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Synthesis and Characterization of a Series of Mononuclear Tantalum(V) Hydride Compounds Containing Aryloxide Ligation

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A series of seven-coordinate, mononuclear tantalum−hydride compounds $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(Cl)_{3-\mathit{n}}(H)_\mathit{n}}]$ (**1**, $n = 1$; **2**, $n = 2$; **3**, $n = 3$; $\mathrm{OC_6H_3Pr^i_2\text{-}2,6}$ = 2,6-diisopropylphenoxide; L = tertiary phosphines) can be obtained either by hydrogenolysis of the corresponding tantalum alkyl substrate, producing **2** and **3**, or by reacting the trichloride $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3}]$ with one (for **1**) or two (for **2**) equiv of $\mathrm{Bu^n_3SnH}$ in the presence of ligand. The hydrogenolysis of the substrate $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2C_6H_4\text{-}4Me)_3}]$ in the presence of $\mathrm{PMe_2Ph}$ or $\mathrm{PMePh_2}$ produces the complexes $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(H)_3(L)_2}]$ (**3a**, L = $\mathrm{PMe_2Ph}$; **3b**, L = $\mathrm{PMePh_2}$), while the compounds $[\mathrm{Ta(OC_6H_3Ph_2\text{-}2,6)_2(R)_3}]$ (R = $\mathrm{CH_2C_6H_4\text{-}4Me}$, $\mathrm{CH_2SiMe_3}$) produce $[\mathrm{Ta(OC_6H_3Cy_2\text{-}2,6)_2(H)_3(L)_2}]$ (**3c**, L = $\mathrm{PMe_2Ph}$; **3d**, L = $\mathrm{PMePh_2}$) with the 2,6-dicyclohexylphenoxide ligand being generated by intramolecular hydrogenation of the *ortho* phenyl rings in the 2,6-diphenylphenoxide substrate. The hydrogenolysis of the bisalkyl $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(CH_2C_6H_4\text{-}4Me)_2}]$ in the presence of $\mathrm{PMe_2Ph}$ produces the six-coordinate $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(PMe_2Ph)(H)_2}]$, **4b**, which will exchange the phosphine ligand to produce a series of substituted derivatives. A related series of six-coordinate dihydride compounds $[\mathrm{Ta(OC_6H_3Bu^t_2\text{-}2,6)_2(L)(Cl)(H)_2}]$, **5**, are produced by addition of $\mathrm{Bu^nSnH}$ (2 Sn per Ta) to $[\mathrm{Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_3}]$ in the presence of added L. Single-crystal X-ray diffraction analyses of seven-coordinate **1**, **2b**, and **3c** (all cases L = $\mathrm{PMe_2Ph}$) show them to adopt pentagonal bipyramidal geometries with *trans* axial aryloxide ligands. In monohydride **1** the unique hydride ligand is *cis* to both phosphine ligand, while in dihydride **2b** the hydride ligands are mutually *cis* but *trans* to the chloride group within the pentagonal plane. A crystallographic 2-fold axis in trihydride **3c** passes through the unique Ta−H bond and bisects the remaining *cis* hydride ligands within the pentagonal plane. The solution ^{1}H NMR spectra of **1**, **2**, and **3** are consistent with the solid state structure being maintained in solution. Furthermore, analysis and simulation of the downfield hydride resonances in **2** and **3** show these seven-coordinate molecules to be stereochemically rigid on the NMR time scale. The coupling constants obtained from simulations conclusively rule out the formulation of **2** or **3** as containing η^2-$\mathrm{H_2}$ ligands. The solid state structures of six-coordinate $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(PMe_2Ph)(H)_2}]$, **4b**, and $[\mathrm{Ta(OC_6H_3Bu^t_2\text{-}2,6)_2(PMePh_2)(Cl)(H)_2}]$, **5c**, show a geometry severely distorted from octahedral. In both compounds the mutually *trans* hydride ligands are bent toward the phosphine ligand with H−Ta−P angles of 66(2)° and 69(1)° for **4a** and 56(2)° and 62(2)° for **5b**. A steric origin to this distortion is ruled out by the structure of **5b** in which the hydride ligands are bent toward the bulky phosphine ligand and away from the Ta−Cl bond. Strong support for the distorted structures of **4** and **5** comes from solution and solid state infrared spectra where two sharp $\bar{\nu}$(Ta−H) vibrations are observed. Analysis of the intensity ratio for the symmetric and asymmetric bands yields predicted H−Ta−H angles very close to these observed in the solid state structure. The summary of the crystal data is as follows for $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(PMe_2Ph)_2(Cl)_2(H)}]$, **1**, at 20 °C: a = 26.025(4) Å, b = 10.7954(5) Å, c = 18.509(3) Å, β = 128.31(1)°, Z = 4, d_{calcd} = 1.438 g cm^{-3} in space group $C2/c$. For $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(PMe_2Ph)_2(Cl)(H)_2}]$, **2b**, at 20 °C: a = 9.735(1) Å, b = 24.310(3) Å, c = 17.735(2) Å, β = 90.76(1)°, Z = 4, d_{calcd} = 1.344 g cm^{-3} in space group $P2_1/n$. For $[\mathrm{Ta(OC_6H_3Cy_2\text{-}2,6)_2(PMe_2Ph)_2(H)_3}]$, **3c**, at 20 °C: a = 24.065(3) Å, b = 13.530(2) Å, c = 20.263(3) Å, β = 131.633(9)°, Z = 4, d_{calcd} = 1.313 g cm^{-3} in space group $C2/c$. For $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(PMe_2Ph)(H)_2}]$, **4b**, at 20 °C: a = 10.637(1) Å, b = 12.820(2) Å, c = 31.799(4) Å, β = 98.76(1)°, Z = 4, d_{calcd} = 1.322 g cm^{-3} in space group $P2_1/n$. For $[\mathrm{Ta(OC_6H_3Bu^t_2\text{-}2,6)_2(PMePh_2)(Cl)(H)_2}]$, **5c**, at −100 °C, a = 10.851(5) Å, b = 18.110(7) Å, c = 20.09(1) Å, β = 96.67(5)°, Z = 4, d_{calcd} = 1.404 g cm^{-3} in space group $P2_1/n$.

Introduction

The study of transition metal hydride compounds remains an extremely active area of chemical research.[1] This interest stems not only from the important chemical reactivity demonstrated by these species but also by their structural and spectroscopic properties.[2] Another facet to this chemistry has been added with the discovery and characterization of η^2-dihydrogen complexes.[3] During our studies of the early d-block organometallic

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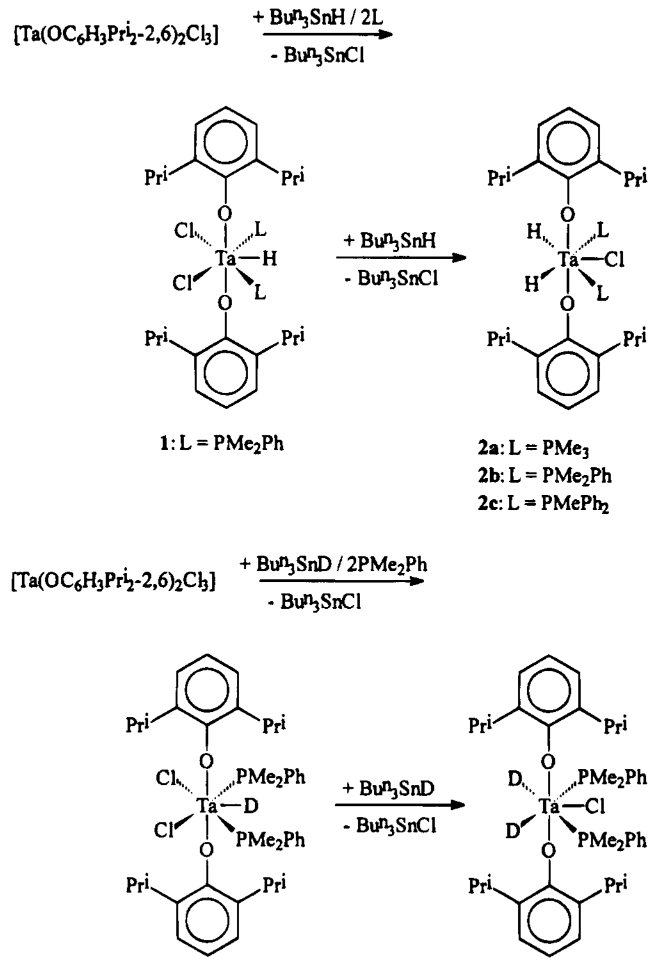
chemistry associated with bulky aryloxide ligation we have demonstrated the ability of mixed hydrido aryloxides of niobium and tantalum to carry out the catalytic hydrogenation of arene rings along with other unsaturated substrates.[4] In this paper we report on the synthesis, structure and spectroscopic properties of an extensive series of mononuclear hydride compounds of tantalum(V).[5]

Results and Discussion

Synthesis of Compounds. There are numerous methods in the literature for the formation of transition metal hydride bonds.[1] Using as our basic starting materials the chloro aryloxides $[Ta(OC_6H_3R_2\text{-}2,6)_nCl_{5-n}]$ ($R = Pr^i$, $n = 2, 3$; $R = Ph$, $n = 2, 3$; and $R = Bu^t$, $n = 2$)[6,7] we have evaluated many of these methods for the generation of the corresponding hydride derivatives. We find that two synthetic procedures are superior for the formation of hydrido aryloxides in high yield. The first involves addition of $Bu^n{}_3SnH$ to the corresponding chloride in the presence of phosphine ligands.[8] The second involves initial formation of the corresponding alkyl intermediate followed by hydrogenolysis, again in the presence of a suitable phosphine ligand.[5k,9]

The trichloride $[Ta(OC_6H_3Pr^i{}_2\text{-}2,6)_2Cl_3]$ forms a 1:1 adduct in hydrocarbon solution with phosphine ligands.[10] In the presence of an excess (>2 equiv) of PMe_2Ph, the addition of $Bu^n{}_3SnH$ to these mixtures does not lead to any detectable evolution of hydrogen gas. Instead sequential formation of the seven-coordinate mono- and dihydrido derivatives **1** and **2b** occurs (Scheme 1). The

Scheme 1



slightly soluble monohydride **1** is obtained in >80% yield directly from an unstirred reaction mixture, while formation of **2b** requires the stirring of a suspension of

