</sub>ITa(CSiMe<sub>3</sub>=CMeCPh=CHI) (**24**). The iodine

appears to only attack the less hindered side of the metallacycle. This ring-opened butadienyl product formed from the reaction of the metallacycle **23** with  $I_2$  is different from the the 1,4-diiodo-1,3-dienes which are formed in high yield from the iodination of  $(\eta^5-C_5H_5)_2Zr(CR=CR=CR=CR)$  complexes.<sup>77</sup> The butadienyl fragment can be removed from the metal to yield a 1-iodo-1,3-diene from the reaction of an  $Et_2O$  solution of **24** with a 10%  $H_2O/Acetone$  solution.

### SUMMARY AND CONCLUSIONS

$Ta(DIPP)_3Cl_2(OEt_2)$  can be reduced by two electrons in the presence of the bulky alkynes  $Me_3SiC\equiv CMe$  and  $PhC\equiv CPh$  to provide the pale yellow acetylene adducts  $(DIPP)_3Ta(Me_3SiC\equiv CMe)$  (**14**) and  $(DIPP)_3Ta(PhC\equiv CPh)$  (**16**). The reduction of  $Ta(DIPP)_3Cl_2(OEt_2)$  in the presence of the smaller internal alkynes  $EtC\equiv CEt$  or  $PrC\equiv CPr$  or the terminal alkynes  $Me_3CC\equiv CH$  or  $Me_3SiC\equiv CH$  affords the metallacyclopentadienes  $(DIPP)_3Ta(\overline{CR=CR'CR=CR'})$  (**17**,  $R = R' = Et$ ; **18**,  $R = R' = Pr$ ; **19**,  $R = Me_3C$ ,  $R' = H$ ; **20**,  $R = Me_3Si$ ,  $R' = H$ ) directly. The molecular structure of **16** is approximately tetrahedral ( $L-Ta-L$  angles average  $109.4^\circ$ ) and features very short  $Ta-C_{alkyne}$  distances ( $2.070(3)$  Å and  $2.076(3)$  Å) and an elongated "C≡C" bond ( $1.346(5)$  Å) which indicate a strongly bound and substantially reduced alkyne ligand. The molecular structure of the metallacycle **17** is a trigonal bipyramid ( $L_{ax}-Ta-L_{ax} = 164.9(3)^\circ$ ) with the metallacyclic  $\alpha$  carbons occupying one axial and one equatorial position. Although the alkyne complex  $(DIPP)_3Ta(Me_3SiC\equiv CMe)$  (**14**) will not react with an additional equivalent of  $Me_3SiC\equiv CMe$ , it will react with the smaller alkynes  $MeC\equiv CMe$ ,  $Me_3CC\equiv CH$ , and  $PhC\equiv CH$  to afford the cross-coupled metallacycle products  $(DIPP)_3Ta(\overline{MeC=CSiMe_3CMe=CMe})$  (**21**),  $(DIPP)_3Ta(\overline{MeC=CSiMe_3CH=CCMe_3})$  (**22**), and  $(DIPP)_3Ta(\overline{CSiMe_3=CMeCPh=CH})$  (**23**) which are formed much in the same way as other cross-coupled products that have been

observed by several other groups. Compound **23** can be iodinated to provide the ring-opened butadienyl product  $(\text{DIPP})_3\text{ITa}(\text{CSiMe}_3=\text{CMeCPh=CHI})$  (**24**).

The alkyne adducts **14** and **16** can be considered as relevant models for alkyne cyclotrimerization using group 5 metals. Unlike Schrock's cyclopentadienyl tantalum alkyne complex which does not react with additional equivalents of alkyne,<sup>34</sup> the tantalum tris phenoxide alkyne adducts react with another equivalent of alkyne to form the next higher cyclooligomer. This reactivity can be partially attributed to the enhanced electrophilicity of the complex resulting when Cp ligands are replaced by phenoxide ligands. The metallacyclopentadienes do not react with further equivalents of alkyne to produce arene complexes. This lack of reactivity can be explained by steric effects. With three 2,6-diisopropylphenoxide ligands and the metallacycle attached to the metal center, the coordination sphere of the metal is too crowded to coordinate another alkyne ligand. Reducing the steric congestion around the metal center by having only two phenoxide ligands allows its reaction with the third equivalent of alkyne to produce the arene.<sup>68</sup> The coupling reactions which produce metallacyclopentadienes show a high degree of regioselectivity. This selectivity is most likely due to minimization of steric interactions around the metallacycle ring. These cross-coupling reactions may provide a viable approach to synthesizing substituted 1,3-dienes which may prove useful in organic synthesis.

## EXPERIMENTAL

**Preparations.**  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (**14**). To a  $-40$  °C solution of 1.0 g (1.12 mmol) of  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  in 20 mL of diethyl ether was added 0.34 mL (2.32 mmol) of  $\text{Me}_3\text{SiC}\equiv\text{CMe}$  and 1.00 mL (2.3 mmol) of 0.50% Na/Hg. The solution was stirred at room temperature for 24 h. The resulting mixture was filtered through Celite, and all

volatiles were removed from the filtrate in vacuo to provide the product as a yellow oil. This oil was pure by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and was used without further purification in the following preparations. Since this compound has not been induced to crystallize, no analyses were attempted.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.09-6.90 (m, 9 H,  $\text{H}_{\text{aryl}}$ ), 3.46 (spt, 6 H,  $\text{CHMe}_2$ ), 2.54 (s, 3 H,  $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ), 1.17 (d, 36 H,  $\text{CHMe}_2$ ), -0.005 (s, 9 H,  $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  226.0 ( $\text{C}_{\text{alkyne}}$ ), 224.4 ( $\text{C}'_{\text{alkyne}}$ ), 158.2 ( $\text{C}_{\text{ipso}}$ ), 137.7 ( $\text{C}_o$ ), 124.5 ( $\text{C}_m$ ), 123.1 ( $\text{C}_p$ ), 27.3 ( $\text{CHMe}_2$ ), 24.6 ( $\text{MeC}\equiv\text{CSiMe}_3$ ), 23.8 ( $\text{CHMe}_2$ ), 0.5 ( $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ). IR: 1574 br, 1558 br, 1430 s, 1323 s, 1245 s, 1186 s, 1105 m, 1091 sh, 1038 m, 1022 m, 917 sh, 892 s, 870 m, 837 s, 786 m, 743 s, 700 m.

**(DIPP)Ta( $\text{Me}_3\text{SiC}\equiv\text{CMe}$ )(THF) (15).** To a  $-40$  °C solution of 1.0 g (1.12 mmol) of  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  in 20 mL of diethyl ether was added 0.34 mL (2.32 mmol) of  $\text{Me}_3\text{SiC}\equiv\text{CMe}$  and 1.00 mL (2.3 mmol) of 0.50% Na/Hg. The solution was stirred at room temperature for 24 h. The resulting mixture was filtered through Celite, and all volatiles were removed from the filtrate in vacuo to provide the product as a yellow oil weighing 0.84 g (1.02 mmol). The oil was reconstituted in 5 mL of pentane and cooled to  $-40$  °C. 2 mL of THF was added to the cold solution and upon cooling to  $-40$  °C for 24 h 0.46 g (0.51 mmol, 50% yield) of pale yellow crystals was filtered off, washed with ca. 5 mL of cold pentane, and dried in vacuo. This THF adduct was prepared strictly for analysis and was not used in any subsequent preparations.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.10-6.92 (m, 9 H,  $\text{H}_{\text{aryl}}$ ), 3.71 (br, 4 H,  $\text{C}_\alpha\text{H}_2$ , THF), 3.44 (spt, 6 H,  $\text{CHMe}_2$ ), 2.55 (s, 3 H,  $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ), 1.33 (br, 4 H,  $\text{C}_\beta\text{H}_2$ , THF), 1.17 (d, 36 H,  $\text{CHMe}_2$ ), 0.12 (s, 9 H,  $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  235.9 ( $\text{C}_{\text{alkyne}}$ ), 216.8 ( $\text{C}'_{\text{alkyne}}$ ), 158.4 ( $\text{C}_{\text{ipso}}$ ), 137.8 ( $\text{C}_o$ ), 123.6 ( $\text{C}_m$ ), 122.4 ( $\text{C}_p$ ), 70.0 (coincident  $\text{C}_\alpha$  and  $\text{C}_\alpha'$ , THF), 27.0 ( $\text{CHMe}_2$ ), 25.5 (coincident  $\text{C}_\beta$  and  $\text{C}_\beta'$ , THF), 24.1 ( $\text{CHMe}_2$ ), 23.7 ( $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ), 0.70 ( $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ). Anal. Calcd. for  $\text{C}_{46}\text{H}_{71}\text{O}_4\text{SiTa}$ : C,

61.59; H, 7.98. Found: C, 61.72; H, 8.28.

**(DIPP)<sub>3</sub>Ta(PhC≡CPh) (16).** To a -40 °C solution of 3.00 g (3.50 mmol) of Ta(DIPP)<sub>3</sub>Cl<sub>2</sub>(OEt<sub>2</sub>) in 50 mL of diethyl ether was added 1.00 g (5.61 mmol) of diphenylacetylene and 2.00 mL (7.1 mmol) of 0.59% Na/Hg. This mixture was stirred 24 h at room temperature, over which time the solution developed an orange color. After this time the mixture was filtered through Celite, the solvent was removed from the filtrate in vacuo to provide a yellow oil. This oil was dissolved in pentane, and upon cooling the solution to -40 °C, pale yellow crystals of impure product were formed. The crystals were filtered off and dried in vacuo, and excess diphenylacetylene was removed by sublimation (5 X 10<sup>-5</sup> Torr, room temperature). From 1.35 g of impure product that was isolated in this manner, 1.22 g (1.37 mmol, 39% yield) of pure product was obtained.

Recrystallization from pentane at -40 °C provided analytically pure samples. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.24-6.85 (m, 19 H, H<sub>aryl</sub> and C<sub>6</sub>H<sub>5</sub>), 3.60 (spt, 6 H, CHMe<sub>2</sub>), 1.11 (d, 36 H, CHMe<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 216.0 (C<sub>alkyne</sub>), 157.7 (C<sub>ipso</sub>, DIPP), 142.0 (C<sub>ipso</sub> C<sub>6</sub>H<sub>5</sub>), 137.8 (C<sub>o</sub>, DIPP), 129.1, 128.2 (C<sub>o</sub> and C<sub>m</sub>, C<sub>6</sub>H<sub>5</sub>), 127.9 (C<sub>p</sub>, C<sub>6</sub>H<sub>5</sub>), 123.4 (C<sub>m</sub>, DIPP), 123.3 (C<sub>p</sub>, DIPP), 27.3 (CHMe<sub>2</sub>), 23.5 (CHMe<sub>2</sub>). IR: 1580 br w, 1428 s, 1358 m, 1320 s, 1248 s, 1194 s, 1103 m, 1098 sh, 1052 w, 1038 m, 1022 w, 90 sh, 915 sh, 890 s, 870 m, 800 sh, 786 m, 760 w, 742 s, 697 s. Hydrolysis of **16** produced only *cis*-stilbene. Partial <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.20 (m, 10 H, C<sub>6</sub>H<sub>5</sub>CHC=CHC<sub>6</sub>H<sub>5</sub>) 6.45 (s, 2 H, C<sub>6</sub>H<sub>5</sub>CHC=CHC<sub>6</sub>H<sub>5</sub>).

**(DIPP)<sub>3</sub>Ta(CEt=CEtCEt=CEt) (17).** To a -40 °C solution of 0.99 g (1.15 mmol) of Ta(DIPP)<sub>3</sub>Cl<sub>2</sub>(OEt<sub>2</sub>) in 20 mL of diethyl ether were added 0.53 mL (4.7 mmol) of 3-hexyne and 0.76 mL of 0.52% Na/Hg. 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 the addition of 5 mL of acetonitrile, orange crystals started to form. This sample was stored at  $-40\text{ }^{\circ}\text{C}$  for 16 h to complete crystallization and afford (0.79 g, 0.90 mmol, 78% yield) of orange crystals which were filtered off, washed with a minimal volume of cold acetonitrile, and dried in vacuo. Recrystallization of this compound from  $\text{Et}_2\text{O}/\text{MeCN}$  at  $-40\text{ }^{\circ}\text{C}$  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, 6 H,  $\text{C}_\alpha\text{CH}_2\text{CH}_3$ ), 0.92 (t, 6 H,  $\text{C}_\beta\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{H}_5\text{CD}_3$ , 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,  $\text{C}_\text{o}$ ), 123.8 (d,  $\text{C}_\text{p}$ ), 123.7 (d,  $\text{C}_\text{m}$ ), 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,  $\text{C}_\alpha\text{CH}_2\text{CH}_3$  and  $\text{C}_\beta\text{CH}_2\text{CH}_3$  are coincident). 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, 65.47; H, 8.16. Found: C, 65.95; H, 8.27.

**(DIPP) $_3$ Ta(CPr=CPrCPr=CPr) (18)**. To a  $-40\text{ }^{\circ}\text{C}$  solution of 1.03 g (1.20 mmol) of  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  in 20 mL of diethyl ether were added 0.70 mL (4.77 mmol) of 4-octyne and 0.86 mL (2.40 mmol) of 0.47% Na/Hg. The solution was stirred at room temperature for 16 h over which time the color slowly changed from yellow to orange. After this time, the solution was filtered through Celite and the solvent was removed in vacuo to afford an orange oil. The oil was reconstituted in ca. 5 mL of diethyl ether and upon the addition of 5 mL of acetonitrile, orange crystals began to form. This sample was stored at  $-40\text{ }^{\circ}\text{C}$  for 16 h to complete crystallization and afford (0.31 g, 0.33 mmol, 28% yield) of orange diamond shaped crystals which were filtered off, washed with a minimal volume of cold acetonitrile, and dried in vacuo. Recrystallization of this compound from  $\text{Et}_2\text{O}/\text{MeCN}$  solution at  $-40\text{ }^{\circ}\text{C}$  provided analytically pure samples.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 318K):  $\delta$  7.08-6.91

(m, 9 H,  $H_{\text{aryl}}$ ), 3.64 (br spt, 6 H,  $\text{CHMe}_2$ ), 2.76 (m, 4 H,  $C_{\alpha}\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.15 (m, 4 H,  $C_{\beta}\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.55 (m, 4 H,  $C_{\alpha}\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.35 (m, 4 H,  $C_{\beta}\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.20 (d, 36 H,  $\text{CHMe}_2$ ), 0.97 (t, 6 H,  $C_{\alpha}\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.58 (t, 6 H,  $C_{\beta}\text{CH}_2\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 318K):  $\delta$  203.9 ( $C_{\alpha}$ ), 162.3 ( $C_{\beta}$ ), 157.4 ( $C_{\text{ipso}}$ ), 138.6 ( $C_{\text{o}}$ ), 123.8 ( $C_{\text{p}}$ ), 123.7 ( $C_{\text{m}}$ ), 39.3 ( $C_{\alpha}\text{CH}_2\text{CH}_2\text{CH}_3$ ), 32.2 ( $C_{\beta}\text{CH}_2\text{CH}_2\text{CH}_3$ ), 27.5 ( $\text{CHMe}_2$ ), 24.8 ( $C_{\alpha}\text{CH}_2\text{CH}_2\text{CH}_3$  and  $C_{\beta}\text{CH}_2\text{CH}_2\text{CH}_3$  are coincident), 24.4 ( $\text{CHMe}_2$ ), 15.4 ( $C_{\alpha}\text{CH}_2\text{CH}_2\text{CH}_3$ ), 14.7 ( $C_{\beta}\text{CH}_2\text{CH}_2\text{CH}_3$ ). IR: 1576 w, 1321 s, 1246 s, 1187 s, 1153 sh, 1103 m, 1092 m, 1062 w, 1038 m, 1010 w, 952 w, 928 sh, 918 sh, 905 s, 892 s, 874 s, 800 w, 787 m, 750 sh, 742 s, 721 w, 709 m, 699 m. Anal. Calcd. for  $\text{C}_{52}\text{H}_{79}\text{O}_3\text{Ta}$ : C, 66.93; H, 8.53. Found: C, 66.46; H, 8.63.

(DIPP) $_3$ Ta( $\overline{\text{CCMe}_3=\text{CHCCMe}_3=\text{CH}}$ ) (19). To a  $-40\text{ }^\circ\text{C}$  solution of 1.02 g (1.19 mmol) of Ta(DIPP) $_3$ Cl $_2$ (OEt $_2$ ) in 20 mL of diethyl ether were added 0.57 mL (4.6 mmol) of 3,3-dimethyl-1-butyne and 0.66 mL (2.4 mmol) of 0.59% Na/Hg. The solution was stirred at room temperature for 48 h over which time a golden brown color developed. After this time, the solution was filtered through Celite and the solvent was removed in vacuo to afford a golden, frothy oil. The oil was reconstituted in pentane and cooled to  $-40\text{ }^\circ\text{C}$  for 48 h. Golden brown crystals (0.47 g, 0.54 mmol, 45% yield, 2 crops) were collected, washed with a minimal volume of cold pentane, and dried in vacuo. Recrystallization of this compound from pentane at  $-40\text{ }^\circ\text{C}$  provided analytically pure samples.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.68, 7.56 (d,  $^4J_{\text{HH}} = 2.1\text{ Hz}$ , 1 H each,  $C_{\beta}\text{H}$  and  $C_{\alpha}\text{H}$ ), 7.11-6.86 (m, 9 H,  $H_{\text{aryl}}$ ), 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,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  218.0 ( $C_{\alpha}\text{CMe}_3$ ), 183.9 ( $C_{\beta}\text{CMe}_3$ ), 180.2 ( $C_{\alpha}\text{H}$ ), 157.8 ( $C_{\text{ipso}}$ ), 139.8, 138.2, 137.3 ( $C_{\text{o}}$ ), 135.5 ( $C_{\beta}\text{H}$ ), 124.3, 124.1 ( $C_{\text{p}}$ ), 123.6, 123.4 ( $C_{\text{m}}$ ), 41.1, 37.0 ( $\text{CMe}_3$ ), 31.5, 29.1 ( $\text{CMe}_3$ ), 28.0, 27.2, 25.2 ( $\text{CHMe}_2$ ),

24.7, 23.7, 23.4 ( $\underline{\text{CHMe}_2}$ ). 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.

$(\text{DIPP})_3\text{Ta}(\overline{\text{CSiMe}_3=\text{CHCSiMe}_3=\text{CH}})$  (20). To a  $-40\text{ }^\circ\text{C}$  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 trimethylsilylacetylene and 0.33 mL (1.13 mmol) of 0.59% Na/Hg. The reaction was allowed to stir 24 h at room temperature. The yellow solution was filtered through Celite, and the solvent was removed in vacuo to afford a yellow oil. The oil was dissolved in pentane and cooled to  $-40\text{ }^\circ\text{C}$  for 24 h to provide yellow crystals (0.29 g, 0.32 mmol, 54% yield) which were filtered off, washed with a minimal volume of cold pentane, and dried in vacuo. This sample was sufficiently pure for elemental analysis, but the compound can be recrystallized from pentane at  $-40\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 318K):  $\delta$  8.56 and 8.35 (d,  $^4J_{\text{HH}} = 1.5\text{ Hz}$ , 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,  $\underline{\text{CHMe}_2}$ ), 1.20 (d, 36 H,  $\underline{\text{CHMe}_2}$ ), 0.12 and 0.10 (s, 9 H each,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ , 318K):  $\delta$  212.6 ( $\underline{\text{C}_\alpha\text{SiMe}_3}$ ), 202.6 ( $\text{C}_\alpha\text{H}$ ), 180.8 ( $\underline{\text{C}_\beta\text{SiMe}_3}$ ), 157.8 ( $\text{C}_{\text{ipso}}$ ), 153.3 ( $\text{C}_\beta\text{H}$ ), 138.4 ( $\text{C}_\alpha$ ), 124.0 ( $\text{C}_\beta$ ), 123.7 ( $\text{C}_\text{m}$ ), 27.8 ( $\underline{\text{CHMe}_2}$ ), 24.2 ( $\underline{\text{CHMe}_2}$ ), 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.

$(\text{DIPP})_3\text{Ta}(\overline{\text{CMe}=\text{CSiMe}_3\text{CMe}=\text{CMe}})$  (21). To a  $-40\text{ }^\circ\text{C}$  solution of 0.56 g (0.68 mmol) of  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (14) 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

affording an orange oil. The oil was reconstituted in a minimal volume of pentane, and the solution was cooled to  $-40\text{ }^{\circ}\text{C}$  for 24 h. The orange crystals that formed (0.084 g, 0.10 mmole, 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 (br, 6 H,  $\text{CHMe}_2$ ), 2.33, 2.19, 1.92 (s, 3 H each,  $\text{C}_{\alpha}$ ,  $\text{C}_{\beta}$ ,  $\text{C}_{\beta}\text{Me}$ ), 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 ( $\text{C}_{\alpha}$ ), 195.4 ( $\text{C}_{\alpha}$ ), 170.1 ( $\text{C}_{\beta}$ ), 157.3 ( $\text{C}_{\text{ipso}}$ ), 149.8 ( $\text{C}_{\beta}$ ), 138.3 ( $\text{C}_o$ ), 123.7 ( $\text{C}_p$ ), 123.1 ( $\text{C}_m$ ), 27.6 ( $\text{CHMe}_2$ ), 24.1 ( $\text{CHMe}_2$ ), 23.7, 23.4 ( $\text{C}_{\alpha}\text{Me}$  and  $\text{C}_{\beta}\text{Me}$ ), 19.4 ( $\text{C}_{\alpha}\text{Me}$ ), 3.3 ( $\text{SiMe}_3$ ). IR: 1576 w, 1535 w, 1320 s, 1244 s, 1188 s, 1092 m, 1079 sh, 1052 w, 1038 m, 905 s, 896 s, 870 m, 832 s, 787 m, 750 sh, 742 s, 707 m, 670 w. Anal. Calcd. for  $\text{C}_{46}\text{H}_{69}\text{O}_3\text{SiTa}$ : C, 62.85; H, 7.91. Found: C, 62.89; H, 8.10. Hydrolysis of **21** yielded **Z,E-CHMe=C(SiMe<sub>3</sub>)CMe=CHMe**. Partial  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.92, 5.98 (q,  $^3J_{\text{HH}} = 7.0$  Hz, 1 H each,  $\text{CHMe}$ ), 1.76 (d, 3 H,  $\text{CHMe}$ ), 1.63 (s, 3 H, Me), 1.59 (d, 3 H,  $\text{CHMe}$ ), 0.15 (s, 9 H,  $\text{SiMe}_3$ ).

(DIPP)<sub>3</sub>Ta( $\overline{\text{CMe=CSiMe}_3\text{CH=CCMe}_3}$ ) (**22**). To a room temperature solution of 0.87 g (1.05 mmol) of (DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) (**14**) in 10 mL of diethyl ether was added 0.30 mL of 3,3-dimethyl-1-butyne. The solution changed color from yellow to orange over several min. After being stirred 24 h at room temperature, 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  $-40\text{ }^{\circ}\text{C}$  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 a minimal volume of cold pentane, and dried in vacuo. This sample was sufficiently pure for analyses but could be recrystallized from pentane at  $-40\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  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,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  210.8 ( $\text{C}_\alpha$ ), 157.3 ( $\text{C}_{\text{ipso}}$ ), 138.4, 137.6 ( $\text{C}_\beta$  and  $\text{C}_\gamma$ ), 124.0, 123.7 ( $\text{C}_p$ ), 122.7, 122.6 ( $\text{C}_m$ ), 114.8 ( $\text{C}_q$ ), 39.9 ( $\text{CMe}_2$ ), 31.3 ( $\text{CMe}_3$ ), 27.9, 26.8, 26.6 ( $\text{CHMe}_2$ ), 25.9 ( $\text{C}_\beta\text{Me}$ ), 24.6, 24.3, 23.9 ( $\text{CHMe}_2$ ), -0.42 ( $\text{SiMe}_3$ ). 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 **22** yielded *Z,E*- $\text{CHMe}=\text{CSiMe}_3\text{CH}=\text{CH}(\text{CMe}_3)$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.23 (q, 1 H,  $\text{CHMe}=\text{CSiMe}_3$ ), 5.92, 5.52 (d,  $^3J_{\text{HH}} = 16\text{Hz}$ , 1 H each,  $\text{CHCMe}_3=\text{CH}$ ), 1.82 (d, 3 H,  $\text{C}_\alpha\text{Me}$ ), 1.02 (s, 9 H,  $\text{CMe}_3$ ), 0.19 (s, 9 H,  $\text{SiMe}_3$ ).

**(DIPP) $_3$ Ta( $\overline{\text{CSiMe}_3=\text{CMeCPh}=\text{CH}}$ ) (23)**. To a room temperature solution of 0.77 g (0.93 mmol) of **(DIPP) $_3$ Ta( $\text{Me}_3\text{SiC}\equiv\text{CMe}$ ) (14)** 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 the solvent was removed in vacuo to afford an orange oil. The oil was reconstituted in pentane and cooled to  $-40\text{ }^\circ\text{C}$  for 24 h. The orange brown cubes which formed (0.36 g, 0.38 mmol, 41% yield) were collected, washed with a minimal volume of cold pentane, and dried in vacuo. Recrystallization of this compound from pentane at  $-40\text{ }^\circ\text{C}$  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  $\text{C}_6\text{H}_5$ ), 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 (broad d, 24 H,  $\text{CHMe}_2$ ), 0.92 (br, 12 H,  $\text{CHMe}_2$ ), 0.26 (s, 9 H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  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  $\text{C}_\beta\text{Ph}$ ), 158.3, 155.4 ( $\text{C}_{\text{ipso}}$  DIPP), 143.4 ( $\text{C}_{\text{ipso}}$ ,  $\text{C}_6\text{H}_5$ ), 139.7, 138.0, 137.6 ( $\text{C}_\gamma$ , DIPP), 128.4 ( $\text{C}_\gamma$ ,  $\text{C}_6\text{H}_5$ ), 127.4 ( $\text{C}_p$ ,  $\text{C}_6\text{H}_5$ ), 127.3 ( $\text{C}_m$ ,  $\text{C}_6\text{H}_5$ ), 124.2 ( $\text{C}_p$ , DIPP), 123.9, 123.7 ( $\text{C}_m$ , DIPP), 28.2, 27.9, 27.2 ( $\text{CHMe}_2$ ), 25.4 ( $\text{C}_\beta\text{Me}$ ), 24.7, 24.4, 24.2, 23.9 ( $\text{CHMe}_2$ ), 1.9 ( $\text{SiMe}_3$ ). 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  $C_{50}H_{69}O_3SiTa$ : C, 64.78; H, 7.50. Found: C, 64.87; H, 7.68. Hydrolysis of **23** yielded  $E\text{-CH}(\text{SiMe}_3)=\text{CMeCPh}=\text{CH}_2$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.50, 5.30, 5.15 (s, 1 H each,  $\text{CH}_2=\text{CPh}$  and  $\text{CHSiMe}_3=\text{CMe}$ ), 2.03 (s, 3 H,  $\text{C}_\beta\text{Me}$ ), 0.13 (s, 9 H,  $\text{C}_\alpha\text{SiMe}_3$ ).

