

distances and angles were kept fixed: Zr-Cl = 2.55 Å, Zr-S = 2.72 Å, Zr-(centroid of C₅H₅) = 2.22 Å, cyclopentadienyl C-C = 1.40 Å, C-H = 1.08 Å, C-S = 1.71 Å, S-C-S = 115.7°. The angle between the normals to the planes of the two η-C₅H₅ rings was set equal to 138°.

Registry No. (η-C₅H₅)₂ZrCl[S₂CN(C₂H₅)₂], 66943-46-2; (η-C₅H₅)₂ZrCl[S₂CN(CH₃)₂], 66943-45-1.

Supplementary Material Available: A listing of structure factor amplitudes for (η-C₅H₅)₂ZrCl[S₂CN(C₂H₅)₂] (10 pages). Ordering information is given on any current masthead page.

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Comparison of the Eight-Coordinate Structures of d¹ TaCl₄(dmpe)₂ and d⁰ TaCl₄(dmpe)₂⁺

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The structures of [P(CH₃)₄][TaCl₄(dmpe)₂]₃Cl₄·4(CH₃)₂S (1) and TaCl₄(dmpe)₂ (2) have been determined by X-ray crystallography to examine the structural effects of adding one d electron to the d⁰ cation TaCl₄(dmpe)₂⁺. The TaCl₄(dmpe)₂⁺ ion has a structure of the dodecahedral type previously found for similar Ta^V complexes; the bond lengths and angles are as follows: Ta-Cl, 2.430 (3) Å; Ta-P, 2.691 (5) Å; P-Ta-P, 72.1 (2)°; Cl-Ta-Cl, 145.4 (2)°. The neutral molecule, 2, has a structure that is approximately square antiprismatic with the following bond lengths: Ta-Cl, 2.505 [3] Å; Ta-P, 2.653 [2] Å. Compound 1 forms cubic crystals in the space group $I\bar{4}3m$ with a unit cell edge of 16.726 (7) Å, a cell volume of 4679 (6) Å³, and Z = 2. The Ta atoms reside on positions of $\bar{4}2m$ symmetry. Compound 2 forms orthorhombic crystals in the space group *P*2₁2₁2 with unit cell dimensions *a* = 10.765 (2) Å, *b* = 11.297 (4) Å, *c* = 9.595 (3) Å, *V* = 1167 (3) Å³, and Z = 2. The molecules have a crystallographic twofold axis of symmetry.

Introduction

Coordination number 8 can be considered uncommon only in a relative sense. There are, in fact, many examples of it, and several geometric forms are well-known.^{1,2} We are concerned here with a question that is simple in concept but rarely answerable experimentally: What will be the effect of adding one electron to a given eight-coordinate species on its structure? We were led to our particular study of this question in the following way.

In the course of preparing the new compound³ Ta₂Cl₆(dmpe)₂, where dmpe represents Me₂PCH₂CH₂PMe₂, we isolated a very small amount of a beautifully crystalline yellow compound, 1. A crystallographic study of this compound showed that it contains the [TaCl₄(dmpe)₂]⁺ ion, which has a dodecahedral structure of the type previously reported¹ for several [MX₄(diars)₂]⁺ ions with M = Nb and Ta, X = Cl and Br, and diars = *o*-(Me₂As)₂C₆H₄. In these structures the diars ligands span the positions marked X in Figure 1 and the four halide ions occupy the Y positions. The symmetries of these molecules are essentially *D*_{2d} although this is not crystallographically rigorous. In our [TaCl₄(dmpe)₂]⁺ ion crystallographic $\bar{4}2m$ symmetry of the TaCl₄P₂ core was found.

Since the neutral, homologous compound TaCl₄(dmpe)₂ had already been reported,⁴ we recognized an opportunity to see what effects the presence of one d electron would have on the structure. It had previously been claimed⁵ from powder diffraction work that NbCl₄(diars)₂ retained the dodecahedral geometry of the [NbCl₄(diars)₂]⁺ ion, but no quantitative information about bond lengths or bond angles was likely to be obtainable for NbCl₄(diars)₂ since it was reported⁵ to be impossible to find a solvent from which to recrystallize it.

We have been able to obtain the detailed crystal structure of TaCl₄(dmpe)₂ (2) and find that the geometry is not dodecahedral but square antiprismatic.

