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Reactions of Alkynes and Olefins with Tantalum Hydrides Containing Aryloxy Ancillary Ligation: Relevance to Catalytic Hydrogenation[†]

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The reactivity of the three hydride compounds [Ta(OC₆H₃Ph₂-2,6)₂(H)₂Cl(PMe₃)₂] (**1**), [Ta(OC₆H₃Prⁱ-2,6)₂(H)₂Cl(PMe₂Ph)₂] (**2**), and [Ta(OC₆H₃Bu^t-2,6)₂(H)₂Cl(PMePh)₂] (**3**) toward olefins and alkynes has been investigated. The reactivity observed is highly dependent on the nature of the ancillary aryloxy ligands. The 2,6-diphenylphenoxide **1** reacts with styrene to produce 1 equiv of ethylbenzene and the styrene adduct [Ta(OC₆H₃Ph₂-2,6)(η²-CH₂=CHPh)Cl(PMe₃)₂] (**5**). In contrast, **1** reacts with 3-hexyne to eliminate H₂ along with formation of the analogous alkyne complex **6**. Structural studies of **5** and **6** show a square-pyramidal geometry with an axial olefin (alkyne) unit lying along the Cl–Ta–P axis. Structural parameters support a tantalacyclopentadiene (tantalacyclopentadiene) bonding picture for these molecules. Compound **5** is converted back into **1** under H₂ along with formation of PhEt. The dihydride **2** reacts with styrene to form 1 equiv of PhEt, H₂, and the dehydrogenation product [Ta(OC₆H₃Prⁱ-η²-CMe=CH₂)(OC₆H₃Prⁱ-2,6)Cl(PMe₂Ph)₂] (**7**). The related adduct [Ta(OC₆H₃Prⁱ-η²-CMe=CH₂)(OC₆H₃Prⁱ-2,6)Cl(PEt₃)₂] (**9**) was isolated by treatment of [Ta(OC₆H₃Prⁱ-2,6)₂Cl₃] with PEt₃/Bu₃SnH and was structurally characterized. Labeling studies show that the H₂ generated comes exclusively from the aryloxy *o*-Prⁱ group which was dehydrogenated. Both hydrides initially attached to the metal are transferred to the olefin substrate. In the case of the 2,6-di-*tert*-butylphenoxide compound **3**, reaction with styrene generates the mono-cyclometalated compound [Ta(OC₆H₃Bu^tCMe₂CH₂)(OC₆H₃Bu^t-2,6)(CH₂CH₂Ph)Cl] (**9**). Structural studies of **9** confirm the presence of a phenethyl group. The related *trans*-phenylvinyl compound **10** is produced when **3** is reacted with phenylacetylene. Addition of 2,6-dimethylphenyl isocyanide (xyNC) to **10** produces the bis(iminoacyl) derivative **11**, in which xyNC has inserted into the cyclometalated carbon as well as the Ta–CH=CHPh bond in **10**. Structural studies of **11** confirmed the *trans* arrangement of the hydrogen atoms in the phenylvinyl group. Mechanistic studies of the formation of **10** and **11** show the presence of two competing pathways. The first involves direct elimination of H₂ from the dihydride and formation of an intermediate olefin/alkyne adduct. The product then arises by CH bond activation of the aryloxy with the hydrogen transferring to a carbon atom of the tantalacyclopentadiene (tantalacyclopentadiene) ring. The second pathway involves insertion of olefin/alkyne into a Ta–H bond followed by CH bond activation by the remaining hydride.

Introduction

It has been demonstrated that hydride derivatives of niobium and tantalum containing aryloxy ligation possess the ability to catalyze the hydrogenation of a variety of arene substrates.¹ This discovery has led us to pursue studies that may give insights into the key steps within the catalytic cycle. Previous work has shown that cyclohexene and 1,3-cyclohexadiene are hydrogenated many orders of magnitude faster than arenes.² Furthermore, stable 1,3-cyclohexadiene com-

pounds of niobium and tantalum have been isolated and implicated as key intermediates in arene hydrogenation. As an extension of this work, we have investigated the reactivity of isolated hydride aryloxides of tantalum with olefins and alkynes.³ In this paper we report the results of this study, hinting at the plethora of reaction pathways that are available to these systems.

Results and Discussion

Synthesis and Characterization of Compounds.

The reactivity of the previously synthesized⁴ hydrides

[†] Dedicated to Professor Richard A. Walton on the occasion of his 60th birthday.

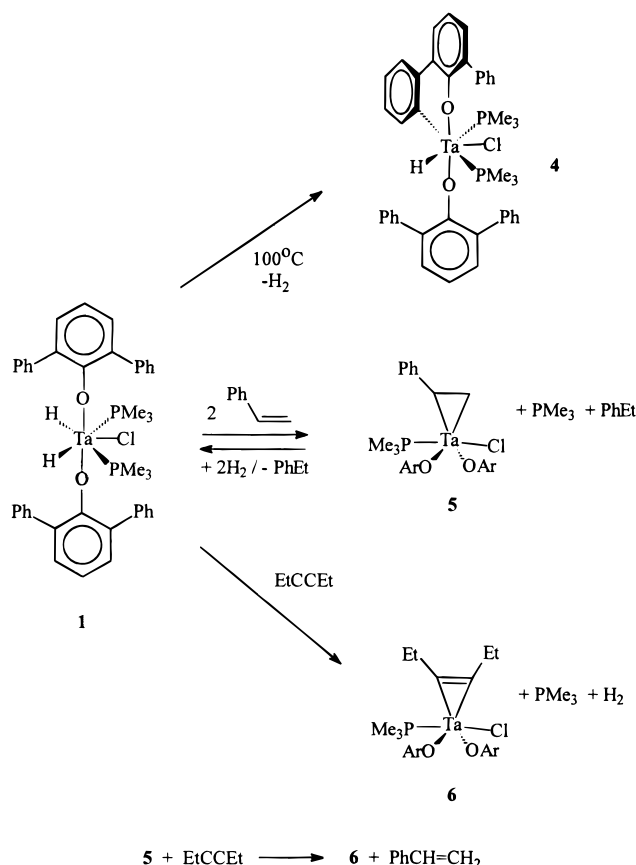
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Scheme 1



$[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph}_2-2,6)_2(\text{H})_2\text{Cl}(\text{PMe}_3)_2]$ (**1**), $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i_2-2,6)_2(\text{H})_2\text{Cl}(\text{PMe}_2\text{Ph})_2]$ (**2**), and $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t_2-2,6)_2(\text{H})_2\text{Cl}(\text{PMePh}_2)]$ (**3**) are the focus of this paper. Seven-coordinate **1** and **2** have been shown to adopt pentagonal-bipyramidal structures both in solution and the solid state with trans, axial aryloxy ligands. In the case of six-coordinate **3** a dramatic distortion from octahedral geometry is observed and the underlying electronic reasons for the distortion have been investigated.⁵ During the course of this study we discovered that compound **1** is thermally unstable. After 24 h a C_6D_6 solution of **1** is converted into a 50/50 mixture of **1** and a new hydride product. The conversion is complete within minutes at 100°C , yielding the mono-cyclometalated derivative **4** (Scheme 1), which shows a sharp Ta–H resonance as a doublet of doublets at δ 18.68 ppm in the ^1H NMR spectrum and nonequivalent phosphine ligands in the ^{31}P NMR spectrum. The solid-state structure of **4** (Figure 1, Table 1) shows pentagonal-bipyramidal geometry with trans, axial oxygen atoms. The structure is closely related to that of the precursor **1**, except that the Ta–C bond of a cyclometalated 2,6-diphenylphenoxide ligand has replaced one of the original Ta–H groups. Detailed analysis of the ^1H NMR spectra of **1** and **2** indicates that the molecules are stereochemically rigid.⁴ This results in an AA'XX' spectrum for the hydride ligands coupled not only to each other but the magnetically nonequivalent phosphine ligands. Simulation of the pattern yields all four (H,H', H,P, H,P', and P,P') coupling constants. The

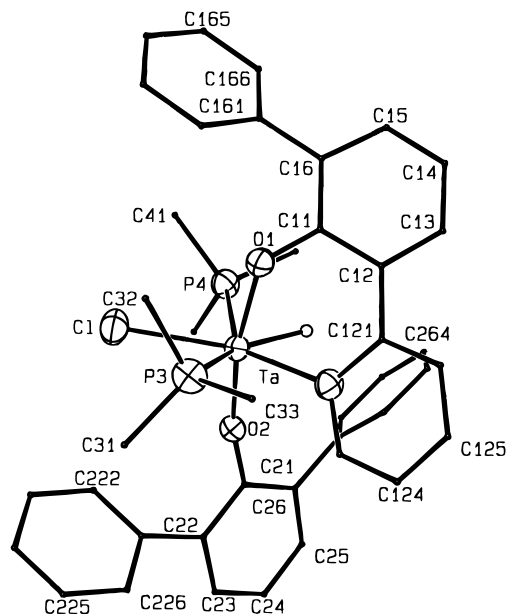


Figure 1. Molecular structure of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph}-\eta^1\text{-C}_6\text{H}_4)(\text{OC}_6\text{H}_3\text{Ph}_2-2,6)(\text{H})\text{Cl}(\text{PMe}_3)_2]$ (**4**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph}-\eta^1\text{-C}_6\text{H}_4)(\text{OC}_6\text{H}_3\text{Ph}_2-2,6)(\text{H})\text{Cl}(\text{PMe}_3)_2]$ (**4**)