**(DIPP)<sub>3</sub>(I)Ta(CSiMe<sub>3</sub>=CMeCPh=CHI) (24)**. To a  $-40\text{ }^\circ\text{C}$  solution of 0.24 g (0.26 mmol) of **(DIPP)<sub>3</sub>Ta(CSiMe<sub>3</sub>C=CMeCPh=CH) (23)** 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 which turned to yellow after several h. After this solution was stirred for 24 h at room temperature, the solvent was removed in vacuo leaving a frothy, yellow oil. The oil was reconstituted in pentane and cooled to  $-40\text{ }^\circ\text{C}$  for 24 h, and the resulting yellow crystals (0.17 g, 0.14 mmol, 54% yield) were collected, washed with a minimal volume of cold pentane, and dried in vacuo. The product was sufficiently pure for analysis but could be recrystallized from pentane at  $-40\text{ }^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.86 (s, 1 H,  $\text{C}_8\text{H}$ ), 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 ( $\text{C}_\delta$ ), 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 ( $\text{C}_o$ , DIPP), 129.0 ( $\text{C}_o$ ,  $\text{C}_6\text{H}_5$ ), 128.8 ( $\text{C}_p$ ,  $\text{C}_6\text{H}_5$ ), 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 ( $\text{C}_q$ ), 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  $C_{50}H_{69}I_2O_3SiTa$ : C, 50.85; H, 5.89. Found: C, 50.54; H, 6.05. Hydrolysis of **24** yielded  $E,Z\text{-CHSiMe}_3=\text{CMeCPh}=\text{CHI}$ . Partial  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  5.49 and 4.96 (s, 1 H each,  $\text{CHSiMe}_3$  and  $\text{CPh}=\text{CHI}$ ), 1.92 (d,  $^4J_{\text{HH}} = 0.7\text{ Hz}$ , 3 H,  $\text{CMe}$ ), 0.32 (d,  $^4J_{\text{HH}} = 0.9\text{ Hz}$ , 9 H,  $\text{SiMe}_3$ ).

**CHAPTER 4**  
**HETEROATOM COUPLING REACTIONS WITH A TANTALUM ALKYNE**  
**ADDUCT**

**INTRODUCTION**

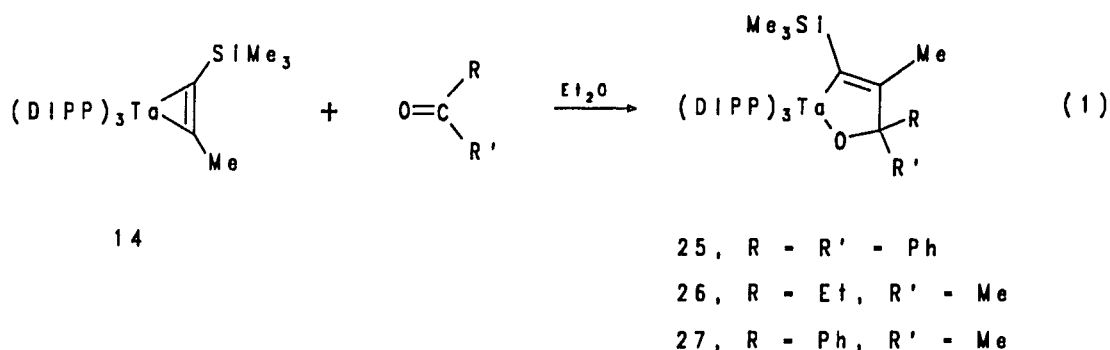
The formation of carbon-carbon bonds using transition metal templates to couple two organic fragments together to form a more complex molecule is a powerful tool for organic synthesis. Recently, the use of middle-to-low valent early transition metals<sup>71,77-85</sup> to reductively couple two organic molecules has arisen. As described in the previous chapter, the  $d^2$  alkyne adduct  $(DIPP)_3Ta(Me_3SiC\equiv CMe)$  (**14**) can be employed to cross-couple two different alkynes to make substituted 1,3-dienes. Similar coupling reactions using heteroatom substrates (aldehydes, ketones, and nitriles) are of interest because they can provide routes to the formation of vicinal diamines,<sup>66,86</sup> polyfunctionalized aromatic compounds (from benzyne),<sup>87</sup> allylic amines,<sup>88</sup> 2-amino alcohols,<sup>66</sup> and other products derived from metallacyclic intermediates.<sup>67,76,80-83</sup> This chapter describes the products from heteroatom coupling reactions with **14**.

**RESULTS AND DISCUSSION**

**Cross-Coupling Reactions of  $(DIPP)_3Ta(Me_3SiC\equiv CMe)$  (**14**) with Aldehydes and Ketones.** Reduction of  $Ta(DIPP)_3Cl_2(OEt_2)$  with 2 equivalents of Na/Hg in the presence of  $Me_3SiC\equiv CMe$  results in the isolation of the alkyne adduct  $(DIPP)_3Ta(Me_3SiC\equiv CMe)$  (**14**) as a yellow oil in high yield.<sup>66,86</sup> With the successful cross-coupling reactions of **14** with smaller alkynes,<sup>25-28,66,86</sup> I decided to try reactions involving unsaturated substrates containing heteroatoms, i.e. aldehydes, ketones, and nitriles.

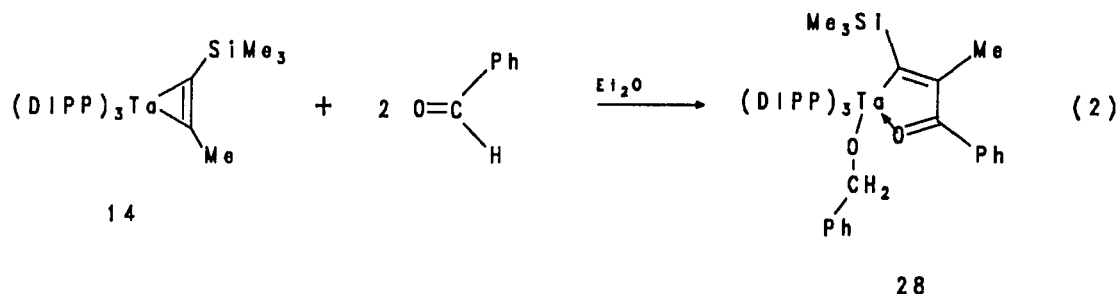
The reaction of  $(DIPP)_3Ta(Me_3SiC\equiv CMe)$  (**14**) with acetophenone, benzophenone, or methyl ethyl ketone in  $Et_2O$  results initially in red-orange solutions which quickly change

to pale yellow or white, and from which the metallacycles **25-27** can be isolated as white microcrystals (equation 1). The regioselectivity presented in equation 1 for compounds **25-27** is based upon the product obtained from the hydrolysis ( $\text{H}_2\text{O}/\text{acetone}$ , 1:9 v/v) of **25**, which provides (E)- $\text{Me}_3\text{SiCH}=\text{CMeCPh}_2\text{OH}$ , rather than (Z)- $\text{MeCH}=\text{C}(\text{SiMe}_3)\text{CPh}_2\text{OH}$ ,



expected for the opposite regioisomer.<sup>30,32,34,36,38,39</sup> These reactions most likely proceed by initial coordination of the ketone via an oxygen lone pair which could be reflected in the rapid color change to red-orange followed by the coupling to the acetylene ligand in which the solution color changes to pale yellow or white, which is consistent with the oxophilic nature of the tantalum center. In addition, no  $\nu(\text{C}=\text{O})$  mode is observed in the IR spectra of **25-27** between 1800 and 1600  $\text{cm}^{-1}$  indicating that these complexes are not simply  $\eta^1$ -bound ketones. Similar coupling reactions with zirconocene alkyne, cycloalkyne, and benzyne reagents have been reported by Buchwald.<sup>71,77,84,85</sup>

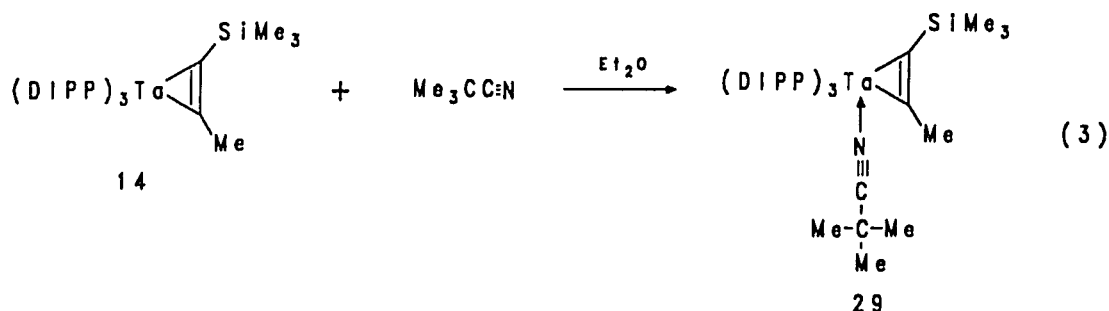
The  $\text{Me}_3\text{SiC}\equiv\text{CMe}$  adduct **14** also reacts with 2 equivalents of benzaldehyde to provide red-orange crystals of **28**, which on the basis of its analysis and spectroscopic properties similar to those of the product from the analogous reaction of the  $\text{PhC}\equiv\text{CPh}$  adduct **16** with benzaldehyde is formulated as the benzyl alkoxide complex  $(\text{DIPP})_3\text{-}(\text{PhCH}_2\text{O})\overline{\text{Ta}}(\text{C}(\text{SiMe}_3)=\text{CMeCPh}=\text{O})$  (equation 2). The diagnostic spectroscopic features of



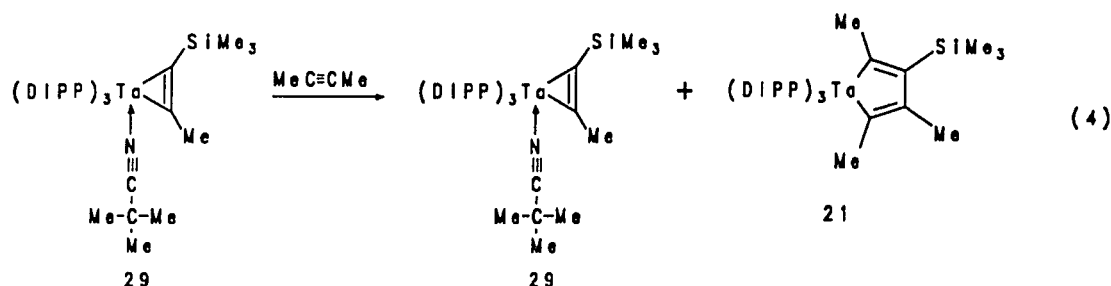
**28** include a singlet at  $\delta$  6.30 in the  $^1\text{H}$  NMR spectrum that integrates for 2 protons, a signal at  $\delta$  77.5 in the  $^{13}\text{C}$  NMR attached-proton-test spectrum which indicates a carbon with 2 attached protons, and a signal at  $\delta$  257.4 in the  $^{13}\text{C}$  NMR spectrum which can be assigned to a quaternary carbon doubly bonded to an oxygen. All of these data implicate the *transfer* of a hydride from one aldehyde to the other in a type of Meerwein-Ponndorf-Verley/Oppenauer hydride transfer reaction.<sup>89</sup> An X-ray crystal structure determination of  $(\text{DIPP})_3(\text{PhCH}_2\text{O})\text{Ta}(\text{CPh}=\text{CPh}=\text{O})$  was carried out in order to unambiguously characterize the products of these reactions.<sup>74</sup> A series of isotopically labeled cross-over experiments using the  $\text{PhC}\equiv\text{CPh}$  adduct and deuterated benzaldehyde were performed which confirmed that the hydride transfer indeed comes from the coordinated benzaldehyde ligand and not from exogeneous sources of hydrogen.

#### Cross-Coupling Reactions of $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$ (14) with Nitriles.

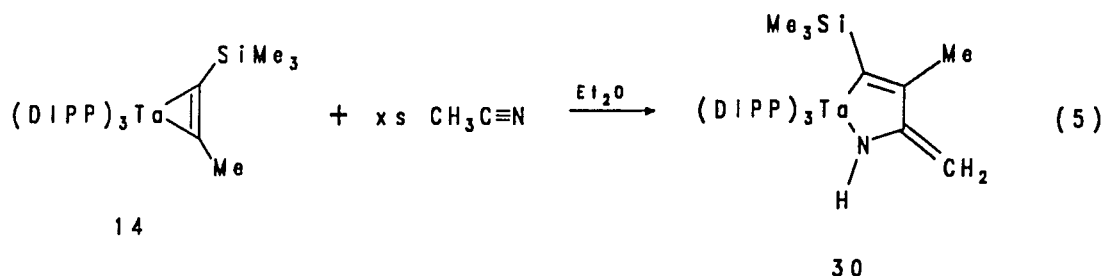
Reaction of the alkyne complex  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (14) with *t*-butyl cyanide results in the isolation of an  $\eta^1$ -nitrile adduct **29** (equation 3). Complex **29** is readily identified by its IR spectrum with a medium intensity  $\nu(\text{C}\equiv\text{N})$  stretch at  $2264\text{ cm}^{-1}$  compared to  $2225\text{ cm}^{-1}$  in free  $\text{Me}_3\text{CC}\equiv\text{N}$ . Heating a toluene solution of **29** in an effort to couple the nitrile and alkyne ligands together resulted only in the isolation of the starting material.<sup>65</sup> 2-Butyne was added to a diethyl ether solution of **29** which produced some of the cross-



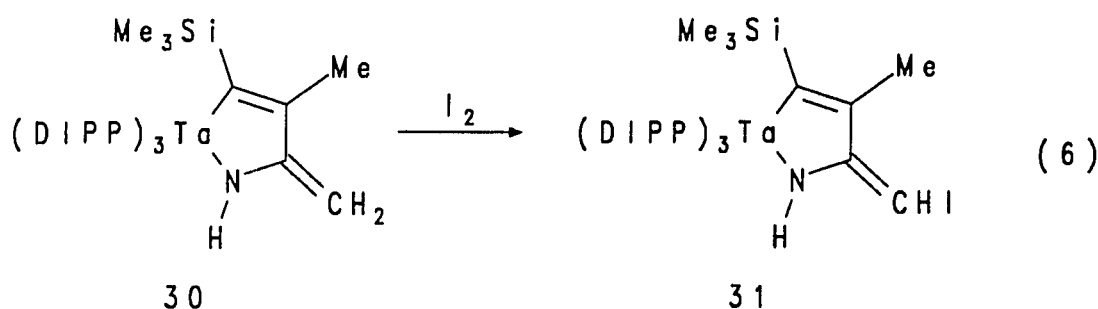
coupled product  $(\text{DIPP})_3\text{Ta}(\text{MeC}=\text{CSiMe}_3\text{CMe}=\text{CMe})$  (21) and starting material (equation 4).



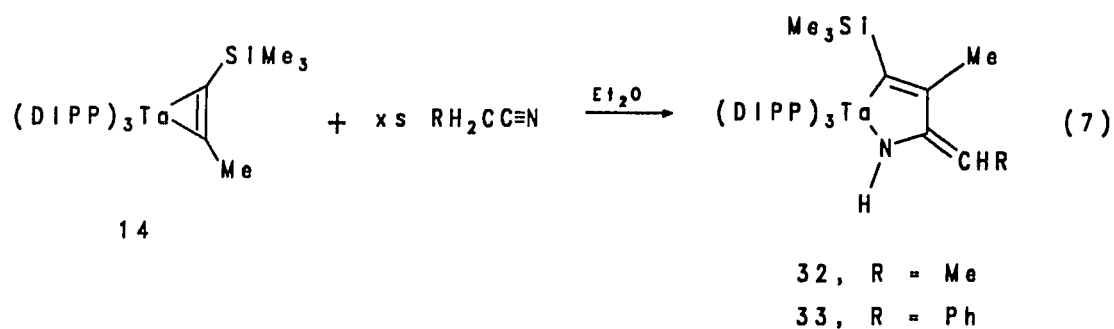
In an initial attempt to crystallize the  $\text{Me}_3\text{SiC}\equiv\text{CMe}$  adduct (14), the oil was dissolved in a minimal volume of  $\text{Et}_2\text{O}$  and excess acetonitrile and cooled to  $-40^\circ\text{C}$ . Pale yellow crystals were isolated and the  $^1\text{H}$  NMR spectrum of these crystals had an unusual feature. Instead of a singlet of intensity 3 due to the methyl protons from acetonitrile if an  $\eta^1$ -nitrile adduct had formed, three singlets at  $\delta$  7.42, 3.93, and 3.57 which integrated for one proton each was found instead. The  $^1\text{H}$  NMR spectrum coupled with a weak intensity IR stretch at  $3320\text{ cm}^{-1}$  ( $\nu(\text{N-H})$ ) and a  $^{13}\text{C}$  NMR signal at  $\delta$  90.6 with 2 attached protons led to the formulation of this compound as the metallacycloenamine complex,  $(\text{DIPP})_3\text{Ta}(\text{CSiMe}_3\text{CMeC}(\text{=CH}_2)\text{NH})$  (30) (equation 5). In an effort to remove the metallacyclic fragment from the metal center,  $\text{I}_2$  was added to a diethyl ether solution of 30. Instead of removing the organic fragment from the metal or producing a ring



-opened product similar to the reaction of  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}=\text{CMeCPh}=\text{CH})$  (**23**) with  $\text{I}_2$ , the iodine simply replaces one of the exo methylene hydrogens (equation 6). Proof of this

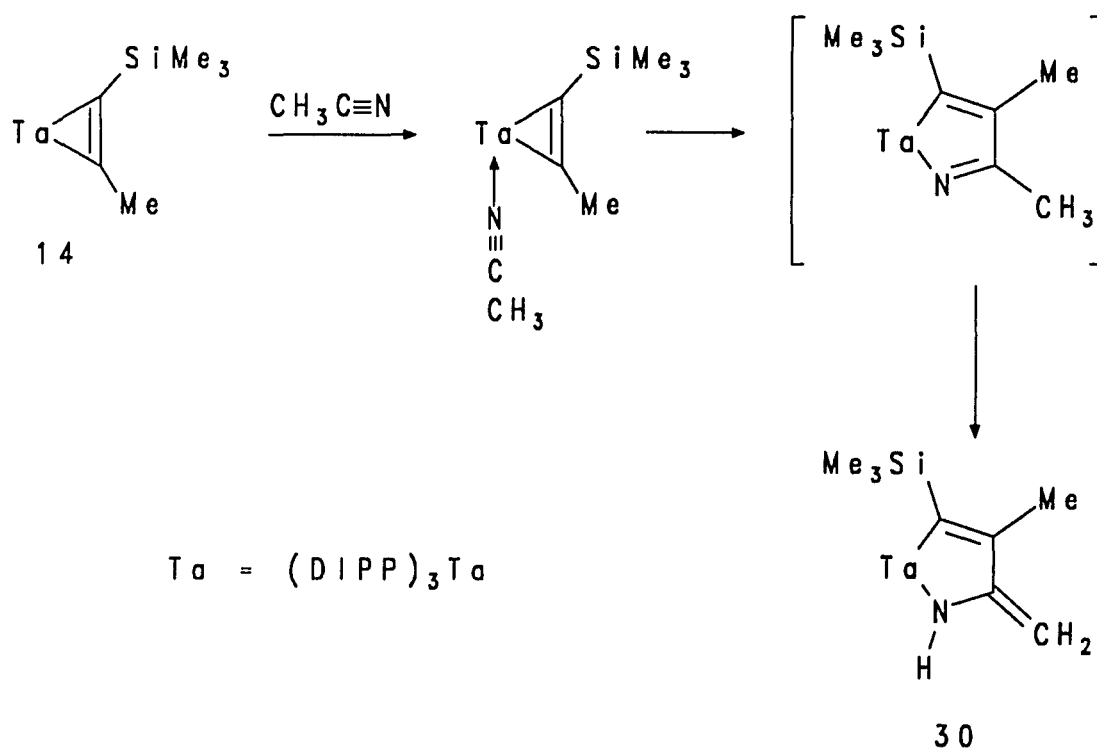


replacement is clearly seen in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the compound. In the  $^1\text{H}$  NMR spectra of **30**, two singlets at  $\delta$  3.90 and 3.56 are attributed to the exo methylene protons. In contrast, the  $^1\text{H}$  NMR spectrum of **31** has only one signal at  $\delta$  4.98. The off-resonance decoupled  $^{13}\text{C}$  NMR spectrum of **31** has a doublet at  $\delta$  59.1 indicative of only one attached proton. Upon reacting the  $\text{Me}_3\text{SiC}\equiv\text{CMe}$  adduct **14** with other nitriles containing  $\alpha$  hydrogens, the metallacycloenamine complexes **32** and **33** are formed (equation 7). The formation of the metallacycloenamine appears to proceed through an intermediate metallacyclic imine complex followed by a 1,3-hydrogen shift from the alkyl group of the original nitrile to the nitrogen atom of the metallacyclic imine (Scheme 4.1). Since an  $\eta^1$ -nitrile adduct of the reaction of **14** and acetonitrile could not be isolated,



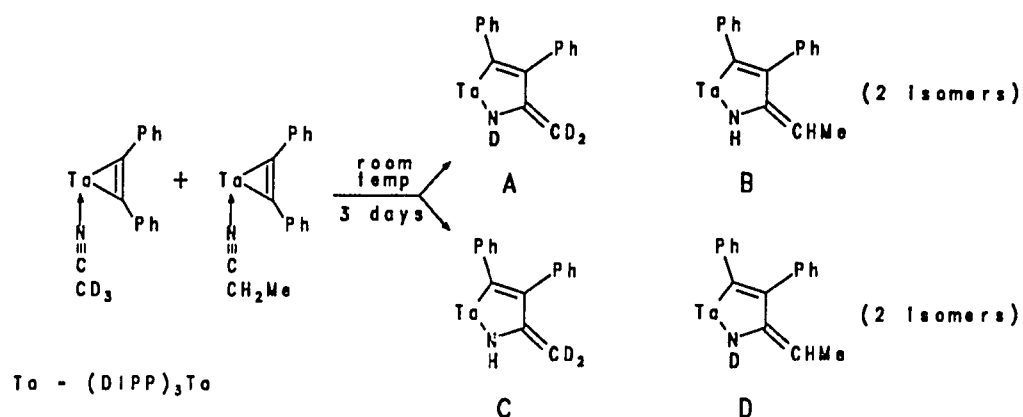
crossover experiments using  $\text{CD}_3\text{C}\equiv\text{N}$  and the  $\text{PhC}\equiv\text{CPh}$  adduct **16** were performed to elucidate whether the tautomerization process is intra- or intermolecular,

**Scheme 4.1**



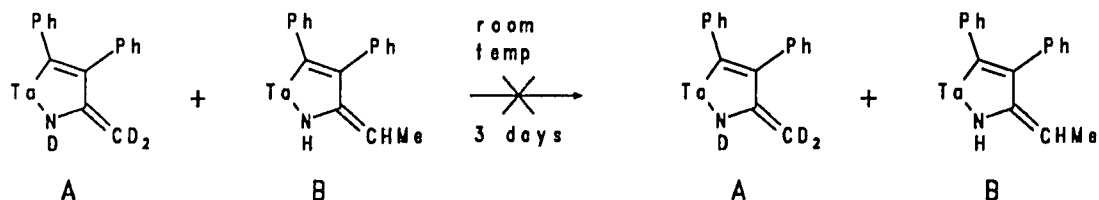
the results of which are outlined in Scheme 4.2.<sup>75</sup> In a control experiment, a 50/50

Scheme 4.2



mixture of **A** and **B** in Et<sub>2</sub>O was allowed to stir for 3 days (Scheme 4.3). No H/D

Scheme 4.3

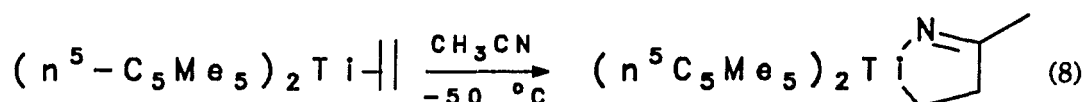


exchange was observed (<sup>1</sup>H NMR) between the two metallacyclic enamines providing evidence for the metallacyclic imine intermediate. The H/D exchange observed in the products in Scheme 4.2 can only be explained if this intermediate undergoes the hydrogen transfer and that the transfer occurs through some *intermolecular* process. Since the metallacycloenamines themselves do not undergo a similar exchange, the hydrogen transfer must occur before they are formed.

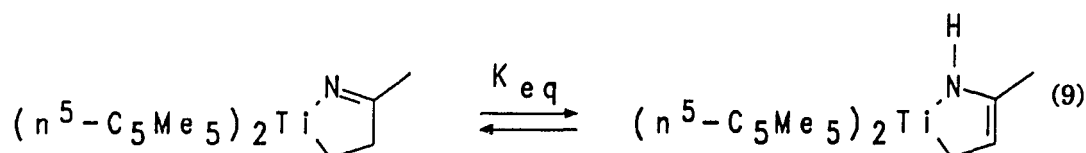
These results differ from those seen by Bercaw using a related titanocene system, (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(η-C<sub>2</sub>H<sub>4</sub>).<sup>80d</sup> Reaction of (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(η-C<sub>2</sub>H<sub>4</sub>) with acetonitrile at -50 °C

produces the metallacycloimine complex  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiN}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2$  (equation 8).

Warming solutions of the metallacycloimine to  $-10\text{ }^\circ\text{C}$  or above results in an equilibrium



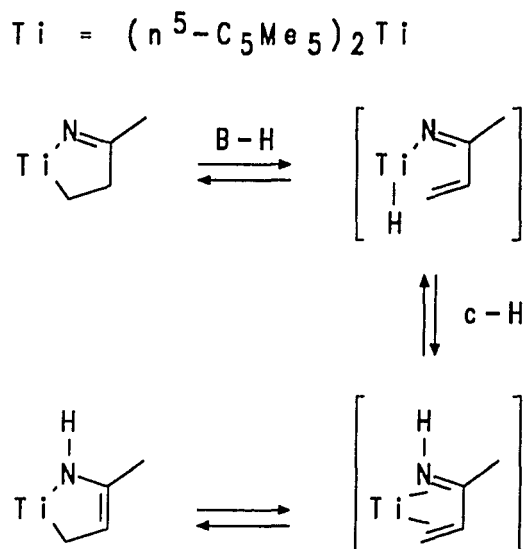
between the metallacycloimine and its metallacycloenamine tautomer (equation 9). From labeling and crossover experiments with  $^{15}\text{N}$ ,  $^{13}\text{C}$ , and  $^2\text{H}$ , the mechanism of this



tautomerization is an *intramolecular* 1,3 hydrogen shift which contrasts with the *intermolecular* process in this tantalum system. This difference between the two systems may be explained by the reversible  $\beta$ -hydrogen eliminations from the  $\beta$ -methylene carbon of the imine and from the  $\alpha$ -nitrogen of the enamine in the titanium system (Scheme 4.4). This type of reaction is not possible in the tantalum system since the ring carbon  $\beta$  to the nitrogen has a methyl group instead of a hydrogen attached to it. Therefore, these tantalum complexes must undergo an intermolecular abstraction of a proton from the alkyl group of another metallacycloenamine molecule.

