breathing mode always is more intense than the ring-stretching mode (ratio 1.2-1.5). In the complexes with a second or third metal coordinated through the exocyclic oxygen(s) of 1-MeU, the relative intensities of these two modes are inverted (Table V).

Conclusion

Three aspects of the results described here appear to be noteworthy.

(1) Binding of a heterometal to the exocyclic oxygens of a N(3)-platinated 1-methyluracilate ligand is not restricted to a cis arrangement of two 1-MeU ligands. Although an arrangement of this kind, as found for example in Pt_2,Ag,L_4 and Pt_4,Ag,L_4, may contribute to the formation of these complexes, the results presented here indicate that this favorable steric factor is not a prerequisite for the formation of heteronuclear complexes in general. Thus, the ligating properties of N(3)-platinated 1-MeU and 1-MeT should be attributed primarily to the favorable charge distribution in these ligands, similar to the situation with N(3)-mercurated 1-MeT as shown by Guay and Beauchamp.[26]

(2) Association of small building blocks of dinuclear or, as in the present case, tetranuclear units, which has previously been found to occur through intermolecular hydrogen bonding[7,12,13] or metal-metal interactions,[14] can also be accomplished through anion bridging. Though nitrate bridging in the compound described here certainly is restricted to the solid state, there is the possibility that anions with good coordinating properties could act in such a way in solution as well.

(3) The solution behavior of the head-head and the head-tail dimers *cis*-$[(NH_3)_2Pt(1\text{-MeU})]_2^{2+}$ in the presence of Ag(I) shows that the Pt-O bonds in these complexes are labile. The Pt-O bonds are cleaved not only by strongly coordinating anions such as Cl^-, which compete with oxygen for Pt(II),[12] but also by cations such as Ag(I), which then compete with Pt(II) for oxygen donors of the 2,4-pyrimidinedione ligands.

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft, DFG, and the Technische Universität München. We thank J. Riede for his assistance with the X-ray measurements and Drs. P. and L. G. Marzilli for helpful comments.

Registry No. *cis*-**1**(NO_3), 85715-80-6; *cis*-**2**$(NO_3)_2$ (head-tail dimer), 75790-29-3; *cis*-**2**$(NO_3)_2$ (head-head dimer), 85886-74-4; *cis*-$[(NH_3)_4Pt_2(1\text{-MeU})_2Ag_2](NO_3)_4\cdot 2H_2O$, 89637-18-3; *cis*-$(NH_3)_2Pt(1\text{-MeU})_2$, 83350-97-4; *cis*-$[(NH_3)_2Pt(1\text{-MeU})(9\text{-EtG})]^+$, 89637-19-4; *cis*-$[(NH_3)_2Pt(1\text{-MeU})X]^+$ (X = 1-methylcytosine), 89637-20-7.

Supplementary Material Available: Tables of atomic and thermal parameters and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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(26) Guay, F.; Beauchamp, A. *Inorg. Chim. Acta* **1982**, *66*, 57.

Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109, and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Paramagnetic Hydride Complexes of Niobium(IV) and Tantalum(IV)[1]

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Received August 24, 1983

The d^3 complexes $TaCl_2(PMe_3)_4$ and $NbCl_2(PMe_3)_4$ are prepared by reduction of MCl_5 with sodium amalgam in diethyl ether in the presence of excess PMe_3 and isolated as brown crystalline solids in 60 and 25% yields, respectively. Red-brown $NbCl_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] is obtained in 90% yield via reduction of $NbCl_4(dmpe)_2$ in THF. These MCl_2 adducts, as well as the previously reported $TaCl_2(dmpe)_2$, all react readily with dihydrogen at 25 °C. Paramagnetic, eight-coordinate M(IV) hydride complexes, $MCl_2H_2L_4$, are isolated from the $TaCl_2(PMe_3)_4$, $TaCl_2(dmpe)_2$, and $NbCl_2(dmpe)_2$ reactions. The yields of $TaCl_2H_2(PMe_3)_4$ (red), $TaCl_2H_2(dmpe)_2$ (red-orange), and $NbCl_2H_2(dmpe)_2$ (red-orange) range from 75 to 90%. These d^1 hydrides have been characterized by infrared and electron spin resonance spectroscopy, by magnetic susceptibility, and, in the case of the two tantalum complexes, by low-temperature X-ray crystallography. $TaCl_2H_2(PMe_3)_4$ adopts a distorted dodecahedral geometry in the solid state while $TaCl_2H_2(dmpe)_2$ is more appropriately described as a distorted square-antiprismatic complex. The hydride ligands in both complexes were located and refined. Crystal data (at -160 °C) are as follows: for $TaCl_2H_2(PMe_3)_4$, monoclinic space group *Cc*, $a = 15.127$ (3) Å, $b = 12.005$ (3) Å, $c = 12.410$ (2) Å, $\beta = 92.49$ (1)°, $V = 2251.6$ Å^3, $Z = 4$, $d_{calcd} = 1.647$ g cm^{-3}; for $TaCl_2H_2(dmpe)_2$, orthorhombic space group $P2_12_12_1$, $a = 9.781$ (4) Å, $b = 15.842$ (8) Å, $c = 13.832$ (6) Å, $V = 2143.3$ Å^3, $Z = 4$, $d_{calcd} = 1.717$ g cm^{-3}.

Introduction

The first paramagnetic hydride complexes of niobium and tantalum, viz., Cp_2MH_2 (M = Nb, Ta) and $TaH_4(dmpe)_2$, were reported in 1974 by Kochi, Parshall, and their coworkers.[3,4] They were prepared by reacting the corresponding M(V) hydrides with photogenerated *tert*-butoxy radicals (eq 1 and 2) and characterized low-temperature electron spin

$$2Cp_2MH_3 + t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2Cp_2MH_2 + 2\text{-}t\text{-BuOH} \quad (1)$$

$$2TaH_5(dmpe)_2 + t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2TaH_4(dmpe)_2 + 2\text{-}t\text{-BuOH} \quad (2)$$

resonance (ESR) spectroscopy. None of these 17-electron, d^1 species was sufficiently stable at ambient temperature to permit isolation, a feature that necessarily frustrated any thorough investigation of their physicochemical properties, structural chemistry, and reactivity.[5]

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[1] Paper presented, in part, at the 186th National Meeting of the American Chemical Society, Washington, DC, Aug 1983.

[2] (a) The University of Michigan. (b) Indiana University.

[3] Elson, I. H.; Kochi, J. K.; Klabunde, U.; Manzer, L. E.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 7374.

[4] dmpe is an acronym for 1,2-bis(dimethylphosphino)ethane or $Me_2PCH_2CH_2PMe_2$.

[5] The reactions of metastable Cp_2NbH_2 with several olefins have been studied by ESR. See: Elson, I. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 1263.

During the course of our investigations on the synthesis and reactions of low-valent niobium and tantalum complexes we had the good fortune to "rediscover" paramagnetic group 5 hydrides. Eight-coordinate $TaCl_2H_2(PMe_3)_4$, $TaCl_2H_2(dmpe)_2$, and $NbCl_2H_2(dmpe)_2$ were prepared by reacting the corresponding six-coordinate tantalum(II) and niobium(II) dichloro phosphine monomers with molecular hydrogen. The feature that distinguishes these new 17-electron hydrides from their predecessors is that they all were isolated as thermally stable crystalline solids. In this paper we will describe the syntheses and properties of these interesting inorganic radicals. Some of these results have appeared in preliminary form.[6]

Results

Preparation of Tantalum(II) and Niobium(II) Complexes. Tantalum pentachloride is reduced smoothly by sodium amalgam in ether in the presence of excess (5–6 equiv) trimethylphosphine to give brown, air-sensitive $TaCl_2(PMe_3)_4$ (**1**) (eq 3). Yields as high as 70% have been obtained by our

$$TaCl_5 + 3Na/Hg + PMe_3\ (excess) \xrightarrow{OEt_2} TaCl_2(PMe_3)_4 + 3Na/Hg \quad (3)$$

procedure but are more typically in the range of 60% for 20–40-mmol scale reactions. The use of excess phosphine is necessary to suppress the dimerization of *mer*-$TaCl_3(PMe_3)_3$,[7] an intermediate in the reduction. Once the tantalum(III) dimer, $[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2$,[7,8] is formed, it cannot be reduced to tantalum(II) complexes. An analogous reduction of $NbCl_5$ or $NbCl_4{\cdot}2PMe_3$[9] gave poor, but reproducible yields (20–30%) of brown, air-sensitive $NbCl_2(PMe_3)_4$ (**2**) even when a larger excess of PMe_3 was used. The niobium(III) dimer, $[NbCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2$,[10] is the major product of this reduction. This binuclear complex, like its tantalum analogue, is essentially insoluble in diethyl ether and does not interfere with the workup of **2**. The ^1H NMR spectra of **1** and **2** show broad PMe_3 resonances at δ 1.98 and δ −0.84, respectively, which suggest that both have trans-octahedral geometries. This was confirmed by X-ray crystallography for **1**.[6a]