| | | | |
|----------------|-----------|----------------|-----------|
| Ta–Cl | 2.500(1) | Ta–C(122) | 2.220(5) |
| Ta–P(3) | 2.729(2) | Ta–H | 1.7(4) |
| Ta–P(4) | 2.603(1) | O(1)–C(11) | 1.347(6) |
| Ta–O(1) | 1.947(3) | O(2)–C(21) | 1.376(6) |
| Ta–O(2) | 1.910(3) | | |
| Cl–Ta–P(3) | 75.45(5) | P(4)–Ta–O(1) | 85.8(1) |
| Cl–Ta–P(4) | 77.47(5) | P(4)–Ta–O(2) | 91.8(1) |
| Cl–Ta–O(1) | 95.8(1) | P(4)–Ta–C(122) | 130.6(1) |
| Cl–Ta–O(2) | 94.8(1) | P(4)–Ta–H | 66(1) |
| Cl–Ta–C(122) | 151.5(1) | O(1)–Ta–O(2) | 168.43(2) |
| Cl–Ta–H | 143(1) | O(1)–Ta–C(122) | 83.4(2) |
| P(3)–Ta–P(4) | 148.62(5) | O(1)–Ta–H | 79(1) |
| P(3)–Ta–O(1) | 81.5(1) | O(2)–Ta–C(122) | 89.7(2) |
| P(3)–Ta–O(2) | 105.9(1) | O(2)–Ta–H | 90(1) |
| P(3)–Ta–C(122) | 76.3(1) | C(122)–Ta–H | 65(1) |
| P(3)–Ta–H | 138(1) | | |

coupling constants obtained for **4** are totally consistent with the previous conclusions. Hence, the H,P and H,P' coupling constants of 83 and 8 Hz as well as the P,P' coupling of 108 Hz are comparable in magnitude to those calculated for dihydrides such as **1** and **2**.⁴ The pathway of cyclometalation of the aryloxy ligand in **1** is relevant to the other reactivity in this paper and is discussed in more detail in the mechanistic section below.

The addition of excess styrene to C_6D_6 solutions of **1** leads to the slow formation of the new organometallic product **5** as monitored by ^1H NMR spectroscopy. The solution was also found to contain uncoordinated PMe_3 (^{31}P NMR) and 1 equiv of ethylbenzene per tantalum (Scheme 1). Compound **5** was structurally characterized and can be seen to contain 1 equiv of styrene π -bound to the metal center (Figure 2, Table 2). The C–C distance of 1.452(7) Å for the bound styrene in **5** is significantly elongated over the distance of 1.339 Å found for ethylene but is comparable to the value of 1.477 Å found in $[\text{Cp}^*\text{Ta}(\eta^2\text{-C}_2\text{H}_4)(=\text{CHCMe}_3)(\text{PMe}_3)]$.⁶

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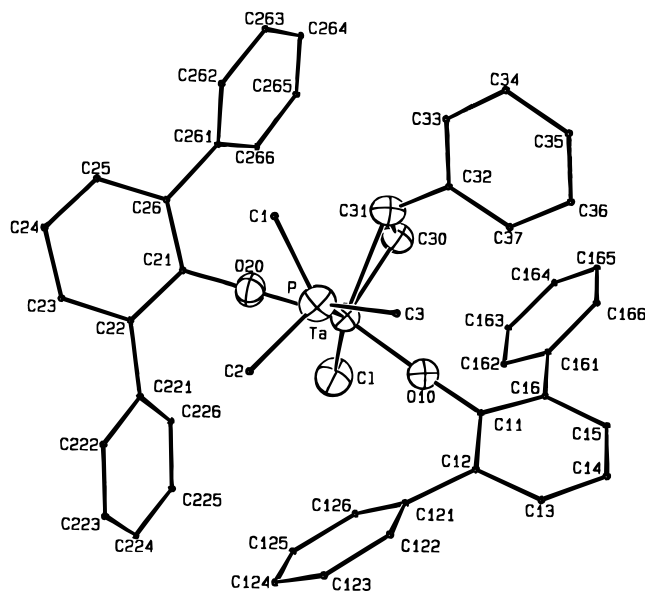


Figure 2. Molecular structure of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2(\eta^2\text{-CH}_2=\text{CHPh})\text{Cl}(\text{PMe}_3)]$ (**5**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2(\eta^2\text{-CH}_2=\text{CHPh})\text{Cl}(\text{PMe}_3)]$ (5**)**

| | | | |
|----------------|-----------|----------------|----------|
| Ta–Cl | 2.442(1) | Ta–C(30) | 2.131(5) |
| Ta–O(10) | 1.895(3) | Ta–C(31) | 2.242(5) |
| Ta–O(20) | 1.915(3) | C(30)–C(31) | 1.452(7) |
| Ta–P | 2.609(1) | | |
| Cl–Ta–O(10) | 88.6(1) | P–Ta–C(30) | 117.7(1) |
| Cl–Ta–O(20) | 89.1(1) | P–Ta–C(31) | 79.1(1) |
| Cl–Ta–P | 150.88(5) | O(10)–Ta–O(20) | 158.9(1) |
| Cl–Ta–C(30) | 91.3(1) | O(10)–Ta–C(30) | 98.4(2) |
| Cl–Ta–C(31) | 129.7(1) | O(10)–Ta–C(31) | 101.5(2) |
| P–Ta–O(10) | 89.6(1) | O(20)–Ta–C(30) | 102.6(2) |
| P–Ta–O(20) | 82.3(1) | O(20)–Ta–C(31) | 96.0(2) |
| C(30)–Ta–C(31) | 38.7(2) | | |

This parameter along with the Ta–C distances supports a tantalacyclopropane description of the bonding in **5**.⁷ The molecular structure of **5** is best described as square pyramidal with trans-basal aryloxides. The π -bound styrene occupies the axial site, and its C–C vector lies along the P–Ta–Cl plane. The phenyl substituent is proximal to the phosphine ligand. The Ta–CHPh distance of 2.242(5) Å is slightly longer than the Ta–CH₂ distance of 2.131(5) Å, possibly for steric reasons. In the ¹³C NMR spectrum of **5** the Ta–CH₂ carbon appears as a doublet (²*J* coupling to ³¹P), while the Ta–CHPh carbon is a singlet. This is consistent with the same structure being adopted in solution as is observed in the solid state. Studies of the olefin complexes $[(\text{ArO})_2\text{Ti}(\eta^2\text{-olefin})(\text{PR}_3)]$ show stronger ³¹P coupling to the distal carbon of the olefin (larger P–Ti–C angle).⁸ The PMe₃ protons in **5** appear upfield as a sharp doublet at δ –0.01 ppm. This upfield shifting is due to the diamagnetic anisotropy of the adjacent 2,6-diphenylphenoxide ligands.

When a solution of **5** in the presence of an extra 1 equiv of PMe₃ is exposed to H₂ at ambient temperatures, regeneration of dihydride **1** is observed (¹H and ³¹P

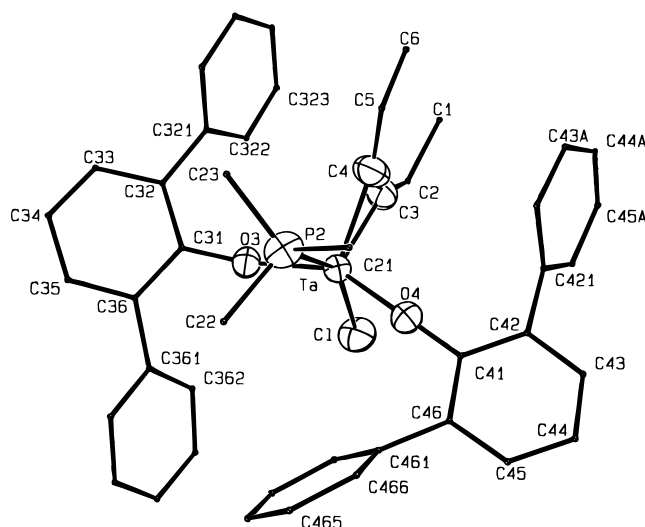


Figure 3. Molecular structure of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2(\eta^2\text{-EtC}\equiv\text{CEt})\text{Cl}(\text{PMe}_3)]$ (**6**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2(\eta^2\text{-EtC}\equiv\text{CEt})\text{Cl}(\text{PMe}_3)]$ (6**)**

| | | | |
|--------------|-----------|--------------|----------|
| Ta–Cl | 1.913(2) | C(1)–C(2) | 1.405(4) |
| Ta–P(2) | 2.633(1) | C(2)–C(3) | 1.500(6) |
| Ta–O(3) | 1.926(2) | C(3)–C(4) | 1.291(6) |
| Ta–O(4) | 1.913(2) | C(4)–C(5) | 1.504(7) |
| Ta–C(3) | 2.045(3) | C(5)–C(6) | 1.352(9) |
| Ta–C(4) | 2.092(4) | | |
| O(4)–Ta–O(3) | 148.2(1) | C(3)–Ta–C(4) | 36.3(2) |
| O(3)–Ta–Cl | 89.45(7) | C(3)–C(4)–Ta | 73.5(2) |
| O(4)–Ta–Cl | 88.28(8) | O(3)–Ta–C(3) | 105.2(1) |
| O(3)–Ta–P(2) | 82.38(7) | O(3)–Ta–C(4) | 106.5(1) |
| O(4)–Ta–P(2) | 84.37(8) | O(4)–Ta–C(3) | 106.5(1) |
| Cl–Ta–P(2) | 150.98(4) | O(4)–Ta–C(4) | 100.8(1) |