Another group 4 metallocene system used by Buchwald,  $(\eta^5\text{-C}_5\text{Me}_5)\text{Zr}(\text{benzynes})$ , also couples nitriles to produce azametallacyclopentenes (metallacyclic enamines). These complexes are not observed to undergo any unusual hydrogen shifts. This zirconium

Scheme 4.4



benzyne system also successfully couples *t*-butyl cyanide to form a metallacycle, whereas in my tantalum system only an  $\eta^1$ -nitrile adduct could be formed. However, these zirconacycles are known to dimerize in the solid state (Figure 4.1).<sup>90</sup>

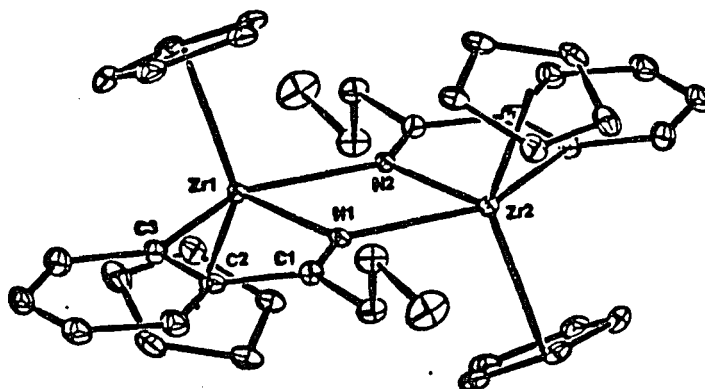


Figure 4.1 ORTEP of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{C}_6\text{H}_4\text{CPr}=\text{N})]_2$ <sup>90</sup>

#### SUMMARY AND CONCLUSIONS

The electrophilic metal center in  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (14) coordinates with

aldehydes, ketones, and nitriles to afford a variety of products. Reaction of **14** with benzaldehyde produced the Meerwein-Ponndorf-Verley hydride transfer product  $(\text{DIPP})_3(\text{PhCH}_2\text{O})\overline{\text{Ta}(\text{C}(\text{SiMe}_3)=\text{CMeCPh}=\text{O})}$  (**28**). Reactions with ketones produced the metallacyclic complexes  $(\text{DIPP})_3\overline{\text{Ta}(\text{C}(\text{SiMe}_3)=\text{CMeC}(\text{RR}')\text{O})}$  (**25**,  $\text{R} = \text{R}' = \text{Ph}$ ; **26**,  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Et}$ ; **27**,  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Ph}$ ) which when hydrolyzed provide alcohols. An  $\eta^1$ -nitrile adduct,  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})(\text{Me}_3\text{CC}\equiv\text{N})$  (**25**), is formed from the reaction of t-butyl cyanide with **14**. Reaction of **14** with nitriles containing  $\alpha$ -hydrogens affords the metallacycloenamines  $(\text{DIPP})_3\overline{\text{Ta}(\text{C}(\text{SiMe}_3)=\text{CMe}(=\text{CHR})\text{NH})}$  (**26**,  $\text{R} = \text{H}$ ; **28**,  $\text{R} = \text{Me}$ ; **29**,  $\text{R} = \text{Ph}$ ) which should yield ketones upon their hydrolysis.

All these reactions proceed in such a way as to produce only one of the possible regioisomers. The driving force for these reactions presumably is the strength of the resulting Ta-O and Ta-N bonds that are formed from the coupling of the heteroatom molecules to the substantially reduced alkyne adduct.

## EXPERIMENTAL

**Preparations.**  $(\text{DIPP})_3\overline{\text{Ta}(\text{CSiMe}_3=\text{CMeCPh}_2\text{O})}$  (**25**). 1.07 g (1.30 mmol) of  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (**14**) was dissolved in 10 mL of diethyl ether and a slight excess of benzophenone (0.26 g, 1.40 mmol) was added. An immediate color change from yellow to red orange was observed upon  $\text{Ph}_2\text{C}=\text{O}$  addition and within 15 min, the solution color had changed back to yellow. The solution was allowed to stir at room temperature for 24 h over which time the white product was observed to precipitate. The white powder (0.61 g, 0.60 mmol, 52% yield) was filtered off, washed with pentane, and dried in vacuo. Analytically pure samples were obtained by recrystallization from  $\text{Et}_2\text{O}$ /pentane solution at  $-40\text{ }^\circ\text{C}$ .  $^1\text{H NMR}(\text{C}_6\text{D}_6)$ :  $\delta$  7.28-6.95 (m, 21 H,  $\text{H}_{\text{aryl}}$  (DIPP) and  $\text{C}_6\text{H}_5$ ), 3.49 (spt, 6 H,  $\text{CHMe}_2$ ), 2.21 (s, 3 H,  $\text{C}_\beta\text{Me}$ ), 1.09 (d, 36 H,  $\text{CHMe}_2$ ), 0.13 (s, 9 H,  $\text{C}_\alpha\text{SiMe}_3$ ).  $^{13}\text{C}$

NMR( $C_6D_6$ ):  $\delta$  207.5 ( $C_\alpha$ ), 174.3 ( $C_\beta$ ), 157.0 ( $C_{ipso}$  DIPP), 147.5 ( $C_{ipso}$   $C_6H_5$ ), 138.3 ( $C_o$ , DIPP), 128.3, 128.2, 126.9 ( $C_o$ ,  $C_p$ ,  $C_m$ ,  $C_6H_5$ ), 123.9, 123.8 ( $C_p$ ,  $C_m$ , DIPP), 109.8 ( $C_\gamma$ ), 27.7 ( $CHMe_2$ ), 24.8 ( $C_\beta Me$ ), 24.4 ( $CHMe_2$ ), 2.1 ( $SiMe_3$ ); IR: 1580 m, 1532 w, 1312 br,m, 1175 s, 1105 br,m, 1076 sh,m, 1036 m, 1022 sh,w, 982 w, 960 w, 915 m, 898 m, 886 m, 868 w, 843 br,m, 825 sh,w, 788 w, 772 w, 692 m, 638 w; Anal. Calcd. for  $C_{55}H_{73}SiO_4Ta$ : C, 65.59; H, 7.30. Found: C, 65.00; H, 7.28.

$(DIPP)_3Ta(\overline{CSiMe_3=CMeC(Me)EtO})$  (26). To a  $-40$  °C solution of 0.45 g (0.55 mmole) of  $(DIPP)_3Ta(Me_3SiC\equiv CMe)$  (14) in 10 mL of diethyl ether was added 0.05 mL (0.56 mmole) of methyl ethyl ketone. An immediate color change from yellow to white was observed. The solution was allowed to stir 24 h at room temperature after which the solvent was removed in vacuo producing an oil. The oil was reconstituted in pentane and white microcrystals immediately precipitated out. The white crystals (0.17 g, 0.19 mmole, 35% yield) were filtered off, washed with a minimal volume of cold pentane, and dried in vacuo. The product was sufficiently pure for analyses but could be recrystallized from  $Et_2O$ /pentane at  $-40$  °C.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  7.09-6.90 (m, 9 H,  $H_{aryl}$ ), 3.63 (spt 6 H,  $CHMe_2$ ), 1.72 (s, 3 H,  $C_\beta Me$ ), 1.65, 1.50 (m, 1 H each,  $C_\gamma CH_2CH_3$ ), 1.33 (s, 3 H,  $C_\gamma Me$ ), 1.25, 1.16 (d, 18 H each  $CHMe_2$ ), 0.74 (t, 3 H,  $C_\gamma CH_2CH_3$ ), 0.14 (s, 9 H,  $SiMe_3$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  199.0 ( $C_\alpha$ ), 178.1 ( $C_\beta$ ), 156.8 ( $C_{ipso}$ ), 138.4 ( $C_o$ ), 123.7 ( $C_m$ ), 123.6 ( $C_p$ ), 105.4 ( $C_\gamma$ ), 33.4 ( $C_\gamma Me$ ), 27.2 ( $CHMe_2$ ), 25.0 ( $C_\gamma CH_2CH_3$ ), 24.4 ( $CHMe_2$ ), 20.8 ( $C_\beta Me$ ), 8.2 ( $C_\gamma CH_2CH_3$ ), 2.2 ( $SiMe_3$ ). IR: 1578 w, 1549 w, 1320 m, 1297 w, 1248 s, 1183 s, 1153 m, 1101 m, 1054 w, 1038 m, 1002 w, 982 m, 928 m, 912 s, 900 s, 888 s, 872 m, 842 s, 828 s, 800 w, 787 m, 742 s, 710 m, 695 m, 672 w. Anal. Calcd. for  $C_{46}H_{71}O_4SiTa$ : C, 61.59; H, 7.98. Found: C, 61.23; H, 8.17.

$(DIPP)_3Ta(\overline{CSiMe_3=CMeC(Me)PhO})$  (27). To a  $-40$  °C solution of 0.45 g (0.55

mmole) of  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (**14**) in 10 mL of diethyl ether was added 0.07 mL (0.60 mmole) of acetophenone. An immediate color change from yellow to orange red was observed upon acetophenone addition and within seconds the solution color changed to pale yellow. The solution was allowed to stir 24 h at room temperature after which the solvent was removed in vacuo to afford a pale yellow oil. The oil was reconstituted in pentane and cooled to  $-40\text{ }^\circ\text{C}$ . Off white crystals (0.20 g, 0.21 mmole, 38% yield) were filtered off, washed with a minimal volume of cold pentane, and dried in vacuo.

Analytically pure samples were obtained by recrystallization from pentane at  $-40\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.38 (d, 2 H,  $\text{H}_o$   $\text{C}_6\text{H}_5$ ), 7.11-6.89 (m, 12 H,  $\text{H}_{\text{aryl}}$  DIPP and  $\text{H}_m$ ,  $\text{H}_p$   $\text{C}_6\text{H}_5$ ), 3.58 (spt, 6 H,  $\text{CHMe}_2$ ), 2.02 (s, 3 H,  $\text{C}_\beta\text{Me}$ ), 1.72 (s, 3 H,  $\text{C}_\gamma\text{Me}$ ), 1.18, 1.11 (d, 18 H each,  $\text{CHMe}_2$ ), 0.11 (s, 9 H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  202.1 ( $\text{C}_\alpha$ ), 176.0 ( $\text{C}_\beta$ ), 156.8 ( $\text{C}_{\text{ipso}}$  DIPP), 147.3 ( $\text{C}_{\text{ipso}}$   $\text{C}_6\text{H}_5$ ), 138.5 ( $\text{C}_o$  DIPP), 128.2, 126.7, 125.9 ( $\text{C}_o$ ,  $\text{C}_p$ ,  $\text{C}_m$   $\text{C}_6\text{H}_5$ ), 123.8 ( $\text{C}_m$ ,  $\text{C}_p$  DIPP), 105.0 ( $\text{C}_\gamma$ ), 32.3 ( $\text{C}_\gamma\text{Me}$ ), 27.5 ( $\text{CHMe}_2$ ), 24.5, 24.3 ( $\text{CHMe}_2$ ), 22.8 ( $\text{C}_\beta\text{Me}$ ), 2.1 ( $\text{SiMe}_3$ ). IR: 1684 m, 1586 w, 1318 m, 1243 s, 1180 s, 1096 m, 1080 sh, 1067 sh, 1038 m, 1023 w, 985 w, 942 m, 902 s, 866 m, 839 s, 802 w, 787 m, 743 s, 721 m, 710 m, 695 m. Anal. Calcd. for  $\text{C}_{50}\text{H}_{71}\text{O}_4\text{SiTa}$ : C, 63.54; H, 7.57. Found: C, 64.09; H, 8.04.

$(\text{DIPP})_3(\text{PhCH}_2\text{O})\overline{\text{Ta}(\text{CSiMe}_3=\text{CMeCPh}=\text{O})}$  (**28**). 0.87 g (1.05 mmol) of  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (**14**) was dissolved in 10 mL of diethyl ether. Benzaldehyde (0.24 mL, 2.32 mmol) was added and the mixture was stirred at room temperature overnight (ca. 24 h), over which time the solution color changed to red orange. The solvent was removed in vacuo to provide a red orange oil. The oil was reconstituted in pentane (ca. 8 mL) and upon cooling this solution to  $-40\text{ }^\circ\text{C}$ , 0.41 g (0.40 mmol, 34% yield) of red orange, crystalline product was obtained. Analytically pure samples were obtained by recrystallization from pentane at  $-40\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR( $\text{C}_6\text{D}_6$ ):  $\delta$  7.67 (d, 2 H,  $\text{H}_o$   $\text{C}_\gamma(\text{C}_6\text{H}_5)$ ), 7.28-6.84 (m, 17 H,  $\text{H}_{\text{aryl}}$ )

DIPP and  $H_m$  and  $H_p$   $C_\gamma(C_6H_5)$ , 6.30 (s, 2 H,  $OCH_2C_6H_5$ ), 3.91 (spt, 2 H,  $CHMe_2$ ), 3.55 (spt, 4 H,  $CHMe_2$ ), 1.92 (s, 3 H,  $C_\beta Me$ ), 1.17 (d, 12 H,  $CHMe_2$ ), 1.15 (d, 12 H,  $CHMe_2$ ), 0.95 (d, 12 H,  $CHMe_2$ ), 0.37 (s, 9 H,  $SiMe_3$ ).  $^{13}C$  NMR( $C_6D_6$ ):  $\delta$  208.0 ( $C_\alpha$ ), 205.9 ( $C_\beta$ ), 156.9, 156.6 ( $C_{ipso}$ , DIPP), 150.8 ( $C_\gamma$ ), 140.6 ( $C_{ipso}$   $OCH_2C_6H_5$ ), 139.7, 138.7 ( $C_o$ , DIPP), 137.2 ( $C_{ipso}$   $C_\gamma(C_6H_5)$ ), 132.6, 129.1, 128.7 ( $C_p$ ,  $C_o$ ,  $C_m$   $C_\gamma(C_6H_5)$ ), 128.5, 127.8, 126.5 ( $C_o$ ,  $C_p$ ,  $C_m$   $OCH_2(C_6H_5)$ ), 123.7, 123.3 ( $C_p$ , DIPP), 122.5, 121.8, ( $C_m$ , DIPP), 77.5 ( $OCH_2(C_6H_5)$ ), 26.6, 25.1 ( $CHMe_2$ ), 24.6, 24.2 ( $CHMe_2$ ), 23.9 ( $C_\beta Me$ ), 2.8 ( $C_\alpha SiMe_3$ ); IR: 1591 m, 1538 m, 1320 s, 1300 w, 1270 m, 1268 sh, 1250 s, 1190 s, 1122 m, 103 w, 1086 w, 1053 m, 1038 w, 1020 w, 992 w, 978 s, 916 w, 903 m, 890 m, 882 m, 858 m, 842 m, 826 m, 785 s, 751 sh, 742 s, 727 w, 706 m, 691 m, 628 w, 608 w; Anal. Calcd. for  $C_{56}H_{75}SiO_5Ta$ : C, 64.84; H, 7.29. Found C, 64.88; H, 7.34.

**(DIPP) $_3$ Ta(Me $_3$ SiC $\equiv$ CMe)(N $\equiv$ CCMe $_3$ ) (29).** To a solution of 0.58g (0.70 mmol) of (DIPP) $_3$ Ta(Me $_3$ SiC $\equiv$ CMe) (14) in 10 mL of diethyl ether was added 0.10 mL (0.91mmol) of trimethylacetone nitrile. The solution underwent a color change from yellow to yellow orange in a few min. The solution was allowed to stir for 24 h at room temperature. The solvent was removed in vacuo producing a yellow, frothy oil which was reconstituted in pentane and cooled to -40 °C for 12 h. Pale yellow, needlelike crystals (0.24g, 0.26 mmol, 38% yield, 2 crops) were filtered off, washed with a minimal volume of cold pentane, and dried in vacuo. The product was sufficiently pure for analyses but could be recrystallized from pentane at -40 °C.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  7.13-6.89 (m, 9 H,  $H_{aryl}$ ), 3.51 (spt, 6 H,  $CHMe_2$ ), 2.77 (s, 3 H,  $C_{alkyne}Me$ ), 1.23 (d, 36 H,  $CHMe_2$ ), 0.50 (s, 9 H,  $NCCMe_3$ ), 0.23 (s, 9 H,  $SiMe_3$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  222.6, 197.1 ( $C_{alkyne}$ ), 159.1 ( $C_{ipso}$ ), 138.0 ( $C_o$ ), 132.5 ( $NCCMe_3$ ), 123.2 ( $C_p$ ), 121.2 ( $C_m$ ), 28.5 ( $NCCMe_3$ ), 27.0 ( $CHMe_2$ ), 26.8 ( $NCCMe_3$ ), 24.3 ( $CHMe_2$ ), 22.5 ( $C_{alkyne}Me$ ), 0.80 ( $SiMe_3$ ). IR: 2264 w, 1607 m, 1580 m, 1430 sh, 1320 s,

1248 s, 1190 s, 1104 m, 1088 m, 1037 m, 1000 w, 928 w, 883 s, 861 s, 840 m, 825 m, 785 m, 743 s, 692 s. Anal. Calcd. for  $C_{47}H_{72}NO_3SiTa$ : C, 62.22; H, 7.99. Found: C, 61.89; H, 7.75.

**(DIPP)<sub>3</sub>Ta(CSiMe<sub>3</sub>=CMeC(=CH<sub>2</sub>)NH) (30).** To a solution of 0.90 g (1.1 mmol) of (DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) (14) in 10 mL of diethyl ether was added 0.30 mL (0.57 mmol) of acetonitrile. The solution was allowed to stir for 24 h at room temperature after which time the solvent was removed in vacuo producing a yellow, frothy oil. The oil was reconstituted in 3 mL of diethyl ether and 3.5 mL of MeCN. Pale yellow crystals started to form immediately. The solution was cooled to -40 °C to complete crystallization. The crystals (0.52 g, 0.60 mmol, 63.4% yield) were filtered off, washed with a minimal volume of cold MeCN, and dried in vacuo. The product was sufficiently pure for analyses but could be recrystallized from Et<sub>2</sub>O/MeCN at -40 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, 263K): δ 7.37 (s, 1 H, NH), 7.08-6.93 (m, 9 H, H<sub>aryl</sub>), 3.90, 3.56 (s, 1 H each, C=CH<sub>2</sub>), 3.88, 3.65, 2.95 (spt, 2 H each, CHMe<sub>2</sub>), 1.98 (s, 3 H, C<sub>β</sub>Me), 1.38, 1.34, 1.24, 1.21 (d, 6 H each, CHMe<sub>2</sub>), 0.90 (br d, 12 H, CHMe<sub>2</sub>), 0.29 (s, 9 H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, 263K): δ 208.5 (C<sub>α</sub>), 167.2 (C<sub>β</sub>), 159.5, 157.0, 156.6 (C<sub>ipso</sub>), 153.2 (C<sub>γ</sub>), 139.7, 138.7, 137.5 (C<sub>o</sub>), 124.0 (C<sub>p</sub>), 123.6 (C<sub>m</sub>), 90.6 (C<sub>γ</sub>=CH<sub>2</sub>), 27.5, 27.4, 27.2 (CHMe<sub>2</sub>), 24.8, 24.7, 24.0, 23.7 (CHMe<sub>2</sub>), 20.2 (C<sub>β</sub>Me), 2.0 (SiMe<sub>3</sub>). IR: 3320 w, 1583 m, 1515 w, 1320 m, 1300 sh, 1252 br s, 1180 s, 1140 m, 1090 m, 1050 w, 1035 m, 994 w, 976 w, 926 w, 897 m, 888 sh, 870 sh, 847 m, 830 m, 803 w, 783 m, 740 s, 696 m. Anal. Calcd. for  $C_{44}H_{66}NO_3SiTa$ : C, 61.02; H, 7.68; N, 1.62. Found: C, 61.10; H, 7.61; N, 1.64.

**(DIPP)<sub>3</sub>Ta(C(SiMe<sub>3</sub>)=CMeC(=CHI)NH) (31).** To a -40 °C solution of 0.65 g (0.75 mmol) of (DIPP)<sub>3</sub>Ta(CSiMe<sub>3</sub>=CMeC(=CH<sub>2</sub>)NH) (26) in 10 mL of diethyl ether was added 0.18 g of I<sub>2</sub> (0.71 mmol). The pale yellow solution immediately changed color to dark red

brown. The solution was allowed to stir for 24 h at room temperature after which the solvent was removed in vacuo producing a frothy oil. The oil was reconstituted in Et<sub>2</sub>O/MeCN (ca. 1:3) and upon cooling to -40 °C, golden yellow crystals formed. The crystals (0.24 g, 0.24 mmol, 32% yield) were filtered off, washed with a minimal volume of cold MeCN, and dried in vacuo. The product was sufficiently pure for analyses but could be recrystallized from Et<sub>2</sub>O/MeCN at -40 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.74 (s, 1 H, NH), 7.07-6.91 (m, 9 H, H<sub>aryl</sub>), 4.98 (s, 1 H, C=CHI), 3.86, 3.60, 2.95 (spt, 2 H each, CHMe<sub>2</sub>), 1.83 (s, 3 H, C<sub>β</sub>Me), 1.36, 1.20 (d, 12 H each, CHMe<sub>2</sub>), 0.95 (br s, 12 H, CHMe<sub>2</sub>), 0.27 (s, 9 H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 208.7 (s, C<sub>α</sub>), 167.8 (s, C<sub>β</sub>), 157.0 (s, C<sub>ipso</sub>), 155.9 (s, C<sub>γ</sub>), 139.6, 138.7, 137.5 (s, C<sub>o</sub>), 124.2, 124.0 (d, C<sub>p</sub>), 123.7, 123.6 (d, C<sub>m</sub>), 59.1 (d, C=CHI), 27.4, 26.8 (d, CHMe<sub>2</sub>), 24.8, 23.8, 23.5 (q, CHMe<sub>2</sub>), 20.0 (s, C<sub>β</sub>), 1.9 (q, SiMe<sub>3</sub>). IR: 3282 m, 1579 w, 1556 m, 1510 br w, 1337 s, 1291 w, 1243 s, 1179 s, 1138 sh, 1085 s, 1052 w, 1035 m, 990 m, 926 w, 899 s, 885 sh, 862 s, 838 s, 795 w, 784 m, 741 s, 692 m, 677 w, 668 sh, 643 w, 617 m. Anal. Calcd. for C<sub>44</sub>H<sub>65</sub>INO<sub>3</sub>SiTa: C, 53.28; H, 6.60; I, 12.79. Found: C, 53.33; H, 6.77; I, 12.82.

(DIPP)<sub>3</sub>Ta(CSiMe<sub>3</sub>=CMeC(=CHMe)NH) (32). To a -40 °C solution of 0.50 g (0.61 mmole) of (DIPP)<sub>3</sub>Ta(Me<sub>3</sub>SiC≡CMe) (14) in 10 mL of diethyl ether was added 0.10 mL (1.40 mmole) of propionitrile. The solution was allowed to stir 24 h at room temperature after which the solvent was removed in vacuo producing a pale yellow solid. The solid was dissolved in a minimal volume of pentane and cooled to -40 °C. Pale yellow crystals (0.12 g, 0.14 mmole, 23 % yield) were filtered off, washed with a minimal volume of cold pentane, and dried in vacuo. The product was sufficiently pure for analyses but could be recrystallized from pentane at -40 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.56 (s, 1 H, NH), 7.10-6.92 (m, 9 H, H<sub>aryl</sub>), 4.37 (q, 1 H, C=CHCH<sub>3</sub>), 3.92, 3.71, 2.99 (br, 2 H each, CHMe<sub>2</sub>), 1.99 (s, 3 H,

$C_{\beta}Me$ ), 1.42 (d, 3 H,  $C=CHCH_3$ ), 1.38, 1.24, 0.92 (br, 12 H each,  $CHMe_2$ ), 0.33 (s, 9 H,  $SiMe_3$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  207.1 ( $C_{\alpha}$ ), 161.5 ( $C_{\beta}$ ), 160.2, 157.1 ( $C_{ipso}$ ), 154.1 ( $C_{\gamma}$ ) 139.7, 139.0, 137.7 ( $C_o$ ), 124.1, 123.9, 123.6 ( $C_m$  and  $C_p$ ), 100.7 ( $C_{\gamma}=CH(Me)$ ), 27.4 ( $CHMe_2$ ), 26.8, 24.8, 23.6 ( $CHMe_2$ ), 19.7 ( $C_{\beta}Me$ ), 11.3 ( $C=CHMe$ ), 2.1 ( $SiMe_3$ ). IR: 1614 w, 1578 w, 1512 m, 1320 s, 1300 sh, 1242 s, 1182 s, 1132 w, 1106 m, 1092 m, 1055 m, 1038 m, 997 w, 950 vw, 928 m, 898 s, 873 s, 847 s, 799 w, 788 m, 743 s, 720 vw, 703 m, 698 m. Anal. Calcd. for  $C_{45}H_{68}O_3NSiTa$ : C, 60.88; H, 7.89; N, 1.61. Found: C, 61.90; H, 8.19; N, 1.59.

(DIPP) $_3$ Ta( $\overline{SiMe_3C=CMeC(=CHPh)NH}$ ) (33). To a -40 °C solution of 0.96 g (1.17 mmole) of (DIPP) $_3$ Ta( $Me_3SiC\equiv CMe$ ) (14) in 10 mL of diethyl ether was added 0.14 mL (1.21 mmole) of benzyl cyanide. The solution underwent a color change from yellow to bright yellow over the course of 1 h. The solution was allowed to stir for 4 h at room temperature after which the solvent was removed in vacuo to produce a yellow oil. The oil was reconstituted in pentane and cooled to -40 °C. Bright yellow crystals (0.61 g, 0.65 mmole, 56% yield, 2 crops) were filtered off, washed with a minimal volume of cold pentane, and dried in vacuo. The product was sufficiently pure for analyses but could be recrystallized from pentane at -40 °C.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  8.52 (s, 1 H, NH), 7.08-6.80 (m, 14 H,  $H_{aryl}$  and  $C_6H_5$ ), 5.50 (s, 1H,  $C=CHPh$ ), 3.92, 3.73, 2.94 (spt, 2 H each,  $CHMe_2$ ), 2.12 (s, 3 H,  $C_{\beta}Me$ ), 1.38 (br, 12 H,  $CHMe_2$ ), 1.24, 1.20 (d, 6 H each,  $CHMe_2$ ), 0.79 (d, 12 H,  $CHMe_2$ ), 0.35 (s, 9 H,  $SiMe_3$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  209.4 ( $C_{\alpha}$ ), 161.1 ( $C_{\beta}$ ), 157.1 ( $C_{ipso}$  DIPP), 154.0 ( $C_{\gamma}$ ), 139.7, 138.8, 137.6 ( $C_o$  DIPP), 137.3 ( $C_{ipso}$   $C_6H_5$ ), 128.9, 128.6 ( $C_m$  and  $C_p$   $C_6H_5$ ), 125.8 ( $C_o$   $C_6H_5$ ), 124.1, 123.8, 123.6, ( $C_m$  and  $C_p$  DIPP), 106.2 ( $C_{\gamma}=CHPh$ ), 27.5, 27.4 ( $CHMe_2$ ), 26.9, 24.8, 23.9, 23.7 ( $CHMe_2$ ), 20.2 ( $C_{\beta}Me$ ), 2.2 ( $SiMe_3$ ). IR: 3342 w, 1592 w, 1515 w, 1348 w, 1320 s, 1256 sh, 1246 sh, 1239 s, 1183 s, 1092 s, 1054 vw, 1038 w, 992 w, 928 sh, 912 sh, 902 s, 890 m, 878 w, 855 s, 832s, 796 w, 788 m, 743 s, 710 w, 696 m,

667 vw, 633 m, 622 m. Anal. Calcd. for  $C_{50}H_{70}O_3NSiTa$ : C, 63.95; H, 7.51; N, 1.49.

Found: C, 63.87; H, 7.75; N, 1.53.

