

## Structural Distortions in Six-Coordinate Adducts of Niobium(V) and Tantalum(V)

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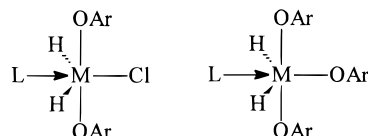
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The mixed chloro-aryloxide compounds  $[M(OC_6H_3Pr^{i-2,6})_2Cl_2]_2$  ( $M = Nb$  (**1a**),  $Ta$  (**1b**); both structurally characterized) and  $[M(OC_6H_3Pr^{i-2,6})_3Cl_2]$  ( $M = Nb$  (**2a**),  $Ta$  (**2b**)) react with pyridine (py) and  $PMe_2Ph$  to produce a series of adducts *cis-mer*- $[MCl_3(OC_6H_3Pr^{i-2,6})_2(L)]$  ( $M, L$ : Nb, py (**3a**);  $Ta$ , py (**3b**); Nb,  $PMe_2Ph$  (**4a**);  $Ta$ ,  $PMe_2Ph$  (**4b**)) and *trans-mer*- $[MCl_2(OC_6H_3Pr^{i-2,6})_3(L)]$  ( $M, L$ : Nb, py (**5**); Nb,  $PMe_2Ph$  (**6a**);  $Ta$ ,  $PMe_2Ph$  (**6b**)). The assigned geometric arrangement of ligands is based upon  $^1H$  NMR studies and single-crystal X-ray diffraction analyses of **3a**, **3b**, **4**, **6a**, and **6b**. The salt complex  $[HPMe_2Ph]^+[mer-NbCl_3(OC_6H_3Pr^{i-2,6})_3]^-$  (**7**) has also been isolated and structurally characterized. The structural parameters for the neutral adducts are compared with those of previously reported hydrido aryloxides of tantalum. A small but consistent distortion away from octahedral geometry involving the bending of mutually *trans* anionic ligands toward the neutral donor group is observed. Theoretical analysis at several levels of theory (RHF, MP2, and DFT) on model compounds  $[Ta(OH)_2(H)_2(PH_3)(X)]$  ( $X = Cl, OH, H$ ) show a distortion involving bending of the *trans*-hydride groups toward the  $PH_3$  ligand for  $X = Cl$  and  $OH$ . This distortion can be accounted for in terms of an improvement in both  $X$  p to metal d  $\pi$ -bonding and  $Ta-H$   $\sigma$ -bonding. The contribution of  $\sigma$ -bonding effects is clearly shown in the case of  $X = H$ , where again a bend of the two hydride ligands toward the  $Ta-P$  bond is calculated. A smaller distortion of the  $Cl$  ligands in *trans-mer*- $[Ta(OH)_3(Cl)_2(PH_3)]$  is also predicted.

## Introduction

The sovereignty of the octahedral geometry in transition metal six-coordination has slowly been undermined. Besides the burgeoning class of trigonal prismatic structures,<sup>1–9</sup> large deformations from octahedral geometry have been observed for distinct categories of complexes containing formally  $d^n$ ,  $n < 6$  electron counts.<sup>10–13</sup> A particularly significant subset of these molecules is those containing a  $d^4$  configuration. Theoretical studies have rationalized the observed deformations in terms

of electronic factors, in particular the  $\pi$ -accepting/donating capacity of the coordinated ligands.<sup>10–14</sup> Recent studies of the six-coordinate dihydride compounds *trans-mer*- $[Ta(H)_2(OC_6H_3Pr^{i-2,6})_3(L)]$  and *trans-trans*- $[TaCl(H)_2(OC_6H_3Bu^{i-2,6})_2(L)]$  have shown an interesting coordination environment about the metal center.<sup>15</sup> Specifically, the two hydride ligands in these  $d^0$  molecules are bent toward the donor ligand  $L$ , a distortion that cannot be justified on steric grounds. The infrared spectra of these compounds confirm the X-ray diffraction data.<sup>15</sup>



As an extension of this work, we report here our investigation of the reaction of the chloride compounds  $[M(OC_6H_3Pr^{i-2,6})_2Cl_2]_2$  and  $[M(OC_6H_3Pr^{i-2,6})_3Cl_2]$  ( $M = Nb, Ta$  with various donor ligands). An evaluation of the solid state structures of the simple pyridine and phosphine adducts has been undertaken to quantitate any significant distortions from octahedral geometry. Theoretical analysis of a number of these systems has also been undertaken in an attempt to identify the underlying electronic principles that account for the observed deformations.

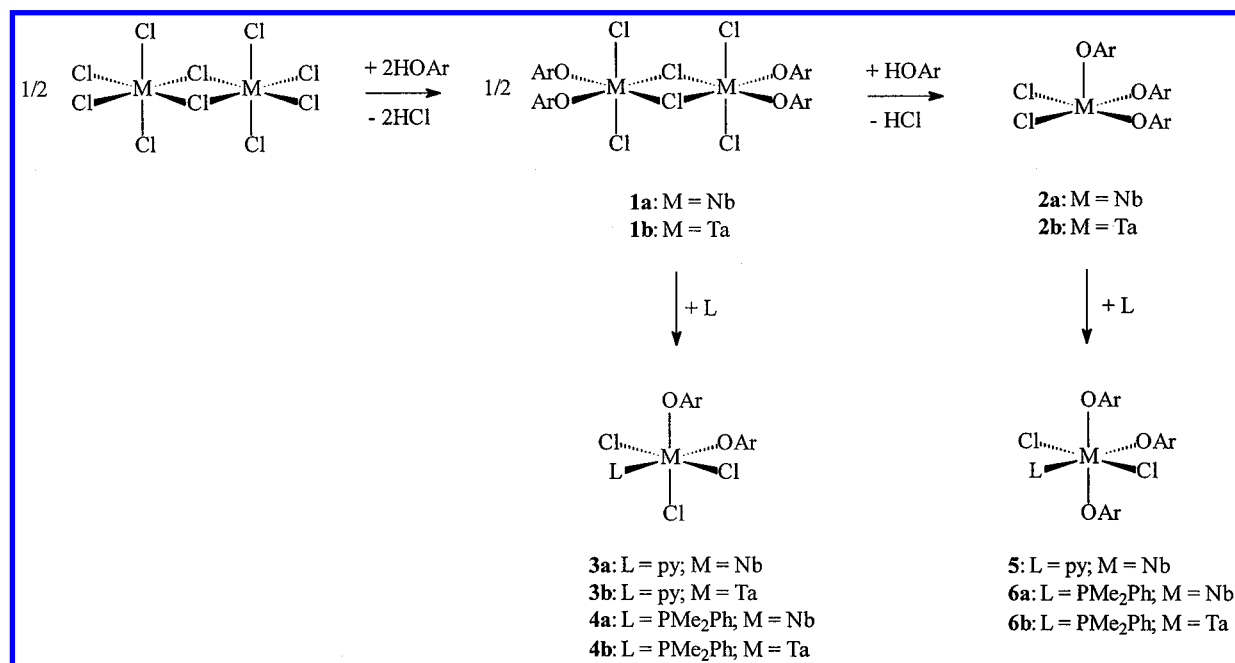
## Results and Discussion

**Synthesis and Spectroscopic Properties of New Compounds.** The mixed chloro aryloxides of Nb(V) and Ta(V) are important starting materials for studying the organometallic

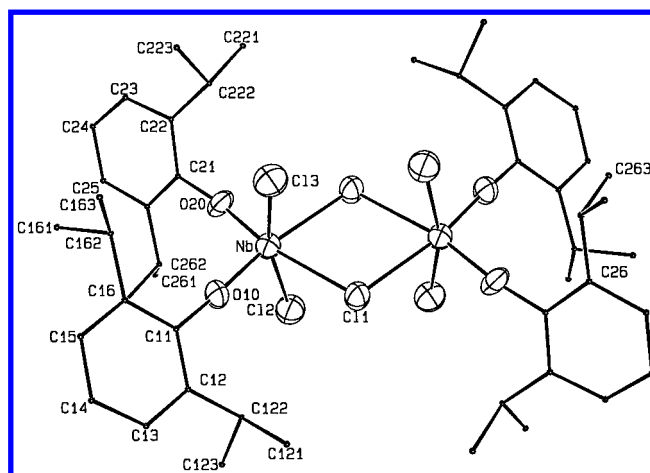
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<sup>§</sup> Université de Paris-Sud. Present address: Laboratoire de Structure et Dynamique des Systèmes Moléculaires et Solides, UMR 5636, Université de Montpellier 2, 34095 Montpellier Cedex 5, France.  
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## Scheme 1



chemistry of these metals.<sup>16,17</sup> The pentachlorides [MCl<sub>5</sub>]<sub>2</sub> (M = Nb, Ta) will react with 2,6-diisopropylphenol (2 equiv) in hydrocarbon solvents to generate the corresponding trichloride compounds [M(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>2</sub>Cl<sub>3</sub>]<sub>2</sub> (M = Nb (**1a**), Ta (**1b**)) (Scheme 1). The solid state structures of the niobium compound (Figure 1, Table 1) and isomorphous tantalum compound (Table 1) show them to adopt a dimeric structure with bridging chloride ligands. The dimerization results in a pseudooctahedral environment about each metal center (Figure 1) with the aryloxy ligands mutually *cis* and *trans* to the two bridging chloride groups. The solid state structure of **1** contrasts with that observed previously for the trichloride compounds [Ta(OC<sub>6</sub>H<sub>3</sub>-



**Figure 1.** Molecular structure of [NbCl<sub>3</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>2</sub>]<sub>2</sub> (**1a**). An identical labeling scheme is adopted for isomorphous **1b**, Table 1.

