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# Synthesis, Characterization, Low-Temperature (50 K) Neutron Diffraction Structure, and Reactivity of Chlorodihydridotetrakis(trimethylphosphine)tantalum(III)

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Dichlorodihydridotetrakis(trimethylphosphine)tantalum(IV), $TaCl_2H_2(PMe_3)_4$, is reduced under argon by sodium amalgam in the presence of $PMe_3$ to give green $TaClH_2(PMe_3)_4$ (**1a**) in 70% yield. **1a** has been characterized by IR spectroscopy, variable-temperature $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopy, and low-temperature (50 K) neutron crystallography. In the solid state, **1a** is a slightly distorted pentagonal bipyramid with two axial phosphines. The hydride ligands are coordinated in a cis configuration in the pentagonal plane with a H–Ta–H angle of 66.2 (6)° and Ta–H distances of 1.79 (1) and 1.80 (1) Å. **1a** reacts readily with $Me_2PCH_2CH_2PMe_2$ (dmpe) to give $TaClH_2(dmpe)_2$ (**2**) and with ethylene to give $TaCl(C_2H_4)(PMe_3)_4$ (**3**). It also reacts with dinitrogen to given the $\mu$-dinitrogen complex $[TaClH_2(PMe_3)_3]_2(\mu\text{-}N_2)$ (**4a**) and with carbon monoxide to provide $TaCl(CO)_3(PMe_3)_3$ (**5**). The latter complex has been characterized by low-temperature (−160 °C) X-ray crystallography. In the solid state, **5** is a capped (by Cl) trigonal prism with three $PMe_3$ ligands and one CO on the capped quadrilateral face and two CO ligands on the remaining edge. Crystal data are as follows: for **1a** (at 50 K), monoclinic space group $P2_1/a$, $a = 18.436$ (4) Å, $b = 9.139$ (2) Å, $c = 12.376$ (3) Å, $\beta = 97.90$ (3)°, $V = 2106.1$ Å$^3$, $Z = 4$; for **5** (at −160 °C), monoclinic space group $P2_1/n$, $a = 17.684$ (3) Å, $b = 13.904$ (5) Å, $c = 18.522$ (5) Å, $\beta = 117.60$ (2)°, $V = 2018.0$ Å$^3$, $Z = 8$.

## Introduction

We recently reported[2-5] some simple paramagnetic hydride complexes of niobium(IV) and tantalum(IV) that were prepared by reacting *trans*-$TaCl_2(PMe_3)_4$ and *trans*-$MCl_2(dmpe)_2$ (M = Ta, Nb; dmpe= 1,2-bis(dimethylphosphino)ethane) with molecular hydrogen. Of these 17-electron complexes, dodecahedral $TaCl_2H_2(PMe_3)_4$ is the most interesting from a chemical standpoint because it decomposes in solution at elevated temperatures to the quadruply hydrogen-bridged tantalum(IV) dimer[6] $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$, and because it can be reduced to an exceptionally reactive 16-electron tantalum(III) monomer, $TaClH_2(PMe_3)_4$. In this paper we provide preparative details and low-temperature neutron structural data and describe some of the reaction chemistry associated with this seven-coordinate, monomeric reduction product. Some of these results have been described in preliminary communications.[2,7]

## Results and Discussion

**Preparation and Characterization of $TaClH_2(PMe_3)_4$.** Reduction of $TaCl_2H_2(PMe_3)_4$[4] with sodium amalgam in ether containing THF and trimethylphosphine provides, after workup and recrystallization from ether, green, air-sensitive $TaClH_2(PMe_3)_4$ (**1a**) in ca. 70% yield (eq 1). The analogous deuteride,

$$TaCl_2X_2(PMe_3)_4 + Na/Hg \xrightarrow[PMe_3]{OEt_2/THF} TaClX_2(PMe_3)_4 + NaCl \quad (1)$$

**1a**, X = H
**1b**, X = D

**1b**, was prepared in the same manner, starting from $TaCl_2D_2(PMe_3)_4$.[4] The yield quoted above is an improvement over that reported in our original communication.[2] We have found, by trial and error, that a 6:1 mixture of ether/THF facilitates the reduction of $TaCl_2H_2(PMe_3)_4$ and provides a cleaner product than that obtained in pure diethyl ether. Larger proportions of THF had a deleterious effect on the reaction; in pure THF the yield of **1a** was nil. In addition, **1a** is sensitive to dinitrogen (vide infra), so all solvents must be rigorously degassed.

The infrared spectrum of **1a** (Nujol mull) shows a strong metal hydride stretch at 1662 cm$^{-1}$, which shifts to 1191 cm$^{-1}$ in the IR spectrum of **1b** ($\nu_{Ta-H}/\nu_{Ta-D} = 1.40$). Two broad resonances were observed in the 25 °C proton NMR spectrum of **1a** (in benzene-$d_6$)—one at $\delta$ 1.46 (36 H) and one at $\delta$ 0.23 (2 H). These resonances are attributable to the $PMe_3$ hydrogens and the hydride ligands, respectively. The $^1H$ NMR spectrum of **1b** shows only the resonance at $\delta$ 1.46. The fact that P–H coupling cannot be detected at room temperature in the hydride resonance suggests that the phosphine ligands are labile[8] and that **1a** exchanges rapidly with free phosphine on the NMR time scale. At −80 °C in toluene-$d_8$ the hydride resonance is a quintet ($J_{PH} = 37.5$ Hz) and the original, broad $PMe_3$ resonance splits into two signals at $\delta$ 1.41 (18 H) and $\delta$ 1.36 (18 H) (Figure 1). The −80 °C $^{31}P\{^1H\}$ NMR spectrum of **1a** shows two triplets of equal area (an $A_2X_2$ spin system) with $J_{PP'} = 29.6$ Hz. The quintet hydride pattern is maintained down to −120 °C (methylcyclohexane-$d_{14}$/toluene-$d_8$), suggesting that there is a fluxional process that time averages the hydride ligand environments. We will return to this point after describing the neutron diffraction structure of **1a**, which was pursued because neither the spectroscopic data nor the X-ray diffraction structure (the hydrides were not located[2]) unambiguously define the stereochemistry of this seven-coordinate complex.

**Neutron Diffraction Structure of $TaClH_2(PMe_3)_4$.** In the solid state (at 50 K), $TaClH_2(PMe_3)_4$ is composed of discrete mononuclear units, and there are no unusual intermolecular contacts. Final atomic positional parameters are listed in Table I and selected bond distances and angles are provided in Table II. An ORTEP drawing of the molecule that indicates the numbering scheme used in Table II is shown in Figure 2. A second ORTEP drawing, depicting the inner coordination sphere atoms, is provided in Figure 3.

The molecule has virtual, but not crystallographically imposed, $C_{2v}$ symmetry and is best described as a distorted pentagonal-bipyramidal complex. A least-squares analysis of the pentagonal plane composed of Ta, Cl(2), P(4), P(5), H(37), and H(38)

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(8) **1a** is not stable in solution. After several hours at 25 °C, decomposition is evidenced by a change in the color of the solution from green to brown. The nature of the decomposition product(s) has not been determined.

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**Table I.** Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $TaClH_2(PMe_3)_4$

