

# Transition Metal Polyhydride Complexes. 9. The Effect of Ligand $\sigma$ - and $\pi$ -Bonding on the H–Ta–H Bond Angle in Six-Coordinate Tantalum(V) Dihydride Complexes

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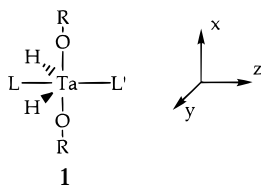
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In the known structures of the pseudo-octahedral complexes  $[\text{Ta}(\text{OR})_2\text{L}'(\text{H})_2\text{L}]^+$ , with  $\text{L} = \text{PR}_3$  and  $\text{L}' = \text{Cl}^-$ ,  $\text{OR}^-$ , the “trans” hydrides are bent away from the sterically less demanding ligand ( $\text{L}'$ ) toward the bulkier phosphine group ( $\text{L}$ ). Here, ab initio calculations on a series of analogous model complexes ( $\text{R} = \text{H}$ ;  $\text{L}, \text{L}' = \text{OH}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{CS}$ ,  $\text{BF}$ ,  $\text{N}_2$ ,  $\text{CH}_3^-$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{CH}_3\text{CN}$ ,  $\text{NH}_2^-$ , and  $\text{H}^-$ ) are used to examine the effect of the  $\sigma$ - and  $\pi$ -bonding of the ligands  $\text{L}$  and  $\text{L}'$  on the direction of H–Ta–H bending. While the trend in the trans influence, which dominates the Ta–L bond length of the ligand trans to  $\text{L}'$ , originates primarily from  $\sigma$ -bonding, the direction of the distortion of the “trans” hydrides originates primarily from the relative  $\pi$ -acceptor ability of the ligand  $\text{L}$  to that of the ligand  $\text{L}'$ . Generally, as the ligands are varied, the hydrides will bend toward the stronger  $\pi$ -acceptor ( $\text{L}$  vs  $\text{L}'$ ). With certain ligand pairs the possibility of two isomers exists, one with hydrides bent toward  $\text{L}$  and another with hydrides bent toward  $\text{L}'$ .

## Introduction

In transition metal hydride complexes the hydride ligand adopts an interesting variety of structural motifs from  $\mu$ -hydrogen bridges to dihydrogen ligands. Unfortunately, the small size and fluxional behavior of the ligand can limit accurate structural determinations except by neutron diffraction. Quantum chemistry provides a convenient methodology to examine systems for which experimental methods are less than adequate.<sup>1</sup> Previous studies have demonstrated the reliability of second-order Møller–Plesset (MP2) perturbation theory for determining geometries and relative energies for second- and third-row transition metal polyhydride complexes.<sup>2</sup>



The X-ray crystallographic studies of the recently synthesized<sup>3</sup> tantalum dihydride complexes (**1**;  $\text{L} = \text{PR}_3$ ,  $\text{L}' = \text{Cl}^-$ ,  $\text{OR}^-$ ) show that their “trans” hydride ligands bend away from an octahedral-like geometry by  $\sim 20$ – $30^\circ$ . By using the intensities of the M–H stretching

bands,<sup>4</sup> vibrational studies<sup>3</sup> also confirm that the H–M–H bond angle was much less than  $180^\circ$ . On steric grounds one might expect the hydrides to bend toward the least bulky ligand ( $\text{L}' = \text{Cl}^-$ ,  $\text{OC}_6\text{H}_3\text{Pr}_2\text{-2,6}^-$ ), but in both complexes the hydrides bend toward the more bulky phosphine ( $\text{L}$ ), even for  $\text{L} = \text{PMeCy}_2$ . Originally, the geometry was rationalized in terms of primary (covalent) and secondary (dative) bonding effects as described by Haaland<sup>5a</sup> and Alcock<sup>5b</sup> and elaborated upon by Buhro.<sup>5c</sup> By using this reasoning, the unusual structure of these Ta complexes could be rationalized as a combination of a trigonal bipyramidal arrangement of the primary ligands (trans aryloxy ligands, ligand  $\text{L}'$  and hydrides) and a secondary ligand ( $\text{L} = \text{phosphine}$ ) weakly bound between the hydrides. The primary/secondary bonding argument was developed to interpret anomalous structural features in main group chemistry and considers primarily  $\sigma$ -bonding effects. Similar arguments have been invoked in transition metal chemistry to explain the trans influence<sup>6</sup> observed in platinum chemistry.<sup>7</sup>

Alternatively, these Ta complexes can be analyzed as a pseudo-octahedral arrangement of ligands in which the hydrides undergo a pseudo-second-order Jahn–Teller (PSOJT) distortion.<sup>8</sup> Since hydrides prefer to bond through d-orbitals or sd hybrids, most trans

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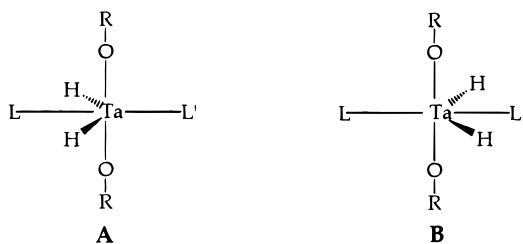
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hydrides will undergo a PSOJT distortion if there are empty low-lying d-orbitals available. One example is the  $d^2$  pseudo-octahedral complex  $\text{CpOsH}_5$ .<sup>21,8c</sup> This complex has two empty d-orbitals, which allow the "trans" equatorial hydride ligands to bend away from the Cp ring to an H–Os–H angle of  $\sim 130^\circ$ , an angle similar to that found in **1** with  $L' = \text{OR}^-$ . Unfortunately, at this level the PSOJT effect can only predict when a hydride system can distort. It cannot determine the direction of the distortion, as it does not incorporate the relative  $\sigma$ - and  $\pi$ -donor (acceptor) characteristics of the other ligands. A brief theoretical analysis along these lines was included as part of a study<sup>9</sup> of six-coordinate niobium and tantalum complexes.

In this study, we perform ab initio calculations on the model complexes  $[\text{Ta}(\text{OH})_2\text{L}'(\text{H})_2\text{L}]$  in which the ligands L and L' are varied in order to determine the effect of  $\pi$ -donor (acceptor) ability and  $\sigma$ -bonding trans influence on the PSOJT distortion of the hydride ligands. The results on alternative ligands, which bond either covalently or datively and include varying amounts of  $\sigma$ -/ $\pi$ -bonding effects, allow trends to be established that may be useful in future experimental studies. In addition, we predict that some of these complexes have two isomers, A and B. A study of the analogous metal complexes  $(\text{M}(\text{OH})_3(\text{H})_2(\text{PH}_3))$ ,  $\text{M} = \text{Re}(d^2)$ ,  $\text{Ir}(d^4)$ ,  $\text{Au}(d^6)$  shows how changes in d occupancy affect this distortion.