The dmpe derivatives, $TaCl_2(dmpe)_2$ (**3**) and $NbCl_2(dmpe)_2$ (**4**), were prepared by reduction of the tetrachlorides, $MCl_4(dmpe)_2$,[9,11] with sodium amalgam in THF (eq 4), and both

$$MCl_4(dmpe)_2 + 2Na/Hg \xrightarrow{THF} \underset{\substack{\mathbf{3},\ M = Ta\\ \mathbf{4},\ M = Nb}}{MCl_2(dmpe)_2} + 2NaCl \quad (4)$$

were obtained in high yield (ca. 90%). The tantalum(II) complex has been reported previously,[11] but $NbCl_2(dmpe)_2$ is a new compound. Complexes **3** and **4** are very air sensitive in the solid state but are otherwise thermally stable, sublimable red-brown crystalline solids. Both show strong parent ions in their mass spectra, with the correct isotope patterns expected for dichlorides. They are soluble in toluene, THF, and hot hexane.

The dmpe complexes can also be prepared by metathesis of **1** and **2** with 2 equiv of the bidentate phosphine in THF or hexane (eq 5). We had hoped that this reaction would provide binuclear products, i.e., $M_2Cl_4(dmpe)_2$, but there is no evidence that these are formed. In fact, reaction 5 is quantitative. The search for Nb^3–Nb and Ta^3–Ta triple bonds continues.

$$MCl_2(PMe_3)_4 + 2dmpe \xrightarrow{THF} MCl_2(dmpe)_2 + 4PMe_3 \quad (5)$$

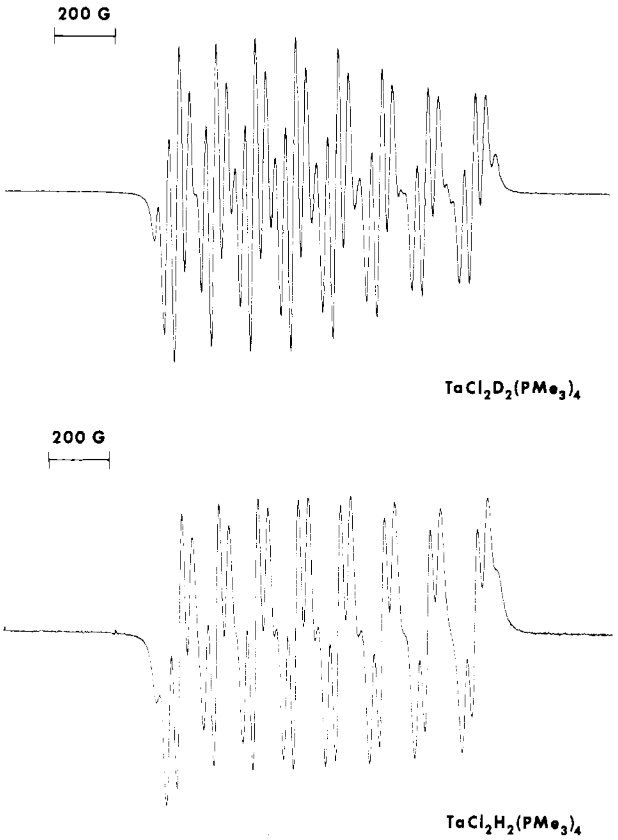

Figure 1. ESR spectra of $TaCl_2X_2(PMe_3)_4$.

We suspect, but cannot offer direct experimental evidence, that the dmpe complexes also have trans-octahedral geometries. We have, thus, far, been unable to grow X-ray quality crystals of these materials, and the ^1H NMR spectra were very broad and uninformative.

Formation of $MCl_2H_2L_4$ Complexes. Ether solutions of **1**, in the presence of free trimethylphosphine, react readily with dihydrogen (40 psi H_2, 25 °C, 4 h) to provide red air-sensitive $TaCl_2H_2(PMe_3)_4$ (**5a**) in ca. 75% recrystallized yield (eq 6).

$$TaCl_2(PMe_3)_4 + X_2 \xrightarrow{OEt_2} \underset{\substack{\mathbf{5a},\ X = H\\ \mathbf{5b},\ X = D}}{TaCl_2X_2(PMe_3)_4} \quad (6)$$

The deuteride, **5b**, was prepared in the same manner. We add free phosphine to suppress the slow dimerization of **5a** to the quadruply hydrogen-bridged tantalum(IV) dimer $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$[12] (vide infra). The solid-state infrared spectra (Nujol mull) of **5a** and **5b** show strong terminal M–H (D) stretching modes at 1690 and 1212 cm^{-1}, respectively ($\nu_{Ta\text{-}H}/\nu_{Ta\text{-}D}$ = 1.39). The room-temperature magnetic moment (Gouy method) of **5a** is 1.74 μ_B, indicative of a d^1 complex with an orbitally nondegenerate ground state. In Figure 1 we show the X-band ESR spectra obtained for dilute toluene solutions of **5a** and **5b**. An octet of quintets is observed in both spectra; i.e., we have hyperfine coupling to one tantalum nucleus (^{181}Ta, $I = {}^7/_2$, ~100% abundance) and four equivalent ^{31}P nuclei ($I = {}^1/_2$, 100% abundance). Hydride coupling was not resolved in the spectrum of **5a**, but a computer simulation[13] of the experimental spectrum yielded a value of $\langle a \rangle_H$ on the

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(6) (a) Luetkens, M. L., Jr.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1983**, *105*, 4474. (b) Luetkens, M. L., Jr.; Elcesser, W. L.; Huffman, J. C.; Sattelberger, A. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1072.

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

(8) Sattelberger, A. P.; Wilson, R. B., Jr.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 4179.

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(13) Ahn, M. K. *QCPE* **1966**, *11*, 83.

Table I. Hyperfine Coupling Constants for $MCl_2H_2P_4$ Complexes

radical	hyperfine coupling const,[a] G $\langle a\rangle_M$	$\langle a\rangle_P$	$\langle a\rangle_H$	line width, G	$\langle g\rangle^{a,b}$	ref
$NbCl_2H_2(dmpe)_2$	109.0	25.5	11.1[c]	18	1.96	*d*
$TaCl_2H_2(dmpe)_2$	126.0	25.8	6.0[c]	13	1.97	*d*
$TaCl_2H_2(PMe_3)_4$	139.4	33.9	6.4[c]	18	1.95	*d*
$TaH_4(dmpe)_2$	106.3	32.9	*e*	18	1.99	*f*

[a] Hyperfine coupling constants and isotropic *g* factors are all corrected to second order by using the Briet–Rabi equation. [b] ±0.01. [c] From computer simulations[13] of the experimental spectra. [d] This work. [e] Not resolved. [f] Reference 3.

order of 6.4 G. Hyperfine coupling constants, isotropic *g* values, and line widths for all of our paramagnetic group 5 hydrides are given in Table I, together with the parameters reported for $TaH_4(dmpe)_2$.[3]

Ether solutions of $NbCl_2(PMe_3)_4$ (**2**) also react readily with dihydrogen (40 psi H_2, 25 °c, 4 h), but no paramagnetic species could be isolated from the yellow-brown solutions even when a large excess of free phosphine was added prior to hydrogenation. $[NbCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$ was the only product isolated from the reaction and most likely arises from the rapid decomposition of transient $NbCl_2H_2(PMe_3)_4$ (eq 7). Support

$$NbCl_2(PMe_3)_4 + H_2 \xrightarrow{OEt_2} [NbCl_2H_2(PMe_3)_4] \rightarrow 0.5[NbCl_2(PMe_3)_2]_2(\mu\text{-}H)_4 + 2PMe_3 \quad (7)$$

for this hypothesis comes from two sources: (1) Our successful isolation and characterization of $NbCl_2H_2(dmpe)_2$ (vide infra) proves that H_2 will add to a monomeric niobium(II) center. (2) Cyclohexane solutions of **5a** provide quantitative yields of $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$ on thermolysis (81 °C, 1 h).[6a] These quadruply hydrogen-bridged M(IV) dimers will be the subjects of a future publication.[14]