| atom | $x$ | $y$ | $z$ | $U_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Ta(1) | 0.1053 (2) | 0.4177 (5) | 0.7586 (3) | 0.007 (1) |
| Cl(2) | 0.1293 (2) | 0.4029 (5) | 0.9574 (3) | 0.012 (1) |
| P(3) | 0.0091 (3) | 0.5962 (8) | 0.7014 (5) | 0.010 (2) |
| P(4) | 0.2064 (3) | 0.6009 (8) | 0.8004 (5) | 0.011 (2) |
| P(5) | 0.0128 (3) | 0.2310 (8) | 0.7951 (5) | 0.011 (2) |
| P(6) | 0.1842 (3) | 0.2446 (8) | 0.6803 (5) | 0.011 (2) |
| C(7) | −0.0206 (3) | 0.6853 (7) | 0.8191 (4) | 0.015 (2) |
| C(8) | 0.0297 (3) | 0.7507 (7) | 0.6209 (4) | 0.014 (2) |
| C(9) | −0.0790 (3) | 0.5483 (7) | 0.6253 (4) | 0.014 (2) |
| C(10) | 0.1888 (3) | 0.7476 (7) | 0.8898 (4) | 0.016 (2) |
| C(11) | 0.2933 (3) | 0.5399 (7) | 0.8742 (5) | 0.015 (2) |
| C(12) | 0.2396 (3) | 0.6997 (7) | 0.6906 (4) | 0.016 (2) |
| C(13) | 0.0477 (3) | 0.0721 (7) | 0.8723 (4) | 0.017 (2) |
| C(14) | −0.0444 (3) | 0.1433 (7) | 0.6823 (4) | 0.014 (2) |
| C(15) | −0.0560 (3) | 0.2869 (6) | 0.8792 (4) | 0.014 (2) |
| C(16) | 0.1452 (3) | 0.0995 (7) | 0.5928 (4) | 0.015 (2) |
| C(17) | 0.2533 (3) | 0.3048 (7) | 0.5992 (4) | 0.016 (2) |
| C(18) | 0.2405 (3) | 0.1444 (7) | 0.7879 (4) | 0.017 (2) |
| H(1) | 0.0241 (6) | 0.7391 (16) | 0.8672 (10) | 0.032 (4) |
| H(2) | −0.0618 (7) | 0.7640 (17) | 0.7924 (11) | 0.038 (4) |
| H(3) | −0.0443 (9) | 0.6133 (17) | 0.8686 (11) | 0.042 (5) |
| H(4) | 0.0400 (9) | 0.7159 (17) | 0.5413 (10) | 0.042 (5) |
| H(5) | −0.0157 (8) | 0.8293 (15) | 0.6102 (11) | 0.035 (4) |
| H(6) | 0.0778 (8) | 0.8053 (17) | 0.6625 (12) | 0.037 (4) |
| H(7) | −0.1166 (7) | 0.6375 (18) | 0.6171 (11) | 0.037 (4) |
| H(8) | −0.0722 (7) | 0.5144 (18) | 0.5436 (9) | 0.035 (4) |
| H(9) | −0.1037 (7) | 0.4620 (15) | 0.6679 (11) | 0.033 (4) |
| H(10) | 0.2363 (7) | 0.8143 (14) | 0.9121 (11) | 0.031 (4) |
| H(11) | 0.1455 (7) | 0.8154 (15) | 0.8492 (11) | 0.034 (4) |
| H(12) | 0.1706 (8) | 0.7071 (18) | 0.9636 (9) | 0.040 (4) |
| H(13) | 0.3192 (6) | 0.4645 (19) | 0.8255 (11) | 0.040 (4) |
| H(14) | 0.3307 (7) | 0.6278 (16) | 0.8962 (11) | 0.032 (4) |
| H(15) | 0.2825 (7) | 0.4865 (18) | 0.9459 (10) | 0.037 (4) |
| H(16) | 0.2628 (9) | 0.6259 (16) | 0.6363 (11) | 0.040 (4) |
| H(17) | 0.1955 (7) | 0.7574 (17) | 0.6434 (11) | 0.036 (4) |
| H(18) | 0.2817 (7) | 0.7763 (16) | 0.7210 (11) | 0.035 (4) |
| H(19) | 0.0034 (7) | 0.0054 (15) | 0.8912 (12) | 0.037 (4) |
| H(20) | 0.0820 (7) | 0.0111 (15) | 0.8256 (12) | 0.036 (4) |
| H(21) | 0.0812 (7) | 0.1104 (17) | 0.9449 (10) | 0.038 (4) |
| H(22) | −0.0781 (7) | 0.2239 (15) | 0.6360 (10) | 0.031 (4) |
| H(23) | −0.0097 (7) | 0.0966 (18) | 0.6271 (10) | 0.037 (4) |
| H(24) | −0.0808 (7) | 0.0641 (17) | 0.7118 (10) | 0.037 (4) |
| H(25) | −0.0936 (7) | 0.3641 (17) | 0.8371 (10) | 0.034 (4) |
| H(26) | −0.0883 (7) | 0.1969 (16) | 0.9015 (11) | 0.036 (4) |
| H(27) | 0.0282 (7) | 0.3392 (19) | 0.9525 (10) | 0.038 (4) |
| H(28) | 0.1146 (9) | 0.1458 (18) | 0.5199 (10) | 0.044 (5) |
| H(29) | 0.1887 (7) | 0.0307 (16) | 0.5697 (13) | 0.040 (4) |
| H(30) | 0.1091 (8) | 0.0348 (16) | 0.6345 (12) | 0.040 (5) |
| H(31) | 0.2856 (7) | 0.2195 (18) | 0.5742 (11) | 0.037 (4) |
| H(32) | 0.2266 (7) | 0.3607 (16) | 0.5268 (9) | 0.034 (4) |
| H(33) | 0.2888 (7) | 0.3830 (18) | 0.6444 (11) | 0.038 (4) |
| H(34) | 0.2069 (7) | 0.0867 (21) | 0.8376 (12) | 0.046 (5) |
| H(35) | 0.2755 (7) | 0.0672 (19) | 0.7542 (11) | 0.041 (5) |
| H(36) | 0.2740 (8) | 0.2153 (18) | 0.8403 (12) | 0.043 (5) |
| H(37) | 0.1301 (6) | 0.4974 (14) | 0.6371 (9) | 0.030 (3) |
| H(38) | 0.0530 (6) | 0.3518 (13) | 0.6349 (9) | 0.024 (3) |

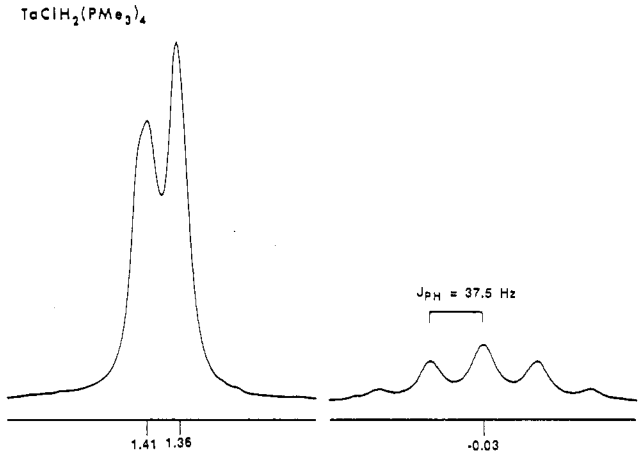

**Figure 1.** 360-MHz $^1H$ NMR spectrum of **1a** recorded in toluene-$d_8$ at −80 °C.

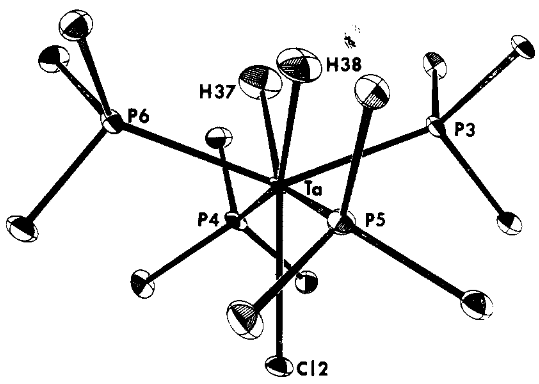

**Figure 2.** ORTEP drawing of $TaClH_2(PMe_3)_4$. Methyl hydrogens have been omitted for clarity. Atomic ellipsoids are drawn at the 50% probability level.

**Table II.** Selected Bond Distances (Å) and Bond Angles (deg) for $TaClH_2(PMe_3)_4$

| | | | |
|---|---|---|---|
| Ta(1)–Cl(2) | 2.443 (5) | Ta(1)–H(37) | 1.792 (11) |
| Ta(1)–P(3) | 2.464 (8) | Ta(1)–H(38) | 1.802 (12) |
| Ta(1)–P(4) | 2.527 (8) | H(37)–H(38) | 1.963 (17) |
| Ta(1)–P(5) | 2.521 (8) | av P–C | 1.822 [1][a] |
| Ta(1)–P(6) | 2.458 (8) | av C–H | 1.081 [2][a] |
| Cl(2)–Ta(1)–P(3) | 110.6 (3) | H(37)–Ta(1)–H(38) | 66.2 (6) |
| Cl(2)–Ta(1)–P(4) | 78.8 (2) | H(37)–Ta(1)–P(3) | 74.6 (5) |
| Cl(2)–Ta(1)–P(5) | 79.3 (2) | H(37)–Ta(1)–P(4) | 68.0 (4) |
| Cl(2)–Ta(1)–P(6) | 109.0 (2) | H(37)–Ta(1)–P(6) | 73.1 (5) |
| P(3)–Ta(1)–P(4) | 94.8 (3) | H(38)–Ta(1)–P(3) | 72.9 (4) |
| P(3)–Ta(1)–P(5) | 92.2 (3) | H(38)–Ta(1)–P(5) | 67.7 (4) |
| P(3)–Ta(1)–P(6) | 140.5 (3) | H(38)–Ta(1)–P(6) | 73.6 (4) |
| P(4)–Ta(1)–P(5) | 158.1 (3) | av C–P–C | 99.9 [3][a] |
| P(4)–Ta(1)–P(6) | 93.7 (3) | av P–C–H | 110.4 [2][a] |
| P(5)–Ta(1)–P(6) | 94.0 (3) | av H–C–H | 108.5 [2][a] |

[a] A number in brackets is equal to $[\sum_m \Delta_i^2/m(m-1)]^{1/2}$, where $\Delta_i$ is the deviation of the $i$th value in a set of $m$ such values from the arithmetic mean.

indicates deviations of less than ±0.02 Å. Coplanarity is also indicated by the fact that the angles in this plane around tantalum sum to 360.0°. The plane composed of Ta, P(3), and P(6) is perpendicular to the pentagonal plane. However, in this plane, the phosphines are displaced from the normal by approximately 20° (see Figure 2).

