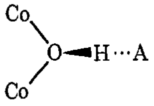
TABLE VI
SHORT CONTACTS, D···A, BETWEEN THE NONHYDROGEN ATOMS OF THE CATION AND ATOMS OF SURROUNDING GROUPS[a]

D	A	H	D···A, Å	D–H···A, deg
O(1)	O(11, b)		3.15	
	O(11)	H(1)	3.16	178
N(2)	O(5)	H(4)	3.10	127
	O(5, a)	H(4)	3.11	140
	O(10, d)	H(5)	3.06	161
N(3)	O(11, b)	H(6)	2.99	143
	O(12, b)	H(6)	3.14	160
	O(5, a)	H(7)	2.99	164
N(4)	O(13)	H(8)	3.28	144
	O(7)	H(9)	3.12	155
N(5)	O(13, c)	H(10)	3.08	121
	O(3, c)	H(11)	2.96	148
N(2′)	O(8, c)	H(12)	2.99	157
	O(4, e)	H(13)	3.25	135
	O(2, e)	H(13)	3.30	169
N(3′)	O(2, e)	H(14)	3.11	141
	O(14)		2.99	
N(4′)	O(3, c)	H(16)	3.00	113
	O(13, c)	H(17)	3.00	143
N(5′)	O(3)	H(18)	2.99	138
	O(14)	H(19)	3.23	145
C(5′)	O(4, e)	H(35)	3.14	143

[a] Hydrogen atoms not too far from the D···A line and angles D–H···A are also given. Symmetry code: no letter, coordinates are given in Tables II and III; (a) $1 - x, -y, 1 - z$; (b) $1 - x, -y, -z$; (c), $-1 + x, y, z$; (d) $-1/2 + x, 1/2 - y, 1/2 + z$; (e) $-1/2 + x, 1/2 - y, -1/2 + z$; (f) $x, y, z - 1$.

H(15) of the amine groups in the en ligands seem to participate in hydrogen bonds. The N–H···A distances for some of these bonds are rather long, however, and the angles at some of the H atoms are considerably less than 180°, suggesting only weak interactions. There are two amine hydrogen atoms [H(4) and H(6)] which appear to be shared by two acceptor oxygen atoms each. The water molecule oxygen, O(14), forms four close contacts, three of which can be considered as hydrogen bonds: O(14)–H(37)···O(6, f) = 3.04 Å; O(14)–H(36)···O(8, e) = 2.88 Å; N(5′)–H(19)···O(14) = 3.23 Å (for symmetry code, see Table VI). The fourth contact, of 2.99 Å to N(3′), does not involve a hydrogen atom. The two hydrogen atoms of the bridging μ-NH_2 group are not engaged in hydrogen bonding, as there are no suitable hydrogen-bond acceptors. The μ-OH group oxygen, O(1), has a suitable hydrogen-bond acceptor: the nitrate oxygen, O(11), 3.16 Å away. The hydrogen atom H(1) [whose coordinates were calculated on the basis of a tetrahedral sp^3 configuration around O(1) and which was put arbitrarily on that side of the central ring where it can form a hydrogen bond to O(11)] deviates only slightly from the O(1)···O(11) line, the O–H···O angle being about 178°. A similar geometry of a arrangement has been observed for cation **3** in its tetrachloride tetrahydrate salt.[15] The shortest nonbonded contact (3.14 Å) between a nitrate group and a carbon atom of the en ring is between O(4, e) and C(5′). This contact, with a C–H···O angle of 143° at H(35), may be regarded as an accidental result of the molecular packing rather than hydrogen bonding. All other C···O contacts in this structure exceed 3.2 Å. The closest contact between oxygen atoms of different nitrate groups, 2.82 Å, is between O(3) and O(13).



Acknowledgments.—This work was carried out under Grant GP-5768 from the National Science Foundation. We are grateful to Dr. W. P. Schaefer for helpful advice and to Dr. S. Samson for help in the use and maintenance of the X-ray equipment.