**CHAPTER 5**  
**PREPARATION, PROPERTIES, AND BONDING ANALYSIS**  
**OF TANTALUM (II)  $\eta^6$ -ARENE COMPLEXES**

**INTRODUCTION**

Arene complexes of the transition metals<sup>91,92</sup> have proven essential to the understanding of aromatic C-H bond activation,<sup>93,94</sup> arene hydrogenation<sup>95-97</sup> and exchange reactions,<sup>98,99</sup> and alkyne cyclotrimerization chemistry.<sup>100-102</sup> Well-categorized examples of ( $\eta^6$ -arene)ML<sub>2</sub> complexes<sup>92</sup> are typically restricted to late transition metal, 18 electron species as exemplified by [( $\eta^6$ -arene)RhL<sub>2</sub>]<sup>+</sup>,<sup>103</sup> ( $\eta^6$ -arene)RuL<sub>2</sub>,<sup>104</sup> ( $\eta^6$ -arene)FeL<sub>2</sub>,<sup>105</sup> and ( $\eta^6$ -arene)NiR<sub>2</sub>.<sup>106</sup> While "electron deficient" arenes are well-known, particularly in the early metals,<sup>107</sup> the only electron deficient late transition metal ( $\eta^6$ -arene)ML<sub>2</sub> species seem to be the 17 electron ( $\eta^6$ -arene)CoR<sub>2</sub> derivatives.<sup>108</sup>

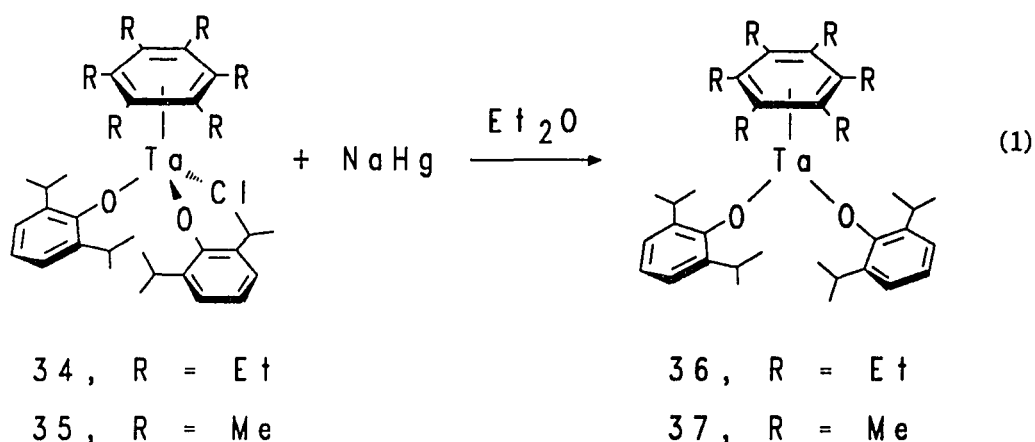
Tantalum (III) arenes of the form ( $\eta^6$ -C<sub>6</sub>R<sub>6</sub>)Ta(OR)<sub>2</sub>Cl<sup>7,44</sup> had been prepared and it was discovered that they undergo a facile one-electron reduction to afford the paramagnetic tantalum (II) complexes ( $\eta^6$ -C<sub>6</sub>R<sub>6</sub>)Ta(OR)<sub>2</sub>.<sup>109</sup> Since the electron count at the metal center is a nominal 13 electrons, these molecules represent extremely electron deficient ( $\eta^6$ -arene)ML<sub>2</sub>-type complexes. Further interest in these species arises since the arene ligand was assembled at the metal center by alkyne cyclization chemistry<sup>100-102,110</sup> and since they represent rare examples of tantalum (II) organometallics.<sup>111</sup> The molecular structure of one of these species, ( $\eta^6$ -C<sub>6</sub>Et<sub>6</sub>)Ta(DIPP)<sub>2</sub> (DIPP = 2,6-diisopropylphenoxide), has been determined and is shown to exhibit some unusual structural properties. A collaboration with Thomas A. Albright and John B. Koeiner at the University of Houston was undertaken to perform molecular orbital calculations at the extended Hückel and ab initio level on ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)Ta(OH)<sub>2</sub> which were used to investigate the bonding and

geometric distortions for these molecules.

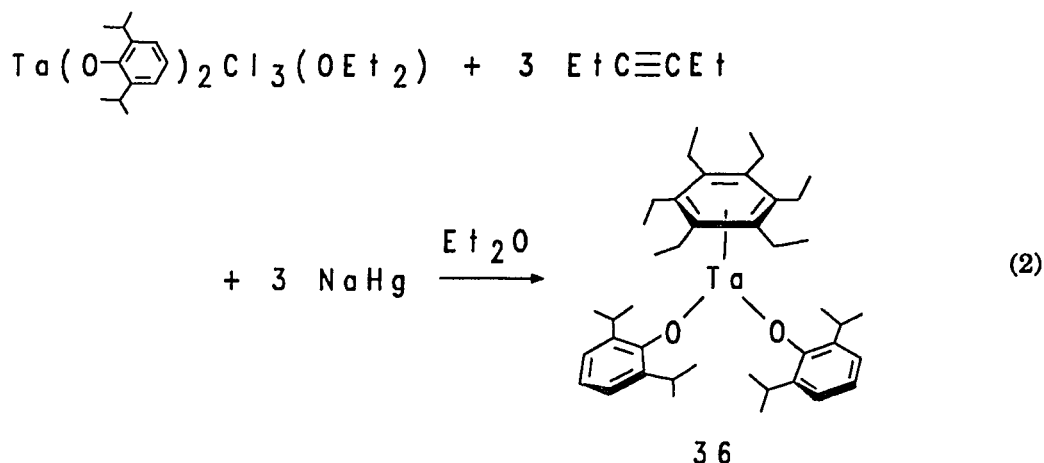
## RESULTS AND DISCUSSION

### Synthesis and Reactivity of Tantalum (II) Arene Complexes.

$\text{Ta}(\text{DIPP})_2\text{Cl}_3(\text{OEt}_2)$  (DIPP = 2,6-diisopropylphenoxide) can be reduced by two electrons in the presence of  $\text{RC}\equiv\text{CR}$  ( $\text{R} = \text{Me}, \text{Et}$ ) to afford the blue tantalum (III) arene complexes ( $\eta^6\text{-C}_6\text{R}_6$ ) $\text{Ta}(\text{DIPP})_2\text{Cl}$  (**34**,  $\text{R} = \text{Et}$ ; **35**,  $\text{R} = \text{Me}$ ). As outlined in equation 1, both ( $\eta^6\text{-C}_6\text{R}_6$ ) $\text{Ta}(\text{DIPP})_2\text{Cl}$  compounds may be reduced further by one electron to provide the paramagnetic tantalum (II) monomers, ( $\eta^6\text{-C}_6\text{R}_6$ ) $\text{Ta}(\text{DIPP})_2$  (**36**,  $\text{R} = \text{Et}$ ; **37**,  $\text{R} = \text{Me}$ ) in good yield. ( $\eta^6\text{-C}_6\text{Et}_6$ ) $\text{Ta}(\text{DIPP})_2$  (**36**) can be crystallized as maroon crystals in



66% yield from cold pentane solutions. Since this hexaethylbenzene derivative is available in higher yield and is easier to isolate and purify than ( $\eta^6\text{-C}_6\text{Me}_6$ ) $\text{Ta}(\text{DIPP})_2$  (**37**), most of the reactivity studies (vide infra) were performed with **36** rather than **37**. Alternatively, **36** can be prepared directly from  $\text{Ta}(\text{DIPP})_2\text{Cl}_3(\text{OEt}_2)$  upon its reduction by three electrons in the presence of  $\text{EtC}\equiv\text{CEt}$ , (equation 2). The intermediate blue color in this reaction as well as the results of reaction 1 leave little doubt as to the intermediacy of



$(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2\text{Cl}$  (**34**) in equation 2.

Magnetic moment measurements (Evans method<sup>112</sup>) on solutions of **36** and **37** yield values for  $\mu_{\text{eff}}$  of around  $2.1 \mu_{\text{B}}$  for both compounds, which suggests the  $d^3$  metal centers contain one unpaired electron with an orbital contribution to the moment.  $(\eta^6\text{-C}_6\text{Et}_6)\text{-Ta}(\text{DIPP})_2$  (**36**) exhibits an ESR signal (X-band, toluene solution) at room temperature ( $\langle g \rangle = 2.01$ , peak to peak separation = 2200 G), although hyperfine coupling to  $^{181}\text{Ta}$  ( $I = 7/2$ , 99.988% abundant) was not resolved. This behavior of compound **36** can be contrasted to that of  $d^3 \text{TaCl}_2(\text{PMe}_3)_4$  which is ESR silent<sup>113</sup> and  $\text{TaCl}_2(\text{dmpe})_2$ , the ESR signal of which shows well resolved hyperfine structure under similar experimental conditions.<sup>114,115</sup> Hyperfine coupling in **36** becomes apparent at low temperature (frozen toluene soln,  $-196^\circ\text{C}$ ), and a small  $g$  anisotropy is observed; overlapping  $g$  values complicate the spectrum, but  $\langle g_{\text{avg}} \rangle \approx 1.94$  and  $\langle a \rangle_{\text{Ta}} \approx 220 \text{ G}$ .  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2$  is quite easily oxidized as is evident from a cyclic voltammetry experiment. Scanning through an irreversible oxidation wave at  $E_{\text{p,a}} = -0.58 \text{ V vs. Ag/AgCl}$  (THF solution containing  $0.1 \text{ M n-Bu}_4\text{PF}_6$  as supporting electrolyte) gives rise to several irreversible, ill-defined electrochemical processes, most likely reflecting the instability of the resulting

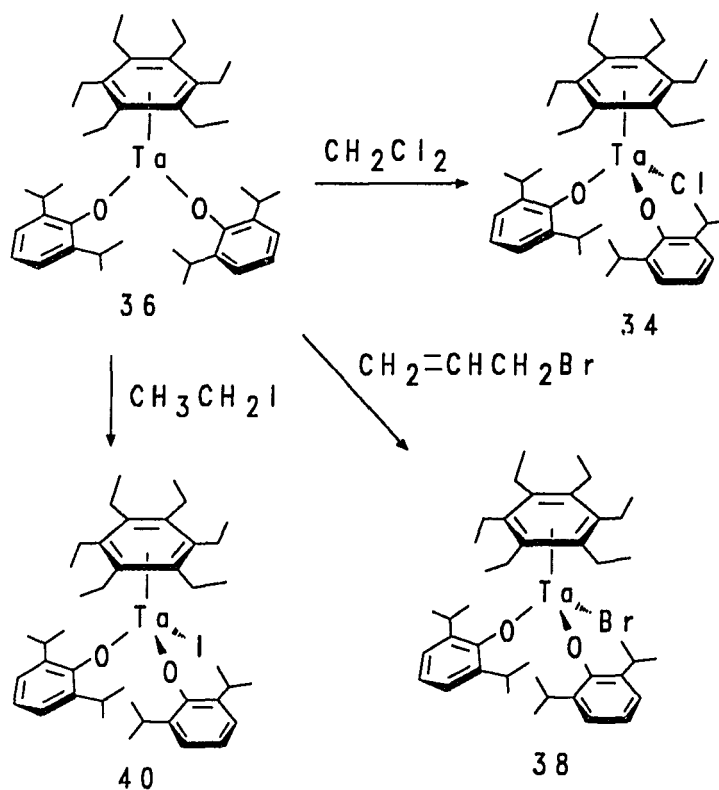
cation under the experimental conditions, perhaps including the reaction of this cation with unoxidized **36**. This remarkably accessible oxidation can be compared to that of the tantalum (III) compound  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{DIPP})_2\text{Cl}$  (**35**) which oxidizes at  $E_{p,a} = + 0.10$  V vs Ag/AgCl.<sup>116</sup> Accordingly,  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2$  can be oxidized with  $\text{PCl}_5$  in  $\text{Et}_2\text{O}$  solution to afford the starting complex  $\text{Ta}(\text{DIPP})_2\text{Cl}_3(\text{OEt}_2)$  along with  $\text{C}_6\text{Et}_6$  in near quantitative yields.

Paramagnetic  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2$  (**36**) is much more stable thermally than its diamagnetic tantalum (III) analogues.<sup>110</sup> Although they are exceedingly air and moisture sensitive, solutions of **36** remain intact for months when stored under  $\text{N}_2$  at room temperature. We anticipated that **36** would be highly reactive towards one-electron oxidants. However, few reactions were discovered of any synthetic utility. The principal reaction pathway involved the labilization of the  $\text{C}_6\text{Et}_6$  ring in reactions from which no tractable organometallic products were isolated. Examples include the reactions of **36** with 1 equiv of  $\text{NO}(\text{g})$  and the photolysis of **36** with  $\text{Me}_3\text{COOCMe}_3$ . The attempted thermal reactions of **36** with *t*-butyl peroxide gave no reaction.

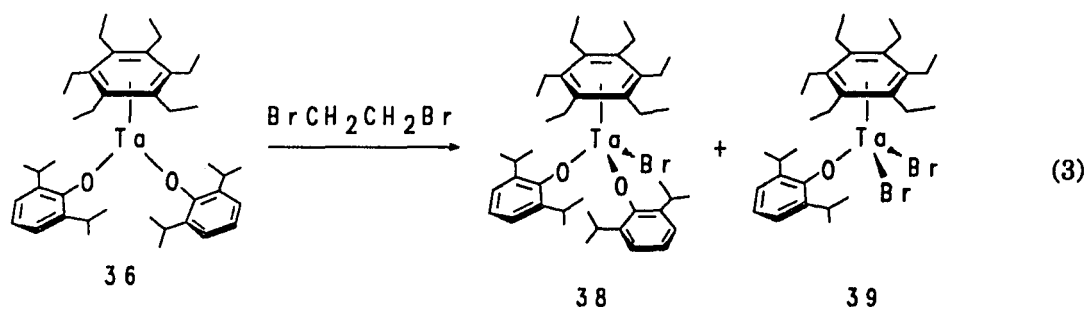
Scheme 5.1 outlines the one-electron oxidative addition reaction of  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2$  (**36**) with alkyl and allyl halides to afford the tantalum (III) products  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2\text{X}$  (**34**, X = Cl; **38**, X = Br; **40**, X = I). An immediate reaction ensues between **36** and  $\text{CH}_2=\text{CHCH}_2\text{Br}$  to afford moderate yields of blue  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2\text{Br}$  (**38**), Scheme 5.1. The same product is obtained upon reaction of **36** with other organic bromides, e.g.  $\text{CH}_2\text{Br}_2$ ,  $\text{BrCH}_2\text{CH}_2\text{Br}$ , and  $\text{CH}_3\text{CHBr}_2$ , but in each of these cases, the product is contaminated with varying amounts of a diamagnetic green product. The reaction conditions can be manipulated to optimize the yield of this product. Thus, when 10 equiv of 1,2-dibromoethane are reacted with **36** for 15 min, a green, crystalline

compound which we formulate as the tantalum (III) dibromide complex ( $\eta^6$ -

Scheme 5.1



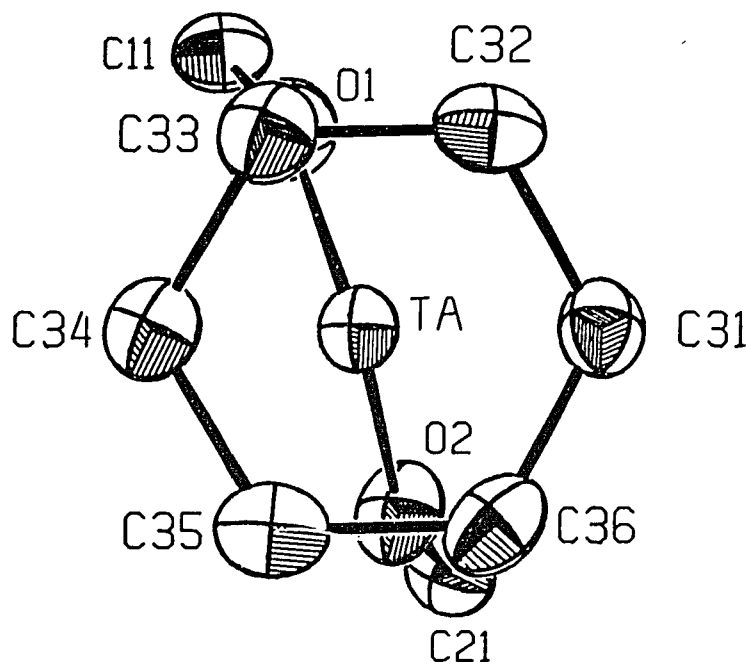
C<sub>6</sub>Et<sub>6</sub>Ta(DIPP)Br<sub>2</sub> (**39**) is obtained in 32% yield, equation 3. It is likely that **39**



arises from the reaction of the kinetic product ( $\eta^6$ -C<sub>6</sub>Et<sub>6</sub>)Ta(DIPP)<sub>2</sub>Br (**38**) with excess 1,2-



Selected bond distances and angles are listed in Tables 5.1 and 5.2, respectively. The tantalum atom in this "two-legged piano stool" geometry is coordinated to two phenoxide ligands with Ta-O(1) = 1.917(4) Å and Ta-O(2) = 1.916(4) Å, and with Ta-O-C<sub>ipso</sub> angles of 159.6(4)° and 158.2(4)°, respectively. The most striking structural feature of **36** is the severe bending of the arene ligand which results in C(31) and C(34) making close approaches to the metal (2.205(5) and 2.219(5) Å, respectively) while the remaining tantalum-carbon distances (average 2.386 Å) are more similar to those in known tantalum η<sup>6</sup>-hexamethylbenzene complexes.<sup>118</sup> Atoms C(31) and C(34) are well within the range of known Ta-C(sp<sup>3</sup>) σ bonds of a metal-alkyl.<sup>118</sup> The extent of folding of the ring



**Figure 5.2.** ORTEP drawing of the local coordination of (η<sup>6</sup>-C<sub>6</sub>Et<sub>6</sub>)Ta(DIPP)<sub>2</sub> (DIPP = 2,6-diisopropylphenoxide), viewing down the C<sub>6</sub>Et<sub>6</sub>(centroid)-Ta axis from an orientation perpendicular to the best arene plane. Atoms are shown as 50% ellipsoids.

**Table 5.1** Selected Bond Distances (Å) in  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2$ <sup>a</sup> (**36**)

Ta-O(1)	1.917(4)	O(1)-C(11)	1.355(7)
Ta-O(2)	1.916(4)	O(2)-C(21)	1.368(6)
Ta-C(31)	2.205(5)	C(31)-C(32)	1.486(7)
Ta-C(32)	2.346(5)	C(31)-C(36)	1.455(8)
Ta-C(33)	2.424(5)	C(32)-C(33)	1.403(7)
Ta-C(34)	2.219(5)	C(33)-C(34)	1.448(7)
Ta-C(35)	2.349(5)	C(34)-C(35)	1.486(7)
Ta-C(36)	2.426(5)	C(35)-C(36)	1.399(8)

**Table 5.2** Selected Bond Angles (deg) in  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2$  (**36**)

O(1)-Ta-O(2)	96.1(2)	C(32)-C(33)-C(34)	120.1(5)
O(1)-Ta-Arene <sup>b</sup>	129.7(1)	C(33)-C(34)-C(35)	116.4(5)
O(2)-Ta-Arene <sup>b</sup>	134.2(1)	C(34)-C(35)-C(36)	120.1(5)
Ta-O(1)-C(11)	159.6(4)	C(35)-C(36)-C(31)	119.7(5)
C(31)-C(32)-C(33)	119.8(5)		

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

<sup>b</sup>"Arene" is the centroid of the  $\text{C}_6\text{Et}_6$  ligand calculated by averaging the x, y, and z coordinates of all carbon atoms in the arene ring.

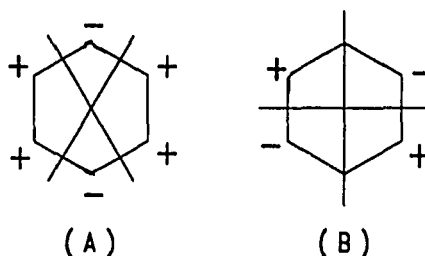
may be measured by the C(31)-C(32)-C(33)-C(34) plane which assumes an angle of 20.8 degrees out of planarity with C(34)-C(35)-C(36)-C(31). Arene bending to this extent is rare. Table 5.3 gives a compilation of selected folded arenes. Non-planarity of this type (with two carbons closer to the metal) in  $\eta^6$ -arene ligands has also been observed in complexes of titanium,<sup>107a</sup> rhodium,<sup>103a</sup> ruthenium,<sup>104b</sup> and niobium,<sup>119-121</sup> but only in the case of related tantalum complexes  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{DIPP})_2\text{Cl}^7$  (**35**) and  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{DIPP})\text{Cl}_2$ <sup>110</sup> is bending more severe than in (**36**) (fold angles 34.4 and 26.8°, respectively). Additionally, the arene ligand features considerable  $\pi$  electron localization as indicated by the short C(32)-C(33) and C(35)-C(36) bonds (1.403(7) and 1.399(8) Å, respectively), while all other carbon-carbon bond lengths within the ring average 1.468 Å. The bending,  $\pi$  localization, and bond length effects are no doubt principally electronic in origin, as the

**Table 5.3** Data for  $\eta^6$ -Arene Ligands that Show Folding upon Coordination

complex	fold angle $\Theta$ , deg		degree of $\pi$ -localization $\Delta_{(C-C)_{avg}-(C=C)_{avg}}$ , Å	ref
	inverted boat	boat		
$(C_6Me_6)Ta(DIPP)_2Cl$		34.4	0.075	7
$(C_6Me_6)Ta(DIPP)Cl_2$		26.8	0.087	110
$(C_6Et_6)Ta(DIPP)_2$		20.8	0.067	109
$[(C_6Me_6)_3Nb_3Cl_6]^+$		22.6	0.12	121
$[(C_6Me_6)_3Nb_3Cl_6]^{2+}$		17.8	0.044	119
$(C_6H_6)Ru(1,5-COD)$		5.2	0.045	104b
$(C_6Me_3H_3)Ni(C_6H_5)_2$	5.5		*	106a
$(C_6H_5Me)Ni(C_6H_5)_2$	8.2		*	108
$[(C_6H_5Me)Mo(SMe)_2]_2^{2+}$	9.6		*	122
$(C_6H_5Me)MoMe_2(PPhMe_2)_2$	10.9		*	123



arene  $\pi^*$  orbital (A) seems to be populated selectively by metal  $\delta$  functions over (B).

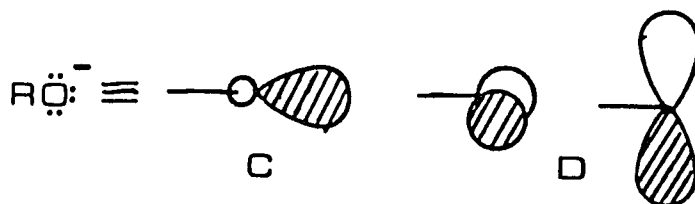
**Figure 5.3** Arene  $\pi^*$  Molecular Orbitals

Two other structural features are noteworthy. First, the arene ring shows a distortion towards a twist-boat structure as C(33) and C(36) lie 0.05 Å above the least squares C(32)-C(33)-C(35)-C(36) plane, while C(32) and C(35) lie 0.05 Å below that plane. Secondly, as seen in Figure 2, the Ta-O- $C_{ipso}$  linkages neither perfectly eclipse nor stagger the C-C bonds of the arene ring. To understand the bonding and structural features of **36**,

Albright and Koenier have undertaken a molecular orbital study of the model compound  $(\eta^6\text{-C}_6\text{H}_6)\text{Ta}(\text{OH})_2$ , the results of which are summarized in the following section.

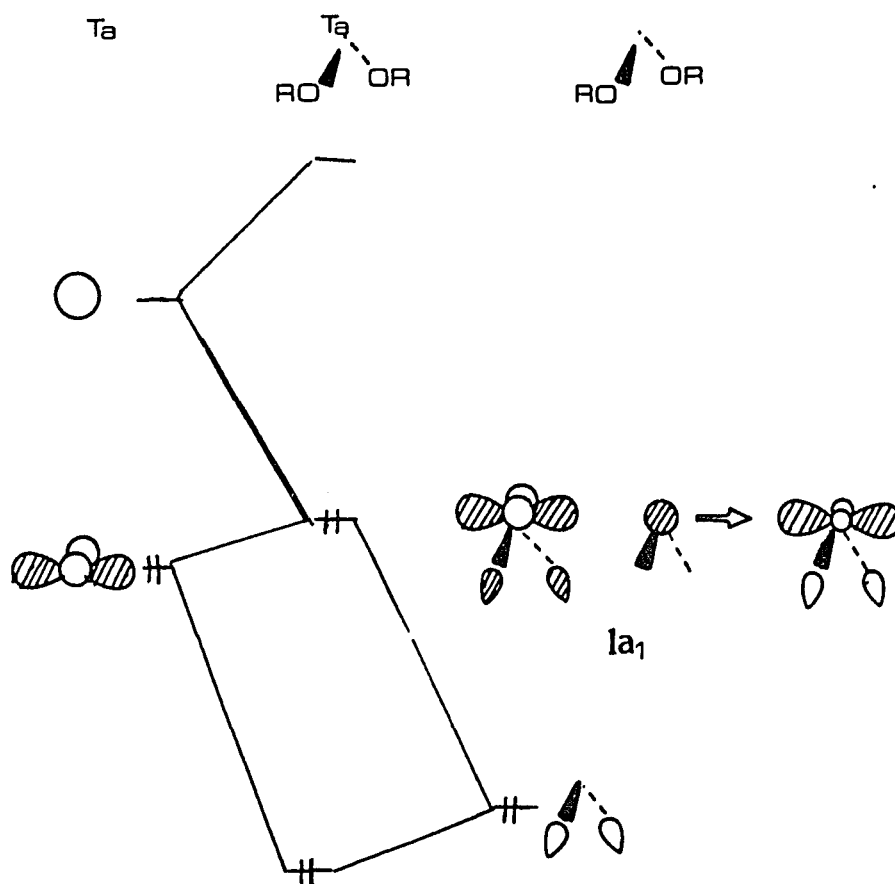
**Computational Study of  $(\eta^6\text{-C}_6\text{H}_6)\text{Ta}(\text{OH})_2$ .** The electronic reasons that the arene ligand in 18 electron  $(\eta^6\text{-arene})\text{ML}_2$  complexes distorts towards a nonplanar, boat-like geometry have been established.<sup>106a,124,125</sup> Since the HOMO in this molecule is metal d centered and antibonding to a benzene  $\pi$  orbital, this antibonding is reduced when the arene distorts to a boat geometry. Consistent with this argument is the fact that upon removal of the electrons from the HOMO to give a 16 electron complex, the arene ring returns to planarity.<sup>92</sup> For the 13 electron,  $(\eta^6\text{-arene})\text{Ta}(\text{OR})_2$  molecules considered here this orbital is also clearly not occupied. Albright and Koenier used molecular orbital calculations at the extended Hückel and ab initio levels to discern the electronic driving force for the peculiar twist boat deformation observed in  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2$  (**3**).

An idealized orbital interaction diagram for an  $(\eta^6\text{-C}_6\text{H}_6)\text{Ta}(\text{OR})_2$  molecule is given in Figure 5.4. Two of the benzene  $\pi$  and two  $\pi^*$  orbitals are shown on the right side of the Figure. The fragment orbitals for an  $\text{ML}_2$  unit, where L is a  $\sigma$  donor or has  $\pi$  acceptor functions, have been described elsewhere.<sup>106a,124-126</sup> In this particular case, however, the alkoxide group possesses a  $\sigma$  donor orbital, (C), as well as two excellent  $\pi$  donor orbitals, (D). The presence of the  $\pi$  donor functions requires some additional discussion.



The highest lying fragment orbital,  $b_2$ , on the left side of Figure 5.4, is primarily  $xz$  antibonding to the alkoxide  $\sigma$  donor set. Furthermore, significant metal  $x$  character mixes

into this orbital to hybridize it towards the benzene. At lower energies are the  $2a_1$ ,  $a_2$  and  $b_1$  fragment levels. Each is primarily metal d in character, antibonding to the appropriate symmetry-adapted  $\pi$  donor set on the alkoxide ligands as shown in Figure 5.4. The lowest energy fragment orbital for  $Ta(OR)_2$  is  $1a_1$ . This orbital is  $x^2-y^2$  and, most importantly to the ensuing discussion, contains metal s character. What is central to the discussion of arene bending is the fact that the  $x^2-y^2/s$  hybridization in  $1a_1$  reduces the amplitude of this fragment orbital in the  $Ta(OR)_2$  plane and increases the amplitude in the plane orthogonal to it.



