Such d-orbital contributions have recently been put forth[26] as the explanation for the short Pt–As bond lengths of 2.38 Å. in Pt(diarsine)$_2$I$_2$[27] and in Pt(diarsine)$_2$Cl$_2$.[26] Since the covalent radius of As is some 0.10 Å. longer than that of P, the contraction of the Pt–As bonds is similar to that of the Pt–P bonds found here. Nevertheless, there is sufficiently little information on M–P and M–Cl distances (where M is a second or third row transition element) so that very little can be said with certainty about the bonding in this platinum compound. It is not possible to assess the relative importance of the *trans* effect or of d-orbital contributions, or in fact of any other effects that one might fancy. Yet, on the basis of the spreading of the P–Pt–Cl angles from the presumably ideal value of 90° to 92.6 and 94.5° there is the indication of some steric interaction between Cl and P. (A similar deviation of the angles from 90° was observed in the bromo compound.[4]) Hence any factor that tends to shorten the Pt–P bond distance will, through steric effects, lengthen the Pt–Cl distance and *vice versa*.

(26) N. C. Stephenson, *Acta Cryst.*, **17**, 1517 (1964).
(27) N. C. Stephenson, *J. Inorg. Nucl. Chem.*, **24**, 791 (1963).

Of some interest in this regard is that the Pt, P, Cl portion of the molecule is significantly nonplanar. The best least-squares plane[28] through these four atoms has the equation $3.528x - 15.805y + 1.336z = 5.572$ (monoclinic coordinates). The deviations from this plane are Pt, 0.005 ± 0.001; Cl, −0.021 ± 0.010; P$_1$, −0.095 ± 0.008; and P$_2$, −0.096 ± 0.008 Å. A careful examination of the intermolecular distances suggests no explanation for a lack of planarity in terms of packing distortions. (In fact all intermolecular contacts appear to be normal, and hence are not tabulated here.) The only explanation for this lack of planarity that we can suggest involves the intramolecular steric repulsions of P and Cl.

The geometry of the diphenylethylphosphine ligand closely resembles that found previously for the triphenylphosphine ligand.[7,20,21]

Acknowledgment.—We are indebted to H. B. Gray, who kindly supplied the crystals, for his diligent laboratory work.

(28) W. C. Hamilton, *Acta Cryst.*, **14**, 185 (1961).

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A Five-Coordinated d^6 Complex: Structure of Dichlorotris(triphenylphosphine)ruthenium(II)[1]

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A complete X-ray structure determination of dichlorotris(triphenylphosphine)ruthenium(II), RuCl$_2$[P(C$_6$H$_5$)$_3$]$_3$, has been carried out in order to ascertain if in this compound the Ru(II) (d^6) is five-coordinated. The compound crystallizes in space group C_{2h}^5-P2$_1$/c of the monoclinic system in a cell of dimensions a = 18.01, b = 20.22, c = 12.36 Å., β = 90.5°. The observed density is 1.43 g./cm.^{3}, and the density calculated for four molecules in the cell is 1.415 g./cm.^{3}. There are no crystallographic symmetry conditions imposed on the molecule. The structure consists of the packing of individual monomeric molecules. In these molecules the Ru lies toward the center of a distorted square pyramid which consists of *trans* Cl atoms and *trans* P atoms in the base and an apical P atom. The apical Ru–P distance of 2.23 Å. is about 0.16 Å. shorter than the basal Ru–P distances. This is the only known example from X-ray structural studies of a five-coordinated d^6 complex, and it probably occurs not because of an inherent tendency toward five-coordination, but rather because the unused octahedral site about the square-pyramidal configuration is effectively blocked by a phenyl ring.

