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Preparation and Structural Characterization of Phosphine Adducts of Tantalum(IV) Chloride

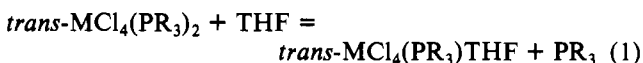
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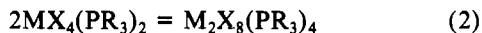
Three complexes of empirical formula $\text{TaCl}_4(\text{PR}_3)_n$, with $\text{PR}_3 = \text{PMe}_2\text{Ph}$, PMe_3 , and PET_3 , have been synthesized and characterized by X-ray crystallography. The $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$ molecule, which has a cis phosphine arrangement, crystallizes in space group $P2_1/c$ with $a = 15.466$ (4) Å, $b = 10.080$ (2) Å, $c = 14.086$ (6) Å, $\beta = 97.32$ (3)°, and $Z = 4$. The molecule has Ta-Cl distances of 2.360 (3) and 2.386 (3) Å trans to phosphorus, 2.319 (3) and 2.322 (3) Å for Cl trans to Cl, and Ta-P distances of 2.641 (3) and 2.651 (3) Å. The P-Ta-P angle is 97.7 (1)°, the largest Cl-Ta-Cl angle is 159.6 (1)°, and the angle between the Ta-Cl bonds trans to phosphorus is 90.4 (1)°. The seven-coordinate $\text{TaCl}_4(\text{PMe}_3)_3$ molecule is a capped octahedron with virtual C_{3v} symmetry. The space group for this compound is $P2_1/c$ with $a = 15.000$ (3) Å, $b = 11.714$ (3) Å, $c = 11.606$ (3) Å, $\beta = 91.56$ (2)°, and $Z = 4$. The unique chlorine atom, Cl(1), caps the P_3 face and is closer to the Ta atom than the other three chlorine atoms. The average Ta-Cl distance for the latter is equal to 2.447 [8] Å. The molecule $\text{TaCl}_4(\text{PET}_3)_2$ is a trans isomer with the metal atom on a crystallographic inversion center, and all angles between nonequivalent atoms are very close to 90°. It forms crystals ($P2_1/n$) with $a = 8.032$ (1) Å, $b = 12.851$ (2) Å, $c = 10.357$ (4) Å, $\beta = 98.55$ (2)°, and $Z = 2$. Of the three tantalum(IV) adducts only one, *trans*- $\text{TaCl}_4(\text{PET}_3)_2$, is structurally analogous to its niobium congener. The PMe_2Ph and PMe_3 compounds of tantalum are each drastically different in structure from the niobium complexes with the same phosphine. The adduct *cis*- $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$ is the first cis molecule of the $\text{MCl}_4(\text{PR}_3)_2$ type; the homologous niobium compound has a binuclear structure with eight-coordinate metal atoms. The $\text{TaCl}_4(\text{PMe}_3)_3$ complex appears to be the only structurally characterized seven-coordinate PR_3 monomer of TaCl_4 ; the PMe_3 adduct of NbCl_4 is dinuclear, consisting of two square-antiprismatic $\text{NbCl}_4(\text{PMe}_3)_2$ units sharing a face formed by four chlorine atoms.

Introduction

One might have supposed, a priori, that a systematic study of the phosphine adducts of the niobium(IV) and tantalum(IV) halides would provide little more than a routine exercise, with the chief task being to establish whether a cis or trans compound, $\text{MX}_4(\text{PR}_3)_2$, would be formed in any given case. Before our own studies in this area were begun, there was but a small amount of information available and it did not arouse any expectation that more interesting game might be afoot. In 1976, Manzer¹ reported the preparation of a few compounds of niobium, but aside from their stoichiometry, which was $\text{NbCl}_4(\text{PR}_3)_2$, with $\text{R} = \text{Me}$, Et , they remained essentially uncharacterized. The studies of Samuel, Labauze, and Livage,^{2,3} in which some tantalum as well as niobium compounds were studied, suggested that in those few cases studied, i.e., for the tetrachlorides with the phosphines PET_3 and PBu_3 , the adducts were *trans*- $\text{MCl}_4(\text{PR}_3)_2$ molecules. The susceptibility of these to replacement of one phosphine by a donor solvent molecule such as THF (eq 1) was also recognized.