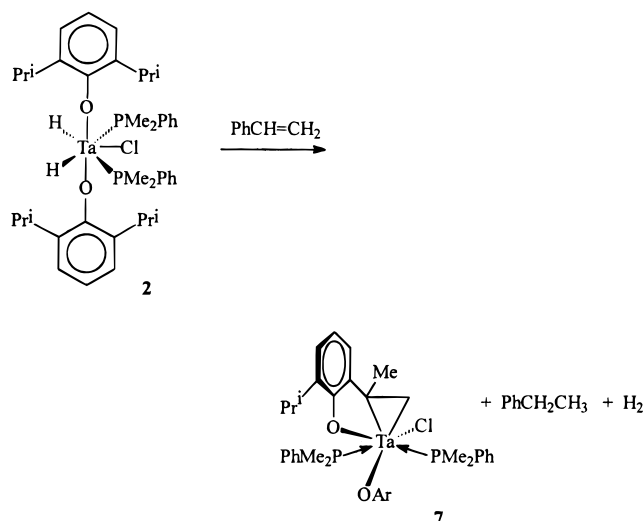
NMR) along with 1 equiv of ethylbenzene (Scheme 1). In the presence of an excess of styrene, **5** acts as a hydrogenation catalyst precursor, yielding ethylbenzene at rates varying from 1 equiv/day (room temperature, 20 psi H₂) to 1 equiv/h (room temperature, 1200 psi H₂). Exhaustive hydrogenation of 20 equiv of styrene by **5** can occur in the presence of 1 equiv of PMe₃ over 24 h (room temperature, 1200 psi H₂) with re-formation of **1** as determined by ³¹P NMR analysis of the final reaction mixture.

Compound **1** reacts readily with 3-hexyne to generate the corresponding alkyne adduct **6** (Scheme 1). However, in this case no hexene is produced. Instead, H₂ is detected in solution (¹H NMR), and in fact bubbles of gas are observed upon addition of 3-hexyne to a concentrated C₆D₆ solution of **1**. Compound **6** adopts a structure in the solid state similar to that observed for **5** (Figure 3, Table 3). The axially, π -bound hexyne unit lies along the P–Ta–Cl plane with trans-basal aryloxides. The C–C distance of 1.291(6) Å is elongated over a typical alkyne distance but is still 0.1 Å shorter than that found in olefins. However, as with related early d-block metal derivatives of alkynes, a tantalacyclopropane description is justified. The solution spectroscopic properties of **6** are consistent with the molecule adopting an structure identical with that found in the solid state. Furthermore, the presence of two sharp sets of C≡T signals shows that the alkyne unit is not undergoing rotation on the NMR time scale. In the ¹H NMR spectrum the nonequivalent hexyne protons appear as

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Scheme 2



two sets of quartets (nondiastereotopic CH_2) and triplets (CH_3). Hence, a virtual plane runs through the unit with each end being nonequivalent. The $\text{Ta}(\eta^2\text{-EtC}\equiv\text{CEt})$ carbon atoms give rise to a doublet at δ 188.5 ppm (2J coupling to ^{31}P) and a singlet at δ 195.0 ppm.

The addition of 3-hexyne to a C_6D_6 solution of the styrene complex **5** was found to slowly (^1H and ^{31}P NMR) form the alkyne adduct **6** and free styrene (Scheme 1). However, even in the presence of a large excess of styrene the alkyne adduct **6** failed to form any detectable amounts of **5**. This clearly demonstrates a much stronger affinity of the metal and this particular ligand set for 3-hexyne over styrene.

The addition of styrene to the di-isopropylphenoxide **2** generates both 1 equiv of ethylbenzene and H_2 (Scheme 2). The organometallic product **7** was identified spectroscopically as containing an aryloxy chelated to the metal via an α -methylvinyl group generated by dehydrogenation of an original isopropyl substituent. Previous studies have shown that dehydrogenation of the ortho substituents of 2,6-diisopropylphenoxide can occur at d^2 niobium metal centers.⁷ The proposed structure for $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i_2-\eta^2\text{-CMe=CH}_2)(\text{OC}_6\text{H}_3\text{Pr}^i_2-2,6)\text{Cl}(\text{PMe}_2\text{Ph})_2]$ (**7**) is given strong support in the structurally characterized complex $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i_2-2,6)(\text{OC}_6\text{H}_3\text{Pr}^i_2-\eta^2\text{-CMe=CH}_2)\text{Cl}(\text{PET}_3)_2]$ (**8**), which was obtained during the reaction of the trichloride $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i_2-2,6)\text{Cl}_3]$ with $\text{PET}_3/\text{Bu}_3\text{SnH}$. Compound **8** adopts a structure (Figure 4, Table 4) that is very similar to that of the previously reported dcpm derivative.⁹ Furthermore, complex **7** is also generated when **2** is added to either 1,3-cyclohexadiene or cyclohexene, yielding cyclohexene or cyclohexane, respectively.² In the proton-decoupled ^{13}C NMR spectra of **7** the $\eta^2\text{-CMe=CH}_2$ carbon atoms appear as two doublets (2J coupling to ^{31}P) at δ 71.9 and 68.2 ppm, respectively. In the ^1H NMR spectrum the methyl peak is a sharp singlet, while the methylene protons appear as overlapping multiplets due to their similar chemical shifts. The possible mechanism of formation of **7** is discussed below.

The addition of styrene to the dihydride **3** results in formation of the mono-cyclometalated product **9**, which

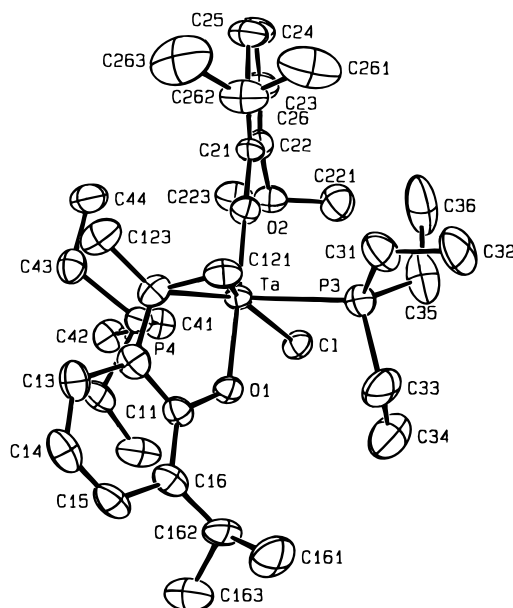


Figure 4. Molecular structure of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i_2-2,6)(\text{OC}_6\text{H}_3\text{Pr}^i_2-\eta^2\text{-CMe=CH}_2)\text{Cl}(\text{PET}_3)_2]$ (**8**).

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i_2-2,6)(\text{OC}_6\text{H}_3\text{Pr}^i_2-\eta^2\text{-CMe=CH}_2)\text{Cl}(\text{PET}_3)_2]$ (**8**)

| | | | |
|----------------|----------|----------------|----------|
| Ta—Cl | 2.484(2) | Ta—C(121) | 2.193(7) |
| Ta—O(1) | 1.981(5) | Ta—C(122) | 2.295(7) |
| Ta—O(2) | 1.922(5) | Ta—P(3) | 2.651(2) |
| O(2)—Ta—O(1) | 178.1(2) | O(2)—Ta—C(121) | 96.4(3) |
| O(1)—Ta—C(121) | 82.8(3) | O(2)—Ta—C(122) | 102.4(3) |
| O(1)—Ta—C(122) | 75.9(2) | Cl—Ta—O(1) | 85.0(2) |
| Cl—Ta—O(2) | 96.4(2) | Cl—Ta—C(121) | 153.1(2) |
| Cl—Ta—C(122) | 156.0(2) | Ta—O(1)—C(11) | 123.2(5) |
| Ta—O(2)—C(21) | 177.6(5) | | |

also contains a phenethyl group attached to the metal center (Scheme 3). No ethylbenzene is detected in the ^1H NMR spectrum of the reaction mixture. However, a singlet at δ 4.48 ppm (C_6D_6) can be assigned to H_2 generated during the reaction. Uncoordinated PMePh_2 is also observed. The solid-state structure of **9** (Figure 5, Table 5) shows a trigonal-bipyramidal geometry about the metal center with the oxygen atom of the cyclometalated aryloxy and the chloro group in axial positions. The phenethyl ligand can be clearly seen to contain the phenyl substituent attached to the β -carbon. The presence of the cyclometalated aryloxy is indicated by the presence of an AB pattern and a pair of methyl singlets in the ^1H NMR spectrum assignable to the $\text{Ta}-\text{CH}_2\text{CMe}_2$ protons.¹⁰ The protons of the *tert*-butyl groups attached to the nonmetalated aryloxy appear as two broad resonances due to restricted rotation about the $\text{Ta}-\text{O}-\text{Ar}$ bonds within the crowded coordination sphere. The $\text{Ta}-\text{CH}_2\text{CH}_2\text{Ph}$ methylene protons are all diastereotopic and appear as two multiplets centered at δ 3.75 (β) and 2.40 ppm (α). The results of labeling studies are discussed in the mechanistic section. The $^1J(^1\text{H}-^{13}\text{C})$ coupling constant of 119 Hz measured for the $\alpha\text{-CH}_2\text{CHPh}$ carbon in the ^{13}C NMR spectrum appears normal.