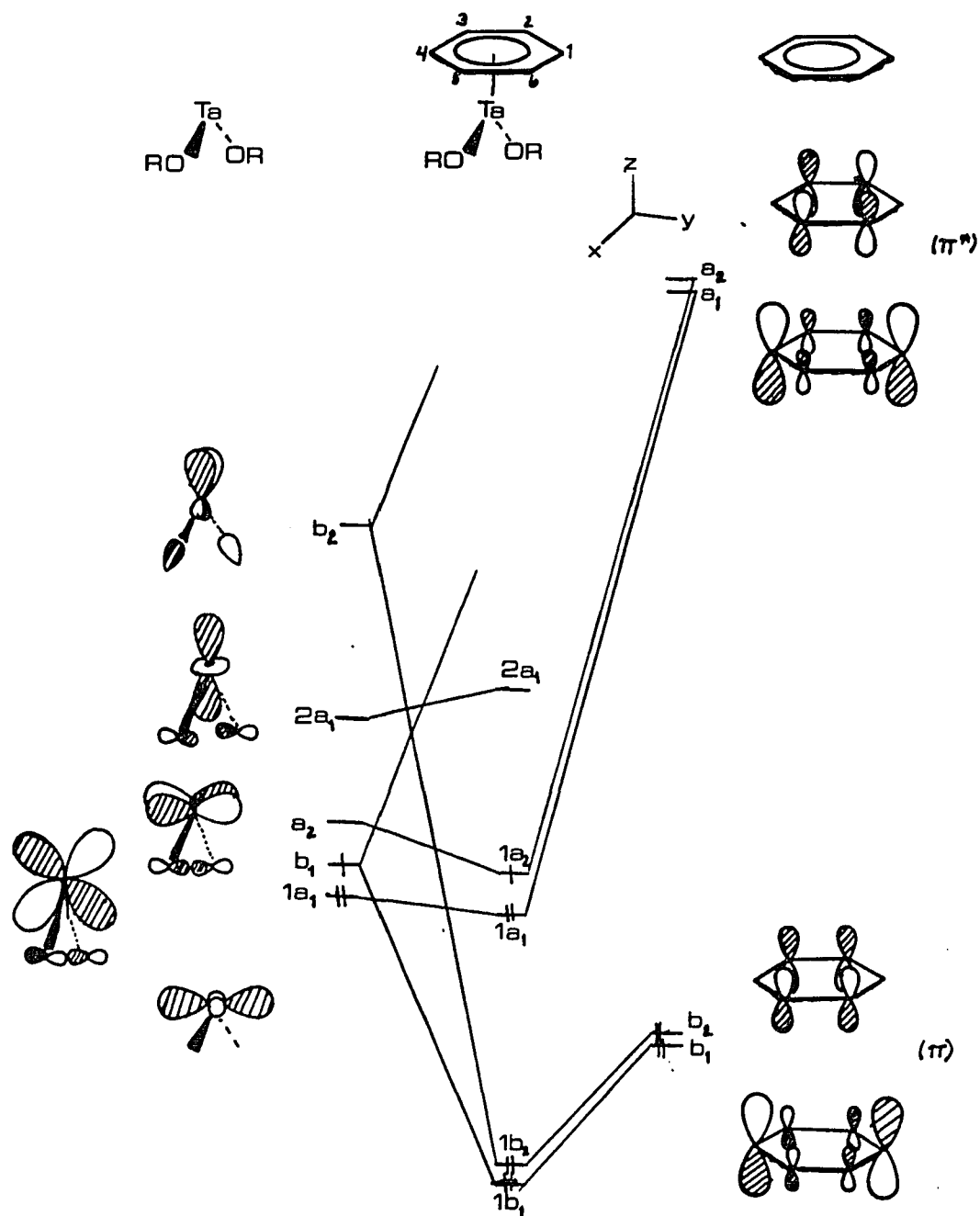
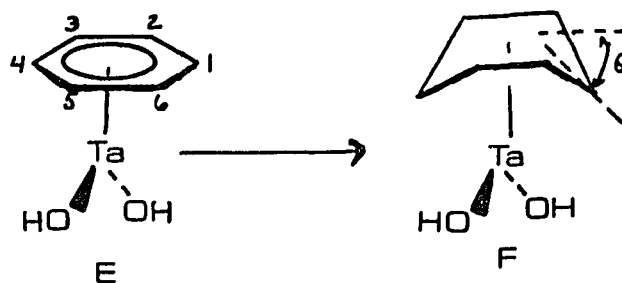


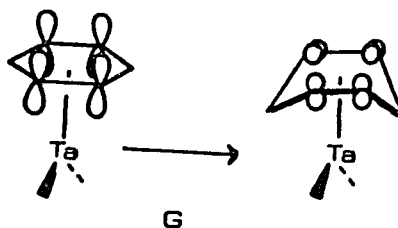
Figure 5.4 An orbital interaction diagram for  $(\eta^6\text{-C}_6\text{H}_6)\text{Ta}(\text{OR})_2$ .

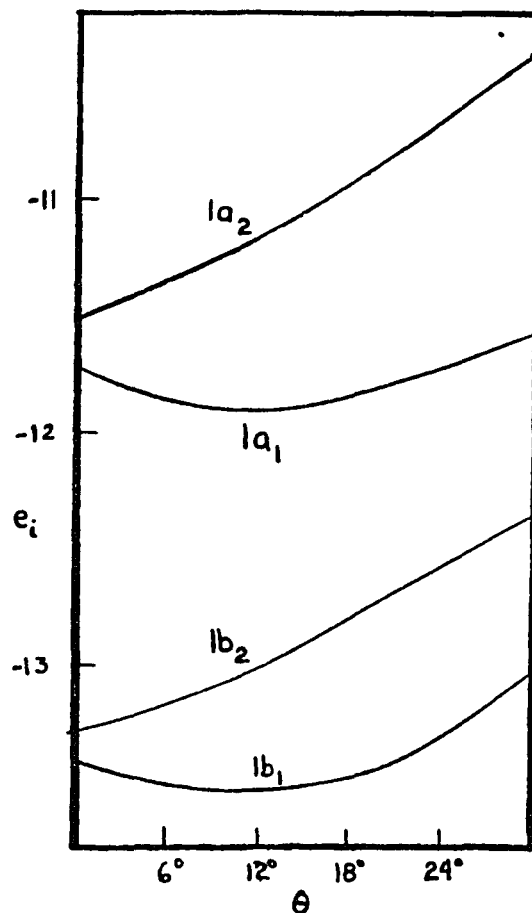
Returning to Figure 5.4, the two benzene  $\pi$  orbitals are stabilized by the  $b_2$  and  $b_1$  fragment orbitals on  $\text{Ta}(\text{OR})_2$ . The  $1a_1$  and  $1a_2$  fragment orbitals have  $\delta$  symmetry with respect to the benzene. They are, therefore, stabilized by the benzene  $\pi^*$  set. Finally, the  $\text{Ta}(\text{OR})_2$   $2a_1$  orbital remains essentially nonbonding. Notice that the  $1a_1$  molecular orbital lies lower in energy than  $1a_2$ . This level ordering is ensured because  $1a_1$  is nonbonding but  $1a_2$  is clearly antibonding to the alkoxide ligand set. Consequently molecular  $1a_1$  is filled and  $1a_2$  is singly occupied for this  $d^3$  complex.

Let us now consider the changes which occur for the occupied molecular orbitals in Figure 5.4 when the planar benzene ligand is distorted to a boat geometry. A Walsh diagram based upon extended Hückel calculations for going from (E) to (F) is shown in Figure 5.5. Here  $\Theta$  is defined as the angle made between the C(2)-C(1)-C(6) and C(3)-



C(4)-C(5) planes with the C(2)-C(3)-C(5)-C(6) plane. The molecular  $1b_2$  and  $1a_2$  orbitals rise in energy as  $\Theta$  increases. The reason for this is rather simple. As  $\Theta$  increases the  $z$  atomic orbitals on C(2), C(3), C(5) and C(6) reorient themselves as shown in a somewhat exaggerated manner in (G). Overlap between the  $b_2$  and  $a_2$  fragment orbitals





**Figure 5.5** A plot of the orbital energy,  $e_i$ , for the four occupied molecular orbitals in Figure 5.4 versus  $\Theta$ , defined in (F) for  $(\eta^6\text{-C}_6\text{H}_6)\text{Ta}(\text{OH})_2$ .

(Figure 5.4) on  $\text{Ta}(\text{OH})_2$  and the appropriate  $\pi$  and  $\pi^*$  orbitals on the benzene is reduced. The molecular  $1b_1$  and  $1a_1$  orbitals initially are stabilized as  $\Theta$  increases. Here there is increased overlap between the atomic  $z$  orbitals at C(1) and C(4) with the  $1a_1$  and  $b_1$  fragment orbitals on  $\text{Ta}(\text{OH})_2$ . At large values of  $\Theta$ , lower lying  $\sigma$  levels on the benzene skeleton also begin to mix into the molecular  $1b_1$  and  $1a_1$  orbitals which causes them to be destabilized. At small to intermediate values of  $\Theta$ , the energetic behavior of  $1b_1$  and  $1b_2$  approximately cancel one another. The same would be true for the  $1a_2$  and  $1a_1$  levels;

however,  $1a_1$  is doubly occupied whereas  $1a_2$  is occupied with a single electron. Therefore, the distortion from (E) to (F) results in a net stabilization. At the ab initio level all internal coordinates were optimized within a  $C_{2v}$  symmetry constraint, except that in structure (E) the benzene ring was also forced to remain planar with equal C-C and C-H bond lengths. It was found that (F) is 5.9 kcal/mol more stable than (E) with optimized value of  $\Theta = 17.9^\circ$ . With the hybridization in the  $1a_1$  fragment orbital on  $Ta(OR)_2$  there is now stronger bonding to C(2), C(3), C(5) and C(6). Consequently the folding of these carbon atoms downward, towards Ta, serves to further stabilize molecular  $1a_1$ .

The peculiar twist-boat conformation in **36** is, therefore, tied to the hybridization presented in the  $x^2-y^2$  orbital on Ta along with the fact that the  $1a_1$  molecular orbital in Figure 5.4 is doubly occupied, whereas  $1a_2$  is occupied with a single electron. The substantial buckling of the arene ring and its C-C bond localization underscore the fact that there is extremely strong  $\delta$  type bonding between the arene and Ta in these complexes compared to the situation that exists for other 16-18 electron  $(\eta^6\text{-arene})ML_n$  systems.<sup>106a,124-126</sup> The addition of another electron to  $1a_2$  should then cause the arene to return to planarity and greatly reduce the rotational barrier around the arene-Ta axis.

## SUMMARY AND CONCLUSIONS

The arene ligand in compounds **34** - **40** was successfully prepared by alkyne cyclization chemistry, whereas all other niobium and tantalum arene complexes are either trinuclear clusters derived from Fischer-Hafner synthesis, bis(arene) compounds and their derivatives arising from metal vapor synthesis, or the tetracarbonyl cations.<sup>91</sup> The one electron reductions of **34** and **35** result in the formation of rare Ta (II)  $(\eta^6\text{-arene})ML_2$  paramagnetic complexes **36** and **37**.  $(\eta^6\text{-C}_6\text{Et}_6)Ta(\text{DIPP})_2$  (**36**) undergoes one-electron oxidative addition reactions with alkyl and allyl halides to afford compounds **34**, **38**, and

40. An x-ray structural study of **36** shows the  $\eta^6$ -arene ligand to be characterized by a boat-like distortion exhibiting 1,4-diene  $\pi$ -localization. From the molecular orbital calculations at the ab initio levels, it was found that the boat-like deformation of the benzene ligand is primarily due to maximization of the overlap between an s hybridized  $x^2-y^2$  orbital at the metal and  $\pi^*$  on the benzene. The  $C_2$  deformation of the remaining four carbon atoms in the benzene ligand is tied to rotation of the  $ML_2$  unit about the metal-benzene axis. At the ab initio level, a fully optimized structure was found to lie 19.8 kcal/mol lower in energy than one where the benzene ligand was constrained to be planar.

## EXPERIMENTAL

**Preparations.** ( $\eta^6$ - $C_6Et_6$ )Ta(DIPP) $_2$ Cl (**34**). A solution of 2.00 g (2.79 mmol) of Ta(DIPP) $_2$ Cl $_3$ (OEt $_2$ ) in 50 mL of diethyl ether was prepared and cooled to -40 °C. To this stirred solution were added 1.00 mL (8.80 mmol) of 3-hexyne and 2.00 mL (5.60 mmol) of a 0.47% NaHg. After being stirred at room temperature for 1 h, the resulting blue solution was filtered through Celite (Et $_2$ O wash) and the solvent was removed from the filtrate in vacuo. The resulting blue solid was washed with 5-10 mL of cold pentane, filtered off, and dried in vacuo to provide 1.22 g (1.49 mmol, 53% yield) of product. This compound was recrystallized from toluene/pentane solutions at -40 °C to afford analytically pure samples.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  7.11-6.93 (A $_2$ B m, 6 H, H $_{aryl}$ ), 3.23 (spt, 4 H, CHMe $_2$ ), 2.37 (q, 12 H, CH $_2$ CH $_3$ ), 1.19 (d, 24 H, CHMe $_2$ ), 1.09 (t, 12 H, CH $_2$ CH $_3$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  156.1 ( $C_{ipso}$ ), 137.1 ( $C_o$ ), 126.8 ( $C_6Et_6$ ), 123.6 ( $C_m$ ), 122.4 ( $C_p$ ), 25.7 (CHMe $_2$ ), 25.1 (CHMe $_2$ ), 23.9 (CH $_2$ CH $_3$ ), 17.7 (CH $_2$ CH $_3$ ). IR (Nujol): 1580 w, 1435 s, 1320 m, 1254 s, 1193 sh, 1182 s, 1098 m, 1091 m, 1038 m, 930 w, 904 s, 885 w, 861 m, 820 w, 788 m, 742 s, 700 m. Anal. Calcd. for C $_{42}$ H $_{64}$ ClO $_2$ Ta: C, 61.72; H, 7.89. Found: C, 62.30; H, 8.21.

**( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)Ta(DIPP)<sub>2</sub>Cl (35).** To a -40 °C solution of 2.00 g (2.79 mmol) of Ta(DIPP)<sub>2</sub>Cl<sub>3</sub>(OEt<sub>2</sub>) in 25 mL of diethyl ether were added 0.65 mL (8.80 mmol) of 2-butyne and 2.10 mL (5.60 mmol) of 0.46% NaHg. The reaction mixture was shaken for 5 min and the resulting blue solution was filtered through Celite and the solvent was removed from the filtrate in vacuo. The resulting blue solid was washed with 5-10 mL of cold pentane, filtered, and dried in vacuo to provide 1.35 g (1.84 mmol, 66% yield) of blue powder. <sup>1</sup>H NMR(C<sub>6</sub>D<sub>6</sub>):  $\delta$ 7.09-6.92 (m, 6 H, H<sub>aryl</sub>), 3.19 (spt, 4 H, CHMe<sub>2</sub>), 2.02 (s, 18 H, C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>), 1.18 (d, 24 H, CHMe<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$ 156.7 (C<sub>ipso</sub>), 136.7 (C<sub>o</sub>), 123.6 (C<sub>m</sub>), 122.3 (C<sub>p</sub>), 120.6 (C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>), 26.2 (CHMe<sub>2</sub>), 24.8 (CHMe<sub>2</sub>), 16.2 (C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>). IR (Nujol): 1580 w, 1567 w, 1325 sh, 1320 m, 1255 sh, 1245 s, 1196 sh, 1182 s, 1092 m, 1038 m, 931 w, 908 s, 882 m, 855 s, 786 m, 741 s, 694 m. Anal. Calcd. for C<sub>36</sub>H<sub>52</sub>ClO<sub>2</sub>Ta: C, 58.97; H, 7.15. Found: C, 59.18; H, 7.29.

**( $\eta^6$ -C<sub>6</sub>Et<sub>6</sub>)Ta(DIPP)<sub>2</sub> (36).** i) **From ( $\eta^6$ -C<sub>6</sub>Et<sub>6</sub>)Ta(DIPP)<sub>2</sub>Cl (34).** To a room temperature solution of 1.00 g (1.22 mmol) of ( $\eta^6$ -C<sub>6</sub>Et<sub>6</sub>)Ta(DIPP)<sub>2</sub>Cl (34) in 20 mL of diethyl ether was added excess Na/Hg (0.80 mL, 2.44 mmol, of a 0.46% amalgam). After being stirred for 24 h, this mixture was filtered through Celite and the solvent removed from the filtrate in vacuo to afford a red solid. Upon dissolving this solid in minimal pentane and cooling the solution to -40 °C, dark red cubes (0.63 g, 0.81 mmol, 66%) were filtered off, washed with minimal cold pentane, and dried in vacuo. Samples of compound obtained in this fashion were analytically pure. ii) **From Ta(DIPP)<sub>2</sub>Cl<sub>3</sub>(OEt<sub>2</sub>).** To a -40 °C solution of 1.00 g (1.40 mmol) of Ta(DIPP)<sub>2</sub>Cl<sub>3</sub>(OEt<sub>2</sub>) in 25 mL of diethyl ether were added 0.50 mL (4.40 mmol) of 3-hexyne and 2.00 mL (5.60 mmol) of 0.50% NaHg. The reaction was allowed to stir for 24 h at room temperature. The dark red solution was filtered through Celite and the filtrate was pumped to dryness. The resulting dark red

solid was dissolved in pentane and cooled to  $-40\text{ }^{\circ}\text{C}$ . 0.35 g (0.45 mmol, 32% yield) of maroon crystals was filtered off, washed with a minimal volume of cold pentane, and dried in vacuo.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ): All resonances are broad, featureless signals (peak width at half maximum (in Hz) in parentheses):  $\delta$  9.70 (40), 4.73 (135), 4.06 (80), 3.77 (90). IR (CsI): 1588 m-w, 1453 sh, 1434 s, 1380 m, 1359 m, 1336 s, 1326 s, 1268 s, 1258 s, 1206 s, 1104 m, 1057 m, 1044 m, 904 s, 875 m, 823 m, 791 m, 748 s, 707 m-s, 593 m-w, 419 w, 258 w. Molecular weight ( $\text{Et}_2\text{O}$  solution): calcd. for monomer, 781.9; found  $809 \pm 80$ . Magnetic moment ( $\text{C}_6\text{D}_6$  solution):  $\mu_{\text{eff}} = 2.14 \mu_{\text{B}}$ . Anal. Calcd. for  $\text{C}_{42}\text{H}_{64}\text{O}_2\text{Ta}$ : C, 64.52; H, 8.25; Cl, 0.00. Found: C, 65.01; H, 8.57; Cl,  $<0.05$ .

$(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{DIPP})_2$  (**37**). To a room temperature solution of 1.19 g (1.62 mmol) of  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ta}(\text{DIPP})_2\text{Cl}$  (**35**) in 20 mL of diethyl ether was added 0.70 mL (3.24 mmol) of a 0.50% NaHg. This mixture was stirred for 24 h, as a gradual color change from blue to deep red was observed. The solution was then filtered through Celite and the filtrate was pumped to dryness. The resulting red solid was dissolved in ca. 10 mL of pentane and upon cooling to  $-40\text{ }^{\circ}\text{C}$ , 0.37 g (0.53 mmol, 32% yield) of red brown plates were obtained. The product was collected, washed with minimal cold pentane, and dried in vacuo. This product was analytically pure.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ): All resonances are broad, featureless signals (peak width at half maximum (in Hz) in parentheses):  $\delta$  9.68 (30), 6.14 (20), 4.27 (65). IR (Nujol): 1580 w, 1430 s, 1328 s, 1256 s, 1200 s, 1106 m, 1088 m, 1036 m, 929 w, 895 s, 870 m, 786 m, 743 s, 698 m. Magnetic moment ( $\text{C}_6\text{D}_6$  solution):  $\mu_{\text{eff}} = 2.07 \mu_{\text{B}}$ . Anal. Calcd. for  $\text{C}_{36}\text{H}_{52}\text{O}_2\text{Ta}$ : C, 61.97; H, 7.51. Found: C, 61.62; H, 7.63.

$(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2\text{Br}$  (**38**). To a room temperature solution of 0.25 g (0.32 mmol) of  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2$  (**36**) in 10 mL of diethyl ether was added 0.03 mL (0.32 mmol) of allyl bromide, whereupon the solution immediately turned blue. After being

stirred for 5 min, the blue solution was pumped to dryness. The resulting blue solid was washed with 3-5 mL of cold pentane, filtered off, and dried in vacuo to provide 0.14 g (0.16 mmol, 50% yield) of product. Analytically pure compound was obtained upon recrystallizing the product from pentane at -40 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.11-6.93 (A<sub>2</sub>B m, 6 H, H<sub>aryl</sub>), 3.21 (spt, 4 H, CHMe<sub>2</sub>), 2.40 (q, 12 H, CH<sub>2</sub>CH<sub>3</sub>), 1.19 (d, 24 H, CHMe<sub>2</sub>), 1.10 (t, 18 H, CH<sub>2</sub>CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  156.6 (C<sub>ipso</sub>), 137.0 (C<sub>o</sub>), 126.7 (C<sub>6</sub>Et<sub>6</sub>), 123.6 (C<sub>m</sub>), 122.4 (C<sub>p</sub>), 25.8 (CHMe<sub>2</sub>), 25.2 (CHMe<sub>2</sub>), 24.3 (CH<sub>2</sub>CH<sub>3</sub>), 17.9 (CH<sub>2</sub>CH<sub>3</sub>). IR (Nujol): 1580 w, 1430 s, 1318 m, 1250 s, 1242 sh, 1185 sh, 1180 s, 1096 m, 1090 m, 1048 m-w, 902 m-s, 885 w, 859 m, 784 w, 741 s, 697 w. Anal. Calcd for C<sub>42</sub>H<sub>64</sub>BrO<sub>2</sub>Ta: C, 58.53; H, 7.48. Found: C, 58.45; H, 7.60.

( $\eta^6\text{-C}_6\text{Et}_6$ )Ta(DIPP)Br<sub>2</sub> (**39**). To a solution of 0.25 g (0.32 mmol) of ( $\eta^6\text{-C}_6\text{Et}_6$ )Ta(DIPP)<sub>2</sub> (**36**) in 10 mL of diethyl ether was added 0.12 mL (1.40 mmol) of 1,2-dibromoethane, resulting in an immediate color change from red to blue. After being stirred for 15 min at room temperature, the solvent was removed in vacuo to provide a turquoise oil. The oil was reconstituted in room temperature pentane and in min, 0.05 g (0.07 mmol, 22% yield) of green crystals formed. The product was filtered off, leaving a blue filtrate which was shown to contain ( $\eta^6\text{-C}_6\text{Et}_6$ )Ta(DIPP)<sub>2</sub>Br (**38**). Since samples of ( $\eta^6\text{-C}_6\text{Et}_6$ )Ta(DIPP)Br<sub>2</sub> (**39**) obtained in this fashion were always contaminated with varying amounts of ( $\eta^6\text{-C}_6\text{Et}_6$ )Ta(DIPP)<sub>2</sub>Br (**38**) which could not be separated by fractional crystallization or chromatography, no elemental analyses were attempted.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.06-6.90 (m, 3 H, H<sub>aryl</sub>), 3.51 (spt, 2 H, CHMe<sub>2</sub>), 2.09 (q, 12 H, CH<sub>2</sub>CH<sub>3</sub>), 1.32 (d, 12 H, CHMe<sub>2</sub>), 0.93 (t, 18 H, CH<sub>2</sub>CH<sub>3</sub>).

( $\eta^6\text{-C}_6\text{Et}_6$ )Ta(DIPP)<sub>2</sub>I (**40**). To a room temperature solution of 0.25 g (0.32 mmol) of ( $\eta^6\text{-C}_6\text{Et}_6$ )Ta(DIPP)<sub>2</sub> (**36**) in 10 mL of diethyl ether was added 0.03 mL (0.32 mmol) of

iodoethane, whereupon the solution immediately turned purple. After being stirred for 5 min, the solvent was removed in vacuo and the resulting oil was reconstituted in 3 mL of pentane. Cooling this solution to -40 °C for 24 h afforded 0.13 g (0.14 mmol, 45% yield) of dark blue crystals. The crystals were collected, washed with minimal cold pentane, and dried in vacuo. Samples obtained in this fashion were analytically pure.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.11-6.92 ( $\text{A}_2\text{B}$  m, 6 H,  $\text{H}_{\text{aryl}}$ ), 3.19 (spt, 4 H,  $\text{CHMe}_2$ ), 2.42 (q, 12 H,  $\text{CH}_2\text{CH}_3$ ), 1.20 (d, 24 H,  $\text{CHMe}_2$ ), 1.11 (t, 18 H,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  157.3 ( $\text{C}_{\text{ipso}}$ ), 136.8 ( $\text{C}_o$ ), 126.0 ( $\text{C}_6\text{Et}_6$ ), 123.7 ( $\text{C}_m$ ), 122.5 ( $\text{C}_p$ ), 25.9 ( $\text{CHMe}_2$ ), 25.4 ( $\text{CHMe}_2$ ), 25.1 ( $\text{CH}_2\text{CH}_3$ ), 18.1 ( $\text{CH}_2\text{CH}_3$ ). IR (CsI): 1587 w, 1536 w, 1455 sh, 1433 s, 1381 m, 1360 m, 1323 s, 1256 s, 1195 s, 1104 s, 1045 m, 909 s, 892 m, 866 s, 827 w, 792 m, 747 s, 706 m, 624 w, 601 m, 590 m, 429 w, 343 m, 314 m-w, 301 m-w, 259 w. Anal. Calcd. for  $\text{C}_{42}\text{H}_{64}\text{IO}_2\text{Ta}$ : C, 55.51; H, 7.10. Found: C, 56.02; H, 7.43.

## CHAPTER 6

### CONCLUSIONS

#### Mechanistic Summary

The use of an early transition metal system supported by phenoxide ligands instead of the conventionally used cyclopentadienyl ligand allowed the isolation of purported intermediates in the cyclotrimerization of alkynes by controlling the steric and electronic environment at the metal center. Use of the tris phenoxide starting material  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  and the sterically demanding alkynes  $\text{PhC}\equiv\text{CPh}$  and  $\text{Me}_3\text{SiC}\equiv\text{CMe}$  allowed the isolation of acetylene adducts (compound **A**, Scheme 1.1) which are generally accepted as the first intermediates in a cyclotrimerization pathway. Upon reducing  $\text{Ta}(\text{DIPP})_3\text{Cl}_2(\text{OEt}_2)$  by two electrons in the presence of smaller internal or terminal alkynes, metallacyclopentadienes (compound **C**, Scheme 1.1), the next higher cyclooligomer in the reaction pathway were isolated. The tris phenoxide starting material proved to be too sterically congested to allow the isolation of either a 7-metallanorbornadiene or a metallacycloheptatriene (compounds **E** or **D**, Scheme 1.1) complex. Reducing the steric congestion around the metal center by using only two of the bulky phenoxide ligands instead of three allowed the isolation of 7-metallanorbornadiene (**E**) complexes from the cyclotrimerization of 2-butyne or 3-hexyne upon reducing  $\text{Ta}(\text{DIPP})_2\text{Cl}_3(\text{OEt}_2)$ .

With the successful isolation of compounds along the cyclotrimerization pathway, it was necessary to test the validity of these complexes as models by studying their reactivity. The stability of the highest oxidation state in early transition metals made purported intermediates like the alkyne adducts reactive. The substantially reduced nature of the alkyne ligand along with the electrophilic nature of the metal center (due to the phenoxide ligands) allowed the alkyne adduct  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (**14**) to couple

a variety of small alkynes to produce metallacyclopentadiene complexes. This conversion of an alkyne adduct to a metallacyclopentadiene has been observed in many group 4 and group 8-10 metal systems<sup>15,24,77</sup> but not in any of the group 5 adducts prepared to date.<sup>26,34</sup> No group 6 systems have undergone similar metallacyclization reactions including the alkyne adducts discussed in Chapter 2. The enhanced reactivity of the group 5 systems may be attributed to the greater electrophilicity of the metal when supported by phenoxide instead of cyclopentadienyl ligands. These compounds are both coordinatively as well as electronically unsaturated which allows them to react further whereas most of the group 4 systems previously studied are supported by cyclopentadienyl ligands which increase the sterics and electron count at the metal center.