### Theoretical Details

The model complexes simplified the experimental ones by replacing the R-groups on the phosphine and aryloxy with hydrogens to produce  $[\text{Ta}(\text{OH})_2\text{L}'(\text{H})_2\text{L}]^+$ . Calculations were performed on complexes with  $L = \text{PH}_3$ ;  $L' = \text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{CS}$ ,  $\text{BF}$ ,  $\text{N}_2$ ,  $\text{CH}_3^-$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{CH}_3\text{CN}$ ,  $\text{NH}_2^-$ , and  $\text{H}^-$  and on those mixed ligands where both L and L' ligands were chosen from the above list for L'. In separate calculations on the trihydroxide complex  $[\text{M}(\text{OH})_3(\text{H})_2\text{PH}_3]$ , the tantalum was replaced by the following metals in the +5 oxidation state:  $\text{Re}(d^2)$ ,  $\text{Ir}(d^4)$ , and  $\text{Au}(d^6)$ .

Geometries were optimized at the MP2 level<sup>10</sup> for isomer A and isomer B. In the cases where one of these isomers would not converge to a local minimum within the constraints of the calculation (i.e., there was no second isomer), the geometry was calculated with the H–M–H bond angle constrained to  $180^\circ$  (pseudo-octahedral) in order to estimate the relative energy of the stable isomer. Frequency calculations (MP2) were performed on selected systems to determine whether the optimized geometry was a minimum on the potential energy surface.

The atoms of the nonhydride ligands were represented by valence double- $\zeta$  basis sets<sup>11</sup> with effective core potentials

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**Table 1.** MP2 Relative Energies of Isomer A to Isomer B,  $\Delta E_{\text{AB}}$ , and MP2 Relative Energies for the Minimum Energy Isomer to the Pseudo-Octahedral Geometries,  $\Delta E_{\text{Oh}}^a$  for  $[\text{Ta}(\text{OH})_2\text{L}(\text{H})_2\text{PH}_3]^+$

L'	$\Delta E_{\text{AB}}$ (kcal/mol)	$\Delta E_{\text{Oh}}$ (kcal/mol)	L'	$\Delta E_{\text{AB}}$ (kcal/mol)	$\Delta E_{\text{Oh}}$ (kcal/mol)
$\text{F}^-$	<i>b</i>	−26.62	$\text{CH}_3\text{CN}$	−8.80	
$\text{OH}^-$	<i>b</i>	−23.17	$\text{NH}_3$	−8.41	−28.74
$\text{NH}_2^-$ <sup>c</sup>	<i>b</i>	−19.53	$\text{N}_2$	−5.97	
$\text{Cl}^-$	−26.59	−30.20	$\text{H}^-$	−4.76	−26.14
$\text{Br}^-$	−24.18	−39.92	$\text{NH}_2^-$ <sup>d</sup>	−4.64	
$\text{NC}^-$	−21.60		$\text{PH}_3$	0.00	−29.67
$\text{I}^-$	−21.37	−29.66	$\text{CO}$	2.57	−40.26
$\text{CH}_3^-$	−16.46	−25.13	$\text{CS}$	3.84	
$\text{CN}^-$	−13.69	−36.26	$\text{BF}$	12.79	

<sup>a</sup>  $\Delta E_{\text{Oh}}$  is defined as the difference in energy between the isomer (A or B) with the lowest energy and the pseudo-octahedral structure. <sup>b</sup> These complexes do not possess minima for isomer B. <sup>c</sup> Ligand is coplanar with trans hydroxide ligands. <sup>d</sup> Ligand is coplanar with "trans" hydride ligands.

(ECP) where applicable. Hydride ligands (including  $L' = \text{H}^-$ ) were described in a triple- $\zeta$  basis set (311).<sup>12</sup> Metal basis sets were double- $\zeta$  quality with a triple- $\zeta$  representation of the d-orbitals (541/541/211) and were used in conjunction with the corresponding Ermler–Christiansen ECP<sup>13</sup> that includes 60 electrons ( $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14}$ ). The  $(n+1)s$ - and  $(n+1)p$ -orbitals were included in the metal valence set in accordance with previous work<sup>14</sup> in this group. All calculations were performed with the GAMESS-UK code<sup>15</sup> on an SGI Power Challenge or a Cray J90 at the Supercomputer Facility at Texas A&M University.

### Results and Discussion

In addition to calculations on models of the experimental complexes  $[\text{Ta}(\text{OH})_3(\text{H})_2(\text{PH}_3)]$  and  $[\text{Ta}(\text{OH})_2\text{Cl}(\text{H})_2(\text{PH}_3)]$ , studies were also performed on a long series of complexes  $[\text{Ta}(\text{OH})_2\text{L}'(\text{H})_2(\text{PH}_3)]^+$ , where  $L' = \text{F}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CO}$ ,  $\text{CN}^-$ ,  $\text{CS}$ ,  $\text{BF}$ ,  $\text{N}_2$ ,  $\text{CH}_3^-$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{CH}_3\text{CN}$ ,  $\text{NH}_2^-$ , and  $\text{H}^-$ , to determine the effect of various degrees of the ligand's (L')  $\sigma$ - and  $\pi$ -bonding on the structure and energy of isomers A and B. Several mixed (non-phosphine) complexes,  $[\text{Ta}(\text{OH})_2\text{L}'(\text{H})_2\text{L}]^+$ , were also studied, where both L and L' were chosen from the above list. The relative energies of isomer A to isomer B,  $\Delta E_{\text{AB}}$ , and the structural data for the most stable isomers are in Tables 1 and 2, respectively.

In the results and discussion below we have grouped the complexes according to their structural similarity.