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The Crystal and Molecular Structure of *cis*-Dichlorobis(dimethylphenylphosphine)palladium(II)[1]

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The crystal and molecular structure of *cis*-dichlorobis(dimethylphenylphosphine)palladium(II) has been determined from 1722 independent, nonzero reflections using conventional, three-dimensional, single-crystal techniques. The compound crystallizes in the space group $P4_2/n$ with four molecules in a unit cell of dimensions $a = b = 9.324 \pm 0.004$ Å and $c = 21.485 \pm 0.004$ Å ($\rho_{calcd} = 1.612 \pm 0.003$ g/cm^3 and $\rho_{obsd} = 1.61 \pm 0.01$ g/cm^3). The structure is approximately cis square planar with a slight tetragonal distortion of 4.3°. A strong "trans effect" is evident. The Pd–P distance of 2.260 ± 0.002 Å is 0.12 Å shorter while the Pd–Cl distance of 2.362 ± 0.003 Å is 0.08 Å longer than the respective, expected values. The shortest Pd–Pd distance is 6.6 Å.

Introduction

It has been observed that square-planar complexes of the type PdX_2Y_2, where X is a halide, very often adopt the trans configuration.[2] In fact, only recently have any cis complexes of this type been characterized. The cis chloro complexes usually form pale yellow or colorless crystals while crystals of the trans complexes are decidedly more yellow.[3] However, a recent far-infrared study by Keiter[4] of $PdCl_2(P(CH_3)_2C_6H_5)_2$, which forms

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2708.

(2) (a) A. G. Booth, *Advan. Inorg. Chem. Radiochem.*, **6**, 37 (1964); (b) N. A. Bailey and R. Mason, *J. Chem. Soc.*, 2594 (1968).

(3) G. E. Coates and C. Parkin, *ibid.*, 421 (1963).

(4) R. Keiter, Ph.D. Dissertation, University of Maryland, 1966.

TABLE I

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	$^3/_4$	$^1/_4$	0.25309 (3)	69 (1)	79 (1)	12 (0)	− 1 (1)	0	0
P	0.8863 (2)	0.3716 (2)	0.3222 (1)	66 (2)	74 (2)	16 (0)	−12 (2)	2 (1)	−2 (1)
Cl	0.8977 (2)	0.3462 (2)	0.1742 (1)	151 (3)	145 (3)	17 (0)	−26 (2)	17 (1)	2 (1)
C_1	0.8162 (7)	0.4163 (7)	0.3973 (3)	79 (8)	79 (8)	17 (2)	−21 (7)	0 (3)	−5 (3)
C_2	0.702 (1)	0.511 (1)	0.4011 (4)	122 (12)	164 (14)	25 (2)	6 (10)	3 (4)	−10 (5)
C_3	0.650 (1)	0.556 (1)	0.4583 (6)	159 (15)	186 (16)	35 (3)	27 (12)	22 (6)	−21 (6)
C_4	0.712 (1)	0.513 (1)	0.5114 (5)	185 (18)	287 (23)	20 (2)	−67 (17)	19 (6)	−38 (6)
C_5	0.823 (1)	0.417 (1)	0.5103 (4)	212 (18)	239 (20)	15 (2)	−87 (16)	−13 (5)	11 (5)
C_6	0.8759 (9)	0.3678 (9)	0.4527 (4)	113 (11)	165 (13)	18 (2)	−43 (10)	−11 (4)	6 (4)
C_7	0.933 (1)	0.5498 (9)	0.2942 (4)	187 (15)	107 (11)	22 (2)	−75 (10)	4 (5)	7 (4)
C_8	0.4411 (8)	0.2143 (9)	0.3340 (4)	74 (9)	170 (14)	37 (3)	35 (9)	17 (4)	16 (5)
H_2	0.655	0.544	0.360	5.0					
H_3	0.570	0.631	0.463	5.0					
H_4	0.668	0.550	0.552	5.0					
H_5	0.872	0.382	0.550	5.0					
H_6	0.964	0.301	0.453	5.0					

[a] Estimated standard deviations are given in parentheses right adjusted to the least significant figure of the preceding number. [b] β's are × 10^4 and have the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

distinctly yellow crystals, indicated that this compound was probably not trans but no configuration could be assigned from the spectra. Therefore we undertook a crystal structure investigation to determine if the complex is square planar and, if so, which isomer is present. The resultant cis square-planar structure provides an opportunity to study the effects of trans-moiety interchange on Pd–ligand bonds and to make some limited comparisons to similar effects in platinum compounds.