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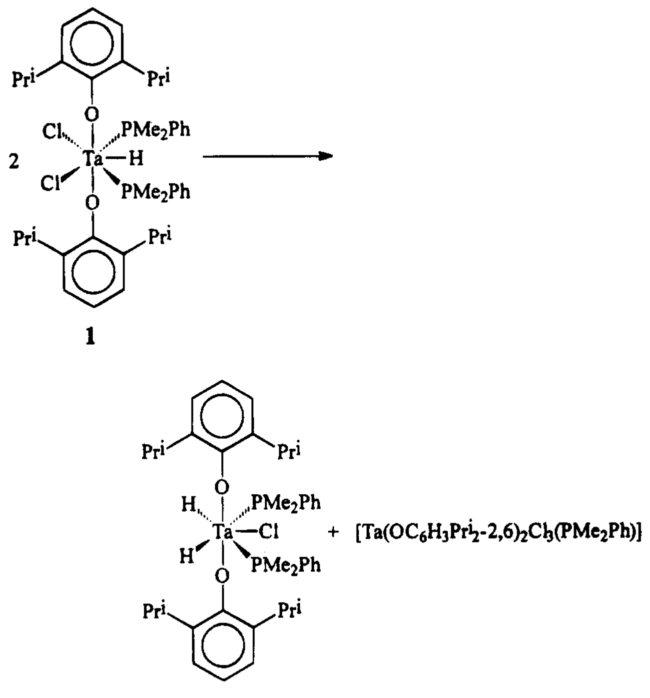
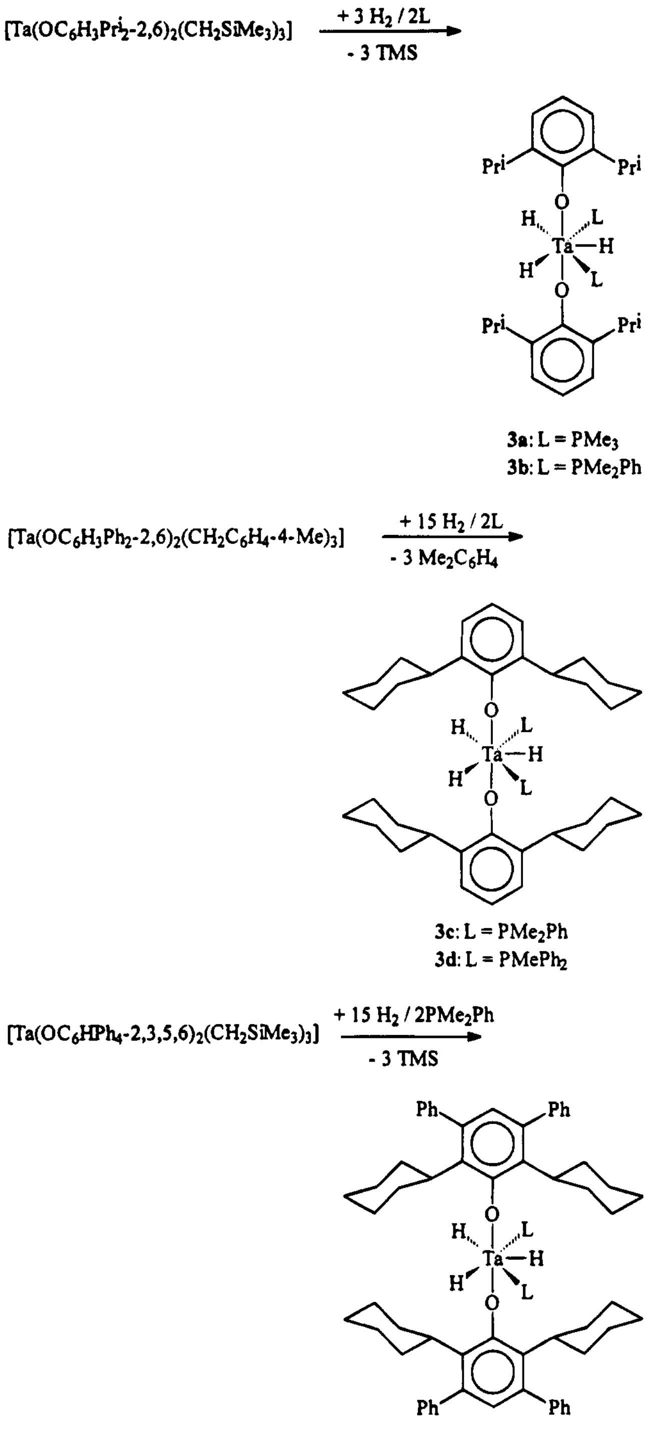
Scheme 2



1

2b

Scheme 3



3a: L = PMe_3
3b: L = PMe_2Ph

3c: L = PMe_2Ph
3d: L = $PMePh_2$

3e

1 in the presence of an excess of Bu^n_3SnH. The procedure can be used to obtain the corresponding deuterium-labeled compounds by using Bu^n_3SnD as reagent (Scheme 1).

A suspension of sparingly soluble **1** in C_6D_6 was found (^1H and ^{31}P NMR) to produce **2** upon heating for several hours at 90 °C along with 1 equiv of the monophosphine adduct of the trichloride and free phosphine (Scheme 2). This ligand exchange reaction presumably proceeds via an intermediate containing two tantalum metal centers bridged by chloro and hydrido ligands. In the presence of an excess of Bu^n_3SnH, the final chloride ligand in **2** is not replaced. The corresponding trihydride compounds **3** can, however, be obtained by the hydrogenolysis of the tris(4-methylbenzyl) complex $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2C_6H_4\text{-}4Me)_3]$[11] in the presence of a suitable phosphine ligand (Scheme 3). The use of 2,6-diphenylphenoxide and 2,3,5,6-tetraphenylphenoxide alkyl substrates for reaction with H_2 leads to the formation of the corresponding 2,6-dicyclohexylphenoxide and 2,6-dicyclohexyl-3,5-diphenylphenoxide trihydride derivatives due to the intramolecular hydrogenation of the *ortho* phenyl rings (Scheme 3). The hydrogenolysis method can also be applied to the synthesis of the dihydride complexes **2** (Scheme 4). In the case of the monochloride precursor $[Ta(OC_6H_3Ph_2\text{-}2,6)_2Cl(CH_2SiMe_3)_2]$ the dihydride product obtained after 24 h contained unhydrogenated aryloxide ligands (Scheme 4).

Two sets of six-coordinate dihydride complexes were obtained either by the hydrogenolysis of the bisalkyl $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(CH_2C_6H_4\text{-}4Me)_2]$ or by treating the trichloride $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_3]$ with Bu^n_3SnH/L in benzene solution (Scheme 5).

Some alternative methods have been evaluated for the synthesis of the tantalum–hydride compounds **1**–**5**. The

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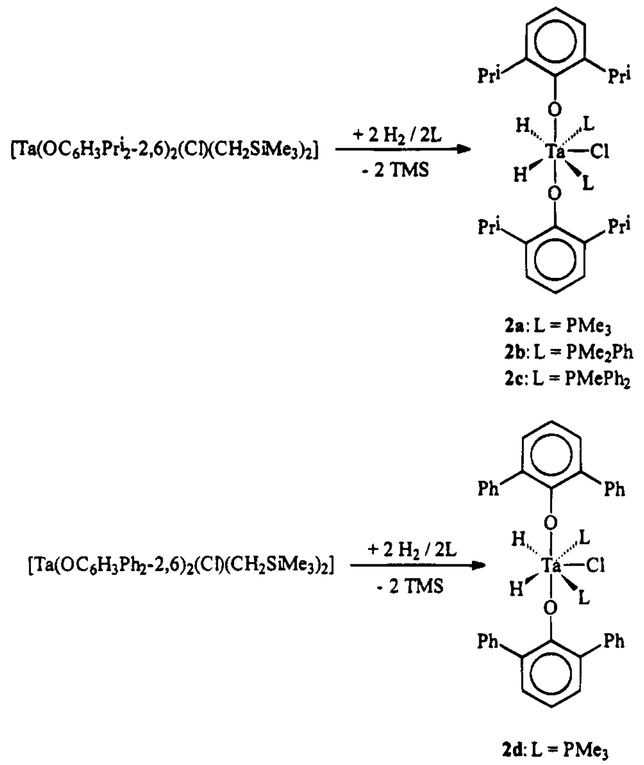
Scheme 4



2a: L = PMe_3
2b: L = PMe_2Ph
2c: L = $PMePh_2$

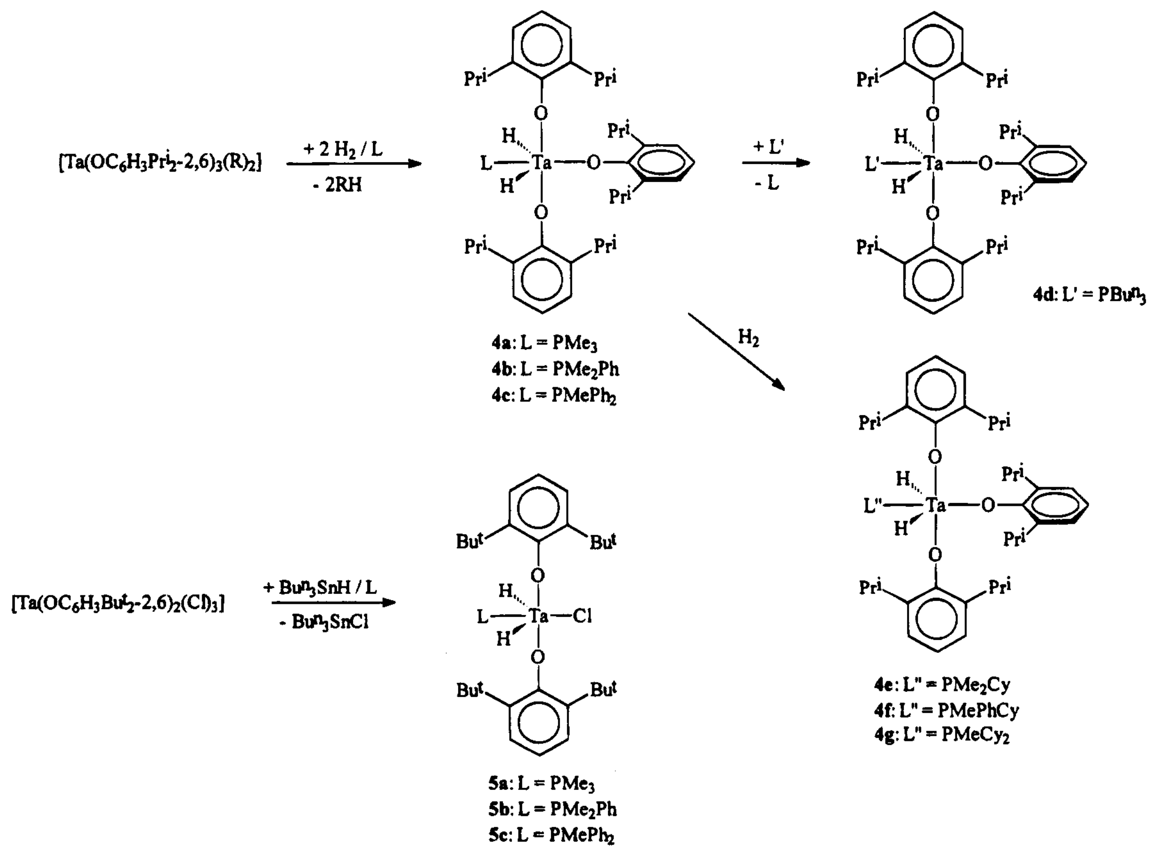
2d: L = PMe_3

addition of hydride reagents such as $LiBH_4$ and $LiAlH_4$ to hydrocarbon solutions of phosphine ligands and halides such as [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl$_3$] will generate detectable amounts of hydrido complexes such as **1** and **2** in solution (^{1}H NMR), but isolation of the compounds from the reaction mixtures was not convenient. The work of Wolczanski et al. has shown that siloxy hydrides of tantalum can be obtained by sodium amalgam reduction of the corresponding chloride precursor under an H_2 atmosphere.[5a] We find that hydride compounds such as **4** are generated by this procedure, although again yields of isolated material are lower than these obtained via hydrogenolysis of the alkyl precursor.