Hexane solutions of the dmpe complexes **3** and **4** react smoothly with hydrogen or deuterium (40 psi H_2, 25 °C, 4 h) and deposit sparingly soluble red-orange precipitates (eq 8) in ca. 90% yield. The tantalum hydrides **6a** and **6b** have

$$\begin{array}{lll} MCl_2(dmpe)_2 + X_2 \xrightarrow{C_6H_{14}} & MCl_2X_2(dmpe)_2 & (8) \\ \mathbf{3},\ M = Ta & \mathbf{6a},\ M = Ta,\ X = H & \\ \mathbf{4},\ M = Nb & \mathbf{6b},\ M = Ta,\ X = D & \\ & \mathbf{7a},\ M = Nb,\ X = H & \\ & \mathbf{7b},\ M = Nb,\ X = D & \end{array}$$

also been isolated from the reactions of **5a** and **5b** with 2 equiv of dmpe in THF. All of these paramagnetic hydrides are moderately air sensitive in the solid state and very sensitive in solution. Thermally they are quite robust; **6a** and **7a** decompose, without melting, at 190 and 145 °C, respectively. A weak parent ion (P^+) was observed in the mass spectrum of **6a**, but P^+ could not be detected in the spectrum of **7a**. Both complexes show strong $P\text{-}H_2^+$ ions. The solid-state infrared spectra of **6a** and **7a** show ν_{M-H} at 1650 and 1610 cm^{-1}, respectively; for **6b** and **7b**, the M–D stretching modes were located at 1185 and 1180 cm^{-1}, respectively.

The room-temperature magnetic moments (Gouy method) for **6a** and **7a** (1.73 and 1.72 μ_B) were close to the value expected for d^1 complexes with no orbital contributions to the moment, and both complexes and their deuterium analogues gave beautiful ESR spectra in toluene at 25 °C. The X-band spectra of **6a** and **6b** are very similar to those of **5a** and **5b** and are included as supplementary material (see Table I for spectral parameters). In Figure 2, the X-band spectra of **7a** and **7b** are presented. A decet of quintets pattern can be seen

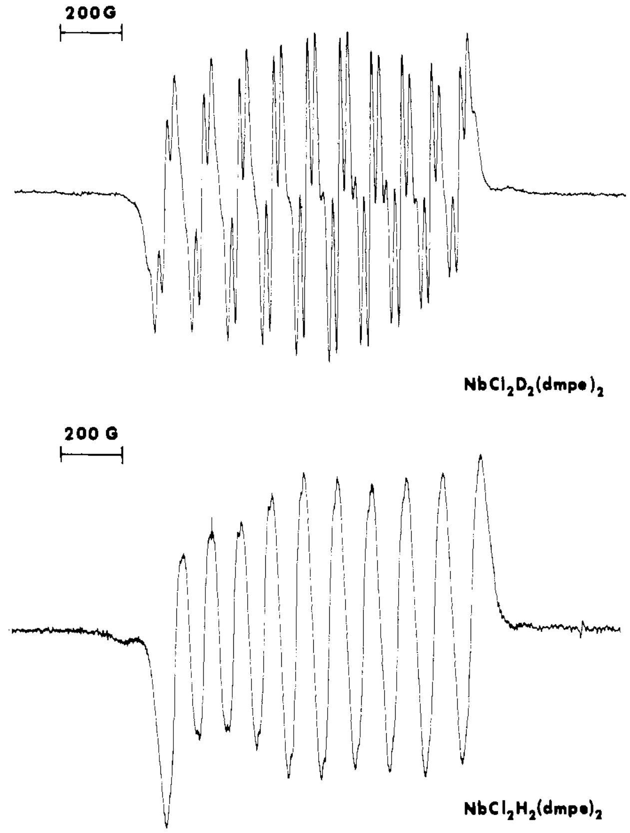

Figure 2. ESR spectra of $NbCl_2X_2(dmpe)_2$.

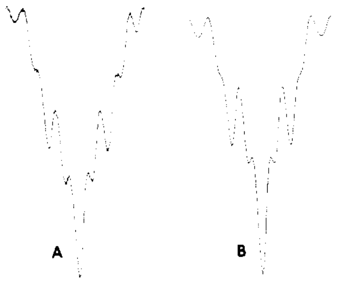

Figure 3. A portion ($m_I = +^1/_2$) of the second-derivative ESR spectrum of $NbCl_2H_2(dmpe)_2$ (A) and a computer simulation (B).[13] See text for discussion.

in the spectrum of **7b**. Here we have hyperfine coupling to ^{93}Nb, an $I = {}^9/_2$ nucleus (100% abundance), and four equivalent ^{31}P nuclei. ^1H and ^{31}P coupling are barely discernible in the first-derivative ESR spectrum of **7a** but can be clearly seen in the second-derivative spectrum. A portion of that spectrum, i.e., the $m_{Nb} = +^1/_2$ line (A), is shown in Figure 3 together with a computer simulation (B) of the quintet of triplets pattern. The values of $\langle a\rangle_P$ and $\langle a\rangle_H$ are respectively 25.5 and 11.1 G.

With the spectroscopic characterization of our paramagnetic hydrides well in hand, we decided to collect X-ray data on $TaCl_2H_2(PMe_3)_4$ (**5a**) and $TaCl_2H_2(dmpe)_2$ (**6a**). Our objectives were (1) to define the stereochemistry of these 8-coordinate tantalum(IV) complexes and observe the structural consequences of the exchange of four PMe_3 for two dmpe ligands and (2) to locate and refine the terminal hydride ligands. Both of these objectives were attained as described in the next section.

Solid-State Structures. In the crystalline state, $TaCl_2H_2(PMe_3)_4$ is composed of discrete mononuclear units and there are no unusual intermolecular contacts. Final atomic positional parameters are listed in Table II, and selected bond distances and angles are provided in Table IV. An ORTEP drawing of

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[14] Wilson, R. B., Jr.; Luetkens, M. L., Jr.; Huffman, J. C.; Sattelberger, A. P., in preparation.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for $TaCl_2H_2(PMe_3)_4$ (5a)[a]

atom	*x*	*y*	*z*	B_{iso}, Å^2
Ta(1)	−214*	−2709.9 (2)	1038*	11
Cl(2)	−1287 (4)	−1105 (4)	701 (4)	21
Cl(3)	873 (3)	−1101 (4)	1396 (4)	18
P(4)	21 (5)	−2305 (3)	−1016 (5)	18
P(5)	−1711 (4)	−3718 (4)	1008 (4)	16
P(6)	1277 (4)	−3719 (4)	1076 (4)	14
P(7)	−426 (3)	−2311 (4)	3092 (5)	14
C(8)	527 (10)	−3353 (13)	−1840 (11)	17
C(9)	656 (8)	−1090 (11)	−1232 (8)	16
C(10)	−1003 (11)	−1992 (14)	−1885 (12)	22
C(11)	−2658 (12)	−3046 (11)	1668 (16)	26
C(12)	−1696 (9)	−5129 (10)	1576 (12)	18
C(13)	−2242 (11)	−3951 (13)	−267 (11)	25
C(14)	2246 (10)	−3185 (10)	435 (12)	18
C(15)	1789 (9)	−3960 (13)	2479 (9)	20
C(16)	1244 (11)	−5127 (13)	574 (12)	26
C(17)	548 (12)	−2066 (13)	3893 (12)	24
C(18)	−1115 (11)	−1062 (10)	3411 (13)	26
C(19)	−928 (17)	−3356 (15)	3962 (17)	32
H(1)	−38 (7)	−406 (9)	20 (8)	22
H(2)	−6 (7)	−383 (9)	205 (8)	32

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. B_{iso} values are ×10. Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609. Parameters marked by an asterisk were not varied.