### Synthetic Utility

The alkyne adduct  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (**14**) demonstrated a high degree of cross-coupling regioselectivity in that only one of the four possible isomers from the reaction with another alkyne was formed. Unlike some of the group 4 systems which are intolerant to terminal alkynes<sup>127</sup>, the tantalum complex **14** was highly successful coupling with terminal alkynes. These cross-coupled metallacyclopentadienes also were shown to react with  $\text{I}_2$  to form mono-iodinated butadienyl fragments. Therefore, the products from these cross-coupled reactions show this to be a viable route to substituted 1,3-butadienes and 1-iodo-1,3-butadienes as detailed in Chapter 3. The alkyne adduct **14** was also shown in Chapter 4 to couple to other unsaturated organic molecules, namely aldehydes, ketones, and nitriles to afford heterosubstituted metallacycles. These coupled products could provide routes to vinyl alcohols, secondary amines, and imines.

### Future Directions

Carbon-carbon bond forming reactions are a major topic of current and no doubt

future interest. The coupling reactions between the alkyne adduct  $(\text{DIPP})_3\text{Ta}(\text{Me}_3\text{SiC}\equiv\text{CMe})$  (14) and a variety of unsaturated organic molecules including heteroatom molecules make this a viable method for organic synthesis. The current system relies heavily on steric control that only allows the isolation of alkyne adducts for bulky alkynes, the use of smaller alkynes affords the isolation of metallacyclopentadienes. Development of a way to trap alkyne adducts of less sterically demanding alkynes would help to generalize this system to allow other substituents in the cross-coupled products. Use of Lewis bases, such as THF, pyridine, or phosphines may prevent the smaller alkynes from metallacyclizing. The success of these reactions also seems to be metal dependent. Attempts to extend this chemistry from group 5 to group 6 were made. However, under similar reaction conditions, the tungsten phenoxide analogue failed to produce any cyclooligomers higher than an alkyne adduct, and these adducts proved to be unreactive toward additional alkyne, ketones, and nitriles.

The current system is composed of multiple steps with isolation at each stage. Development of a "one-pot" method would be helpful in making this system more attractive to the organic chemist, but the reduction conditions employed in preparing the alkyne adducts are too harsh for many heteroatomic functional groups. Preparation of an isolable  $d^2$  reagent like Pedersen's  $\text{NbCl}_3(\text{DME})^{66}$  would be necessary for the "one-pot" method to work. Another problem with the current system is that it is not catalytic. The current method of removing the organic fragment from the metal is by hydrolysis which converts the tantalum phenoxide portion of the molecule into free phenol and tantalum oxide. A way of reductively eliminating the organic fragment with regeneration of some  $d^2$   $\text{Ta}(\text{DIPP})_3$  reagent would be more ideal.  $\text{PCl}_5$  has been used to remove the arene from  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2$  presumably forming  $\text{Ta}(\text{DIPP})_2\text{Cl}_3$  as the other product. A similar

methodology needs to be developed for the metallacycles.

Since the cyclization and C-H activation chemistry that was so successful in the group 5 system could not be applied to group 6, some alteration to the system should be made. With the successful preparation of a bis-imide complex of Ta<sup>128</sup>, a bis imide of tungsten instead of a mixed imido-alkoxide complex might be used in cyclization reactions. If both imido ligands are coordinated in a linear fashion, contributing up to four electrons each to the tungsten metal center, perhaps the metal center will be more electrophilic and undergo chemistry similar to that seen in the tantalum phenoxide system.

**APPENDIX A**  
**EXPERIMENTAL DETAILS**

**SYNTHESIS AND PURIFICATION**

**General Details.** All experiments were performed under a nitrogen atmosphere by either standard Schlenk techniques<sup>129</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>130</sup> and transferred to the drybox or reaction vessel without exposure to air.

**Reagents.** The source and purification method of all reagents used are found in Table A.1. Most liquid reagents were dried by passing them down a short column (ca. 5-6 cm) of activated alumina.

**Table A.1** Source and Purification of Reagents

<u>Reagent</u>	<u>Source</u>	<u>Purification Method</u>
TaCl <sub>5</sub> (resub.)	Alfa	none
WCl <sub>6</sub> (resub.)	Alfa	none
HDIPP	Aldrich	vacuum distillation
HDMP	Aldrich	none
n-BuLi (1.6M)	Aldrich	none
Me <sub>3</sub> SiCl	Petrarch	none
Me <sub>3</sub> SiOMe	Petrarch	none
(Me <sub>3</sub> Si) <sub>2</sub> O	Petrarch	none
(Me <sub>3</sub> Si) <sub>2</sub> NH	Petrarch	none
MeC≡CMe	Farchan	dried over activated Al <sub>2</sub> O <sub>3</sub>
EtC≡CEt	Farchan	dried over activated Al <sub>2</sub> O <sub>3</sub>

**Table A.1** Source and Purification of Reagents (cont.)

<u>Reagent</u>	<u>Source</u>	<u>Purification Method</u>
$\text{Me}_3\text{CC}\equiv\text{CH}$	Farchan	dried over activated $\text{Al}_2\text{O}_3$
$\text{Me}_3\text{SiC}\equiv\text{CMe}$	Farchan	dried over activated $\text{Al}_2\text{O}_3$
$\text{Me}_3\text{SiC}\equiv\text{CH}$	Farchan	dried over activated $\text{Al}_2\text{O}_3$
$\text{PhC}\equiv\text{CPh}$	Aldrich	none
$\text{MeC}\equiv\text{N}$	Baxter	distilled over $\text{CaH}_2$
$\text{EtC}\equiv\text{N}$	Aldrich	dried over activated $\text{Al}_2\text{O}_3$
$\text{Me}_3\text{CC}\equiv\text{N}$	Aldrich	dried over activated $\text{Al}_2\text{O}_3$
$\text{PhCH}_2\text{C}\equiv\text{N}$	Aldrich	dried over activated $\text{Al}_2\text{O}_3$
$\text{PhCHO}$	Aldrich	dried over activated $\text{Al}_2\text{O}_3$
$\text{MeCOEt}$	Aldrich	dried over activated $\text{Al}_2\text{O}_3$
$\text{MeCOPh}$	Aldrich	dried over activated $\text{Al}_2\text{O}_3$
$\text{Ph}_2\text{C}=\text{O}$	Aldrich	none
pyridine	Mallinckrodt	none
$\text{PCl}_5$	Aldrich	none
$\text{EtI}$	Aldrich	dried over activated $\text{Al}_2\text{O}_3$
$\text{H}_2\text{C}=\text{CHCH}_2\text{Br}$	Aldrich	dried over activated $\text{Al}_2\text{O}_3$
$\text{BrCH}_2\text{CH}_2\text{Br}$	Aldrich	dried over activated $\text{Al}_2\text{O}_3$

## PHYSICAL MEASUREMENTS.

### NUCLEAR MAGNETIC RESONANCE

Routine  $^1\text{H}$  (250 MHz) and  $^{13}\text{C}$  (62.9 MHz) NMR spectra were recorded at probe temperature (unless otherwise specified) on a Bruker WM-250 spectrometer in 5 mm tubes. Most variable temperature experiments were performed on a Bruker AM-250 spectrometer in 5 mm tubes for proton spectra and 10 mm tubes for carbon-13 spectra. Chemical shifts are referenced to protio solvent impurities ( $\delta$  7.15,  $\text{C}_6\text{D}_6$ ; 7.24,  $\text{CDCl}_3$ ; 2.09,  $\text{C}_6\text{D}_5\text{CD}_3$ ; 0.00  $\text{Me}_4\text{Si}$  (0.2%, added to  $\text{CDCl}_3$ )) or solvent  $^{13}\text{C}$  resonances ( $\delta$  128.0,  $\text{C}_6\text{D}_6$ ; 77.0,  $\text{CDCl}_3$ ; 20.4,  $\text{C}_6\text{D}_5\text{CD}_3$ ; ) and are reported in ppm downfield of  $\text{Me}_4\text{Si}$ . Multiplicities for  $^{13}\text{C}$  resonances (when reported) were obtained from off-resonance decoupled spectra. Attached proton tests (APT) were routinely obtained and used for assigning carbon resonances but are not listed. Some assignments were based on relative intensities in the broad-band decoupled spectra.

All NMR samples were prepared under a nitrogen atmosphere in a drybox. Deuterated solvents were purchased from Aldrich and were dried over a short column (ca. 5-6 cm) of activated alumina (basic) prior to use. The samples were dried in vacuo, dissolved in the appropriate solvent, transferred to an NMR tube, capped, and the cap was wrapped with Parafilm before removing the sample from the drybox. Spectra were generally obtained within 48 hours of removing the samples from the drybox.

### MAGNETIC MOMENTS

Magnetic moment measurements were performed by the Evans method<sup>112a</sup> on  $\text{C}_6\text{D}_6$  solutions (250 MHz) at probe temperature, and frequency shifts were measured for solvent protio impurity resonances. Diamagnetic corrections ( $\chi_{\text{dia}}$ ) were calculated from Pascal's constants.<sup>112b</sup>

## ELECTRON SPIN RESONANCE SPECTROSCOPY

X-Band (9.5 GHz) ESR spectra were recorded on fluid solutions (room temperature) or frozen glasses (liquid nitrogen temperature) in toluene using a Varian E-3 spectrometer. To minimize the dielectric loss due to moisture condensation in the resonance cavity for measurements made at liquid nitrogen temperature, a nitrogen stream was set to flow continuously down through the microwave resonance cavity. All samples were prepared in the drybox using the following method. A known amount of solid was dissolved in a known volume of toluene. The toluene solution was then placed in a 2 mm quartz tube with a rubber septum for a cap. The cap was then wrapped with Parafilm, and the sample was removed from the drybox.

## INFRARED SPECTROSCOPY

Infrared spectra (reported in  $\text{cm}^{-1}$ ) were recorded as Nujol mulls between 4000 and 600  $\text{cm}^{-1}$  using a Perkin-Elmer 1310 spectrometer or as CsI pellets between 4000 and 180  $\text{cm}^{-1}$  using a Perkin-Elmer 983 spectrometer and were not assigned (except for key resonances), but used as fingerprints (w = weak, m = medium, s = strong intensities; sh = shoulder, br = broad, v = very).

All nujol mulls were prepared in the drybox by the following method. First, the sample was crushed to a fine powder with an agate mortar and pestle. A small amount of Nujol was then added and mixed until a homogeneous paste was formed. The mull was then placed between two NaCl plates before it was removed from the drybox. A spectrum was taken immediately. Samples prepared in this fashion were sufficiently stable to obtain spectra (12 minute scan) without significant decomposition.

Cesium Iodide pellets were also prepared in the drybox. A mixture of the sample and CsI (ca. 1:10) were crushed to a fine homogeneous powder using an agate mortar and

pestle. A small amount of the mixture was then placed in a pellet press and hand tightened before removing from the drybox. The sample was fully compressed outside the box to yield a transparent disc. A spectrum immediately taken showed no significant decomposition.

#### ELEMENTAL ANALYSES

Elemental analyses (C, H, N, and halide) were performed by Desert Analytics of Tucson, Arizona. All samples were stored cold, handled under nitrogen, and combusted with tungstic anhydride.

#### ELECTROCHEMISTRY

Cyclic voltammetry experiments were performed under a nitrogen atmosphere using a BioAnalytical Systems CV-27 Voltammograph and recorded on a Houston Instruments Model 100 X-Y recorder. Measurements were taken at a Pt-disk electrode in THF solutions containing 0.1 M  $n\text{-Bu}_4\text{NPF}_6$  as supporting electrolyte. Voltammograms were recorded at room temperature at a sweep rate of 150 mV/s.  $E_{1/2}$  values (taken as  $(E_{p,a} + E_{p,c})/2$ ) are referenced to Ag/AgCl and are uncorrected for junction potentials.

#### MOLECULAR ORBITAL CALCULATIONS

The extended Hückel calculations<sup>131</sup> used a modified Wolfsberg-Helmholz formula<sup>132</sup> with the parameters listed in Table A.17 taken from the literature.<sup>133</sup> The following bond lengths were used: C-H, 1.08 Å; C-C, 1.45; Ta-O, 1.92; O-H, 0.96; and Ta-benzene centroid, 1.91 for  $(\eta^6\text{-C}_6\text{H}_6)\text{Ta}(\text{OH})_2$ .

**Table A.2** Parameters for the Extended Hückel Calculations.

Orbital	$H_{ii}, \text{eV}$	$\xi_1$	$\xi_2$	$C_1^a$	$C_2^a$
Ta 5d	-12.10	4.762	1.938	0.6815	0.5774
6s	-10.10	2.280			
6p	-6.86	2.241			
C 2s	-21.40	1.625			
2p	-11.40	1.625			
O 2s	-32.30	2.275			
2p	-14.80	2.275			
H 1s	-13.60	1.300			

<sup>a</sup>Coefficients used in the double-zeta expansion.

The C-C-C, C-C-H and Ta-O-H angles were idealized at 120.0°, 120.0°, and 180.0°, respectively. The O-Ta-O angle was fixed at 96.1°. The ab initio UHF SCF calculations on  $(\eta^6\text{-C}_6\text{H}_6)\text{Ta}(\text{OH})_2$  utilized the GAUSSIAN 82 package.<sup>134</sup> A relativistic core potential was employed for the 1s to 5s electrons on Ta.<sup>135</sup> An associated double zeta basis<sup>135</sup> was used for the valence region of the form (341/321/21). The standard 3-21G basis<sup>136</sup> was used for C, O, and H. All geometric parameters were fully optimized within a  $C_{2v}$  or  $C_2$  symmetry constraint. The values of  $\langle s^2 \rangle$  ranged from 0.7767 to 0.7501 for the fully optimized geometries.

## PROTONOLYSIS REACTIONS

Assistance in characterization was obtained through hydrolyzing many of these complexes. A typical hydrolysis was performed by the following method. A slight excess (approximately 0.5 mL) of a water/acetone solution (ca. 10% v/v) was added to a diethyl ether solution of the complex until a white precipitate formed and the color faded (about one hour). After this time, the solution was dried overnight with  $\text{MgSO}_4$ . The white

solids (presumably hydrated  $\text{Ta}_2\text{O}_5$  and  $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ ) were removed by filtration through Celite, and the volatiles were removed from the filtrate in vacuo to provide a colorless or pale yellow oil. Purification of the resulting mixture 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.

**APPENDIX B**  
**X-RAY CRYSTALLOGRAPHY DATA**

**X-Ray Structural Determination of (DIPP)<sub>3</sub>Ta(PhC≡CPh) (16).**

A yellow irregular crystal of C<sub>50</sub> H<sub>61</sub> Ta O<sub>3</sub> having approximate dimensions of 0.70 x 40 x 0.25 mm 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 with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Syntex P2<sub>1</sub> diffractometer equipped with a graphite crystal incident beam monochromator. Table B.1 summarizes the crystal data and structure refinement results. As a check on crystal and electronic stability 2 check reflections were measured after every 98 data reflections. The slope of the least-squares line through a plot of intensity versus time was  $-74 \pm 4$  counts/hour which corresponds to a total loss in intensity of 11.0%. An anisotropic decay correction was applied. The correction factors on I ranged from 0.984 to 1.118 with an average value of 1.046. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient was  $24.3 \text{ cm}^{-1}$  for Mo K $\alpha$  radiation. An empirical absorption correction was made using the method described by Walker and Stuart<sup>137</sup> with the correction factors on I ranging from 0.903 to 1.109. Intensities of equivalent reflections were averaged. 8 reflections were rejected from the averaging process because their intensities differed significantly from the average. The agreement factors for the averaging of the 783 observed and accepted reflections was 2.1% based on intensity and 1.4% based on F<sub>o</sub>. The structure was solved using the Patterson heavy-atom method which revealed the position of the Ta atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen

atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined in full-matrix least-squares. The highest peak in the final difference Fourier had a height of  $0.41 \text{ e}/\text{\AA}^3$ ; the minimum negative peak had a height of  $-0.47 \text{ e}/\text{\AA}^3$ . All calculations were performed on a VAX computer using SDP/VAX.<sup>138</sup>

**Table B.1** Details of the X-Ray Diffraction Study for  
 (DIPP)<sub>3</sub>Ta(PhC≡CPh) (16).

molecular formula	C <sub>50</sub> H <sub>61</sub> TaO <sub>3</sub>
molecular weight	890.99
triclinic space group	P $\bar{1}$
unit cell volume, Å <sup>3</sup>	2272.6
a, Å	11.339 (3)
b, Å	12.308 (2)
c, Å	17.989 (4)
α, deg	84.02 (2)
β, deg	88.42 (2)
γ, deg	65.55 (2)
Z	2
calculated density, g cm <sup>-3</sup>	1.30
crystal dimensions, mm	0.70 x 0.40 x 0.25
data collection temp, °C	23 ± 1
Mo Kα radiation, λ, Å	0.71073
monochromator	graphite, crystal
absorption coefficient, cm <sup>-1</sup>	24.3
2θ range, deg	2-50
total no. of reflns measd	8528, 8068 unique
no. of reflns measd with I > 3σ(I)	6746
scan type	θ-2θ
scan rate, deg min <sup>-1</sup>	4-12
parameters refined	487
R	0.023
R <sub>w</sub>	0.027

**Table B.2** Positional Parameters and Their Estimated  
Standard Deviations

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>B (Å<sup>2</sup>)</u>
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)

**Table B.2** Positional Parameters and Their Estimated  
Standard Deviations (cont.)

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>B (Å<sup>2</sup>)</u>
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)

**Table B.2** Positional Parameters and Their Estimated  
Standard Deviations (cont.)

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>B(Å<sup>2</sup>)</u>
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)

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

**Table B.3** Bond Distances in Angstroms

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>
Ta	O1	1.869 (2)	C24	C25	1.380 (8)
Ta	O2	1.912 (2)	C25	C26	1.409 (6)
Ta	O3	1.889 (2)	C26B	C26A	1.526 (7)
Ta	C4	2.070 (3)	C26	C26A	1.507 (6)
Ta	C5	2.076 (3)	C26A	C26C	1.535 (6)
O1	C11	1.384 (4)	C31	C32	1.393 (5)
O2	C21	1.383 (4)	C31	C36	1.404 (5)
O3	C31	1.371 (4)	C32A	C32C	1.507 (8)
C4	C5	1.346 (5)	C32A	C32B	1.524 (7)
C4	C41	1.472 (5)	C32A	C32	1.514 (6)
C5	C51	1.463 (5)	C32	C33	1.397 (6)
C11	C12	1.397 (5)	C33	C34	1.372 (7)
C11	C16	1.395 (5)	C34	C35	1.377 (7)
C12	C12A	1.518 (6)	C35	C36	1.387 (6)
C12	C13	1.386 (6)	C36	C36A	1.506 (6)
C12B	C12A	1.517 (7)	C36A	C36C	1.474 (9)
C12A	C12C	1.533 (7)	C36A	C36B	1.496 (7)
C13	C14	1.358 (7)	C41	C42	1.408 (6)
C14	C15	1.378 (7)	C41	C46	1.375 (6)
C15	C16	1.397 (6)	C42	C43	1.380 (7)
C16A	C16B	1.535 (7)	C43	C44	1.371 (9)
C16A	C16	1.512 (6)	C44	C45	1.368 (9)
C16A	C16C	1.519 (7)	C45	C46	1.399 (6)
C21	C22	1.406 (5)	C51	C52	1.398 (6)
C21	C26	1.392 (5)	C51	C56	1.392 (6)
C22B	C22A	1.527 (7)	C52	C53	1.391 (6)
C22	C22A	1.504 (6)	C53	C54	1.376 (8)

Table B.3 Bond Distances in Angstroms (cont.)

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>
C22	C23	1.395(5)	C54	C55	1.367(8)
C22A	C22C	1.532(6)	C55	C56	1.380(6)
C23	C24	1.364(7)			

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

**Table B.4** Bond Angles in Degrees

<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>
O1	Ta	O2	103.7(1)	C15	C16	C16A	123.0(4)
O1	Ta	O3	117.0(1)	O2	C21	C22	116.6(3)
O1	Ta	C4	114.0(1)	O2	C21	C26	119.5(4)
O1	Ta	C5	101.1(1)	C22	C21	C26	123.9(4)
O2	Ta	O3	100.0(1)	C21	C22	C22A	120.0(3)
O2	Ta	C4	94.6(1)	C21	C22	C23	116.3(4)
O2	Ta	C5	132.3(1)	C22A	C22	C23	123.5(4)
O3	Ta	C4	121.1(1)	C22B	C22A	C22	109.9(4)
O3	Ta	C5	104.0(1)	C22B	C22A	C22C	109.6(4)
C4	Ta	C5	37.9(1)	C22	C22A	C22C	114.7(4)
Ta	O1	C11	158.8(2)	C22	C23	C24	121.5(5)
Ta	O2	C21	148.1(2)	C23	C24	C25	121.0(4)
Ta	O3	C31	156.7(2)	C24	C25	C26	120.8(5)
Ta	C4	C5	71.3(2)	C21	C26	C25	116.3(4)
Ta	C4	C41	151.9(3)	C21	C26	C26A	120.5(4)
C5	C4	C41	136.8(3)	C25	C26	C26A	123.1(4)
Ta	C5	C4	70.8(2)	C26B	C26A	C26	110.0(4)
Ta	C5	C51	153.6(3)	C26B	C26A	C26C	111.0(4)
C4	C5	C51	135.1(3)	C26	C26A	C26C	114.5(5)
O1	C11	C12	119.4(3)	O3	C31	C32	117.9(3)
O1	C11	C16	117.4(3)	O3	C31	C36	119.3(3)
C12	C11	C16	123.2(3)	C32	C31	C36	122.7(3)
C11	C12	C12A	122.2(4)	C32C	C32A	C32B	111.9(5)
C11	C12	C13	116.6(4)	C32C	C32A	C32	110.5(4)
C12A	C12	C13	121.2(4)	C32B	C32A	C32	113.4(4)
C12	C12A	C12B	110.6(4)	C31	C32	C32A	121.8(3)
C12	C12A	C12C	112.7(5)	C31	C32	C33	117.6(4)

**Table B.4** Bond Angles in Degrees (cont.)

<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>
C12B	C12A	C12C	109.8(4)	C32A	C32	C33	120.7(4)
C12	C13	C14	121.8(4)	C32	C33	C34	120.9(4)
C13	C14	C15	121.0(4)	C33	C34	C35	120.2(4)
C14	C15	C16	120.3(4)	C34	C35	C36	121.8(4)
C16B	C16A	C16	112.6(4)	C31	C36	C35	116.8(4)
C16B	C16A	C16C	110.1(4)	C31	C36	C36A	121.3(3)
C16	C16A	C16C	111.6(4)	C35	C36	C36A	121.9(4)
C11	C16	C15	117.1(4)	C36	C36A	C36C	112.7(5)
C11	C16	C16A	119.9(3)	C36	C36A	C36B	113.0(4)
C36C	C36A	C36B	110.2(6)	C5	C51	C52	120.5(4)
C4	C41	C42	119.6(4)	C5	C51	C56	121.6(4)
C4	C41	C46	121.6(4)	C52	C51	C56	117.8(4)
C42	C41	C46	118.8(4)	C51	C52	C53	120.0(4)
C41	C42	C43	119.9(5)	C52	C53	C54	120.9(5)
C42	C43	C44	120.5(5)	C53	C54	C55	119.4(4)
C43	C44	C45	120.4(5)	C54	C55	C56	120.4(5)
C44	C45	C46	119.9(5)	C51	C56	C55	121.4(5)
C41	C46	C45	120.5(5)				

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

**X-Ray Structural Determination of (DIPP)<sub>3</sub>Ta(CEt=CEtCEt=CEt) (17).**

A red orange irregular crystal of C<sub>48</sub> H<sub>71</sub> Ta O<sub>3</sub> was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Syntex P2<sub>1</sub> diffractometer equipped with a graphite crystal incident beam monochromator. Table B.5 summarizes the crystal data and structure refinement results. As a check on crystal and electronic stability, 3 representative reflections were measured after every 46 reflections. The intensities of these standards remained constant within experimental error throughout data collection. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient was  $23.7 \text{ cm}^{-1}$  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 the use of an absorption correction. Intensities of equivalent reflections were averaged. The agreement factors for the averaging of the 345 observed and accepted reflections were 3.8% based on intensity and 2.9% based on  $F_o$ . The structure was solved using the Patterson heavy-atom method which revealed the position of the Ta atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined in full-matrix least-squares. The highest peak in the final difference Fourier had a height of  $0.71 \text{ e/\AA}^3$ ; the minimum negative peak had a height of  $-1.16 \text{ e/\AA}^3$ . All calculations were performed on a VAX computer using SDP/VAX.<sup>138</sup>

**Table B.5** Details of the X-Ray Diffraction Study for  
 (DIPP)<sub>3</sub>Ta(CEt=CEtCEt=CEt) (17).

molecular formula	C <sub>48</sub> H <sub>71</sub> TaO <sub>3</sub>
molecular weight	877.05
monoclinic space group	P2 <sub>1</sub> /n
unit cell volume, Å <sup>3</sup>	4655.9
a, Å	14.340 (15)
b, Å	16.332 (22)
c, Å	19.929 (11)
β, deg	94.05 (7)
Z	4
calculated density, g cm <sup>-3</sup>	1.25
crystal dimensions, mm	0.50 x 0.30 x 0.50
data collection temp, °C	23 ± 1
Mo Kα radiation, λ, Å	0.71073
monochromator	graphite, crystal
absorption coefficient, cm <sup>-1</sup>	23.7
2θ range, deg	2-50
total no. of reflns measd	9088, 8245 unique
no. of reflns measd with I > 3σ(I)	3191
scan type	θ-2θ
scan rate, deg min <sup>-1</sup>	2-8
parameters refined	469
R	0.046
R <sub>w</sub>	0.045

**Table B.6** Positional Parameters and Their Estimated  
Standard Deviations

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)

**Table B.6** Positional Parameters and Their Estimated  
Standard Deviations (cont.)

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>B (Å<sup>2</sup>)</u>
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)

**Table B.6** Positional Parameters and Their Estimated  
Standard Deviations (cont.)

Atom	x	y	z	B(Å <sup>2</sup> )
C64	0.319(1)	0.434(1)	0.0874(8)	7.6(5)