Solid State Structures of the Tantalum Hydride Compounds. Single-crystal X-ray diffraction analyses of representative examples of each class of compound **1**–**5** have been carried out. In each case the hydride ligands about the metal were located and refined. Furthermore the position of these hydride ligands was also supported by spectroscopic studies (*vide infra*). ORTEP views of the five molecules are shown in Figures 1–5, while selected interatomic distances and angles are collected in Tables 1–5.

The seven-coordinate compounds **1**, **2b**, and **3c** adopt a pentagonal bipyramidal arrangement of ligands about the tantalum metal centers. In all three molecules there are two mutually *trans* axial aryloxide ligands; O–Ta–O angles of 174.7(3)° in **1**, 178.6(2)° in **2b**, and 179.2(5)° in **3c**. The Ta–O distances are essentially identical for all three compounds at 1.90 Å (av). The Ta–O–Ar angles are all greater than 170°. Large angles at oxygen are typical of aryloxide derivatives of Ta(V).[11] The pentagonal planes of all three compounds contain the two phosphine ligands in nonadjacent positions. The angles within this plane reflect the steric requirements of the phosphine, chloride, and hydride ligands present. In **1** the H–Ta–P angles are compressed to 65.92(3)°, while the Cl–Ta–Cl angle is opened up to 86.66(7)°. In monochloride **2b**, the mutually *cis* hydride ligands are separated by 61(3)° while the Cl–Ta–P angles open up

Scheme 5



4a: L = PMe_3
4b: L = PMe_2Ph
4c: L = $PMePh_2$

4d: L' = PBu^n_3

4e: L" = PMe_2Cy
4f: L" = PMePhCy
4g: L" = $PMeCy_2$

5a: L = PMe_3
5b: L = PMe_2Ph
5c: L = $PMePh_2$

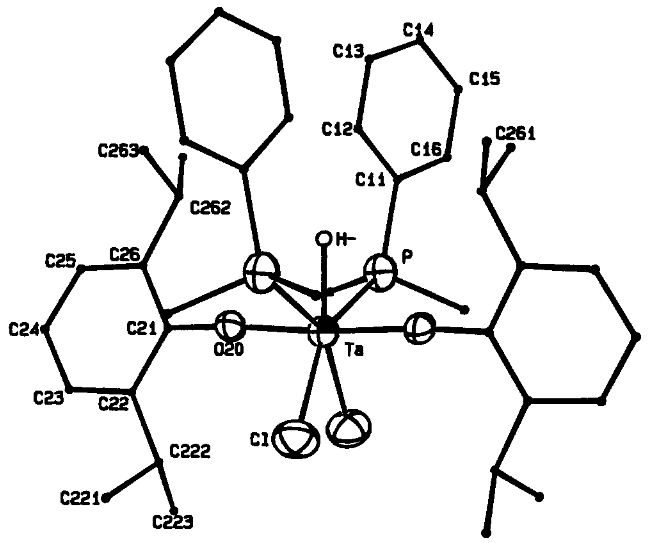


Figure 1. Molecular structure of $[Ta(OC_6H_3Pr^i{}_2\text{-}2,6)_2(H)(Cl)_2(PMe_2Ph)_2]$, **1**. Selected interatomic distances and angles are contained in Table 1. The molecule contains a crystallographically imposed 2-fold rotation axis.

to 84.03(9)° and 84.88(8)°. The trihydride **3c** is closest to adopting a true pentagonal bipyramidal structure with an H(1)–Ta–H(1)′ angle of 75(5)° and *cis* H–Ta–P angles of 65(3)° and 77.49(7)°.

In compounds **2b** and **3c** the *cis* H–Ta–H angles of 61(3)° and 75(5)° are too large for there to be any significant interaction between the hydrogen ligands. This structural data combined with the spectroscopy of those colorless compounds strongly argues against their formulation as η^2-dihydrogen derivatives of Ta(III).[2]

The solid state structures of six-coordinate **4b** and **5c** are of particular interest. It can be seen (Figures 4 and 5) that both compounds adopt related structures. There are two mutually *trans* aryloxide ligands, O–Ta–O angles of 173.3(1)° and 172.2(1)°, and a phosphine ligand *trans* to either an aryloxide oxygen atom **4b**, P–Ta–O(30) = 174.5(1)°, or a chloride group **5c**, P–Ta–Cl = 174.96(5)°. This results in a square planar arrangement for the $[TaO_3P]$ and $[TaO_2PCl]$ cores in **4b** and **5c** respectively. The two hydride ligands are positioned above and below this plane. The location and refinement of these hydrides show that they are distorted away from the positions predicted for an octahedral geometry. Instead in both cases the hydrides are bent toward the phosphine ligand with acute H–Ta–P angles of 66(2)° and 69(1)° in **4b** and 56(2)° and 62(2)° in **5c**. The positioning of these hydride ligands is supported by the infrared spectroscopy (*vide infra*) of **4** and **5** where analysis of the intensity of the two observed $\bar{\nu}$(Ta–H) bands is consistent with the H–Ta–H angles of only 135(3)° in **4b** and 118(2)° in **5c** predicted by the X-ray diffraction studies.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for $[Ta(OC_6H_3Pr^i{}_2\text{-}2,6)_2H(Cl)_2(PMe_2Ph)_2]$, 1

Ta–H⁻	1.70(7)	Ta–P	2.647(1)
Ta–Cl	2.478(1)	Ta–O(20)	1.902(3)
Cl–Ta–H⁻	139(3)	Cl–Ta–O(20)	87.82(9)
P–Ta–H⁻	65(3)	P–Ta–P	131.84(6)
O(20)–Ta–H⁻	87(5)	P–Ta–O(20)	92.19(9)
Cl–Ta–Cl	86.66(7)	P–Ta–O(20)	85.94(9)
Cl–Ta–P	153.84(5)	O(20)–Ta–O(20)	175.4(2)
Cl–Ta–P	73.73(4)	Ta–O(20)–C(21)	174.7(3)

The Ta–O(aryloxide) distances of 1.888(3) and 1.896(3) Å in **5c** are slightly shorter on average than the distances in **1**, **2b**, **3c**, and **4b**. In all five compounds the Ta–P distances span the very narrow range of 2.615(3) to 2.655(1) Å.

The pentagonal bipyramidal structures adopted by the seven-coordinate hydrides **1**, **2**, and **3** can be rationalized using steric and electronic arguments. The formation of a pentagonal bipyramid requires the use of seven atomic orbitals (s, p_x, p_y, p_z, d_{z^2}, d_{xy}, and $d_{x^2-y^2}$) on the metal center for σ-bonding. The *trans* axial arrangement of the bulky aryloxide groups not only minimizes steric crowding but also allows π-donation from the oxygen atoms into the vacant d_{xz} and d_{yz} pair of atomic orbitals on tantalum. The arrangement of

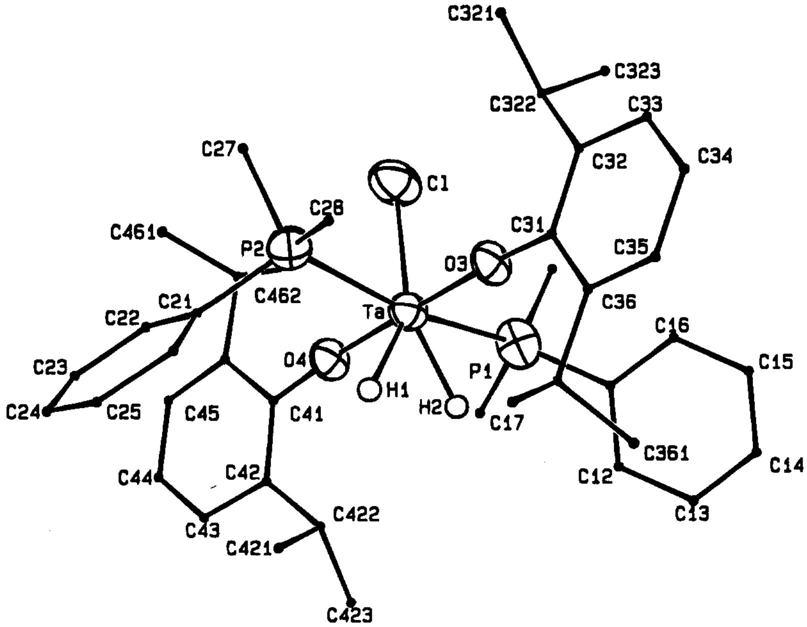


Figure 2. Molecular structure of $[Ta(OC_6H_3Pr^i{}_2\text{-}2,6)_2(Cl)(H)_2(PMe_2Ph)_2]$, **2b**. Selected interatomic distances and angles are contained in Table 2.