Experimental Section

The solvents, CH₂Cl₂ and THF, were dried over P₂O₅ and potassium benzophenone ketyl, respectively. The compound TaCl₄(dmpe)₂ (2) was prepared by the literature method⁴ with bis(dimethylphosphino)ethane, dmpe, purchased from Strem Chemicals. All materials were handled under argon with use of Schlenk and vacuum-line techniques. Ta₂Cl₆(SMe₂)₃ was prepared as described previously.⁶

Preparation of [P(CH₃)₄][TaCl₄(dmpe)₂]₃Cl₄·4(CH₃)₂S (1). An addition funnel was charged with 4 equiv⁷ of dmpe (0.45 mL, 2.70 mmol) followed by 10 mL of CH₂Cl₂ and attached to a flask containing Ta₂Cl₆(SMe₂)₃ (0.5 g, 0.66 mmol) dissolved in 20 mL of CH₂Cl₂. The contents of the addition funnel were added to the flask slowly, and the solution was allowed to stand at 25 °C for 24 h, yielding a yellow-brown solution and a red precipitate. The solvent was removed by vacuum distillation, and the resulting orange-brown solid was extracted with hexane (2 × 10 mL) to remove excess dmpe. The solid was redissolved in CH₂Cl₂ and filtered through a Celite pad, leaving the insoluble red material behind. After the solution had stood 5 days at 25 °C, a deep yellow solution over a large amount of red solid⁵ was obtained. Intermixed with the red solid were cubic yellow crystals of 1 of suitable quality for X-ray analysis, in ca. 5% yield. Crystals of 1 were mildly moisture sensitive (decomposition in moist air in <10 h).

X-ray Crystallography of Compound 1. Geometric and intensity data were obtained from a crystal of dimensions 0.30 × 0.30 × 0.25 mm. The crystal was sealed inside a glass capillary tube and mounted on an automated four-circle diffractometer (Enraf-Nonius CAD-4) equipped with a Mo X-ray tube (λ $\bar{\alpha}$ = 0.71073 Å) and a graphite monochromator.

Unit cell dimensions and the orientation matrix were given by a least-squares fit of these parameters to the goniometer positions of 25 well-centered reflections in the range 29.8° < 2θ < 38.5°. The

(1) Kepert, D. L. *Prog. Inorg. Chem.* 1978, 24, 179.

(2) Burdett, J. K.; Hoffmann, R.; Fay, R. C. *Inorg. Chem.* 1978, 17, 2553.

(3) Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Inorg. Chem.* 1983, 22, 375.

(4) Datta, S.; Wreford, S. S. *Inorg. Chem.* 1977, 16, 1134.

(5) Clark, R. J. H.; Kepert, D. L.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* 1965, 2865.

(6) Cotton, F. A.; Najjar, R. C. *Inorg. Chem.* 1981, 20, 2716.

(7) When less dmpe was used, a complex mixture of products that could not be separated was obtained.

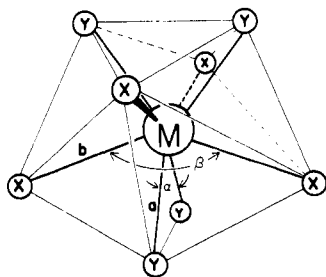


Figure 1. Dodecahedral form of eight-coordination. The nonequivalent subsets of ligand positions are designated X and Y, and four independent parameters, a , b , α , and β , that completely define the structure under the restrictions of D_{2d} symmetry are also shown.

Table I. Crystallographic Parameters for 1 and 2

parameter	1	2
space group	$I\bar{4}3m$	$P2_12_12$
a , Å	16.726 [7] ^a	10.765 (2)
b , Å		11.297 (4)
c , Å		9.595 (3)
V , Å ³	4679 (6)	1167 (3)
d_{calcd} , g/cm ³	1.737	1.357
d_{obsd} , g/cm ³	1.763	1.344
Z	2	2
fw	2350.6	623.0
cryst size, mm	0.30 × 0.30 × 0.25	0.30 × 0.26 × 0.25
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	44.7	53.8
2θ range, deg	0–50	0–50
no. of unique data	468	1076
no. of data with $F_o^2 > 3\sigma(F_o^2)$	306	1025
no. of variables	45	96
R_1^b	0.046	0.0406
R_2^c	0.059	0.0515
esd ^d	1.761	1.660
largest shift ^e	0.23	0.23

^a Length a is given as the average of the three computed values; the deviation in square brackets is determined by $[\sum_{i=1}^3 \Delta_i^2/2]^{1/2}$, where Δ_i is the deviation of the i th value from the mean. ^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^d $\text{Esd} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$. ^e Largest shift/esd, final cycle.

cubic Laue class $m\bar{3}m$ was established unambiguously by axial photography of three members each of the forms of zone axes $\langle 100 \rangle$ and $\langle 110 \rangle$; all of the photographs had the appropriate mirror symmetry.