The tantalum–phosphorous bonds in **1a** can be divided into two sets: axial and equatorial. The average Ta–P bond distance for the axial ligands [P(3) and P(6), 2.46 Å] is 0.06 Å shorter than the average Ta–P bond length of the equatorial phosphines [P(4) and P(5), 2.52 Å]. Similar observations, namely, longer M–P bonds in the hydride plane, have been reported for pentagonal-bipyramidal $OsH_4(PMe_2Ph)_3$,[9] and dodecahedral $TaCl_2H_2(PMe_3)_4$.[4] In both cases, the trans influence of the hydrides was invoked to account for the longer bonds. It should be added, however, that a theoretical investigation of the idealized pentagonal bipyramid predicts marginally stronger axial bonds.[10] For comparison purposes, we note that the axial and equatorial Ta–P bond lengths in **1a** are both shorter than the average Ta–P bond length (2.596 (4) Å) in the binuclear tantalum(III) hydride complex $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_2$.[6] Because the metal center in **1a** is electron rich relative to the Ta centers in the binuclear complex ($H^-$ is a better electron donor than $Cl^-$), this difference in Ta–P bond lengths could be a reflection of increased metal-to-phosphorus $\pi$-back-bonding in the monomeric system.

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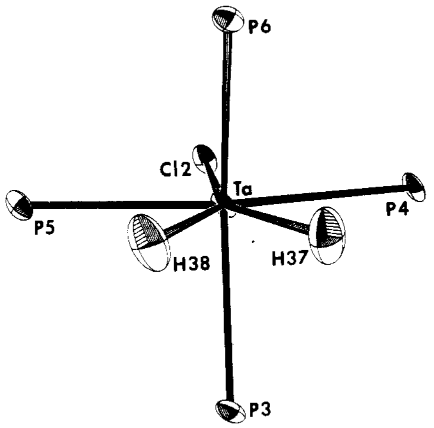
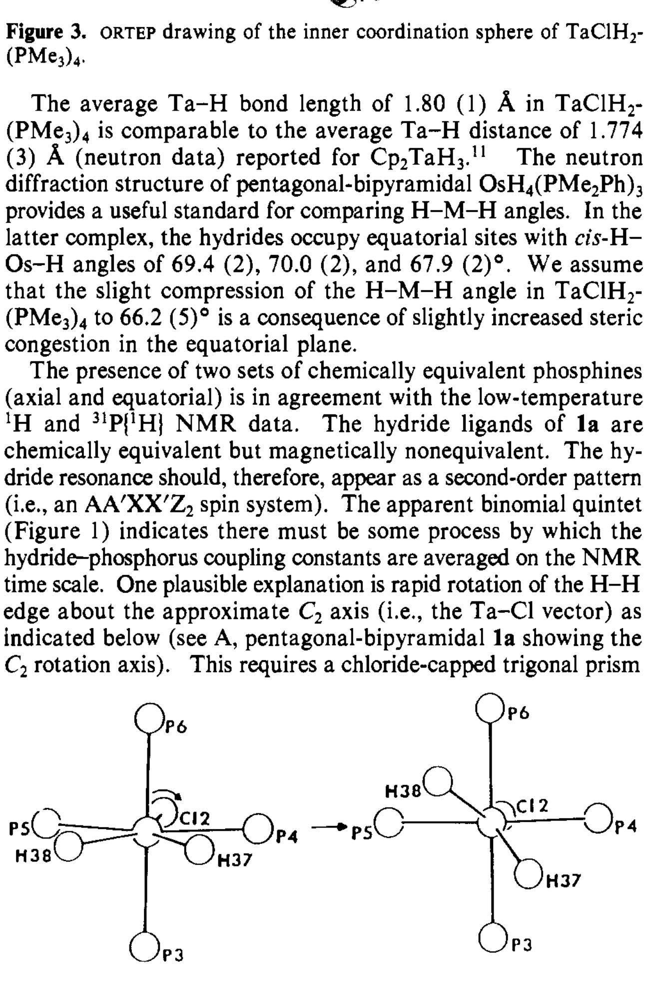


**Figure 3.** ORTEP drawing of the inner coordination sphere of $TaClH_2(PMe_3)_4$.

The average Ta–H bond length of 1.80 (1) Å in $TaClH_2(PMe_3)_4$ is comparable to the average Ta–H distance of 1.774 (3) Å (neutron data) reported for $Cp_2TaH_3$.[11] The neutron diffraction structure of pentagonal-bipyramidal $OsH_4(PMe_2Ph)_3$ provides a useful standard for comparing H–M–H angles. In the latter complex, the hydrides occupy equatorial sites with *cis*-H–Os–H angles of 69.4 (2), 70.0 (2), and 67.9 (2)°. We assume that the slight compression of the H–M–H angle in $TaClH_2(PMe_3)_4$ to 66.2 (5)° is a consequence of slightly increased steric congestion in the equatorial plane.

The presence of two sets of chemically equivalent phosphines (axial and equatorial) is in agreement with the low-temperature $^1H$ and $^{31}P\{^1H\}$ NMR data. The hydride ligands of **1a** are chemically equivalent but magnetically nonequivalent. The hydride resonance should, therefore, appear as a second-order pattern (i.e., an $AA'XX'Z_2$ spin system). The apparent binomial quintet (Figure 1) indicates there must be some process by which the hydride–phosphorus coupling constants are averaged on the NMR time scale. One plausible explanation is rapid rotation of the H–H edge about the approximate $C_2$ axis (i.e., the Ta–Cl vector) as indicated below (see A, pentagonal-bipyramidal **1a** showing the $C_2$ rotation axis). This requires a chloride-capped trigonal prism as an intermediate (see B, capped-trigonal-prismatic orientation formed by 45° rotation of the H–H edge); the process may therefore be viewed as a rapid traverse from a pentagonal bipyramid to a capped trigonal prism. Extended Hückel calculations by Hoffmann and co-workers[10] indicate that the energy difference between idealized pentagonal-bipyramidal and capped-trigonal-prismatic $ML_7$ structures is very small, i.e., less than 5 kcal/mol.

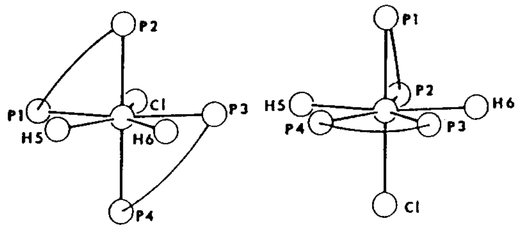


(A) (B)

**Reactions of $TaClH_2(PMe_3)_4$. (1) With dmpe.** The dmpe analogue of **1a** is best prepared by metathesis in hexane (eq 2).

$$\underset{\mathbf{1a}}{TaClH_2(PMe_3)_4} + 2dmpe \xrightarrow{C_6H_{14}} \underset{\mathbf{2}}{TaClH_2(dmpe)_2} + 4PMe_3 \qquad (2)$$

This reaction is accompanied by a dramatic color change (green to orange) and orange crystalline $TaClH_2(dmpe)_2$ (**2**) is obtained in ≥90% yield. The presence of terminal hydride ligands was verified by IR spectroscopy ($\nu_{Ta-H} = 1630\ cm^{-1}$), but the hydride resonance was not located in the $^1H$ NMR spectrum, which is complex. The −80 °C $^{31}P\{^1H\}$ NMR spectrum was somewhat more informative. Three broad resonances were observed at δ +18.3, +20.2, and +22.1 in a 1:2:1 area ratio. This information, coupled with our knowledge of the neutron structure of **1a**, allows us to suggest a reasonable structure for **2**. Let us assume for the moment that the phosphorus stereochemistry in **1a** and **2** is the same, and draw structure C. This isomer has $C_2$ symmetry (the $C_2$ axis is along the Ta–Cl bond and bisects the H–Ta–H angle), which means that the axial phosphorus atoms are chemically equivalent as are the equatorial phosphorus atoms. We expect the $^{31}P\{^1H\}$ NMR spectrum of this isomer to show only two resonances, which is clearly not in agreement with the observed spectrum. Alternatively, we can draw a structure (D) that has $C_s$ symmetry. The chelated equatorial phosphorus atoms of this isomer are chemically equivalent, but the two phosphorus atoms of the second dmpe ligand are clearly nonequivalent. The spin system can be labeled $ABC_2$ or $AMX_2$. The former is more appropriate here because of the small chemical shift differences and the fact that we observe broad, unresolved signals. It is interesting to note that Hoffmann and co-workers[10] predicted that the best σ donors should occupy the equatorial plane of a pentagonal bipyramid. The reduced steric requirements of dmpe no doubt facilitate this possibility in **2**.