Experimental Section

A sample of this compound was kindly supplied by R. Keiter and the yellow crystals were used without further purification. Inspection of the crystals showed them to be square plates with sharply defined faces. The a and b axes were approximately coincident with the face diagonals of the plates. Weissenberg and precession photographs indicated a tetragonal space group with $4/m$ Laue symmetry. Systematic extinctions were of the types $00l$, $l = 2n + 1$, and $hk0$, $h + k = 2n + 1$. These conditions indicate the space group to be $P4_2/n$. In addition, systematically weak reflections of the types $h + k = 2n + 1$ and $l = 2n + 1$ for general hkl reflections were observed.

The unit cell dimensions were determined by a least-squares fit of 13 independent reflections whose 2θ values were determined from Weissenberg photographs using Mo Kα_1 radiation (λ 0.70783 Å) at 25°. The Weissenberg films were calibrated with Al powder lines (a_0 = 4.03310 Å). The values obtained were $a = b = 9.324 \pm 0.004$ Å and $c = 21.485 \pm 0.004$ Å. The measured density was 1.61 ± 0.02 g/cm³ obtained by flotation techniques in a solution of diiodomethane and 1-bromopropane. The calculated density with four molecules per unit cell (V_c = 1868 ± 2 Å³) is 1.62 ± 0.01 g/cm³.

A crystal of approximate dimensions 0.02 × 0.02 × 0.01 cm was selected for use in data collection. The crystal was mounted such that the (110) axis would be coincident with the ϕ axis of the diffractometer. Data were collected at room temperature using a Hilger-Watts four-circle diffractometer equipped with a scintillation counter employing Zr-filtered Mo Kα (λ 0.7107 Å) radiation. All independent data within a 2θ sphere of 60° ($\sin\theta)/\lambda = 0.70$) were measured using a θ–2θ coupled step scan with a 5° takeoff angle. Stationary-counter measurements of the background for half the scan time were made at the beginning and the end of each scan. The scan range was over 50 steps of 0.02° in 2θ, 1 step/0.4096 sec, and was increased by 1 step/deg of increase in 2θ to ensure complete integration over the entire peak. The scan range was observed to be adequate by inspection of the background measurements. No appreciable decrease in the intensities of three standard reflections, which were measured periodically throughout the data taking period, was observed.

The measured intensities were corrected for background, Lorentz, and polarization effects and for absorption[5] (μ = 14.2 cm^{-1}); minimum and maximum transmission factors were 0.67 and 0.87, respectively. The standard deviations were assigned to the intensities according to the formula

$$\sigma(I) = (C_t + C_b + (0.05C_t)^2 + (0.10C_b)^2 + (0.05C_n)^2)^{1/2}/A$$

where C_t, C_b, C_n, and A are the total counts, background counts, net counts, and the value of the absorption coefficient, respectively. The quadratic terms correspond to the estimated systematic errors in intensity and background and absorption corrections of 5, 10, and 5%, respectively. The standard deviations in the structural amplitudes were obtained by the method of finite differences[6]

$$\sigma(F_o) = ((I + \sigma(I))^{1/2} - I^{1/2})/(Lp)^{1/2}$$

where Lp is the Lorentz–polarization factor. Of the 2877 measured reflections, 1155 were found to have values of F_o less than $3\sigma(F_o)$. These reflections were considered to be unobserved and were not included in the refinement.