Our first report in this field⁴ showed that there is an additional, entirely unsuspected, structural facet to this problem, namely the formation of dinuclear species (eq 2). This was



first disclosed in the case of $\text{NbCl}_4(\text{PMe}_2\text{Ph})_2$, and the dinuclear molecule was shown to consist of two square-antiprismatic $\text{NbCl}_6(\text{PR}_3)_2$ units sharing a square Cl_4 face. We next showed⁵ that $\text{NbCl}_4(\text{PMe}_3)_2$ forms a similar dimer, whereas crystalline $\text{NbCl}_4(\text{PET}_3)_2$ consists of trans monomers.

In the meantime, we had found that $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$ does not dimerize in the solid but instead consists of cis monomers, the first such structure known in this series of compounds. This one lack of parallel structural behavior between niobium and

tantalum homologues, $\text{MCl}_4(\text{PMe}_2\text{Ph})_2$, naturally led us to undertake a more general enquiry as to the similarities and differences in the behavior of the two elements in this sort of chemistry.

In this paper we report our results on three $\text{TaCl}_4(\text{PR}_3)_n$ compounds, including the one mentioned above. Once again a surprising disparity has been found, and another new facet has been discovered, namely, seven-coordination in $\text{TaCl}_4(\text{PMe}_3)_3$, although $\text{TaCl}_4(\text{PET}_3)_2$ is homologous to its niobium counterpart. Our work with the tantalum compounds also has implications with regard to some earlier reports on other types of phosphine complexes of tantalum halides.⁶

Experimental Section

All manipulations were carried out under an atmosphere of argon. Standard vacuum line and Schlenk techniques were used. TaCl_5 and the phosphine ligands were purchased from Aldrich and Strem Chemicals, Inc., respectively, and used as received. As with the Nb(IV) phosphine adducts,¹⁻⁵ all products were extremely sensitive to oxygen and/or moisture and traces of air caused immediate formation of blue oily deposits. The phosphine adducts of Ta^{IV} , as well as Nb^{IV} , can usually be prepared readily by a reduction of corresponding pentahalides with sodium amalgam. The procedures described here were used because of their convenience at the time and are not necessarily the optimal ones.

Preparation of $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$. This compound was obtained by following a procedure that has previously been reported to yield $\text{Ta}_2\text{Cl}_6(\text{PMe}_2\text{Ph})_4$.⁶ It was scaled down by a factor of 2, and a different method of product isolation was employed. A 100-mL three-neck flask was charged with TaCl_5 (1.5 g, 4.1 mmol), Mg turnings (0.15 g, 6.2 mmol), 19 mL of CH_2Cl_2 , and PMe_2Ph (1.8 mL, 12.5 mmol). Since no apparent change had occurred after stirring for several hours, a drop of mercury was added to the mixture. The deep red solution then changed slowly to green, and MgCl_2 began to precipitate. Stirring was continued for 3 days and the mixture then filtered to afford a clear, dark green solution. As the volume of this solution was reduced slowly under vacuum to ca. 1-2 mL, an orange solid crystallized out. The resulting slurry was transferred onto a frit, and as the liquid drained off, orange crystals of *cis*- $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$ were obtained (1.9 g, 3.1 mmol, 75% yield).

Preparation of $\text{TaCl}_4(\text{PMe}_3)_3$. $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$ (1.2 g, 2.0 mmol) was dissolved in 10 mL of CH_2Cl_2 . Upon addition of trimethyl-

(1) Manzer, L. E. *Inorg. Chem.* 1977, 16, 525.

(2) Samuel, E.; Labauze, G.; Livage, J. *Nouv. J. Chem.* 1977, 1, 93.

(3) Labauze, G.; Samuel, E.; Livage, J. *Inorg. Chem.* 1980, 19, 1384.

(4) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* 1984, 23, 945.

(5) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* 1984, 23, 3592.

(6) Hubert-Pfaltzgraf, L. G.; Tsunoda, M.; Riess, J. G. *Inorg. Chim. Acta* 1981, 52, 231.

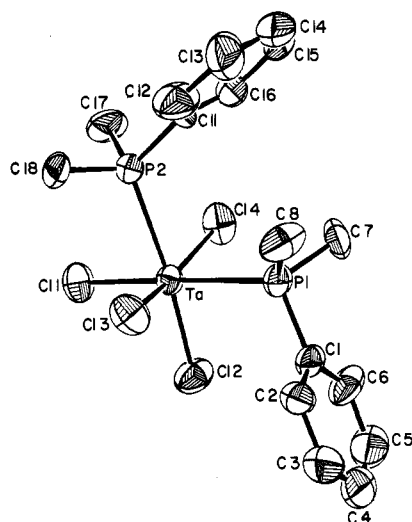


Figure 1. ORTEP drawing of $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$. Atoms are represented by ellipsoids of thermal vibrations at the 40% probability level.

phosphine (1 mL, 11 mmol) the green color of the solution became darker. The solution was reduced in volume to ca. 5 mL, filtered, and stored in a refrigerator at -20°C . After several days large black crystals (dark red in transmitted light) were obtained; yield 0.47 g, 0.85 mmol, 42%.