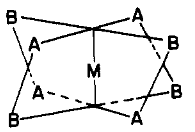
Table III. Fractional Coordinates and Isotropic Thermal Parameters for $TaCl_2H_2(dmpe)_2$ (6a)[a]

atom	*x*	*y*	*z*	B_{iso}, Å^2
Ta(1)	6726.0 (4)	1325.3 (2)	2456.0 (3)	12
Cl(2)	4706 (3)	2092 (2)	1696 (2)	18
Cl(3)	7295 (3)	2758 (2)	3206 (2)	19
P(4)	7889 (3)	1900 (2)	931 (2)	17
P(5)	5187 (3)	93 (2)	2068 (2)	17
P(6)	9225 (3)	1113 (2)	2798 (2)	21
P(7)	5216 (3)	1206 (2)	3977 (2)	16
C(8)	9726 (16)	9726 (16)	1580 (9)	23
C(9)	7243 (16)	1539 (8)	−216 (9)	25
C(10)	7952 (14)	3042 (8)	760 (10)	25
C(11)	3769 (13)	24 (9)	2920 (10)	23
C(12)	4186 (17)	68 (10)	922 (10)	26
C(13)	5935 (14)	−967 (8)	2111 (11)	26
C(14)	10313 (13)	1672 (8)	1920 (11)	24
C(15)	9893 (14)	1491 (12)	3939 (13)	35
C(16)	9859 (13)	17 (8)	2762 (10)	25
C(17)	4294 (16)	191 (10)	3939 (9)	23
C(18)	6039 (14)	1196 (9)	5138 (9)	27
C(19)	3883 (14)	1974 (9)	4151 (8)	21
H(1)	762 (10)	49 (6)	165 (17)	0 (19)
H(2)	702 (10)	47 (6)	319 (7)	0 (19)

[a] See footnote to Table II.

5a, giving the atom-numbering scheme for the inner coordination sphere, is shown in Figure 4. It is very difficult to get a "feel" for the ligand stereochemistry in this complex from the single ORTEP drawings, regardless of the orientation selected, so we have provided a stereoview of **5a** in Figure 5 (top).

5a has virtual, but not crystallographically imposed, C_2 symmetry and is best described as a distorted dodecahedral complex. A regular dodecahedron is characterized by two orthogonal trapezoidal arrays of ligands (see I). In deciding which of the idealized 8-coordinate polyhedra, i.e., the dodecahedron or the square antiprism, **5a** could "best" be identified with, we followed[15] the suggestions of Lippard and Russ and (1) computed trapezoidal least-squares planes for a dodecahedron, (2) calculated the angle between these assumed planes, and (3) compared this angle with the values of 90° for the idealized dodecahedron and 77.4° for the idealized square antiprism. For **5a**, least-squares planes were calculated for the trapezoids composed of Ta, Cl2, Cl3, P5, and P6 *and* Ta, H1, H2, P4, and P7. Some distances and the deviations



I

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for $TaCl_2H_2L_4$

	L = PMe_3	L = $^1/_2$ dmpe
Ta(1)–H(1)	1.94 (11)	1.94 (10)
Ta(1)–H(2)	1.85 (11)	1.71 (10)
Ta(1)–Cl(2)	2.542 (5)	2.546 (3)
Ta(1)–Cl(3)	2.563 (5)	2.557 (3)
Ta(1)–P(4)	2.633 (6)	2.564 (3)
Ta(1)–P(5)	2.567 (5)	2.523 (3)
Ta(1)–P(6)	2.559 (5)	2.512 (3)
Ta(1)–P(7)	2.628 (6)	2.577 (3)
P–C (methyl)	1.83 [1][a]	1.822 [8][a]
P–C (methylene)		1.844 [9][a]
C–C		1.50 [2][a]
H(1)–Ta(1)–H(2)	77 (6)	74 (4)
Cl(2)–Ta(1)–Cl(3)	81.8 (1)	85.0 (1)
Cl(2)–Ta(1)–P(4)	79.2 (2)	80.5 (1)
Cl(2)–Ta(1)–P(5)	78.4 (2)	79.5 (1)
Cl(2)–Ta(1)–P(6)	156.6 (2)	153.7 (1)
Cl(2)–Ta(1)–P(7)	85.3 (2)	85.8 (1)
Cl(3)–Ta(1)–P(4)	85.2 (2)	85.5 (1)
Cl(3)–Ta(1)–P(5)	156.5 (2)	154.6 (1)
Cl(3)–Ta(1)–P(6)	78.2 (2)	80.3 (1)
Cl(3)–Ta(1)–P(7)	78.4 (2)	81.9 (1)
P(4)–Ta(1)–P(5)	103.3 (2)	111.4 (1)
P(4)–Ta(1)–P(6)	87.1 (2)	76.8 (1)
P(4)–Ta(1)–P(7)	158.9 (1)	162.2 (1)
P(5)–Ta(1)–P(6)	123.6 (1)	121.1 (1)
P(5)–Ta(1)–P(7)	87.4 (2)	77.0 (1)
P(6)–Ta(1)–P(7)	102.3 (1)	113.2 (1)
Ta–P–C (methyl)	117.3 [8][a]	118.2 [4][a]
Ta–P–C (methylene)		110.3 [8][a]
P–C–C		109.8 [2][a]

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

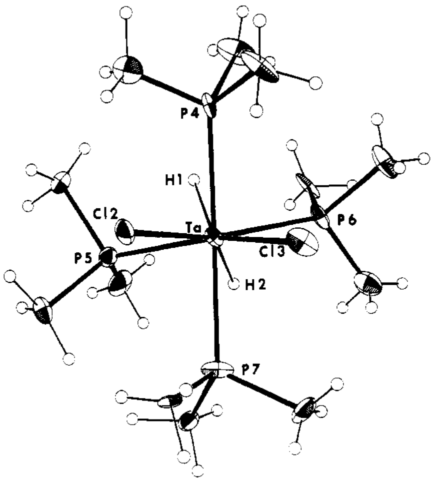


Figure 4. ORTEP drawing of $TaCl_2H_2(PMe_3)_4$. The view is down an approximate C_2 axis of symmetry. Each non-hydrogen atom is represented by a thermal vibration ellipsoid enclosing 50% of its electron density.

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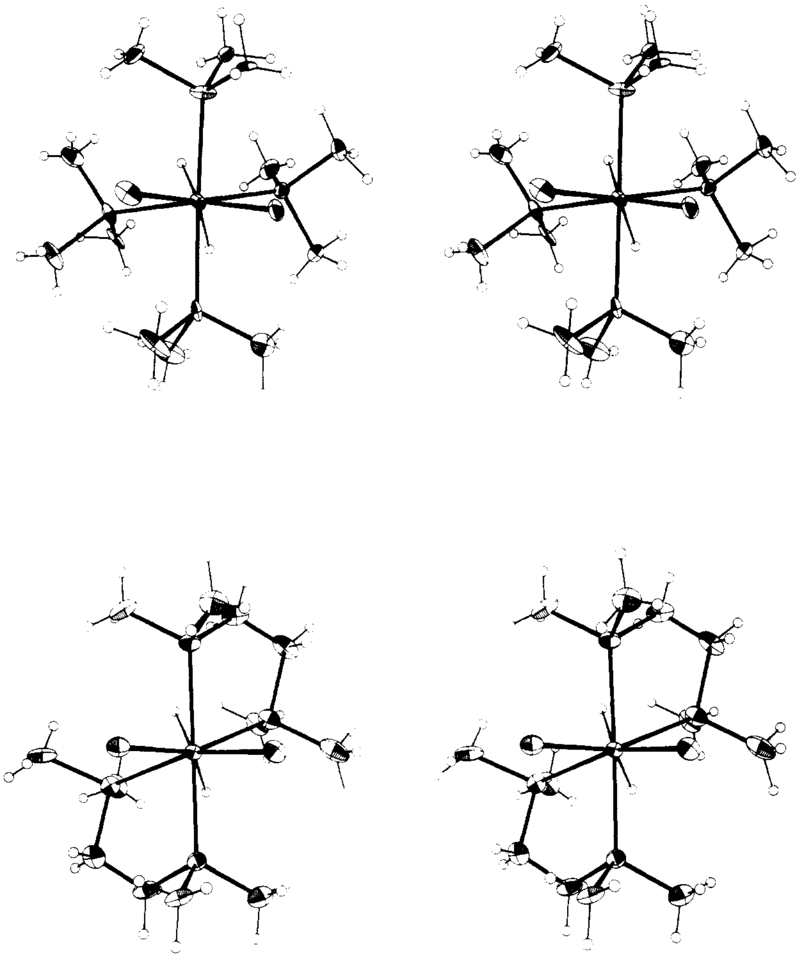
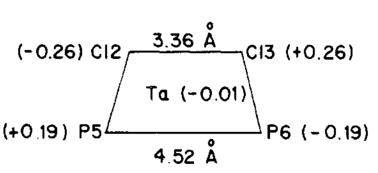


Figure 5. ORTEP stereoviews of $TaCl_2H_2(PMe_3)_4$ (top) and $TaCl_2H_2(dmpe)_2$.