Parameters pertaining to data collection and other crystallographic parameters are summarized in Table I. In all, the intensities of 1492 reflections in the range $0 < 2\theta \leq 50^\circ$ were measured by the 2θ - ω scan technique. Three reflections were used as intensity standards and were measured after every 1 h of X-ray exposure. Three orientation standards were recentered after each 100 intensity measurements. Lorentz and polarization corrections were applied to the data, and structure factors and their standard deviations were derived by routine procedures.⁸ An empirical absorption correction⁹ was based on azimuthal scans of nine strong reflections with χ (Eulerian) near 90° . No decay correction was necessary. Equivalent reflections were averaged, resulting in a net total of 468 unique data.

Reflections with indices (hkl) such that the sum $h + k + l$ is odd were systematically absent from the data. There were no other systematic absences, and so the choice of space group was limited to three possibilities: $I432$ (No. 211), $I\bar{4}3m$ (No. 217), and $Im\bar{3}m$ (No. 229). Three space groups having the same systematic absence but belonging to the Laue group $m\bar{3}$ rather than $m\bar{3}m$ were ruled out for that reason and for additional considerations related to the structure which emerged later.

Table II. Positional Parameters and Their Estimated Standard Deviations^a for 1

atom	x	y	z
Ta(1)	0.0000	0.5000	0.5000
Cl(1)	0.0432 (3)	0.4019	0.4019 (3)
Cl(2)	0.1455 (5)	0.1455 (5)	0.1455 (5)
P(1)	0.1301 (4)	0.5670 (3)	0.4330 (3)
P(2)	0.5000	0.5000	0.5000
C(1)	0.220 (2)	0.528 (1)	0.472 (1)
C(2)	0.144 (1)	0.671 (1)	0.448 (2)
C(3)	0.441 (2)	0.441 (2)	0.441 (2)
S(1A)	0.270 (4)	0.270 (4)	0.270 (4)
S(1B)	0.315 (2)	0.315 (2)	0.220 (3)
C(4)	0.267 (1)	0.267 (1)	0.376 (2)

^a Given in parentheses for the least significant digits.

Table III. Bond Distances (Å) for 1^a

Ta(1)–Cl(1)	2.430 (3)	C(1)–C(1')	1.33 (3)
–P(1)	2.691 (5)	P(2)–C(3)	1.722 (13)
P(1)–C(1)	1.76 (2)	S(1A)–C(4)	1.78 (3)
–C(2)	1.77 (2)	S(1B)–C(4)	1.52 (3)

^a Estimated standard deviations in the least significant digits are given in parentheses.

Table IV. Bond Angles (deg) for 1^a

P(1)–Ta(1)–P(1)'	72.1 (2)	Ta(1)–P(1)–C(2)	117.3 (7)
–P(1)''	130.8 (2)	C(1)–P(1)–C(2)	101 (1)
Cl(1)–Ta(1)–Cl(1)'	145.4 (2)	C(2)–P(1)–C(2)	105 (2)
–Cl(1)''	95.1 (2)	P(1)–C(1)–C(1)'	121.4 (5)
–P(1)	71.3 (2)	C(3)–P(2)–C(3)'	109.5 ^b
–P(1)'	143.4 (1)	C(4)–S(1A)–C(4)'	93 (2)
–P(1)''	76.1 (1)	–C(4)''	93 (2)
Ta(1)–P(1)–C(1)	112.6 (5)	C(4)–S(1B)–C(4)'	116 (3)

^a Estimated standard deviations in the least significant digits are given in parentheses. ^b This angle is fixed by symmetry.

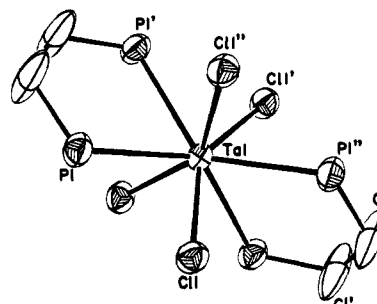


Figure 2. The $[\text{TaCl}_4(\text{dmpe})_2]^+$ ion as found in compound 1. The atoms are represented by thermal ellipsoids enclosing 40% of the electron density, and the labeling scheme is identified.