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

**Table B.7** General Displacement Parameter Expressions - U's

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Ta	0.0476(2)	0.0338(2)	0.0436(2)	-0.0000(5)	0.0088(2)	-0.0014(5)
O1	0.073(5)	0.047(6)	0.037(4)	0.002(5)	0.007(4)	0.007(4)
O2	0.036(4)	0.050(5)	0.055(4)	-0.001(4)	0.008(3)	-0.002(5)
O3	0.083(6)	0.055(5)	0.055(5)	-0.020(5)	0.024(4)	0.019(5)
C11	0.055(8)	0.037(7)	0.054(7)	-0.008(6)	-0.017(6)	0.003(6)
C12	0.059(7)	0.045(8)	0.041(6)	-0.001(7)	-0.005(6)	0.012(6)
C12A	0.081(9)	0.062(9)	0.069(9)	0.012(8)	0.023(8)	-0.007(8)
C12B	0.09(1)	0.06(1)	0.16(2)	-0.02(1)	0.01(1)	-0.03(1)
C12C	0.11(1)	0.06(1)	0.14(1)	0.00(1)	-0.03(1)	-0.03(1)
C13	0.082(9)	0.07(1)	0.045(7)	0.001(9)	0.002(7)	-0.001(8)
C14	0.09(1)	0.08(1)	0.059(8)	-0.011(8)	0.002(8)	0.016(8)
C15	0.11(1)	0.051(9)	0.08(1)	0.003(9)	-0.012(9)	0.009(9)
C16A	0.12(1)	0.039(8)	0.08(1)	0.009(9)	0.009(9)	0.001(8)
C16	0.081(9)	0.048(8)	0.045(7)	0.004(8)	-0.015(7)	0.014(7)
C16B	0.27(2)	0.06(1)	0.11(1)	-0.02(1)	-0.01(2)	-0.01(1)
C16C	0.15(2)	0.12(2)	0.13(2)	0.03(1)	-0.00(1)	-0.02(1)
C21	0.035(7)	0.066(9)	0.074(9)	0.010(6)	-0.002(6)	-0.007(7)
C22B	0.18(2)	0.14(1)	0.07(1)	-0.00(2)	0.02(1)	0.00(1)
C22	0.074(9)	0.07(1)	0.067(8)	0.017(8)	-0.018(7)	-0.003(8)
C22C	0.11(1)	0.13(2)	0.11(1)	0.03(1)	0.01(1)	0.02(1)
C22A	0.08(1)	0.07(1)	0.08(1)	0.023(8)	-0.008(8)	0.022(8)
C23	0.08(1)	0.15(2)	0.072(9)	-0.00(1)	-0.031(8)	-0.02(1)
C24	0.064(9)	0.19(2)	0.10(1)	-0.06(1)	-0.003(9)	-0.00(1)
C25	0.08(1)	0.14(2)	0.08(1)	-0.05(1)	-0.006(9)	0.01(1)
C26	0.065(8)	0.062(8)	0.062(8)	-0.012(9)	-0.001(7)	-0.011(9)
C26A	0.065(8)	0.09(1)	0.059(8)	-0.015(8)	-0.002(7)	0.001(8)
C26B	0.10(1)	0.14(2)	0.08(1)	0.00(1)	0.007(9)	-0.04(1)

**Table B.7** General Displacement Parameter Expressions - U's (cont.)

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C26C	0.14(1)	0.12(1)	0.10(1)	-0.04(1)	-0.01(1)	0.03(1)
C31	0.050(7)	0.077(9)	0.041(7)	-0.005(7)	0.013(6)	0.001(7)
C32A	0.14(1)	0.11(1)	0.07(1)	-0.01(1)	0.033(9)	0.03(1)
C32B	0.12(1)	0.18(2)	0.24(2)	0.01(2)	0.06(1)	-0.05(2)
C32C	0.22(2)	0.13(2)	0.18(2)	0.01(2)	0.08(2)	-0.02(2)
C32	0.08(1)	0.055(9)	0.08(1)	-0.011(8)	0.007(8)	0.011(8)
C33	0.12(1)	0.10(1)	0.09(1)	-0.02(1)	0.01(1)	0.02(1)
C34	0.19(2)	0.08(1)	0.09(1)	-0.02(1)	0.01(1)	0.055(9)
C35	0.07(1)	0.07(1)	0.11(1)	0.005(9)	-0.004(9)	0.02(1)
C36B	0.10(1)	0.35(3)	0.11(2)	-0.00(2)	0.02(1)	-0.03(2)
C36C	0.28(3)	0.13(2)	0.13(2)	-0.07(2)	0.04(2)	-0.02(1)
C36	0.055(8)	0.045(8)	0.069(9)	0.002(7)	0.019(7)	0.011(7)
C36A	0.063(8)	0.057(8)	0.11(1)	-0.018(8)	0.026(8)	-0.006(9)
C41	0.051(7)	0.068(9)	0.11(1)	-0.007(8)	0.017(7)	-0.038(9)
C42	0.055(8)	0.12(1)	0.12(1)	0.03(1)	0.014(8)	-0.03(1)
C43	0.071(9)	0.072(9)	0.08(1)	0.021(8)	0.028(7)	-0.022(8)
C44	0.070(8)	0.056(8)	0.050(8)	0.004(7)	0.012(7)	-0.010(7)
C51	0.07(1)	0.12(2)	0.30(2)	-0.00(1)	0.07(1)	-0.06(2)
C52	0.08(1)	0.18(2)	0.28(2)	0.05(1)	0.00(1)	-0.15(1)
C53	0.09(1)	0.12(1)	0.16(1)	0.03(1)	0.04(1)	-0.06(1)
C54	0.09(1)	0.070(9)	0.054(8)	0.006(9)	0.010(7)	-0.031(8)
C61	0.08(1)	0.26(3)	0.33(3)	-0.05(2)	-0.00(2)	-0.05(3)
C62	0.08(1)	0.26(2)	0.44(3)	0.09(1)	-0.01(2)	-0.22(2)
C63	0.16(1)	0.20(2)	0.21(2)	-0.02(1)	0.11(1)	-0.13(1)
C64	0.10(1)	0.09(1)	0.10(1)	-0.03(1)	0.01(1)	-0.03(1)

The form of the anisotropic displacement parameter is:  
 $\exp[-2\pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2)*(\cos \gamma) + 2hlacU(1,3)*(\cos \beta) + 2klbcU(2,3)*(\cos \alpha)\}]$  where a,b,c, $\alpha$ , $\beta$ , and  $\gamma$  are reciprocal lattice constants.

**Table B.8** Bond Distances in Angstroms

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>
Ta	O1	1.858 (4)	C25	C26	1.38 (1)
Ta	O2	1.920 (5)	C26	C26A	1.50 (1)
Ta	O3	1.845 (5)	C26A	C26B	1.50 (1)
Ta	C41	2.166 (9)	C26A	C26C	1.55 (1)
Ta	C44	2.147 (8)	C31	C32	1.36 (1)
O1	C11	1.392 (9)	C31	C36	1.39 (1)
O2	C21	1.364 (9)	C32A	C32B	1.49 (2)
O3	C31	1.38 (1)	C32A	C32C	1.48 (2)
C11	C12	1.41 (1)	C32A	C32	1.53 (1)
C11	C16	1.41 (1)	C32	C33	1.43 (1)
C12	C12A	1.49 (1)	C33	C34	1.30 (2)
C12	C13	1.39 (1)	C34	C35	1.36 (2)
C12A	C12B	1.51 (1)	C35	C36	1.39 (1)
C12A	C12C	1.53 (1)	C36B	C36A	1.42 (2)
C13	C14	1.34 (1)	C36C	C36A	1.46 (2)
C14	C15	1.38 (1)	C36	C36A	1.51 (1)
C15	C16	1.40 (1)	C41	C42	1.32 (1)
C16A	C16	1.49 (1)	C41	C51	1.61 (2)
C16A	C16B	1.53 (1)	C42	C43	1.49 (1)
C16A	C16C	1.49 (2)	C42	C52	1.51 (1)
C21	C22	1.44 (1)	C43	C44	1.35 (1)
C21	C26	1.39 (1)	C43	C53	1.49 (1)
C22B	C22A	1.57 (1)	C44	C54	1.53 (1)
C22	C22A	1.49 (1)	C51	C61	1.28 (3)
C22	C23	1.38 (1)	C52	C62	1.39 (3)
C22C	C22A	1.49 (1)	C53	C63	1.47 (2)
C23	C24	1.34 (1)	C54	C64	1.52 (1)

Table B.8 Bond Distances in Angstroms (cont.)

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<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>
C24	C25	1.36(2)			

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

**Table B.9** Bond Angles in Degrees

<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>
O1	Ta	O2	96.9 (2)	C22A	C22	C23	124.8 (9)
O1	Ta	O3	124.3 (2)	C22B	C22A	C22	110.7 (9)
O1	Ta	C41	89.8 (3)	C22B	C22A	C22C	109.0 (9)
O1	Ta	C44	118.5 (3)	C22	C22A	C22C	111.3 (9)
O2	Ta	O3	98.4 (2)	C22	C23	C24	125. (1)
O2	Ta	C41	164.9 (3)	C23	C24	C25	119. (1)
O2	Ta	C44	89.2 (3)	C24	C25	C26	123. (1)
O3	Ta	C41	88.9 (4)	C21	C26	C25	117.0 (9)
O3	Ta	C44	115.0 (3)	C21	C26	C26A	121.7 (8)
C41	Ta	C44	75.7 (4)	C25	C26	C26A	120.6 (9)
Ta	O1	C11	165.2 (5)	C26	C26A	C26B	112.8 (8)
Ta	O2	C21	170.8 (5)	C26	C26A	C26C	112.3 (8)
Ta	O3	C31	174.6 (5)	C26B	C26A	C26C	111.2 (9)
O1	C11	C12	118.3 (7)	O3	C31	C32	117.0 (9)
O1	C11	C16	117.7 (8)	O3	C31	C36	119.7 (7)
C12	C11	C16	124.0 (8)	C32	C31	C36	123.4 (9)
C11	C12	C12A	120.7 (7)	C32B	C32A	C32C	108. (1)
C11	C12	C13	115.2 (8)	C32B	C32A	C32	112. (1)
C12A	C12	C13	124 (1)	C32C	C32A	C32	112. (1)
C12	C12A	C12B	110.3 (8)	C31	C32	C32A	123.7 (9)
C12	C12A	C12C	113.0 (9)	C31	C32	C33	116. (1)
C12B	C12A	C12C	109.4 (9)	C32A	C32	C33	120 (1)
C12	C13	C14	124 (1)	C32	C33	C34	122. (1)
C13	C14	C15	118.6 (9)	C33	C34	C35	120. (1)
C14	C15	C16	123 (1)	C34	C35	C36	123. (1)
C16	C16A	C16B	114 (1)	C31	C36	C35	115.2 (9)
C16	C16A	C16C	111 (1)	C31	C36	C36A	121.4 (8)

**Table B.9** Bond Angles in Degrees (cont.)

<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>
C16B	C16A	C16C	111.(1)	C35	C36	C36A	123(1)
C11	C16	C15	115(1)	C36B	C36A	C36C	113.(1)
C11	C16	C16A	121.7(9)	C36B	C36A	C36	113(1)
C15	C16	C16A	123.5(8)	C36C	C36A	C36	114(1)
O2	C21	C22	119.6(9)	Ta	C41	C42	117.0(8)
O2	C21	C26	118.1(8)	Ta	C41	C51	120.9(8)
C22	C21	C26	122.2(8)	C42	C41	C51	121.(1)
C21	C22	C22A	120.7(8)	C41	C42	C43	115.1(9)
C21	C22	C23	114.2(9)	C41	C42	C52	125.(1)
C43	C42	C52	119.5(9)	C43	C44	C54	119.9(8)
C42	C43	C44	116.3(8)	C41	C51	C61	113.(2)
C42	C43	C53	121.3(9)	C42	C52	C62	116.(2)
C44	C43	C53	122.3(9)	C43	C53	C63	113.(1)
Ta	C44	C43	115.7(7)	C44	C54	C64	112.7(8)
Ta	C44	C54	124.2(6)				

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

**Table B.10** Least-Squares Planes

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Plane 1					
Atom	X	Y	Z	Distance	Esd
C11	3.7638	4.2102	-2.6705	-0.0263 +- 0.0114	
C12	4.1360	3.2371	-3.6159	0.0167 +- 0.0110	
C13	4.5724	3.7361	-4.8367	0.0053 +- 0.0122	
C14	4.6250	5.0422	-5.1420	-0.0174 +- 0.0134	
C15	4.1873	5.9553	-4.2075	0.0084 +- 0.0148	
C16	3.7295	5.5898	-2.9351	0.0134 +- 0.0126	
Chi Squared =			10.9		
Plane 2					
Atom	X	Y	Z	Distance	Esd
C21	6.3541	4.0963	1.2877	0.0181 +- 0.0122	
C22	6.7524	3.7654	2.6350	-0.0174 +- 0.0133	
C23	8.0490	4.1295	2.9487	0.0123 +- 0.0166	
C24	8.8767	4.8046	2.1383	-0.0068 +- 0.0199	
C25	8.4491	5.1137	0.8796	0.0069 +- 0.0161	
C26	7.1821	4.8067	0.4230	-0.0130 +- 0.0137	
Chi Squared =			5.6		
Plane 3					
Atom	X	Y	Z	Distance	Esd
C31	2.9380	0.6624	1.8907	-0.0040 +- 0.0116	
C32	2.3499	0.6718	3.1140	0.0073 +- 0.0137	
C33	2.2926	-0.5820	3.8041	0.0008 +- 0.0166	
C34	2.7739	-1.6748	3.2914	-0.0126 +- 0.0189	
C35	3.3188	-1.6480	2.0483	0.0162 +- 0.0142	
C36	3.4556	-0.4831	1.3002	-0.0076 +- 0.0119	

**Table B.10** Least-Squares Planes (cont.)

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	Chi Squared =	2.6			
Plane	4				
Atom	X	Y	Z	Distance	Esd
C44	2.7688	5.1938	1.6841	0.0358 +- 0.0125	
Ta	3.2465	3.5146	0.4347	-0.1262 +- 0.0005	
O1	3.3917	3.7862	-1.3977	0.0458 +- 0.0074	
O3	3.0123	1.8646	1.2251	0.0446 +- 0.0080	
	Chi Squared =	55385.2			
Plane	5				
Atom	X	Y	Z	Distance	Esd
Ta	3.2465	3.5146	0.4347	-0.0071 +- 0.0005	
C41	1.0940	3.7001	0.2827	-0.0046 +- 0.0137	
C42	0.5287	4.6772	0.9616	0.0186 +- 0.0165	
C43	1.4551	5.4820	1.7991	-0.0285 +- 0.0138	
C44	2.7688	5.1938	1.6841	0.0217 +- 0.0120	
	Chi Squared =	185.7			

Table B.10 Least-Squares Planes (cont.)Dihedral Angles Between Planes:

<u>Plane No.</u>	<u>Plane No.</u>	<u>Dihedral Angle</u>
1	2	98.85 +- 0.46
1	3	8.41 +- 1.67
1	4	10.21 +- 0.81
1	5	82.40 +- 0.41
2	3	90.48 +- 0.48
2	4	103.86 +- 0.44
2	5	103.86 +- 0.38
3	4	16.59 +- 0.69
3	5	83.52 +- 0.44
4	5	89.88 +- 0.37

**X-Ray Structural Determination of  $(\eta^6\text{-C}_6\text{Et}_6)\text{Ta}(\text{DIPP})_2$  (36).**

A maroon-red irregular crystal of  $\text{C}_{42}\text{H}_{64}\text{TaO}_2$  having approximate dimensions of 0.35 x 0.45 x 0.40 mm was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Syntex P2<sub>1</sub> diffractometer equipped with a graphite crystal incident beam monochromator. Table B.11 summarizes the crystal data and structure refinement results. As a check on crystal and electronic stability 3 check reflections were measured after every 97 data reflections. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient was  $27.8 \text{ cm}^{-1}$  for Mo  $K\alpha$  radiation. An empirical absorption correction based on a series of psi-scans was applied to the data. Relative transmission coefficients ranged from 0.882 to 0.998 with an average value of 0.912. Intensities of equivalent reflections were averaged. 12 reflections were rejected from the averaging process because their intensities differed significantly from the average. The agreement factors for the averaging of the 673 observed and accepted reflections was 4.0% based on intensity and 2.4% based on  $F_o$ . The structure was solved using the Patterson heavy-atom method which revealed the position of the Ta atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined in full-matrix least-squares. The final difference Fourier had a height of  $1.03 \text{ e/\AA}^3$ ; the minimum negative peak had a height of  $-0.79 \text{ e/\AA}^3$ . All calculations were performed on a VAX computer using SDP/VAX.<sup>138</sup>

**Table B.11** Details of the X-Ray Diffraction Study for

<u>(<math>\eta^6</math>-C<sub>6</sub>Et<sub>6</sub>)Ta(DIPP)<sub>2</sub> (36).</u>	
molecular formula	C <sub>42</sub> H <sub>64</sub> TaO <sub>2</sub>
molecular weight	781.93
monoclinic space group	P2 <sub>1</sub> /c
unit cell volume, Å <sup>3</sup>	3953.3
a, Å	12.396 (4)
b, Å	17.344 (6)
c, Å	18.622 (4)
β, deg	99.11 (2)
z	4
calculated density, g cm <sup>-3</sup>	1.31
crystal dimensions, mm	0.35 x 0.45 x 0.40
data collection temp, °C	23 ± 1
Mo Kα radiation, λ, Å	0.71073
monochromator	graphite, crystal
absorption coefficient, cm <sup>-1</sup>	27.8
2θ range, deg	2-50
total no. of reflns measd	7748, 7008 unique
no. of reflns measd with I > 3σ(I)	4581
scan type	θ-2θ
scan rate, deg min <sup>-1</sup>	2-8
parameters refined	406
R	0.029
R <sub>w</sub>	0.033

**Table B.12** Positional Parameters and Their Estimated Standard Deviations

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>B(Å<sup>2</sup>)</u>
Ta	0.21250 (2)	0.46254 (1)	0.25865 (1)	2.355 (3)
O1	0.2224 (3)	0.5254 (2)	0.1753 (2)	3.69 (8)
O2	0.3453 (3)	0.4982 (2)	0.3159 (2)	3.40 (8)
C11	0.2675 (5)	0.5658 (3)	0.1252 (3)	3.2 (1)
C12	0.2999 (5)	0.5267 (4)	0.0662 (3)	3.9 (1)
C12A	0.2806 (5)	0.4406 (4)	0.0554 (3)	4.3 (1)
C12B	0.3851 (8)	0.3960 (5)	0.0613 (6)	9.3 (3)
C12C	0.2059 (9)	0.4252 (6)	-0.0154 (5)	9.2 (3)
C13	0.3490 (6)	0.5697 (4)	0.0167 (4)	4.9 (2)
C14	0.3630 (6)	0.6470 (4)	0.0248 (4)	5.2 (2)
C15	0.3278 (6)	0.6850 (4)	0.0824 (4)	5.1 (2)
C16A	0.2427 (6)	0.6890 (4)	0.1952 (4)	5.1 (2)
C16	0.2800 (5)	0.6460 (3)	0.1337 (3)	4.0 (1)
C16C	0.3358 (7)	0.7313 (5)	0.2431 (4)	6.7 (2)
C16B	0.1489 (8)	0.7444 (5)	0.1667 (6)	8.6 (3)
C21	0.4257 (4)	0.5489 (3)	0.3437 (3)	3.1 (1)
C22B	0.5987 (7)	0.4405 (5)	0.2610 (5)	6.8 (2)
C22	0.5161 (5)	0.5578 (3)	0.3074 (3)	3.6 (1)
C22A	0.5278 (5)	0.5116 (4)	0.2404 (4)	4.1 (1)
C22C	0.5739 (7)	0.5594 (4)	0.1833 (4)	6.1 (2)
C23	0.5964 (5)	0.6094 (4)	0.3368 (4)	5.0 (2)
C24	0.5877 (6)	0.6508 (4)	0.3985 (4)	6.1 (2)
C25	0.4975 (6)	0.6417 (4)	0.4328 (4)	5.2 (2)
C26A	0.3180 (5)	0.5815 (3)	0.4451 (3)	3.8 (1)
C26	0.4152 (5)	0.5906 (3)	0.4068 (3)	3.6 (1)
C26B	0.2402 (6)	0.6497 (5)	0.4276 (5)	6.4 (2)

**Table B.12** Positional Parameters and Their Estimated  
Standard Deviations (cont.)

Atom	x	y	z	B(Å <sup>2</sup> )
C26C	0.3492(6)	0.5695(5)	0.5263(4)	6.1(2)
C31	0.0763(4)	0.4530(3)	0.3213(3)	2.8(1)
C32	0.0224(4)	0.4463(3)	0.2445(3)	2.7(1)
C33	0.0567(4)	0.3895(3)	0.1994(3)	3.0(1)
C34	0.1546(4)	0.3452(3)	0.2241(3)	2.8(1)
C35	0.1879(4)	0.3385(3)	0.3041(3)	3.0(1)
C36	0.1421(4)	0.3874(3)	0.3509(3)	3.1(1)
C311	0.0264(5)	0.5081(4)	0.3709(3)	3.9(1)
C312	-0.0752(5)	0.4765(5)	0.3989(4)	5.8(2)
C321	-0.0684(5)	0.5027(4)	0.2155(4)	4.3(1)
C322	-0.0297(6)	0.5789(4)	0.1881(4)	5.1(2)
C331	0.0046(5)	0.3871(4)	0.1202(3)	4.5(1)
C332	-0.1008(7)	0.3398(5)	0.1067(5)	7.4(2)
C341	0.1926(5)	0.2829(3)	0.1765(3)	3.8(1)
C342	0.1254(6)	0.2080(4)	0.1736(4)	5.0(2)
C351	0.2710(5)	0.2772(3)	0.3343(4)	4.3(1)
C352	0.3898(6)	0.3016(5)	0.3384(5)	6.6(2)
C361	0.1782(5)	0.3799(4)	0.4332(3)	4.3(1)
C362	0.1127(7)	0.3171(5)	0.4651(4)	6.4(2)

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

**Table B.13** General Displacement Parameter Expressions - U's

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Ta	0.02937(8)	0.02827(8)	0.03232(8)	-0.0034(1)	0.00646(7)	-0.0025(1)
O1	0.059(2)	0.037(2)	0.046(2)	-0.001(2)	0.015(2)	0.007(2)
O2	0.036(2)	0.048(2)	0.044(2)	-0.013(2)	0.004(2)	-0.015(2)
C11	0.040(3)	0.043(3)	0.039(3)	-0.004(3)	0.001(2)	0.010(2)
C12	0.054(3)	0.052(4)	0.042(3)	-0.011(3)	0.009(3)	0.006(3)
C12A	0.073(4)	0.051(4)	0.045(3)	-0.014(3)	0.021(3)	0.004(3)
C12B	0.109(6)	0.051(5)	0.20(1)	0.003(5)	0.052(6)	-0.012(6)
C12C	0.168(9)	0.097(6)	0.074(6)	-0.054(6)	-0.012(6)	-0.006(5)
C13	0.070(4)	0.069(4)	0.053(3)	-0.010(4)	0.022(3)	0.011(3)
C14	0.065(4)	0.065(4)	0.070(4)	-0.008(3)	0.018(3)	0.029(3)
C15	0.063(4)	0.046(3)	0.086(5)	-0.003(3)	0.014(4)	0.016(4)
C16A	0.074(4)	0.040(3)	0.083(5)	0.007(3)	0.018(4)	0.006(4)
C16	0.049(3)	0.041(3)	0.063(4)	-0.002(3)	0.010(3)	0.014(3)
C16C	0.114(6)	0.055(4)	0.087(5)	-0.009(4)	0.016(5)	0.000(4)
C16B	0.118(6)	0.079(5)	0.130(8)	0.046(5)	0.019(6)	0.006(6)
C21	0.039(3)	0.029(3)	0.047(3)	-0.003(2)	0.000(2)	-0.001(3)
C22B	0.094(6)	0.069(5)	0.095(6)	0.024(4)	0.019(5)	0.012(4)
C22	0.036(3)	0.044(3)	0.055(3)	-0.004(2)	0.004(3)	0.003(3)
C22A	0.035(3)	0.060(4)	0.061(4)	-0.002(3)	0.006(3)	0.002(3)
C22C	0.096(5)	0.080(5)	0.063(4)	-0.009(4)	0.030(3)	0.013(4)
C23	0.051(3)	0.068(4)	0.070(4)	-0.029(3)	0.004(3)	0.002(4)
C24	0.076(4)	0.074(4)	0.078(5)	-0.043(4)	-0.001(4)	-0.018(4)
C25	0.081(4)	0.057(4)	0.062(4)	-0.031(3)	0.010(4)	-0.013(3)
C26A	0.055(3)	0.042(3)	0.048(3)	0.000(3)	0.007(3)	-0.009(3)
C26	0.047(3)	0.043(3)	0.048(3)	-0.001(3)	0.006(3)	-0.003(3)
C26B	0.069(5)	0.075(5)	0.101(6)	0.004(4)	0.017(4)	-0.002(5)
C26C	0.078(5)	0.099(6)	0.059(4)	0.006(5)	0.014(4)	0.005(4)

**Table B.13** General Displacement Parameter Expressions - U's (cont.)

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C31	0.031(2)	0.038(3)	0.038(2)	-0.001(2)	0.008(2)	-0.003(3)
C32	0.018(2)	0.042(3)	0.043(3)	-0.008(2)	-0.001(2)	0.004(2)
C33	0.033(3)	0.042(3)	0.039(3)	-0.006(3)	0.005(2)	-0.004(3)
C34	0.033(3)	0.036(3)	0.039(3)	-0.010(2)	0.005(2)	-0.005(2)
C35	0.031(3)	0.037(3)	0.044(3)	-0.008(2)	0.001(2)	0.007(3)
C36	0.039(3)	0.049(3)	0.029(2)	-0.010(3)	0.007(2)	-0.001(3)
C311	0.048(3)	0.057(4)	0.050(3)	-0.000(3)	0.022(2)	-0.014(3)
C312	0.057(3)	0.104(6)	0.067(4)	0.002(4)	0.030(3)	-0.009(4)
C321	0.040(3)	0.071(4)	0.052(4)	0.016(3)	0.000(3)	-0.001(3)
C322	0.067(4)	0.062(4)	0.062(4)	0.029(3)	0.001(3)	-0.001(4)
C331	0.056(4)	0.056(4)	0.054(4)	-0.003(3)	-0.005(3)	-0.012(3)
C332	0.069(5)	0.093(6)	0.103(6)	-0.012(4)	-0.036(4)	-0.024(5)
C341	0.056(3)	0.035(3)	0.056(3)	-0.006(3)	0.018(3)	-0.007(3)
C342	0.079(4)	0.043(3)	0.072(4)	-0.015(3)	0.019(4)	-0.009(3)
C351	0.062(4)	0.039(3)	0.060(4)	0.011(3)	0.004(3)	0.003(3)
C352	0.057(4)	0.074(5)	0.111(6)	0.020(4)	-0.011(4)	0.006(5)
C361	0.061(4)	0.065(4)	0.035(3)	-0.006(3)	0.005(3)	0.004(3)
C362	0.102(5)	0.092(5)	0.050(4)	-0.017(5)	0.016(4)	0.022(4)

The form of the anisotropic displacement parameter is:  
 $\exp[-2\pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2)*(\cos \gamma) + 2hlacU(1,3)*(\cos \beta) + 2klbcU(2,3)*(\cos \alpha)\}]$  where a,b,c, $\alpha$ , $\beta$ , and  $\gamma$  are reciprocal lattice constants.