**$[\text{Ta}(\text{OH})_3(\text{H})_2(\text{PH}_3)]$  and  $[\text{Ta}(\text{OH})_2\text{Cl}(\text{H})_2(\text{PH}_3)]$ .** Their MP2 geometries are compared to the experimental geometries in Table 3, and the first of these two complexes is shown in Figure 1a. As expected, X-ray

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**Table 2. Structural Parameters at the MP2 Level for Minimum Energy Structures of [Ta(OH)<sub>2</sub>L'(H)<sub>2</sub>PH<sub>3</sub>]<sup>+</sup>**

L'	d(Ta–P), Å	d(Ta–O <sub>trans</sub> ), Å	d(Ta–L'), Å	d(Ta–H), Å	∠(H–Ta–H), deg	∠(O <sub>trans</sub> –Ta–O <sub>trans</sub> ), deg	∠(Ta–O <sub>trans</sub> –H), deg
OH <sup>−</sup>	2.783	1.915	1.919	1.804	135.7	172.3	173.6
F <sup>−</sup>	2.760	1.905	1.958	1.789	133.5	179.7	167.5
Cl <sup>−</sup>	2.720	1.903	2.434	1.783	132.8	179.3	165.0
Br <sup>−</sup>	2.715	1.903	2.589	1.784	132.9	179.0	165.4
I <sup>−</sup>	2.712	1.903	2.778	1.784	132.8	179.5	165.5
CH <sub>3</sub> <sup>−</sup>	2.883	1.906	2.209	1.796	132.0	179.5	174.3
NH <sub>2</sub> <sup>− a</sup>	2.823	1.910	2.000	1.816	137.6	178.7	177.0
NH <sub>2</sub> <sup>− b</sup>	2.830	1.929	2.012	1.791	132.0	167.9	164.7
H <sup>−</sup>	2.839	1.904	1.816	1.791	131.5	171.4	160.7
BF	2.822	1.887	2.249 (1.302)	1.776	125.8 <sup>c</sup>	167.8	178.2
CO	2.782	1.884	2.241 (1.189)	1.765	129.8 <sup>c</sup>	167.0	177.0
CS	2.813	1.888	2.191 (1.589)	1.772	129.9 <sup>c</sup>	164.2	177.4
N <sub>2</sub>	2.658	1.875	2.483 (1.186)	1.758	131.8	156.0	176.9
CN <sup>−</sup>	2.763	1.901	2.210 (1.238)	1.779	131.5	175.0	161.3
NC <sup>−</sup>	2.743	1.899	2.104 (1.236)	1.781	132.0	175.0	162.8
CH <sub>3</sub> CN	2.686	1.884	2.268	1.763	131.4	165.3	178.0
NH <sub>3</sub>	2.704	1.890	2.308	1.764	131.5	165.2	175.6
PH <sub>3</sub>	2.682	1.887	2.792	1.763	131.4 <sup>c</sup>	163.8	178.9

<sup>a</sup> Ligand is coplanar with trans hydroxide ligands. <sup>b</sup> Ligand is coplanar with “trans” hydride ligands. <sup>c</sup> Bond angle is bisected by ligand L' rather than PH<sub>3</sub>.

**Table 3. Comparison of Selected Experimental<sup>a</sup> and Theoretical (MP2) Parameters for [Ta(OR)<sub>2</sub>L'(H)<sub>2</sub>(PR'<sub>3</sub>)<sup>+</sup>, L' = OR<sup>−</sup>, Cl<sup>− b</sup>**

parameter	exptl L' = OR <sup>− b</sup>	theor L' = OR <sup>− b</sup>	exptl L' = Cl <sup>−</sup>	theor L' = Cl <sup>−</sup>
d(Ta–H, av), Å	1.74(4)	1.804	1.73(5)	1.783
d(Ta–P), Å	2.650	2.783	2.655	2.720
d(Ta–O <sub>trans</sub> , av), Å	1.902	1.915	1.892	1.903
d(Ta–L'), Å	1.912	1.919	2.397	2.434
∠(H1–Ta–H2), deg	135.(3)	135.7	118.(2)	132.8
∠(Ta–O <sub>ax</sub> –R), deg	153.6	150.8		
∠(Ta–O <sub>trans</sub> –R, av), deg	165.1(4)	173.6	160.8(1) <sup>c</sup>	165.0
∠(P–Ta–L'), deg	174.5	179.3	175.0	179.0

<sup>a</sup> See ref 3. <sup>b</sup> Exptl: R = C<sub>6</sub>H<sub>5</sub><sup>3</sup>Pr<sub>2</sub>-2,6; PR'<sub>3</sub> = PMe<sub>2</sub>Ph. Theor: R = H; PR'<sub>3</sub> = PH<sub>3</sub>. <sup>c</sup> See ref 9.

diffraction gives M–H bond distances that are too short by about 0.05 Å. For the trihydroxide model the calculated H–Ta–H bond angle is almost identical to that of the experimental complex, but for the chloride the calculated angle is 15° larger than the experimental one. This large discrepancy between theory and experiment may result from the difficulty of determining the hydrogen atom positions in this X-ray diffraction analysis.

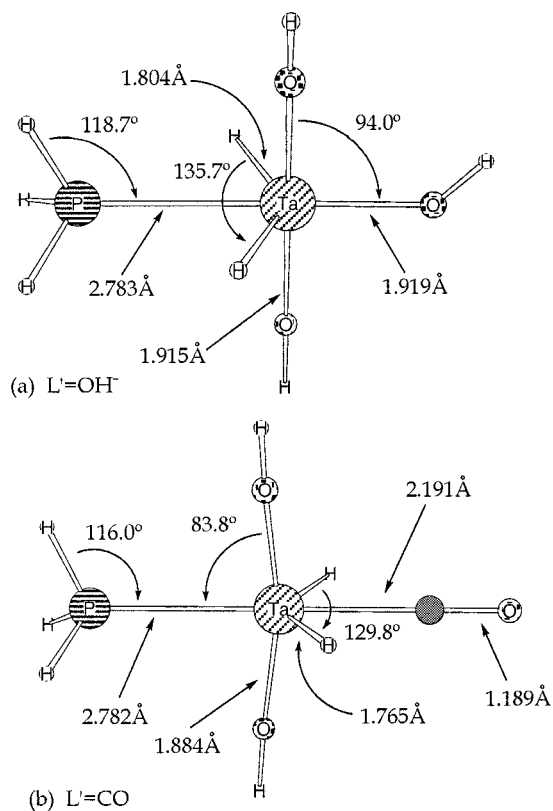
In agreement with the experiment the Ta–O bond distances for the trans hydroxides (Ta–O<sub>trans</sub>) are slightly shorter than that for the axial hydroxide (trans to PH<sub>3</sub>) and the Ta–O<sub>trans</sub>–H bond angles are almost linear. For a mer pseudo-octahedral system with three σ-bonding ligands and three multiply bonding ligands, group-theoretical studies<sup>16</sup> indicate that the multiply bonded ligands will have a maximum bond order of 2.0. By using both the empty d<sub>xy</sub> and d<sub>xz</sub> the axial RO–M–OR π-bonding can be described as two three-center, four-electron bonds, which in valence bond terms is equivalent to partial triplet-bond character. In other words, the resonance forms RO≡M–OR ↔ RO–M≡OR are important additions to the more traditional RO=M=OR resonance form. Because of this symmetric delo-

calized π-structure with some triple-bond character, one would expect M–O–R angles near 180°.<sup>17</sup> Since the hydrides use the d<sub>yz</sub> in forming their Ta–H bonds, it is unavailable for bonding to the axial OR. Thus, the Ta–O axial bond will have little or no triple-bond character and, therefore, will be bent.