Positions of the tantalum atoms in the unit cell were derived from a Patterson map and found to be $(0, \frac{1}{2}, \frac{1}{2})$ and its symmetry-related equivalents. Of the space groups under consideration, only $I\bar{4}3m$ was found to have symmetry at these positions consistent with the chemical moiety at hand. The structure was completed and refined in this space group. Positional and thermal parameters for the dodecahedral Ta complex, the chloride ion, and the $\text{P}(\text{CH}_3)_4^+$ moiety were assigned by routine computational procedures. For the part of the structure that was finally refined as a disordered $\text{S}(\text{CH}_3)_2$ molecule, several alternative assignments were attempted. In most cases, refinements of models for this region of the unit cell were divergent and/or led to unacceptable derived parameters. The model that converged to an acceptable result consisted of a disordered pair of sulfur atoms—one on a half-occupied site of symmetry $3m$ and one on a one-third-occupied site of symmetry m —with methyl groups on fully occupied sites of symmetry m . (The site occupancy factors were fixed so as to maintain the stoichiometry of $\text{S}(\text{CH}_3)_2$.) The least-squares refinement converged with the results listed in Table I.

Table II gives the positional parameters from the refinement. Tables III and IV contain the bond distances and bond angles, respectively. A thermal ellipsoid plot of the monomeric tantalum complex is shown

(8) Crystallographic calculations were done on the PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX, with programs from the Enraf-Nonius structure determination package.

(9) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* 1968, **A24**, 351.

Table V. Positional Parameters and Their Estimated Standard Deviations for **2^a**

atom	x	y	z	B, Å ²
Ta(1)	0.500	0.500	0.74234 (5)	1.98 (1)
Cl(1)	0.5316 (3)	0.3257 (3)	0.5841 (4)	4.02 (7)
Cl(2)	0.6517 (3)	0.3968 (3)	0.8981 (4)	3.93 (7)
P(1)	0.6196 (3)	0.6673 (3)	0.8818 (4)	3.18 (7)
P(2)	0.7139 (3)	0.5321 (3)	0.6096 (4)	3.36 (7)
C(1)	0.781 (1)	0.675 (1)	0.826 (1)	4.5 (3)
C(2)	0.789 (1)	0.667 (1)	0.666 (1)	4.3 (3)
C(22)	0.701 (2)	0.549 (2)	0.415 (1)	5.8 (4)
C(11)	0.625 (2)	0.650 (2)	1.072 (1)	5.0 (4)
C(23)	0.840 (2)	0.418 (1)	0.632 (2)	5.3 (4)
C(12)	0.570 (2)	0.821 (1)	0.859 (2)	4.7 (4)

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

Table VI. Bond Distances (Å) for **2^a**

Ta(1)–Cl(1)	2.509 (3)	P(1)–C(11)	1.840 (11)
–Cl(2)	2.502 (3)	–C(12)	1.826 (13)
–P(1)	2.650 (3)	P(2)–C(2)	1.812 (12)
–P(2)	2.656 (3)	–C(22)	1.880 (11)
P(1)–C(1)	1.824 (13)	–C(23)	1.886 (14)
		C(1)–C(2)	1.54 (2)

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

in Figure 2. The numerical values of the thermal vibration parameters and a table of the structure factors are available as supplementary material.

X-ray Crystallography of Compound 2. A crystal was sealed in a capillary under nitrogen and mounted on a Syntex P1 automated diffractometer. A summary of data collection and refinement parameters is presented in Table I. The usual Lorentz and polarization corrections as well as an empirical absorption correction⁹ were applied to the data. After identification of the unit cell as orthorhombic, belonging to space group $P2_12_12$ (from the systematic absences $h00$, $h = 2n + 1$, and $0k0$, $k = 2n + 1$), the heavy-atom positions were obtained by direct methods (MULTAN program) and refined by full-matrix least squares. Carbon atoms were then found in difference maps, and the structure was refined, without hydrogen atoms, to convergence. Refinement of this arbitrarily chosen enantiomorph converged to the following figures of merit: $R_1 = 0.052$, $R_2 = 0.064$, and $esd = 2.08$. There were several reflections for which I_o and I_c disagreed for no obvious reason. The opposite enantiomorph was then refined and shown by the significantly improved figures of merit (Table I) to be the correct one. The final electron density difference map contained no peaks over $0.7 \text{ e } \text{Å}^{-3}$ except for one of $3.9 \text{ e } \text{Å}^{-3}$ that was within 1 Å of the tantalum atom. The positional parameters for this model are listed in Table V, and the bond lengths and bond angles are given in Tables VI and VII, respectively. A thermal ellipsoid plot of the molecular structure is displayed in Figure 3. The components of the anisotropic thermal vibration tensor and a table of structure factors for the correct enantiomorph are available as supplementary material.