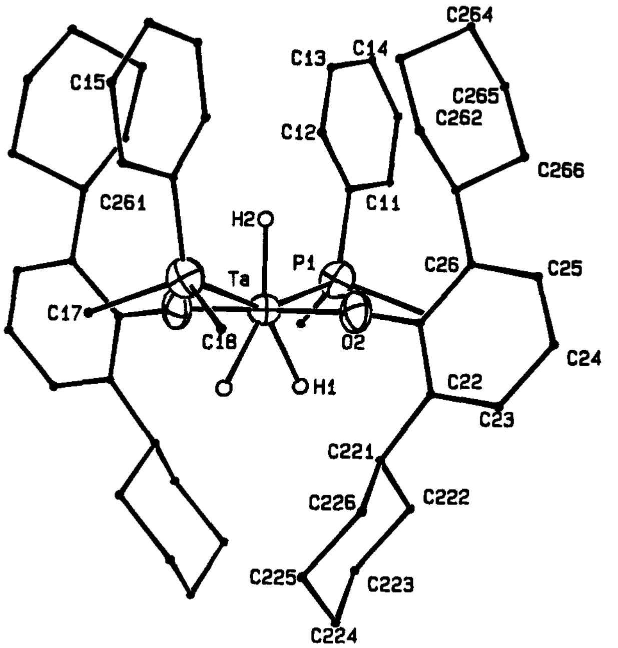


Figure 3. Molecular structure of [Ta(OC$_6$H$_3$Cy$_2$-2,6)$_2$(H)$_3$(PMe$_2$Ph)$_2$], **3c**. Selected interatomic distances and angles are contained in Table 3. The molecule contains a crystallographically imposed 2-fold rotation axis.

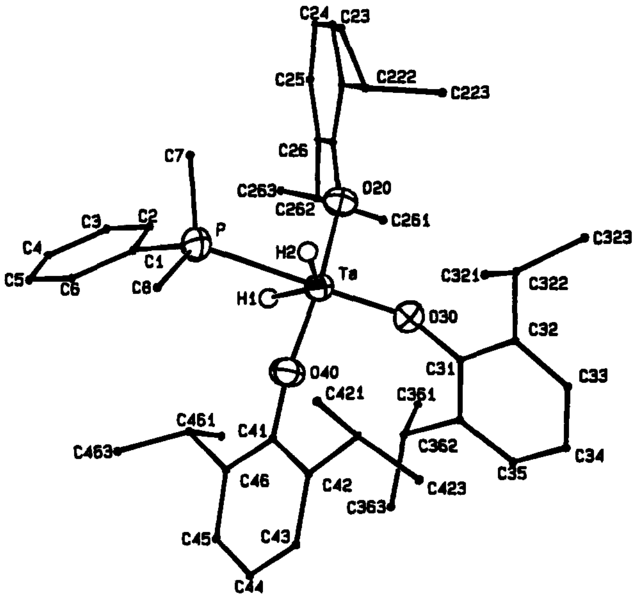


Figure 4. Molecular structure of [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$(H)$_2$(PMe$_2$Ph)], **4a**. Selected interatomic distances and angles are contained in Table 4.

ligands within the pentagonal plane can be rationalized on steric grounds.

The structures adopted by six-coordinate **4b** and **5c** are intriguing. The bending of the hydride ligands toward the phosphine group cannot be rationalized on steric grounds; in **5c** a steric argument would predict a bending toward the chloride group. Despite the acute P–Ta–H angles in **4b** and **5c** the hydride ligands still lie 2.2–2.5 Å away from the phosphorus atom, which is too far (typical P–H bond distances are 1.4 Å) for any electronic interaction. A better description of the molecular structures of **4b** and **5c** involves a pentagonal bipyramidal arrangment of the "anionic" groups (hydride, chloride, aryloxide) with the phosphine ligand coordinated between the two equatorial hydride groups.

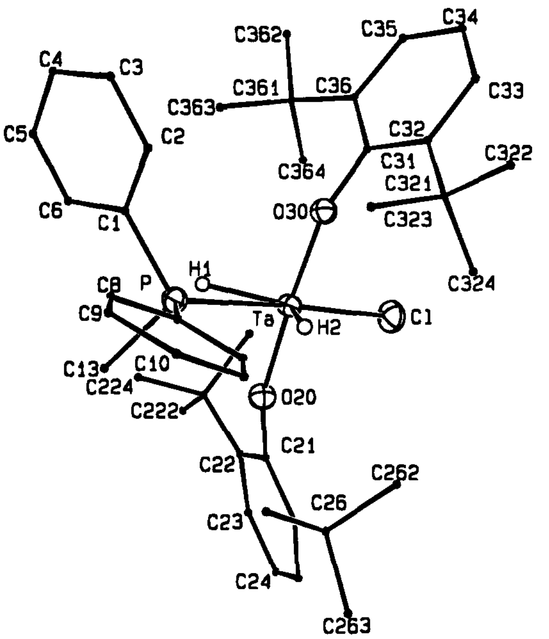


Figure 5. Molecular structure of [Ta(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$(Cl)(H)$_2$(PMePh$_2$)], **5c**. Selected interatomic distances and angles are contained in Table 5.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl(H)$_2$(PMe$_2$Ph)$_2$], 2b

Ta–H(1)	1.90(9)	Ta–P(2)	2.617(3)
Ta–H(2)	1.76(7)	Ta–O(3)	1.899(5)
Ta–Cl	2.532(2)	Ta–O(4)	1.900(5)
Ta–P(1)	2.616(3)		
H(1)–Ta–H(2)	61(3)	Cl–Ta–P(2)	84.88(8)
Cl–Ta–H(1)	152(3)	Cl–Ta–O(3)	91.2(2)
Cl–Ta–H(2)	146(2)	Cl–Ta–O(4)	90.2(2)
P(1)–Ta–H(1)	123(3)	P(1)–Ta–P(2)	168.86(8)
P(1)–Ta–H(2)	62(2)	P(1)–Ta–O(3)	90.1(2)
P(2)–Ta–H(1)	68(3)	P(1)–Ta–O(4)	90.1(2)
P(2)–Ta–H(2)	129(2)	P(2)–Ta–O(3)	89.1(2)
O(3)–Ta–H(1)	95(3)	P(2)–Ta–O(4)	90.9(2)
O(3)–Ta–H(2)	92(2)	O(3)–Ta–O(4)	178.6(2)
O(4)–Ta–H(1)	84(3)	Ta–O(3)–C(31)	174.2(5)
O(4)–Ta–H(2)	87(2)	Ta–O(3)–C(41)	71.4(5)
Cl–Ta–P(1)	84.03(9)		

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for [Ta(OC$_6$H$_3$Cy$_2$-2,6)$_2$(H)$_3$(PMe$_2$Ph)$_2$] 3c

Ta–H(1)	1.77(9)	Ta–P(1)	2.615(3)
Ta–H(2)	1.6(2)	Ta–O(2)	1.901(6)
H(1)–Ta–H(1)	75(5)	O(2)–Ta–H(2)	90.4(3)
H(1)–Ta–H(2)	143(3)	P(1)–Ta–P(1)	155.0(1)
P(1)–Ta–H(1)	65(3)	P(1)–Ta–O(2)	89.0(2)
P(1)–Ta–H(1)	140(3)	P(1)–Ta–O(2)	91.2(2)
P(1)–Ta–H(2)	77(3)	O(2)–Ta–O(2)	179.2(5)
O(2)–Ta–H(1)	84(3)	Ta–O(2)–C(21)	172.1(8)
O(2)–Ta–H(1)	95(3)		

The adoption of unexpected structures by some s- and p-block metal derivatives has been attributed to the presence of primary (typically covalent) and secondary (typically dative) bonds.[12] The secondary bonds are argued to be less stereochemically active than the primary bonds in determining the adopted structure. A similar argument can be applied to compounds **4b** and **5c** and a number of other transition metal compounds in the literature.[13]

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[12] Goel, S. C.; Chiang, M. Y.; Buhro, W. E. *J. Am. Chem. Soc.* **1990**, *112*, 6724. (b) Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992. (c) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for [Ta($OC_6H_3Pr^i_2$-2,6)$_3$(H)$_2$(PMe_2Ph)], 4b

Ta−H(1)	1.74(4)	Ta−O(20)	1.907(3)
Ta−H(2)	1.83(6)	Ta−O(30)	1.912(4)
Ta−P	2.650(1)	Ta−O(40)	1.897(3)
H(1)−Ta−H(2)	135(3)	P−Ta−O(20)	89.3(1)
P−Ta−H(1)	69(1)	P−Ta−O(30)	174.5(1)
P−Ta−H(2)	66(2)	P−Ta−O(40)	85.4(1)
O(20)−Ta−H(1)	89(1)	O(20)−Ta−O(30)	92.0(2)
O(20)−Ta−H(2)	91(2)	O(20)−Ta−O(40)	173.3(1)
O(30)−Ta−H(1)	116(1)	O(30)−Ta−O(40)	93.6(2)
O(30)−Ta−H(2)	109(2)	Ta−C(20)−C(21)	160.7(3)
O(40)−Ta−H(1)	86(1)	Ta−O(30)−C(31)	153.6(3)
O(40)−Ta−H(2)	91(2)	Ta−O(4)−C(41)	169.5(4)

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for [Ta($OC_6H_3Bu^t_2$-2,6)$_2$Cl(H)$_2$($PMePh_2$)], 5c

Ta−H(1)	1.73(5)	Ta−P	2.655(1)
Ta−H(2)	1.54(5)	Ta−O(20)	1.896(3)
Ta−Cl	2.397(1)	Ta−O(30)	1.888(3)
H(1)−Ta−H(2)	118(2)	O(30)−Ta−H(1)	99(2)
Cl−Ta−H(1)	128(2)	O(30)−Ta−H(2)	88(2)
Cl−Ta−H(2)	113(2)	Cl−Ta−P	174.96(5)
P−Ta−H(1)	56(2)	Cl−Ta−O(20)	86.5(1)
P−Ta−H(2)	62(2)	Cl−Ta−O(30)	86.5(1)
O(20)−Ta−H(1)	83(2)	P−Ta−O(20)	92.7(1)
O(20)−Ta−H(2)	99(2)	P−Ta−O(30)	94.6(1)
O(20)−Ta−O(30)	172.2(1)		

NMR Spectroscopic Properties. The most important spectroscopic feature of these compounds is due to the tantalum hydride ligands in the ^{1}H NMR spectrum (Table 6). The resonances due to the other ligands in the ^{1}H, ^{13}C, and ^{31}P NMR spectra are unexceptional and are consistent with the observed solid state structures. The hydride ligands in compounds **1**−**5** resonate to low field in the δ 10−20 ppm region of the ^{1}H NMR spectrum. In sparingly soluble monohydride **1** the hydride ligand appears as a sharp triplet at δ 18.93 ppm due to coupling to the two equivalent ^{31}P nuclei, $^2J(^{31}P-{}^1H) = 88.0$ Hz. In dihydrides **2** a multiplet is observed for the two equivalent hydride ligands (Figure 6). The position of the multiplet is highly sensitive to the nature of the phosphine ligand, moving to higher field as the basicity of the phosphine ligand increases. Analysis of these multiplets shows them to contain 10 resolvable lines with some of the lines being very weak. The peaks were successfully simulated as being half of an AA′XX′ pattern (the X nucleus being phosphorus). This simulation (Figure 7) and the derived coupling constants (Table 7) have some important ramifications. The generation of an AA′XX′ pattern necessitates a lack of exchange on the NMR time scale between the chemically identical, but magnetically nonequivalent, hydride ligands. The multiplet for the hydride ligands in **2b** was found to remain essentially unchanged at temperatures up to 80 °C. This indicates that molecules **2** exhibit stereochemical rigidity on the ^{1}H NMR time scale. Any facile processes involving formation of an η^2-dihydrogen complex in **2** followed by rotation can be excluded. The values of the coupling constants derived from the simulation are also informative. The H−H coupling constants of 6−7 Hz are too low to indicate significant interaction between these ligands. The magnitudes of the P−P coupling constants were confirmed by the ^{31}P NMR spectrum of a mixture of **2b** and added PMe$_3$. A well-resolved AB pattern for the mixed (PMe_2Ph)(PMe_3) complex was observed with a ^2J coupling constant of 158 Hz, comparable in magnitude to these derived from the simulation studies.