(in parentheses) from planarity in the former trapezoid are shown in II. When we deleted the hydride ligands from the second trapezoid (their positions are known less accurately than the Cl and P atoms) and recalculated the angle between the first trapezoid and the plane defined by Ta, P4, and P7, a value of 85.9° was obtained. The designation of **5a** as a distorted dodecahedral complex therefore seem justified.



II

The M(IV), group 6 complexes $MoH_4(PMePh_2)_4$,[16] $WH_4(PEtPh_2)_4$,[17] and $[MoH_2(NCMe)_2(PMe_2Ph)_4](BF_4)_2$[18] are the closest analogues to **5a** that have been structurally characterized, and they provide useful standards for comparative purposes. The tetrahydrides have metal-ligand coordination spheres that are clearly dodecahedral, and the P-M-P angles, within the MH_2P_2 trapezoids, range from 139.1 to 144.1°. The P-Mo-P angles in the molybdenum(IV) cation, whose structure most closely resembles that of **5a**, are 157.3 (MoH_2P_2 plane) and 117.1° (MoN_2P_2 plane). Caulton et al.[18] have rationalized these changes in P-Mo-P, relative to the MH_4P_4 complexes, as a structural response to the presence of acetonitrile ligands in two of the A sites of the dodecahedron. The same arguments hold for **5a**, where the P-Ta-P angles are 158.9° for the TaH1H2P4P7 plane and 123.6° for the TaCl2Cl3P5P6 plane; i.e., the P5-Ta-P6 angle decreases because of the larger Cl ligands at the A sites of this trapezoid, and the P4-Ta-P7 angle opens in response to the presence of Cl ligands in the orthogonal plane.

The Ta-P bond lengths in **5a** fall into two sets: those in the TaCl2Cl3P5P6 plane average 2.56 Å while those in the TaH1H2P4P7 plane average 2.63 Å. A similar trend, i.e., longer M-P bonds in the hydride plane, was noted for $[MoH_2(NCMe)_2(PMe_2Ph)_4]^{2+}$ and attributed to a "torsional distortion caused by packing of the non-C_{3v} substitution pattern on the PRR_2' phosphines".[18] This argument cannot be applied to **5a**—we have no bulky phosphines and there are no unusual hydrogen contacts. Instead, we favor a trans influence of the hydride ligands on P4 and P7.

The hydride ligands in **5a** were located by difference Fourier techniques, and their positional and isotropic thermal parameters were refined. The final values obtained for Ta-H1 and Ta-H2 were 1.94 (11) and 1.85 (11) Å, and the H1-Ta-H2 bond angle was calculated to be 77 (6)°. Reported metal-hydrogen bond lengths range from 1.4 to 2.0 Å and center around 1.7 Å[19] (cf. $MoH_4(PMePh_2)_4$,[16] where the average Mo-H distance is 1.70 Å). The most accurate Ta-H bond length data available comes from the neutron diffraction study of Cp_2TaH_3.[20] Here the mean Ta-H bond length is 1.774

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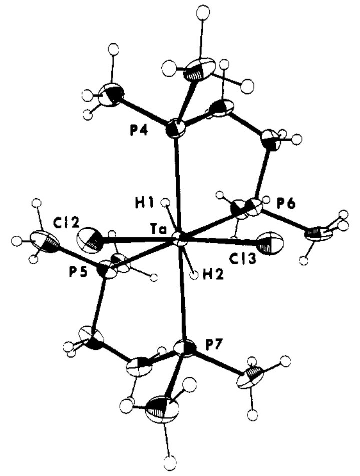

Figure 6. ORTEP drawing of $TaCl_2H_2(dmpe)_2$. The view is down an approximate C_2 axis of symmetry. Each non-hydrogen atom is represented by a thermal vibration ellipsoid enclosing 50% of its electron density.

(3) Å. In the hydride-bridged dimers, $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_2$[12] and $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$,[14,21] we have found Ta–H distances ranging from 1.81 to 1.97 Å (X-ray data).

We turn now to the structure of $TaCl_2H_2(dmpe)_2$ (**6a**). In the solid state this compound is composed of discrete mononuclear units. Final atomic positional parameters are given in Table III, and selected bond distances and angles are provided in Table IV. The atom-numbering scheme for the inner coordination sphere is consistent with the that used for **5a**. An ORTEP drawing of the molecule (same perspective as **5a**, Figure 4) is shown in Figure 6, and a stereoview is provided in Figure 5 (bottom).

6a also has virtual C_2 symmetry, but it is best described as a distorted square-antiprismatic complex. This follows from the fact that the angle between the supposed dodecahedral trapezoids composed of Ta, Cl2, Cl3, P5, and P6 *and* Ta, H1, H2, P4, and P7 is 81.2°. If we delete the hydride ligands, the angle between least-squares planes is 78.4°, i.e., very close to 77.4°, the angle for the idealized square antiprism. Why the structural change? Table IV provides an answer. We see that, in the dmpe complex, the P4–Ta–P6 and P5–Ta–P7 angles (76.9° average) are ca. 10° smaller and the P4–Ta–P5 and P6–Ta–P7 angles (112.3° average) are ca. 10° larger than their counterparts in the PMe_3 complex. These changes are certainly a reflection of the fact that the phosphorus atoms are now tied into chelate rings. The only other substantive difference between **5a** and **6a** is in the tantalum–phosphorus bond lengths. The Ta–P bonds in **6a** are 0.04–0.07 Å shorter than their counterparts in **5a**. The ligand cone angles[22] of PMe_3 and dmpe are 118 and 107°, respectively, and this could account for the differences; i.e., with the more compact dmpe ligand the repulsive forces in the coordination sphere are reduced and the phosphorus atoms can move closer to the tantalum center.

The compound $TaCl_4(dmpe)_2$ provides a useful standard for comparison to the structure of **6a**. In the solid state,[23] the tetrachloride is approximately square antiprismatic and mean Ta–Cl and Ta–P bond lengths are 2.505 [4] Å and 2.653 [3] Å, respectively. These distances are appreciably different from those in **6a**, and the changes are in opposite directions. In **6a**, the Ta–Cl bonds are 0.04–0.05 Å longer and the Ta–P bonds are 0.07–0.14 Å shorter than in $TaCl_4(dmpe)_2$. While there are, doubtless, several possible explanations for these bond length changes, we favor a simple and qualitative one: when two chloride ligands in $TaCl_4(dmpe)_2$ are replaced with two hydrides, the repulsive forces in the coordination sphere will be reduced. In addition, the ligand exchange should lower the effective charge on the metal and thereby decrease its attraction for the remaining halogens. As the latter move away from the metal, the repulsive interactions are further reduced. The net result is that the phosphorus atoms can be much closer to the metal center in **6a** than they can in $TaCl_4(dmpe)_2$.

There is one final point to be raised in this section, and it concerns the relationship of the solution ESR data to the solid-state structures. Both **5a** and **6a** [and, presumably, $NbCl_2H_2(dmpe)_2$] show two types of M–P distances, differing by ca. 0.06 Å, in the solid state, yet the solution ESR spectra all show hyperfine coupling to four equivalent ^{31}P nuclei. We have examined the solution spectra down to −60 °C, and there were no significant changes in the ^{31}P hyperfine patterns or coupling constants. These 8-coordinate complexes may be fluxional on the ESR time scale,[24] but we cannot rule out the possibility that the coupling constant differences are too small to resolve.

Discussion

With the exception of $TaCl_2(dmpe)_2$,[11] the adducts of MCl_2 (M = Nb, Ta) reported here are new compounds. Together, they represent the only well-defined coordination complexes of niobium and tantalum in the +2 oxidation state. The syntheses are straightforward, and the yields range from 25 to 90%. The worst yield was obtained for $NbCl_2(PMe_3)_4$, where a significant fraction of the initial niobium [$NbCl_5$ or $NbCl_4(PMe_3)_2$[9]] is lost in the form of $[NbCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2$.[10] We also lose some tantalum to $[TaCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2$[7,8] in the $TaCl_2(PMe_3)_4$ synthesis, but the yields of the latter are much more acceptable. The problem in both systems is that the phosphine ligands on the intermediate $MCl_3(PMe_3)_3$[7] complexes are labile (eq 9a) and the formation of

$$MCl_3(PMe_3)_3 \rightleftharpoons MCl_3(PMe_3)_2 + PMe_3 \qquad (9a)$$

$$MCl_3(PMe_3)_2 \rightarrow 0.5[MCl_2(PMe_3)_2]_2(\mu\text{-}Cl)_2 \qquad (9b)$$

M(III) dimers, which cannot be reduced under the prevailing experimental conditions, is irreversible (eq 9b). No M(III) dimers are observed in the reductions of $MCl_4(dmpe)_2$. The formation of $[MCl_2(dmpe)]_2(\mu\text{-}Cl)_2$[25] would require the loss of a chelating phosphine from $MCl_3(dmpe)_2$, and this is unlikely.