(C) (D)

**(2) With Ethylene.** Toluene-$d_8$ solutions of **1a** react rapidly with 2 equiv of ethylene at −60 °C to give the known[12] violet ethylene complex, *trans*-$TaCl(C_2H_4)(PMe_3)_4$ (**3**) in quantitative ($^1H$ NMR) yield (eq 3). Ethane (δ 0.80) is the only other product

$$\underset{\mathbf{1a}}{TaClH_2(PMe_3)_4} + 2C_2H_4 \xrightarrow[-60\ °C]{C_7D_8} \underset{\mathbf{3}}{TaCl(C_2H_4)(PMe_3)_4} + C_2H_6 \qquad (3)$$

observed by NMR. In the presence of excess ethylene, **3** is unstable and reacts to form the butadiene complex Ta(1,3-butadiene)$(C_2H_4)Cl(PMe_3)_2$.[13]

**(3) With Dinitrogen.** Schrock and co-workers have shown[12] that **3** and Ta(=CH-*t*-Bu)$Cl(PMe_3)_4$ react slowly with dinitrogen to provide $[TaCl(C_2H_4)(PMe_3)_3]_2(\mu-N_2)$ and [Ta(=CH-*t*-Bu)$Cl(PMe_3)_2]_2(\mu-N_2)$, respectively. The μ-$N_2$ ligand in these complexes is "imido-like"; i.e., the Ta(μ-$N_2$)Ta linkage is best described as Ta=N—N=Ta. The X-ray structure[14] of a related complex, viz., [Ta(=CH-*t*-Bu)($CH_2$-*t*-Bu)$(PMe_3)_2]_2(\mu-N_2)$, supports this description; here the Ta=N distance is 1.84 Å and the N—N distance is 1.298 Å.

Because **1a**, **3**, and Ta(=CH-*t*-Bu)$Cl(PMe_3)_4$ are formally isoelectronic, we thought that **1a** would react with $N_2$ to give a μ-$N_2$ complex. This is indeed the case. When **1a** is dissolved in ether and the solution is exposed to dinitrogen (40 psi, 25 °C, 12 h), the dinitrogen complex $[TaClH_2(PMe_3)_3]_2(\mu-N_2)$ (**4a**) precipitates as an air-sensitive, mustard yellow powder in ca. 90% yield (eq 4). One mole of $PMe_3$ per mole of Ta is liberated ($^1H$ NMR) in the reaction. (Complex **2** is stable in the presence of

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(11) Wilson, R. D.; Koetzle, T. F.; Hart, D. W.; Kvick, A.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1775.

(12) Rocklage, S. M.; Turner, H. W.; Fellman, J. D.; Schrock, R. R. *Organometallics* **1982**, *1*, 703.

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(14) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 2899.

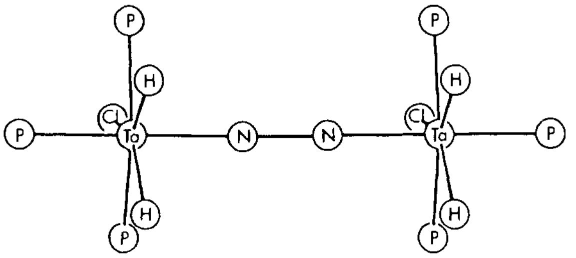
$$\underset{\substack{\mathbf{1a},\ X = H\\ \mathbf{1b},\ X = D}}{2TaClX_2(PMe_3)_4} + N_2 \xrightarrow{OEt_2} \underset{\substack{\mathbf{4a},\ X = H\\ \mathbf{4b},\ X = D}}{[TaClX_2(PMe_3)_3]_2(\mu\text{-}N_2)} + 2PMe_3 \quad (4)$$

$N_2$.) **4a** is sparingly soluble in toluene, hexane, and ethers. A deuterium analogue, **4b**, was prepared in a similar fashion from **1b** and $N_2$. The infrared spectrum of **4a** (Nujol mull) shows a strong terminal metal–hydride stretch at 1585 $cm^{-1}$, which shifts to 1140 $cm^{-1}$ in the IR spectrum of **4b** ($\nu_{Ta-H}/\nu_{Ta-D} = 1.39$).

A $^{15}N$-labeled complex was prepared from **1a** and $^{15}N_2$ (96 atom % $^{15}N$). The mid-IR spectra (Nujol mulls) of the two $\mu$-$N_2$ derivatives differ in only one respect: a medium-strength band located at 853 $cm^{-1}$ in the IR spectrum of the $^{14}N_2$ complex shifts to 829 $cm^{-1}$ in the spectrum of the $^{15}N_2$ complex. Similar bands are observed at 825 and 793 $cm^{-1}$ in the IR spectra of the $[TaCl(C_2H_4)(PMe_3)_3]_2(\mu\text{-}^{14}N_2)$ and its $^{15}N_2$ analogue, respectively, and have been assigned as a mode characteristic of the entire Ta=N—N=Ta linkage.[12]

The room-temperature proton NMR spectrum of **4a** consists of three resonances: a complex hydride multiplet at $\delta$ 8.34 (4 H), a $PMe_3$ doublet at $\delta$ 1.67 (18 H), and a "filled-in" $PMe_3$ doublet at $\delta$ 1.44 (36 H). The $^{31}P\{^1H\}$ NMR spectrum (25 °C) shows two signals: a triplet at $\delta$ −3.0 ($J_{PP'}$ = 5.4 Hz) and a doublet at $\delta$ −23.1 ($J_{PP'}$ = 5.4 Hz) (an $AX_2$ spin system). Selective $^1H$ decoupling of the phosphine methyl resonances converts the $\delta$ −3.0 triplet to a triplet of triplets ($J_{PH}$ = 66 Hz) and the $\delta$ −23.1 doublet to a complex multiplet.

On the basis of the preceding spectroscopic data, the structure of **4a** is believed to be that shown as structure E, namely two



(E)

pentagonal pyramids joined by a $\mu$-$N_2$ ligand. The observation of only two types of $PMe_3$ ligands indicates that the ends of the molecule are free to rotate. Regrettably, we have been unable to grow crystals of this material that are suitable for X-ray diffraction.

**(4) With Carbon Monoxide.** Diethyl ether solutions of **1a** react smoothly with carbon monoxide (40 psi, 25 °C, 8 h) according to the stoichiometry of eq 5. Analytically pure, red-orange

$$\underset{\mathbf{1a}}{TaClH_2(PMe_3)_4} + 3CO \xrightarrow{Et_2O} \underset{\mathbf{5}}{TaCl(CO)_3(PMe_3)_3} + H_2 + PMe_3 \quad (5)$$

$TaCl(CO)_3(PMe_3)_3$ (**5**) is isolated in 90% yield after solvent removal, extraction of the solid residue with warm hexane, and evaporation of the filtrate. Moderately air-sensitive **5** is soluble in toluene, ethers, and methylene chloride, and slightly soluble in hexane. The infrared spectrum of **5** in hexane solution shows three sharp C–O stretching modes at 1962, 1862, and 1843 $cm^{-1}$.

Complex **5** is stereochemically nonrigid in solution. At room temperature in toluene-$d_8$ a single "phosphine" resonance is observed in the $^1H$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of **5**. In addition, a single carbonyl resonance is observed at $\delta$ +258.7 in the $^{13}C\{^1H\}$ NMR spectrum. When the sample is cooled to −80 °C, apparent limiting spectra are obtained: (1) two methyl resonances, in a 1:2 area ratio at $\delta$ 1.14 and 0.92 in the proton NMR spectrum; (2) an $AX_2$ pattern ($\delta_A$ −10.4, $\delta_X$ −24.9, $J_{AX}$ = 50.7 Hz) in the $^{31}P\{^1H\}$ NMR spectrum (Figure 4); (3) two broad carbonyl resonances at $\delta$ 269.5 (1 CO) and $\delta$ 254.8 (2 CO) in the $^{13}C\{^1H\}$ NMR spectrum. The preceding data suggest that **5** has $C_s$ or mirror symmetry but do not unambiguously define the stereochemistry of this seven-coordinate complex. An X-ray diffraction study was therefore initiated.