Introduction

Of the two dozen or so five-coordinated transition metal complexes that have been established by X-ray diffraction studies, none is a d^6 complex.[2] This is not surprising, for it has frequently been noted[3] that the spin-paired d^6 configuration is an especially favorable one for the formation of octahedral complexes. Of the relatively few d^6 complexes thought to be five-coordinated that are reported in the literature, the case for five-coordinated Os(II) in dibromotris(triphenylphosphine)osmium(II) seems one of the most convincing. This compound was prepared by Vaska[4] in 90% yield from the reaction of (NH$_4$)$_2$OsBr$_6$ with triphenylphosphine in 2-methoxyethanol at 25°. In a similar manner Vaska[5] has prepared dichlorotris(triphenylphosphine)ruthenium(II). From magnetic, molecular weight, conductivity, and spectroscopic measurements Vaska concludes that these compounds are diamagnetic, monomeric, and are not hydrides. A preliminary X-ray examination by Pollack[6] indicated that the

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.
(2) J. A. Ibers, *Ann. Rev. Phys. Chem.*, in press.
(3) For example, see R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961).
(4) L. Vaska, *Chem. Ind.* (London), 1402 (1963).
(5) L. Vaska, private communication.
(6) S. S. Pollack, as quoted by Vaska.[5]

TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $RuCl_2[P(C_6H_5)_3]_3$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.23919 (7)[b]	0.48707 (6)	0.30760 (10)	0.00146 (5)	0.00111 (4)	0.00321 (12)	−0.00014 (4)	0.00009 (6)	0.00008 (6)
P_1	0.2410 (2)	0.5878 (2)	0.4062 (3)	0.0019 (2)	0.0012 (1)	0.0028 (4)	−0.0002 (1)	−0.0001 (2)	0.0000 (2)
P_2	0.1891 (2)	0.3833 (2)	0.2444 (3)	0.0017 (2)	0.0015 (2)	0.0031 (4)	−0.0001 (1)	0.0000 (2)	−0.0005 (2)
P_3	0.3279 (2)	0.5057 (2)	0.1866 (3)	0.0018 (2)	0.0016 (2)	0.0038 (4)	−0.0001 (1)	−0.0001 (2)	0.0002 (2)
Cl_1	0.1230 (2)	0.5276 (2)	0.2408 (3)	0.0021 (2)	0.0016 (1)	0.0054 (4)	0.0002 (1)	−0.0003 (2)	−0.0003 (2)
Cl_2	0.3234 (2)	0.4353 (2)	0.4315 (3)	0.0027 (2)	0.0017 (2)	0.0051 (4)	0.0002 (1)	−0.0008 (2)	0.0004 (2)

Group	x_c[c]	y_c	z_c	δ	ϵ	η	B, Å.^{2}
P_1R_1[d]	0.1377 (5)	0.5418 (4)	0.6067 (6)	1.280 (8)	5.742 (7)	1.083 (8)	3.6 (2)
P_1R_2	0.1623 (4)	0.7152 (4)	0.2996 (6)	1.008 (13)	1.079 (7)	4.225 (13)	3.3 (2)
P_1R_3	0.3801 (5)	0.6535 (4)	0.5368 (6)	0.472 (7)	−0.016 (7)	2.595 (6)	4.0 (2)
P_2R_1	0.0841 (4)	0.3334 (4)	0.4380 (7)	2.655 (8)	5.667 (8)	1.850 (8)	3.6 (2)
P_2R_2	0.2661 (4)	0.2381 (4)	0.2451 (6)	5.298 (21)	1.210 (6)	2.940 (21)	3.2 (2)
P_2R_3	0.0964 (5)	0.3935 (3)	0.0217 (7)	1.473 (8)	0.535 (7)	4.664 (8)	3.5 (2)
P_3R_1	0.4675 (4)	0.5891 (4)	0.2840 (5)	3.708 (7)	0.103 (6)	0.406 (6)	3.4 (2)
P_3R_2	0.2901 (5)	0.5890 (4)	−0.0304 (6)	4.964 (7)	6.207 (8)	5.287 (6)	3.8 (2)
P_3R_3	0.4113 (4)	0.3779 (4)	0.0853 (6)	−0.130 (15)	5.163 (7)	4.087 (14)	3.1 (2)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbers in parentheses here and in succeeding tables are standard deviations in the least significant digits. [c] x_c, y_c, z_c are the fractional coordinates of the ring centers. The angles δ, ϵ, η (in radians) are defined in the text. [d] P_1R_1 is phosphorus 1, ring 1, etc.

osmium and ruthenium compounds are probably isomorphous, since they crystallize in monoclinic cells of similar dimensions. It seemed of especial interest to determine the molecular structure of one of these compounds because of the possibility of establishing for the first time the existence of a five-coordinated d^6 complex. The detailed knowledge of the conformation of the ligands about ruthenium or osmium is of interest, because five-coordinated compounds have been studied infrequently,[2] and five-coordinated ruthenium and osmium not at all. Since higher accuracy in the determination could be expected, we undertook a study of the ruthenium compound.