Bu<sup>i</sup>-2,6)<sub>2</sub>Cl<sub>3</sub>]<sub>2</sub><sup>16b</sup> and [Nb(OC<sub>6</sub>HPh<sub>4</sub>-2,3,5,6)<sub>2</sub>Cl<sub>3</sub>]<sub>2</sub><sup>16a</sup> which were found to be mononuclear in the solid state, adopting a square pyramidal geometry about the metal center with one axial and one equatorial aryloxy ligand. The binuclear structure observed for the diisopropylphenoxide **1a** presumably is a result of the slightly lower steric requirements of this aryloxy ligand compared to the more bulky 2,6-di-*tert*-butylphenoxide and 2,3,5,6-tetraphenylphenoxide ligands. The substitution of a third aryloxy into the coordination sphere of the metal occurs when **1** is refluxed with a further 1 equiv of 2,6-diisopropylphenol in benzene solvent (Scheme 1) to produce [M(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>3</sub>Cl<sub>2</sub>] (M = Nb (**2a**), Ta (**2b**)). Although the exact structure of **2** is unknown, a related compound [Ta(OC<sub>6</sub>H<sub>3</sub>Bu<sup>i</sup><sub>2</sub>-2,6)<sub>3</sub>Cl<sub>2</sub>] has been shown to adopt a square pyramidal structure in the solid state with an axial aryloxy and two mutually *trans* basal aryloxy ligands.<sup>18</sup>

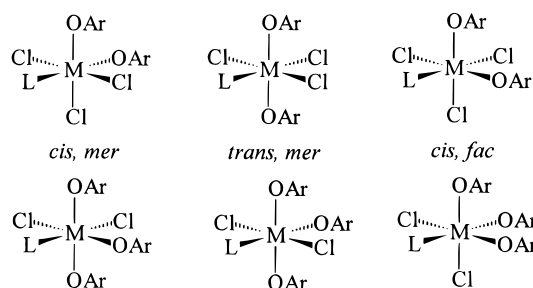
The trichloride compounds **1** react rapidly in hydrocarbon solvents with a variety of oxygen,<sup>19</sup> nitrogen,<sup>19</sup> and phosphorus donor ligands to generate the corresponding adducts. In the case of pyridine (py) and the phosphine ligand PMe<sub>2</sub>Ph, the

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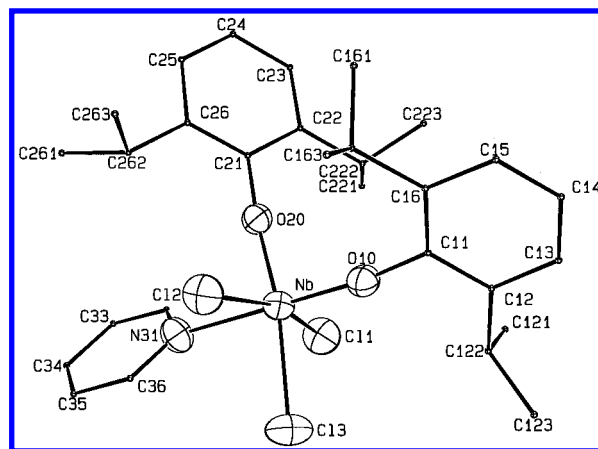
**Table 1.** Selected Bond Distances (Å) and Angles (deg) for  $[\text{MCl}_3(\text{OC}_6\text{H}_3\text{Pr}^i_2\text{-2,6})_2]_2$  (M = Nb (**1a**), Ta (**1b**))

	<b>1a</b>	<b>1b</b>
M—O(10)	1.816(7)	1.815(12)
M—O(20)	1.816(7)	1.791(14)
M—Cl(2)	2.347(3)	2.335(6)
M—Cl(3)	2.359(3)	2.352(6)
M—Cl(1)	2.550(3)	2.533(6)
M—Cl(1)'	2.622(3)	2.613(6)
O(20)—M—O(10)	101.1(3)	101.0(6)
O(20)—M—Cl(2)	97.0(3)	95.1(5)
O(20)—M—Cl(3)	95.7(3)	97.0(5)
O(20)—M—Cl(1)	90.2(3)	90.3(4)
O(20)—M—Cl(1)'	168.6(3)	168.1(4)
O(10)—M—Cl(2)	94.1(3)	93.7(5)
O(10)—M—Cl(3)	91.6(3)	91.7(5)
O(10)—M—Cl(1)	168.6(3)	168.7(4)
O(10)—M—Cl(1)'	90.3(3)	90.9(4)
Cl(2)—M—Cl(3)	164.82(12)	165.6(2)
Cl(2)—M—Cl(1)	86.22(11)	86.4(2)
Cl(2)—M—Cl(1)'	83.26(11)	83.6(2)
Cl(3)—M—Cl(1)	85.43(11)	85.7(2)
Cl(3)—M—Cl(1)'	82.66(11)	82.9(2)
Cl(1)—M—Cl(1)'	78.41(10)	77.8(2)
M—Cl(1)—M	101.59(10)	102.2(2)
MJ—O(10)—C(11)	172.8(8)	173.0(14)
M—O(20)—C(21)	168.6(8)	170.5(16)

**Chart 1.** Possible Isomers of  $[\text{M}(\text{OAr})_2\text{Cl}_3(\text{L})]$  and  $[\text{M}(\text{OAr})_3\text{Cl}_2(\text{L})]$ 

products **3** and **4** (Scheme 1) can be obtained as orange (niobium compounds) or yellow (tantalum compounds) crystalline materials. Spectroscopic (NMR) studies of adducts **3** and **4** show that they adopt a *cis-mer* structure in solution. The  $^1\text{H}$  NMR spectra of the pyridine adducts **3**, show well resolved, sharp signals for the pyridine ligand and two nonequivalent aryloxide groups. Furthermore neither of the aryloxide  $\text{CHMe}_2$  groups is diastereotopic. These data are consistent with a solution structure in which one of the aryloxide ligands is *trans* to the pyridine donor group while the other aryloxide ligand is *cis* and rules out both the *trans-mer* and *cis-fac* isomeric forms for the solution structures of **3**. (See Chart 1.)

The tantalum phosphine adduct **4b** also shows a sharp set of well-resolved ligand signals in the solution  $^1\text{H}$  NMR spectra. Again two nonequivalent aryloxides are observed, indicating that a structure similar to that of the pyridine adduct is present. However, for the niobium compound **4a**, the signals due to the aryloxide ligands are broad at ambient temperatures in the  $^1\text{H}$  NMR spectrum. Upon cooling of the solution (toluene- $d_8$ ), the

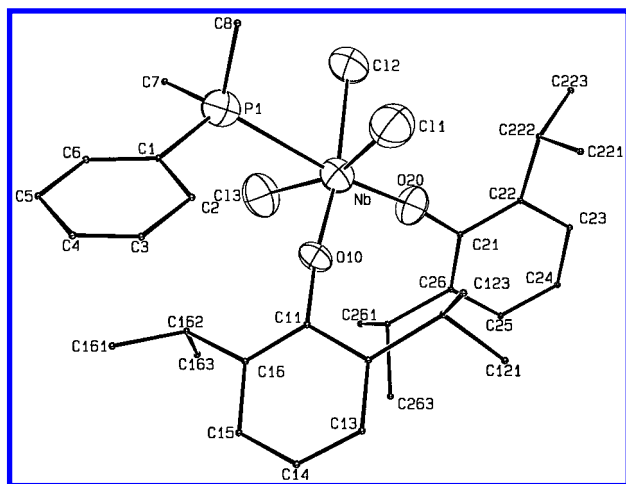
**Figure 2.** Molecular structure of *cis-mer*- $[\text{NbCl}_3(\text{OC}_6\text{H}_3\text{Pr}^i_2\text{-2,6})_2(\text{py})]$  (**3a**). An identical labeling scheme is adopted for isomorphous **3b**, Table 2.**Table 2.** Selected Bond Distances (Å) and Angles (deg) for *cis-mer*- $[\text{MCl}_3(\text{OC}_6\text{H}_3\text{Pr}^i_2\text{-2,6})_2(\text{py})]$  (M = Nb (**3a**), Ta (**3b**))