Preparation of $\text{TaCl}_4(\text{PEt}_3)_2$. To a slurry of TaCl_5 (3.6 g, 10 mmol) in 30 mL of toluene was added triethylphosphine (3.2 mL, 22 mmol) and sodium amalgam (0.23 g, 10 mmol of Na in 5 mL of mercury). When it was stirred, the solution turned green within several minutes. After 12 h the solution was filtered, reduced in volume to about 15 mL, and stored in a refrigerator at -5°C . Orange crystals of the PEt_3 adduct formed overnight; yield 2.7 g, 4.8 mmol, 48%.

X-ray Crystallography. Single-crystal X-ray analyses have been carried out by application of general procedures that are fully described elsewhere.⁷ The relevant data pertaining to the structure determinations are summarized in Table I. Polarization, Lorentz, and empirical (ψ -scan) absorption corrections were applied to the intensity data. In all three cases the position of the Ta atom was determined from a three-dimensional Patterson function. The remaining non-hydrogen atoms were located by series of alternating difference Fourier syntheses and least-squares refinements. Following the assignment of anisotropic thermal parameters, the structures were refined to convergence. No peaks of chemical significance were present in the final difference Fourier maps.

Tables of observed and calculated structure factors for all three compounds are available as supplementary material.

Results and Discussion

Solid-State Structures and Synthesis. Positional and isotropic equivalent thermal parameters are listed in Table II. Tables III–VI present important interatomic distances and angles. Tables of anisotropic thermal parameters and complete listings of bond distances and angles are included in the supplementary material. ORTEP drawings of each of the three molecules are shown in Figures 1–3.

$\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$. The molecule of *cis*- $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$ resides on a general position thus giving four formula units per unit cell. It has a typical pseudooctahedral geometry with some deviation from ideal 90° and 180° angles. The most significant among the latter is a ca. 20° deviation from linearity for Cl(3) and Cl(4). It is caused by the repulsive forces from the other chlorine atoms. There is an evident trans effect resulting in the elongation of the Ta–Cl bonds involving chlorine atoms opposite to phosphine ligands. These effects are not unexpected, and therefore the molecule can be considered to have no unusual features, except for the important

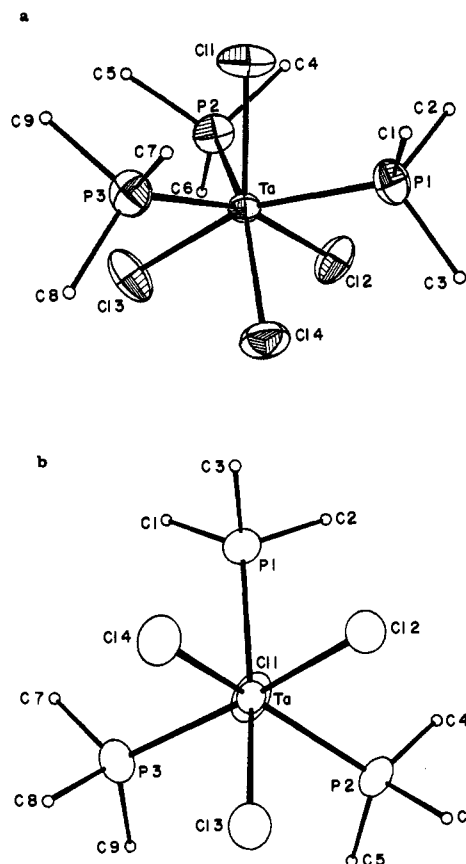


Figure 2. (a) ORTEP drawing of the $\text{TaCl}_4(\text{PMe}_3)_3$ molecule. The thermal ellipsoids enclose 40% of electron density. Methyl carbon atoms were assigned arbitrarily small thermal parameters for the sake of clarity. (b) As above; a view down the Ta–Cl(1) bond.