Collection and Reduction of the X-Ray Data

Well-developed black crystals of $RuCl_2[P(C_6H_5)_3]_3$ were very kindly supplied by L. Vaska. On the basis of an optical examination and an X-ray examination using Weissenberg and precession photography we established that the compound crystallizes in the monoclinic system in a cell of dimensions $a = 18.01 \pm 0.04$, $b = 20.22 \pm 0.04$, $c = 12.36 \pm 0.02$ Å., $\beta = 90.5 \pm 0.3°$. The observed extinctions are $0k0$ for k odd and $h0l$ for l odd, and the space group is very probably C_{2h}^5-$P2_1/c$. A density of 1.415 g./cm.^{3} calculated for four molecules in the unit cell agrees satisfactorily with that of 1.43 g./cm.^{3} measured by Pollack[6] by the flotation method. Thus no crystallographic conditions need be imposed on the molecules.

No difficulty was encountered in grinding spheres of the material. Integrated intensity data were collected at room temperature with Cu Kα radiation by the equi-inclination Weissenberg technique from a spherical crystal of radius 0.083 mm. (calculated weight, 339 μg.). The layers $hk0$ through $hk8$ were photographed. Intensities of 1778 independent reflections accessible within the angular range $\theta_{Cu} \leq 42°$ were estimated visually. These were reduced to values of the structure amplitudes F_o by application of the usual Lorentz-polarization factor and of a relatively constant correction for absorption ($\mu R = 0.442$). These F_o values were brought to an approximate common scale through a modification of Wilson's procedure.

Solution of the Structure

The positions of the Ru and other heavy atoms were deduced from a three-dimensional Patterson function (sharpened and origin-removed).[7] Refinement of these positions led to a conventional agreement factor R ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 43%. (Note that the compound contains 68% carbon by weight, and so structure factors based only on the Ru, P, and Cl positions lack contributions from a significant fraction of the scatterers in the structure.) The positions of the phenyl rings were detected in a subsequent difference Fourier map based on this refinement of the heavy-atom positions.

The structure was refined by the least-squares procedure. In this refinement the phenyl rings were treated as rigid groups[8,9] and were restricted to their well-known geometry (D_{6h} symmetry, C–C = 1.392, C–H = 1.08 Å.). This procedure was followed not only to make the calculations feasible, but also because we believe that it is physically more reasonable than the imposition of no geometrical restrictions on the phenyl rings. The variable parameters for each ring are, in addition to a single over-all isotropic thermal parameter, the fractional coordinates of the ring center x_c, y_c, z_c, and three angles, δ, ϵ, and η, which are successive counter clockwise rotations about internal orthogonal axes $\mathbf{a}_2'$, $\mathbf{a}_1'$, and $\mathbf{a}_3'$ of the phenyl ring which bring about alignment (except for translation) of this coordinate system with a stationary orthogonal coordinate system $\mathbf{A}$. The origin of the orthogonal internal coordinate system $\mathbf{a}'$ is chosen at the center of the phenyl ring, $\mathbf{a}_3'$ is normal to the plane of the ring, and $\mathbf{a}_1'$ intersects a vertex of the ring. The stationary orthogonal coordinate system $\mathbf{A}$ has $\mathbf{A}_2$ parallel to $\mathbf{a}_2$,

(7) Programs for the I.B.M. 7090 used in this work were local modifications of Zalkin's FORDAP Fourier-summation program and the Busing–Levy ORFLS least-squares program, together with various local programs.

(8) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963).

(9) S. J. La Placa and J. A. Ibers, *Acta Cryst.*, in press.