In the trihydride **3**, two multiplets in the ratio of 2:1 are observed in the ^{1}H NMR spectrum for the two chemically distinct hydride ligands. The unique hydride appears as a triplet of triplets due to coupling to both phosphines and the other two hydride ligands. The $\{^{31}P\}^1H$ NMR spectrum shows the small ^2J coupling between the chemically nonequivalent hydride ligands (Figure 8). The more complex pattern for the remaining two hydrides can again can be ascribed to the stereochemical rigidity of these molecules.

In both seven-coordinate compounds **2** and **3**, restricted rotation about the Ta−O−Ar bond is evidenced by the presence of nonequivalent resonances for the *ortho* substituents on the aryloxide ligands (Figure 6).

Vibrational Spectroscopy. The existence of tantalum−hydride ligands in these compounds can be detected by the presence of bands in the 1550−1950 cm^{-1} region of the infrared spectrum. The detection and assignment of $\bar{\nu}$(M−H) bands in the infrared spectra of metal−hydride compounds can be challenging.[1a] The monohydride **1** shows a single, sharp infrared band at 1850 cm^{-1}. In dihydrides **2** and trihydrides **3** the tantalum−hydride bands are broader and weaker. The most interesting infrared spectra are those of six-coordinate dihydrides **4** and **5**. In both sets of compounds two well-resolved $\bar{\nu}$(Ta−H) vibrations are observed. In the case of highly soluble **4**, the spectra are due to *solutions* of the compound in Nujol. In the case of **5**, however, the spectra are due to mulls (Figure 9). The use of infrared spectroscopy as a structural tool for inorganic compounds has excellent precedence in metal−carbonyl chemistry. A common text book illustration involves the angular dependence of the intersities of the symmetric and asymmetric stretching vibrations for two carbonyl ligands.[14] An identical analysis should apply to metal−hydride compounds. In practice it is unusual to be able to obtain vibrational spectra of hydrides in which simple $\bar{\nu}$(M−H) stretching vibrations are not strongly coupled to other ligand vibrations or metal−hydride bends. In compounds **4** and **5** the presence of two tantalum−hydride stretches is consistent with a nonlinear arrangement of hydride ligands (Figure 9). If one assigns the higher frequency band to the symmetric stretch, then the intensity ratio of the two bands yields an estimate of the H−Ta−H angle (Figure 10). The angles estimated by this analysis (typically within 10°) are consistent with the values determined from the X-ray diffraction 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. Tributyltin hydride and tributyltin deuteride were purchased from Aldrich Chemical Co. Phosphines were all purchased from Strem Chemical Co. and were

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(13) (a) Fryzuk, M. D.; Carter, A.; Rettig, S. J. *Organometallics* **1992**, *11*, 469. (b) Kobriger, L. M.; McMullen, A. K.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1989**, *8*, 77.

(14) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; p 1037.

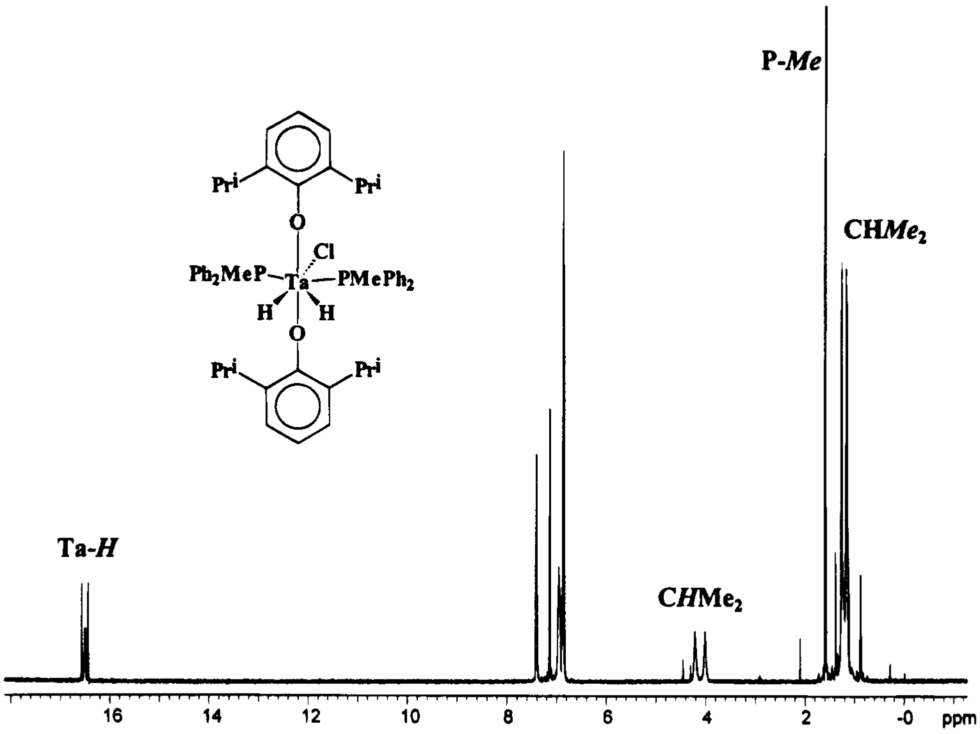

Figure 6. ^1H NMR (500 MHz) spectrum of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(Cl)(H)_2(PMePh_2)_2]$, **2c**.

Table 6. Selected NMR Data for Tantalum–Hydride Compounds

	δ(Ta−H)	$^2J(^{31}P-^1H)$/Hz	δ(Ta−P)
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2H(Cl)_2(PMe_2Ph)_2]$, **1**	18.93 (t)	88	7.8
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl(H)_2(PMe_3)_2]$, **2a**	15.89 (m)		−12.3
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl(H)_2(PMe_2Ph)_2]$, **2b**	16.55 (m)		−3.7
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl(H)_2(PMePh_2)_2]$, **2c**	17.77 (m)		7.6
$[Ta(OC_6H_3Ph_2\text{-}2,6)_2Cl(H)_2(PMe_3)_2]$, **2d**	16.73 (m)		−12.4
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(H)_3(PMe_3)_2]$, **3a**	13.20 (m); 12.32 (tt)		−12.0
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(H)_3PMe_2Ph)_2]$, **3b**	13.54 (m); 12.80 (tt)		3.2
$[Ta(OC_6H_3Cy_2\text{-}2,6)_2(H)_3(PMe_2Ph)_2]$, **3c**	13.00 (m); 12.98 (tt)		2.3
$[Ta(OC_6H_3Cy_2\text{-}2,6)_2(H)_3(PMePh_2)_2]$, **3d**	13.52 (m); 13.34 (tt)		22.5
$[Ta(OC_6HPh_2\text{-}3,5\text{-}Cy_2\text{-}2,6)_2(H)_3(PMe_2Ph)_2]$, **3e**	13.76 (m); 13.15 (tt)		−2.2
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(H)_2(PMe_3)]$, **4a**	14.46 (d)	63	−17.4
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(H)_2(PMe_2Ph)]$, **4b**	14.89 (d)	60	−6.5
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(H)_2(PMePh_2)]$, **4c**	15.34 (d)	59	8.2
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(H)_2(PBu^n_3)]$, **4d**	14.67 (d)	59	10.7
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(H)_2(PMe_2Cy)]$, **4e**	14.65 (d)	60	−3.6
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(H)_2(PMePhCy)]$, **4f**	15.23 (d)	58	11.9
$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(H)_2(PMeCy_2)]$, **4g**	14.82 (d)	57	18.2
$[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl(H)_2(PMe_3)]$, **5a**	17.12 (d)	77	−5.6
$[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl(H)_2(PMe_2Ph)]$, **5b**	17.47 (d)	76	3.9
$[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl(H)_2(PMePh_2)]$, **5c**	17.69 (d)	74	24.1

dried over 3 Å molecular sieves prior to use. $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]$, $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl_3]$, $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_3(CH_2C_6H_4\text{-}p\text{-}CH_3)_2]$, $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl(CH_2SiMe_3)_2]$, $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2SiMe_3)_3]$, $[Ta(OC_6H_3Ph_2\text{-}2,6)_2Cl(CH_2SiMe_3)_2]$, $[Ta(O\text{-}C_6H_3Ph_2\text{-}2,6)_2(R)_3]$, ($R = CH_2SiMe_3$, $CH_2C_6H_4\text{-}p\text{-}CH_3$), and $[Ta(OC_6HPh_4\text{-}2,3,5,6)_2(CH_2SiMe_3)_3]$ were prepared by reported procedures.[6,7,15] The ^1H and ^{31}P NMR spectra were recorded on Varian Associates Gemini 200 and General Electric QE-300 spectrometers and were referenced to 85% H_3PO_4 using protio impurities of commercial benzene-d_6 as an internal standard. The infrared spectra were obtained using a Perkin-Elmer 1800 Fourier transform infrared spectrophotometer. High-pressure operations were performed with a Parr Instrument Co. model 4561 300 mL stainless steel high-pressure minireactor connected to a Parr 4841 temperature controller. Microanalyses were obtained in-house at Purdue. Considerable difficulties were encountered in obtaining accurate microanalytical data for some of these compounds. In particular, the values for the percentage of carbon were consistently found to be low, a fact we ascribe to the possible formation of metal carbides on combustion. Due to the similarity of some of the synthetic procedures, only representative methods will be presented for each type of compound.