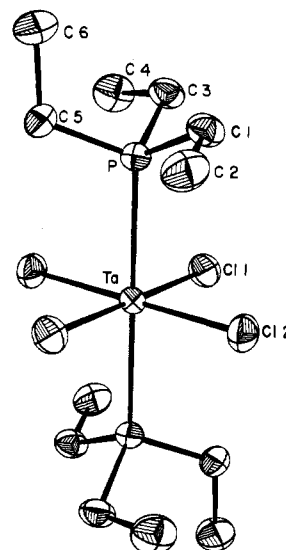


Figure 3. ORTEP drawing of the $\text{TaCl}_4(\text{PEt}_3)_2$ molecule. The thermal ellipsoids enclose 40% of electron density.

fact that it is the first *cis* molecule containing phosphine ligands.

The *cis* arrangement of neutral donor ligands is known to occur among other complexes of the type MX_4L_2 , where $\text{M} = \text{Nb}, \text{Ta}$, $\text{X} = \text{halogen}$, $\text{L} = \text{a } \sigma \text{ donor}$.⁸

The preparation of this compound by a procedure that has been reported⁶ to give Ta^{III} species undoubtedly calls for some

(7) See for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

(8) Miller, D. A.; Bereman, R. D. *Coord. Chem. Rev.* **1972**, *9*, 107 and references cited therein. See especially: Fowler, G. W. A.; Tidmark, D. J.; Walton, R. A. *Inorg. Chem.* **1969**, *8*, 631.

Table I. Crystallographic Data

	TaCl ₄ (PMe ₂ Ph) ₂	TaCl ₄ (PMe ₃) ₃	TaCl ₄ (PEt ₃) ₂
formula	TaCl ₄ P ₂ C ₁₆ H ₂₂	TaCl ₄ P ₃ C ₉ H ₂₇	TaCl ₄ P ₂ C ₁₂ H ₃₀
fw	599.06	551.00	559.08
space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /n
systematic absences	0k0, k ≠ 2n; h0l, l ≠ 2n	0k0, k ≠ 2n; h0l, l ≠ 2n	0k0, k ≠ 2n; h0l, h + l ≠ 2n
a, Å	15.466 (4)	15.000 (3)	8.032 (1)
b, Å	10.080 (2)	11.714 (3)	12.851 (2)
c, Å	14.086 (6)	11.606 (3)	10.357 (4)
β, deg	97.32 (3)	91.56 (2)	98.55 (2)
V, Å ³	2178 (2)	2038 (2)	1057.0 (9)
Z	4	4	2
d _{calcd} , g/cm ³	1.826	1.795	1.756
cryst size, mm	0.5 × 0.5 × 0.45	0.4 × 0.4 × 0.2	0.3 × 0.3 × 0.15
μ(Mo Kα), cm ⁻¹	56.261	60.767	57.893
data collecn instrument	Syntex P1	Syntex P1	CAD-4
radiation (monochromated in incident beam)		Mo Kα (λ = 0.710 73 Å)	
orientation reflns: no.; range (2θ), deg	15, 16.05–29.24	15, 16.50–26.63	25, 10.18–27.14
temp, °C		22	
scan method		w-2θ	
data collecn range, 2θ, deg		4 ≤ 2θ ≤ 50	
no. of unique data, total with F _o ² > 3σ(F _o ²)	2092, 1914	3008, 2425	1432, 1266
no. of parameters refined	208	154	88
transmission factors, max, min	0.9990, 0.9219	0.9991, 0.7853	0.9992, 0.8823
R ^a	0.0305	0.0372	0.0298
R _w ^b	0.0445	0.0500	0.0406
quality of fit indicator ^c	0.978	1.014	1.112
largest shift/esd, final cycle	0.05	0.0	0.0
largest peak, e/Å ³	0.539	0.873	0.841

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|)^2$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$.