Solution and Refinement of the Structure

Since the space group $P4_2/n$ has eightfold general positions, the molecule is required to have, at least, C_2 or C_s symmetry and it was necessary to place the palladium atoms in special positions. From a consideration of the systematically weak reflections of the type $l = 2n + 1$ for general hkl reflections, the palladium atoms were placed in the fourfold special position denoted by the Wyckoff symbol "e;" that is, on the twofold axis perpendicular to the ab plane. The origin was placed at the center of symmetry. Analysis of the Patterson map confirmed this supposition and allowed ready determination of the z coordinates of the palladium atoms. Three possible sets of chlorine and phosphorus atom positions were present due to pseudomirroring. The correct set was determined by trial and error. These atoms gave a value of the discrepancy factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.28 for a structure factor calculation with the heavy atoms alone. The carbon atoms were located from a three-dimensional electron density map. The structure was refined isotropically to an R of 0.154 using a modified version of ORFLS[7,8] and unit weights. At this point weights were

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(5) F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Saunderson, "NRC Crystallographic Programs for the IBM 360 System," National Research Council of Canada, Ottawa, Canada, 1966.

(6) D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 1660 (1964).

(7) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(8) Scattering factor tables used were those of H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964), and those in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1965.

changed to those based on individual statistics of the reflection ($w = 1/\sigma^2(F_o)$). The ring hydrogen atoms were added in calculated positions assuming 1.0 Å for the C–H distance. No attempt was made to refine hydrogen positions. The structure refined anisotropically to a final R of 0.088 and a final weighted discrepancy index, $R_w = (\Sigma w(F_o - F_c)^2)^{1/2}/(\Sigma wF_o^2)^{1/2}$, of 0.058. Convergence was assumed when no parameter shift was greater than 0.1 of that parameter's estimated standard deviation. A final difference electron density map showed no residual electron density above 1.4 e$^-$/Å^3.

In Table I are the final values of the positional and thermal parameters and their respective estimated standard deviations[9] which were derived from the inverse matrix. In Table II are given the root mean square amplitudes of vibration while we have deposited[10] the values of the observed and calculated structure factors on an absolute scale. The configuration of the molecule along with the numbering scheme used is shown in Figure 1.[11] Selected intramolecular distances and angles are given in Table III (see also Figure 2).

TABLE II

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å × 10^3)

Atom	Min	Inter-med	Max	Atom	Min	Inter-med	Max
Pd	169	174	187	C_4	176	259	397
P	158	185	199	C_5	179	246	376
Cl	175	245	284	C_6	180	215	294
C_1	157	196	215	C_7	158	234	320
C_2	224	240	279	C_8	160	251	325
C_3	202	296	324				

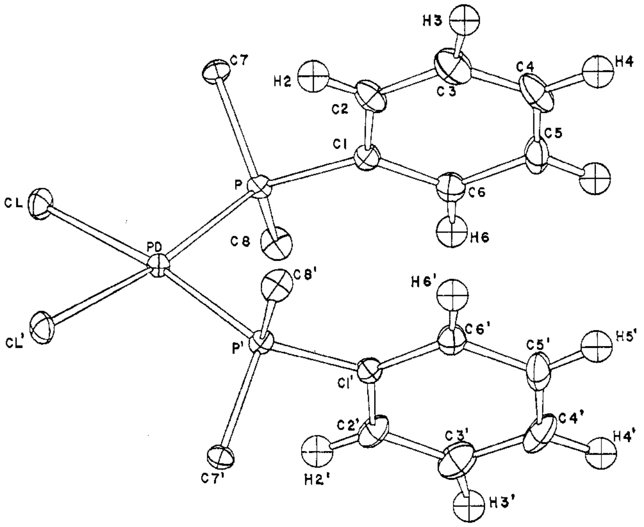

Figure 1.—The perspective drawing of *cis*-dichlorobis(dimethylphenylphosphine)palladium(II). Anisotropic thermal vibration is indicated by 50% probability ellipsoids.