	<b>3a</b>	<b>3b</b>
M—O(10)	1.832(3)	1.841(4)
M—O(20)	1.852(3)	1.848(5)
M—Cl(1)	2.379(1)	2.370(2)
M—Cl(2)	2.373(1)	2.366(2)
M—Cl(3)	2.403(1)	2.399(2)
M—N(31)	2.331(4)	2.315(6)
Cl(1)—M—Cl(2)	164.34(5)	164.90(7)
Cl(1)—M—Cl(3)	85.95(5)	86.03(8)
Cl(1)—M—O(10)	97.1(1)	97.1(2)
Cl(1)—M—O(20)	92.9(1)	92.6(2)
Cl(1)—M—N(31)	82.8(1)	82.8(2)
Cl(2)—M—Cl(3)	85.96(5)	86.12(8)
Cl(2)—M—O(10)	96.9(1)	96.3(2)
Cl(2)—M—O(20)	92.9(1)	93.1(2)
Cl(2)—M—N(31)	83.3(1)	83.8(2)
Cl(3)—M—O(10)	94.2(1)	94.3(2)
Cl(3)—M—O(20)	170.4(1)	170.6(2)
Cl(3)—M—N(31)	86.1(1)	86.1(2)
O(10)—M—O(20)	95.4(1)	95.0(2)
O(10)—M—N(31)	179.6(1)	179.6(2)
O(20)—M—N(31)	84.3(1)	84.6(2)
M—O(10)—C(11)	173.0(3)	173.8(5)
M—O(20)—C(21)	174.8(3)	174.0(5)

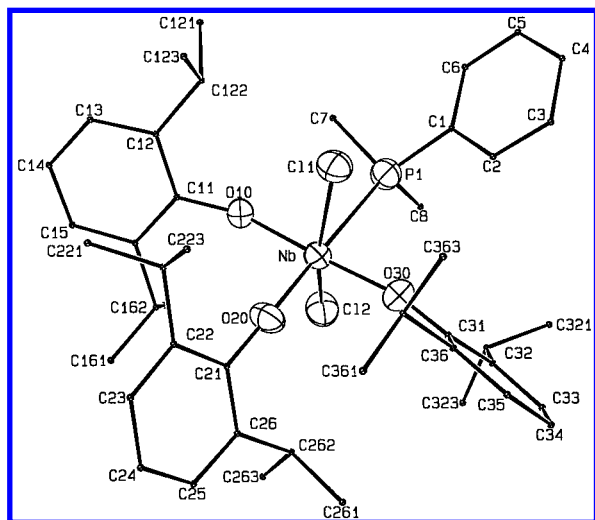
spectra become sharp, and at  $-20^\circ\text{C}$ , well-resolved signals are obtained for the aryloxide and phosphine ligands very similar to those observed for the tantalum analog. This result indicates that, in the case of the niobium phosphine adduct, stereochemical nonrigidity is present, allowing exchange of the nonequivalent aryloxide ligands. Furthermore, it can be shown by  $^{31}\text{P}$  NMR that rapid exchange of coordinated and free phosphine occurs at  $30^\circ\text{C}$  for solutions of compound **3a** to which has been added  $\text{PMe}_2\text{Ph}$ . Single-crystal X-ray diffraction analyses of the isomorphous pyridine adducts **3a** and **3b** (Figure 2, Table 2) and the niobium—phosphine adduct **4a** (Figure 3, Table 3) have been carried out and confirm that the *cis-mer* arrangement of ligands inferred from solution spectroscopic studies is present in the solid state. These structures are discussed in more detail below.

The addition of pyridine or  $\text{PMe}_2\text{Ph}$  to hydrocarbon solutions of the dichlorides **2** also leads to the formation of 1:1 adducts (Scheme 1).<sup>19</sup> These compounds are formulated as *trans-mer*- $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i_2\text{-2,6})_3\text{Cl}_2(\text{py})]$  **5** and *trans-mer*- $[\text{M}(\text{OC}_6\text{H}_3\text{Pr}^i_2\text{-2,6})_3\text{Cl}_2(\text{PMe}_2\text{Ph})]$  (M = Nb (**6a**), Ta (**6b**)) on the basis of their  $^1\text{H}$  NMR spectra and X-ray diffraction studies (Figure 4, Table 4). In the case of the pyridine complex **5** and the tantalum complex **6b**, two sharp sets of nondiastereotopic aryloxide

(19) A series of diethyl ether complexes of tantalum were reported by Wigley et al. (see refs 17a–c), e.g. *cis-mer*- $[\text{TaCl}_3(\text{OAr})_2(\text{OEt}_2)]$  and *trans-mer*- $[\text{TaCl}_2(\text{OAr})_3(\text{OEt}_2)]$  (OAr = 2,6-dimethyl- and 2,6-diisopropylphenoxide). A series of quinoline (quin) complexes *cis-mer*- $[\text{TaCl}_3(\text{OC}_6\text{H}_3\text{Pr}^i_2\text{-2,6})_2(\text{quin})]$  and *trans-mer*- $[\text{TaCl}_2(\text{OC}_6\text{H}_3\text{Pr}^i_2\text{-2,6})_3(\text{quin})]$  were also reported by Wigley et al. (see refs 17d,f). A number of tetrahydrofuran complexes of mixed chloro aryloxides of niobium were structurally characterized by Nakamura et al.: (a) Kanehisa, N.; Kai, N.; Yasuda, H.; Nakayama, Y.; Takei, K.; Nakamura, A. *Chem. Lett.* **1990**, 2167. (b) Yasuda, H.; Nakayama, Y.; Takei, K.; Nakamura, A.; Kai, N.; Kanehisa, N. *J. Organomet. Chem.* **1994**, 473, 105.



**Figure 3.** Molecular structure of *cis-mer*-[NbCl<sub>3</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>2</sub>(PMe<sub>2</sub>-Ph)] (**4a**).



**Figure 4.** Molecular structure of *trans-mer*-[NbCl<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>3</sub>(PMe<sub>2</sub>-Ph)] (**6a**). An identical labeling scheme is adopted for isomorphous **6b**, Table 4.

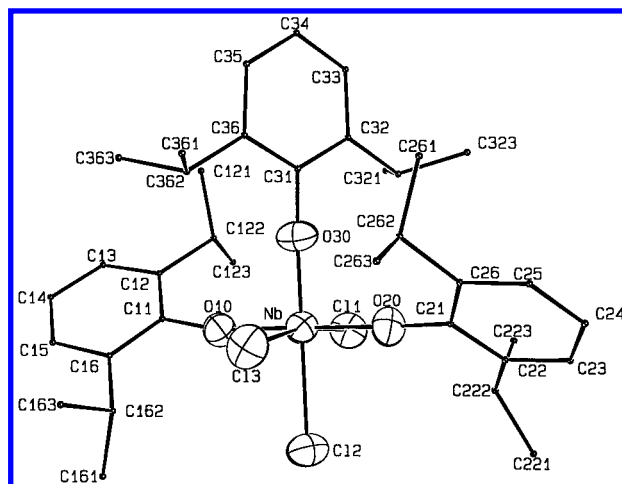
**Table 3.** Selected Bond Distances (Å) and Angles (deg) for *cis-mer*-[NbCl<sub>3</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>2</sub>(PMe<sub>2</sub>-Ph)] (**4a**)

Nb—O(10)	1.83(2)	Nb—Cl(2)	2.425(7)
Nb—O(20)	1.82(2)	Nb—Cl(3)	2.374(7)
Nb—Cl(1)	2.366(8)	Nb—P(1)	2.742(8)
Cl(1)—Nb—Cl(2)	86.2(3)	Cl(3)—Nb—O(10)	92.4(6)
Cl(1)—Nb—Cl(3)	161.5(3)	Cl(3)—Nb—O(20)	98.5(6)
Cl(1)—Nb—O(10)	92.7(6)	Cl(3)—Nb—P(1)	81.6(2)
Cl(1)—Nb—O(20)	98.5(6)	O(10)—Nb—O(20)	96.6(7)
Cl(1)—Nb—P(1)	80.5(3)	O(10)—Nb—P(1)	91.6(5)
Cl(2)—Nb—Cl(3)	86.1(3)	O(20)—Nb—P(1)	171.8(6)
Cl(2)—Nb—O(10)	171.3(5)	Nb—O(10)—C(11)	172.6(16)
Cl(2)—Nb—O(20)	92.0(6)	Nb—O(20)—C(21)	172.0(19)
Cl(2)—Nb—P(1)	79.8(3)		

CHMe<sub>2</sub> resonances in the ratio of 2:1 are present in the <sup>1</sup>H NMR spectrum. In contrast, the corresponding resonances for **6a** are broad, implying that, as with **4a** above, exchange of nonequivalent aryloxy ligands can occur on the NMR time scale possibly via phosphine dissociation.

During studies of the reaction of the niobium trichloride [Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>2</sub>Cl<sub>3</sub>]<sub>2</sub> (**1a**) with PMe<sub>2</sub>Ph, a few crystals of a new product were isolated and identified by X-ray diffraction as the salt complex *mer*-[HPMe<sub>2</sub>Ph]<sup>+</sup>[Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>3</sub>Cl<sub>3</sub>]<sup>−</sup> (**7**) (Figure 5, Table 5).

**Solid State Structures.** The M—O (aryloxy) and M—Cl distances as well as the M—O—C (aryloxy) angles in the



**Figure 5.** Molecular structure of *mer*-[HPMe<sub>2</sub>Ph]<sup>+</sup>[NbCl<sub>3</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>3</sub>]<sup>−</sup> (**7**).