**Table III.** Fractional Coordinates (×$10^4$) and Isotropic Thermal Parameters (×10 $Å^2$) for $TaCl(CO)_3(PMe_3)_3$[a]

| atom | *x* | *y* | *z* | $B_{iso}$ |
|---|---|---|---|---|
| Ta(1) | 1498.5 (2) | 2214.6 (3) | 3524.0 (2) | 11 |
| Cl(2) | 2418 (2) | 3312 (2) | 3154 (2) | 22 |
| P(3) | 2151 (2) | 897 (2) | 2988 (2) | 17 |
| P(4) | 1320 (2) | 3890 (2) | 4095 (2) | 15 |
| P(5) | 190 (2) | 2835 (2) | 2152 (2) | 16 |
| C(6) | 2595 (6) | 1754 (7) | 4513 (6) | 19 |
| O(7) | 3177 (4) | 1448 (5) | 5075 (4) | 30 |
| C(8) | 1235 (5) | 1895 (6) | 4448 (6) | 13 |
| O(9) | 1127 (4) | 1705 (5) | 5001 (4) | 19 |
| C(10) | 671 (6) | 1090 (7) | 3213 (6) | 15 |
| O(11) | 205 (4) | 426 (4) | 3047 (4) | 21 |
| C(12) | 2273 (7) | −292 (7) | 3446 (7) | 24 |
| C(13) | 3232 (7) | 1126 (9) | 3143 (9) | 37 |
| C(14) | 1598 (7) | 641 (8) | 1907 (6) | 25 |
| C(15) | 526 (7) | 4035 (7) | 4454 (6) | 19 |
| C(16) | 1214 (7) | 5007 (7) | 3535 (7) | 25 |
| C(17) | 2301 (7) | 4117 (8) | 5019 (7) | 29 |
| C(18) | −699 (6) | 3405 (7) | 2239 (6) | 23 |
| C(19) | −407 (6) | 1912 (8) | 1398 (6) | 26 |
| C(20) | 403 (7) | 3696 (7) | 1532 (6) | 23 |
| Ta(1)′ | 1938.1 (2) | 2569.8 (3) | 8896.1 (2) | 13 |
| Cl(2)′ | 1127 (2) | 4124 (2) | 8778 (2) | 24 |
| P(3)′ | 623 (2) | 1891 (2) | 8983 (2) | 19 |
| P(4)′ | 3094 (2) | 3850 (2) | 9028 (2) | 16 |
| P(5)′ | 1389 (2) | 2801 (2) | 7305 (2) | 17 |
| C(6)′ | 2311 (6) | 2447 (7) | 10138 (6) | 19 |
| O(7)′ | 2534 (6) | 2334 (5) | 10818 (4) | 34 |
| C(8)′ | 3066 (6) | 1842 (7) | 9444 (6) | 19 |
| O(9)′ | 3706 (5) | 1434 (5) | 9787 (5) | 31 |
| C(10)′ | 1841 (6) | 1191 (7) | 8469 (6) | 18 |
| O(11)′ | 1771 (5) | 424 (5) | 8206 (4) | 27 |
| C(12)′ | 711 (8) | 689 (8) | 9390 (7) | 31 |
| C(13)′ | 298 (7) | 2560 (8) | 9639 (7) | 26 |
| C(14)′ | −363 (7) | 1835 (9) | 8037 (7) | 29 |
| C(15)′ | 4053 (7) | 3472 (7) | 8971 (7) | 27 |
| C(16)′ | 2830 (7) | 4949 (7) | 8439 (6) | 25 |
| C(17)′ | 3556 (7) | 4329 (8) | 10059 (6) | 27 |
| C(18)′ | 2206 (7) | 2599 (8) | 6976 (6) | 25 |
| C(19)′ | 546 (7) | 1983 (8) | 6622 (6) | 25 |
| C(20)′ | 925 (7) | 3956 (8) | 6829 (6) | 30 |

[a] Isotropic thermal parameters were calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

**X-ray Diffraction Structure of $TaCl(CO)_3(PMe_3)_3$.** In the solid state (at −160 °C), **5** is composed of discrete mononuclear units and there are no unusual intermolecular contacts. Final atomic positional parameters are listed in Table III. and selected bond distances and angles are provided in Table IV. There are two crystallographically independent, but structurally very similar molecules in the asymmetric unit. An ORTEP drawing of one of these is shown in Figure 5. The same numbering scheme was used for both of the independent molecules.

The overall geometry is best described as a capped trigonal prism, with Cl(2) in the capping position, P(3), P(4), P(5), and C(6) in the capped quadrilateral face, and C(8) and C(10) on the remaining edge. The Ta–P(3,4,5) bond lengths are 2.595 (3), 2.638 (3), and 2.666 (3) Å, respectively, and the Ta–C(6,8,10) bond lengths are 2.06 (1), 2.02 (1), and 2.04 (1) Å, respectively. Both the Ta–P and Ta–C distances in **5** are comparable to those found[15a] in the capped (by $PMe_3$) octahedral Ta(I) complex $[Ta(CO)_3(PMe_3)_4]^+$. The angles subtended from the capping chloride to P(3), P(4), P(5), and C(6) average 83.6°; those to C(8) and C(10) average 145.1°. These average values are in good agreement with those calculated by Hoffmann et. al.[10] for a

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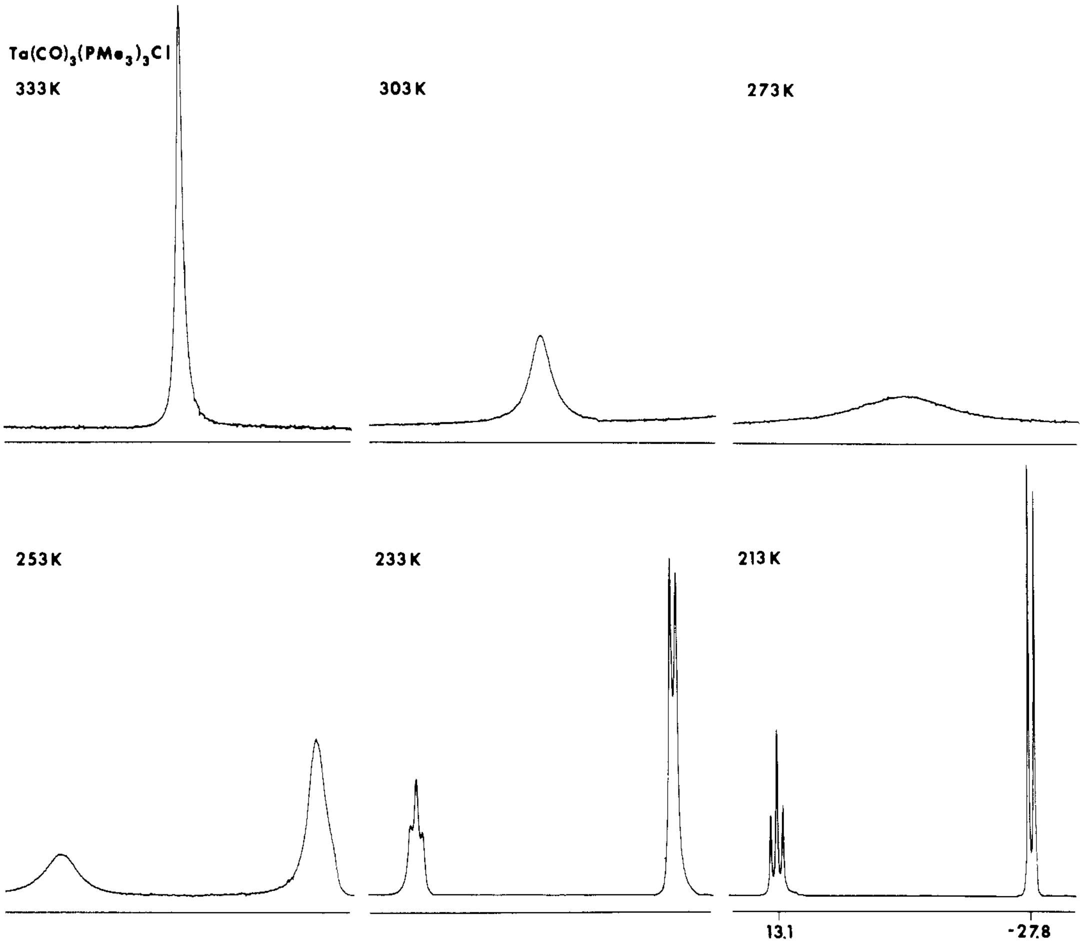

Figure 4. Variable-temperature 145.8-MHz $^{31}P\{^1H\}$ NMR spectra of $TaCl(CO)_3(PMe_3)_3$ recorded in toluene-$d_8$.