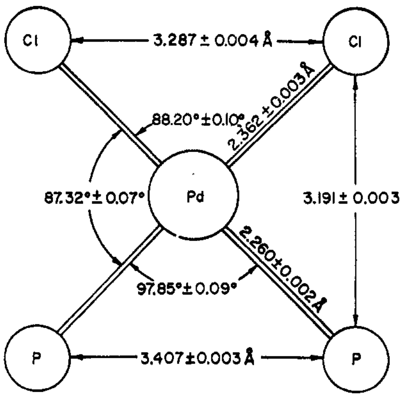

Figure 2.—The arrangement of palladium and its four neighbors along with cogent distances and angles.

TABLE III

SELECTED DISTANCES (Å) AND ANGLES (DEG) WITH STANDARD DEVIATIONS IN PARENTHESES

Atoms	Distance	Atoms	Angle	Atoms	Angle
P–Cl	3.191 (3)	Cl–Pd–Cl′	88.2 (1)	P–C_1–C_2	118.8 (6)
P–P′	3.407 (3)	Cl–Pd–P	87.32 (7)	P–C_1–C_6	123.4 (5)
Cl–Cl′	3.287 (4)	P–Pd–P′	97.85 (9)	P–C_1–C_4	174.6 (5)
P–C_1	1.791 (7)	Pd–P–C_1	120.2 (2)	C_6–C_1–C_2	117.7 (7)
P–C_7	1.819 (7)	Pd–P–C_7	112.0 (3)	C_1–C_2–C_3	121.0 (8)
P–C_8	1.815 (8)	Pd–P–C_8	111.7 (3)	C_2–C_3–C_4	120.6 (9)
C_1–C_2	1.38 (1)	C_1–P–C_7	100.0 (3)	C_3–C_4–C_5	120.6 (9)
C_2–C_3	1.39 (1)	C_1–P–C_8	107.4 (4)	C_4–C_5–C_6	119.4 (8)
C_3–C_4	1.34 (2)	C_7–P–C_8	103.8 (6)	C_5–C_6–C_1	120.6 (8)
C_4–C_5	1.37 (2)				
C_5–C_6	1.41 (2)				
C_6–C_1	1.39 (1)				

Description of the Structure

The complex has a crystallographic twofold axis (C_2) and is described as approximately cis square planar. However there are slight but significant distortions since ∠Cl–Pd–Cl′ (prime denotes atom at $\bar{x}$, $\bar{y}$, z) has closed 2° and ∠P–Pd–P′ has opened some 8° from their theoretical value of 90°. The chlorine atoms are +0.13 and −0.13 Å from the least-squares plane defined by the palladium and its four nearest neighbors while the phosphorus atoms are ±0.12 Å from the plane. This is best viewed as a tetragonal distortion of 4.3°. The dihedral angle between the planes defined two phosphorus atoms and the palladium and the two chlorine atoms and the palladium is 171.3 ± 0.1°. The equations of the two planes in the form $ax + by + cz - d = 0$ use the values ($a = -0.66$, $b = 0.746$, $c = 0.00$, $d = -2.92$) and ($a = -0.546$, $b = 0.838$, $c = 0.00$, $d = -1.86$), respectively.

The six carbon atoms in the phenyl ring show no significant deviations from the least-squares plane with the values $a = 0.642$, $b = 0.766$, $c = -0.025$, and $d = 7.64$. The largest deviation from the plane is 0.02 Å by C_4 which is not statistically significant. The angles within the ring are all within three esd's of the normal value of 120°. The ring bond distances also agree well with the expected value[12] of 1.396 Å with the exception of the C_3–C_4 distance which is slightly short.

Discussion

The apparent deviations in this complex from the ideal square-planar configuration can be primarily attributed to overcrowding caused by the bulky phosphorus ligands cis to each other. The phenyl rings of

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[9] W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[10] A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N. W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microche.

[11] C. K. Johnson, "ORTEP: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[12] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 260.