**Table 4.** Selected Bond Distances (Å) and Angles (deg) for *trans-mer*-[MCl<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>3</sub>(PMe<sub>2</sub>-Ph)] (M = Nb (**6a**), Ta (**6b**))

	<b>6a</b>	<b>6b</b>
M—O(10)	1.913(2)	1.913(2)
M—O(20)	1.868(2)	1.863(2)
M—O(30)	1.894(2)	1.897(2)
M—Cl(1)	2.3823(9)	2.3713(8)
M—Cl(2)	2.3792(9)	2.3690(8)
M—P(1)	2.7666(9)	2.7574(9)
Cl(1)—M—Cl(2)	158.74(3)	159.87(3)
Cl(1)—M—O(10)	88.63(6)	88.50(7)
Cl(1)—M—O(20)	102.53(7)	101.86(7)
Cl(1)—M—O(30)	89.17(7)	89.15(7)
Cl(1)—M—P(1)	81.00(3)	81.61(3)
Cl(2)—M—O(10)	89.92(7)	89.93(6)
Cl(2)—M—O(20)	98.70(7)	98.24(7)
Cl(2)—M—O(30)	91.60(7)	91.51(6)
Cl(2)—M—P(1)	77.76(3)	78.28(3)
O(10)—M—O(20)	90.83(9)	91.43(10)
O(10)—M—O(30)	177.36(9)	176.77(10)
O(10)—M—P(1)	88.89(6)	88.26(7)
O(20)—M—O(30)	91.07(9)	91.22(10)
O(20)—M—P(1)	89.32(7)	89.20(7)
O(30)—M—P(1)	89.32(7)	89.20(7)
M—O(10)—C(11)	159.9(2)	158.9(2)
M—O(20)—C(21)	175.8(2)	175.7(2)
M—O(30)—C(31)	165.5(2)	164.9(2)

**Table 5.** Selected Bond Distances (Å) and Angles (deg) for *mer*-[HPMe<sub>2</sub>Ph]<sup>+</sup>[NbCl<sub>3</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>3</sub>]<sup>−</sup> (**7**)

Nb—O(10)	1.884(3)	Nb—Cl(1)	2.407(1)
Nb—O(20)	1.914(3)	Nb—Cl(2)	2.492(1)
Nb—O(30)	1.865(3)	Nb—Cl(3)	2.440(1)
Cl(1)—Nb—Cl(2)	85.61(4)	Cl(3)—Nb—O(10)	90.03(9)
Cl(1)—Nb—Cl(3)	169.84(4)	Cl(3)—Nb—O(20)	89.42(9)
Cl(1)—Nb—O(10)	89.55(9)	Cl(3)—Nb—O(30)	94.4(1)
Cl(1)—Nb—O(20)	90.86(9)	O(10)—Nb—O(20)	179.0(1)
Cl(1)—Nb—O(30)	95.8(1)	O(10)—Nb—O(30)	90.7(1)
Cl(2)—Nb—Cl(3)	84.24(4)	O(20)—Nb—O(30)	90.2(1)
Cl(2)—Nb—O(10)	90.02(9)	Nb—O(10)—C(11)	168.2(3)
Cl(2)—Nb—O(20)	89.14(9)	Nb—O(20)—C(21)	174.8(3)
Cl(2)—Nb—O(30)	178.4(1)	Nb—O(30)—C(31)	176.7(3)

compounds obtained in this study are comparable to those found in other aryloxy and chloride derivatives of Nb(V) and Ta(V).<sup>16m</sup> It is interesting to note that the tantalum—ligand distances are consistently shorter than the corresponding niobium—ligand distances in the isomorphous pairs of compounds **1** and **3** (Tables 1 and 2) although the differences are within 3σ of the experimental errors. There are presently far fewer structurally characterized pyridine and related N-heterocyclic donor ligand complexes of Nb and Ta than phosphine com-

**Table 6.** Selected Structural Parameters for Six-Coordinate Derivatives of Nb and Ta

species	L–M–X( <i>trans</i> ), deg	L–M–X( <i>cis</i> ), deg	$\Sigma\alpha$ , deg	ref
[NbCl <sub>5</sub> (NCH)]	178.52(7)	82.06(5), 83.49(5), 82.06(5), 83.49(5)	–28.9	29
[NbCl <sub>5</sub> (PMe <sub>2</sub> Ph)] <sup>–</sup>	178.1(2)	83.5(3), 85.5(3), 87.4(4), 88.0(4)	–15.5	30
<i>trans</i> -[TaCl <sub>4</sub> {OSi(C <sub>6</sub> H <sub>4</sub> Me-2,6)}(OEt <sub>2</sub> )]	177.5(1)	83.7(1), 84.2(1), 84.7(1), 86.8(1)	–20.6	31
<i>trans</i> -[NbCl <sub>4</sub> (OC <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> -2,6)(THF)]	180.0	84.9(1), 84.9(1), 84.9(1), 84.9(1)	–19.4	19
<i>cis-mer</i> -[NbCl <sub>3</sub> (OC <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> -2,6) <sub>2</sub> (THF)]	177.4(3)	84.5(2), 84.7(2), 85.0(2), 86.3(2)	–19.4	19
<i>cis-mer</i> -[NbCl <sub>3</sub> (OC <sub>6</sub> H <sub>3</sub> Ph <sub>2</sub> -2,6) <sub>2</sub> (THF)]	172.0(2)	83.0(2), 88.1(1),	–19.4	19
<i>cis-mer</i> -[NbCl <sub>3</sub> (OC <sub>6</sub> H <sub>3</sub> Pr <sub>2</sub> -2,6) <sub>2</sub> (py)] ( <b>3a</b> )	179.6(1)	82.8(1), 83.3(1), 84.3(1), 86.1(1)	–23.5	<i>a</i>
<i>cis-mer</i> -[TaCl <sub>3</sub> (OC <sub>6</sub> H <sub>3</sub> Pr <sub>2</sub> -2,6) <sub>2</sub> (py)] ( <b>3b</b> )	179.6(2)	82.8(2), 83.8(2), 84.6(2), 86.1(2)	–22.6	<i>a</i>
<i>cis-mer</i> -[NbCl <sub>3</sub> (OC <sub>6</sub> H <sub>3</sub> Pr <sub>2</sub> -2,6) <sub>2</sub> (PMe <sub>2</sub> Ph)] ( <b>4a</b> )	171.8(6)	79.8(3), 80.5(3), 81.6(2), 91.6(5)	–26.4	<i>a</i>
<i>cis-mer</i> -[TaCl <sub>3</sub> (NMe <sub>2</sub> ) <sub>2</sub> (HNMe <sub>2</sub> )]	169.3(2)	78.5(1), 79.2(2), 89.6(1), 91.0(2)	–21.6	32
<i>trans-trans</i> -[TaCl(H) <sub>2</sub> (OC <sub>6</sub> H <sub>3</sub> Bu <sub>2</sub> -2,6) <sub>2</sub> (PMePh <sub>2</sub> )]	174.96(5)	56(2), 62(2), 92.7(1), 94.6(1)	–54.7	15
<i>trans-mer</i> -[NbCl <sub>2</sub> (OC <sub>6</sub> H <sub>3</sub> Pr <sub>2</sub> -2,6) <sub>3</sub> (PMe <sub>2</sub> Ph)] ( <b>6a</b> )	176.45(7)	77.76(3), 81.00(3), 88.89(6), 89.32(7)	–23.0	<i>a</i>
<i>trans-mer</i> -[TaCl <sub>2</sub> (OC <sub>6</sub> H <sub>3</sub> Pr <sub>2</sub> -2,6) <sub>3</sub> (PMe <sub>2</sub> Ph)] ( <b>6b</b> )	176.51(7)	78.28(3), 81.61(3), 88.26(7), 89.20(7)	–22.7	<i>a</i>
<i>trans-mer</i> -[Ta(H) <sub>2</sub> (OC <sub>6</sub> H <sub>3</sub> Pr <sub>2</sub> -2,6) <sub>3</sub> (PMe <sub>2</sub> Ph)]	174.5(1)	69(1), 66(2), 89.3(1), 85.4(1)	–50.3	15
<i>mer</i> -[NbCl <sub>3</sub> (OC <sub>6</sub> H <sub>3</sub> Pr <sub>2</sub> -2,6) <sub>3</sub> ] <sup>–</sup> <b>7</b>	178.4(1)	84.24(4), 85.61(4), 89.14(9), 90.02(9)	–11.0	<i>a</i>

<sup>a</sup> This work.