Frequency calculations (MP2) performed on these complexes confirm that the geometries are minima on their respective potential energy surfaces. The experimental frequencies (ν(M–H)) for the L' = OR<sup>−</sup> complex fall between 1794 and 1846 cm<sup>−1</sup> for the symmetric stretch and 1742–1758 cm<sup>−1</sup> for the asymmetric stretch. Unscaled theoretical (MP2) frequencies give similar results (1802 cm<sup>−1</sup> (symm) and 1750 cm<sup>−1</sup> (asym)). However, the agreement between theory and experiment for the chloride complex is not as good. The experimental frequencies range between 1884 and 1922 cm<sup>−1</sup> and 1800–1820 cm<sup>−1</sup> for the symmetric and asymmetric stretch, respectively, while the unscaled theoretical (MP2) frequencies are 1988 cm<sup>−1</sup> (symm) and 1916 cm<sup>−1</sup> (asym). Careful examination of the theoretical frequencies did not reveal any obvious error in the theoretical results. The discrepancy between theory and

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**Figure 1.** Selected structural parameters for (a) [Ta(OH)<sub>3</sub>-(H)<sub>2</sub>PH<sub>3</sub>] and (b) [Ta(OH)<sub>2</sub>(CO)(H)<sub>2</sub>PH<sub>3</sub>]<sup>+</sup> calculated at the MP2 level. Distances are given in angstroms (Å).

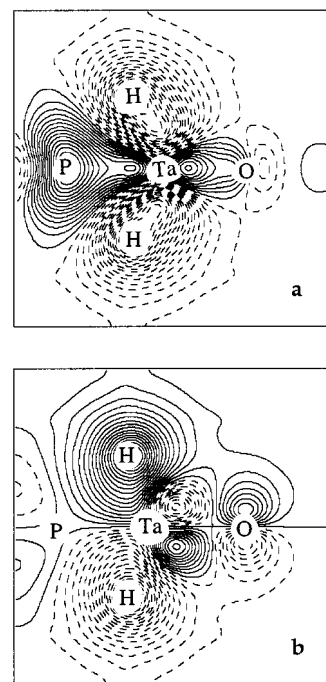
experiment may be attributed to experimental problems, because the chloride samples were Nujol mulls, while the aryloxide samples were solutions, or because the chloride spectrum was misassigned and has a band at about 1988 cm<sup>-1</sup>.

As the tantalum complexes [Ta(OH)<sub>2</sub>L'(H)<sub>2</sub>L] are d<sup>0</sup> (12e<sup>-</sup>) complexes, all of the d-orbitals are available for bonding (i.e., there are no d "lone" pairs). In C<sub>2v</sub> symmetry (C<sub>2</sub> = z axis) the hydride orbitals in **1** form a<sub>1</sub> and b<sub>2</sub> combinations. The hydride representations can bond to hybrids constructed from the 5d<sub>x<sup>2</sup>-y<sup>2</sup></sub> (a<sub>1</sub>) or 6s (a<sub>1</sub>) orbitals and the 5d<sub>yz</sub> (b<sub>2</sub>) or 6p<sub>y</sub> (b<sub>2</sub>) orbitals. The a<sub>1</sub> hybrid formed from the 5d<sub>x<sup>2</sup>-y<sup>2</sup></sub> and 6s will tend to favor 180° angles for the H-Ta-H framework. However, the two b<sub>2</sub> orbitals have maximum overlap with the hydride ligands at quite different angles. The observed angle will, in part, be dependent on the mixing shown in eq 1.

$$\phi_{b_2} = (\sqrt{1 + \alpha^2})^{-1}(5d_{yz} \pm \alpha 6p_y) \quad (1)$$

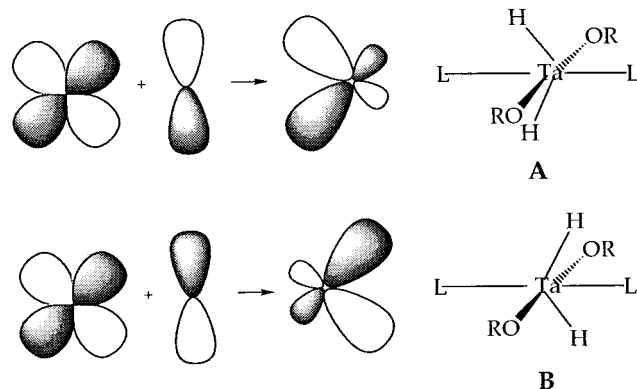
If the b<sub>2</sub> interactions were weak so that the bonding arose primarily from the a<sub>1</sub> interactions or if the b<sub>2</sub> interactions were dominated by the 6p<sub>y</sub>, the H-Ta-H angle would be 180°. However, as the importance of the 5d<sub>yz</sub> increases, the H-Ta-H angle will bend away from 180° toward 90°. If one begins at the geometry where H-Ta-H is 180°, one can describe the distortion to smaller angles in terms of a PSOJT effect.<sup>8c</sup>

The direction of the distortion will depend on the sign of the mixing in eq 1 as illustrated in Scheme 1. Our results will show that this direction is dominated by the relative π-donor (acceptor) strength of the two trans



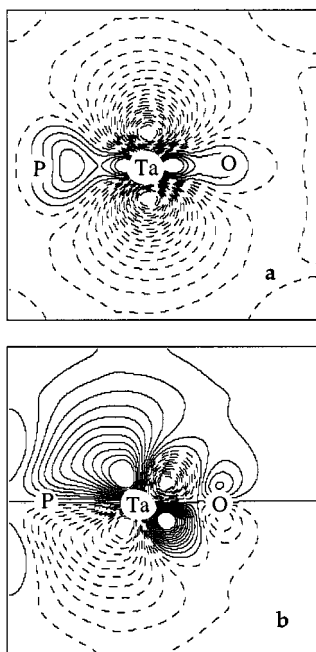
**Figure 2.** (a) Plot of HOMO-1 (a<sub>1</sub>) and (b) HOMO (b<sub>2</sub>) for [Ta(OH)<sub>3</sub>(H)<sub>2</sub>PH<sub>3</sub>] in the yz plane showing the Ta-H bonding orbitals distorted toward PH<sub>3</sub>.