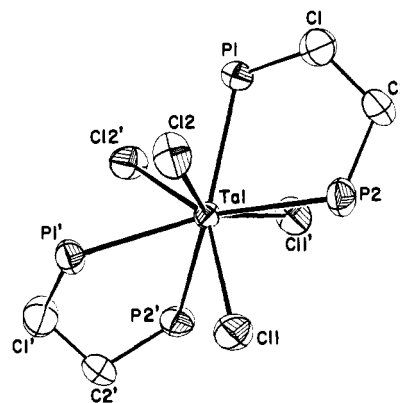
Results and Discussion

Compound 1. The origin and precise composition of compound **1** pose questions for which we do not have definitive answers. It is only a minor product of a preparative procedure that produces largely $\text{Ta}_2\text{Cl}_6(\text{dmpe})_2$; it presumably arises by adventitious oxidation of a small amount of the tantalum from Ta^{III} to Ta^{V} . The Cl/Ta ratio of 16/3 is much higher than that in the starting material, $\text{Ta}_2\text{Cl}_6(\text{Me}_2\text{S})_3$, but since **1** is formed in such small quantity, this is acceptable as is the incorporation of what appears to be $\text{S}(\text{CH}_3)_2$ of crystallization, since there is a relatively large quantity of the latter available. The identification of $\text{S}(\text{CH}_3)_2$ in **1** is not incontrovertible because of the disorder in the entities so identified. The postulated $[\text{P}(\text{CH}_3)_4]^+$ ion causes some misgivings both because of its origin, which is uncertain though not at all impossible to imagine, and because of its P–C distance of 1.72

Table VII. Bond Angles in (deg) for **2^a**

Cl(1)–Ta(1)–Cl(1)'	105.6 (2)	P(2)–Ta(1)–P(2)'	122.7 (1)
Cl(1)–Ta(1)–Cl(2)	84.7 (1)	Ta(1)–P(1)–C(1)	110.5 (4)
Cl(1)–Ta(1)–Cl(2)'	144.65 (9)	Ta(1)–P(1)–C(11)	116.1 (5)
Cl(1)–Ta(1)–P(1)	143.07 (9)	Ta(1)–P(1)–C(12)	118.3 (4)
Cl(1)–Ta(1)–P(1)'	79.1 (1)	C(1)–P(1)–C(11)	105.6 (6)
Cl(1)–Ta(1)–P(2)	72.50 (9)	C(1)–P(1)–C(12)	101.6 (6)
Cl(1)–Ta(1)–P(2)'	73.77 (9)	C(11)–P(1)–C(12)	103.2 (6)
Cl(2)–Ta(1)–Cl(2)'	106.6 (2)	Ta(1)–P(2)–C(2)	111.0 (4)
Cl(2)–Ta(1)–P(1)	73.4 (1)	Ta(1)–P(2)–C(22)	115.1 (5)
Cl(2)–Ta(1)–P(1)'	71.5 (1)	Ta(1)–P(2)–C(23)	118.6 (5)
Cl(2)–Ta(1)–P(2)	77.54 (9)	C(2)–P(2)–C(22)	104.0 (6)
Cl(2)–Ta(1)–P(2)'	142.06 (9)	C(2)–P(2)–C(23)	102.6 (7)
P(1)–Ta(1)–P(1)'	119.3 (1)	C(22)–P(2)–C(23)	103.7 (7)
P(1)–Ta(1)–P(2)	73.96 (9)	P(1)–C(1)–C(2)	110.0 (9)
P(1)–Ta(1)–P(2)'	139.5 (1)	P(2)–C(2)–C(1)	108.7 (9)

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

**Figure 3.** The $\text{TaCl}_4(\text{dmpe})_2$ molecule as found in compound **2**.

(1) Å, which is shorter than the normal values, viz., $\geq 1.80 \text{ Å}$. However, the carbon atoms do not appear to be disordered or undergo excessive thermal motion, nor have we found any other chemically credible entity that could be refined more satisfactorily.

However, the fact that the structural study of **1** leaves some ambiguities concerning the $[\text{P}(\text{CH}_3)_4]^+$ ion and the disorder and/or uncertainty concerning the $\text{S}(\text{CH}_3)_2$ molecules is annoying in a minor way but fundamentally irrelevant to our purpose in this paper. That purpose is to compare the structures of $[\text{TaCl}_4(\text{dmpe})_2]^+$ and $\text{TaCl}_4(\text{dmpe})_2$. The structure of **1** provides an entirely adequate picture of the former, whatever its inadequacies in other respects. Let us turn then to a consideration of the structure of this d^0 , eight-coordinate species, which is depicted in Figure 2.