plexes. The M–N(py) distances of 2.331(4) and 2.315(6) Å in **3a** and **3b** can be compared with values of 2.291(21) Å in [TaCl<sub>2</sub>Me<sub>3</sub>(bipy)],<sup>20</sup> 2.420(12) Å in [NbBr<sub>4</sub>(CF<sub>3</sub>CCCF<sub>3</sub>)(py)]<sup>–</sup>,<sup>21</sup> 2.479(4) Å in [Nb(NBu)<sub>4</sub>Cl<sub>4</sub>(py)]<sup>–</sup>,<sup>22</sup> 2.28(2) Å in [Ta{C(Me)C(Me)CHCMe<sub>3</sub>}OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>3</sub>(py)],<sup>23</sup> 2.348(6) and 2.408(6) Å in [Ta(NAr)(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)Cl<sub>2</sub>(py)<sub>2</sub>],<sup>24</sup> and 2.316(14) and 2.324(15) Å in [Ta(NSiBu<sub>3</sub>)<sub>2</sub>Me(py)<sub>2</sub>].<sup>25</sup> The Nb–P distances of 2.742(8) and 2.7666(9) Å in **4a** and **6** are among the longest niobium–phosphine distances so far reported. They are only slightly shorter than one of the Nb–P distances of 2.787(1) Å in [CpNbCl<sub>3</sub>(dppe)]<sup>26</sup> and compare with values of 2.74–2.75 Å found in a series of phosphine adducts of niobium cluster compounds.<sup>27,28</sup> The adducts **3a**, **3b**, **4a**, **6a**, and **6b** (Figures 2–4) structurally characterized in this study are examples of a class of six-coordinate derivatives of Nb and Ta of general formula [MX<sub>5</sub>L] where X represents either a single type of monoanionic ligand or a set of monoanionic ligands, e.g. halide, hydride, alkoxide, aryloxy, siloxide, amide groups, etc. The previously characterized six-coordinate hydride compounds *trans-mer*-[Ta(H)<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>3</sub>(PMe<sub>2</sub>Ph)] and *trans-trans*-[TaCl(H)<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>Bu<sub>2</sub>-2,6)<sub>2</sub>(PMePh<sub>2</sub>)] are highly distorted in the solid state with acute H–Ta–P angles of 56(2)–69(1)°. In Table 6 are collected the L–M–X angles (*cis* and *trans*) for these compounds along with the corresponding parameters for the new molecules obtained in this study and certain related Nb and Ta derivatives in the literature.<sup>15,19,10–32</sup> It can be seen that there is a consistent distortion in which some or all of the *cis* groups are bent toward the donor ligand. This is clearly evident in the simple formonitrile complex [NbCl<sub>5</sub>(NCH)]<sup>29</sup> (all

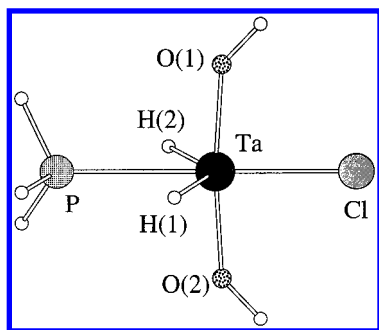
ligands being sterically very innocent) where all four *cis*-chloride groups form angles of 82–83° with the nitrile ligand (Table 6). The resulting structure can hence be best described as a square pyramidal arrangement of chloride groups to which a nitrile group is bound axially. Similar, but less pronounced distortions are evident in the d<sup>1</sup> anion [NbCl<sub>5</sub>(PMe<sub>2</sub>Ph)]<sup>–</sup> and the monosiloxide *trans*-[TaCl<sub>4</sub>{OSi(C<sub>6</sub>H<sub>4</sub>Me-2,6)}(OEt<sub>2</sub>)]<sup>31</sup> (Table 6). The pyridine adducts *cis-mer*-[MCl<sub>3</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>2</sub>(py)] (M = Nb (**3a**), Ta (**3b**)) obtained in this study and the 2,6-dimethylphenoxide complex *cis-mer*-[NbCl<sub>3</sub>(OC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)<sub>2</sub>(THF)]<sup>19</sup> possess solid state structures in which the three chloride ligands and one aryloxy oxygen atom are bent toward the neutral donor group. In the related complex *cis-mer*-[NbCl<sub>3</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>2</sub>(PMe<sub>2</sub>Ph)] (**4a**), all three chloride ligands form angles of 80–82° with the *cis*-phosphine ligand while the angle formed with the aryloxy group is 91.6(5)°. In *trans-mer*-[MCl<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>3</sub>(PMe<sub>2</sub>Ph)] (**6**), the two *trans*-chloride ligands are distinctly bent toward the PMe<sub>2</sub>Ph group although not as dramatically as the hydride groups in *trans-mer*-[Ta(H)<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)<sub>3</sub>(PMe<sub>2</sub>Ph)] or *trans-trans*-[TaCl(H)<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>Bu<sub>2</sub>-2,6)<sub>2</sub>(PMePh<sub>2</sub>)] (Table 6).

In order to more readily quantitate this specific distortion from octahedral geometry we introduce the parameter  $\Sigma\alpha$  defined as follows:  $\Sigma\alpha = \sum[(\text{cis-L-M-X}) - 90]$  (Table 6). All of the group 5 metal derivatives can be seen to have negative values of  $\Sigma\alpha$  (as defined), consistent with the bending of these groups toward the donor ligand. We have also evaluated this parameter for all of the species [MCl<sub>5</sub>(L)]<sup>*n*–</sup> contained in the Cambridge Crystallographic Database (Table 7).<sup>33–49</sup> A definite trend is evident, with the value of  $\Sigma\alpha$  becoming less negative as the

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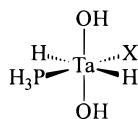
**Figure 6.** Optimized structure (DFT/B3LYP) in  $C_s$  symmetry for  $[\text{Ta}(\text{OH})_2(\text{H})_2(\text{PH}_3)(\text{Cl})]$ . Distances and angles are contained in Table 8.

**Table 7**

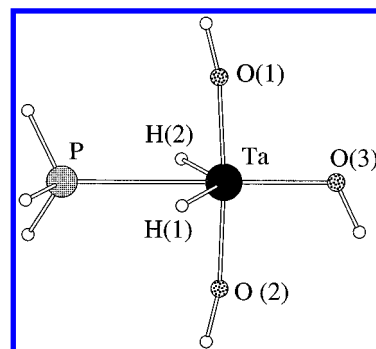
compd/anion	$d^n$	$\text{cis-L-M-Cl, deg}$	$\Sigma\alpha, \text{deg}$	ref
$[\text{NbCl}_5(\text{NCH})]$	$d^0$	82.0, 82.0, 83.5, 83.5	-29.0	29
$[\text{TiCl}_5(\text{THF})]^-$	$d^0$	85.1, 85.2, 85.8, 86.5	-17.4	33
$[\text{ZrCl}_5(\text{THF})]^-$	$d^0$	84.0, 85.4, 86.0, 88.4	-16.2	34
$[\text{ZrCl}_5(\text{THF})]^-$	$d^0$	84.3, 85.3, 85.8, 88.8	-15.8	35
$[\text{HfCl}_5(\text{THF})]^-$	$d^0$	86.1, 86.1, 86.2, 87.7	-13.9	36
$[\text{NbCl}_5(\text{PMe}_2\text{Ph})]^-$	$d^1$	83.5, 85.5, 87.3, 88.0	-15.7	31
$[\text{MoCl}_5(\text{OH}_2)]^{2-}$	$d^3$	86.2, 87.6, 87.6, 92.9	-5.7	37
$[\text{ReCl}_5(\text{OH}_2)]^-$	$d^3$	87.5, 87.5, 88.5, 88.5	-8.0	38
$[\text{ReCl}_5(\text{NCMe})]^-$	$d^3$	86.3, 87.1, 87.7, 89.4	-9.5	39
$[\text{ReCl}_5(\text{PEt}_3)]^-$	$d^3$	87.8, 87.8, 98.9, 89.9	-4.6	40
$[\text{TaCl}_5(\text{PEt}_3)]^-$	$d^3$	85.9, 86.8, 89.8, 90.1	-7.4	41
$[\text{TaCl}_5(\text{PPh}_3)]^-$	$d^3$	85.3, 87.8, 90.3, 91.3	-5.3	42
$[\text{FeCl}_5(\text{OH}_2)]^{2-}$	$d^5$	85.7, 86.3, 86.6, 90.2	-11.2	43
$[\text{RuCl}_5(\text{imidazole})]^{2-}$	$d^5$	89.7, 89.7, 90.0, 90.0	-0.6	44
$[\text{IrCl}_5(\text{pyrazine})]^{2-}$	$d^6$	89.8, 89.8, 90.0, 91.3	+0.9	45
$[\text{PtCl}_5(\text{OH}_2)]^-$	$d^6$	88.0, 88.0, 91.6, 91.6	-0.8	46
$[\text{PtCl}_5(\text{NH}_3)]^-$	$d^6$	87.3, 88.1, 89.2, 89.5	-5.9	47
$[\text{PtCl}_5(\text{py})]^-$	$d^6$	88.1, 89.6, 90.4, 90.8	-1.1	48
$[\text{PtCl}_5(\text{PEt}_3)]^-$	$d^6$	89.7, 90.3, 90.7, 93.4	+4.1	49

number of electrons in the formally nonbonding orbitals ( $t_{2g}$  in  $O_h$  symmetry) increases.

**Theoretical Analysis and Discussion.** Calculations were carried out on the model compounds  $[\text{Ta}(\text{OH})_2(\text{H})_2(\text{PH}_3)(\text{X})]$  ( $\text{X} = \text{OH}, \text{Cl}$ ) in which the two hydroxides and hydrides are maintained in a mutually transoid geometry. The OH groups (called axial in the following discussion) were maintained in the plane containing Ta, P, and X.