Treatment of **3** with phenylacetylene leads to the related cyclometalated species **10** (Scheme 3). Besides

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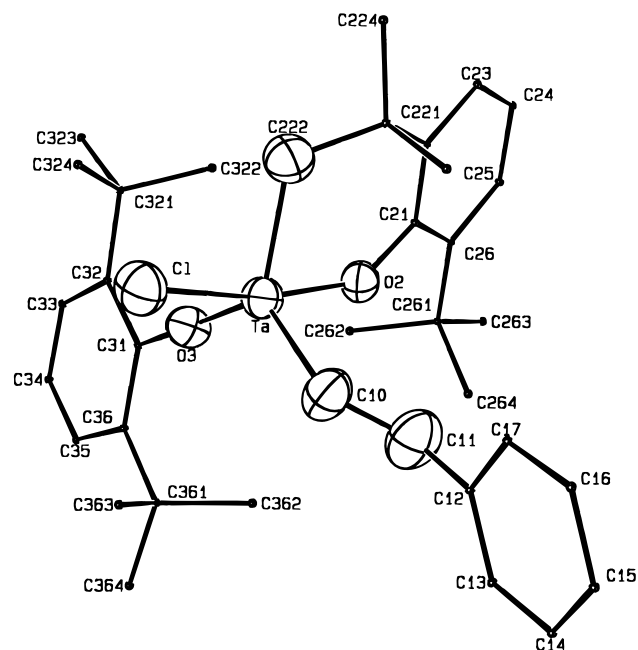
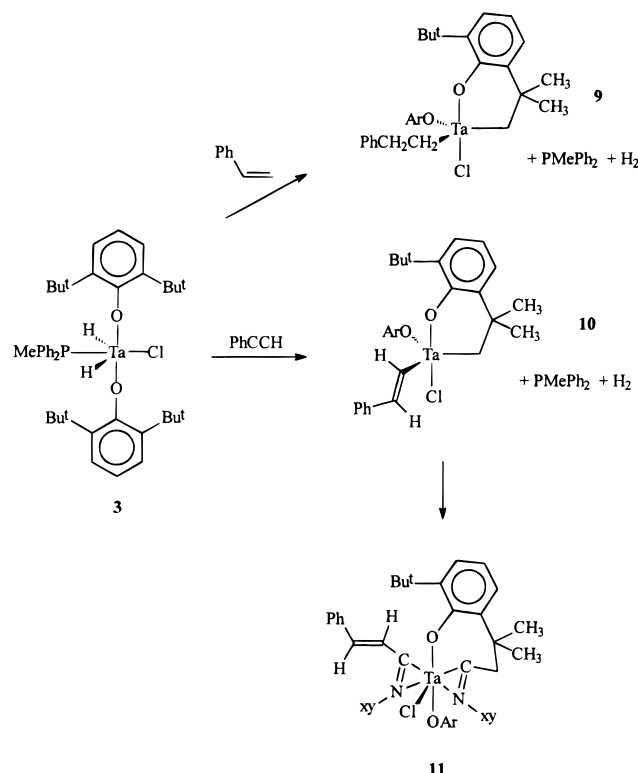


Figure 5. Molecular structure of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{CMe}_2\text{-CH}_2)(\text{OC}_6\text{H}_3\text{Bu}^t\text{-2,6})(\text{CH}_2\text{CH}_2\text{Ph})\text{Cl}]$ (**9**).

Scheme 3



the presence of the aryloxy ligand signals, a sharp pair of doublets are observed in the ^1H NMR spectrum of **10** at δ 9.48 and 8.48 ppm. These are assigned as being due to the α - and β -protons of a β -phenylvinyl ligand. The 3J coupling of 18 Hz between these protons indicates they are mutually *trans*, as shown in Scheme 3 and supported by the solid-state structure (Figure 6, Table 6). The α -vinyl carbon $\text{Ta}-\text{CH}=\text{CHPh}$ of this group resonates at δ 203.5 ppm. This is the region typical for vinyl groups attached to early d-block metals, and the $^1J(^1\text{H}-^{13}\text{C})$ coupling constant of 133 Hz implies

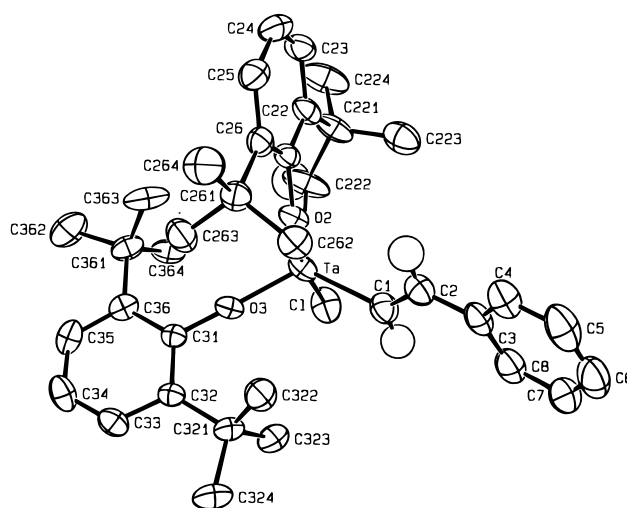


Figure 6. Molecular structure of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{CMe}_2\text{-CH}_2)(\text{OC}_6\text{H}_3\text{Bu}^t\text{-2,6})(\text{CH}=\text{CHPh})\text{Cl}]$ (**10**).

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{CMe}_2\text{-CH}_2)(\text{OC}_6\text{H}_3\text{Bu}^t\text{-2,6})(\text{CH}_2\text{CH}_2\text{Ph})\text{Cl}]$ (9**)**

| | | | |
|--------------|----------|-----------------|----------|
| Ta-Cl | 2.383(2) | Ta-C(10) | 2.145(7) |
| Ta-O(2) | 1.873(4) | Ta-C(222) | 2.171(7) |
| Ta-O(3) | 1.863(4) | | |
| Cl-Ta-O(2) | 166.4(1) | O(2)-Ta-C(10) | 94.5(2) |
| Cl-Ta-O(3) | 93.4(1) | O(2)-Ta-C(222) | 81.6(2) |
| Cl-Ta-C(10) | 87.2(2) | O(3)-Ta-C(10) | 124.0(2) |
| Cl-Ta-C(222) | 85.5(2) | O(3)-Ta-C(222) | 121.5(2) |
| O(2)-Ta-O(3) | 96.8(2) | C(10)-Ta-C(222) | 114.4(3) |

Table 6. Selected Bond Distances (Å) and Angles (deg) for $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{CMe}_2\text{-CH}_2)(\text{OC}_6\text{H}_3\text{Bu}^t\text{-2,6})(\text{CH}=\text{CHPh})\text{Cl}]$ (10**)**

| | | | |
|------------------|------------|--------------|------------|
| Ta-Cl | 2.369(1) | Ta-C(1) | 2.124(5) |
| Ta-O(2) | 1.871(3) | Ta-O(3) | 1.863(3) |
| Ta-C(222) | 2.173(5) | C(1)-C(2) | 1.333(7) |
| O(3)-Ta-O(2) | 98.8(1) | O(2)-Ta-C(1) | 92.84(18) |
| O(3)-Ta-C(1) | 121.38(17) | O(2)-Ta-Cl | 164.83(10) |
| O(3)-Ta-Cl | 93.56(10) | C(2)-C(1)-Ta | 126.2(4) |
| C(221)-C(222)-Ta | 119.9(4) | | |

no agostic interaction with the metal is occurring for the α -CH bond.¹¹

Both **9** and **10** can be synthesized on a larger scale by treating a mixture of the trichloride $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{-2,6})_2\text{Cl}_3]$ and styrene or phenylacetylene with Bu^n_3SnH in benzene solvent. Previous work has shown that only two of the Ta-Cl bonds in the trichloride react with the hydride reagent to form Ta-H bonds.⁴ It is therefore possible that the dihydride $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{-2,6})_2(\text{H})_2\text{Cl}]$ is first generated in the reaction mixtures prior to reaction with olefin or alkyne. Treatment of **10** with excess 2,6-dimethylphenyl isocyanide (xyNC) led to the new product **11**, in which the isocyanide has inserted into both the vinyl and metalated Ta-C bonds (Scheme 3). The presence of two η^2 -iminoacyl groups is indicated by the appearance of two resonances at δ 243.0 and 228.2 ppm in the ^{13}C NMR spectrum.¹² The solid-state structure of **11** (Figure 7, Table 7) confirms the molecular structure and also confirms the *trans* orientation of the original phenyl-vinyl group (Figure 8). If one considers

(11) Zwertler, R.; Hyla-Kryspin, I.; Gleiter, R.; Kruger, C.; Erker, G. *Organometallics* **1990**, *9*, 517.

(12) Rothwell, I. P.; Durfee, L. D. *Chem. Rev.* **1988**, *88*, 1059.

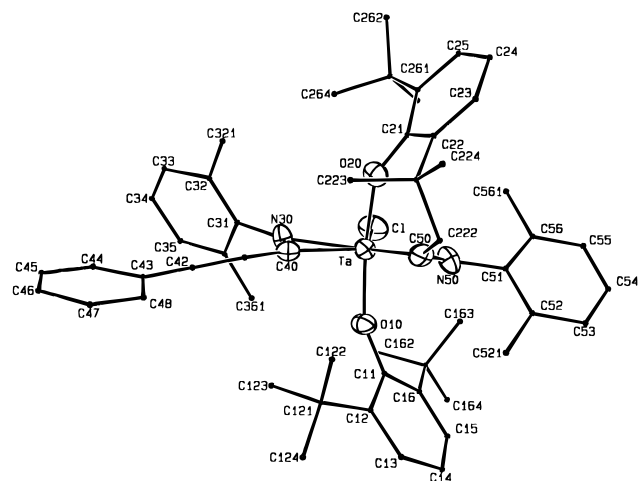


Figure 7. Molecular structure of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{-}2,6)(\text{OC}_6\text{H}_3\text{-Bu}^t\text{CMe}_2\text{CH}_2\text{-}\eta^2\text{-C=Nxy})(\text{PhCH=CH-}\eta^2\text{-C=Nxy})\text{Cl}]$ (**11**).