**Table B.14** Bond Distances in Angstroms

<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Distance</u>
Ta	O1	1.917(4)	C22	C23	1.385(8)
Ta	O2	1.916(4)	C22A	C22C	1.530(9)
Ta	C31	2.205(5)	C23	C24	1.37(1)
Ta	C32	2.346(5)	C24	C25	1.38(1)
Ta	C33	2.424(5)	C25	C26	1.381(8)
Ta	C34	2.219(5)	C26A	C26	1.501(8)
Ta	C35	2.349(5)	C26A	C26B	1.528(9)
Ta	C36	2.426(5)	C26A	C26C	1.515(9)
O1	C11	1.355(7)	C31	C32	1.486(7)
O2	C21	1.368(6)	C31	C36	1.455(8)
C11	C12	1.402(8)	C31	C311	1.526(7)
C11	C16	1.407(8)	C32	C33	1.403(7)
C12	C12A	1.521(9)	C32	C321	1.523(8)
C12	C13	1.399(8)	C33	C34	1.448(7)
C12A	C12B	1.50(1)	C33	C331	1.516(8)
C12A	C12C	1.51(1)	C34	C35	1.486(7)
C13	C14	1.36(1)	C34	C341	1.519(7)
C14	C15	1.39(1)	C35	C36	1.399(8)
C15	C16	1.379(9)	C35	C351	1.524(8)
C16A	C16	1.499(9)	C36	C361	1.533(7)
C16A	C16C	1.53(1)	C311	C312	1.538(9)
C16A	C16B	1.54(1)	C321	C322	1.52(1)
C21	C22	1.406(8)	C331	C332	1.53(1)
C21	C26	1.404(8)	C341	C342	1.539(8)
C22B	C22A	1.528(9)	C351	C352	1.52(1)
C22	C22A	1.508(9)	C361	C362	1.533(9)

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

**Table B.15** Bond Angles in Degrees

<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>
O1	Ta	O2	96.1 (2)	C12	C12A	C12B	112.4 (6)
O1	Ta	C31	128.6 (2)	C12	C12A	C12C	110.6 (6)
O1	Ta	C32	99.7 (2)	C12B	C12A	C12C	112.1 (8)
O1	Ta	C33	94.5 (2)	C12	C13	C14	121.0 (7)
O1	Ta	C34	110.3 (2)	C13	C14	C15	120.3 (6)
O1	Ta	C35	147.3 (2)	C14	C15	C16	121.7 (6)
O1	Ta	C36	162.8 (2)	C16	C16A	C16C	112.9 (6)
O2	Ta	C31	113.1 (2)	C16	C16A	C16B	110.8 (7)
O2	Ta	C32	149.4 (2)	C16C	C16A	C16B	111.2 (7)
O2	Ta	C33	166.9 (2)	C11	C16	C15	117.3 (6)
O2	Ta	C34	131.8 (2)	C11	C16	C16A	122.4 (6)
O2	Ta	C35	104.1 (2)	C15	C16	C16A	120.3 (6)
O2	Ta	C36	98.8 (2)	O2	C21	C22	118.5 (5)
C31	Ta	C32	37.9 (2)	O2	C21	C26	119.3 (5)
C31	Ta	C33	65.2 (2)	C22	C21	C26	122.2 (5)
C31	Ta	C34	81.1 (2)	C21	C22	C22A	121.8 (5)
C31	Ta	C35	65.6 (2)	C21	C22	C23	117.3 (6)
C31	Ta	C36	36.2 (2)	C22A	C22	C23	120.9 (6)
C32	Ta	C33	34.2 (2)	C22B	C22A	C22	110.4 (6)
C32	Ta	C34	65.4 (2)	C22B	C22A	C22C	110.4 (6)
C32	Ta	C35	75.2 (2)	C22	C22A	C22C	112.5 (6)
C32	Ta	C36	63.1 (2)	C22	C23	C24	121.5 (6)
C33	Ta	C34	36.0 (2)	C23	C24	C25	120.2 (6)
C33	Ta	C35	63.0 (2)	C24	C25	C26	121.3 (6)
C33	Ta	C36	72.0 (2)	C26	C26A	C26B	110.2 (5)
C34	Ta	C35	37.8 (2)	C26	C26A	C26C	113.0 (6)
C34	Ta	C36	65.0 (2)	C26B	C26A	C26C	111.8 (6)

**Table B.15** Bond Angles in Degrees (cont.)

<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>	<u>Atom 1</u>	<u>Atom 2</u>	<u>Atom 3</u>	<u>Angle</u>
C35	Ta	C36	34.0(2)	C21	C26	C25	117.6(6)
Ta	O1	C11	159.6(4)	C21	C26	C26A	122.1(5)
Ta	O2	C21	158.2(4)	C25	C26	C26A	120.3(6)
O1	C11	C12	119.3(5)	Ta	C31	C32	76.2(3)
O1	C11	C16	118.9(6)	Ta	C31	C36	80.2(3)
C12	C11	C16	121.7(6)	Ta	C31	C311	133.7(4)
C11	C12	C12A	121.3(5)	C32	C31	C36	116.3(5)
C11	C12	C13	117.9(6)	C32	C31	C311	117.9(5)
C12A	C12	C13	120.8(6)	C36	C31	C311	121.1(5)
Ta	C32	C31	65.9(3)	Ta	C35	C34	66.3(3)
Ta	C32	C33	75.9(3)	Ta	C35	C36	76.0(3)
Ta	C32	C321	129.5(4)	Ta	C35	C351	130.7(4)
C31	C32	C33	119.8(5)	C34	C35	C36	120.1(5)
C31	C32	C321	119.1(5)	C34	C35	C351	119.2(5)
C33	C32	C321	121.1(5)	C36	C35	C351	120.7(5)
Ta	C33	C32	69.9(3)	Ta	C36	C31	63.6(3)
Ta	C33	C34	64.3(3)	Ta	C36	C35	70.0(3)
Ta	C33	C331	130.1(4)	Ta	C36	C361	132.4(4)
C32	C33	C34	120.1(5)	C31	C36	C35	119.7(5)
C32	C33	C331	118.6(5)	C31	C36	C361	120.2(5)
C34	C33	C331	120.1(5)	C35	C36	C361	119.2(5)
Ta	C34	C33	79.7(3)	C31	C311	C312	114.5(5)
Ta	C34	C35	75.8(3)	C32	C321	C322	114.9(5)
Ta	C34	C341	134.9(4)	C33	C331	C332	113.4(6)
C33	C34	C35	116.4(5)	C34	C341	C342	113.8(5)
C33	C34	C341	120.9(5)	C35	C351	C352	114.7(5)
C35	C34	C341	117.8(5)	C36	C361	C362	111.1(5)

Numbers in parentheses are estimated standard deviations.

**Table B.16** Least-Squares Planes

Plane 1				
C31	-0.0007	7.8565	5.9088	0.2051 +- 0.0051
C32	-0.4429	7.7412	4.4950	0.0138 +- 0.0049
C33	0.1157	6.7555	3.6674	-0.0828 +- 0.0054
C34	1.2559	5.9872	4.1211	0.2020 +- 0.0052
C35	1.4326	5.8713	5.5923	0.0367 +- 0.0053
C36	0.7276	6.7200	6.4525	-0.0697 +- 0.0056
C311	-0.7653	8.8122	6.8199	0.1159 +- 0.0062
C321	-1.4833	8.7184	3.9631	-0.0495 +- 0.0066
C331	-0.2976	6.7134	2.2095	-0.1985 +- 0.0066
C341	1.8674	4.9064	3.2457	0.0906 +- 0.0059
C351	2.3740	4.8084	6.1466	-0.0329 +- 0.0063
C361	0.9323	6.5883	7.9662	-0.2308 +- 0.0066
Chi Squared = 6365.1				
	----- Other Atoms -----			
Ta	1.8718	8.0225	4.7559	1.8848 +- 0.0002
Plane 2				
C31	-0.0007	7.8565	5.9088	0.1547 +- 0.0051
C32	-0.4429	7.7412	4.4950	-0.0278 +- 0.0049
C33	0.1157	6.7555	3.6674	-0.1251 +- 0.0054
C34	1.2559	5.9872	4.1211	0.1507 +- 0.0052
C35	1.4326	5.8713	5.5923	-0.0234 +- 0.0053
C36	0.7276	6.7200	6.4525	-0.1291 +- 0.0056
Chi Squared = 2886.4				
	----- Other Atoms -----			
Ta	1.8718	8.0225	4.7559	1.8340 +- 0.0002

**Table B.16** Least-Squares Planes (cont.)

---

Plane	3				
	C32	-0.4429	7.7412	4.4950	0.0506 +- 0.0049
	C33	0.1157	6.7555	3.6674	-0.0507 +- 0.0054
	C35	1.4326	5.8713	5.5923	0.0509 +- 0.0053
	C36	0.7276	6.7200	6.4525	-0.0508 +- 0.0056
	Chi Squared =	371.1			
		----- Other Atoms -----			
	Ta	1.8718	8.0225	4.7559	1.9104 +- 0.0002
Plane	4				
	C31	-0.0007	7.8565	5.9088	-0.0194 +- 0.0051
	C32	-0.4429	7.7412	4.4950	0.0402 +- 0.0049
	C33	0.1157	6.7555	3.6674	-0.0408 +- 0.0054
	C34	1.2559	5.9872	4.1211	0.0200 +- 0.0052
	Chi Squared =	152.0			
Plane	5				
	C31	-0.0007	7.8565	5.9088	0.0221 +- 0.0050
	C34	1.2559	5.9872	4.1211	-0.0217 +- 0.0052
	C35	1.4326	5.8713	5.5923	0.0449 +- 0.0053
	C36	0.7276	6.7200	6.4525	-0.0453 +- 0.0055
	Chi Squared =	174.9			
Plane	6				
	C33	0.1157	6.7555	3.6674	0.0000 +- 0.0055
	C34	1.2559	5.9872	4.1211	0.0000 +- 0.0052
	C35	1.4326	5.8713	5.5923	0.0000 +- 0.0054

**Table B.16** Least-Squares Planes (cont.)

---

Plane 7				
C31	-0.0007	7.8565	5.9088	0.0000 +- 0.0050
C32	-0.4429	7.7412	4.4950	0.0000 +- 0.0048
C36	0.7276	6.7200	6.4525	0.0000 +- 0.0054
Plane 8				
C31	-0.0007	7.8565	5.9088	0.0000 +- 0.0051
C32	-0.4429	7.7412	4.4950	0.0000 +- 0.0049
C33	0.1157	6.7555	3.6674	0.0000 +- 0.0054
Plane 9				
C32	-0.4429	7.7412	4.4950	0.0000 +- 0.0050
C33	0.1157	6.7555	3.6674	0.0000 +- 0.0054
C34	1.2559	5.9872	4.1211	0.0000 +- 0.0052
Plane 10				
C35	1.4326	5.8713	5.5923	0.0000 +- 0.0053
C36	0.7276	6.7200	6.4525	0.0000 +- 0.0055
C31	-0.0007	7.8565	5.9088	0.0000 +- 0.0050
Plane 11				
C34	1.2559	5.9872	4.1211	0.0000 +- 0.0052
C35	1.4326	5.8713	5.5923	0.0000 +- 0.0053
C36	0.7276	6.7200	6.4525	0.0000 +- 0.0056
Plane 12				
C21	4.2641	9.5203	6.3198	-0.0019 +- 0.0053

**Table B.16** Least-Squares Planes (cont.)

C22	5.4920	9.6745	5.6526	0.0046 +- 0.0057
C23	6.4006	10.5698	6.1933	-0.0025 +- 0.0070
C24	6.1111	11.2886	7.3273	-0.0024 +- 0.0075
C25	4.8920	11.1304	7.9580	0.0052 +- 0.0068
C26	3.9475	10.2434	7.4804	-0.0030 +- 0.0058
Chi Squared =	1.8			
Plane 13				
C11	2.9466	9.8126	2.3025	-0.0110 +- 0.0056
C12	3.5224	9.1350	1.2180	0.0101 +- 0.0059
C13	4.2768	9.8809	0.3066	-0.0006 +- 0.0069
C14	4.4270	11.2220	0.4562	-0.0081 +- 0.0069
C15	3.8207	11.8810	1.5148	0.0073 +- 0.0071
C16	3.0763	11.2048	2.4583	0.0023 +- 0.0062
Chi Squared =	9.3			
Plane 14				
O1	2.2409	9.1132	3.2231	0.0000 +- 0.0037
Ta	1.8718	8.0225	4.7559	0.0000 +- 0.0002
O2	3.3494	8.6409	5.8078	0.0000 +- 0.0038
Plane 15				
C11	2.9466	9.8126	2.3025	0.0814 +- 0.0056
O1	2.2409	9.1132	3.2231	-0.1190 +- 0.0037
Ta	1.8718	8.0225	4.7559	-0.0093 +- 0.0002
O2	3.3494	8.6409	5.8078	0.1380 +- 0.0038
C21	4.2641	9.5203	6.3198	-0.0910 +- 0.0052
Chi Squared =	4789.9			

Table B.16 Least-Squares Planes (cont.)Dihedral Angles Between Planes:

<u>Plane No.</u>	<u>Plane No.</u>	<u>Dihedral Angle</u>
1	2	0.41 +- 2.40
1	3	0.46 +- 2.74
1	4	10.83 +- 0.79
1	5	9.98 +- 0.77
1	6	17.26 +- 1.08
1	7	17.65 +- 0.89
1	8	7.41 +- 2.60
1	9	16.02 +- 0.79
1	10	164.23 +- 0.57
1	11	6.53 +- 3.12
1	12	74.65 +- 0.14
1	13	115.84 +- 0.14
1	14	89.15 +- 0.10
1	15	88.07 +- 0.09
2	3	0.17 +- 5.25
2	4	10.42 +- 0.93
2	5	10.39 +- 0.85
2	6	17.17 +- 1.11
2	7	17.72 +- 0.93
2	8	7.08 +- 2.80
2	9	15.63 +- 0.86
2	10	163.84 +- 0.62
2	11	6.82 +- 3.05
2	12	74.25 +- 0.17
2	13	115.43 +- 0.17
2	14	89.28 +- 0.13
2	15	88.24 +- 0.12
3	4	10.43 +- 1.08
3	5	10.38 +- 0.99
3	6	17.01 +- 1.18
3	7	17.89 +- 0.97
3	8	7.17 +- 2.87
3	9	15.67 +- 0.94
3	10	163.88 +- 0.71
3	11	6.72 +- 3.21
3	12	74.20 +- 0.20
3	13	115.40 +- 0.20
3	14	89.45 +- 0.17
3	15	88.40 +- 0.16
4	5	20.81 +- 0.56
4	6	19.39 +- 1.01
4	7	21.01 +- 0.92
4	8	5.63 +- 3.63
4	9	5.76 +- 2.73
4	10	153.55 +- 0.56
4	11	16.44 +- 1.31
4	12	64.69 +- 0.21
4	13	105.22 +- 0.22
4	14	91.42 +- 0.17
4	15	91.29 +- 0.16
5	6	20.64 +- 1.00
5	7	19.85 +- 0.80

Table B.16 Least-Squares Planes (cont.)Dihedral Angles Between Planes:

<u>Plane No.</u>	<u>Plane No.</u>	<u>Dihedral Angle</u>
5	8	16.85 +- 1.24
5	9	25.90 +- 0.58
5	10	173.64 +- 1.55
5	11	6.32 +- 3.39
5	12	83.90 +- 0.21
5	13	125.58 +- 0.22
5	14	87.11 +- 0.17
5	15	85.19 +- 0.16
6	7	34.89 +- 0.83
6	8	21.30 +- 1.26
6	9	24.48 +- 0.87
6	10	158.25 +- 0.96
6	11	14.71 +- 1.88
6	12	67.28 +- 0.36
6	13	109.68 +- 0.41
6	14	106.29 +- 0.33
6	15	104.96 +- 0.32
7	8	15.75 +- 1.56
7	9	21.85 +- 1.04
7	10	154.54 +- 0.72
7	11	22.11 +- 1.14
7	12	82.56 +- 0.35
7	13	118.87 +- 0.25
7	14	71.76 +- 0.34
7	15	71.03 +- 0.33
8	9	9.27 +- 2.44
8	10	157.04 +- 0.98
8	11	13.88 +- 1.99
8	12	70.12 +- 0.34
8	13	110.15 +- 0.35
8	14	87.00 +- 0.33
8	15	86.57 +- 0.33
9	10	148.21 +- 0.61
9	11	22.01 +- 1.05
9	12	61.50 +- 0.37
9	13	100.94 +- 0.35
9	14	89.51 +- 0.26
9	15	89.89 +- 0.24
10	11	169.69 +- 2.07
10	12	92.26 +- 0.34
10	13	50.03 +- 0.42
10	14	90.74 +- 0.25
10	15	93.16 +- 0.22
11	12	77.90 +- 0.36
11	13	119.88 +- 0.38
11	14	92.06 +- 0.35
11	15	90.45 +- 0.35
12	13	42.43 +- 0.29
12	14	122.76 +- 0.18
12	15	127.22 +- 0.18
13	14	111.81 +- 0.18
13	15	116.84 +- 0.17
14	15	5.24 +- 1.27

## APPENDIX C

## LIST OF ABBREVIATIONS

Å = Angstrom  
Anal = analysis  
Ar = 2,6-diisopropylphenyl  
br = broad  
<sup>t</sup>bu or <sup>t</sup>Bu = tertiary butyl  
Calcd = calculated  
Cp = cyclopentadienyl ( $\eta^5\text{-C}_5\text{H}_5$ )  
Cp\* = pentamethylcyclopentadienyl ( $\eta^5\text{-C}_5\text{Me}_5$ )  
d = doublet (NMR)  
DIPP = 2,6-diisopropylphenoxide  
DME = dimethoxyethane  
DMP = 2,6-dimethylphenoxide  
ESR = electron spin resonance  
Et = ethyl  
g = grams  
h = hours  
Hz = hertz  
<sup>i</sup>Pr = isopropyl  
IR = infrared  
L = ligand  
m = medium (IR) or multiplet (NMR) or meta (<sup>13</sup>C NMR)  
Me = methyl  
mL = milliliter  
mmol = millimole  
NMR = nuclear magnetic resonance  
o = ortho (<sup>13</sup>C NMR)  
p = para (<sup>13</sup>C NMR)  
Ph = phenyl  
ppm = part per million  
Pr = propyl  
py = pyridine  
q = quartet (NMR)  
R = alkyl  
s = strong (IR) or singlet (NMR)  
spt = septet (NMR)  
sh = shoulder  
t = triplet (NMR)  
THF = tetrahydrofuran  
THT = tetrahydrothiophene  
TMS = trimethylsilyl  
v = very  
w = weak  
X = halogen

**APPENDIX D**  
**REAGENT SYNTHESSES**

**Preparations. LiDMP.** The lithium phenoxide salt  $\text{Li}(\text{O}-2,6\text{-C}_6\text{H}_3\text{Me}_2)$  was prepared by dissolving 15.0 g (0.12 mmol) of 2,6-dimethylphenol in 250 mL of pentane and cooling the solution to 0 °C. 76 mL (0.12 mmol) of 1.6 M n-BuLi in hexanes was diluted with 100 mL of pentane. The n-BuLi solution was added to the phenol in a dropwise manner over 30 min. A white precipitate formed after most of the n-BuLi had been added. The solution was allowed to warm to room temperature and was stirred for 12 h. The white precipitate was allowed to settle, and the pentane was cannula transferred away from the solid. The resulting white pasty solid was washed with fresh pentane, filtered, and dried in vacuo to produce 14.97 g (0.12 mmol, 95% yield) of LiDMP.

**LiDIPP(OEt<sub>2</sub>).** The lithium phenoxide salt  $\text{Li}(\text{O}-2,6\text{-C}_6\text{H}_3\text{-}^i\text{Pr}_2)$  was prepared by diluting 50 mL (0.27 mmol) of 2,6-diisopropylphenol with 250 mL of pentane and cooling the solution to 0 °C. 166 mL (0.27 mmol) of 1.6 M n-BuLi in hexanes was diluted with 150 mL of pentane. The n-BuLi solution was added to the phenol in a dropwise manner over 1.5 h. A white precipitate formed when most of the n-BuLi was added. The solution was allowed to warm to room temperature and stir for 12 h. The pentane was removed in vacuo producing a white solid (LiDIPP, ether free). The solid was then completely dissolved in 500 mL of diethyl ether. The Et<sub>2</sub>O was removed in vacuo to produce a solid with a faint yellow tint. The solid was washed with pentane, filtered, and dried in vacuo to produce 64.58 g (0.25 mmol, 93% yield) of white, crystalline LiDIPP(OEt<sub>2</sub>). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.12-6.77 (m, 3 H, H<sub>aryl</sub>), 3.48 (spt, 2 H, CHMe<sub>2</sub>), 2.86 (q, 4 H, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 1.29 (d, 12 H, CHMe<sub>2</sub>), 0.68 (t, 6 H, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 136.0 (C<sub>o</sub>), 123.2

(br,  $C_m$ ), 115.4 (br,  $C_p$ ), 65.2 ( $O(\underline{CH}_2CH_3)_2$ ), 27.4 ( $\underline{CHMe}_2$ ), 23.9 ( $\underline{CHMe}_2$ ), 14.2 ( $O(\underline{CH}_2CH_3)_2$ ). The  $C_{ipso}$  resonance was not observed.

**TMSDMP.** Both TMSDMP and TMSDIPP can be prepared from their respective phenols by a procedure analogous to that reported for other trimethylsilyl ethers.<sup>139</sup> A mixture of HO-2,6- $C_6H_3Me_2$  (50.1 g, 0.41 mol), TMSCl (72.8 g, 0.67 mol), and  $TMS_2NH$  (32.5 g, 0.20 mol) were combined in a large flask in 200 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 cooled to room temperature, filtered, and the reaction volatiles were removed in vacuo with gentle heating (at ca. 60 °C) to afford an oil. Heating and vacuum were continued for 6-8 h for complete removal of the pyridine, after which time the oil was filtered again to provide 54 g (0.28 mol, 68% yield) of pure TMSDMP as a pale brown oil.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  6.94-6.75 (m, 3 H,  $H_{aryl}$ ), 2.16 (s, 6 H,  $C_6H_3\underline{Me}_2$ ), 0.14 (s, 9 H,  $SiMe_3$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  153.0 ( $C_{ipso}$ ), 128.9 ( $C_m$ ), 128.5 ( $C_o$ ), 121.8 ( $C_p$ ), 17.9 ( $C_6H_3\underline{Me}_2$ ), 0.9 ( $SiMe_3$ ).

**TMSDIPP.** This reagent can be prepared as described in the above procedure but was actually prepared using the procedure described below. 15.0 g (0.06 mol) of  $LiDIPP(OEt_2)$  was dissolved in 250 mL of diethyl ether. 6.81 g (0.06 mol) of TMSCl was added to the ether solution in a dropwise manner. Upon addition of the TMSCl, the solution immediately went from clear and colorless to cloudy and white. The solution was allowed to stir 24 h at room temperature. The solution was filtered through Celite, and the solvent was removed in vacuo leaving behind 13.53 g (0.05 mol, 93% yield) of a pale yellow oil.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.07-6.92 (m, 3 H,  $H_{aryl}$ ), 3.23 (spt, 2 H,  $\underline{CHMe}_2$ ), 1.19 (d, 12 H,  $\underline{CHMe}_2$ ), 0.26 (s, 9H,  $SiMe_3$ ).  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  139.0 ( $C_o$ ), 123.3 ( $C_m$ ), 121.8

(C<sub>p</sub>), 26.9 (CHMe<sub>2</sub>), 23.4 (CHMe<sub>2</sub>), 0.75 (SiMe<sub>3</sub>). The C<sub>ipso</sub> was not observed.

**Ta(DIPP)<sub>2</sub>Cl<sub>3</sub>(OEt<sub>2</sub>)**. The ether-free analogue of this complex has been reported,<sup>140</sup> 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 10.05 g (28.06 mmol) of TaCl<sub>5</sub> in 250 mL of benzene was added 50 mL of diethyl ether, which resulted in the immediate dissolution of the TaCl<sub>5</sub>. 14.21 g (55.0 mmol) of LiDIPP(OEt<sub>2</sub>) was weighed out and added all at once to the tantalum solution. Upon the addition of the lithium salt, a series of color changes (from brown to orange to yellow) and the precipitation of LiCl were observed. After being stirred for 24 h at room temperature, the solution was filtered through Celite, and the solvent was removed in vacuo producing a yellow frothy oil. Upon the addition of 50 mL of pentane to the oil, a yellow solid immediately precipitated out. The solvent was again removed in vacuo to yield a yellow solid. The solid was collected, washed with pentane, and dried in vacuo to produce 17.50 g (24.44 mmol, 87% yield) of product sufficiently pure for further reactions. Additional crops of solid may be obtained by concentrating the filtrate and cooling to -40 °C (up to 92% yield.) <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.03-6.81 (m, 6 H, H<sub>aryl</sub>), 4.25 (br q, 4 H, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 4.03 (br, 4 H, CHMe<sub>2</sub>), 1.20 (d, 24 H, CHMe<sub>2</sub>), 12.0 (t, 6 H, O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 140.7 (C<sub>o</sub>), 125.8 (C<sub>p</sub>), 124.2 (C<sub>m</sub>), 69.0 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 26.4 (CHMe<sub>2</sub>), 24.8 (CHMe<sub>2</sub>), 12.0 (O(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>). The C<sub>ipso</sub> resonance has not been observed. Anal. Calcd. for C<sub>28</sub>H<sub>44</sub>O<sub>3</sub>Cl<sub>3</sub>Ta: C, 46.97; H, 6.19. Found: C, 47.26; H, 6.35.

**Ta(DIPP)<sub>3</sub>Cl<sub>2</sub>(OEt<sub>2</sub>)**. To a slurry of 10.00 g (27.92 mmol) of TaCl<sub>5</sub> in 250 mL of benzene was added 50 mL of diethyl ether, which resulted in the immediate dissolution of the TaCl<sub>5</sub>. 21.31 g (82.50 mmol) of LiDIPP(OEt<sub>2</sub>) was weighed out and added all at once to the tantalum solution. Upon the addition of the lithium salt, a series of color changes

(from brown to orange to yellow) and the precipitation of LiCl were observed. After being stirred for 24 h at room temperature, the solution was filtered through Celite, and the solvent was removed in vacuo producing a yellow frothy oil. Upon the addition of 50 mL of pentane to the oil, a yellow solid immediately precipitated out. The solvent was again removed in vacuo to yield a yellow solid. The solid was collected, washed with pentane, and dried in vacuo to produce 15.17 g (17.69 mmol, 74% yield) of product sufficiently pure for further reactions. Additional crops of solid may be obtained by concentrating the filtrate and cooling to -40 °C (up to 80% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.09-6.89 (m, 9 H,  $\text{H}_{\text{aryl}}$ ), 4.28 (br, 4 H,  $\text{O}(\underline{\text{CH}_2\text{CH}_3})_2$ ), 3.78 (br, 6 H,  $\underline{\text{CH}}\text{Me}_2$ ), 1.37 (t, 6 H,  $\text{O}(\text{CH}_2\underline{\text{CH}_3})_2$ ), 1.07 (br d, 36 H,  $\underline{\text{CH}}\text{Me}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  155.2 (br,  $\text{C}_{\text{ipso}}$ ), 139.7 ( $\text{C}_o$ ), 123.5 (coincident  $\text{C}_m$  and  $\text{C}_p$ ), 66.8 ( $\text{O}(\underline{\text{CH}_2\text{CH}_3})_2$ ), 26.0 ( $\underline{\text{CH}}\text{Me}_2$ ), 24.5 ( $\underline{\text{CH}}\text{Me}_2$ ), 12.2 ( $\text{O}(\text{CH}_2\underline{\text{CH}_3})_2$ ). Anal. Calcd. for  $\text{C}_{40}\text{H}_{61}\text{O}_4\text{Cl}_2\text{Ta}$ : C, 56.01; H, 7.17. Found: C, 56.11; H, 7.31.

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12 H, Me), 1.19 (d, 12 H,  $\text{CHMe}_2$ ), 1.06 (t, 6 H,  $\text{C}_{\text{alkyne}}\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  191.8 ( $\text{C}_{\text{acet}}$ ), 161.4 ( $\text{C}_{\text{ipso}}$  DMP), 144.2 ( $\text{C}_o$  NAr), 128.2 ( $\text{C}_m$ ,  $\text{C}_p$  DMP are coincident), 127.4 ( $\text{C}_o$  DMP), 124.6 ( $\text{C}_p$  NAr), 121.9 ( $\text{C}_m$  NAr), 27.8 ( $\text{CHMe}_2$ ), 26.3 ( $\text{C}(\text{CH}_2\text{CH}_3)_2$ ), 23.4 ( $\text{CHMe}_2$ ), 17.3 (Me), 13.7 ( $\text{C}(\text{CH}_2\text{CH}_3)_2$ ).

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