$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2H(Cl)_2(PMe_2Ph)_2]$, 1. To a suspension of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]$ (2.0 g, 3.12 mmol) in benzene (5 mL) was added (dimethylphenyl)phosphine (1.08 g, 7.79 mmol) followed by tri-*n*-butyltin hydride (1.36 g, 4.67 mmol). The resulting clear yellow mixture was allowed to stand for 15 h to yield the crystalline product. The colorless crystals were washed with hexane and dried *in vacuo*; yield: 2.14 g (88.6%). Anal. Calcd for $C_{40}H_{57}Cl_2P_2O_2Ta$: C, 54.37; H, 6.50; Cl, 8.03; P, 7.01. Found: C, 54.17; H, 6.51; Cl, 7.89. ^1H NMR (C_6D_6, 30 °C): 7.63 (m, 4H, P-*Ph ortho*); 6.62–6.85 (m, 12H, aromatics); 3.61 (septet, 2H, C*H*Me); 2.78 (septet, 2H, C*H*Me); 1.94 (t, 12H, P-*Me*); 1.64 (d, 12H, CH*Me*); 1.52 (d, 12H, CH*Me*). IR (Nujol): 1850 cm^{-1} (Ta−H).

$[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2Cl(H)_2(PMe_3)_2]$, 2a. This compound was obtained by the hydrogenolysis of $[Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2\text{-}$

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(15) Parkin, B. C.; Clark, J. R.; Fanwick, P. E.; Rothwell, I. P. Results to be published.

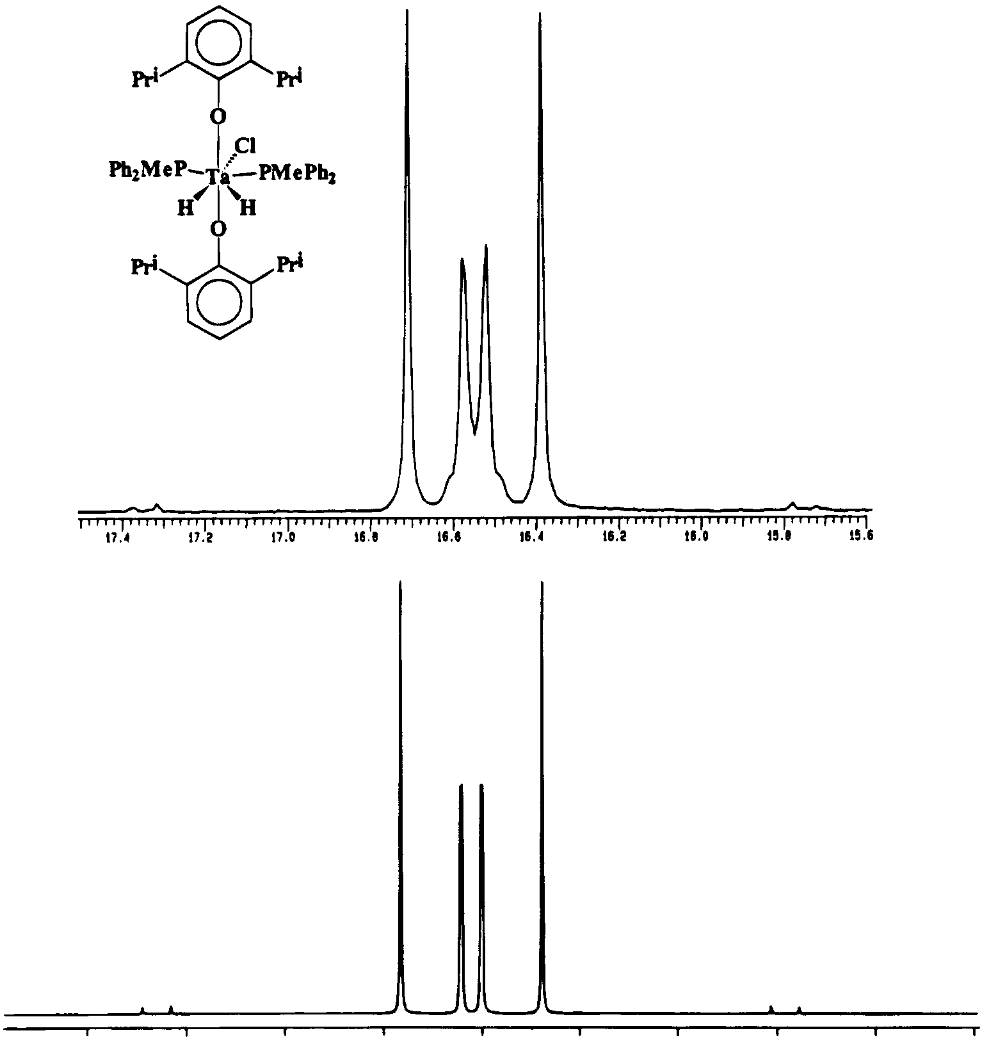

Figure 7. Observed and simulated spectra for the hydride ligands (AA'XX' pattern) in the ^{1}H NMR spectrum of [Ta(OC$_6$H$_3$-Pr$^i_2$-2,6)$_2$(Cl)(H)$_2$(PMePh$_2$)$_2$], **2c**. The coupling constants used in the simulation are contained in Table 7.

Table 7. Coupling Constants Obtained by Simulation for Dihydrides 2

	${}^2J({}^{31}\mathrm{P'}-{}^1\mathrm{H})$	${}^2J({}^{31}\mathrm{P}-{}^1\mathrm{H})$	${}^2J({}^1\mathrm{H}-{}^1\mathrm{H})$	${}^2J({}^{31}\mathrm{P}-{}^{31}\mathrm{P})$
[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl(H)$_2$(PMe$_3$)$_2$], **2a**	65.8	7.0	−7.4	163.6
[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl(H)$_2$(PMe$_2$Ph)$_2$], **2b**	64.4	7.2	−7.9	159.0
[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl(H)$_2$(PMePh$_2$)$_2$], **2c**	65.0	7.0	−6.2	156.7

SiMe$_3$)$_2$Cl] in the presence of PMe$_3$ using a procedure analogous to that used for compound **2b**. Anal. Calcd for C$_{30}$H$_{54}$ClO$_2$P$_2$Ta: C, 49.69; H, 7.51; Cl, 4.89; P, 8.54. Found: C, 49.32; H, 7.40; Cl, 4.44; P, 8.07. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 6.87−7.17 (m, 6H, aromatics); δ 4.24 (septet, 2H, C*H*Me); δ 4.20 (septet, 2H, C*H*Me); δ 1.33 (d, 24H, CH*Me*); δ 1.21 (t, 18H, P-*Me*), ${}^2J({}^{31}\mathrm{P}-{}^1\mathrm{H})$ = 7.4 Hz. IR (Nujol): 1764, 1730 cm^{-1}, br (Ta−H).

[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl(H)$_2$(PMe$_2$Ph)$_2$], 2b, by Hydrogenolysis. To a solution of [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$(CH$_2$SiMe$_3$)$_2$-Cl] (0.30 g, 0.40 mmol) in cyclohexane (3 mL) was added (dimethylphenyl)phosphine (0.24 g, 1.20 mmol). The solution was placed in a glass flask within the high-pressure reactor, pressurized to 1200 psi of H$_2$, and heated unstirred at 80 °C for 24 hrs. The pressure reactor was allowed to cool slowly to ambient temperatures before being depressurized and opened in the drybox. Decanting the brown supernatant gave pale yellow crystals of product, which were washed with hexane and dried *in vacuo*. In a number of runs the yield of **2b** varied from 35%−65%. Anal. Calcd for C$_{40}$H$_{58}$ClO$_2$P$_2$Ta: C, 56.57; H, 6.88; Cl, 4.17; P, 7.29. Found: C, 56.63; H, 7.23; Cl, 4.61; P, 7.14. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 7.42 (m, 4H, P-*Ph ortho*); δ 6.82−6.95 (m, 12 H, aromatics); δ 4.21 (septet, 2H, C*H*Me); δ 4.02 (septet, 2H, C*H*Me); δ 1.60 (t, 12H, P-*Me*), ${}^2J({}^{31}\mathrm{P}-{}^1\mathrm{H})$ = 4.1 Hz; δ 1.23 (d, 12H, CH*Me*); δ 1.17 (d, 12H, CH*Me*). IR (Nujol): 1848, 1754 cm^{-1}, br (Ta−H).

[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl(H)$_2$(PMe$_2$Ph)$_2$], 2b, by Addition of Bu$_3$SnH. To a suspension of [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl$_3$] (2.0 g, 3.11 mmol) in benzene (5 mL) was added (dimethylphenyl)-phosphine (1.08 g, 7.81 mmol) followed by tri-*n*-butyltin hydride (2.72 g, 9.35 mmol). The resulting clear yellow mixture was stirred for 20 h to generate a dark orange solution. Removal of benzene solvent led to the crude product as a white solid, which was washed with hexane and dried *in vacuo* to yield 1.1 g (42%).

[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$Cl(H)$_2$(PMePh$_2$)$_2$], 2c. This compound was obtained by the hydrogenolysis of [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_2$(CH$_2$SiMe$_3$)$_2$Cl] in the presence of PMePh$_2$ using a procedure analogous to that used for compound **2b**. Anal. Calcd for C$_{50}$H$_{62}$ClO$_2$P$_2$Ta: C, 61.70; H, 6.42; Cl, 3.64; P, 6.36. Found: C, 61.30; H, 6.72; Cl, 3.65; P, 6.07. ^{1}H NMR (C$_6$D$_6$, 30 °C): δ 7.69 (m, 8H, P-*Ph ortho*); δ 6.77−7.21 (m, 18H, aromatics); δ 4.02 (septet, 4H, C*H*Me); δ 2.07 (t, 6H, P-*Me*), ^{2}J (P−H) = 4.4 Hz; δ 1.11 (d, 12H, CH*Me*); δ 1.02 (d, 12H, CH*Me*). IR (Nujol): 1852, 1796, 1758 cm^{-1}, br (Ta−H).