### Scheme 1



ligands in the TaH<sub>2</sub> plane (L and L'). With a strong π-donor ligand as L', the φ<sub>b<sub>2</sub></sub> orbital will polarize away from L' and favor isomer A, while with a strong π-acceptor as L', this orbital will polarize toward L' and favor isomer B. From the PSOJT viewpoint, the low-lying, empty 5d<sub>yz</sub> orbital, which causes the distortion by stabilizing the filled b<sub>2</sub> hydride combination, will have the stronger interaction when the H's are located in the maximum of this orbital, which is polarized toward the better acceptor and away from the better donor (L or L').

The hydride bonding orbitals for the L = PH<sub>3</sub>, L' = OH<sup>-</sup> complex are shown in Figures 2a (a<sub>1</sub>, HOMO-1) and 2b (b<sub>2</sub>, HOMO). In the b<sub>2</sub> orbital plot, one side of the metal d-orbital is bonding to the hydrides, while the opposite side is antibonding to the hydroxide π-orbital. Figure 3 shows the same two orbitals from a calculation where the hydrides on the MP2-optimized structure have been replaced by electrons (i.e., double deprotonation of the dihydride to form Ta(OH)<sub>3</sub>PH<sub>3</sub><sup>2-</sup>). The plot of the a<sub>1</sub> orbital (Figure 3a) appears as the expected atomic orbital or sd hybrid. Although this orbital favors

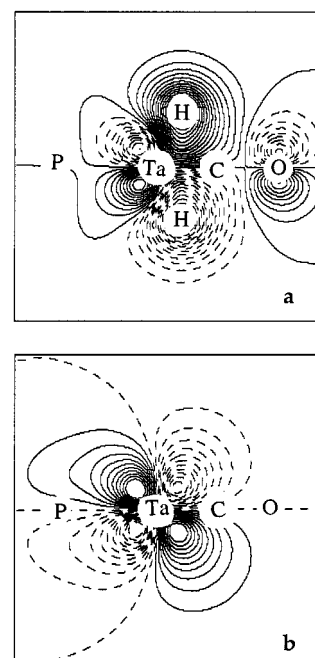


**Figure 3.** (a) Plot of HOMO-1 ( $a_1$ ) and (b) HOMO ( $b_2$ ) for  $[\text{Ta}(\text{OH})_3\text{PH}_3]^{2-}$  in the  $yz$  plane. Comparison with Figure 2 shows that the distortion of the trans hydrides originates in the  $b_2$  orbital.

a linear H–Ta–H framework, its large lobes could be used in either a trans or a bent hydride complex without significant loss of bonding. However, the  $b_2$  orbital (Figure 3b) shows a node in the region of a linear H–Ta–H framework and significant distortion of the lobes in a direction away from the antibonding interaction with the oxygen  $\pi$ -orbital. This plot reflects the mixing of the  $b_2$  orbital described in eq 1 where the  $x$ – $y$  mirror plane of the orbital is lost as a result of asymmetric ligand  $\pi$ -bonding to the metal. The most stable  $\phi_{b_2}$  orbital is the one polarized away from the  $\pi$ -donor toward the  $\pi$ -acceptor. Thus, protonation will occur with the hydrogens bent toward the  $\pi$ -acceptor and away from the  $\pi$ -donor.

**$[\text{Ta}(\text{OH})_2(\text{H})_2(\text{PH}_3)_2]^+$ .** This complex presents a problem for the original primary/secondary bonding explanation for the bend H–Ta–H system, as both trans ligands are identical and dative. The results of the MP2 geometry optimization show that, even here, the molecule distorts so that the hydrides are not trans to one another. As the two key ligands in this case are identical, the trans influence cannot be the origin of the distortion. Interestingly, the Ta–P bond that bisects the H–Ta–H bond angle is about 0.1 Å shorter than the other Ta–P bond. This difference in bond lengths is opposite that expected from the primary/secondary bonding argument, as it would predict that the Ta–P bond toward which the hydrides bend would be the weaker (and longer) of the two bonds. The fact that this bond length is shorter shows that the direction of the PSOJT distortion is due to the  $\pi$ -bonding of L to the metal as the shorter bond allows more interaction between the metal  $d_\pi$ -orbital and the  $\pi$ -accepting orbital of the phosphine ligand.

**$[\text{Ta}(\text{OH})_2\text{L}(\text{H})_2(\text{PH}_3)]^+$ ,  $\text{L}' = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-$ .** There is a very strong interaction between the F  $p_\pi$ -orbitals and the metal  $d_\pi$ -orbitals, such that isomer B



**Figure 4.** Plot of HOMO for (a)  $[\text{Ta}(\text{OH})_2(\text{CO})(\text{H})_2\text{PH}_3]^+$  and (b)  $[\text{Ta}(\text{OH})_2(\text{CO})\text{PH}_3]^-$  in the  $yz$  plane showing the distortion of the  $b_2$  orbital toward CO.

in Scheme 1 does not exist. The strong metal–fluoride  $\sigma$ -bond increases the trans influence on the  $\text{PH}_3$ , as seen in a longer Ta–P bond compared with the other halides. The other halide ligands are less covalently bound than fluoride, and both isomers are stable. The  $\Delta E_{\text{AB}}$  values show a slowly progressing decrease. The Ta–P bond length also decreases from Cl to I, indicating that the trans influence on  $\text{PH}_3$  decreases as the halide becomes softer.

**$[\text{Ta}(\text{OH})_2(\text{H})_3(\text{PH}_3)]$ .** As shown in the previous theoretical study,<sup>9</sup> when  $\text{L}' = \text{H}^-$ , the trans hydride ligands distort toward the phosphine and form a structure similar to that seen for  $\text{L} = \text{Cl}^-$  or  $\text{OR}^-$ . However, these workers did not appreciate the significance of a second isomer. While the  $\text{L}' = \text{H}^-$ ,  $\text{Cl}^-$ , and  $\text{OR}^-$  complexes do have similar structures, the difference in the energy  $\Delta E_{\text{AB}}$  is much larger for the  $\pi$ -donating complexes than for the  $\text{L}' = \text{H}^-$  complex (by more than 20 kcal/mol in the case of  $\text{Cl}^-$ ). As noted in the case where both L and  $\text{L}'$  are phosphine ligands, the distortion of the trans hydrides is an intrinsic property of these complexes. Since the  $\text{PH}_3$  ligand is a better  $\pi$ -acceptor than either  $\text{Cl}^-$  or  $\text{H}^-$ , the structures of these two complexes are similar, but the relative energy of the other isomer is related to the difference in  $\pi$ -donor abilities of  $\text{Cl}^-$  and  $\text{H}^-$ .