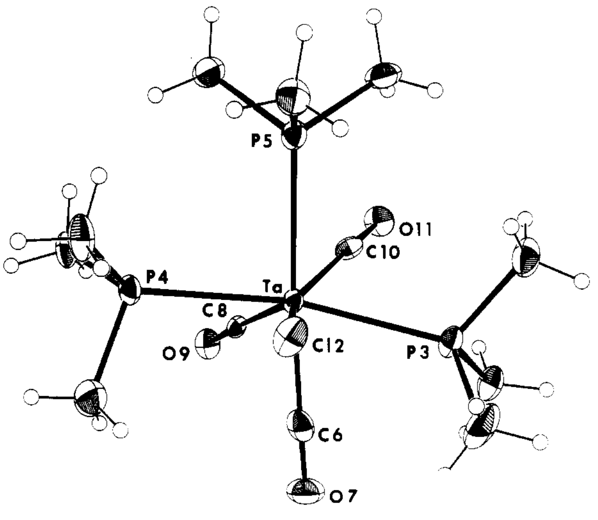

Figure 5. ORTEP drawing of $TaCl(CO)_3(PMe_3)_3$. Non-hydrogen atomic ellipsoids are drawn at the 50% probability level.

$d^4$-$ML_7$ capped trigonal prism, i.e., 82 and 148°.

Note that **5** has only $C_1$ symmetry in the solid state. In order to explain the low-temperature NMR data, we postulate rotation of the edge carbonyls about the Ta–Cl axis, i.e., another example of the capped-trigonal-prismatic–pentagonal-bipyramidal traverse, one which, in this case, averages the environments of the edge carbonyls and the trans phosphine ligands on the quadrilateral face.

We reiterate here that monomeric, non-cyclopentadienyl carbonyl complexes of niobium(I) and tantalum(I) are very rare and that the only well-characterized examples reported prior to our work[7] were the $MX(CO)_2(R_2PCH_2CH_2PR_2)_2$ (R = alkyl) compounds described by Tebbe,[16] Schrock,[17] Wreford,[18] and Leigh.[19] These adopt capped-trigonal-prismatic structures when X, the capping ligand, is a halide, pseudohalide, or alkyl ligand and capped-octahedral geometries when X is a hydride. As an aside, we note that the dmpe hydride complex **2** can be converted, in essentially quantitative yield, to Wreford and Datta's[18a] $TaCl(CO)_2(dmpe)_2$ (see Experimental Section). The synthetic utility of these compounds for further explorations of low-valent group 5 chemistry is necessarily limited by the presence of two, tightly bound chelating phosphines. We anticipate that **5** and other $MX(CO)_3L_3$ complexes (M = Nb, Ta; X = monoanionic ligand; L = neutral 2-electron donor) will be considerably more useful from a synthetic standpoint than the $MX(CO)_2(R_2PCH_2CH_2PR_2)_2$ systems. Recent work from this group (Michigan and Los Alamos)[15] and by Templeton and co-workers[20] at The University of North Carolina has already demonstrated some of their potential.

## Summary

We have shown here that it is possible to reduce the eight-coordinate $d^1$ hydride complex $TaCl_2H_2(PMe_3)_4$ to a seven-coordinate $d^2$ hydride, $TaClH_2(PMe_3)_4$. Our neutron diffraction analysis of **1a** has defined its stereochemistry as that of a slightly distorted pentagonal bipyramid, and we have demonstrated that **1a** is a useful synthon in low-valent tantalum chemistry. Future papers in this series will examine other aspects of the chemistry of **1a**, including its transformation to $Ta(BH_4)H_2(PMe_3)_4$, the first

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(16) (a) Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 5823. (b) Meakin, P.; Guggenberger, L. J.; Tebbe, F. N.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1025.

(17) Schrock, R. R. *J. Organomet. Chem.* **1976**, *121*, 373.

(18) (a) Datta, S.; Wreford, S. S. *Inorg. Chem.* **1977**, *16*, 1134. (b) Brown, L. D.; Datta, S.; Kouba, J. K.; Smith, L. K.; Wreford, S. S. *Inorg. Chem.* **1978**, *17*, 729.

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**Table IV.** Selected Bond Distances (Å) and Bond Angles (deg) for $TaCl(CO)_3(PMe_3)_3$

| | | | |
|---|---|---|---|
| Ta(1)–Cl(2) | 2.545 (2) | Ta(1)′–Cl(2)′ | 2.547 (3) |
| Ta(1)–P(3) | 2.595 (3) | Ta(1)′–P(3)′ | 2.583 (3) |
| Ta(1)–P(4) | 2.638 (3) | Ta(1)′–P(4)′ | 2.635 (3) |
| Ta(1)–P(5) | 2.666 (3) | Ta(1)′–P(5)′ | 2.661 (3) |
| Ta(1)–C(6) | 2.059 (10) | Ta(1)′–C(6)′ | 2.086 (10) |
| Ta(1)–C(8) | 2.021 (9) | Ta(1)′–C(8)′ | 2.038 (10) |
| Ta(1)–C(10) | 2.035 (10) | Ta(1)′–C(10)′ | 2.051 (10) |
| C(6)–O(7) | 1.153 (12) | C(6)′–O(7)′ | 1.144 (12) |
| C(8)–O(9) | 1.156 (11) | C(8)′–O(9)′ | 1.159 (12) |
| C(10)–O(11) | 1.179 (11) | C(10)′–O(11)′ | 1.156 (12) |
| av P–C | 1.823 [3][a] | av P′–C′ | 1.822 [3][a] |
| Cl(2)–Ta(1)–P(3) | 82.4 (1) | Cl(2)′–Ta(1)′–P(3)′ | 80.1 (1) |
| Cl(2)–Ta(1)–P(4) | 77.8 (1) | Cl(2)′–Ta(1)′–P(4)′ | 79.5 (1) |
| Cl(2)–Ta(1)–P(5) | 86.0 (1) | Cl(2)′–Ta(1)′–P(5)′ | 84.3 (1) |
| Cl(2)–Ta(1)–C(6) | 88.3 (3) | Cl(2)′–Ta(1)′–C(6)′ | 92.4 (3) |
| Cl(2)–Ta(1)–C(8) | 141.9 (3) | Cl(2)′–Ta(1)′–C(8)′ | 147.8 (3) |
| Cl(2)–Ta(1)–C(10) | 148.2 (3) | Cl(2)′–Ta(1)′–C(10)′ | 144.8 (3) |
| P(3)–Ta(1)–P(4) | 159.1 (1) | P(3)′–Ta(1)′–P(4)′ | 157.4 (1) |
| P(3)–Ta(1)–P(5) | 101.9 (1) | P(3)′–Ta(1)′–P(5)′ | 103.7 (1) |
| P(3)–Ta(1)–C(6) | 73.6 (3) | P(3)′–Ta(1)′–C(6)′ | 74.6 (3) |
| P(3)–Ta(1)–C(8) | 119.1 (3) | P(3)′–Ta(1)′–C(8)′ | 119.3 (3) |
| P(3)–Ta(1)–C(10) | 74.8 (3) | P(3)′–Ta(1)′–C(10)′ | 76.5 (3) |
| P(4)–Ta(1)–P(5) | 83.4 (1) | P(4)′–Ta(1)′–P(5)′ | 83.7 (1) |
| P(4)–Ta(1)–C(6) | 99.0 (3) | P(4)′–Ta(1)′–C(6)′ | 96.8 (3) |
| P(4)–Ta(1)–C(8) | 74.8 (3) | P(4)′–Ta(1)′–C(8)′ | 75.6 (3) |
| P(4)–Ta(1)–C(10) | 126.1 (3) | P(4)′–Ta(1)′–C(10)′ | 126.1 (3) |
| P(5)–Ta(1)–C(6) | 173.2 (3) | P(5)′–Ta(1)′–C(6)′ | 176.5 (3) |
| P(5)–Ta(1)–C(8) | 116.1 (2) | P(5)′–Ta(1)′–C(8)′ | 112.4 (3) |
| P(5)–Ta(1)–C(10) | 77.6 (3) | P(5)′–Ta(1)′–C(10)′ | 76.3 (3) |
| C(6)–Ta(1)–C(8) | 70.7 (4) | C(6)′–Ta(1)′–C(8)′ | 71.0 (4) |
| C(6)–Ta(1)–C(10) | 105.7 (4) | C(6)′–Ta(1)′–C(10)′ | 106.0 (4) |
| C(8)–Ta(1)–C(10) | 69.7 (4) | C(8)′–Ta(1)′–C(10)′ | 67.4 (4) |
| Ta(1)–C(6)–O(7) | 175.3 (8) | Ta(1)′–C(6)′–O(7)′ | 176.4 (9) |
| Ta(1)–C(8)–O(9) | 176.6 (7) | Ta(1)′–C(8)′–O(9)′ | 177.0 (9) |
| Ta(1)–C(10)–O(11) | 178.5 (7) | Ta(1)′–C(10)′–O(11)′ | 178.1 (8) |
| av Ta–P–C | 116.6 [14][a] | av Ta′–P′–C′ | 116.6 [15][a] |
| av C–P–C | 101.4 [4][a] | av C′–P′–C′ | 101.3 [3][a] |

[a] A number in brackets is equal to $[\sum_m \Delta_i^2/m(m-1)]^{1/2}$, where $\Delta_i$ is the deviation of the *i*th value in a set of *m* such values from the arithmetic mean.

tantalum borohydride complex.[15a]

## Experimental Section

**Reagents.** Tantalum pentachloride was purchased from Pressure Chemical and sublimed under high vacuum to remove nonvolatile impurities. Toluene, THF, and ether were dried and freed from dissolved molecular oxygen by distillation under argon from a solution of solvent, benzophenone, and sodium or potassium. Normal hexane was purified by stirring it over saturated $KMnO_4$ in 10% sulfuric acid and then sequentially washing it with water, saturated $Na_2CO_3$, and water. After predrying over $MgSO_4$, it was filtered and distilled under argon from Na/K alloy. The complexes $TaCl_2H_2(PMe_3)_4$ and $TaCl_2D_2(PMe_3)_4$ were prepared and purified by literature methods.[4] Nitrogen-15-enriched $N_2$ was obtained from Los Alamos laboratory stock.