[Ta(OC$_6$H$_3$Ph$_2$-2,6)$_2$Cl(H)$_2$(PMe$_3$)$_2$], 2d. This compound

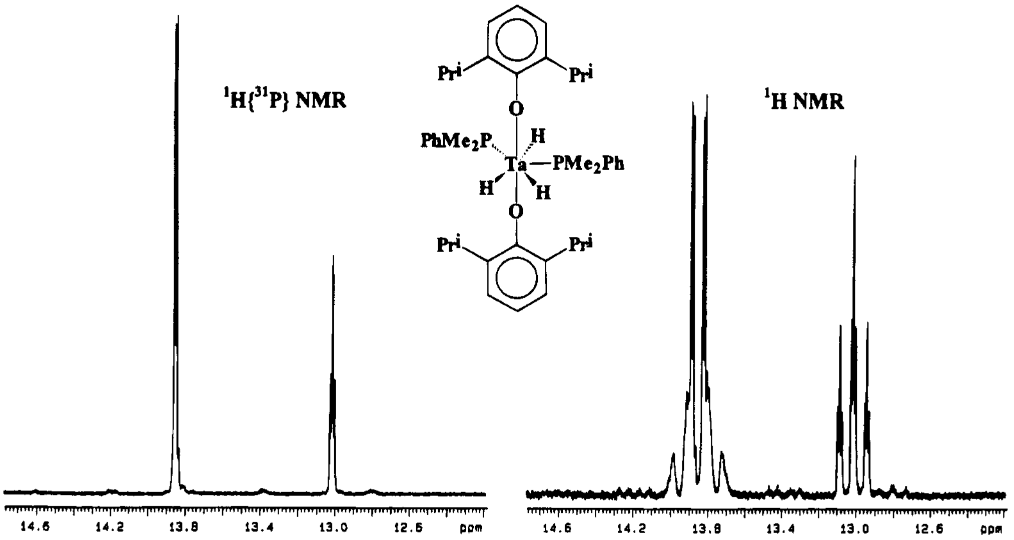

Figure 8. ^{1}H{^{31}P} and ^{1}H NMR (500 MHz) spectra of the hydride resonances in $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(H)_3(PMe_2Ph)_2}]$, **3b**.

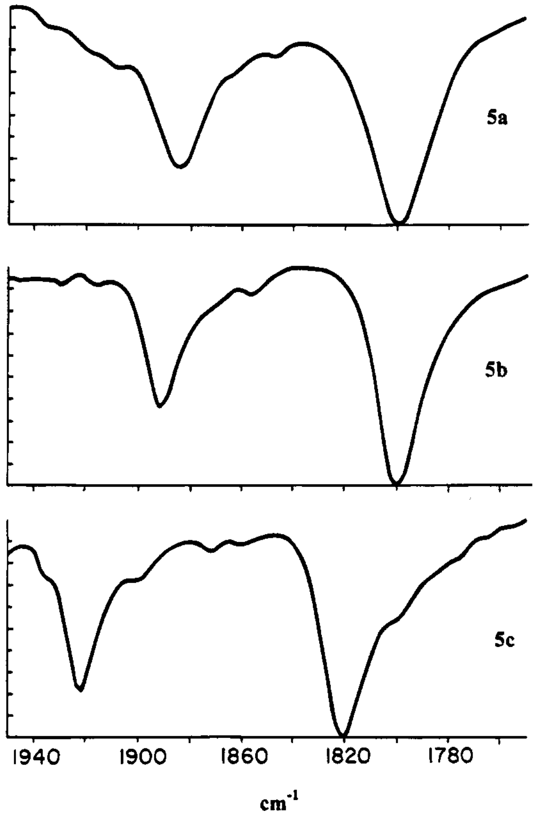

Figure 9. Infrared spectra (Nujol mulls) of dihydrides **5a–c** showing the symmetric and asymmetric ν(Ta–H) vibrations.

was obtained by the hydrogenolysis of $[\mathrm{Ta(OC_6H_3Ph_2\text{-}2,6)_2(CH_2SiMe_3)_2Cl}]$ in the presence of $\mathrm{PMe_3}$ using a procedure analogous to that used for compound **2b**. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 6.49–7.75 (m, 26H, aromatics); δ 0.91 (d, 9H, P-*Me*), ^2J(P–H) = 3.73 Hz; δ 0.89 (d, 9H, P-*Me*), ^2J(P–H) = 3.73 Hz. IR (Nujol): 1730 cm^{-1}, br (Ta–H).

$[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(H)_3(PMe_3)_2}]$, 3a. This compound was obtained by the hydrogenolysis of $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2SiMe_3)_3}]$ in the presence of $\mathrm{PMe_3}$ using a procedure analogous to that used for compound **3b**. Anal. Calcd for $\mathrm{C_{30}H_{55}O_2P_2Ta}$: C, 52.17; H, 8.03; P, 8.97. Found: C, 53.80; H, 8.30. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 6.86–7.00 (m, 6H, aromatics); δ 4.18 (septet, 2H, C*H*Me); δ 3.95 (septet, 2H, C*H*Me); δ 1.35 (d, 18 H, P-*Me*), ^2J(^{31}P–^{1}H) = 7.4 Hz; δ 1.31 (d, 12H, CH*Me*); δ 1.21 (d, 12H, CH*Me*).

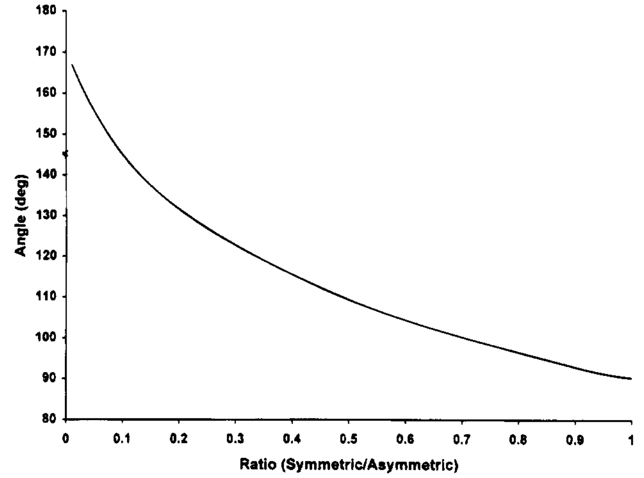

Figure 10. Plot showing the calculated relationship of the ratio of symmetric/asymmetric intensities with the angle between two vibrationally coupled ligands.

$[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(H)_3(PMe_2Ph)_2}]$, 3b. To a cyclohexane (3 mL) solution of $[\mathrm{Ta(OC_6H_3Pr^i_2\text{-}2,6)_2(CH_2SiMe_3)_3}]$ (0.15 g, 0.19 mmol) was added (dimethylphenyl)phosphine (0.078 g, 0.56 mmol). The solution was placed in a glass flask within the high-pressure reactor, pressurized to 1200 psi of $\mathrm{H_2}$, and heated unstirred at 80 °C for 24 h. The pressure reactor was allowed to cool slowly to ambient temperatures before being depressurized and opened in the drybox. Decanting the brown supernatant gave colorless crystals of product, which were washed with hexane and dried *in vacuo*. Typical yields: 35–65%. Anal. Calcd for $\mathrm{C_{40}H_{59}O_2P_2Ta}$: C, 58.96; H, 7.30; P, 7.60. Found: C, 58.58; H, 7.50; P, 7.41. ^{1}H NMR ($\mathrm{C_6D_6}$, 30 °C): δ 7.99 (m, 4H, P-*Ph ortho*); δ 6.77–7.10 (m, 12H, aromatics); δ 4.10 (septet, 2H, C*H*Me); δ 3.77 (septet, 2H, C*H*Me); δ 1.67 (d, 12H, P-*Me*), ^2J(^{31}P–^{1}H) = 6.3 Hz; δ 1.26 (d, 12 H, CH*Me*); δ 0.98 (d, 12H, CH*Me*). IR (Nujol): 1648 cm^{-1}, br (Ta–H); 1196 cm^{-1}, (Ta–D).

$[\mathrm{Ta(OC_6H_3Cy_2\text{-}2,6)_2(H)_3(PMe_2Ph)_2}]$, 3c. To a cyclohexane (3 mL) solution of $[\mathrm{Ta(OC_6H_3Ph_2\text{-}2,6)_2(CH_2C_6H_4\text{-}\mathit{p}\text{-}CH_3)_3}]$ (0.50 g, 0.51 mmol) was added (dimethylphenyl)phosphine (0.21 g, 1.52 mmol). The solution was placed in a glass flask within the high-pressure reactor, pressurized to 1200 psi of $\mathrm{H_2}$, and heated unstirred at 80 °C for 24 h. The pressure reactor was allowed to cool slowly to ambient temperatures before being depressurized and opened in the drybox. Decanting the dark-brown supernatant gave colorless crystals of product, which were washed with hexane and dried *in vacuo*. Anal. Calcd for $\mathrm{C_{52}H_{75}O_2P_2Ta}$: C, 64.05; H, 7.75; P, 6.35. Found: C, 63.97;

Table 8. Crystal Data and Data Collection Parameters

formula	$TaCl_2P_2O_2C_{40}H_{57}$	$TaClP_2O_2C_{40}H_{58}$	$TaP_2O_2C_{52}H_{75}$	$TaPO_3C_{44}H_{64}$	$TaClPO_2C_{41}H_{57}$
fw	883.70	849.26	975.07	852.92	829.29
space group	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	26.025(4)	9.735(1)	24.065(3)	10.637(1)	10.851(5)
b, Å	10.7954(5)	24.310(3)	13.530(2)	12.820(2)	18.110(7)
c, Å	18.509(3)	17.735(2)	20.263(3)	31.799(4)	20.09(1)
β, deg	128.31(1)	90.76(1)	131.633(9)	98.76(1)	96.67(5)
V, $Å^3$	4080(2)	4196(1)	4931(3)	4285(2)	3921(6)
Z	4	4	4	4	4
d_{calcd}, g cm^{-3}	1.438	1.344	1.313	1.322	1.404
cryst dimens, mm^3	0.47 × 0.47 × 0.30	0.47 × 0.28 × 0.06	0.44 × 0.20 × 0.05	0.50 × 0.46 × 0.29	0.50 × 0.25 × 0.19
temp, K	293	293	293	293	173
radiation (wavelength)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)
monochromator	graphite	graphite	graphite	graphite	graphite
linear abs coeff, cm^{-1}	29.02	27.56	23.01	26.05	29.09
abs corr appl	empirical	empirical	empirical	empirical	empirical
transmissn factors: min, max	0.64, 1.00	0.78, 1.00	0.65, 1.00	0.76, 1.00	0.68, 1.00
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
h,*k*,*l* range	0−30; 0−12; −21 to 17	−10 to +10; 0−26; 0−19	0−25; 0−14; −21−16	−12 to +12; 0−15; 0−37	−11 to +11; −19 to 0; 0−21
2θ range, deg	4.00−50.00	4.00−45.00	4.00−45.00	4.00−50.00	5.04−45.00
scan width, deg	0.65 + 0.35 tan *θ*	0.57 + 0.35 tan *θ*	0.63 + 0.35 tan *θ*	0.42 + 0.35 tan *θ*	0.50 + 0.92 tan *θ*
Takeoff angle, deg	2.95	2.95	2.95	2.95	3.00
programs used	Enraf-Nonius MolEN	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius MolEN	Enraf-Nonius MolEN
F_{000}	1800.0	1736.0	2024.0	1760.0	1696.0
p-factor used in weighting	0.040	0.040	0.040	0.040	0.040
w no. of data collected	3784	5633	3377	7944	5504
no. of unique data	3784	5633	3377	7944	5332
no. of data with $I > 3.0\sigma(I)$	2631	3571	2213	5127	4111
no. of variables	215	423	264	450	423
largest shift/esd in final cycle	0.00	0.28	0.03	0.03	0.25
R	0.027	0.032	0.048	0.029	0.029
R_w	0.033	0.306	0.053	0.036	0.037
goodness of fit	1.148	0.895	1.148	0.956	1.075