**$[\text{Ta}(\text{OH})_2\text{L}'(\text{H})_2(\text{PH}_3)]^+$ ,  $\text{L}' = \text{CO}, \text{CS}, \text{CN}^-, \text{NC}^-, \text{BF}, \text{N}_2$ .** The results for the complexes with  $\text{L}' = \text{CO}, \text{CS}$ , and  $\text{BF}$  are markedly different from the results on the hydrides and halide complexes. For these ligands, the hydrides bend away from the phosphine as shown in Figure 1b ( $\text{L}' = \text{CO}$ ). The reason for this difference is the  $\pi$ -acceptor strength of these ligands. Examination of the Ta–H  $b_2$  bonding orbital shows that the half of the metal  $d_{yz}$ -orbital facing the CO ligand is augmented by the  $\pi^*$  CO orbital (Figure 4a) reflecting the polarization of the Ta  $b_2$  atomic orbital by the strong  $\pi$ -acceptor, CO. A calculation on the fragment formed by doubly

deprotonating  $[\text{Ta}(\text{OH})_2(\text{H})_2(\text{CO})\text{PH}_3]^+$  shows a similar polarization for this orbital (Figure 4b).

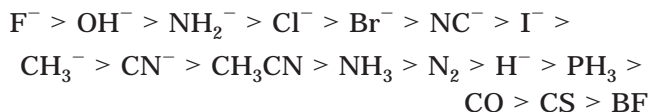
As the difference in the electronegativities of the atoms of a diatomic molecule increases along an iso-electronic series, the  $\pi^*$ -orbital gains more of the character of the atom with the smaller electronegativity. Thus, the trend in  $\pi$ -acceptor ability for the isoelectronic ligands in this series,  $\text{BF} > \text{CO} > \text{N}_2$ , is reflected in the energy differences,  $\Delta E_{\text{AB}}$ , by a decrease of about 10 kcal/mol for each ligand change from BF to  $\text{N}_2$ . However, unlike the other two ligands, the dinitrogen ligand is a sufficiently poor  $\pi$ -acceptor that the H-Ta-H bond angle distorts toward  $\text{PH}_3$ .

As the cyanide and isocyanide ligands are also poor  $\pi$ -acceptors, the hydrides prefer bending toward the phosphine. The greater ability of the isocyanide ligand to  $\pi$ -donate to the metal is reflected in its larger  $\Delta E_{\text{AB}}$ . The neutral  $\text{CH}_3\text{CN}$  ligand gives a structurally similar complex, but  $\Delta E_{\text{AB}}$  is reduced by  $\sim 13$  kcal/mol compared to  $\text{CN}^-$ .

**$[\text{Ta}(\text{OH})_2(\text{CH}_3)(\text{H})_2(\text{PH}_3)]$  and  $[\text{Ta}(\text{OH})_2(\text{NH}_3)(\text{H})_2(\text{PH}_3)]^+$ .** Both  $\text{CH}_3^-$  and  $\text{NH}_3$  have very weak  $\pi$ -donating abilities and differ mainly because the methyl anion is a strong  $\sigma$ -donor (covalent M-C bond) and the amine is a weak  $\sigma$ -donor (dative M-N bond). The hydride ligands in these complexes bend toward the phosphine, but the difference in magnitude of  $\Delta E_{\text{AB}}$  for these two ligands (methyl roughly double that of amine) suggests that the methyl group may hyperconjugate to allow  $\pi$ -donation to the metal. This hyperconjugation can also be viewed as an  $\alpha$ -agostic interaction.

**$[\text{Ta}(\text{OH})_2(\text{NH}_2)(\text{H})_2(\text{PH}_3)]$ .** The  $\text{NH}_2^-$  complex is the most compelling case for the  $\pi$ -donor argument. Two different cases were considered with this ligand:  $\text{NH}_2$  coplanar with hydrides and  $\text{NH}_2$  coplanar with hydroxides. In the former case, the lone pair on the  $\text{NH}_2^-$  ligand cannot affect directly the bond angle of the hydride ligand, as its  $p_\pi$ -orbital is coplanar with the hydroxide ligands. The difference in energy between isomer A and B for this case is only  $-4.64$  kcal/mol, roughly on the order of that for  $L' = \text{H}^-$ , a result indicative of only  $\sigma$ -effects. For the case where the  $\pi$ -orbital of the ligand can interact with the hydride ligands, the effect is so strong that isomer B is not found.

**Overall Trends.** Two series can be constructed from the results of this study. The first trend compares the energy differences of isomer A to isomer B for ligand  $L'$  relative to the phosphine ligand:



The above series can be described in terms of  $\pi$ -donor (acceptor) abilities of the ligands. The strongest  $\pi$ -donor ligands are to the left and their  $\pi$  donor abilities decrease across the series. The hydride ligand is at the crossover point between predominately  $\pi$ -donating ligands and predominately  $\pi$ -accepting ligands. The  $\pi$ -donor ligands push electron density into the  $d_{yz}$ -orbital and distort the vacant orbital away from the donating ligand, thus favoring isomer A. The  $\pi$ -accepting ligands

**Table 4. Tantalum-Phosphine Bond Distances in Decreasing Order for  $[\text{Ta}(\text{OH})_2\text{L}'(\text{H})_2\text{PH}_3]^+$**

$L'$	$d(\text{Ta}-\text{P}), \text{\AA}$	$L'$	$d(\text{Ta}-\text{P}), \text{\AA}$
$\text{CH}_3^-$	2.883	$\text{CN}^-$	2.763
$\text{H}^-$	2.839	$\text{F}^-$	2.760
$\text{NH}_2^-^c$	2.830	$\text{NC}^-$	2.743
$\text{NH}_2^d$	2.823	$\text{Cl}^-$	2.720
$\text{BF}$	2.822	$\text{Br}^-$	2.775
$\text{CS}$	2.813	$\text{I}^-$	2.712
$\text{PH}_3^a$	2.792	$\text{NH}_3$	2.704
$\text{Be}$	2.789	$\text{CH}_3\text{CN}$	2.686
$\text{OH}^-$	2.783	$\text{PH}_3^b$	2.682
$\text{CO}$	2.782	$\text{N}_2$	2.658

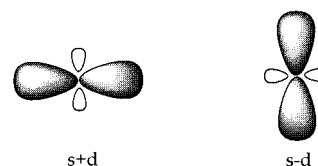
<sup>a</sup> Phosphine closest to hydrides in  $[\text{Ta}(\text{OH})_2(\text{H})_2(\text{PH}_3)_2]^+$ . <sup>b</sup> Phosphine farthest from hydrides in  $[\text{Ta}(\text{OH})_2(\text{H})_2(\text{PH}_3)_2]^+$ . <sup>c</sup> Ligand is coplanar with "trans" hydride ligands. <sup>d</sup> Ligand is coplanar with trans hydroxide ligands.