The calculated structures (Figures 6 and 7) are in excellent agreement with the experimental structures (Table 8). The notable feature is the strong deviation from the octahedral geometry with a P-Ta-H angle of around  $60^\circ$ . The Ta-ligand bond lengths are well reproduced in the theoretical structures with the exception of the Ta-P bond, which is too long (Table 8). This discrepancy is often observed in the calculation of phosphine complexes and does not bear any influence on the other properties of the molecules. The Ta-H bond lengths of 1.76–1.79 Å are well within the average expected values. The significant shortening of one of the Ta-H bond observed in the X-ray structure of  $[\text{Ta}(\text{OC}_6\text{H}_3\text{Bu}^t_2\text{-2,6})_2\text{Cl}(\text{H})_2(\text{PMePh}_2)]^{15}$



**Figure 7.** Optimized structure (DFT/B3LYP) in  $C_s$  symmetry for  $[\text{Ta}(\text{OH})_3(\text{H})_2(\text{PH}_3)]$ . Distances and angles are contained in Table 8.

is not reproduced by the calculations and is undoubtedly a consequence of the X-ray diffraction technique. The calculated bond angles are also in excellent agreement with the solid state structures. The predicted Ta-O-H angles at the axial hydroxides (aryloxides) are as large as those found in the experimental structures, but the Ta-O-H angle at the equatorial O in  $[\text{Ta}(\text{OH})_2(\text{H})_2(\text{PH}_3)(\text{OH})]$  is too small. Since the angle at O must be due to a combination of electronic ( $\pi$  bonds between Ta and O) and steric factors which are not properly incorporated here, one should consider these results with caution.

Since the structure adopted by several electron-deficient species has often been attributed to the presence of  $\pi$ -donor ligands,<sup>14</sup> it was of special interest to calculate the structure of  $[\text{Ta}(\text{OH})_2(\text{H})_2(\text{PH}_3)(\text{H})]$  for a better understanding of the results. The structure was found to be essentially identical to that obtained for  $\text{X} = \text{Cl}$  or  $\text{OH}$  (Table 8). This demonstrates without ambiguity that the presence of a  $\pi$  donor at the X site is not the dominant factor which makes this present structure favorable.

The structures of  $d^0$  complexes have been the subject of numerous controversies. While  $d^6$  saturated hexacoordinated complexes have a structure which is essentially octahedral, this is far from being the case with lesser electrons in the d shell. Disregarding the case of closed-shell  $d^2$  or  $d^4$  complexes, where distortions away from octahedral usually occur<sup>10–13</sup> in part because of the necessity for opening a HOMO–LUMO gap, the case of  $d^0$   $\text{ML}_6$  complexes is considerably more fascinating. In an octahedral geometry, the HOMO–LUMO gap is already significant since it is associated with the energy gap between the occupied M–L  $\sigma$  bond and the empty “ $t_{2g}$ ” orbitals of the metal. The gap depends on the nature of the complex, and one can foresee that second-order Jahn–Teller distortion may occur for specific cases leading to nonoctahedral complexes. The requirement for such distortion is that the energy gap be small in the octahedral geometry. This means that the energy of the M–L  $\sigma$  bonds must be high and/or the energy of the  $t_{2g}$  orbitals must be low and calls for ligands which are bound to the metal by atoms which are not too electronegative. It also calls for ligands which have no  $\pi$ -donor orbitals, since this would raise the energy of the  $t_{2g}$  set. The ideal case is thus  $\text{WMe}_6$ .<sup>1d</sup> It was proposed several years ago that the model  $d^0$   $\text{MH}_6$  complex could have a  $C_{3v}$  geometry with nonequivalent triangular faces within a trigonal prismatic structure.<sup>3,4</sup> Electron diffraction measurements<sup>1c</sup> on  $[\text{WMe}_6]$  followed by more recent ab initio calculations on  $[\text{CrH}_6]$ ,<sup>5</sup>  $[\text{WH}_6]$ ,<sup>6</sup> and  $[\text{WMe}_6]$ <sup>7–9</sup> agreed with the earlier predictions. Very recently, an X-ray determination of  $[\text{WMe}_6]$  (as well as  $[\text{ReMe}_6]$ )<sup>1a</sup> gave a definitive answer to the structure of this complex.

It is of interest to return briefly to the origin of the distortion in  $\text{WMe}_6$ , since a similar argument will be used for the tantalum

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**Table 8.** Comparison of Optimized Theoretical and Experimental<sup>15</sup> Bond Distances (Å) and Angles (deg)

	[Ta(OH) <sub>2</sub> (H) <sub>2</sub> (PH <sub>3</sub> )(Cl)]	[Ta(OAr) <sub>2</sub> (H) <sub>2</sub> (PMePh <sub>2</sub> )(Cl)]		[Ta(OH) <sub>3</sub> (H) <sub>2</sub> (PH <sub>3</sub> )]	[Ta(OAr) <sub>3</sub> (H) <sub>2</sub> (PMe <sub>2</sub> Ph)]
Ta—Cl	2.42	2.397(1)	Ta—O(3)	1.95	1.912(4)
Ta—O	1.91	1.896(3), 1.888(3)	Ta—O(1)	1.90	1.897(3), 1.907(3)
Ta—P	2.72	2.655(1)	Ta—P	2.82	2.650(1)
Ta—H	1.76, 1.77	1.73(5), 1.54(5)	Ta—H	1.78, 1.79	1.74(4), 1.83(6)
P—Ta—H	66.1, 63.4	56(2), 62(2)	P—Ta—H	64.8, 66.6	66(2), 69(1)
Cl—Ta—O	86.7	86.5(1), 86.5(1)	O(3)—Ta—O(2)	92.3	92.0(2), 93.6(2)
Ta—O—H	140.6	160.8(1)	Ta—O(1)—H	168.7	160.7(3), 169.5(4)
			Ta—O(3)—H	114.3	153.6(3)

**Table 9.** Crystal Data and Data Collection Parameters

	1a	1b	3a	3b
formula	Nb <sub>2</sub> Cl <sub>6</sub> O <sub>4</sub> C <sub>48</sub> H <sub>68</sub>	Ta <sub>2</sub> Cl <sub>6</sub> O <sub>4</sub> C <sub>48</sub> H <sub>68</sub>	NbCl <sub>3</sub> O <sub>2</sub> NC <sub>29</sub> H <sub>39</sub>	TaCl <sub>3</sub> O <sub>2</sub> NC <sub>29</sub> H <sub>39</sub>
fw	1107.60	1283.68	632.90	720.95
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)
<i>a</i> , Å	12.735(2)	12.757(6)	11.622(2)	11.648(2)
<i>b</i> , Å	15.527(3)	12.757(6)	13.283(5)	13.273(3)
<i>c</i> , Å	13.620(2)	13.625(9)	20.666(7)	20.624(6)
α, deg	90	90	90	90
β, deg	90.607(14)	90.83(6)	90	90
γ, deg	90	90	90	90
<i>V</i> , Å <sup>3</sup>	2693.0(14)	2703(5)	3190(3)	3188(2)
<i>Z</i>	2	2	4	4
ρ <sub>calc</sub> , g cm <sup>-3</sup>	1.366	1.577	1.318	1.502
temp, K	295	297	293	293
radiation (λ, Å)	Cu Kα (1.541 84)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
<i>R</i>	0.062	0.072	0.031	0.029
<i>R</i> <sub>w</sub>	0.121	0.160	0.036	0.036

	4	6a	6b	7·C <sub>6</sub> H <sub>6</sub>
formula	NbCl <sub>3</sub> PO <sub>2</sub> C <sub>32</sub> H <sub>45</sub>	NbCl <sub>3</sub> PO <sub>3</sub> C <sub>44</sub> H <sub>62</sub>	TaCl <sub>2</sub> PO <sub>3</sub> C <sub>44</sub> H <sub>62</sub>	NbCl <sub>3</sub> PO <sub>3</sub> C <sub>50</sub> H <sub>69</sub>
fw	691.95	833.77	921.81	948.34
space group	<i>Pna</i> 2 <sub>1</sub> (No. 33)	<i>P</i> 1 (No. 2)	<i>P</i> 1 (No. 2)	<i>P</i> 1 (No. 2)
<i>a</i> , Å	19.153(4)	13.1862(9)	13.1685(15)	10.505(2)
<i>b</i> , Å	17.372(5)	13.3274(12)	13.337(2)	12.967(4)
<i>c</i> , Å	10.461(8)	13.4391(16)	13.4210(16)	19.289(3)
α, deg	90	85.553(9)	85.553(12)	83.17(2)
β, deg	90	73.433(9)	73.584(10)	89.35(1)
γ, deg	90	89.794(7)	89.735(12)	89.20(2)
<i>V</i> , Å <sup>3</sup>	3480(4)	2256.5(5)	2253.8(7)	2608(2)
<i>Z</i>	4	2	2	2
ρ <sub>calc</sub> , g cm <sup>-3</sup>	1.320	1.227	1.357	1.207
temp, K	297	296	295	295
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
<i>R</i>	0.062	0.039	0.036	0.046
<i>R</i> <sub>w</sub>	0.114	0.086	0.028	0.052

complexes in this study. In pure *O<sub>h</sub>* geometry, the empty *t<sub>2g</sub>* set is not involved in W—C bonding. A change of geometry which could permit the overlap between those nonbonding orbitals and the ligands can thus stabilize the complex by lowering the energy of some of the orbitals that describe the W—C bonds. This stabilization may only occur if the loss of W—C bonding associated with the diminished overlap between the ligands and the metal orbitals (*p* orbitals of *t<sub>1u</sub>* and *d* orbitals of *e<sub>g</sub>* symmetry) used in the octahedral bonding is not too large.<sup>9</sup> Calculations are thus required to determine which is the dominant effect, but it is clear that a low energy of the *t<sub>2g</sub>* set of orbitals is central to the story. The absence of *π*-donor ligands is thus an important requirement. For this reason, WMe<sub>6</sub> is a distorted trigonal prism while [WCl<sub>6</sub>],<sup>50</sup> [WF<sub>6</sub>],<sup>51</sup> and [CrF<sub>6</sub>]<sup>52</sup> are octahedral.