$\mathbf{A}_1$ parallel to $\mathbf{a}_2 \times \mathbf{a}_3$, and $\mathbf{A}_3$ parallel to $\mathbf{A}_1 \times \mathbf{A}_2$, where $\mathbf{a}$ is the monoclinic axial system. The function minimized was $\Sigma w(F_o - F_c)^2$, where the weights w were assigned in the following way: $I < 10$, w proportional to $(I/F)^2$; $I \geqslant 10$, w proportional to $(10/F)^2$, where I is the raw intensity value for the particular reflection. The atomic scattering factors for the neutral atoms tabulated by Ibers[10] were used. The anomalous parts of the Ru, Cl, and P scattering factors were obtained from Templeton's tabulation[11] and were included in the calculated structure factors.[12] In the initial refinement the Ru, P, and Cl atoms were restricted to isotropic vibration; this refinement converged in two cycles to an R value of 7.5% and to a weighted R factor R' ($R' = (\Sigma w(F_o - F_c)^2/\Sigma w F_o^2)^{1/2}$) of 9.4%. In a subsequent difference Fourier there was a clear indication of some anisotropic thermal motion of the heavy atoms. In a final calculation, the Ru, P, and Cl atoms were allowed to vibrate anisotropically, but the phenyl rings (this time including the contributions from the phenyl hydrogens) were constrained to a single isotropic thermal parameter per ring. This refinement of 117 positional and thermal parameters converged to values of R of 6.3% and R' of 7.5% for the 1778 observed reflections. (Past experience leads us to believe that at least half of this very significant improvement in R' results from the inclusion of scattering from the hydrogen atoms; the rest, of course, results from the assignment of anisotropic thermal motion to the heavy atoms.) The highest peak on the final difference Fourier is only 0.54 e/Å.^{3}, about 10% the height of a carbon atom in this structure. Although there is clear evidence from this final difference Fourier that the phenyl carbon atoms adjacent to phosphorus atoms are vibrating less than those *para*, no attempt was made to derive from this difference Fourier changes in the carbon thermal parameters.

In Table I the final parameters, together with their standard deviations as estimated from the inverse matrix, are listed. The group parameters of Table I lead to the positional parameters for the phenyl carbon atoms given in Table II. (The positional parameters of the hydrogen atoms of the phenyl rings have been omitted, but these can be derived readily from the data of Table I, on the assumption that the C–H distance is 1.08 Å.) The standard deviations assigned to the parameters of Table II are derived from the errors in the group parameters and may be applied to an error analysis of distances not involved in the same ring. The intra-ring distances are, of course, fixed (C–C = 1.392 A.). The tabulation of structure factors (Table III) does not include unobserved reflections, for no value of $|F_c|$ exceeded our estimate of F_{min} for any of the weak reflections accessible on the films. The principal values of the root-mean-square amplitudes of vibration of the heavy atoms are listed in Table IV. The orientations of the vibrational ellipsoids are not given, because they do not appear to conform to any simple picture of the vibrations of the molecule as a whole. These orientations can, of course, be derived from the data of Table I.

TABLE II

DERIVED PARAMETERS FOR GROUP CARBON ATOMS[a]

