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Communications

The Structure of d^0 ML_6 Complexes

In a study of the driving force for agostic bonding, one of us put forth[1] the idea that certain d^0 ML_6 complexes were unstable at an octahedral geometry. Extended Hückel calculations on TiH_6^{2-} and other molecules found that distortions away from an octahedral geometry were in fact stabilizing. This was challenged in a recent communication[2] by Cameron, Fitzgerald, and Zerner on the basis of INDO and ab initio calculations for TiH_6^{2-}. The octahedral geometry was found to be more stable than a C_{2v} variant, one of the distortion modes originally considered;[1] however, the potential was soft when correlation was included at the second-order Møller-Plesset (MP2) level. In this communication we report ab initio calculations on TiH_6^{2-}, CrH_6, and CrF_6 at the MP2 and full MP4 levels.

The central thesis that certain d^0 ML_6 complexes will distort from an octahedral geometry is derived from potential second-order Jahn–Teller forces that serve to mix the t_{1u} HOMO with the t_{2g} LUMO in these molecules. The normal modes available to do this are of t_{2u} and t_{1u} symmetry. Perhaps the most simple t_{2u} deformation is rotation about one 3-fold axis to yield a trigonal-prismatic, D_{3h}, geometry. As shown in Figure 1, this stabilizes two members of the filled t_{1u} set.[3] A further pyramidization from D_{3h} to C_{3v} geometry couples the filled a_2'' and empty a_1' orbitals, stabilizing the former. This is, of course, but one of the *multiple* distortions available to an octahedral system. Many d^2 complexes have structures along the $O_h \rightarrow D_{3h}$ path.[4] A number of d^4 molecules are distorted in a C_{2v} sense.[5] What is intriguing about the d^0 case is that with a spherically symmetrical field at the metal, VSEPR and crystal field arguments clearly favor an octahedral arrangement of ligands. The C_{3v} and D_{3h} geometries are sterically much more demanding than O_h.[6]

We emphasize that *some* d^0 ML_6 compounds will remain octahedral. The necessary conditions for distortion are 3-fold: First, for obvious steric reasons the ligands must not be bulky. Second, the t_{2g}–t_{1u} energy gap should be small since the stabilization afforded to the t_{1u} set is inversely dependent upon this energy difference.[7] In a one-electron sense, there are several lower lying orbitals that are destabilized along the distortion modes given in Figure 1, and these serve as a breaking force for the distortion. A small t_{2g}–t_{1u} energy gap is favored when the ligands are strong σ donors, the ligands possess little or no π-donating capability, and the metal is not too electropositive.[1] Third, the metal–ligand bond should be covalent. An extreme, ionic case simply reduces to a point charges on a sphere problem. The mixing of t_{2g} into t_{1u} serves to increase the overlap (or covalency) in the M–L bond.[1] With these factors in mind we proceed to CrF_6, TiH_6^{2-}, and CrH_6.

The ab initio calculations[8] were carried out with two basis sets. The first, referred to as basis I, started with Huzinaga's (4333/43/4) primitive set[9] for Ti and Cr. The d along with 4s and augmented 4p functions were replaced by ones optimized for molecular environments[10,11] to yield a basis of the form (4333/433/31). Standard 4-31G basis sets for H and F were used.[12,13] Basis II used a Wachters basis[14] for the metal, where the primitive d functions were replaced with an optimized (411) set[10] and the 4s/4p functions were replaced with an augmented set.[11,15] The H atoms used a 6-311 G** basis.[13,16]

With use of basis I at the Hartree–Fock (HF) level, the optimized structure for TiH_6^{2-} with an O_h geometry was found to be in good agreement with that reported by Cameron, Fitzgerald, and Zerner.[2] A stationary point for a C_{3v} structure was not found; the geometry collapsed to D_{3h}. A summary of the geometries and energies for all systems in this study is reported in Table I. The O_h structure was found to be 10.7 kcal/mol more stable than the D_{3h} structure. Using Cameron, Fitzgerald, and Zerner's DZP basis,[2] we find essentially the same result with the O_h geometry to be 8.0 kcal/mol more stable than the optimized D_{3h} one.[17] With

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[1] Demolliens, A.; Jean, Y.; Eisenstein, O. *Organometallics* **1986**, *5*, 1457.

[2] Cameron, A. D.; Fitzgerald, G.; Zerner, M. C. *Inorg. Chem.* **1988**, *27*, 3439.

[3] Hoffmann, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484.