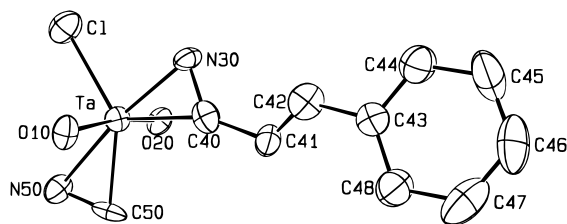


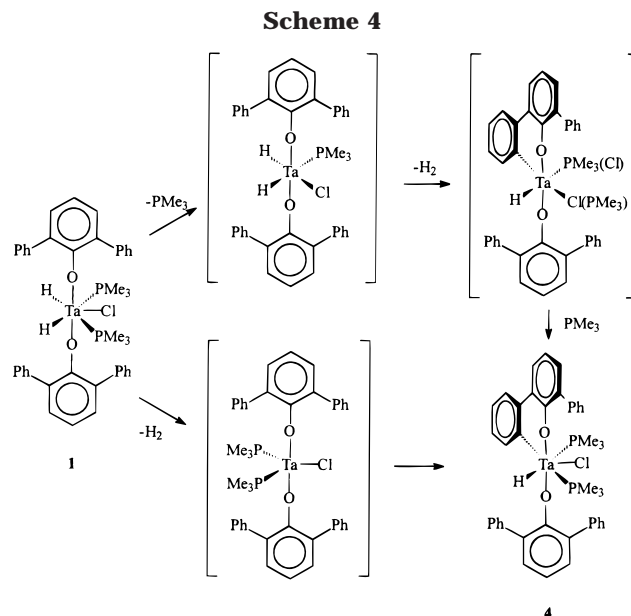
Figure 8. Central coordination sphere of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{-}2,6)(\text{OC}_6\text{H}_3\text{Bu}^t\text{CMe}_2\text{CH}_2\text{-}\eta^2\text{-C=Nxy})(\text{PhCH=CH-}\eta^2\text{-C=Nxy})\text{-Cl}]$ (**11**).

Table 7. Selected Bond Distances (Å) and Angles (deg) for $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{-}2,6)(\text{OC}_6\text{H}_3\text{Bu}^t\text{CMe}_2\text{CH}_2\text{-}\eta^2\text{-C=Nxy})(\text{PhCH=CH-}\eta^2\text{-C=Nxy})\text{Cl}]$ (11**)**

| | | | |
|-------------------|----------|-------------------|----------|
| Ta—Cl | 2.424(3) | Ta—C(40) | 2.14(1) |
| Ta—O(10) | 1.936(7) | Ta—C(50) | 2.11(1) |
| Ta—O(20) | 1.960(8) | C(40)—C(41) | 1.48(2) |
| Ta—N(30) | 2.123(9) | C(41)—C(42) | 1.35(2) |
| Ta—N(50) | 2.20(1) | C(42)—C(43) | 1.45(2) |
| N(30)—C(40) | 1.29(1) | N(50)—C(50) | 1.27(1) |
| C(40)—C(41)—C(42) | 121(1) | C(41)—C(42)—C(43) | 127(1) |
| N(30)—Ta—C(40) | 35.1(4) | N(50)—Ta—C(50) | 34.3(4) |
| Ta—O(10)—C(11) | 153.4(7) | Ta—O(20)—C(12) | 148.6(7) |

the iminoacyl groups to occupy single sites then the structure of **11** is best described as trigonal bipyramidal about the metal center with axial oxygen atoms. The two η^2 -iminoacyl groups and the chloride ligand occupy equatorial sites (Figure 8). An alternative description is as a pentagonal-bipyramidal geometry. The η^2 -iminoacyl groups lie within the equatorial plane of the molecule with the carbon atoms mutually cis. An identical geometry is observed for the related molecule $[\text{Ta}(\text{OC}_6\text{H}_3\text{Me}_2\text{-}2,6)_2(\eta^2\text{-xyNCMe})_2(\text{Me})]$.¹³ The structural parameters for the η^2 -iminoacyl groups are similar to those reported for related molecules.¹³

Mechanism. We have carried out a number of experiments to try and gain mechanistic insight into the reactions outlined in Schemes 1–3. A number of the reactions involve CH bond activation of aryloxide ligands. It is now well-established that such reactions can occur for niobium and tantalum aryloxides either by σ -bond



metathesis at a d^0 metal center or by addition of the CH bond to a d^2 metal intermediate.¹⁴ This mechanistic quandary exists for the conversion of **1** to **4**. It is highly unlikely that σ -bond metathesis¹⁵ could occur directly within seven-coordinate **1**. Besides being sterically crowded, all of the equatorial orbitals within the pentagonal-bipyramidal structure are involved in bonding, while the formally unoccupied d_{xz} and d_{yz} orbitals will be involved in π -bonding to the axial aryloxides. Hence, for σ -bond metathesis to occur, initial dissociation of phosphine would have to occur, yielding an unsaturated intermediate. Alternatively, direct elimination of H_2 is feasible, yielding a five-coordinate d^2 Ta(III) intermediate which can oxidatively add (insert into) the aryloxide CH bond (Scheme 4). To rule out one of these pathways, two C_6D_6 solutions of **1** were monitored over time by ^1H NMR spectroscopy. To one of the solutions was initially added PMe_3 (5 equiv by integration). After 24 h the solution of **1** with no added PMe_3 had converted to a 60/40 mixture of **4**/**1**, as judged by integration of the hydride signals. Only a trace amount of **4** was observed in the solution of **1** to which the PMe_3 had been added. Hence, the dramatic inhibition of CH bond activation by added phosphine argues strongly for the reaction proceeding via initial phosphine dissociation followed by σ -bond metathesis.

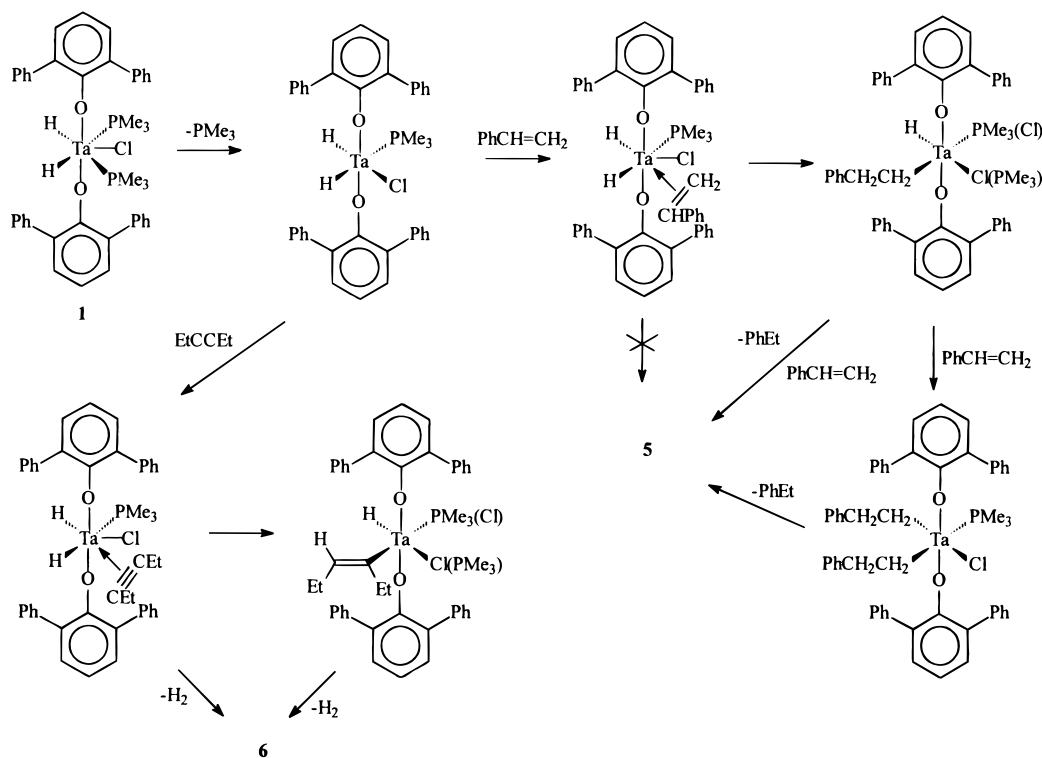
All of the reactions of the hydrides **1**–**3** with olefins and alkynes are inhibited by the presence of excess phosphines. Hence, in all cases it appears that initial dissociation of phosphine has to occur in order to allow the various substrates to coordinate to the metal center. In the case of **1** addition of styrene leads to 1 equiv of ethylbenzene and the complex **5** (Scheme 1). However, 3-hexyne leads to the hexyne adduct **6** with elimination of H_2 . It seems reasonable to assume that both proceed via olefin/alkyne intermediates (Scheme 5). Clearly, insertion of styrene must proceed to generate a phen-

(13) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390.

(14) (a) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153. (b) Steffey, B. D.; Chamberlain, L. R.; Chesnut, R. W.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1989**, *8*, 1419.