Group atom	x	y	z
$P_1R_1C_1$	0.1818 (7)	0.5637 (5)	0.5220 (8)
$P_1R_1C_2$	0.1048 (7)	0.5674 (6)	0.5135 (8)
$P_1R_1C_3$	0.0607 (5)	0.5454 (6)	0.5982 (10)
$P_1R_1C_4$	0.0936 (7)	0.5198 (6)	0.6915 (8)
$P_1R_1C_5$	0.1706 (7)	0.5162 (6)	0.7000 (8)
$P_1R_1C_6$	0.2147 (5)	0.5381 (6)	0.6153 (10)
$P_1R_2C_1$	0.1939 (6)	0.6593 (5)	0.3470 (10)
$P_1R_2C_2$	0.1513 (6)	0.7023 (6)	0.4089 (7)
$P_1R_2C_3$	0.1197 (6)	0.7582 (6)	0.3614 (9)
$P_1R_2C_4$	0.1307 (6)	0.7711 (5)	0.2521 (10)
$P_1R_2C_5$	0.1732 (6)	0.7281 (6)	0.1903 (7)
$P_1R_2C_6$	0.2048 (6)	0.6722 (6)	0.2377 (9)
$P_1R_3C_1$	0.3216 (6)	0.6262 (7)	0.4774 (8)
$P_1R_3C_2$	0.3204 (6)	0.6929 (6)	0.5051 (9)
$P_1R_3C_3$	0.3789 (8)	0.7202 (4)	0.5644 (9)
$P_1R_3C_4$	0.4385 (6)	0.6808 (7)	0.5961 (9)
$P_1R_3C_5$	0.4398 (6)	0.6141 (6)	0.5684 (9)
$P_1R_3C_6$	0.3813 (7)	0.5868 (5)	0.5091 (9)
$P_2R_1C_1$	0.1229 (6)	0.3584 (6)	0.3501 (9)
$P_2R_1C_2$	0.0780 (7)	0.3029 (6)	0.3374 (8)
$P_2R_1C_3$	0.0391 (6)	0.2780 (5)	0.4253 (11)
$P_2R_1C_4$	0.0452 (6)	0.3085 (6)	0.5259 (8)
$P_2R_1C_5$	0.0902 (7)	0.3640 (6)	0.5385 (8)
$P_2R_1C_6$	0.1291 (6)	0.3889 (5)	0.4507 (11)
$P_2R_2C_1$	0.2364 (6)	0.3014 (5)	0.2368 (13)
$P_2R_2C_2$	0.2709 (6)	0.2814 (6)	0.3324 (8)
$P_2R_2C_3$	0.3007 (6)	0.2180 (6)	0.3407 (7)
$P_2R_2C_4$	0.2959 (6)	0.1747 (5)	0.2534 (10)
$P_2R_2C_5$	0.2614 (6)	0.1948 (6)	0.1578 (8)
$P_2R_2C_6$	0.2316 (6)	0.2582 (6)	0.1495 (7)
$P_2R_3C_1$	0.1352 (7)	0.3868 (6)	0.1190 (8)
$P_2R_3C_2$	0.0585 (7)	0.3952 (6)	0.1194 (8)
$P_2R_3C_3$	0.0197 (5)	0.4019 (6)	0.0221 (11)
$P_2R_3C_4$	0.0576 (7)	0.4002 (6)	−0.0755 (8)
$P_2R_3C_5$	0.1343 (7)	0.3919 (6)	−0.0759 (8)
$P_2R_3C_6$	0.1731 (5)	0.3851 (6)	0.0214 (11)
$P_3R_1C_1$	0.4092 (6)	0.5528 (6)	0.2390 (8)
$P_3R_1C_2$	0.4741 (7)	0.5209 (4)	0.2720 (9)
$P_3R_1C_3$	0.5323 (5)	0.5572 (6)	0.3170 (8)
$P_3R_1C_4$	0.5257 (6)	0.6253 (6)	0.3290 (8)
$P_3R_1C_5$	0.4609 (7)	0.6572 (4)	0.2961 (9)
$P_3R_1C_6$	0.4027 (5)	0.6210 (6)	0.2511 (8)
$P_3R_2C_1$	0.3054 (8)	0.5539 (5)	0.0641 (7)
$P_3R_2C_2$	0.3624 (5)	0.5863 (6)	0.0102 (10)
$P_3R_2C_3$	0.3472 (6)	0.6214 (6)	−0.0842 (10)
$P_3R_2C_4$	0.2749 (8)	0.6242 (5)	−0.1249 (7)
$P_3R_2C_5$	0.2179 (5)	0.5918 (6)	−0.0711 (10)
$P_3R_2C_6$	0.2331 (6)	0.5567 (6)	0.0234 (10)
$P_3R_3C_1$	0.3738 (6)	0.4330 (5)	0.1246 (9)
$P_3R_3C_2$	0.3963 (6)	0.4312 (5)	0.0172 (9)
$P_3R_3C_3$	0.4338 (6)	0.3761 (6)	−0.0221 (7)
$P_3R_3C_4$	0.4488 (6)	0.3228 (5)	0.0460 (9)
$P_3R_3C_5$	0.4262 (6)	0.3246 (5)	0.1533 (9)
$P_3R_3C_6$	0.3887 (6)	0.3797 (6)	0.1926 (7)

[a] C_1 is attached to P; other C atoms are numbered in succession so that C_4 is *para* to C_1.