Table II. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations^a

atom	x	y	z	B, Å ²	atom	x	y	z	B, Å ²
(a) TaCl ₄ (PMe ₂ Ph) ₂									
Ta	0.25475 (2)	0.25304 (6)	0.23623 (3)	3.149 (7)	C(6)	-0.0291 (7)	0.280 (1)	0.119 (1)	5.6 (3)
Cl(1)	0.3589 (2)	0.1237 (4)	0.3360 (3)	5.90 (8)	C(7)	0.0872 (8)	0.526 (1)	0.181 (1)	5.9 (3)
Cl(2)	0.1450 (2)	0.0967 (4)	0.2564 (3)	5.80 (8)	C(8)	0.1758 (8)	0.470 (1)	0.0198 (9)	5.6 (3)
Cl(3)	0.2894 (2)	0.1740 (3)	0.0911 (2)	5.29 (8)	C(11)	0.3692 (7)	0.573 (1)	0.167 (1)	4.6 (3)
Cl(4)	0.2248 (2)	0.4026 (4)	0.3532 (2)	5.32 (8)	C(12)	0.3907 (9)	0.589 (1)	0.077 (1)	6.3 (4)
P(1)	0.1374 (2)	0.3897 (3)	0.1222 (2)	3.65 (6)	C(13)	0.3696 (9)	0.712 (1)	0.028 (1)	7.0 (4)
P(2)	0.3886 (2)	0.4134 (3)	0.2276 (3)	4.41 (7)	C(14)	0.3287 (8)	0.810 (1)	0.074 (1)	6.7 (4)
C(1)	0.0447 (7)	0.291 (1)	0.0721 (8)	3.8 (2)	C(15)	0.3070 (7)	0.797 (1)	0.168 (1)	6.1 (4)
C(2)	0.0489 (8)	0.228 (1)	-0.015 (1)	5.4 (3)	C(16)	0.3263 (8)	0.667 (1)	0.216 (1)	6.5 (4)
C(3)	-0.022 (1)	0.151 (1)	-0.057 (1)	7.0 (4)	C(17)	0.4451 (9)	0.455 (1)	0.348 (1)	7.3 (4)
C(4)	-0.0935 (9)	0.137 (1)	-0.010 (1)	8.0 (4)	C(18)	0.4745 (7)	0.336 (1)	0.166 (1)	6.8 (4)
C(5)	-0.0979 (9)	0.202 (1)	0.079 (1)	7.4 (4)					
(b) TaCl ₄ (PMe ₃) ₃									
Ta	-0.25554 (3)	-0.01822 (3)	0.21911 (4)	2.406 (6)	C(2)	-0.0258 (8)	-0.128 (1)	0.284 (1)	6.0 (4)
Cl(1)	-0.2361 (3)	-0.1278 (3)	0.3945 (3)	5.06 (7)	C(3)	-0.0716 (9)	-0.143 (1)	0.038 (1)	6.9 (4)
Cl(2)	-0.1379 (2)	0.1130 (3)	0.1586 (3)	4.79 (7)	C(4)	-0.134 (1)	0.119 (1)	0.475 (1)	6.4 (4)
Cl(3)	-0.3767 (2)	0.1191 (3)	0.1860 (4)	5.61 (8)	C(5)	-0.325 (1)	0.121 (1)	0.498 (1)	7.4 (4)
Cl(4)	-0.2788 (2)	-0.0643 (3)	0.0161 (3)	4.99 (7)	C(6)	-0.240 (1)	0.283 (1)	0.348 (1)	6.2 (4)
P(1)	-0.1199 (2)	-0.1554 (3)	0.1823 (3)	4.05 (7)	C(7)	-0.3791 (9)	-0.305 (1)	0.219 (2)	6.2 (4)
P(2)	-0.2379 (2)	0.1322 (3)	0.3888 (3)	4.03 (7)	C(8)	-0.4813 (9)	-0.128 (1)	0.108 (1)	7.0 (4)
P(3)	-0.3981 (2)	-0.1492 (3)	0.2228 (3)	4.33 (7)	C(9)	-0.4645 (9)	-0.129 (2)	0.353 (1)	7.6 (4)
C(1)	-0.1346 (9)	-0.309 (1)	0.198 (1)	5.5 (3)					
(c) TaCl ₄ (PEt ₃) ₂									
Ta	0.000	0.000	0.000	2.676 (7)	C(2)	0.405 (1)	0.1952 (8)	0.1192 (8)	4.9 (2)
Cl(1)	-0.2643 (3)	0.0817 (2)	-0.0260 (2)	4.17 (4)	C(3)	-0.054 (1)	0.1882 (7)	0.2753 (7)	3.9 (2)
Cl(2)	0.0912 (3)	0.1211 (2)	-0.1478 (2)	4.11 (4)	C(4)	-0.167 (1)	0.1117 (8)	0.3431 (9)	5.2 (2)
P	0.1093 (3)	0.1203 (2)	0.2009 (2)	2.91 (4)	C(5)	0.236 (1)	0.0490 (8)	0.3320 (8)	3.9 (2)
C(1)	0.240 (1)	0.2299 (6)	0.1632 (8)	3.7 (2)	C(6)	0.308 (1)	0.1158 (8)	0.4545 (9)	5.7 (2)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