**Physical and Analytical Measurements.** Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared measurements were made on Perkin-Elmer Model 1330 and Digilab FTS-40 spectrometers. All samples, with the exception of **5**, were run as Nujol mulls between KBr plates. Mass spectra were obtained on a Finnigan Model 4021 GC-mass spectrometer. NMR spectra were run on JEOL FX-90Q, Bruker WM-360, and Bruker AM-200 spectrometers. The $^1H$ spectra are referenced to $Me_4Si$, and $^{31}P$ spectra are referenced to external 85% $H_3PO_4$. Negative chemical shifts are assigned to signals upfield of the reference.

**General Procedures.** Manipulations of air-sensitive reagents and solutions and the workup of reaction products were performed (under argon) using Schlenk techniques, or within the confines of a helium-filled Vacuum Atmospheres HE-43 drybox equipped with a high-capacity recirculation system (MO-40V) and a Dri-Cold freezer maintained at −40 °C.

**$TaClH_2(PMe_3)_4$ (1a).** Because this complex is sensitive to dinitrogen, all solvents were subjected to three freeze–pump–thaw cycles prior to use. Inside the drybox, $TaCl_2H_2(PMe_3)_4$ (7.0 g, 12.5 mmol) was added to a precooled (−40 °C) solution of trimethylphosphine (ca. 1 mL), diethyl ether (120 mL), and THF (20 mL) in a 500-mL Morton flask. Sodium amalgam (4.2 mL of 0.5% amalgam, 12.5 mmol of Na) was added, and the reaction mixture was stirred *vigorously* for 3 h with an overhead mechanical stirrer. The initial red-orange color slowly changed to green. The suspension was filtered through Celite, and the collected solids were rinsed with an additional 50 mL of ether. The combined filtrate was evaporated to dryness, extracted with hexane (ca. 250 mL), and filtered to remove unreacted $TaCl_2H_2(PMe_3)_4$. The combined filtrate was evaporated to dryness in vacuo to afford a light green, microcrystalline product. Yield: 4.6 g, 70%. An analytical sample was obtained by recrystallization from toluene at −40 °C.

Anal. Calcd for $TaClH_2(PMe_3)_4$ ($TaClP_4C_{12}H_{38}$): C, 27.57; H, 7.33; Cl, 6.78. Found: C, 27.63; H, 7.28; Cl 6.77. IR ($cm^{-1}$): 1662 ($\nu_{\mathrm{Ta-H}}$). $^1H$ NMR (ppm, $C_6D_6$, 360 MHz, 25 °C): 1.46 (br s, 36 H, $P(CH_3)_3$), 0.23 (br s, 2 H, Ta–*H*). $^1H$ NMR (ppm, $C_7D_8$, 360 MHz, −80 °C): 1.41 (br s, 18 H, $P(CH_3)_3$), 1.36 (br s, 18 H, $P(CH_3)_3$), −0.03 (quintet, 2 H, $^2J_{PH}$ = 37.5 Hz, Ta–*H*). $^{31}P$ NMR (ppm, $C_7D_8$, 145.8 MHz, $\{^1H\}$, −80 °C): +10.5 (t, 2, $J_{PP'}$ = 29.6 Hz), −5.35 (t, 2, $J_{PP'}$ = 29.6 Hz).

The deuteride, **1b**, was prepared in the same manner as **1a**.

IR ($cm^{-1}$): 1195 ($\nu_{\mathrm{Ta-D}}$).

**$TaClH_2(dmpe)_2$ (2).** This complex was prepared by the following ligand-exchange procedure. Freshly recrystallized $TaClH_2(PMe_3)_4$ (1.56 g, 3.0 mmol) was dissolved in 100 mL of hexane, and dmpe (0.90 g, 6.0 mmol) was added. Immediately, the color changed from green to orange. The solution was stirred for 4 h, filtered, and the filtrate treated with Darco (activated charcoal). This suspension was filtered through Celite and the filtrate evaporated to dryness. The sample was then placed under high vacuum ($10^{-4}$ Torr, 30 °C) to remove residual $PMe_3$. Yield: 1.37 g, 90%.

Anal. Calcd for $TaClH_2(dmpe)_2$ ($TaClP_4C_{12}H_{34}$): C, 27.79; H, 6.61; Cl, 6.84. Found: C, 28.52; H, 6.78; Cl, 7.03. IR ($cm^{-1}$): 1630 ($\nu_{\mathrm{Ta-H}}$). $^{31}P$ NMR (ppm, $C_7D_8$, 36.2 MHz, $\{^1H\}$, −80 °C): +22.1 (br s, 1), +20.2 (br s, 2), +18.3 (br s, 1).

**$TaCl(C_2H_4)(PMe_3)_4$ (3).** On a high-vacuum line, ethylene (0.076 mmol) was condensed (at −196 °C) into a 5-mm NMR tube containing a frozen solution of $TaClH_2(PMe_3)_4$ (20 mg, 0.038 mmol) in toluene-$d_8$. The tube was flame-sealed and placed in the $^1H$ probe, where it was warmed to −60 °C. The ethylene resonance (δ 5.30) decreased in intensity with corresponding increases at δ 2.15 (br quintet, $J_{HP}$ ~ 4 Hz, Ta-$C_2H_4$), 1.31 (br s, $P(CH_3)_3$),[21] and 0.80 (br s, $C_2H_6$). The reaction was complete in ca. 0.5 h.

**$[TaClH_2(PMe_3)_3]_2(\mu\text{-}N_2)$ (4a).** An ether solution (ca. 50 mL) of $TaH_2Cl(PMe_3)_4$ (1.0 g, 1.9 mmol) was transferred to a 90-mL Fischer-Porter reaction vessel. The latter was removed from the drybox, evacuated, and pressurized (40 psi) with $N_2$. After 12 h, the solution was faintly colored and a mustard yellow precipitate had formed. The bomb was returned to the drybox where the precipitate was isolated by filtration, washed with hexane, and dried in vacuo. Yield: 0.78 g, 90%.

Anal. Calcd for $[TaClH_2(PMe_3)_3]_2(\mu\text{-}N_2)$ ($Ta_2Cl_2P_6C_{18}H_{58}N_2$): C, 23.46; H, 6.35; N, 3.04. Found: C, 22.38; H, 6.01; N, 3.09. IR ($cm^{-1}$): 1585 ($\nu_{\mathrm{Ta-H}}$), 853 ($\nu_{\mathrm{Ta=N-N=Ta}}$). $^1H$ NMR (ppm, $C_6D_6$, 360 MHz, 25 °C): 8.54 (m, 4 H, Ta–*H*), 1.67 (d, $^2J_{PH}$ = 8.54 Hz, 18 H, $P(CH_3)_3$), 1.45 (m, $^2J_{PH}$ = 3.36 Hz, 36 H, $P(CH_3)_3$). $^{31}P$ NMR (ppm, $C_6D_6$, 145.8 MHz, $\{^1H\}$, 25 °C): −3.0 (t, 2, $J_{PP'}$ = 5.4 Hz), −23.1 (d, 4, $J_{PP'}$ = 5.4 Hz). $^{31}P$ NMR (ppm, $C_6D_6$, 145.8 MHz, {selective $^1H$}, 25 °C): −3.0 (t of t, $J_{PH}$ = 66.0 Hz), −23.1 (complex m).

The deuteride, **4b**, was prepared in an analogous manner.

IR ($cm^{-1}$): 1140 ($\nu_{\mathrm{Ta-D}}$) ($\nu_{\mathrm{Ta-H}}/\nu_{\mathrm{Ta-D}}$ = 1.39).

A $^{15}N_2$ derivative was prepared from **1a** and $^{15}N_2$ in the same fashion as **4a**.[22]

IR ($cm^{-1}$): 829 ($\nu_{\mathrm{Ta=N-N=Ta}}$).

