Development of Low-Valent Tantalum Chemistry: Syntheses and X-ray Structures of $TaCl_2(PMe_3)_4$, $TaCl_2H_2(PMe_3)_4$, and $TaClH_2(PMe_3)_4$[1]

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The chemistry of the lower oxidation states of niobium and tantalum has undergone a renaissance in the past 3 years, highlighted by new examples of (1) reactive metal-metal multiple bonds,[3] (2) selective olefin polymerization catalysis,[4] (3) μ-dinitrogen complexes,[5] (4) carbon monoxide activation,[6] (5) η^2-CO_2 chemistry,[7] and (6) zerovalent bis(arene) compounds.[8] These are encouraging developments in a long neglected area,[9] but there is still much to be learned about the synthesis, physiochemical properties, and reactivity of both mononuclear and polynuclear complexes in which the formal oxidation states of these metals range between −3[10] and +4. The present work on the rare +2, +3, and +4 oxidation states of tantalum was undertaken with these objectives in mind.

Reduction of tantalum pentachloride with 3 equiv of sodium amalgam in ether containing excess (6–8 equiv) trimethylphosphine gave, after filtration, solvent removal, and recrystallization from toluene (−40 °C), brown air-sensitive crystals[11] of the paramagnetic[12] tantalum(II) monomer $TaCl_2(PMe_3)_4$, **1**, in 60–70% yield (eq 1). A trans-octahedral geometry was tentatively

$$TaCl_5 + 3Na/Hg + PMe_3(\text{excess}) \xrightarrow{OEt_2} \underset{\mathbf{1}}{TaCl_2(PMe_3)_4} + 3NaCl \quad (1)$$

assigned on the basis of a single broad ($\Delta\nu_{1/2}$ = 14 Hz) PMe_3 resonance at δ 1.98 in the proton NMR spectrum of **1** (benzene-d_6) and subsequently confirmed by X-ray crystallography.[13] An ORTEP drawing of **1** is shown in Figure 1 (top). **1** has crystallographically imposed D_{2d} symmetry, and its PMe_3 ligands are alternately puckered about the idealized equatorial plane by ca. ±10°.[14] The Ta–Cl2 and Ta–P3 distances are 2.464 (3) and 2.543 (2) Å, respectively. **1** is only the second reported complex of tantalum(II)[15] and the first for which structural data have been obtained.