In the solid state, $TaCl_2(PMe_3)_4$ adopts a distorted (D_{2d}) trans-octahedral geometry[6a] similar to that observed in $W(CH)Cl(PMe_3)_4$.[26] It is reasonable to assume, on the basis of spectroscopic data and the ready conversion of **1** to **3** and **2** to **4**, that all of the MCl_2 adducts are trans isomers. We will have more to say about the physical properties of these d^3 complexes in another paper.[27] Here we want to discuss their role in the synthesis of M(IV) hydride complexes.

The preparation of transition metal hydride complexes by addition of H_2 to low-valent, coordinatively unsaturated metal complexes has ample precedent at both ends of the periodic table.[28,29] Our hydrogenation reactions are unusual only in

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(25) $[TaCl_2(dmpe)]_2(\mu\text{-}Cl)_2$ has been isolated from the reaction of $Ta_2Cl_6(SC_4H_8)_3$ with dmpe and structurally characterized. See: Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Inorg. Chem.* **1983**, *22*, 375.

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the sense that they involve 6-coordinate, 15-electron starting materials and 8-coordinate, 17-electron products; otherwise, they meet all of the criteria normally associated with oxidative addition reactions.[30] The closest analogy in the literature to the chemistry we describe here, albeit one that does not involve dihydrogen, is the reaction of vanadocene with diphenyl disulfide (eq 10).[31] Here also, a 15-electron monomer is converted into a 17-electron product.

$$Cp_2V + PhSSPh \rightarrow Cp_2V(SPh)_2 \qquad (10)$$

Although the oxidative addition of dihydrogen to the M(II) complexes was expected, the isolation of stable mononuclear M(IV) hydrides was not. We readily admit that the anticipated product from the reaction of *trans*-$TaCl_2(PMe_3)_4$ with H_2 (the first hydrogenation attempted) was the quadruply hydrogen-bridged tantalum(IV) dimer $[TaCl_2(PMe_2)_2]_2(\mu\text{-}H)_4$[12] and not $TaCl_2H_2(PMe_3)_4$. We thought that the latter would rapidly lose phosphine and that the fragments would dimerize to give the μ-H_4 dimer. We know now that this reaction does take place in solution but it is very slow at 25 °C and inhibited by free phosphine. **5a** can be converted to $[TaCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$ at a convenient rate in refluxing cyclohexane (bp 81 °C),[6a] and this method for the preparation of the dimer is a considerable improvement over our previous four-step procedure.[12] It is interesting to note that the reaction of $NbCl_2(PMe_3)_4$ with H_2 did give the "expected" product, i.e., $[NbCl_2(PMe_3)_2]_2(\mu\text{-}H)_4$.[14] Evidently, the phosphine ligands in the paramagnetic intermediate $NbCl_2H_2(PMe_3)_4$ are less tightly bound than in **5a**, and even with a large excess of phosphine, we were unable to prevent the formation of the binuclear complex at 25 °C.[32]

Since PMe_3 must be lost from the $MCl_2H_2(PMe_3)_4$ complexes to form the μ-H_4 dimers and since dmpe is comparatively tightly bound (compare the Ta–P bond lengths in **5a** and **6a**, Table IV), we would expect the $MCl_2H_2(dmpe)_2$ complexes to be stable in solution. This is the case. **6a** and **7a** can be recovered unchanged after 1 h in refluxing *n*-hexane. The high thermal stability of the $MCl_2H_2(dmpe)_2$ compounds suggests that the $MH_4(dmpe)_2$ species also may be isolable. An attempt to prepare them from the reaction of **6a** or **7a** with sodium borohydride in THF was unsuccessful.[33] The reduction of **6a** or **7a** followed by reoxidation with hydrogen is a route we are currently exploring.

Experimental Section

Reagents. Niobium and tantalum pentachloride were purchased from Pressure Chemical and sublimed under high vacuum to remove nonvolatile impurities. Triphenylphosphite (Aldrich, 97%) was purified by distillation (bp 200–201 °C (5 mmHg)) and stored under nitrogen. Di-*n*-butyl ether (Aldrich, 99%) was refluxed over molten sodium for 1 h and then distilled at atmospheric pressure (bp 142 °C). The purified ether was stored under N_2, and all waste was disposed of promptly. 1,2-Bis(dichlorophosphino)ethane was purchased from Strem Chemicals in sealed ampules and used without further purification. Hydrogen (Air Products, 99.995%) and deuterium (Linde, 99.5%) were used as received.

Toluene, THF, and ether were dried and freed from dissolved molecular oxygen by distillation under nitrogen from a solution of the solvent, benzophenone, and sodium or potassium. *n*-Hexane was purified by stirring over saturated $KMnO_4$ in 10% sulfuric acid (2 × 6 h). It was then sequentially washed with water, saturated Na_2CO_3, and water, dried over $MgSO_4$, filtered, and distilled under nitrogen from sodium–potassium alloy.

The complexes $NbCl_4(THF)_2$,[9] $NbCl_4(PMe_3)_2$,[9] $NbCl_4(dmpe)_2$,[9] and $TaCl_2(dmpe)_2$[11] were prepared and purified by literature procedures. 1,2-Bis(dimethylphosphino)ethane was prepared by a slight modification[34] of the method of Burt et al. from $Cl_2PCH_2CH_2PCl_2$.[35] Trimethylphosphine was prepared by the method of Wolfsberger and Schmidbauer[37] with use of the modification[38] suggested by R. R. Schrock.[39] The details of our procedure are reported below.

Physical and Analytical Measurements. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, and Galbraith Laboratories, Knoxville, TN.

Infrared spectral measurements were made on a Perkin-Elmer Model 1330 spectrometer. All samples were run as Nujol mulls between KBr plates. Mass spectra were obtained on a Finnigan Model 4021 GC mass spectrometer. Isotope patterns were calculated by using a local program written by Steve Werness. NMR spectra were run on a Bruker WM-360 spectrometer, and benzene-d_6 was used as a lock solvent and reference. Chemical shifts (δ) are reported from Me_4Si. Electron spin resonance spectra were run on dilute toluene solutions on a Bruker 200E-SRC spectrometer, operating at 9.64 GHz. The g values are reported relative to a 2,2-diphenyl-1-picrylhydrazyl (dpph) standard with $g = 2.0036$. Magnetic susceptibility measurements were performed on a Cahn Ventron R100 Faraday balance.

General Procedures. Manipulations of air-sensitive reagents and solutions and the workup of reaction products were usually performed within the confines of a helium-filled Vacuum Atmospheres HE-43 drybox. The latter is equipped with a high-capacity recirculation system (MO-40V) and a Dri-Cold freezer that is maintained at −40 °C.

PMe_3. An oven-dried 3-L, 3-neck round-bottom flask, equipped with an overhead mechanical stirrer, N_2 gas inlet, and a 500-mL pressure-equalizing dropping funnel was charged with 1.5 L of a 2.1 M solution of methylmagnesium bromide in di-*n*-butyl ether (3.15 mol, excess) under a countercurrent of N_2. The flask was immersed in an ice/salt bath, and the Grignard solution was cooled to 0 °C. Triphenyl phosphite (262 mL, 310 g, 1.0 mol), mixed with an equal volume of the butyl ether, was added dropwise, with vigorous stirring, to the Grignard solution over a 3-h period. The ice/salt bath was replaced periodically in order to maintain the reaction temperature at or below 0 °C. After the addition was complete, the ice bath was removed and the solution was warmed to room temperature. Under a gentle flow of N_2 the dropping funnel was disconnected and replaced with an N_2-purged distillation assembly. The latter consisted of a 15-in. Vigreux column, a distillation head with a 150 °C thermometer, a water-cooled condenser, and a 200-mL Schlenk receiver flask. The Schlenk flask was immersed in a −78 °C bath (dry ice/acetone), and the contents of the reaction flask were slowly brought to a *gentle* reflux. Trimethylphosphine was collected until the still head temperature reached 100 °C. At this point the heating mantle on the 3-L flask was removed, and the entire apparatus was allowed to cool before disconnecting the PMe_3 receiver flask. The product was redistilled into a cold 100-mL Schlenk flask by using a short-path distillation head and an oil bath. Pure PMe_3 boils at 39–40 °C at atmospheric pressure. The yield was ca. 65 g or 85% and the purity was checked by proton NMR. ^1H NMR (C_6D_6, 360 MHz): δ 0.79 ($J_{PH} = 2.75$ Hz).