(15) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

Scheme 5



ethyl group. Reductive elimination of ethylbenzene could then generate an unsaturated intermediate that can coordinate styrene. There is precedence for this pathway in the reactivity of **2** below. An alternative pathway is via a bis(phenethyl) intermediate formed by insertion of 2 equiv of styrene. The final styrene complex **5** is then formed via β -hydrogen abstraction from this bis(alkyl) intermediate. As a possible test of this hypothesis the trichloride [Ta(OC₆H₃Ph₂-2,6)₂Cl₃] was reacted with PhCH₂CH₂MgCl (thf solution, 2 equiv) in benzene in the presence of excess PMe₃. Analysis of the reaction mixture by ³¹P NMR did show trace amounts of **5** with other unidentified products. Hence, this result indicates that under these conditions a bis(phenethyl) species does not lead to **5** in high yield.

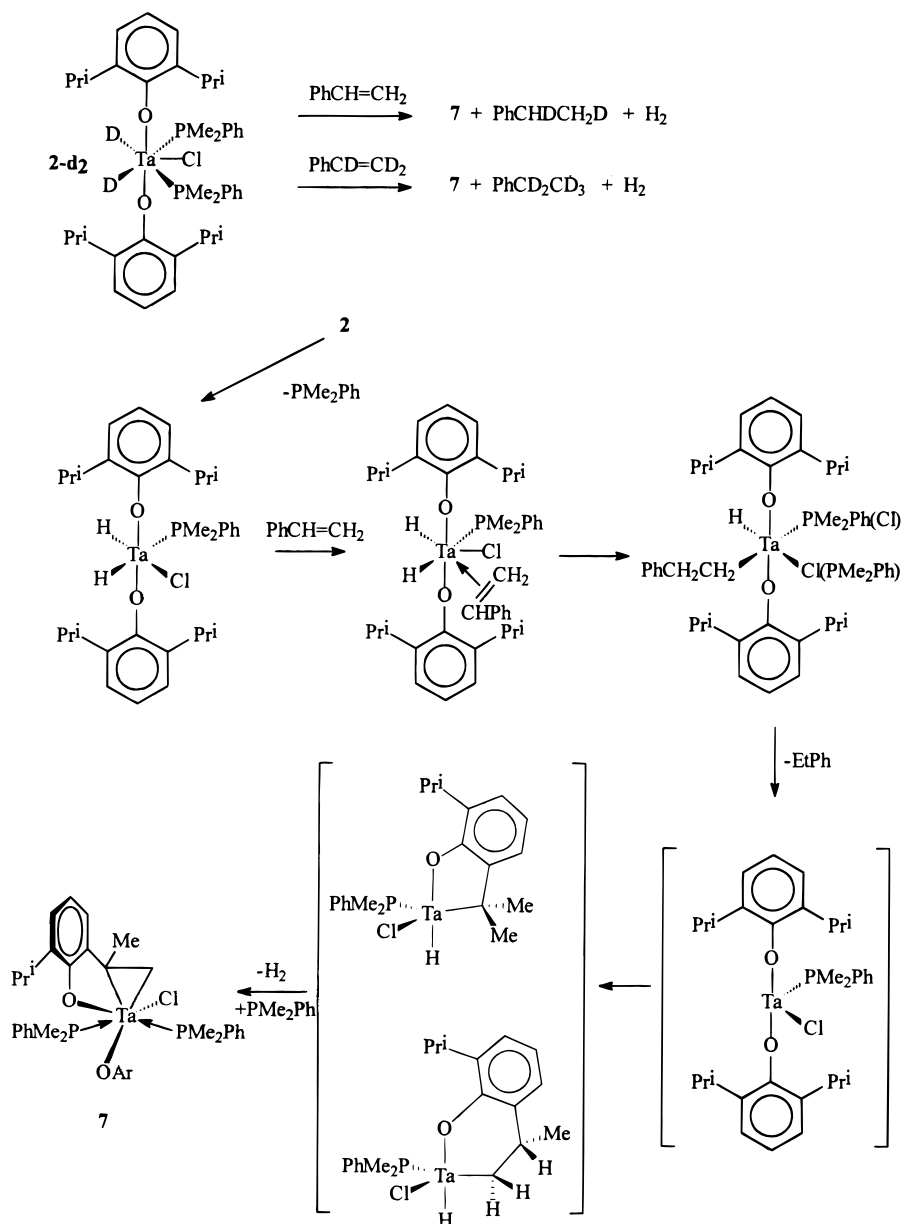
No hexene is detected during the formation of the alkyne adduct **6**. However, there are still two possible pathways for the elimination of H₂. The first involves reductive elimination of H₂ from the d⁰ alkyne adduct, while the second proceeds via an extra step in which CH bond activation occurs from a vinyl hydride intermediate (Scheme 5). We have also shown that **6** can be formed in moderate yield by carrying out the sodium amalgam reduction (2 Na per Ta) of [Ta(OC₆H₃Ph₂-2,6)₂Cl₃] in the presence of PMe₃ and 3-hexyne.

A great deal of mechanistic insight into the reactivity of **2** with styrene has been gained using labeling experiments (Scheme 6). This reaction produces the dehydrogenation product **7** along with 1 equiv of H₂ and ethylbenzene. Treatment of the dideuteride [Ta(OC₆H₃Prⁱ₂-2,6)₂(D)₂Cl(PMe₂Ph)₂] with protio styrene in C₆D₆ solvent was observed to produce H₂ with no detectable amounts of HD (¹H NMR). When the reaction was carried out in C₆H₆, the ²H NMR spectrum showed the formation of PhCHDCH₂D with equal amounts of deuterium label in the methylene and methyl positions. Addition of [Ta(OC₆H₃Prⁱ₂-2,6)₂(D)₂Cl(PMe₂Ph)₂] to

PhCD=CD₂ in C₆D₆ solvent showed no incorporation of H into the ethylbenzene and the formation of H₂ (no detectable HD). These results are consistent with a reaction pathway involving initial insertion of styrene followed by clean elimination of ethylbenzene to generate a d² Ta(III) fragment (Scheme 6). No CH bond activation occurs within the intermediate phenethyl hydride. The low-valent metal center then induces the dehydrogenation of an *o*-Prⁱ group via CH bond activation and β -hydrogen abstraction and elimination of H₂. Some support for this pathway is given by the fact that reduction of [Ta(OC₆H₃Prⁱ₂-2,6)₂Cl₃] with sodium amalgam (2 Na per Ta) in the presence of dcpm leads to an analogue of **7**.⁹ Hence, in the proposed mechanism (Scheme 6) the first equivalent of styrene acts in effect as a reducing agent toward the dihydride to generate the d² metal intermediate. These results also imply that in this case the low-valent species is not trapped by styrene to generate an analogue of **5**.

Similar labeling studies of the reaction of **3** toward styrene and phenylacetylene show a much more complex situation. This reagent only reacts with 1 equiv of substrate to produce mono-cyclometalated **9** and **10** and 1 equiv of H₂ (Scheme 3). The addition of the dideuteride [Ta(OC₆H₃Bu^t₂-2,6)₂(D)₂Cl(PMePh₂)₂]⁴ to PhCD=CD₂ in C₆D₆ produces detectable amounts of HD, as evidenced by a 1:1:1 triplet at δ 4.46 ppm (δ 4.48 for H₂ under these conditions) in the ¹H NMR spectrum. The phenethyl group within the compound **9** generated in this reaction also contained significant amounts of protio label exclusively within the β -methylene group (Scheme 7). Two equal-intensity broad singlets were present at δ 3.68 and 3.73 ppm, assigned to protio label at the two (diastereotopic) Ta-CD₂CHDPh positions. No protio label was observed (¹H NMR) in the α -methylene group. Integration of the phenethyl proton signal versus the Ta-CH₂CMe₂ AB pattern (metalated aryloxy) indi-

Scheme 6



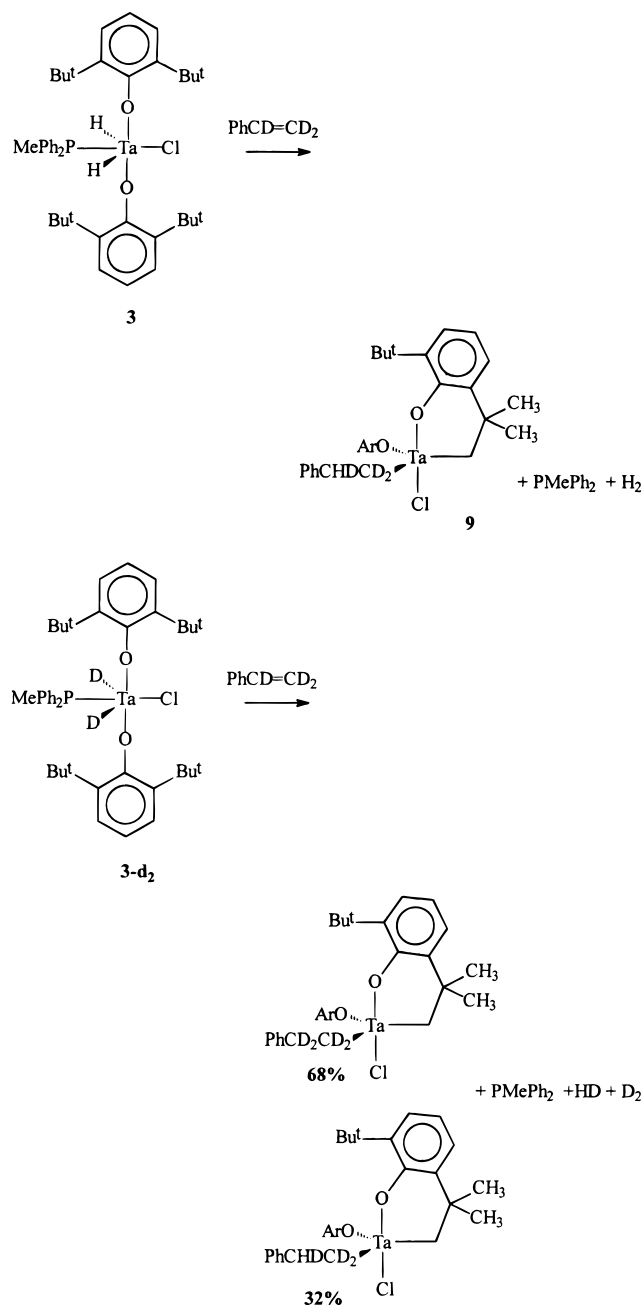
cated the presence of 32% $\text{TaCD}_2\text{CHDPh}$ groups, with the remainder being $\text{TaCD}_2\text{CD}_2\text{Ph}$. The addition of protio **3** to PhCD=CD_2 in C_6D_6 was found to produce exclusively $\text{Ta-CD}_2\text{CHDPh}$ groups along with H_2 (Scheme 7).