**$TaCl(CO)_3(PMe_3)_3$ (5).** A solution of $TaClH_2(PMe_3)_4$ (1.0 g, 1.9 mmol) in diethyl ether (ca. 60 mL) was transferred to a 90-mL Fischer-Porter pressure vessel. The bomb was removed from the drybox, evacuated, and pressurized with CO (40 psi). After the solution was stirred for 12 h, the color had changed from green to orange. The bomb was then returned to the drybox, where the solution was filtered through a medium-porosity frit. The filtrate was evaporated to dryness in vacuo, and the solid residue was recrystallized from warm (40 °C) hexane. Yield: 0.9 g, 89%.

Anal. Calcd for $TaCl(CO)_3(PMe_3)_3$ ($TaClC_{12}H_{27}O_3P_3$): C, 27.26; H, 5.15; Cl, 6.71. Found: C, 26.95; H, 5.10; Cl, 6.80. IR ($cm^{-1}$, hexane solution): 1962, 1862, 1843 ($\nu_{CO}$). $^1H$ NMR (ppm, $C_7D_8$, 360 MHz, −80 °C): 1.14 (d, 9 H, $J_{PH}$ = 8.24 Hz, $P(CH_3)_3$), 0.92 (br s, 18 H, $P'(CH_3)_3$). $^{31}P$ NMR (ppm, $C_7D_8$, 145.8 MHz, $\{^1H\}$, 25 °C): −21.5 (br s). $^{31}P$ NMR (ppm, $C_7D_8$, 145.8 MHz, $\{^1H\}$, −80 °C): −10.4 (t, 1, $J_{PP'}$

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(21) These chemical shifts are similar to those reported in ref 12.

(22) We have not been able to locate the $^{15}N$ NMR resonance of this compound, presumably because of its low solubility in organic solvents. Low solubility has also precluded a molecular weight determination.

**Table V.** Crystal Data for $TaClH_2(PMe_3)_4$

| | | | |
|---|---|---|---|
| mol formula | $TaC_{12}H_{38}ClP_4$ | max (sin $\theta$)/$\lambda$, Å$^{-1}$ | 0.662 |
| mol wt | 522.73 | no. of reflcns | 14 703 |
| color | green | no. of unique reflcns | 2250 |
| temp, K | 50 (1) | merging *R* factor | 0.046 |
| cryst dimens, mm | 2.0 × 2.5 × 4.7 | linear abs coeff, cm$^{-1}$ | 3.2 |
| | | range of transmissn coeff | 0.22–0.67 |
| space group | $P2_1/a$ | | |
| cell dimens | | extinction param, $g \times 10^4$ | 0.03 (1) |
| $a$, Å | 18.436 (4) | | |
| $b$, Å | 9.319 (2) | max extinction coeff | 1.12 |
| $c$, Å | 12.376 (3) | no. of variables | 506 |
| $\beta$, deg | 97.90 (3) | final residuals | |
| molecules/cell | 4 | $R(F)$ | 0.082 |
| cell $V$, Å$^3$ | 2106.1 (8) | $R(F^2)$ | 0.114 |
| $d$(calcd), g cm$^{-3}$ | 1.648 | $R_w(F^2)$ | 0.163 |
| $\lambda$, Å | 1.068 (4) | error in observn of unit wt | 1.278 |
| type of data measd | $\pm h,+k,\pm l$ | | |
| | | max $\Delta/\sigma$, last cycle | 0.0101 |

= 50.7 Hz), −24.9 (d, 2, $J_{PP'}$ = 50.7 Hz). $^{13}C$ NMR (ppm, $C_7D_8$, 90.56 MHz, {$^1H$}, −80 °C): +269.5 (br s, 1, *C*O), +254.8 (br s, 2, *C*O), 16.4 (m, 9, $P(CH_3)_3$).

**$TaCl(CO)_2(dmpe)_2$.** A hexane solution (ca. 10 mL) of $TaClH_2(dmpe)_2$ (0.10 g, 0.19 mmol) was loaded into the 90-mL Fischer-Porter bomb and removed from the drybox. The bomb was evacuated and pressurized with carbon monoxide (40 psi). Over the course of 12 h, a yellow powder slowly precipitated. The vessel was returned to the drybox where the precipitate was filtered, washed with a small amount of hexane, and dried. Yield: 0.105 g, 94%.

The spectroscopic properties (MS, IR, NMR) of this compound were identical with those reported earlier.[18a]

**Neutron Structure Determination of 1a.** Very large single crystals of emerald green **1a** can be grown by cooling saturated toluene solutions to −40 °C and maintaining the sample at this temperature for 1–2 weeks. A crystal with dimensions of 2.0 × 2.5 × 4.7 mm was sealed in a lead glass tube under an argon atmosphere. The glass tube was mounted inside a helium-filled aluminum can, which was screwed on to the cold stage of a Displex closed-cycle helium refrigerator. The temperature of the sample was maintained at 50 (1) K throughout the entire experiment. Data were collected on the 2XE single-crystal neutron diffractometer at the University of Missouri Research Reactor. The unit cell dimensions were determined from 29 well-centered reflections with 30° < 2$\theta$ < 42° (see Table V for crystal data). The integrated intensities of 6048 out of 14 703 reflections were measured on the basis of a prescan criterion of an intensity greater than 1.5 times the background. An analytical absorption correction was applied, and symmetry-related data were averaged to yield 2750 unique reflections.

The non-hydrogen atomic positional parameters that were determined from the X-ray structure[2] were used to calculate phases for a difference Fourier map, from which the locations of most of the hydrogen atoms were obtained. The remaining atoms were located and refined by using conventional least-squares and Fourier techniques. A secondary extinction parameter[23] was included in the final refinements, and all atoms were treated with anisotropic thermal parameters. The neutron scattering lengths used for all atoms were those tabulated by Bacon.[24] Table I contains the atomic positional and equivalent isotropic thermal parameters obtained from the final least-squares cycle. We cannot find any systematic error to account for the relatively large *R* factors but instead believe it to be the result of a small observation to parameter ratio (4.4) and less-than-ideal counting statistics on the data that were used. In the final difference Fourier the highest positive peak was ca. 2.7% of Cl(2), its nearest neighbor, and the highest negative peak was ca. 13% of an average hydrogen in the structure.

**Table VI.** Crystal Data for $TaCl(CO)_3(PMe_3)_3$

| | | | |
|---|---|---|---|
| mol formula | $TaC_{12}H_{27}ClO_3P_3$ | $\lambda$, Å | 0.71069 |
| mol wt | 528.67 | linear abs coeff, cm$^{-1}$ | 57.54 |
| color | red | | |
| temp, °C | −160 (2) | 2$\theta$ range, deg | 6–45 |
| cryst dimens, mm | 0.07 × 0.07 × 0.08 | no. of data with $F_o \geq 2.33\sigma(F_o)$ | 4628 |
| space group | $P2_1/n$ | | |
| cell dimens | | no. of unique data | 5280 |
| $a$, Å | 17.684 (3) | final residuals | |
| $b$, Å | 13.904 (5) | $R(F)$ | 0.0391 |
| $c$, Å | 18.522 (5) | $R_w(F)$ | 0.0405 |
| $\beta$, deg | 117.60 (2) | goodness of fit, last cycle | 0.882 |
| molecules/cell | 8 | | |
| cell $V$, Å$^3$ | 2018.02 | max $\Delta/\sigma$, last cycle | 0.05 |
| $d$(calcd), g cm$^{-3}$ | 1.740 | | |

**X-ray Structure Determination of 5.** General procedures were the same as those described previously.[25]

Red crystals of **5** were grown by slow cooling of a saturated hexane solution to −40 °C. A suitable fragment was cleaved from a large crystal and transferred to the goniostat by using standard inert-atmosphere techniques. Crystal data are presented in Table VI.

The structure was solved by direct methods and Fourier techniques and refined by full-matrix least squares. Most of the hydrogen atoms were visible in a difference Fourier phased on the non-hydrogen atoms, but no attempt was made to refine them. All hydrogen atoms were included as fixed atom contributors in idealized staggered positions. $\psi$-Scans of five peaks indicated that absorption was insignificant; no absorption correction was made. A final difference Fourier revealed three peaks of intensity 1.1–1.5 e/Å$^3$; these were located near the tantalum atoms. All other peaks were less than 0.6 e/Å$^3$.

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**Supplementary Material Available:** Listings of complete bond distances and angles and anisotropic thermal parameters ($U_{ij}$) for **1a** and **5** and calculated hydrogen atom positions for **5** (16 pages); listings of observed and calculated neutron structure factors for **1a** and observed and calculated X-ray structure factors for **5** (37 pages). Ordering information is given on any current masthead page. A complete structural report on **5** (MSC Report No. 83930) is available, in microfiche form only, from the Chemistry Library, Indiana University, Bloomington, IN 47405.

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