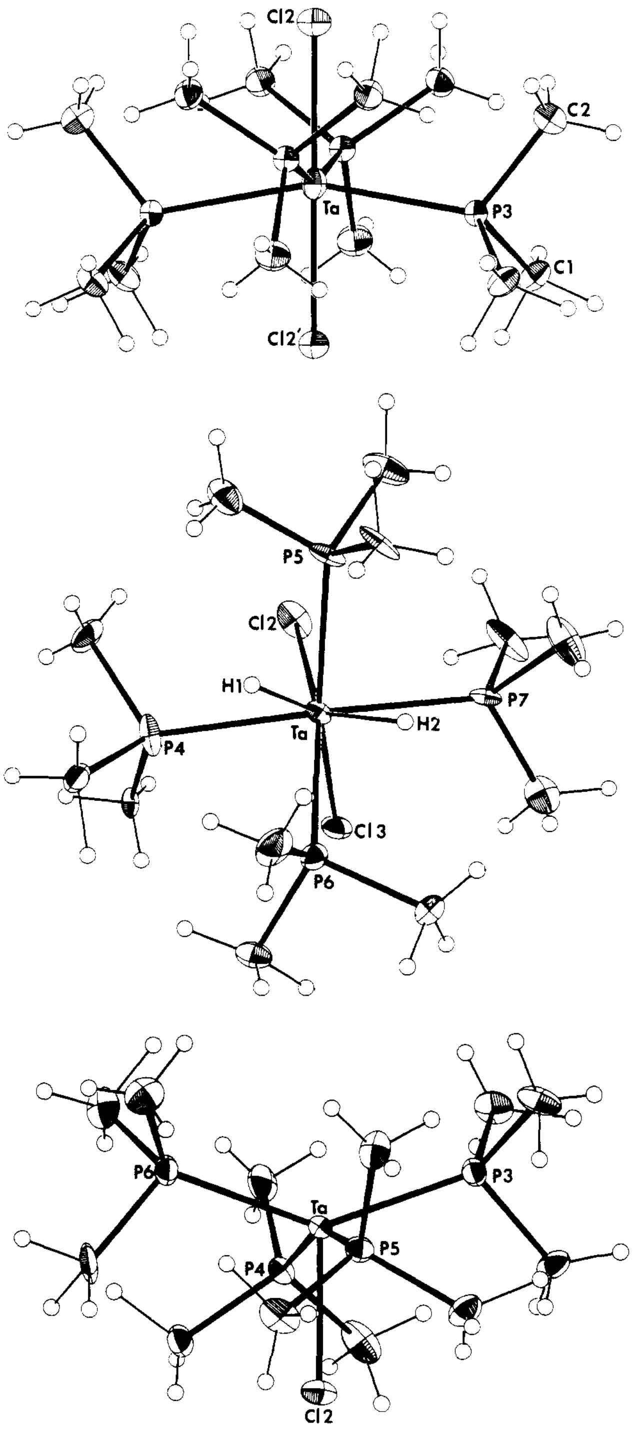

Figure 1. ORTEP drawings of $TaCl_2(PMe_3)_4$ (top), $TaCl_2H_2(PMe_3)_4$ (center), and $TaClH_2(PMe_3)_4$ (bottom).

Ether solutions of **1**, preferably in the presence of free PMe_3, react readily with dihydrogen (40 psi of H_2, 25 °C, 4 h) to provide red, air-sensitive crystals of the paramagnetic tantalum(IV)

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(11) Anal. Calcd for $TaCl_2(PMe_3)_4$ ($TaCl_2P_4C_{12}H_{36}$): C, 25.92; H, 6.52; Cl, 12.75. Found (Galbraith): C, 26.11; H, 6.65; Cl, 12.98.

(12) (a) Magnetic moment[12b,c] ($PhCH_3$ solution) μ_{eff} (296 K) = 1.45 μ_B. (b) Determined by the Evans method (Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005) using Pascal's constants for estimating the diamagnetic correction (Jolly, W. L. "The Synthesis and Characterization of Inorganic Compounds"; Prentice-Hall: New Jersey, 1970; p 371.) (c) A solid-state measurement by the Guoy method gave essentially the same result for this d^3 complex, i.e., 1.49 μ_B. $PhCH_3$ solutions of **1** are EPR-silent at room temperature.

(13) (a) $TaCl_2(PMe_3)_4$ crystallizes (from n-Bu_2O, −40 °C) in the tetragonal space group $I\bar{4}2m$ with $a = b = 9.550$ (3) Å, $c = 12.125$ (5) Å; $V = 1106.1$ Å^3, and ρ(calcd) = 1.67 g cm^{-3} for M_r 556.17 and $z = 2$. Diffraction data were collected at −160 °C by a θ–2θ scan technique described elsewhere.[13b] The structure was solved by trial and error and refined by full-matrix least squares. Final discrepancy indices were $R_F = 3.05\%$ and $R_{wF} = 2.59\%$ for those 480 reflections with $F_o \geq 2.33\sigma(F_o)$. The limits of data collection were $6° < 2\theta < 60°$ (Mo Kα). (b) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755–2762.

(14) The structure of **1** is reminescent of $W(\equiv CH)Cl(PMe_3)_4$. See: Churchill, M. R.; Rheingold, A. L.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 3392–3399 and references therein.

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monomer $TaCl_2H_2(PMe_3)_4$,[16] **2**, in ca. 80% recrystallized ($PhCH_3/PMe_3$, −40 °C) yield (eq 2). The room-temperature

$$\underset{\mathbf{1}}{\mathrm{TaCl_2(PMe_3)_4}} + \mathrm{H_2} \xrightarrow[\mathrm{PMe_3}]{\mathrm{OEt_2}} \underset{\mathbf{2}}{\mathrm{TaCl_2H_2(PMe_3)_4}} \qquad (2)$$