H, 7.99; P, 5.96. ^{1}H NMR (C_6D_6, 30 °C): δ 7.91 (m, 4H, P-*Ph ortho*); δ 6.81−7.18 (m, 12H, aromatics); δ 4.08 (m, 2H, cy-C*H*); δ 3.27 (m, 2H, cy-C*H*); δ 1.06−2.38 (m, 40H, cyclohexyl); δ 1.71 (d, 12H, P-*Me*), $^2J(^{31}P-^1H) = 9.0$ Hz. IR (Nujol): 1654, 1588 cm^{-1}, br (Ta−H); 1193 cm^{-1}, (Ta−D).

[Ta(OC$_6$H$_3$Cy$_2$-2,6)$_2$(H)$_3$(PMePh$_2$)$_2$], 3d. This compound was obtained by the hydrogenolysis of [Ta(OC$_6$H$_3$Ph$_2$-2,6)$_2$(CH$_2$C$_6$H$_4$-*p*-CH$_3$)$_3$] in the presence of PMePh$_2$ using a procedure analogous to that used for compound **3c**. Anal. Calcd for $C_{62}H_{79}O_2P_2Ta$: C, 67.75; H, 7.24; P, 5.64. Found: C, 67.41; H, 7.61; P, 5.79. ^{1}H NMR (C_6D_6, 30 °C): δ 7.96 (m, 8H, P-*Ph ortho*); δ 6.76−7.17 (m, 18H, aromatics); δ 3.80 (m, 2H, cy-C*H*); δ 3.31 (m, 2H, cy-C*H*); δ 1.05−2.12 (m, 40H, cyclohexyl); δ 1.94 (d, 6H, P-*Me*) $^2J(^{31}P-^1H) = 6.5$ Hz. IR (Nujol): 1670, 1596 cm^{-1}, br (Ta−H).

[Ta(OC$_6$HPh$_2$-3,5-Cy$_2$-2,6)$_2$(H)$_3$(PMe$_2$Ph)$_2$], 3e. This compound was obtained by the hydrogenolysis of [Ta(OC$_6$HPh$_4$-2,3,5,6)$_2$(CH$_2$SiMe$_3$)$_3$] in the presence of PMe$_2$Ph using a procedure analogous to that used for compound **3c**. ^{1}H NMR (C_6D_6, 30 °C): δ 7.58 (m, 4H, P-*Ph ortho*); δ 7.01−7.39 (m, 38H, aromatics); δ 6.54 (s, 2H, OC$_6$*H*); δ 4.23 (m, 2H, cy-C*H*); δ 3.88 (m, 2H, cy-C*H*); δ 1.05−2.39 (m, 40H, cyclohexyl); δ 1.92 (d, 12H, P-*Me*), $^2J(^{31}P-^1H) = 6.4$ Hz. IR (Nujol): 1656, 1572 cm^{-1}, br (Ta−H).

[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$(H)$_2$(PMe$_3$)], 4a. This compound was obtained by the hydrogenolysis of [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$(CH$_2$C$_6$H$_4$-*p*-CH$_3$)$_2$] in the presence of PMe$_3$ using a procedure identical to that used for compound **4b**. ^{1}H NMR (C_6D_6, 30 °C): δ 6.9−7.2 (m, 9H, aromatics); δ 3.80 (m, 6H, C*H*Me); δ 1.23 (d, 36 H, CH*Me*); δ 1.06 (d, 9H, P-*Me*).

[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$(H)$_2$(PMe$_2$Ph)], 4b. To a cyclohexane solution (3 mL) of [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$(CH$_2$C$_6$H$_4$-*p*-CH$_3$)$_2$] (1.0 g, 1.08 mmol) was added (dimethylphenyl)phosphine (0.35 g, 2.5 mmol). The solution was placed in a glass flask within the high-pressure reactor, pressurized to 1200 psi of H$_2$, and heated unstirred at 90 °C for 24 h. The pressure reactor was allowed to cool slowly to ambient temperatures before being depressurized and opened in the drybox. Decanting the supernatant left colorless crystals of product, which were washed with hexane and dried *in vacuo* to yield 0.55 g (60%). Anal. Calcd for $C_{44}H_{64}PO_3Ta$: C, 61.96; H, 7.56; P, 3.63. Found: C, 61.82; H, 7.57; P, 3.90. ^{1}H NMR (C_6D_6, 30 °C): δ 7.58 (m, 2H, P-*Ph ortho*); δ 6.8−7.2 (m, 12H, aromatics); δ 3.82 (septet, 4H, C*H*Me); δ 3.73 (septet, 2H, C*H*Me); δ 1.49 (d, 6H, P-*Me*); δ 1.29 (d, 24H, CH*Me*); δ 1.16 (d, 12H, CH*Me*). IR (Nujol): 1824, 1758 cm^{-1}.

[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$(H)$_2$(PMePh$_2$)], 4c. This compound was obtained by the hydrogenolysis of [Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$(CH$_2$C$_6$H$_4$-*p*-CH$_3$)$_2$] in the presence of PMePh$_2$ using a procedure identical to that used for compound **4b**. ^{1}H NMR (C_6D_6, 30 °C): δ 7.37 (m, 4H, P-*Ph ortho*); δ 6.8−7.2 (m, 15H, aromatics); δ 3.81 (septet, 4H, C*H*Me); δ 3.58 (septet, 2H, C*H*Me); δ 1.35 (d, 3H, P-*Me*); δ 1.17 (d, 24H, CH*Me*); δ 1.08 (d, 12H, CH*Me*). IR (Nujol): 1846, 1742 cm^{-1}.

[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$(H)$_2$(PBu$^n_3$)], 4d. This compound was only spectroscopically characterized and was obtained by the addition of PBu$^n_3$ to C_6D_6 solutions of **4b**. ^{1}H NMR (C_6D_6, 30 °C): δ 6.8−7.2 (m, 9H, aromatics); δ 3.77 (m, 6H, C*H*Me); δ 1.72 (pentet, 2H, PCH$_2$*CH$_2$*CH$_2$CH$_3$); δ 1.35 (d, 36H, CH*Me*); δ 1.20 (m, 2H, PCH$_2$CH$_2$*CH$_2$*CH$_3$); δ 0.82 (m, 2H, P*CH$_2$*CH$_2$CH$_2$CH$_3$); δ 0.68 (t, 3H, PCH$_2$CH$_2$CH$_2$*CH$_3$*). IR (Nujol): 1794, 1742 cm^{-1}.

[Ta(OC$_6$H$_3$Pr$^i_2$-2,6)$_3$(H)$_2$(L)] (L = PMe$_2$Cy, 4e; L = PMePhCy, 4f; L = PMeCy$_2$, 4g). These compounds were obtained by exposing solutions of **4b** or **4c** to hydrogen (1200 psi, 90 °C) for extended periods of time. The compounds were not isolated but were characterized in reaction mixtures by ^{1}H and ^{31}P NMR (Table 6).

[Ta(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$Cl(H)$_2$(PMe$_3$)], 5a. This compound was obtained by a procedure analogous to that used for compound **5c**. ^{1}H NMR (C_6D_6, 30 °C): δ 6.84–7.36 (m, 6H, aromatics); δ 1.67 (s, 36H, C*Me*); δ 1.35 (d, 9H, P-*Me*), $^2J(^{31}P-^1H)$ = 8.61 Hz. IR (Nujol): 1884, 1800 cm^{-1} (Ta–H).

[Ta(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$Cl(H)$_2$(PMe$_2$Ph)], 5b. This compound was obtained by a procedure analogous to that used for compound **5c**. ^{1}H NMR (C_6D_6, 30 °C): δ 7.45 (m, 2H, P-*Ph ortho*); δ 6.82–7.33 (m, 9H, aromatics); δ 1.77 (d, 9H, P-*Me*), $^2J(^{31}P-^1H)$ = 8.06 Hz; δ 1.62 (s, 36H, C*Me*). IR (Nujol): 1892, 1800 cm^{-1} (Ta–H).

[Ta(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$Cl(H)$_2$(PMePh$_2$)], 5c. To a suspension of [Ta(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$Cl$_3$] (1.0 g, 1.43 mmol) in benzene (5 mL) was added methyldiphenylphosphine (0.43 g 2.15 mmol) followed by tri-*n*-butyltin hydride (1.04 g, 3.58 mmol), and the resulting mixture was allowed to stand for 24 h. The product crystallized from the mixture, and, after decanting the supernatant, the yellow crystals were washed with hexane and dried *in vacuo* to yield 0.64 g (54%). ^{1}H NMR (C_6D_6, 30 °C): δ 7.68 (m, 4H, P-*Ph ortho*); δ 6.76–7.42 (m, 12H, aromatics); δ 2.02 (d, 3H, P-*Me*), $^2J(^{31}P-^1H)$ = 7.43; δ 1.62 (s, 36H, C*Me*). IR (Nujol): 1922, 1820 cm^{-1} (Ta–H); 1382, 1316 cm^{-1} (Ta–D).

Crystallographic Studies. Crystal data and data collection parameters are contained in Table 8. Further details of the crystallographic study are contained in the supplementary material.

Acknowledgment. We thank the U.S. Department of Energy for financial support of this research.

Supplementary Material Available: Descriptions of experimental procedures and tables of thermal parameters, bond distances and angles, intensity data, torsional angles, and multiplicities for **1**, **2b**, **3c**, **4a**, and **5c** (99 pages). Ordering information is given on any current masthead page.

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