explanation. This outcome was initially interpreted as arising from only partial reduction of the pentachloride. However, repeated attempts to prepare a Ta^{III} product always gave TaCl₄(PMe₂Ph)₂ only. It was also found that the color change (green CH₂Cl₂ solution to orange crystals) is reversible, indicating the absence of Ta^{III} species. Furthermore, a reduction of TaCl₅ with 2 equiv of sodium amalgam yields red material (apparently Ta^{III}) much as reported for the Ta^{III}-PMe₃ sys-

tem.⁹ We are thus inclined to believe that the original identification⁶ of the compound was incorrect, and under the conditions described, the reduction stops at the +4 oxidation state. While we can thus account for some of the previous experimental results,⁶ there are still some that are puzzling.

(9) Sattelberger, A. P.; Wilson, R. B.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 2392.

Table III. Important Bond Distances (Å) and Angles (deg) for $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2^a$

A. Bond Distances			
Ta-Cl(1)	2.386 (3)	Ta-Cl(4)	2.322 (3)
-Cl(2)	2.360 (3)	-P(1)	2.651 (3)
-Cl(3)	2.319 (3)	-P(2)	2.641 (3)
B. Bond Angles			
Cl(1)-Ta-Cl(2)	90.4 (1)	Cl(3)-Ta-Cl(4)	159.6 (1)
-Cl(3)	96.7 (1)	-P(1)	82.1 (1)
-Cl(4)	96.7 (1)	-P(2)	84.2 (1)
-P(1)	178.2 (1)	Cl(4)-Ta-P(1)	84.8 (1)
-P(2)	83.5 (1)	-P(2)	82.2 (1)
Cl(2)-Ta-Cl(3)	97.3 (1)	P(1)-Ta-P(2)	97.7 (1)
-Cl(4)	97.8 (1)		
-P(1)	88.4 (1)		
-P(2)	173.8 (1)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Important Interatomic Distances (Å) for $\text{TaCl}_4(\text{PMe}_3)_2^a$

A. Bonding Contacts			
Ta-Cl(1)	2.417 (3)	Ta-P(1)	2.636 (3)
-Cl(2)	2.458 (3)	-P(2)	2.650 (3)
-Cl(3)	2.449 (3)	-P(3)	2.633 (3)
-Cl(4)	2.433 (3)		
B. Short Nonbonding Contacts			
Cl(1)-P(1)	3.073 (5)	Cl(3)-Cl(4)	3.289 (5)
-P(2)	3.046 (5)	-P(2)	3.103 (5)
-P(3)	3.110 (5)	-P(3)	3.189 (5)
Cl(2)-Cl(4)	3.366 (5)	Cl(4)-P(1)	3.208 (5)
-P(1)	3.167 (4)	-P(3)	3.191 (5)
-P(2)	3.107 (5)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Important Bond Angles (deg) for $\text{TaCl}_4(\text{PMe}_3)_2^a$

Cl(1)-Ta-Cl(2)	120.1 (1)	Cl(3)-Ta-Cl(4)	84.7 (1)
-Cl(3)	123.6 (1)	-P(1)	161.3 (1)
-Cl(4)	135.1 (1)	-P(2)	74.9 (1)
-P(1)	74.8 (1)	-P(3)	77.6 (1)
-P(2)	73.7 (1)	Cl(4)-Ta-P(1)	78.4 (1)
-P(3)	75.9 (1)	-P(2)	151.1 (1)
Cl(2)-Ta-Cl(3)	94.6 (1)	-P(3)	78.0 (1)
-Cl(4)	87.0 (1)	P(1)-Ta-P(2)	117.6 (1)
-P(1)	76.8 (1)	-P(3)	106.1 (1)
-P(2)	74.8 (1)	P(2)-Ta-P(3)	116.1 (1)
-P(3)	163.5 (1)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VI. Important Bond Distances (Å) and Angles (deg) for $\text{TaCl}_4(\text{PEt}_3)_2^a$

A. Bond Distances			
Ta-Cl(1)	2.347 (2)	Ta-P	2.636 (2)
-Cl(2)	2.373 (2)		
B. Bond Angles			
Cl(1)-Ta-Cl(2)	89.61 (8)	Cl(2)-Ta-P	91.50 (7)
-P	91.00 (7)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

For example, could it be that the "olive green crystals" are in fact particles of the Ta^{IV} complex covered by a thin layer of oily mother liquor?