^1H NMR spectrum of **2** (toluene-d_8) shows a single, very broad ($\Delta\nu_{1/2}$ = 160 Hz) PMe_3 resonance at δ −0.96. The latter does not split on cooling to −80 °C, and we were unable to locate the hydride resonance at either temperature. The IR spectrum of **2** (Nujol) shows a strong terminal metal–hydride stretch at 1690 cm^{-1}, which shifts to 1212 cm^{-1} in the IR spectrum of $TaCl_2D_2(PMe_3)_4$. The ESR spectrum of the *deuteride* ($PhCH_3$ solution, 25 °C, 9.64 GHz) is an octet (^{181}Ta, $I = {}^7/_2$, 100% abundance) of quintets: $\langle g \rangle = 1.960$, $\langle a \rangle_{Ta} = 139.4$ G, $\langle a \rangle_P =$ 33.8 G. Hydride coupling in the ESR spectrum of **2** was not resolved, but from the increase in line width we can estimate $\langle a \rangle_H$ to be ca. 6–7 G.

Reaction 2 is a rare example of an oxidative addition reaction connecting paramagnetic monomers[17] and the only one we know of that involves dihydrogen. In addition to **2**, the following *isolable* paramagnetic hydrides have been claimed: $HFe(dppe)_2$,[18] $[HFeCl(dppe)_2]BF_4$,[18] and $HCoL_4^+$.[19] None of these systems has been structurally characterized.

An ORTEP drawing[20] of **2** is shown in Figure 1 (center). The terminal hydride ligands were located directly from difference Fourier maps and were well behaved during least-squares refinement: Ta–H1, 1.94 (11); Ta–H2, 1.85 (11) Å; H1–Ta–H2, 77 (6)°. The overall geometry is best described as dodecahedral with the chloride and hydride ligands in the sterically less demanding "A" sites[21] of the dodecahedron. Selected structural data are as follows: Ta–Cl2, 2.542 (5); Ta–Cl3, 2.563 (5); Ta–P4, 2.633 (6); Ta–P5, 2.567 (5); Ta–P6, 2.559 (5); Ta–P7, 2.628 (6) Å; Cl2–Ta–Cl3, 81.8 (1); P5–Ta–P6 123.6 (1); P4–Ta–P7, 158.9 (1)°.

The solution thermolysis of **2** (cyclohexane, 81 °C, 1 h) provides a single tantalum-containing product in quantitative yield (eq 3).

$$\underset{\mathbf{2}}{\mathrm{TaCl_2H_2(PMe_3)_4}} \xrightarrow[\mathrm{C_6H_{12}}]{\Delta} 0.5\underset{\mathbf{3}}{[\mathrm{TaCl_2(PMe_3)_2}]_2(\mu\text{-H})_4} + 2\mathrm{PMe_3} \qquad (3)$$

The yellow-green product was identified as the quadruply hydrogen-bridged tantalum(IV) dimer $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$, **3**, by spectral comparison (IR, ^1H and ^{31}P NMR) with an authentic sample prepared by an independent and more difficult route.[3b,22]

The reduction of **2** with 1 equiv of sodium amalgam in ether containing free PMe_3 gave, after workup and recrystallization (toluene/PMe_3, −40 °C) green air-sensitive crystals of the diamagnetic tantalum(III) monomer $TaClH_2(PMe_3)_4$,[23] **4**, in ca. 50% yield (eq 4). The IR spectrum (Nujol) of **4** shows a terminal

$$\underset{\mathbf{2}}{\mathrm{TaCl_2H_2(PMe_3)_4}} + \mathrm{Na/Hg} \xrightarrow[\mathrm{PMe_3}]{\mathrm{OEt_2}} \underset{\mathbf{4}}{\mathrm{TaClH_2(PMe_3)_4}} + \mathrm{NaCl} \qquad (4)$$

metal–hydride stretch at 1662 cm^{-1}, which shifts to 1191 cm^{-1} in the deuterium analogue. The proton NMR of **4** (benzene-d_6) shows two resonances at δ 1.46 (36 H) and 0.23 (2 H).[24] The latter disappears in the proton NMR spectrum of $TaClD_2(PMe_3)_4$.