These results imply that two competing pathways are operating for the formation of **9** (Scheme 8). The first pathway involves initial insertion of styrene into one of the Ta-H(D) bonds. The final product then arises via cyclometalation within the phenethyl hydride intermediate. The competing pathway involves initial loss of H_2 (D_2) and formation of a styrene complex. The CH bond activation then involves opening of the tantalacyclopentane ring to generate a phenethyl group. This step, which constitutes about one-third of the reactivity, generates the $\text{Ta-CD}_2\text{CHDPh}$ group in the reaction of the dideuteride with styrene- d_8 .

A similar situation is found for the reaction of **3** toward phenylacetylene. The addition of the labeled compound $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{-2,6})_2(\text{D})_2\text{Cl}(\text{PMePh}_2)_2]$ to $\text{PhC}\equiv\text{CH}$ in C_6D_6 produces two types of β -phenylvinyl

groups (Scheme 9). In the ^1H NMR spectrum a pair of doublets are present due to the formation of Ta-CH=CHPh groups. However, also present is a broad singlet at δ 9.47 ppm, showing the presence of Ta-CH=CDPh groups. Integration of these signals versus the $\text{Ta-CH}_2\text{CMe}_2$ AB pattern showed no deuterium label in the α -CH position of the vinyl group. The ratio of $\text{Ta-CH=CHPh/Ta-CH=CDPh}$ groups is measured as 58/42. Similarly, the addition of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t\text{-2,6})_2(\text{D})_2\text{Cl}(\text{PMePh}_2)_2]$ to $\text{PhC}\equiv\text{CD}$ in C_6D_6 also produces two types of β -phenylvinyl groups (Scheme 9). A singlet at δ 8.44 ppm can be assigned to Ta-CD=CHPh (43%) with the remaining 57% of molecules containing Ta-CD=CDPh groups. As with the styrene reaction, these results imply two competing pathways are operating for the formation of **10**. The first pathway is via elimination of H_2 (D_2) and formation of an alkyne complex which undergoes ring opening via CH bond activation. The second pathway involves insertion followed by elimination of H_2 by CH bond activation by the remaining Ta-H(D) bond. The results

Scheme 7



of the labeling studies in this case show (within error) an approximately equal probability for the two pathways.

Conclusions

All three hydrides **1–3** act as catalysts (precursors) for the hydrogenation of olefins and arenes. This work has identified a number of reactions that have to be considered as potential steps within the catalytic cycle (Scheme 10). All of the steps shown in Scheme 10, which begin with a d^0 metal dihydride, have been observed. Hence, although initial insertion of olefin into a metal–hydride bond can occur, the elimination of H_2 and formation of a metallacyclopropane species must also be considered. Two reaction paths are also possible for the intermediate alkyl hydride. Direct elimination of alkane can occur, or hydrogenolysis of the metal alkyl

can take place to regenerate the initial dihydride. The elimination path generates a d^2 metal species that can either bind with olefin or add H_2 . The actual path followed will clearly be influenced by the concentration of H_2 , and it appears further insight into the mechanism can only be obtained by kinetic studies.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere or in vacuo either in a Vacuum Atmosphere Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium/benzophenone and stored under dry nitrogen. Trimethylphosphine was purchased from Strem Chemical Co., and 1,3-cyclohexadiene and styrene were purchased from Aldrich Chemical Co. All reagents were dried over 3 Å molecular sieves prior to use. The ^1H and ^{13}C NMR spectra were recorded on a Varian Associates Gemini 200 and a General Electric QE-300 spectrometer and were referenced using protio impurities of commercial benzene- d_6 as an internal standard. Microanalytical data were obtained in house at Purdue. All high-pressure reactions were performed in a Parr Model 4561 300 mL internal volume minireactor.

The X-ray diffraction studies were completed in house at Purdue University. Crystal data and data collection parameters are given in Table 8. The crystals were examined under deoxygenated Nujol and mounted in an appropriate size glass capillary surrounded by epoxy resin. They were aligned and indexed, and data were collected in an Enraf-Nonius CAD4 diffractometer. General operating procedures have been reviewed.¹⁶

Preparation of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph-}^i\text{Bu})_2(\eta^1\text{-C}_6\text{H}_5)(\text{OC}_6\text{H}_3\text{Ph-}^i\text{Bu})_2(\text{H})\text{Cl}(\text{PMe}_3)_2]$ (4**).** A suspension of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph-}^i\text{Bu})_2(\text{H})_2\text{Cl}(\text{PMe}_3)_2]$ in C_6D_6 in an NMR tube was heated at 100°C for 4 min. Crystals grew upon cooling, which were washed with hexane and dried in vacuo. ^1H NMR (C_6D_6 , 30°C): δ 18.68 (dd, 1H, Ta–H; $^2J(^{31}\text{P}\text{--}^1\text{H}) = 83$ and 8 Hz); 6.60–7.95 (m, 25H, aromatics); 0.58 (d, 18H, P– Me_3); $^2J(^{31}\text{P}\text{--}^1\text{H}) = 9.3$ Hz. ^{31}P NMR (C_6D_6 , 30°C): δ –0.873 (d), –21.81 (d), $^2J(^{31}\text{P}\text{--}^{31}\text{P}) = 108.1$ Hz.

Preparation of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph-}^i\text{Bu})_2(\eta^2\text{-CH}_2=\text{CHPh})\text{Cl}(\text{PMe}_3)_2]$ (5**).** To a concentrated solution of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph-}^i\text{Bu})_2\text{Cl}(\text{H})_2(\text{PMe}_3)_2]$ (0.2 g, 0.23 mmol) in benzene- d_6 (1 mL) was added styrene (0.12 g, 1.2 mmol). The reaction mixture was allowed to stand for 20 h, and the resulting red solution was layered with hexane (1 mL), yielding the product as red crystals which were washed with hexane and dried in vacuo. Anal. Calcd for $\text{C}_{47}\text{H}_{43}\text{PClO}_2\text{Ta}$: C, 63.34; H, 4.89; Cl, 3.95; P, 3.50. Found: C, 63.26; H, 4.83; Cl, 4.24; P, 3.62. ^1H NMR (C_6D_6 , 30°C): δ 2.01 (m, 1H), 1.55 (m, 1H), 0.62 (m, 1H, $\eta^2\text{-CH}_2=\text{CHPh}$); –0.01 (d, 9H, P– Me_3); $^2J(^{31}\text{P}\text{--}^1\text{H}) = 7.8$ Hz. ^{13}C NMR (C_6D_6 , 30°C): δ 63.1 (d, $^2J(^{13}\text{C}\text{--}^{31}\text{P}) = 8.0$ Hz), 60.1 (s, TaCH_2CHPh). ^{31}P NMR (C_6D_6 , 30°C): δ 1.46.

Preparation of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph-}^i\text{Bu})_2(\eta^2\text{-EtC}\equiv\text{CEt})\text{Cl}(\text{PMe}_3)_2]$ (6**).** **Method 1.** To a suspension of $[\text{Ta}(\text{OC}_6\text{H}_3\text{Ph-}^i\text{Bu})_2(\text{H})_2\text{Cl}(\text{PMe}_3)_2]$ (0.41 g, 0.48 mmol) in benzene was added 3-hexyne (0.117 g, 1.43 mmol, 3.0 equiv), and the solution was allowed to sit overnight. The resulting yellow crystalline solid was dried in vacuo to yield 0.27 g (66%) of **6**. Anal. Calcd for $\text{C}_{45}\text{H}_{45}\text{TaClPO}_2$: C, 62.47; H, 5.24; Cl, 4.10; P, 3.58. Found: C, 61.66; H, 5.10; Cl, 4.39; P, 3.05. ^1H NMR (C_6D_6 , 30°C): δ 6.86–7.50 (m, 26H, aromatics); 2.94 (quartet, 2H, $\text{TaCCH}_2\text{CH}_3$); 1.86 (quartet, 2H, $\text{TaCCH}_2\text{CH}_3$); 1.46 (t, 3H, $\text{TaCCH}_2\text{CH}_3$); 0.67 (t, 3H, $\text{TaCCH}_2\text{CH}_3$); 0.23 (d, 9H, P– Me_3); $^2J(^{31}\text{P}\text{--}^1\text{H}) = 7.98$ Hz. ^{13}C NMR (CDCl_3 , 30°C): δ 195.00 (s, $\text{TaCCH}_2\text{CH}_3$); 188.54 (d, $\text{TaCCH}_2\text{CH}_3$, $^2J(^{31}\text{P}\text{--}^{13}\text{C}) = 15.64$ Hz); 156.87 (s, TaOC); 121.34–139.62 (singlets, $\text{TaOC}_6\text{H}_3\text{Ph-}^i\text{Bu}$); 30.20 (s,

(16) Fanwick, P. E.; Ogilvy, A. E.; Rothwell, I. P. *Organometallics* **1987**, *6*, 73.