The $[\text{TaCl}_4(\text{dmpe})_2]^+$ ion resides on a position of crystallographic $42m$ (D_{2d}) symmetry. As discussed below, a disordering of the carbon atoms of the dmpe ligands is necessary to accommodate this symmetry, but the inner set of heavy atoms, TaCl_4P_4 , has rigorous D_{2d} symmetry. The arrangement is thus precisely that of Figure 1 with $X = \text{Cl}$, $Y = \text{P}$, $a = 2.691$ (5) Å, $b = 2.430$ (3) Å, $\alpha = 72.1$ (2)°, and $\beta = 145.4$ (2)°.

Atom C(1), the methylene carbon of the dmpe ligand, was refined at a position on the same plane that contains P(1) and the central Ta atom. It is not likely, however, that the entire five-membered metal–ligand unit is planar but rather that the methylene carbon atoms lie slightly off the mirror plane in directions perpendicular to it and are disordered. The refinement developed for atom C(1) an anisotropic temperature factor that is roughly uniaxial, with corresponding root-mean-square amplitudes of thermal vibration 0.166, 0.234, and 0.572 Å. Figure 2 shows that the large amplitude of vibration is essentially perpendicular to the mirror plane. An attempt to refine atom C(1) as two half-atoms with positions slightly

away from the plane resulted in coalescence of the disordered pair. With this type of unresolved disorder in the ring conformation there would also have to be a disorder in the positions of the methyl groups of the dmpe ligand, and again, this is probably not resolvable into discrete fractional carbon atoms. It is, therefore, not unexpected that atom C(2), the methyl carbon atom of the dmpe moiety, has root-mean-square amplitudes of vibration larger than normal (0.180, 0.330, 0.448 Å) and quite anisotropic. The abnormally short C(1)–C(1') bond length calculated from the refined coordinates is a consequence of using the centers of the elongated ellipsoids instead of actual nuclear positions. For carbon atoms located 0.32 Å on either side of the P–Ta–P plane, a distance that is consistent with the experimental results, the C–C distance would be 1.50 Å.

The structure of the [TaCl₄(dmpe)₂]⁺ ion closely resembles that of the [TaCl₄(diars)₂]⁺ ion.¹⁰ Using average values consistent with D_{2d} symmetry for the latter, we have the following values of the parameters defined in Figure 1: *a* = 2.761 [2] Å, *b* = 2.40 [1] Å, α = 72.7 [4]°, β = 145.9 [3]°. The angles are not significantly different from those in [TaCl₄(dmpe)₂]⁺. The Ta–As distance may be compared with the Ta–P distance if it is diminished by the accepted difference of 0.11 Å in the single-bond radii of As and P. This gives a projected Ta–P distance of 2.65 [1] Å, which is 0.04 (2) Å shorter than the Ta–P distance we have actually found in [TaCl₄(dmpe)₂]⁺. Similarly, the Ta–Cl distance in the diars compound is 0.03 (1) Å shorter than that in [TaCl₄(dmpe)₂]⁺. These small discrepancies are scarcely significant statistically, and the comparison of the two structures supports the assignment of the same oxidation state, namely V, to the metal atoms in both cases.

Compound 2. The structure of the molecule TaCl₄(dmpe)₂ differs in both symmetry and bond lengths from that of the cation [TaCl₄(dmpe)₂]⁺. The molecule of **2** has a crystallographic symmetry axis of order 2. The P–Ta–P, Cl–Ta–Cl, and P–Ta–Cl angles do not follow the pattern expected for dodecahedral (D_{2d}) symmetry but are in rather good accord with the pattern dictated by a square-antiprismatic (D₂) arrangement, as shown in Figure 4. The principal deviations from exact square-antiprismatic symmetry are, first, a slight puckering of the two nearly parallel P₂Cl₂ planes (Figure 4, top) and, second, a rhombic distortion of the two ideally square P₂Cl₂ arrays (Figure 4, bottom). Both of these distortions may be attributed in large part to the fact that the phosphorus atoms are incorporated in chelate rings.