$\text{TaCl}_4(\text{PMe}_3)_3$. The geometry of this molecule is similar to that of PMe_2Ph adducts of Mo^{IV} and W^{IV} halides.¹⁰⁻¹² It

is seven-coordinate, a capped octahedron with virtual C_{3v} symmetry. The unique chlorine atom, Cl(1), caps the P_3 face and is closer to the Ta atom than the other three chlorine atoms. The average Ta-Cl distance for the latter is equal to 2.447 [8] Å. The Ta-Cl(1) bond with length 2.417 (3) Å may be stronger because of the lack of a trans effect, since there is no ligand positioned at 180° with respect to this unique chlorine. In general, all M-L bonds in the Ta adduct of PMe_3 are significantly shorter than in the dimeric Nb- PMe_3 complex. This may be attributed to a less crowded coordination sphere around tantalum.

A coordination number of seven is very rare for the complexes of Nb and Ta in their oxidation state +4.¹³ Usually these d^1 ions form either six- or eight-coordinate species. Except for NbF_7^{3-} the PMe_3 adduct of TaCl_4 seems to be the only structurally characterized representative of that class of compounds.¹³

$\text{TaCl}_4(\text{PET}_3)_2$. Although this complex is not isomorphous with its Nb analogue, they are qualitatively similar. In each the metal atom is positioned on a crystallographic inversion center and all angles between nonequivalent atoms are very close to 90° . While the M-Cl distances are comparable in the two compounds, with average values equal to 2.360 [13] and 2.366 [9] Å for Ta and Nb, respectively, the Ta-P bonds are shorter by ca. 0.03 Å than the Nb-P bonds.

Comparison of the Niobium and Tantalum Compounds. Of the three tantalum(IV) compounds described here, only one, *trans*- $\text{TaCl}_4(\text{PET}_3)_2$, is structurally analogous to its niobium counterpart. Both the PMe_3 and the PMe_2Ph complexes of tantalum are entirely different in structure from the niobium compounds with the same phosphines. These differences appear to be among the most extreme, if not *the* most extreme, ones ever reported between analogous compounds of the two very similar elements. It is not clear why these differences occur.¹⁴

From another point of view, however, there is a similarity in the behavior of the two elements—or at least tentatively, on the limited data available, such a similarity can be postulated. With the most sterically demanding of the phosphines, PET_3 and PET_2Ph , each metal forms a *trans* octahedral complex. We would venture the prediction that for all phosphines that are comparable to or greater than these in their steric requirements, the *trans*- $\text{MCl}_4(\text{PR}_3)_2$ structure is the preferred one. When smaller phosphines such as PMe_3 and PMe_2Ph are used, the two metals are similar in their response to the extent that they adopt structures that are consistent with the smaller steric requirements. In detail, however, the responses are quite different. For both of these smaller phosphines, niobium gives the dinuclear structure in which a coordination number of eight is achieved. Tantalum instead forms a seven-coordinate complex with PMe_3 and a *cis*- $\text{TaCl}_4(\text{PMe}_2\text{Ph})_2$ molecule with PMe_2Ph . Apparently tantalum is for some reason less able to adopt a dinuclear structure, but it is not known what this reason is. In closing, a few remarks about the solution chemistry of the tantalum compounds are pertinent. As with the Nb^{IV} complexes an unusual green solution-red solid phenomenon was observed for the Ta^{IV} compounds as well. However, the changes do not appear as complex as for the niobium systems, since they were independent of time, concentration, and solvent (within the limits studied). Thus all three Ta species produced green solutions and crystallized as red or orange solids. In contrast, $\text{NbCl}_4(\text{PET}_3)_2$ gives red or brown solutions in toluene (no change of color upon dissolution) while its Ta analogue, which

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(14) It has since been found that $\text{NbCl}_4(\text{PMe}_3)_3$ and $\text{Ta}_2\text{Cl}_8(\text{PMe}_3)_4$ can both be made.

is orange, gives green solutions under similar conditions. As with some other properties of the systems, these differences are puzzling and deserve further study.

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Registry No. *cis*-TaCl₄(PMe₂Ph)₂, 92763-08-1; TaCl₄(PMe₃)₃, 92763-09-2; *trans*-TaCl₄(PEt₃)₂, 73079-36-4.

Supplementary Material Available: Tables of structure factors and anisotropic thermal parameters (*B*'s) and full listings of bond distances and angles for all three compounds (37 pages). Ordering information is given on any current masthead page.