Scheme 8

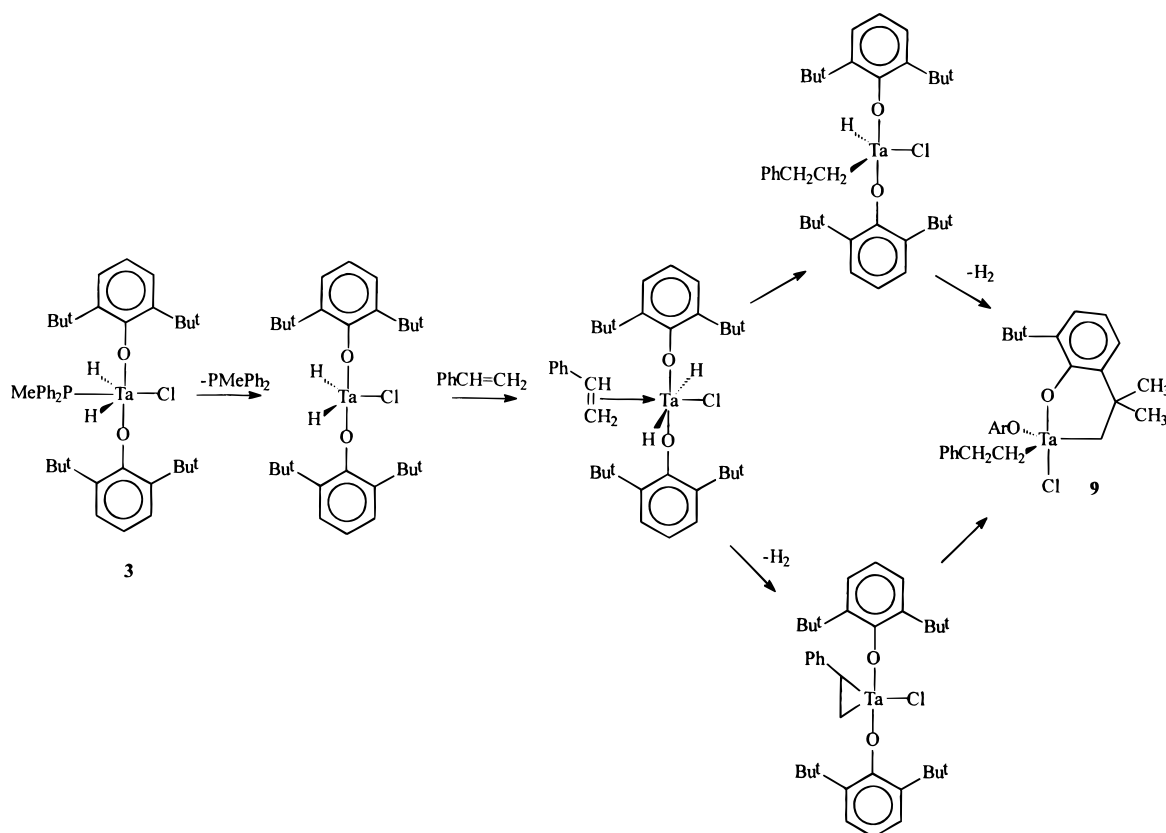


Table 8. Crystal Data and Data Collection Parameters

| | 4 | 5 | 6 | 8 | 9 | 10 | 11 |
|---|--|---|---|---|--|--|--|
| formula | TaClP ₂ O ₂ -C ₄₂ H ₄₄ | TaClPO ₂ C ₄₇ H ₄₃ | TaClPO ₂ C ₄₅ H ₄₅ | TaClP ₂ O ₂ C ₃₆ H ₆₂ | TaClO ₂ C ₃₆ H ₅₀ | TaClO ₂ C ₃₆ H ₄₇ | TaClO ₂ N ₂ -C ₅₉ H ₇₈ |
| fw | 859.17 | 887.24 | 865.23 | 805.24 | 731.20 | 728.18 | 1063.69 |
| space group (No.) | <i>P</i> 2 ₁ / <i>c</i> (14) | <i>P</i> 2 ₁ / <i>n</i> (14) | <i>P</i> 1̄ (2) | <i>P</i> 2 ₁ / <i>c</i> (14) | <i>P</i> 2 ₁ / <i>c</i> (14) | <i>P</i> 2 ₁ / <i>c</i> (14) | <i>P</i> 2 ₁ / <i>n</i> (14) |
| <i>a</i> , Å | 10.959(3) | 9.810(1) | 9.099(2) | 11.092(2) | 10.0577(5) | 16.282(3) | 10.499(3) |
| <i>b</i> , Å | 18.965(5) | 17.858(3) | 9.9130(11) | 30.216(5) | 18.590(2) | 11.548(3) | 18.676(5) |
| <i>c</i> , Å | 19.067(3) | 22.981(84) | 22.2217(14) | 11.589(2) | 18.648(1) | 18.798(4) | 27.583(8) |
| α, deg | 90 | 90 | 84.344(7) | 90 | 90 | 90 | 90 |
| β, deg | 105.528(16) | 100.57(1) | 83.152(11) | 101.697(11) | 90.3(3) | 107.252(16) | 98.29(3) |
| γ, deg | 90 | 90 | 80.687(13) | 90 | 90 | 90 | 90 |
| <i>V</i> , Å ³ | 3818(3) | 3957(2) | 1957.3(9) | 3803.2(2) | 3486.8(8) | 3375.3(3) | 5351(5) |
| <i>Z</i> | 4 | 4 | 2 | 4 | 4 | 4 | 4 |
| ρ _{calcd} , g cm ⁻³ | 1.502 | 1.489 | 1.468 | 1.406 | 1.393 | 1.433 | 1.320 |
| temp, K | 296 | 293 | 296 | 193 | 293 | 193 | 293 |
| radiation (λ, Å) | | | | Mo Kα (0.710 73) | | | |
| <i>R</i> | 0.031 | 0.029 | 0.024 | 0.053 | 0.033 | 0.042 | 0.047 |
| <i>R</i> _w | 0.036 | 0.036 | 0.060 | 0.147 | 0.039 | 0.090 | 0.054 |

TaCCH₂CH₃); 28.21 (s, TaCCH₂CH₃); 12.78 (d, *PMe*₃, ²*J*(³¹P–¹³C) = 19.81 Hz). ³¹P NMR (C₆D₆, 30 °C): δ –6.43 (s).

Method 2. To a sodium amalgam (0.12 g of Na/5 mL of Hg) was added [Ta(OC₆H₃Pr¹-2,6)₂Cl₃] (2.0 g, 2.57 mmol) in benzene (25 mL) and an excess of 3-hexyne. Several equivalents of trimethylphosphine was added via condensation through a vacuum line. This solution was stirred for 3 days, resulting in a yellow-brown solution which was dried in vacuo to give the desired product as a yellow solid, which was washed with hexane to yield 0.70 g (32%).

Preparation of [Ta(OC₆H₃Pr¹-η²-CMe=CH₂)(OC₆H₃-Pr¹-2,6)Cl(PMe₂Ph)₂] (7). To a concentrated solution of [Ta(OC₆H₃Pr¹-2,6)₂Cl(H)₂(PMe₂Ph)₂] (0.2 g, 0.24 mmol) in benzene-*d*₆ (1 mL) was added styrene (0.12 g, 1.2 mmol). The reaction was allowed to stand for 20 h, and a red solution was observed. Removal of the solvent in vacuo left the product as a red oil which could not be purified by recrystallization. ¹H

NMR (C₆D₆, 30 °C): δ 6.78–7.34 (m, 16H, aromatics); 3.72 (septet, 3H, *CHMe*); 3.07 (m, 2H, Ta–CH₂); 2.40 (s, 3H, Ta–CMe); 1.34 (d, 6H, *PMe*, ²*J*(³¹P–¹H) = 7.63 Hz) 1.24 (d, 6H, *PMe*, ²*J*(³¹P–¹H) = 6.90 Hz); 1.04–1.23 (m, 18H, *CHMe*). ¹³C NMR (C₆D₆, 30 °C): δ 156.3 (TaOC); 155.0 (TaOC); 121.8–140.1 (aromatics); 71.95 (d, Ta–CMe), ²*J*(³¹P–¹³C) = 7.1 Hz; 68.2 (d, Ta–CH₂), ²*J*(³¹P–¹³C) = 7.1 Hz; 11.4–26.9 (aliphatics). ³¹P NMR (C₆D₆, 30 °C): δ –0.67 (d), –4.73 (d), ²*J*(³¹P–³¹P) = 145 Hz.

Preparation of [Ta(OC₆H₃Bu^t-CMe₂CH₂)(OC₆H₃Bu^t-2,6)(CH₂CH₂Ph)Cl] (9). To a suspension of [Ta(OC₆H₃Bu^t-2,6)₂Cl₃] (0.5 g, 0.71 mmol) in hexane (5 mL) was added styrene (0.37 g, 3.58 mmol) followed by tri-*n*-butyltin hydride (0.63 g, 2.16 mmol), and the resulting mixture was allowed to stand for 18 h. Removal of the solvent in vacuo left the crude product as a yellow oil. Layering the oil with pentane (3 mL) yielded **9** as yellow crystals that were washed with pentane and dried