$TaCl_2(PMe_3)_4$. Inside the drybox, tantalum pentachloride (7.2 g, 20.1 mmol) was added to a precooled (−20 °C) solution of trimethylphosphine (7.48 g, 98.3 mmol) in diethyl ether (200 mL) in a 500-mL Morton flask. Sodium amalgam (20.3 mL of 0.5%

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(32) All of our hydrogenation reactions were performed at room temperature. $NbCl_2H_2(PMe_3)_4$ might be stable at low temperatures, but we have not investigated this possibility.

(33) These reactions give deep green products that are believed to be $MClH(BH_4)(dmpe)_2$ complexes (Elcesser, W., unpublished results).

(34) Methyl bromide was substituted for methyl iodide in the preparation of the methyl Grignard. The yield of dmpe was essentially the same as reported in ref 35, i.e., ca. 70%.

(35) Burt, R. J.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203. This synthesis is simpler and faster than the one reported by Parshall.[36]

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(37) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149.

(38) Di-*n*-butyl ether is used in place of diethyl ether as the reaction solvent.

(39) Cited in: Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 773.

amalgam, 60.3 mmol of Na) was added, and the reaction mixture was stirred vigorously for 1 h by using an overhead mechanical stirrer. During the course of the reaction, the color changed from yellow to green to red and finally to orange-brown. The suspension was filtered through a 2-in. layer of Celite to remove sodium chloride, and the flask was rinsed with an additional 200 mL of ether (4 × 50 mL). The combined filtrate volume was reduced to ca. 30 mL in vacuo, and the brown microcrystalline product was filtered and dried; yield 6.5g (58%). An analytical sample was obtained by recrystallization from a concentrated toluene solution at −40 °C.

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

$\mathrm{NbCl_2(PMe_3)_4}$. This complex was prepared in the same manner as $\mathrm{TaCl_2(PMe_3)_4}$. Starting with 5.43 g (20.1 mmol) of $\mathrm{NbCl_5}$, 2.35 g or a 25% yield of brown microcrystalline product was obtained. An analytical sample was obtained by recrystallization from toluene. Anal. Calcd for $\mathrm{NbCl_2(PMe_3)_4}$: C, 30.79; H, 7.75; Cl, 15.15. Found: C, 31.02; H, 7.73; Cl, 14.95.

$\mathrm{TaCl_4(dmpe)_2}$. To 2.01 g (5.61 mmol) of $\mathrm{TaCl_5}$, dissolved in a chilled (−40 °C) mixture of toluene and tetrahydrofuran (100 mL total volume, 85 mL of $\mathrm{PhCH_3}$), was added 1.68 g (11.2 mmol) of dmpe. Sodium amalgam (1.91 mL of 0.5% amalgam, 5.62 mmol of Na) and mercury (3 mL) were added to the bright yellow suspension of $\mathrm{TaCl_5(dmpe)}$, and the mixture was warmed to room temperature with vigorous stirring. After 10 h the blue-green suspension was decanted from the mercury and filtered through Celite. The flask was rinsed with toluene (2 × 25 mL), and the combined filtrate was evaporated to dryness, leaving a blue-green solid, yield 3.18 g (91%, average of three preparations).[40] The spectroscopic (ESR, mass spectrum) properties of this compound were identical with those reported earlier.[11]

$\mathrm{TaCl_2(dmpe)_2}$. This complex was prepared by the method of Datta and Wreford[11] or by the following ligand-exchange procedure: $\mathrm{TaCl_2(PMe_3)_4}$ (1.0 g, 1.8 mmol) was dissolved in 20 mL of THF, and dmpe (0.54 g, 3.6 mmol) was added. The solution was stirred for 1 h and then stripped to dryness. The product was dissolved in a minimal amount of hot (50 °C) hexane, the mixture was cooled to −40 °C and filtered, and the resultant solid was washed with cold hexane; yield 0.9 g (91%). Anal. Calcd for $\mathrm{TaCl_2(dmpe)_2(TaCl_2P_4C_{12}H_{32})}$: C, 26.10; H, 5.84. Found: C, 26.34; H, 5.93. Mass spectrum (70 eV): *m/e* 551 ($\mathrm{P^+}$).

$\mathrm{NbCl_2(dmpe)_2}$. To 5.0 g of $\mathrm{NbCl_4(dmpe)_2}$ (9.3 mmol) dissolved in 100 mL of THF was added 7.9 mL of 0.5% sodium amalgam (23.3 mmol Na, excess), and the mixture was stirred vigorously. After 2 h the color had changed from violet to deep brown. The suspension was filtered through Celite, and the flask was rinsed with 2 × 25 mL of fresh THF. The combined filtrate was evaporated to dryness, and the residue was recrystallized from hot hexane; yield 3.9 g (90%) of red-brown crystals. Anal. Calcd for $\mathrm{NbCl_2(dmpe)_2}$: C, 31.06; H, 6.59. Found: C, 30.95; H, 7.02. Mass spectrum (70 eV): *m/e* 463 ($\mathrm{P^+}$). $\mathrm{NbCl_2(dmpe)_2}$ can also be prepared in 95% yield from $\mathrm{NbCl_2(PMe_3)_4}$ by using the procedure described above for $\mathrm{TaCl_2(dmpe)_2}$.

$\mathrm{TaCl_2H_2(PMe_3)_4}$. A solution of $\mathrm{TaCl_2(PMe_3)_4}$ in diethyl ether was prepared as described above and transferred to a Fischer-Porter 500-mL pressure vessel. The latter was sealed, removed from the drybox, and connected to a source of hydrogen and vacuum. The bomb was evacuated and pressurized to 40 psi $\mathrm{H_2}$. After the contents were stirred for 4 h, the color had changed from an orange-brown to red-brown. The vessel was vented, returned to the drybox, and the contents were filtered through Celite. The residue was washed with 2 × 50 mL of ether, and the combined filtrate was concentrated (no heat!) to ca. 20 mL. The red microcrystalline product was filtered and dried; yield 8.4 g (75%). Anal. Calcd for $\mathrm{TaCl_2H_2(PMe_3)_4(TaCl_2P_4C_{12}H_{38})}$: C, 25.82; H, 6.86. Found: C, 25.63; H, 6.68. IR ($\mathrm{cm^{-1}}$): 1690 ($\nu_{\mathrm{Ta-H}}$).

The deuteride $\mathrm{TaCl_2D_2(PMe_3)_4}$ was prepared in the same manner. IR ($\mathrm{cm^{-1}}$): 1212 ($\nu_{\mathrm{Ta-D}}$).

$\mathrm{TaCl_2H_2(dmpe)_2}$. Inside the drybox 1.0 g (1.8 mmol) of $\mathrm{TaCl_2(dmpe)_2}$, 30 mL of *n*-hexane, and a magnetic stir bar were loaded into a 90-mL Fischer-Porter pressure vessel. The latter was removed from the drybox, evacuated, pressurized to 40 psi $\mathrm{H_2}$, and stirred for 4 h. The color changes from brown to red-orange, and a microcrystalline solid precipitates. The bomb was returned to the drybox, and the precipitate was filtered, washed (2 × 5 mL) with hexane, and dried; yield 0.92 g (92%). An analytical sample was recrystallized from toluene/hexane at −40 °C. Anal. Calcd for $\mathrm{TaCl_2H_2(dmpe)_2(TaCl_2P_4C_{12}H_{34})}$: C, 25.82; H, 6.14; Cl, 12.70. Found: C, 25.96; H, 6.20; Cl, 12.53. Mass spectrum (70 eV): *m/e* 553 ($\mathrm{P^+}$), 551 ($\mathrm{P - H_2^+}$). IR ($\mathrm{cm^{-1}}$): 1650 ($\nu_{\mathrm{Ta-H}}$).