The Ta–P and Ta–Cl distances in **2** are appreciably different from those in **1**, but surprisingly, they change in opposite directions. In **2** the Ta–Cl bonds are 0.075 (4) Å longer and the Ta–P bonds 0.038 (5) Å shorter than in **1**. While there are, doubtless, a number of factors that might be implicated in these bond length changes, we may begin by considering the following simple, qualitative explanation. When the formal charge of the tantalum atom is reduced from 5+ to 4+, its attraction for the anionic ligands, Cl[−], is most directly affected, leading to the appreciable increase in Ta–Cl distances. When the Cl atoms have moved away from the metal atom, it is possible for the phosphorus atoms, which are kept at rather large distances (ca. 0.2 Å greater than the Ta–Cl distances) by repulsive forces in the coordination sphere, to move a little closer to the metal atom. This closer approach of the phosphorus atoms may also be encouraged by the formation of metal-to-phosphorus π bonding, a point that will be developed further below.

Why the Structural Change? Now that we have established the fact that a structural change from dodecahedral (DD)

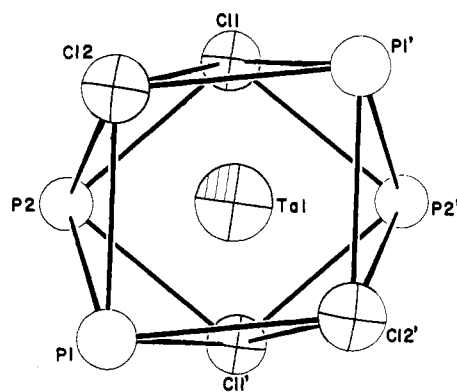
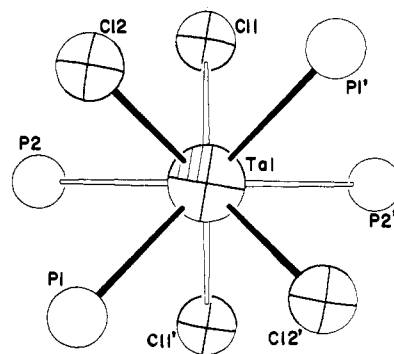
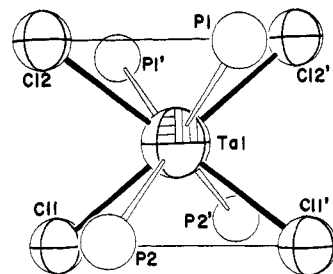


Figure 4. Three views of the TaCl₄P₄ portion of the TaCl₄(dmpe)₂ molecule emphasizing its structure as a distorted square antiprism.

[TaCl₄(dmpe)₂]⁺ to square-antiprismatic (SAP) TaCl₄(dmpe)₂ occurs, it is natural to seek the cause of this change. Since it is well established^{1,2} that the DD and SAP structures are generally of very similar stability, it is clear that it may not be easy to find a simple causal relationship between the addition of one electron and the structural rearrangement.

While there may be no *direct* reason to expect repulsive forces between ligand atoms to change enough to alter the relative stabilities of the DD and SAP arrangements, upon addition of one d electron, there could be an *indirect* effect. This *indirect* effect might arise from the bond length changes. It is possible that, with the Ta–Cl and Ta–P distances favored for the Ta^V complex, the repulsive forces favor the DD stereochemistry, while the altered bond length ratio in the Ta^{IV} case might change the repulsive forces to favor the SAP stereochemistry. There seems little chance of testing this possibility except by some numerical calculations of the sort made by Kepert,¹ which we are not prepared to undertake.

Perhaps a more likely cause of the change is the maximization of metal–ligand π bonding. In the DD configuration the added d electron would occupy a σ-nonbonding orbital (d_{x²−y²} or d_{xy}, depending on the choice of *x* and *y* directions) in which it would not be well suited to give a bonding π interaction with the π-accepting phosphorus atoms, and it might

(10) Dewan, J. C.; Kepert, D. L.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1975, 2031.

actually diminish the strength of any possible Cl→Ta π bonding. However, in the SAP conformation the d electron would presumably occupy the d_{z^2} orbital, which is the uniquely σ -nonbonding orbital but also a potentially Ta-P bonding orbital. Thus, by a relatively small rearrangement of the coordination sphere, in which ligand-ligand repulsive forces would not be much changed, an appreciable increase in π bonding might be secured. This is our current best hypothesis to explain the DD → SAP conformational change observed

in the $[\text{TaCl}_4(\text{dmpe})_2]^+ \rightarrow \text{TaCl}_4(\text{dmpe})_2$ reduction.

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Supplementary Material Available: Tables of anisotropic thermal vibration tensor components and structure factors for both structures (9 pages). Ordering information is given on any current masthead page.