Description of the Structure

The structure described by the cell dimensions, parameters, and symmetry operations of the space group consists of the packing of discrete, monomeric molecules (shortest Ru–Ru distance >9 Å.). The

(10) J. A. Ibers in "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, 1962, Vol. 3, Table 3.3.1.
(11) D. H. Templeton, *ibid.*, Table 3.3.2B.
(12) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR $RuCl_2[P(C_6H_5)_3]_3$

H	K	OBS	CAL
[illegible]	[illegible]	[illegible]	[illegible]

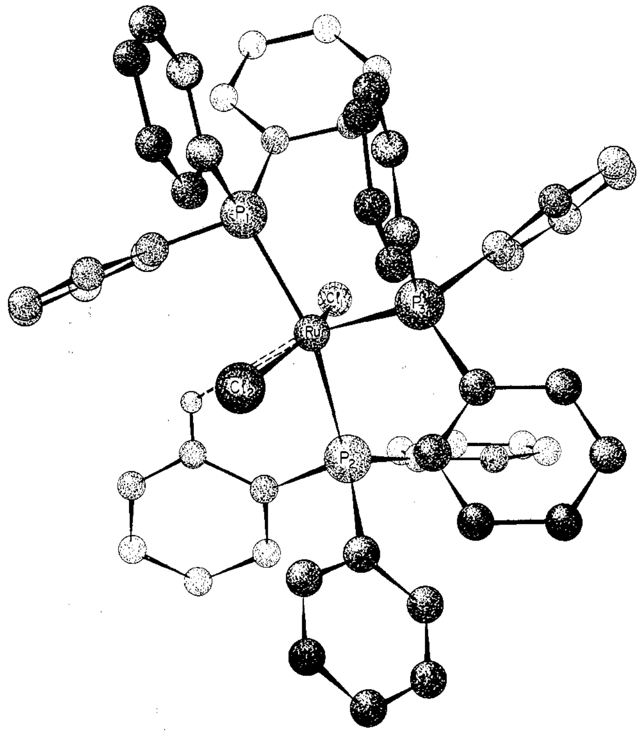

Figure 1.—A perspective view of the structure of $RuCl_2[P(C_6H_5)_3]_3$. Only the hydrogen atom that blocks the unused octahedral site is shown.

Table IV

Root-Mean-Square Amplitudes of Vibration (Å.)

Atom	Min.	Int.	Max.
Ru	0.143 (3)	0.159 (3)	0.162 (3)
P_1	0.145 (11)	0.151 (10)	0.182 (9)
P_2	0.143 (11)	0.166 (10)	0.189 (9)
P_3	0.166 (10)	0.168 (10)	0.186 (9)
Cl_1	0.173 (9)	0.186 (9)	0.214 (8)
Cl_2	0.165 (9)	0.199 (8)	0.228 (8)