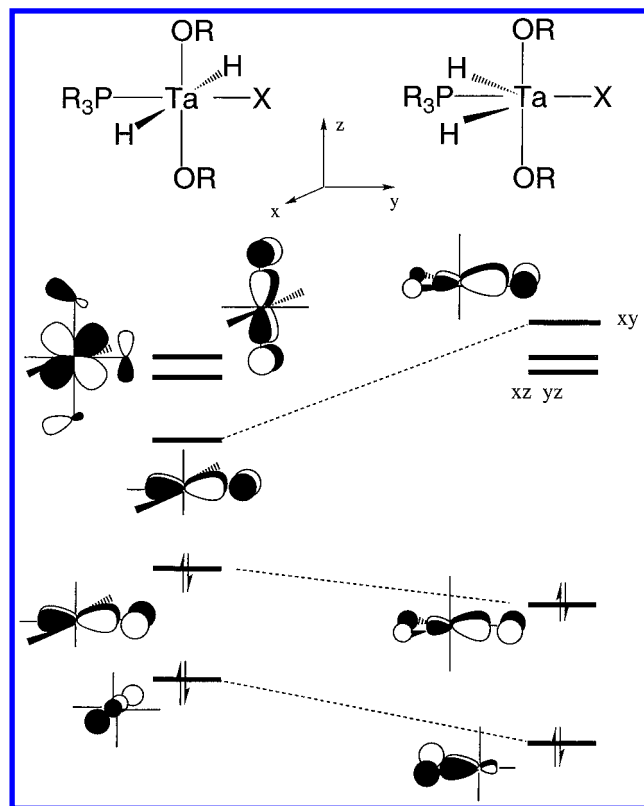
In the present tantalum complexes, drawn in an octahedral geometry in Figure 8, the case of the trihydride (*X* = H) is highly significant. The *d<sub>xy</sub>* orbital is the lowest empty orbital, since it is nonbonding with respect to every lone pair of the alkoxy groups. In contrast, the *d<sub>xz</sub>* and *d<sub>yz</sub>* orbitals are destabilized by the alkoxy lone pairs. Thus *d<sub>xy</sub>* is most able to participate in the stabilization of the *d<sup>0</sup>* species. Moving the two hydrides so that they can overlap with *d<sub>xy</sub>* permits an

increased stabilization of these two Ta—H bonds. This is thus a phenomenon related to that occurring in WMe<sub>6</sub>. When *X* is a *π* donor, the energy of *d<sub>xy</sub>* is raised but the orbital is still at low energy. Moving the hydrides as in Figure 8 now has two effects: reinforcing the Ta—H bonds and improving the Ta—X *π* bonds. The movement of the hydrides forces mixing of *d<sub>xy</sub>* and *p<sub>y</sub>*, which thus creates a hybrid orbital that has improved capacity for Ta—X *π*-bonding. This was previously shown to be the case in the molecules [OsH<sub>3</sub>L<sub>2</sub>(X)].<sup>12</sup> Theoretical studies of the trihydride species [Ta(OH)<sub>2</sub>H<sub>2</sub>(PH<sub>3</sub>)(H)] are highly significant. The fact that this molecule is also predicted to distort (Table 8) implies that the mixing of *d<sub>xy</sub>* and *p<sub>y</sub>* orbitals increases the *σ*-bonding of the two hydride ligands *cis* to the phosphine group.

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**Figure 8.** Qualitative correlation diagram (P-Ta-H decreasing from 90 to 60°) for selected molecular orbitals of  $[\text{Ta}(\text{OR})_2(\text{H})_2(\text{PH}_3)(\text{Cl})]$ .

The above analysis suggests that replacement of the hydride ligands by  $\pi$ -donor groups should diminish or even remove the distortion. Theoretical calculations on *trans-mer*- $[\text{Ta}(\text{OH})_3(\text{Cl})_2(\text{PH}_3)]$ , a model of *trans-mer*- $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_3\text{Cl}_2(\text{PMe}_2\text{Ph})]$  (**6b**), show that in the lowest energy situation the two chloride ligands are indeed bent toward the  $\text{PH}_3$  ligand with P-Ta-Cl  $\approx 10^\circ$ . Since Cl is not a strong  $\pi$  donor, the same effects that are present in the hydride system are still at work here but in a reduced fashion. The adoption of a *cis* arrangement of aryloxo ligands in the adducts *cis-mer*- $[\text{MCl}_3(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_2(\text{L})]$  (**3a**, **3b**, **4a**) precludes direct comparison with *trans-trans*- $[\text{TaCl}(\text{H})_2(\text{OC}_6\text{H}_3\text{Bu}^i\text{-2,6})_2(\text{PMePh}_2)]$ . The small but consistent bending of the chloride ligands toward the donor ligand in  $[\text{MCl}_5(\text{L})]^{n-}$  species for electron-deficient metal centers (Table 7) strongly implicates  $\pi$ -bonding of the axial chloride ligand as the underlying cause. This situation is reminiscent of oxo species  $[\text{M}(\text{O})\text{Cl}_4(\text{L})]^{n-}$ , where bending of the chloride ligands away from the  $\pi$ -donating oxo group occurs.<sup>53</sup>

## 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. The compound  $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_2\text{Cl}_3]_2$  (**1b**) was obtained by previously reported procedures.<sup>16b</sup> Hydrocarbon solvents were dried by distillation from sodium/benzophenone and stored under dry nitrogen. Dimethylphenylphosphine was purchased from Strem Chemical Co., and pyridine was purchased from Aldrich Chemical Co. Both were dried over 3 Å molecular sieves prior to use. The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Varian Associates Gemini 200 and a General Electric QE-300 spectrometer and were referenced either to protio impurities of commercial benzene- $d_6$  or to 85%  $\text{H}_3\text{PO}_4$ . Microanalyses were obtained in-house at Purdue.

**$[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_2\text{Cl}_3]_2$  (**1a**).** To a suspension of  $\text{NbCl}_5$  (21.8 g, 80 mmol) in benzene (200 mL) was slowly added 2,6-diisopropylphenol

(28.7 g, 161 mmol). The resulting mixture was stirred at room temperature for 1.5 h. Removal of benzene solvent gave a red sticky solid, which was washed with hexane and dried *in vacuo* to yield the product as a brick-red powder (31.5 g, 64%). Crystals suitable for X-ray diffraction analysis were obtained by slow cooling of a hot, saturated toluene solution. Anal. Calcd for  $\text{C}_{24}\text{H}_{34}\text{O}_2\text{Cl}_3\text{Nb}$ : C, 52.03; H, 6.15; Cl, 19.24. Found: C, 51.77; H, 6.30; Cl, 19.05.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  7.03–6.86 (m, 6H, aromatics);  $\delta$  4.03 (septet, 4H, CHMe);  $\delta$  1.21 (doublet, 24H, CHMe).

**$[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_3\text{Cl}_2]$  (**2a**).** To a suspension of  $\text{NbCl}_5$  (26 g, 96 mmol) in benzene (250 mL) was slowly added 2,6-diisopropylphenol (55 g, 308 mmol). The resulting mixture was heated to reflux for 6 h, cooled to room temperature, and stirred for an additional 14 h, producing an orange-red suspension. Removal of the benzene solvent *in vacuo* yielded the crude product (60g, 89%) as a light-orange powder. Recrystallization from warm hexane produced red needles of the pure product. Anal. Calcd for  $\text{C}_{36}\text{H}_{51}\text{O}_3\text{Cl}_2\text{Nb}$ : C, 62.25; H, 7.35; Cl, 10.09. Found: C, 61.96; H, 7.63; Cl, 9.94.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  7.07–6.97 (m, 9H, aromatics);  $\delta$  3.65 (septet, 6H, CHMe);  $\delta$  1.25 (d, 36H, CHMe).

**$[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_3\text{Cl}_2]$  (**2b**).** To a solution of  $\text{TaCl}_5$  (26.07 g, 72.8 mmol) in toluene (150 mL) was slowly added 2,6-diisopropylphenol (40.22 g, 225.6 mmol). The resulting mixture was heated to reflux gently for 4 h and then cooled to room temperature, producing a green solution. Removal of the toluene solvent *in vacuo* yielded the crude product as a green crystalline solid. Recrystallization from warm hexane produced green needles of the pure product in moderate yield, 46g (77%). Anal. Calcd for  $\text{C}_{36}\text{H}_{51}\text{O}_3\text{Cl}_2\text{Ta}$ : C, 55.18; H, 6.56; Cl, 9.05. Found: C, 54.83; H, 6.89; Cl, 9.20.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  7.18–6.91 (m, 9H, aromatics);  $\delta$  3.66 (septet, 6H, CHMe);  $\delta$  1.26 (d, 36H, CHMe).