[4] (a) Kepert, D. L. *Prog. Inorg. Chem.* **1977**, *1*, 23. (b) Wentworth, R. A. D. *Coord. Chem. Rev.* **1972**, *9*, 171. (c) For theoretical calculations on some of these deformations, see: Nieke, C.; Reinhold, J. *J. Mol. Struct.* **1985**, *124*, 87.

[5] Kubáček, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320.

[6] McDowell, H. K.; Chiu, H.-L.; Geldard, J. F. *Inorg. Chem.* **1988**, *27*, 1674.

[7] Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

[8] (a) Dupuis, M.; Spangler, D.; Wendoloski, J. J. *National Resource for Computations in Chemistry Software Catalog 1980*; Vol. 1, Program QG01, as modified by M. W. Schmidt and S. T. Elbert. (b) Binkley, J. S.; Frisch, M.; Raghavachari, K.; Fluder, E.; Seeger, R.; Pople, J. A. "GAUSSIAN 82"; Carnegie-Mellon University: Pittsburgh, PA, 1982.

[9] Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatawaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

[10] Rappe, A. K.; Smedley, T. A.; Goddard, W. A., III. *J. Phys. Chem.* **1981**, *85*, 2607.

[11] Pietro, W. J.; Hehre, W. J. *J. Comput. Chem.* **1983**, *4*, 241.

[12] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

[13] A diffuse s function with an exponent of 0.036 was added to the hydrogens for the TiH_6^{2-} calculations; see: Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294. All computations on this molecule had negative eigenvalues for the occupied orbitals with both basis sets.

[14] Wachters, A. J. H. *J. Chem. Phys.* **1977**, *52*, 1033.

[15] Additional 4s/4p functions were added with an exponent of 0.06. The metal basis then is of the form (62111131/511231/411).

[16] Krishman, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

[17] The optimal D_{3h} structure is one with r_1 = 1.83 Å and $\theta = 51.2°$. The vibrational frequencies calculated at the O_h geometry by using this basis are all real; however, the t_{2u} set is quite small (374 cm^{-1}).

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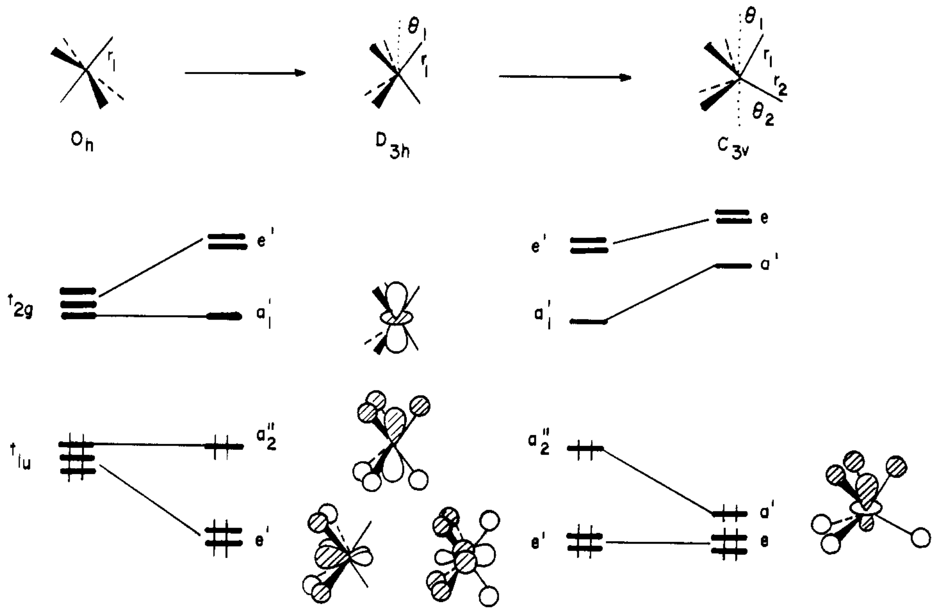

Figure 1. Orbital correlation diagram for a trigonal twist from an O_h to a D_{3h} geometry and pyramidization to a C_{3v} structure.