Ru may be described as being near the center of gravity of a distorted square pyramid, composed of *trans* Cl atoms and *trans* P atoms in the base and of an apical P atom (P_3). This configuration is shown in perspective in Figure 1. The best least-squares plane through the four atoms in the base has the equation $11.073x + 4.618y - 9.396z = 1.551$ (monoclinic coordinates). The base is not strictly planar, since the phosphorus atoms are slightly above it and the chlorine atoms slightly below it. (The distances of P_1, P_2, Cl_1, and Cl_2 from this plane are 0.015, 0.017, −0.016, and −0.014 Å., respectively, all ±0.004 Å.) The Ru is 0.456 Å. above the plane. The important intramolecular distances and angles are given in Table V. (Since there are no unusual intermolecular distances, these are not tabulated.) The basal Ru–P distances (2.37 and 2.41 Å.) are significantly longer than the Rh–P distances (2.32 Å.) found recently[9] in hydridocarbonyltris(triphenylphosphine)rhodium. The apical Ru–P distance of 2.23 Å. is even shorter than the Pt–P distances of 2.26 Å. reported in the platinum hydrides $PtHBr[P(C_2H_5)_3]_2$[13] and $PtHCl[P(C_6H_5)_2C_2H_5]_2$.[14] Moreover, the basal Ru–Cl distances (2.39 Å.) are only slightly shorter than the Pt–Cl distance of 2.42 Å. in the platinum hydride. In the platinum hydrides it is generally assumed that a long Pt–halogen bond (*trans* to hydrogen) is consistent with the high chemical lability of the halogen. There is a general indication, therefore, from the limited comparisons that are possible, that the apical Ru–P bond is severely shortened and that the basal Ru–P and Ru–Cl bonds are somewhat longer than normal. This lengthening of the basal bonds could be purely a steric effect. Clearly steric effects could be minimized if the configuration about Ru were that of a symmetric trigonal bipyramid with Cl at the apices. The apical shortening does not seem to be steric in nature and is probably consistent with the notion of Ballhausen and Gray[15] that there should be strong axial π-bonding in square-pyramidal-type metal complexes. Yet this is not a general phenomenon, for of the dozen or so known examples of square-pyramidal configurations of transition metals, less than half exhibit apical shortening.[2]

(13) P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Cryst.*, **13**, 246 (1960).

Table V

Selected Intramolecular Distances and Angles

Intramolecular distance, Å.		Angles, deg.	
Ru–P_1	2.374 (6)	P_1–Ru–P_2	156.4 (2)
Ru–P_2	2.412 (6)	P_1–Ru–P_3	101.1 (2)
Ru–P_3	2.230 (8)	P_1–Ru–Cl_1	83.7 (2)
Ru–Cl_1	2.387 (7)	P_1–Ru–Cl_2	92.4 (2)
Ru–Cl_2	2.388 (7)	P_1–Ru–H	90
Ru–H[a]	2.59	P_2–Ru–P_3	101.4 (2)
P_1–P_2	4.685 (10)	P_2–Ru–Cl_1	82.1 (2)
P_1–P_3	3.557 (10)	P_2–Ru–Cl_2	93.4 (2)
P_1–Cl_1	3.171 (10)	P_2–Ru–H	70
P_1–Cl_2	3.437 (8)	P_3–Ru–Cl_1	109.9 (2)
P_1–H	3.51	P_3–Ru–Cl_2	92.9 (2)
P_2–P_3	3.594 (8)	P_3–Ru–H	161
P_2–Cl_1	3.151 (8)	Cl_1–Ru–Cl_2	157.2 (2)
P_2–Cl_2	3.494 (11)	Cl_1–Ru–H	86
P_2–H	2.89	Cl_2–Ru–H	71
P_3–Cl_1	3.781 (10)	P_1–Cl_1–P_2	95.5 (2)
P_3–Cl_2	3.348 (8)	Cl_1–P_2–Cl_2	89.4 (2)
P_3–H	4.75	P_2–Cl_2–P_1	85.0 (2)
Cl_1–Cl_2	4.682 (13)	Cl_2–P_1–Cl_1	90.0 (2)
Cl_1–H	3.41		
Cl_2–H	2.90		

[a] H = $P_2R_1H_6$.

A complete interatomic distance calculation reveals that the next closest approach to the Ru atom is made by a hydrogen atom on a β-carbon of phenyl ring 1 attached to phosphorus P_2 (Figure 1). This Ru–H distance is calculated to be 2.59 Å., on the assumption of a normal geometry for the phenyl ring. This distance is about what is expected from van der Waals radii. The triphenylphosphine geometry in this compound, as judged by P–C distances and C–P–C and P–C–C angles,[16] is nearly identical with the geometry