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Pyrazolyl-Bridged Iridium Dimers. 6.¹ Two-Fragment, Two-Center Oxidative Addition of Halogens and Methyl Halides to

trans-Bis(triphenylphosphine)dicarbonylbis(μ -pyrazolyl)diiridium(I)

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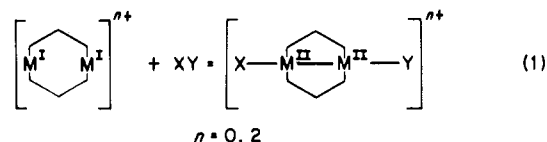
Reaction between *trans*-Ir(PPh₃)₂(CO)Cl and Na(pz) (pzH = C₃N₂H₄, pyrazole) affords the scarlet diiridium complex [Ir(PPh₃)(CO)(μ -pz)]₂ (**1a**) characterized by single-crystal X-ray crystallography, in which the terminal PPh₃ and CO ligands are mutually *trans* across the Ir₂ axis with a formally nonbonded Ir₂ separation of 3.163 (2) Å; the latter is somewhat longer [3.290 (1) Å] in the orange-red hexane solvate (**1b**). A systematic synthesis of the same compound is described, in which reaction of [Ir(COD)Cl]₂ with pzH giving the dimer [Ir(COD)(μ -pz)]₂ (**2**) is followed by treatment with CO and PPh₃ to provide **1** in 82% yield. Reaction of **1** with Ir₂ and Br₂ leads to formation of yellow complexes formulated as 1:1 adducts formed by a two-center oxidative addition, i.e. [Ir(PPh₃)(CO)(X)(μ -pz)]₂ (X = I, Br); with Cl₂ the corresponding product has been characterized crystallographically as [Ir(PPh₃)(CO)(Cl)(4-Cl-pz)]₂ (**9**) in which the *trans* configuration of **1** is retained. Axial substitution at each Ir with Ir-Cl = 2.443 (6) Å has been accompanied by formation of a metal-metal bond [Ir-Ir = 2.737 (1) Å] and electrophilic substitution by Cl of the 4-position in each bridging pyrazolyl-ring system. Reaction between **1** and MeI affords a yellow 1:1 adduct (80% yield) for which a corresponding dimeric structure is proposed having Me attached to Ir(1) and I to Ir(2); by contrast with MeBr, reaction is slower to give an unidentified mixture of products. Crystals of **1a** are triclinic, space group P $\bar{1}$: *a* = 9.992 (4), *b* = 10.402 (4), *c* = 20.278 (8) Å; α = 90.01 (4), β = 90.10 (4), γ = 105.13 (4)°. Modification **1b** crystallizes in P2₁/c: *a* = 15.528 (4), *b* = 9.713 (3), *c* = 30.544 (8) Å; β = 93.98 (2)°. For the addition product (**9**), the space group is P2₁/n: *a* = 15.851 (3), *b* = 28.617 (4), *c* = 11.092 (2) Å; β = 95.82 (2)°.

Introduction

Oxidative-addition reactions have been extensively studied as models for those homogeneous metal-assisted catalytic transformations of organic substrates in which successive alternation with the reverse process, i.e. a reductive-elimination step, is thought to be instrumental in establishing a continuous cycle. Where such circumstances lead to effective catalysis, the metal complexes participating as reactive intermediates may be so labile or present in such low concentration that proper characterization of these species becomes problematic. In other examples of reactions involving oxidative addition, kinetically stable adducts have been obtained that are amenable to structural identification, establishing coordination geometries that by analogy have been projected to transient reactive configurations. A by now classical illustration of this kind of correlation is provided by the difference in properties between six-coordinate *cis*-dihydrido complexes of rhodium and iridium: while examples of the latter have been characterized in the solid state as typical octahedral Ir(III) derivatives,² the former are generated only reversibly,³ in the crucial step of the catalytic hydrogenation of unsaturated compounds by RhCl(PPh₃)₃. Only much more recently however, has it become apparent that oxidative addition may result in attachment of substrate fragments at other than a single metal site, although such events have frequently been hypothesized in relation to cooperativity effects in biological systems as well as in the context of heterogeneous catalytic reactions, especially

reorganization of organic molecules at metal surfaces.

In 1975 the addition of CH₃I to Au₂[(CH₂)₂PMe₂]₂ was claimed by Schmidbaur and Franke,⁴ and in the following year isolation of methyl halide adducts of the binuclear cation Rh₂[CN(CH₂)₃NC]₄²⁺ was reported by Gray et al.⁵ In both cases reaction was taken to result in metal-metal bond formation as represented generally by eq 1, i.e. with a unit in-



crease in the formal oxidation number of each metal center

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