Table I. Summary of the Geometries and Energies with Basis I

molecule	geometry[a] r_1	r_2	θ_1	θ_2	method	total energy[b]	rel energy[c]
TiH_6^{2-} O_h	1.85				HF	−850.743 68	0
D_{3h}	1.84		51.2		HF	−850.726 64	10.7
O_h	1.86				MP2	−851.033 75	1.3
D_{3h}	1.84		51.2		MP2	−851.035 79	0.0
CrH_6 O_h	1.69				MP2	−1045.463 51	155.3
D_{3h}	1.58		43.9		MP2	−1045.679 57	19.7
C_{3v}	1.52	1.55	36.8	75.1	MP2	−1045.711 03	0.0
CrF_6 O_h	1.71				MP2	−1639.087 79	0.0
D_{3h}	1.73		50.6		MP2	−1639.058 31	18.5

[a] The geometrical parameters are defined in Figure 1; *r* values are in angstroms and θ values in degrees. [b] Total energies are listed in hartrees. [c] Relative energies are listed in kcal/mol.

use of basis II, this energy difference is 9.1 kcal/mol (see Table II). Including correlation reverses this prediction. The optimized structure for the D_{3h} geometry is 1.3 kcal/mol more stable than the O_h structure at the MP2 level with basis I and 3.2 kcal/mol with basis II. This difference is increased further to 9.2 kcal/mol at the full fourth-order Møller–Plesset (MP4) level with basis II. Thus, the relative energies appear to be sensitive to the level of correlation.

The situation for CrH_6 is more striking. Stationary points for O_h, D_{3h}, and C_{3v} geometries were located (Table I), and the relative stabilities increase in the order given. The C_{3v} structure is computed to be 174.6 kcal/mol more stable than the O_h one at the MP4 level with basis II (Table II)! In fact, both the O_h and D_{3h} geometries are higher order saddle points, while the C_{3v} structure is a local minimum on the potential energy surface for CrH_6.[18]

To show that trigonal-prismatic or C_{3v} structures are not an artifact of the basis sets or methods used, we have also carried out optimizations of CrF_6 with basis I at the MP2 level. Again, starting from C_3 or C_{3v} geometries resulted in collapse to a D_{3h} structure that was 18.5 kcal/mol higher in energy than the O_h structure. While CrF_6 is a known molecule, its instability has frustrated a precise determination of the structure (an octahedral geometry was found in an Ar matrix).[19] However, a large number of d^0 MX_6 molecules, and this includes MoF_6,[20] WF_6 in the gas and solid states,[21] and the isoelectronic TiF_6^{2-} in three different crystalline environments,[22] are octahedral.[23,24]

Table II. Summary of the Energies with Basis II[a]

molecule	method	total energy[b]	rel energy[c]
TiH_6^{2-} O_h	HF	−851.585 22	0.0
D_{3h}	HF	−851.570 65	9.1
O_h	MP2	−851.789 07	3.2
D_{3h}	MP2	−851.794 16	0.0
O_h	MP4	−851.837 82	9.2
D_{3h}	MP4	−851.852 42	0.0
CrH_6 O_h	MP2	−1046.446 46	158.9
D_{3h}	MP2	−1046.658 06	26.1
C_{3v}	MP2	−1046.699 75	0.0
O_h	MP4	−1046.496 68	174.6
D_{3h}	MP4	−1046.747 08	17.5
C_{3v}	MP4	−1046.774 89	0.0

[a] The geometries used were taken from the optimized structures at the basis I/MP2 level. [b] Total energies are listed in hartrees. [c] Relative energies are listed in kcal/mol.

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(18) The calculated frequencies at the MP2 level with basis I were computed to be all real for the C_{3v} geometry, the D_{3h} geometry had e′ and a_2'' imaginary frequencies, and the t_{1u} and t_{2u} frequencies for the octahedral geometry were imaginary.

(19) Hope, E. G.; Jones, P. J.; Levason, W.; Ogden, J. S.; Tajik, M.; Turff, J. W. *J. Chem. Soc., Dalton Trans.* **1985**, 1443.

(20) (a) Levy, J. H.; Spanger, P. L.; Taylor, J. C.; Wilson, P. W. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1065. (b) Levy, J. H.; Taylor, J. C.; Wilson, P. W. *Ibid.* **1975**, *B31*, 398. (c) Siegel, S.; Northrop, D. A. *Inorg. Chem.* **1966**, *5*, 2187.

(21) (a) Kimura, M.; Schomaker, V.; Smith, D. W.; Weinstock, B. *J. Chem. Phys.* **1968**, *48*, 4001. (b) Levy, J. H.; Taylor, J. C.; Wilson, P. W. *J. Solid State Chem.* **1975**, *15*, 360; *J. Less-Common Met.* **1974**, *45*, 155.

