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

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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]

(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.

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 $[(dippp)\text{-}TaCl_2]_2(\mu\text{-}SMe_2)(\mu\text{-}Cl)_2$ 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 $(dippp)_2Ta_2H_4Cl_2S$ (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 $(dippp)_2Ta_2D_4Cl_2S$ (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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(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. $[(dippp)TaHCl]_2(\mu\text{-}S)(\mu\text{-}H)_2$ 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.

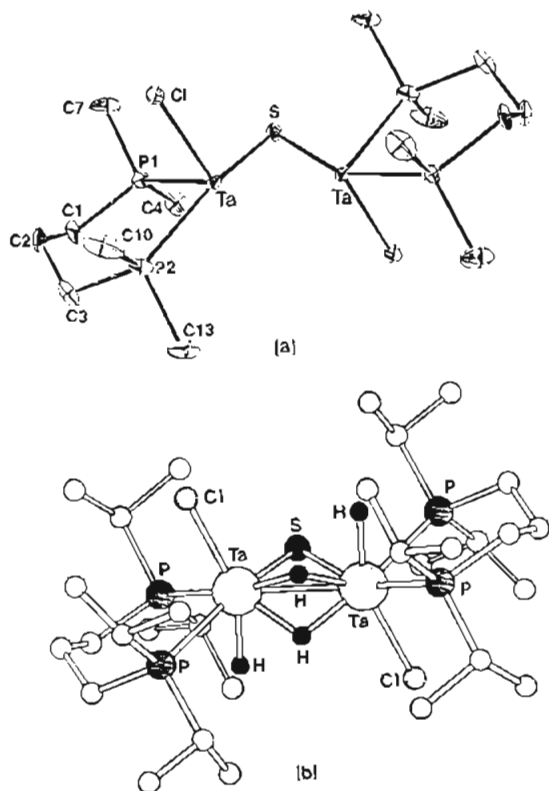**Figure 1.** (a) Molecular structure of [(dippp)TaHCl]$_2$(μ-S)(μ-H)$_2$, **2**. The S atom, which bridges symmetry related Ta atoms, was found to occupy two locations each with 50% site occupancy. Thus the model has a center of symmetry. Only one site occupied by the μ-S is shown. Hydrogen and methyl carbon atoms on the diphosphine ligand have been omitted for clarity. Thermal ellipsoids as drawn represent 10% probability surfaces. Selected bond distances (Å): Ta–Ta, 2.689 (1); Ta–Cl, 2.409 (3); Ta–P1, 2.616 (3); Ta–P2, 2.613 (3); Ta–S, 2.539 (5). Selected angles (deg): Ta–S–Ta, 64.1 (2); S–Ta–P2, 159.4 (1); S–Ta–Cl, 103.0 (2); P2–Ta–P1, 90.1 (1); S–Ta–P1, 75.5 (1). (b) Side view of **2** using Chem 3D showing the likely positions of the bridging and terminal hydrides. The hydrides were placed at a distance of 1.80 Å from the tantalum centers. Hydrogen atoms on the ligand are omitted for clarity.

are two (dippp)TaCl units bridged together by a sulfido ligand. Although the hydrides did not appear in the final difference Fourier analysis, their probable positions are indicated in Figure 1b. The diphosphine ligands lie above and below the plane defined by the two tantalums and the bridging sulfide ligand. The Ta–Ta single bond distance of 2.689 (1) Å is consistent with the presence of two bridging hydrides as is the compressed Ta–S–Ta angle of 64.1 (2)°. The terminal hydrides were placed in the cavity opposite the chlorides. Although the ends of the molecule are related by a C_2 axis (through the S in the Ta$_2$S plane), each phosphorus donor of a particular diphosphine is inequivalent, being either transoid (S–Ta–P2, 159.4 (1)°) or cisoid (S–Ta–P1, 75.5 (1)°) to the bridging sulfide. The solution NMR spectral parameters mentioned above are temperature independent from −80 to +80 °C and are in accord with the solid-state structure.

The formation of [(dippp)TaHCl]$_2$(μ-S)(μ-H)$_2$ (**2**) from **1** involves conversion of a bridging Me$_2$S ligand to a bridging sulfide; analysis of the headspace gas indicates the formation of CH$_3$CH$_3$, and no detectable CH$_4$ (by GCMS). The fact that sulfur–carbon

bond cleavage by group 5 metals is known,[12] combined with the above result, might suggest that complexes having μ-SR$_2$ ligands are unsuitable for accessing polyhydride tantalum complexes,[13] at least by reduction. However, we find that the related tris-(tetrahydrothiophene) complex, Ta$_2$Cl$_6$(THT)$_3$[14] (**3**), can be reduced in a manner analogous to that described above, to generate the binuclear hexahydride [(dippp)TaH$_2$]$_2$(μ-H)$_2$ (**4**) in 40% yield.[15,16] Although we have been unable as yet to grow single crystals of this hexahydride, a hydride-bridged, edge-sharing bioctahedral structure[17] is suggested based on spectral data. In particular, the ^{1}H NMR spectrum[18] consists of a broad triplet at 11.2 ppm of area 2 and a broad singlet at 6.4 ppm of area 4; the resonances for the ligand are typical of a very symmetrical structure as is the singlet at 45.3 ppm in the ^{31}P{^{1}H} NMR spectrum.[9] The IR spectrum (KBr disk) has a medium, broad band at 1739 cm^{-1} and a medium band at 1118 cm^{-1} which shift to 1237 cm^{-1} and 795 cm^{-1} in the hexadeuterio complex. Interestingly, no exchange of the bridging and terminal hydrides of **4** is observed by ^{1}H NMR spectroscopy even at 80 °C.

4   R = Pr^i
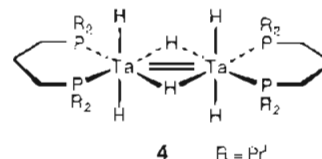
The difference in reactivity between the two bridging thioether complexes of Ta(III) is possibly related to the size of the μ-SR$_2$ ligand. The smaller μ-SMe$_2$ moiety may be more firmly bound to the two tantalum centers than the μ-THT moiety at some critical step in the reduction. How the ethane forms is not known but suggests that this a complex reaction. Full details on the reactivity of these and other coordinatively unsaturated binuclear polyhydrides of Ta will be reported in due course.

Supplementary Material Available: Tables of crystallographic parameters, final positional and anisotropic thermal parameters of non-hydrogen atoms, calculated hydrogen coordinates and isotropic thermal parameters, bond lengths, and bond angles (7 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(14) Templeton, J. L.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 2293.
(15) Anal. Calcd for **4**, Ta$_2$P$_4$C$_{30}$H$_{74}$: C, 39.14; H, 8.10. Found: C, 39.01; H, 8.00.
(16) Better yields of this and other binuclear tantalum polyhydride derivatives can be obtained by the direct reduction of TaCl$_5$ by excess Na/Hg in the presence of a bulky chelating diphosphine under 4 atm of H$_2$.
(17) Cotton, F. A. *Polyhedron* **1987**, *6*, 667.
(18) ^{1}H NMR for **4** (C$_6$D$_6$, ppm): H$_b$, 11.24 (br t, 2, J_{PH} = 55 Hz); H$_t$, 6.42 (br s, 4); ligand resonances, PC*H*Me$_2$, 2.02 (d of sept, 8); 1.56–1.04 (m, 60).

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