Table V. Crystal Data for $\mathrm{TaCl_2H_2L_4}$ Complexes

	L = $\mathrm{PMe_3}$	L = $^1/_2$ dmpe
mol formula	$\mathrm{TaCl_2P_4C_{12}H_{38}}$	$\mathrm{TaCl_2P_4C_{12}H_{34}}$
color	red	red-orange
cryst dimens, mm	0.04 × 0.05 × 0.06	0.04 × 0.10 × 0.10
space group	*Cc*	$P2_12_12_1$
cell dimens		
a, Å	15.127 (3)	9.781 (4)
b, Å	12.005 (3)	15.842 (8)
c, Å	12.410 (2)	13.832 (6)
β, deg	92.49 (1)	90.00
molecules/cell	4	4
V, Å^3	2251.6	2143.3
d_{calcd}, g cm^{-3}	1.647	1.717
λ, Å	0.710 69	0.710 69
mol wt	558.18	554.15
linear abs coeff, cm^{-1}	53.36	56.05
min abs	0.608	0.421
max abs	0.673	0.635
2*θ* range, deg	6–45	6–45
no. of data with $F_o > 2.33\sigma(F_o)$	2418	2000
no. of unique data	2571	2168
final residuals		
R_F	0.0285	0.0358
R_{wF}	0.0293	0.0366
goodness of fit, last cycle	1.083	1.181
max Δ/σ, last cycle	0.05	0.05

The deuteride was prepared similarly. IR ($\mathrm{cm^{-1}}$): 1185 ($\nu_{\mathrm{Ta-D}}$). $\mathrm{TaCl_2H_2(dmpe)_2}$ can also be prepared by from $\mathrm{TaCl_2H_2(PMe_3)_4}$ and 2 equiv of dmpe in minimal THF; yield 95%.

$\mathrm{NbCl_2H_2(dmpe)_2}$. This red-orange complex was prepared in 90% yield by using the same procedure described for the tantalum analogue. Anal. Calcd for $\mathrm{NbCl_2H_2(dmpe)_2}$: C, 30.66; H, 7.29; Cl, 15.08. Found: C, 31.21; H, 7.39; Cl, 14.65. Mass spectrum (70 eV): *m/e* 463 ($\mathrm{P - H_2^+}$). IR ($\mathrm{cm^{-1}}$): 1610 ($\nu_{\mathrm{Nb-H}}$).

The deuteride $\mathrm{NbCl_2D_2(dmpe)_2}$ was prepared by the same procedure. IR ($\mathrm{cm^{-1}}$): 1150 ($\nu_{\mathrm{Nb-D}}$).

X-ray Structure Determinations. General procedures were the same as those described previously.[41]

$\mathrm{TaCl_2H_2(PMe_3)_4}$. X-ray-quality crystals were grown by slow cooling of a saturated toluene solution. Inside a nitrogen-filled glovebag, a crystal was mounted on a glass fiber with silicon grease and transferred to the liquid-nitrogen boil-off cooling system of the diffractometer. Diffraction data were collected at −160 ± 4 °C, and the structure was solved by direct methods (MULTAN) and difference Fourier techniques. An absorption correction was applied to the data, and the structure was refined by full-matrix least squares. All atoms, including the two hydride hydrogens, were located and their positional and thermal parameters (anisotropic for Ta, Cl, P, and C; isotropic for H) refined. A final difference Fourier was remarkably clean, the largest peak being 0.45 e/Å^3. Crystal data are presented in Table V.

$\mathrm{TaCl_2H_2(dmpe)_2}$. Well-formed red-orange blocks were obtained by slow cooling of concentrated toluene solutions. One of these was mounted as described above, transferred to the goniostat, and cooled to −163 ± 4 °C. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares. The data were corrected for the effects of absorption. All atoms, including the hydrogens, were located and their positional and thermal parameters (anisotropic for Ta, Cl, P, and C; isotropic for H) refined. The atomic coordinates reported are for the proper enantiomorph for the crystal chosen, on the basis of residuals for both settings. A final difference Fourier was essentially featureless, the largest peak being 0.7 e/Å^3.

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(40) This yield is a considerable improvement over that reported previously.[11]

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Crystal data are given in Table V.

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Registry No. **1**, 85923-35-9; **2**, 89656-65-5; **3**, 61916-35-6; **4**, 89708-59-8; **5a**, 85939-38-4; **6a**, 89708-60-1; **7a**, 89708-61-2; $TaCl_4(dmpe)_2$, 61916-34-5; $NbCl_4(dmpe)_2$, 61202-65-1; $TaCl_5$, 7721-01-9; $NbCl_5$, 10026-12-7; D, 7782-39-0.

Supplementary Material Available: Listings of phosphine hydrogen atom positions, anisotropic thermal parameters and observed and calculated structure factors for $TaCl_2H_2(PMe_3)_4$ (**5a**) and $TaCl_2H_2(dmpe)_2$ (**6a**) and experimental ESR spectra of **6a** and **6b** (22 pages). Ordering information is given on any current masthead page. Complete structural reports on **5a** (MSC Report No. 82934) and **6a** (MSC Report No. 83913) are available, in microfiche form only, from the Chemistry Library, Indiana University.

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Electrochemical Studies of Antimony(III) and Antimony(V) in Molten Mixtures of Aluminum Chloride and Butylpyridinium Chloride

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Electrochemical studies of Sb, Sb(III), and Sb(V) have been carried out in molten mixtures of $AlCl_3$ and *N*-1-butylpyridinium chloride (BuPyCl) at 40 °C, as a function of melt composition. Analysis of measurements in the acidic melts indicates $SbCl_2^+$ as the dominant species. The reduction of this species on glassy carbon exhibits irreversible behavior. In the basic melts, $SbCl_4^-$ and $SbCl_6^-$ are believed to be the dominant species. The reduction of Sb(III) to Sb on glassy carbon also showed irreversible behavior while its oxidation to Sb(V) revealed a quasi-reversible behavior. No Sb(III) oxidation was observed in the acidic melts.

Introduction

Molten mixtures of $AlCl_3$ and *N*-1-butylpyridinium chloride (BuPyCl) have been shown to be useful and interesting solvents for a variety of electrochemical and spectroscopic studies.[1-7] The mixtures, of composition ranging from 2:1 to 0.75:1 (mol) of $AlCl_3$:BuPyCl, are liquids at essentially ambient temperatures.[2,8] They are ionic liquids, and their composition can be adjusted to change their acid-base properties which, in turn, determine their oxidation-reduction and coordination chemistry. Raman and infrared spectroscopic studies showed that the dominant Al-containing species in the system are $AlCl_4^-$ and $Al_2Cl_7^-$ ions.[8,9] The acid-base equilibrium in these solvents has been studied potentiometrically, by employing Al indicator electrodes, and the equilibrium

$$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^- \qquad (1)$$

was shown to describe the system across the entire range of compositions mentioned above.[10,11] Electrochemical studies of several organic and inorganic solute species in this and similar systems revealed a pronounced dependence of the solute chemistry and electrochemistry on the system acidity.[2,3,6] In the basic (excess BuPyCl) melt, stable chloro complexes of Ni(II), Fe(II), Fe(III), Cu(I), Cu(II), and Co(II) have been reported.[3,6,12,13]

Studies of molten $SbCl_3$ and its mixtures with alkali-metal chloride and/or $AlCl_3$ have reported the formation of several species of antimony.[14-20] As a result of conductance measurements of $AlCl_3$ in molten $SbCl_3$[14] and of KCl in molten $SbCl_3$,[15,16] the presence of $SbCl_2^+$ and $SbCl_4^-$ in these mixtures has been suggested, and the reaction

$$SbCl_3 + AlCl_3 \rightarrow SbCl_2^+ + AlCl_4^- \qquad (2)$$

was proposed for $AlCl_3$ in $SbCl_3$.[14] Raman studies, however, did not give support for the above suggested species and, instead, indicated some interaction between $SbCl_3$ and $AlCl_3$ in their molten equimolar mixture and the possible formation of some higher chloro complexes of antimony in molten mixtures of $SbCl_3$ and KCl.[17] $SbCl_2^+$, produced from reaction 2, has recently been postulated as the species responsible for the chemical oxidation of perylene in molten $SbCl_3$ containing $AlCl_3$.[18] Lower valent Sb species have been suggested as a result of solubility measurements of Sb in molten $SbCl_3$ containing $AlCl_3$[19,20] and CsCl.[20]

We have studied the electrochemistry of Sb in molten mixtures of $AlCl_3$ and BuPyCl to characterize the major species present. Such information would also be useful in any study of organic solutes in solutions of melts containing $SbCl_3$ where the solvent acidity can be varied.[18,21-24]

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