***cis-mer*- $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_2\text{Cl}_3(\text{py})]$  (**3a**).** To a suspension of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_2\text{Cl}_3]_2$  (**1a**) (0.5 g, 2.3 mmol) in benzene (3 mL) was added pyridine (0.75 g, 9.5 mmol). The suspension changed to a dark red solution within 1 min. Removal of the benzene solvent and excess pyridine *in vacuo* produced a red glassy solid. The crude solid was taken up in benzene (7 mL), and the solution was layered with hexane to produce bright red needles of pure product, which were decanted, washed with hexane, and dried *in vacuo*. Anal. Calcd for  $\text{C}_{29}\text{H}_{39}\text{O}_2\text{NCl}_3\text{Nb}$ : C, 55.04; H, 6.21; N, 2.21; Cl, 16.81. Found: C, 55.22; H, 6.45; N, 2.33; Cl, 16.48.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  9.15 (d, 2H, py-ortho);  $\delta$  7.13–6.92 (m, 6H, aromatics);  $\delta$  6.64 (t, 1H, py-para);  $\delta$  6.27 (t, 2H, py-meta);  $\delta$  4.49 (septet, 2H, CHMe);  $\delta$  3.79 (septet, 2H, CHMe);  $\delta$  1.33 (d, 12H, CHMe);  $\delta$  1.07 (d, 12H, CHMe).

***cis-mer*- $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_2\text{Cl}_3(\text{py})]$  (**3b**).** This compound was obtained by a procedure analogous to that used for compound **3a** to yield yellow crystals of product.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  9.19 (d, 2H, py-ortho);  $\delta$  6.86–7.12 (m, 6H, aromatics);  $\delta$  6.60 (t, 1H, py-para);  $\delta$  6.23 (t, 2H, py-meta);  $\delta$  4.43 (septet, 2H, CHMe);  $\delta$  3.71 (septet, 2H, CHMe);  $\delta$  1.33 (d, 12H, CHMe);  $\delta$  1.07 (d, 12H, CHMe).

***cis-mer*- $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_2\text{Cl}_3(\text{PMe}_2\text{Ph})]$  (**4a**).** To a suspension of  $[\text{Nb}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_2\text{Cl}_3]_2$  (**1a**) (1.0 g, 4.6 mmol) in hexane (2 mL) was added  $\text{PMe}_2\text{Ph}$  (0.75 g, 5.4 mmol). Additional hexane was added to just dissolve the dark red product, and the solution was slowly cooled to  $-10^\circ\text{C}$  for 48 h to obtain black needles of product, which were dried *in vacuo*. Anal. Calcd for  $\text{C}_{32}\text{H}_{45}\text{O}_2\text{Cl}_3\text{PNb}$ : C, 55.70; H, 6.52; P, 4.48; Cl, 15.37. Found: C, 55.69; H, 6.57; P, 4.15; Cl, 15.13.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  7.42 (m, 2H, P-Ph ortho);  $\delta$  7.08–6.83 (m, 9H, aromatics);  $\delta$  4.07 (m, br, 4H, CHMe);  $\delta$  1.61 (d, 6H, P-Me),  $^2J(^{31}\text{P}-^1\text{H}) = 9.19$  Hz;  $\delta$  1.18 (s, br, 24H, CHMe).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  -13.35.

***cis-mer*- $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_2\text{Cl}_3(\text{PMe}_2\text{Ph})]$  (**4b**).** To a suspension of  $[\text{Ta}(\text{OC}_6\text{H}_3\text{Pr}^i\text{-2,6})_2\text{Cl}_3]_2$  (0.5 g, 0.39 mmol) in benzene was added dimethylphenylphosphine (0.13 g, 0.94 mmol). The resulting yellow solution was stirred for 1 h. Removal of the benzene solvent yielded the product as a yellow crystalline solid, which was washed with hexane and dried *in vacuo*.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  7.44 (m, 2H, P-Ph ortho);  $\delta$  6.81–7.10 (m, 9H, aromatics);  $\delta$  4.22 (septet, 2H, CHMe);  $\delta$  3.75 (septet, 2H, CHMe);  $\delta$  1.62 (d, 6H, P-Me),  $^2J(^{31}\text{P}-^1\text{H}) = 8.87$  Hz;  $\delta$  1.26 (d, 12H, CHMe);  $\delta$  1.05 (d, 12H, CHMe).  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ , 30 °C):  $\delta$  -11.35.

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**trans-mer-[Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>3</sub>Cl<sub>2</sub>(py)] (5).** To a suspension of [Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>3</sub>Cl<sub>2</sub>] (0.5 g, 0.72 mmol) in benzene (10 mL) was added pyridine (0.07 g, 0.9 mmol), and the resulting mixture was stirred for 5 min, during which a slight color change from bright to dark red was observed. Removal of the benzene solvent *in vacuo* produced the product as a bright red solid. Anal. Calcd for C<sub>41</sub>H<sub>56</sub>O<sub>3</sub>NCl<sub>2</sub>Nb: C, 63.57; H, 7.29; N, 1.81; Cl, 9.15. Found: C, 62.92; H, 7.34; N, 2.00; Cl, 8.84. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 30 °C): δ 8.83 (d, 2H, py-*ortho*); δ 7.17–6.95 (m, 9H, aromatics); δ 6.70 (t, 1H, py-*para*); δ 6.30 (t, 2H, py-*meta*); δ 4.28 (septet, 2H, CHMe); δ 4.01 (septet, 4H, CHMe); δ 1.19 (d, 12H, CHMe); δ 1.18 (d, 24H, CHMe).

**trans-mer-[Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>3</sub>Cl<sub>2</sub>(PMe<sub>2</sub>Ph)] (6a).** To a suspension of [Nb(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>3</sub>Cl<sub>2</sub>] (0.5 g, 0.72 mmol) in benzene (1 mL) was added PMe<sub>2</sub>Ph (0.35 g, 2.5 mmol). After an immediate color change from orange-red to dark bright red, the reaction mixture was covered with a layer of hexane (15 mL). After 72 h, large, cubic, dark red crystals of product were obtained, washed with hexane, and dried *in vacuo*. Anal. Calcd for C<sub>46</sub>H<sub>62</sub>O<sub>3</sub>Cl<sub>2</sub>PNb: C, 63.47; H, 7.44; P, 3.72; Cl, 8.27. Found: C, 63.05; H, 7.65; P, 3.42; Cl, 8.48. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 30 °C): δ 7.41 (m, P-Ph *ortho*); δ 7.17–6.91 (m, 12H, aromatics); δ 4.12–4.04 (m, br, 4H, CHMe); δ 4.03–3.83 (m, br, 2H, CHMe); δ 1.48 (d, 6H, P-Me), <sup>2</sup>J(<sup>31</sup>P–<sup>1</sup>H) = 7.70 Hz; δ 1.15 (s, br, 36H, CHMe). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 30 °C): δ –17.23.

**trans-mer-[Ta(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>3</sub>Cl<sub>2</sub>(PMe<sub>2</sub>Ph)] (6b).** To a suspension of [Ta(OC<sub>6</sub>H<sub>3</sub>Pr<sup>i</sup><sub>2</sub>-2,6)<sub>3</sub>Cl<sub>2</sub>] (1.0 g, 1.22 mmol) in toluene (2 mL) was added PMe<sub>2</sub>Ph (0.25 g, 1.83 mmol). After an immediate change from a green suspension to a yellow solution, the reaction mixture was covered with a layer of hexane (15 mL). After 72 h, yellow crystals of product were obtained, washed with hexane, and dried *in vacuo*. Anal. Calcd for C<sub>44</sub>H<sub>62</sub>O<sub>3</sub>Cl<sub>2</sub>PTa: C, 57.33; H, 6.78; P, 3.36; Cl, 7.69. Found: C, 56.27; H, 6.99; P, 4.94; Cl, 8.44. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 30 °C): δ 7.37 (m, 2H, P-Ph *ortho*); δ 7.13–6.81 (m, 12H, aromatics); δ 4.03 (septet, 4H, CHMe); δ 3.71 (septet, 2H, CHMe); δ 1.51 (d, 6H, P-Me), <sup>2</sup>J(<sup>31</sup>P–<sup>1</sup>H) = 7.60 Hz; δ 1.16 (d, 24H, CHMe) δ 1.09 (d, 12H, CHMe); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 30 °C): δ –12.13.

**Computational Details.** The model systems chosen for study were [Ta(OH)<sub>2</sub>(H)<sub>2</sub>(PH<sub>3</sub>)X] (X = Cl, OH, H with Y = H; X = Cl with Y = OH, Cl). Optimizations of the geometry were carried out with the Gaussian 92 set of programs at the RHF, MP2, and DFT (B3LYP) levels.<sup>54</sup> Effective core potentials (ECPs) from Stoll et al. were chosen for Ta.<sup>55</sup> The ECPs for Cl and P are those of Barthelat et al.<sup>56</sup> and Stevens and Bash, respectively.<sup>57</sup> A triple-ζ-quality basis set<sup>55</sup> was used for the metal, and a double-ζ for all atoms bonded to it with polarization functions for the last.<sup>57,58</sup> The hydrogens of OH and PH<sub>3</sub> were calculated with a (4S)/[1S] basis set.<sup>59</sup> Since the calculations gave essentially the same geometry with the three levels of calculations, only the DFT results are reported here.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for complexes **1a**, **1b**, **3a**, **3b**, **4**, **6a**, **6b**, and **7** are available on the Internet only. Access information is given on any current masthead page.

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