**Table 5. MP2 Relative Energies of Isomer A to Isomer B,  $\Delta E_{\text{AB}}$ , for Mixed Ligand Complexes  $[\text{Ta}(\text{OH})_2\text{L}'(\text{H})_2\text{L}]^+$**

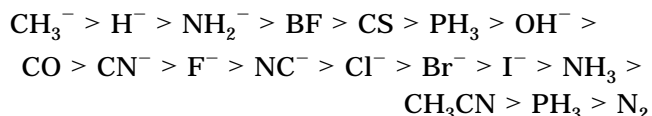
L	$L'$	$\Delta E_{\text{AB}}$ (kcal/mol)	L	$L'$	$\Delta E_{\text{AB}}$ (kcal/mol)
$\text{Cl}^-$	$\text{CO}$	30.40	$\text{CO}$	$\text{BF}$	10.14
$\text{Cl}^-$	$\text{NH}_3$	18.91	$\text{CN}^-$	$\text{NH}_3$	7.24
$\text{Cl}^-$	$\text{H}^-$	17.95	$\text{CN}^-$	$\text{H}^-$	6.43
$\text{NC}^-$	$\text{H}^-$	12.44	$\text{H}^-$	$\text{CO}$	4.79
$\text{CH}_3^-$	$\text{NH}_3$	11.53	$\text{H}^-$	$\text{NH}_3$	0.50
$\text{NH}_3$	$\text{CO}$	11.20	$\text{Cl}^-$	$\text{Br}^-$	0.41

polarize the  $d_{yz}$ -orbital toward the ligand, thus favoring isomer B.

The second trend involves the trans influence of the ligand  $L'$  compared to phosphine in the complex **1**. In the trans influence, we consider a linear combination of the metal s- and d-orbital ( $s+d$ ), which results in two orbitals with their large lobes perpendicular to one another.



For a pair of trans ligands ( $L$  and  $L'$ ), the ligand with the highest  $\sigma$ -donor strength bonds to the  $s+d$  linear combination, leaving the other ligand to form a weaker bond with the metal  $p_z$ -orbital, which results in a longer bond to the weaker  $\sigma$ -donor. In cases where the trans ligands ( $L$  and  $L'$ ) have very weak  $\pi$ -effects, the trans influence should indirectly affect the orientation of the hydride bond angle by influencing the direction of the  $\phi_{b_2}$  linear combination in eq 1. A  $\sigma$ -bonding ligand with a strong trans influence will push more electron density onto the metal and polarize the  $\pi$ -orbitals away from the strong  $\sigma$ -bond. The Ta-P bond distances (Table 4) can serve as a measure of the trans influence of these ligands, which are listed here in decreasing order:



Although one can recognize groups of ligands such as strong  $\sigma$ -donors,  $\pi$ -acceptors, and  $\pi$ -donors, there is no recognizable trend correlating this trans influence and

**Table 6. Structural Parameters at the MP2 Level for Minimum Energy Structures (Isomer B) for Mixed Ligand Complexes [Ta(OH)<sub>2</sub>L(H)<sub>2</sub>L']<sup>+</sup>**

L	L'	d(Ta-L), Å	d(Ta-L'), Å	d(Ta-O <sub>trans</sub> ), Å	d(Ta-H), Å	∠(H-Ta-H), deg	∠(O <sub>trans</sub> -Ta-O <sub>trans</sub> ), deg	∠(Ta-O <sub>trans</sub> -H), deg
Cl <sup>-</sup>	CO	2.422	2.273 (1.193)	1.898	1.786	130.8	175.7	172.0
H <sup>-</sup>	CO	1.818	2.389 (1.194)	1.899	1.794	130.5	174.3	164.8
NH <sub>3</sub>	CO	2.300	2.266 (1.189)	1.887	1.769	130.0	167.9	174.7
CO	BF	2.251 (1.300)	2.490 (1.188)	1.881	1.771	126.5	163.3	179.6
H <sup>-</sup>	NH <sub>3</sub>	1.831	2.437	1.908	1.799	135.0	170.9	157.4
CH <sub>3</sub> <sup>-</sup>	NH <sub>3</sub>	2.223	2.457	1.910	1.805	136.0	179.0	166.9
CN <sup>-</sup>	NH <sub>3</sub>	2.221 (1.238)	2.390	1.904	1.789	135.0	172.2	158.5
Cl <sup>-</sup>	NH <sub>3</sub>	2.437	2.353	1.905	1.791	136.6	179.7	162.0
CN <sup>-</sup>	H <sup>-</sup>	2.386 (1.242)	1.827	1.933	1.792	132.2	159.4	143.2
NC <sup>-</sup>	H <sup>-</sup>	2.303 (1.237)	1.820	1.928	1.791	132.7	158.0	143.0
Cl <sup>-</sup>	H <sup>-</sup>	2.674	1.807	1.928	1.796	134.0	158.2	139.8
Cl <sup>-</sup>	Br <sup>-</sup>	2.466	2.823	1.921	1.784	137.0	177.2	153.0

$\Delta E_{AB}$ , a result that implies that the direction of the distortion (isomer A or B) depends heavily on the  $\pi$ -effects.

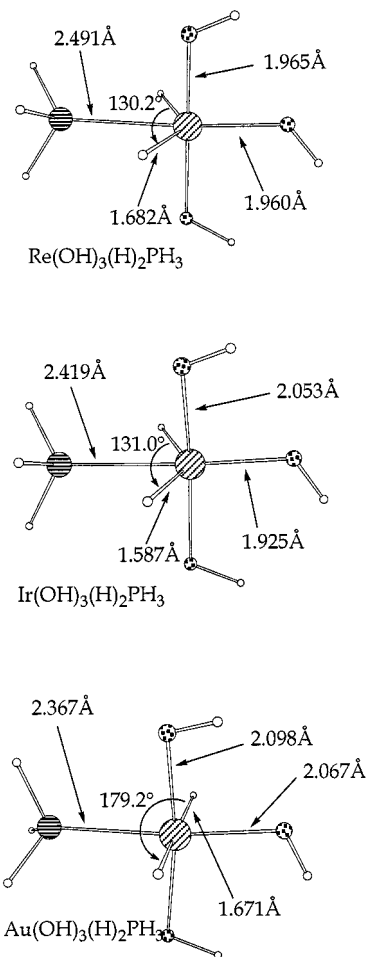
**Mixed Ligands.** By selecting pairs of ligands, we can test the above conclusions by calculating the geometries and relative energies of these mixed ligand complexes. The two ligands are oriented trans to one another with one of the ligands (L) replacing the phosphine. The results of these calculations are given in Tables 5 ( $\Delta E_{AB}$ ) and 6 (geometric parameters).