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(16) The P–C distances range from 1.823 to 1.864 Å. and average 1.848 ± 0.005 Å.; the C–P–C angles range from 95.2 to 105.7° and average 101.6 ± 1.0°; the P–C_1–C_4 angles range from 169.5 to 178.1°. The P–C_1–C_4 angle of 169.5° is for the ring containing the hydrogen in question and it deviates more from 180° than comparable angles in this or the other compounds referred to above. The direction of the deviation is consistent with Ru–H *repulsion;* that is, had the angle been more nearly 180° the Ru–H distance would have been shorter.

of the triphenylphosphine ligand and its derivatives in other transition metal complexes.[9,14,17] Moreover, we have noted previously[9] that within limits, which exclude significant interatomic repulsions, there is no particular dihedral angle between adjacent phenyl rings that is favored. In the present case, then, the filling of the vacant octahedral site by a phenyl ring, and in particular by a phenyl hydrogen, is energetically favorable, and there is no geometrical basis for postulating that this is a weak metal–hydrogen interaction similar to those postulated to account for various spectroscopic anomalies in a variety of different compounds (ferrocenyl alcohols,[18] protonated acylferrocenes,[19] cycloheptadienium complexes,[20] and $(CH_2)_3[Mn(CO)_5]_2$[21]). The evidence for such weak metal–hydrogen interactions is extremely tenuous, and it would be worthwhile examining these compounds in the solid state by diffraction methods. One might find no geometrical basis for this weak metal–hydrogen interaction, other than restricted rotation brought about by a preferred geometry (as in the present case). Unfortunately, the ruthenium and osmium compounds of Vaska are only slightly soluble in most solvents, and, of more interest, the dilute solutions rapidly change color. For these reasons little solution spectroscopy has been carried out. It is tempting to postulate, however, that the color change results from the rotation of the phenyl ring, followed by reaction at the unblocked octahedral site. If this has some basis in fact, then it should be difficult, if not impossible, to prepare the ruthenium or osmium compounds with a less rigid phosphorus ligand, such as triethylphosphine. One fact is certain: since the phenyl ring geometry leaves no room for a hydride hydrogen, the structure found here provides corroborative evidence to that of Vaska's from infrared spectra that the compound is not a hydride.

It is obvious that the preferred configuration about Ru in this compound is not trigonal bipyramidal, but is octahedral or possibly square pyramidal. We believe that dichlorotris(triphenylphosphine)ruthenium(II) is a true five-coordinated d^6 complex, but that its stability probably arises from intramolecular blocking of the unused octahedral site by the phenyl ring.[22]

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(22) NOTE ADDED IN PROOF.—A. Wojcicki has called our attention to a similar argument given by J. Chatt and A. E. Underhill [*J. Chem. Soc.*, 2088 (1963)]. They present evidence that the Rh(III) (d^6) is five-coordinated in bromodi-1-naphthylbis(diethylphenylphosphine)rhodium(III), and they postulate that the stability of the compound results from the shielding of the electron-deficient metal atom by the bulky ligands.

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Studies of Adducts of Metal Salts with Tetraalkyl Alkyldiphosphonates.[1] I. Proton Magnetic Resonance Spectra of Uranyl Nitrate Adducts of Methylenediphosphonates in $CDCl_3$

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Proton magnetic resonance data are given for $CDCl_3$ solutions of uranyl nitrate adducts of tetraalkyl methylenediphosphonates. These data are interpreted in terms of the effects on nearby protons of the anisotropic magnetic field from the uranyl group.

Introduction

In previous communications[2,3] it was reported that some of the proton resonances were doubled in certain organophosphorus esters that contain an aromatic radical. It is the purpose of this paper to report a similar phenomenon for $CDCl_3$ solutions of the uranyl nitrate adducts of certain tetraalkyl methylenediphosphonates, $(RO)_2P(=O)CH_2P(=O)(OR)_2$, and to present some of the inferences that may be drawn concerning the structure of these adducts and the cause of the resonance multiplication.

Uranyl nitrate adducts offer an exceptional opportunity for study in that so many of them can be isolated easily as crystalline solids of well-defined composition. It is therefore possible to be assured that there is no excess of free ester in these adducts. The methylenediphosphonates are of special interest be-

(1) The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.
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