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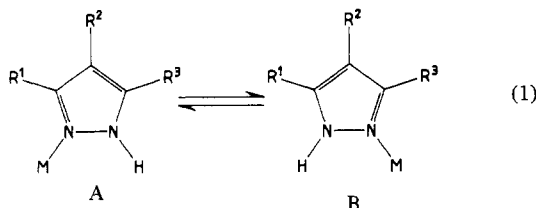
Crystal and Molecular Structures of Tetrafluoroborate Salts of the *cis*-Chlorobis(triethylphosphine)(3-(trifluoromethyl)-5-methylpyrazole)platinum(II) and *cis*-Chlorobis(triethylphosphine)(indazole)platinum(II) Cations

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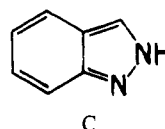
Full X-ray crystallographic data are reported for the Pt(II) cations *cis*-[PtCl(PEt₃)₂(MTMP)]⁺ (**1**) and *cis*-[PtCl(PEt₃)₂(INN)]⁺, acetone monosolvate (**3**) of **2**, MTMP = methyl(trifluoromethyl)pyrazole and INN = indazole, both as BF₄⁻ salts. The Pt-N distances are short compared with those in related cations at 1.95 (3) and 1.96 (3) Å, respectively. In **1** MTMP is bonded to Pt through N², i.e., complexation of 3-(trifluoromethyl)-5-methylpyrazole, while in **2** INN is bound via the N² nitrogen as expected. It is suggested on the basis of ¹³C NMR spectroscopy that neutral MTMP exists in solution as (3-CF₃)(5-CH₃)C₃N₂H₂. Accordingly, deprotonation of MTMP or INN provides access to the neutral pyrazolyl-Pt(II) complexes *cis*-Pt(PEt₃)₂L₂. ¹³C and ³¹P NMR data for the first of which indicate that the product is an isomer in which the Me (rather than the CF₃) substituent of the MTMP heterocycle is closest to Pt.

Earlier we discussed^{2a} the nature of the processes that give rise to temperature-dependent ¹H and ³¹P NMR spectra in cationic palladium(II) complexes incorporating pyrazoles as neutral unidentate ligands. In these systems the fast limit for rearrangement behavior is characterized by equivalence among the N¹ and N² sites (eq 1) for R¹ = R³. We also noted that



the corresponding platinum(II) complexes are nonfluxional and presented details of the crystal and molecular structure of *cis*-[PtCl(PEt₃)₂L][BF₄] for L = 3,5-dimethylpyrazole. Coordination of a neutral, unsymmetrical pyrazole (i.e., R¹ ≠ R³) in a related fashion leads, however, to the situation in which A and B are not identical although they are isomeric, and the exchange represented by eq 1 is nondegenerate, rather than degenerate. In this context we have investigated ligation to Pd or Pt of methyl(trifluoromethyl)pyrazole (MTMP) and indazole (INN). In the first case for the R¹ = Me, R³ = CF₃ configuration A represents a 3-methyl-5-(trifluoromethyl)pyrazole complex while B is the corresponding 3-trifluoromethyl-5-methyl species: similarly, when A implies complexation by INN, then B is a complex of the nonbenzenoid

isomer 2*H*-indazole (2*H*-INN), C. Characterization by X-ray



crystallography of the cationic platinum(II) complexes *cis*-[PtCl(PEt₃)₂L][BF₄], where L = MTMP and INN, forms the substance of the present paper. Transition-metal complexes of MTMP have not been reported previously, and indeed very little of the chemistry of this compound has been investigated despite its straightforward access from the reaction of 1,1,1-trifluoroacetylacetone with hydrazine.^{2b} A limited range of transition-metal complexes of INN are known,³ but none of 2*H*-INN are known. For comparative purposes the formation from the deprotonated heterocycles of platinum(II)-methyl-(trifluoromethyl)pyrazolyl and -indazolyl complexes has also been cursorily examined.

Experimental Section

Synthetic, analytical, and instrumental procedures and preparation of starting materials have been detailed in a previous paper.^{2a} The ¹³C NMR spectrum of MTMP and one Pt(II) complex were measured at 62.89 MHz with a Bruker WM250 spectrometer.

***cis*-[PtCl(PEt₃)₂(MTMP)]⁺[BF₄]⁻ (**1**).** To a solution of [Pt₂Cl₂(PEt₃)₄][BF₄]₂ (0.17 g, 0.15 mmol) in acetone (15 cm³) was added C₃H₅N₂F₃ (MTMP, 0.045 g, 0.30 mmol) in the same solvent (10 cm³). The colorless solution was stirred at ambient temperature (5 h), the solvent removed, and the residue crystallized from CH₂Cl₂/pentane to give the product **1** (0.14 g, 70%).

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