We find that in most cases the hydrides bend toward the stronger  $\pi$ -acceptor given by the  $\Delta E_{AB}$  series.<sup>18</sup> This prediction works well for pairs of ligands chosen from either end of this series. For example, in the Cl<sup>-</sup>/Br<sup>-</sup> complex the hydrides bend toward Br<sup>-</sup>, in the CO/BF complex they bend toward BF, and in the CO/Cl<sup>-</sup> complex they bend toward CO. Generally, it was observed that in cases where one ligand has  $\pi$ -effects and one does not, the effects due to the  $\pi$ -ligand dominate. For the H<sup>-</sup>/CO and NH<sub>3</sub>/CO complexes, the trans hydrides distorted toward CO due to its  $\pi$ -acceptor ability. In the Cl<sup>-</sup>/H<sup>-</sup> complex the trans hydrides bend toward the remaining hydride because the  $\pi$ -donor ability of chloride polarizes the b<sub>2</sub> orbital away from it. As an experimental example, the hydrides in Os(H)<sub>3</sub>-Cl(P<sup>i</sup>Pr)<sub>2</sub> bend toward the third (axial) hydride ligand.<sup>19</sup>

When ligand pairs were chosen from the weak  $\pi$ -effect ligands, the results were not as predictable. In the case of CH<sub>3</sub><sup>-</sup>/NH<sub>3</sub> the trans hydrides bend toward the NH<sub>3</sub> as expected from the comparison with PH<sub>3</sub>. However, the NH<sub>3</sub>/H<sup>-</sup> pair does not reproduce the expected trend, i.e., the "trans" hydrides bend toward NH<sub>3</sub> rather than H<sup>-</sup>. Because the ligand trends were calculated originally with respect to the phosphine ligand, which has some  $\pi$ -accepting ability, the  $\Delta E_{AB}$  trends could be masking the  $\sigma$ -donating effects of ligands with weak  $\pi$ -effects. For ligands with only  $\sigma$ -effects (weak  $\pi$ -effects), we can look to the trend for the trans influence. For these  $\sigma$ -only ligands, the hydrides should bend

(18) It is also notable that the difference in the relative energies listed for the phosphine ligands is generally a good estimate of the relative energies in the mixed complex. Errors were found to be roughly 3 kcal/mol between the estimated and calculated energy difference.

(19) Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.



**Figure 5.** Selected structural parameters for [M(OH)<sub>3</sub>(H)<sub>2</sub>PH<sub>3</sub>], M = Re, Ir, Au, calculated at the MP2 level. Distances are given in angstroms (Å).

toward the ligand with the smallest trans influence, NH<sub>3</sub> for the NH<sub>3</sub>/H<sup>-</sup> case.

**Other Metals.** Calculations were also performed on the trihydroxide complex [M(OH)<sub>3</sub>(H)<sub>2</sub>(PH<sub>3</sub>)] with metals other than Ta. The geometries for these complexes optimized at the MP2 in pseudo-C<sub>2v</sub> symmetry are shown in Figure 5. In the Re(V) complex (d<sup>2</sup>, 14e<sup>-</sup>), the extra pair of electrons occupies the 5d<sub>xz</sub> orbital. There

is little effect on the hydride bonding, but the trans hydroxide ligands become bent due to the reduced ability of the metal to accept  $\pi$ -donation. The M–O<sub>trans</sub> bond order roughly drops to 1.5. If  $C_{2v}$  symmetry is maintained, the iridium(V) complex ( $d^4$ ,  $16e^-$ ) has the  $5d_{xy}$  and  $5d_{xz}$  orbitals occupied with little effect on the orientation of the hydride ligands. However, this complex is not a minimum on the potential energy surface. The optimized minimum is similar to that of the Mo and W  $d^4$ -complexes discussed by Kubáček and Hoffmann.<sup>20</sup> The gold(V) complex ( $d^6$ ,  $18e^-$ ) is a pseudo-octahedron with a  $179.2^\circ$  H–M–H bond angle. Here, the complete occupation of the pseudo- $t_{2g}$  orbitals of the metal forces the  $b_2$  metal–hydride bonding orbital to be constructed from the  $6p_y$  metal orbital. This result demonstrates a condition under which hydrides may be trans to one another, as the unoccupied low-lying d-orbitals required for PSOJT are not present. The results from the Re, Ir, and Au complexes indicate that the observed H–Ta–H angle (but not the direction of the angle) is an intrinsic property of these complexes, due to the d-occupancy of the metal, and not a result of the ligand characteristics. The direction of the angle and the relative stability of isomers A and B are a result of the ligand characteristics.

### Conclusions

Theoretical calculations have been used to show that the direction of the unusual distortion of the “trans”

(20) Kubáček, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320.

hydride ligands toward a bulky phosphine group in a series of tantalum complexes is due primarily to the  $\pi$ -donor (acceptor) properties of the ligands rather than their  $\sigma$ -bonding properties. The hydride ligands are shown to bend toward the stronger  $\pi$ -acceptor and away from the strongest  $\pi$ -donor. In cases where the ligands have weak  $\pi$ -effects, the distortion of the hydrides is determined by the ligand with the strongest trans influence and the hydrides bend toward the weaker  $\sigma$ -donor. A series constructed from calculations on a variety of ligands can be used to predict the orientation of the hydride ligands in similar complexes where ligands other than phosphine are used. In particular, complexes such as  $[\text{Ta}(\text{OR})_2(\text{PR}'_3)(\text{H})_2(\text{PR}''_3)]^+$  and  $[\text{Ta}(\text{OR})_2(\text{H})_3(\text{NR}'_3)]$  would be very interesting to study experimentally, as both complexes have isomers (A and B) of similar enough energy that variations of the substituents could result in direct observation of both isomers. The trihydride has a significantly larger dipole moment for the isomer in which the “trans” hydrides are bent toward the third hydride. Thus, variations in solvent polarity could influence the relative stability of these two isomers.

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