The diversity of behavior offered by these three d^0 ML_6 complexes is easily accommodated by the ideas presented previously. In CrH_6 the ligands are strong σ donors and the bonding is reasonably covalent. The fluorine ligands in CrF_6 are much weaker σ donors (and have some π-donating capability) hence, a return to an octahedral structure is favored. Notice in Table I that the optimized Cr–H bond lengths are much shorter at the C_{3v} (or D_{3h}) geometry than at O_h, in agreement with our idea that a distortion from O_h symmetry will lead to larger M–L overlap. Exactly the reverse is seen for CrF_6, where the bonding is much more ionic. The situation for TiH_6^{2-} is intermediate. Certainly Ti is more electropositive than Cr and the bonding in TiH_6^{2-} is more ionic than in CrH_6.[25] Thus, deformation all the way to C_{3v} is not favored. However, our computations at the highest level point to a D_{3h} geometry being more stable than an O_h one, contrary to a previous assertion.[2] We have recently been informed[26] that the X-ray structure of the related $ZrMe_6^{2-}$ molecule has been completed and that it is indeed trigonal prismatic, in accord with our computations on TiH_6^{2-}. A study of the full potential energy surfaces for these and other d^0 ML_6 molecules will be forthcoming.

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(22) (a) Kojić-Prodić, B.; Matković, B.; Šćavničar, S. *Acta Crystallogr., Sect. B* **1971**, *B27*, 635. (b) Golič, L.; Kaučič, V.; Kojić-Prodić, B. *Ibid.* **1980**, *B36*, 659.

(23) (a) Willing, W.; Müller, U. *Acta Crystallogr., Sect. C* **1987**, *C43*, 1425. Müller, U. *Acta Crystallogr., Sect. A* **1979**, *A35*, 188. (b) Taylor, J. C.; Wilson, P. S. *Acta Crystallogr., Sect. B* **1974**, *B30*, 1216. (c) Smith, D. K.; Landingham, R. L.; Smith, G. S.; Johnson, Q. *Ibid.* **1968**, *B24*, 1563. (d) Schmidbauer, H.; Pichl, R.; Müller, G. *Z. Naturforsch.* **1986**, *41B*, 395.

(24) Ab initio calculations using pseudopotentials on CrF_6, MoF_6, and WF_6 optimized at the O_h geometry have recently been reported; see: Miyoshi, E.; Sakai, Y.; Murakami, A.; Iwaki, H.; Terashima, H.; Shoda, T.; Kawaguchi, T. *J. Chem. Phys.* **1988**, *89*, 4193.

(25) This is borne out from a Mulliken population analysis of TiH_6^{2-} and CrH_6 at either basis set level.

(26) Morse, P. M.; Girolami, G. S. Submitted for publication.

Department of Chemistry
Chungnam National University
Daejeon, 301-764 Korea
Sung Kwon Kang

Department of Chemistry
University of Houston
Houston, Texas 77204-5641
Thomas A. Albright*

Laboratoire de Chimie Theorique
Bâtiment 490
Université de Paris-Sud
91405 Orsay Cedex, France
Odile Eisenstein

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Binuclear Polyhydrides of Tantalum. Reductive Desulfurization of a Bridging Thioether Ligand and Formation of a $Ta_2(\mu\text{-S})$ Unit. X-ray Crystal Structure of $[\{Pr^i_2P(CH_2)_3PPr^i_2\}TaHCl]_2(\mu\text{-S})(\mu\text{-H})_2$

Pentahydride complexes of tantalum of the type TaH_5P_4 (P_2 = dmpe[1a] and P = PMe_3[1b]) are members of a large family of phosphine-stabilized polyhydride complexes having the formula MH_xP_y. Other members of this family include WH_6P_3,[2a] WH_4P_4,[2b] ReH_7P_2,[2c] ReH_5P_3,[2d] OsH_4P_3,[2e] IrH_3P_3,[2f] and IrH_5P_2;[2g] the stoichiometry of these complexes is dependent on the method of preparation, the size of the phosphine ligand, and the amount of the phosphine present. A characteristic feature of all of these systems is that they are coordinatively saturated, and thus any reactivity by these complexes must be preceded by either phosphine dissociation[3] or loss of H_2.[4] In an effort to induce coordinative unsaturation, we have examined the effect of bulky, chelating bidentate phosphines as a possible strategy to make these complexes phosphine deficient. In this paper we describe an approach we have used in an attempt to generate polyhydrides of tantalum stabilized by only two phosphine donors per tantalum. However, the success of the reaction depends critically on the choice of starting material.