An ORTEP drawing of **4**[25] is shown in Figure 1 (bottom). Unfortunately, the hydride ligands were not located by difference Fourier methods, but they must be located in the cavity above the four PMe_3 ligands. Selected structural data are as follows: Ta–Cl2, 2.472 (4); Ta–P3, 2.490 (4); Ta–P4, 2.555 (4); Ta–P5, 2.545 (4); Ta–P6, 2.479 (4) Å; P3–Ta–P6, 140.8 (1); P4–Ta–P5, 157.8 (1)°. Several other monomeric tantalum(III) hydride complexes are known[26,27] in addition to **4**, but only one has been structurally characterized, i.e., pentagonal-bipyramidal $TaH(PPh_2)_2(dmpe)_2$.[27]

Other aspects of the chemistry of **1**, **2**, and **4** are currently under investigation as well as an attempt to develop niobium chemistry along similar lines.

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Registry No. 1, 85923-35-9; **2**, 85939-38-4; **4**, 85923-36-0; $TaCl_5$, 7721-01-9; PMe_3, 594-09-2; H_2, 1333-74-0.

Supplementary Material Available: Fractional coordinates and thermal parameters for **1**, **2**, and **4** (5 pages). Ordering information is given on any current masthead page.

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(16) Anal. Calcd for $TaCl_2H_2(PMe_3)_4$ ($TaCl_2P_4C_{12}H_{38}$): C, 25.82; H, 6.86. Found (Galbraith): C, 25.63; H, 6.68. Magnetic moment: μ_{eff} (298 K) = 1.74 μ_B (Guoy method).

(17) (a) There are several examples in vanadocene chemistry, e.g., $Cp_2V + Ph_2S_2 \rightarrow Cp_2V(SPh)_2$.[17b] (b) Muller, E. G.; Watkins, S. F.; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 73–79.

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(19) Sander, J. R. *J. Chem. Soc., Dalton Trans.*, **1973**, 748–749.

(20) $TaCl_2H_2(PMe_3)_4$ crystallizes (from $PhCH_3$, −40 °C) in the acentric monoclinc space group *Cc* with a = 15.127 (3) Å, b = 12.005 (3) Å, c = 12.410 (2) Å, β = 92.49 (1)°; V = 2251.59 $Å^3$, and ρ(calcd) = 1.647 g cm^{-3} for M_r 558.18 and z = 4. Diffraction data were collected at −160 °C,[13b] and the structure was solved by direct methods (MULTAN), difference Fourier syntheses, and full-matrix least-squares refinement. Final discrepancy indices were R_F = 2.85% and R_{wF} = 2.93% for those 2418 reflections with $F_o > 2.33\sigma(F_o)$. The limits of data collection were $6° < 2\theta < 45°$ (Mo Kα).

(21) Hoard, J. L.; Silverthorn, J. V. *Inorg. Chem.* **1963**, *2*, 235–243.

(22) The solution thermolyses of complexes **1** and **4** are considerably more complex than that of **2**. Both reactions provide multiple products and are still under investigation.

(23) Anal. Calcd for $TaClH_2(PMe_3)_4$ ($TaClP_4C_{12}H_{38}$): C, 27.57; H, 7.33; Cl, 6.78. Found (Schwartzkopf): C, 27.63; H, 7.28; Cl, 6.77.

(24) Variable-temperature ^1H and $^{31}P\{^1H\}$ NMR studies are currently in progress and will be reported in detail elsewhere.

(25) $TaClH_2(PMe_3)_4$ crystallizes (from $PhCH_3$, −40 °C), in the monoclinic space group $P2_1/a$ with a = 18.617 (5) Å, b = 9.428 (2) Å, c = 12.528 (3) Å, β = 97.92 (1)°; V = 2178.04 $Å^3$, and ρ(calcd) = 1.594 g cm^{-3} for M_r 522.73 and z = 4. Diffraction data were collected at −160 °C.[13b] The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares. Final discrepancy indices were R_F = 5.70% and R_{wF} = 5.47; for those 2232 reflections with $F_o \geq 2.33\sigma(F_o)$. The limits of data collection were $6° < 2\theta < 45°$ (Mo Kα).

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Reaction of Acyl Halides with Organotin Hydrides. Mechanism of Aldehyde Formation[1]

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In 1966 Kuivila and Walsh reported that when an acid chloride was mixed at room temperature with tri-*n*-butyltin hydride, there was frequently an exothermic reaction.[4] The major products were the corresponding aldehyde and ester, the relative yields of which depended on both the nature of the acyl moiety and the experimental conditions (eq 1). Kuivila and Walsh carried out a rather

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(4) Kuivila, H. G.; Walsh, E. J., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 571–576.

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