As a starting point, the ability to oxidatively add H_2 to low-valent binuclear Ta(III) complexes[5] appeared attractive. Since the binuclear Ta(III) complex $Ta_2Cl_6(SMe_2)_3$ (**1**) has been reported[6] to be a precursor to low-valent, bioctahedral complexes containing chelating diphosphine ligands, we examined simple displacement reactions of **1**. However, reaction of **1** with the bulky, chelating ligand 1,3-bis(diisopropylphosphino)propane (dippp) does not go to completion even at high temperatures and results in impure complexes having the approximate formula $[(\text{dippp})TaCl_2]_2(\mu\text{-}SMe_2)(\mu\text{-Cl})_2$ with dangling phosphines[7] (by $^{31}P\{^1H\}$ NMR spectroscopy). An alternative synthesis was attempted. The Na/Hg reduction of $Ta_2Cl_6(SMe_2)_3$ in the presence of 2 equiv of dippp under 4 atm of H_2 provided air-sensitive, black crystals in 70% yield. One recrystallization from toluene at −30 °C provided an analytically pure sample[8] of a material having the formula $(\text{dippp})_2Ta_2H_4Cl_2S$ (**2**). The $^{31}P\{^1H\}$ NMR spectrum[9] at 25 °C shows two doublets at 18.8 and 15.6 ppm with some fine structure, indicating that two inequivalent, coordinated phosphines are present. The ^1H NMR spectrum[10] of **2** shows a broad triplet at 12.4 ppm and a broad multiplet at 7.7 ppm, both integrating for two protons, which we attribute to two bridging and two terminal hydrides respectively; both of these resonances are absent in the deuterium analogue $(\text{dippp})_2Ta_2D_4Cl_2S$ (**2**-d_4). The IR spectrum of **2** (KBr disk) shows two strong broad bands at 1759 and 1553 cm^{-1} that shift to 1263 and 1114 cm^{-1}, respectively, for **2**-d_4.

The solid-state structure[11] of **2** (Figure 1a) shows that there

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(1) (a) Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 5823. (b) Tebbe, F. N. U.S. Patent 3 933 876, Jan 20, 1976.

(2) (a) Moss, J. R.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1968**, 632. (b) Bell, B.; Chatt, J.; Leigh, G. J.; Ito, T. *J. Chem. Soc., Chem. Commun.* **1972**, 34. (c) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963. (d) Chatt, J.; Coffey, R. S. *J. Chem. Soc., Chem. Commun.* **1966**, 545. (e) Douglas, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1969**, 624. (f) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1970**, 846. (g) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1970**, 703.

(3) Muralidharan, S.; Ferraudi, G.; Green, M. A.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *244*, 47.

(4) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663.

(5) Sattelberger, A. P.; Wilson, R. B., Jr.; Huffman, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7113.

(6) Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Inorg. Chem.* **1983**, *22*, 375.

(7) Similar complexes containing dangling chelating ligands have been observed: Canich, J. M.; Cotton, F. A. *Inorg. Chem.* **1987**, *26*, 3473.

(8) Anal. Calcd for **2**, $Ta_2SP_4Cl_2C_{30}H_{72}$: C, 35.27; H, 7.10; Cl, 6.94; S, 3.14. Found: C, 34.99; H, 7.10; Cl, 6.98; S, 3.28.

(9) $^{31}P\{^1H\}$ NMR measurements were recorded at 121.4 MHz on a Varian 300 XL spectrometer. Chemical shifts (δ) are in ppm from external $P(OMe)_3$ set at 141.0 ppm.

(10) ^1H NMR for **2** (C_6D_6, ppm): H_b, 12.39 (br t, 2, J_{PH} = 48 Hz); H_t, 7.70 (br m, 2); ligand resonances, $PCHMe_2$, 2.82 (overlapping d of sept, 2); $PCHMe_2$, 2.55 (overlapping d of sept, 2); $PCHMe_2$, 2.06 (overlapping d of sept, 4); 1.64–1.03 (m, 60).

(11) Black crystals of **2** were grown from concentrated THF/hexanes solutions at −30 °C. $[(\text{dippp})TaHCl]_2(\mu\text{-S})(\mu\text{-H})_2$ crystallizes in the monoclinic space group $P2_1/c$, a = 10.730 (2) Å, b = 15.653 (2) Å, c = 13.402 (3) Å, β = 110.78 (2)°, ρ_c = 1.61 g cm^{-3} and Z = 2. The structure was solved by conventional heavy-atom methods and was refined by successive difference Fourier map calculations to $R = 0.0614$ and $R_w = 0.0665$ for 2365 absorption-corrected reflections with $F_o^2 > 3\sigma F_o^2$. Hydrogen atoms were placed in idealized positions during the final refinement. All non-hydrogen atoms were refined anisotropically. Data were collected at 24 °C on a four-cycle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation.

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