TABLE IV

SELECTED METAL–PHOSPHORUS AND METAL–CHLORINE BOND LENGTHS

Pd trans				Pt trans			
Bond	Distance, Å	Compd	Ref	Bond	Distance, Å	Compd	Ref
Pd–P	2.333 ± 0.007	$PdI_2(P(CH_3)_2C_6H_5)_2$	*a*	Pt–P	2.315 ± 0.004	$Pt(P(C_2H_5)_3)_2Br_2$	*d*
Pd–Cl	2.287 ± 0.002	$PdCl_2(DMSO)_2$	*b*	Pt–Cl	2.294 ± 0.009	$Pt(P(C_2H_5)_3)_2Cl_2$	*d*
Pd cis				Pt cis			
Bond	Distance, Å	Compd	Ref	Bond	Distance, Å	Compd	Ref
Pd–P	2.260 ± 0.002	$PdCl_2(P(CH_3)_2C_6H_5)_2$	*c*	Pt–P	2.247 ± 0.008	$PtCl_2(P(CH_2)_3)_2$	*e*
Pd–Cl	2.362 ± 0.003	$PdCl_2(P(CH_3)_2C_6H_5)_2$	*c*	Pt–Cl	2.376 ± 0.009	$PtCl_2(P(CH_2)_3)_2$	*e*
Δ Trans to Cis Pd				Δ Trans to Cis Pt			
Bond	Δ, Å	Bond	Δ, Å	Bond	Δ, Å	Bond	Δ, Å
Pd–P	−0.073	Pd–Cl	+0.075	Pt–P	−0.068	Pt–Cl	+0.082

[a] Reference 2b. [b] Reference 14. [c] This paper. [d] G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966). [e] Reference 16.

the different phosphorus ligands on the same palladium interact sterically with one another. This accounts for the fact that the P–Pd–P′ angle is 98° and the Pd–P–C_1 angle is found to be 120° since in this way steric interactions can be reduced. However, the two rings still approach each other within 3.2 Å (C_6–C_6'), somewhat less than the sum of the van der Waals radii.[12] This interaction could also easily explain the slight screwing of the phenyl rings as indicated by the P–C_1–C_4 angle of 174.6°. In order to accommodate the bulky phosphorus ligands, the chlorine atoms are forced closer together as indicated by the Cl–Pd–Cl′ angle of 88.2°. The Cl–Cl′ distance of 3.287 Å is still greater than the distance of 2.88 Å which is the sum of the van der Waals radii of two chlorine atoms bonded to a common atom.[13] The slight tetragonal distortion may also be attributed to this overcrowding.

The agreement between the three nonequivalent P–C distances is good. The two phosphorus–methyl distances (1.810 ± 0.007, 1.815 ± 0.008 Å) are similar while the phosphorus–ring distance (1.791 ± 0.008 Å) is just slightly shorter as would be expected from the slightly smaller covalent radii for the ring carbon. The C–C distances are within 3σ of their normal values and the Pd–Pd distance of 6.6 Å is so great that any interaction is precluded despite an apparent alignment of the atoms.

The Pd–P bond in this compound (2.260 ± 0.002 Å) is significantly shorter than that of 2.333 ± 0.007 Å found by Bailey and Mason in the trans iodo complex, while the Cl–Pd bond (2.362 ± 0.003 Å) is significantly longer than that of 2.290 ± 0.002 Å found by Bennett, Cotton, and Weaver[14] in $PdCl_2(DMSO)_2$. The predicted values from the sums of the covalent radii are 2.38 and 2.28 Å for the Pd–P and Pd–Cl distances, respectively. Our results generally agree with those expected from a strong "trans effect."[15] That is, the bond trans to a strongly "trans-directing" ligand such as phosphorus is weaker and therefore longer than a bond trans to the somewhat less "trans-directing" chlorine. As has already been noted by Messmer, Amma, and Ibers,[16] these distances may be sensitive to the substituents on the phosphorus as well as variations in the halide used. However, it would be expected that as long as the ligands are similar with respect to their "trans-directing" ability, the effect on either the M–Cl or M–P distance would be similar whether M is Pd or Pt. In Table IV are listed a number of M–Cl and M–P bond lengths involving ligands of similar "trans-directing" ability.[15] As would be expected from the different covalent radii and electronegativities of palladium and platinum, the M–Cl and M–P distances are somewhat different. However, the changes in the bond distances are identical within 1 esd in going from the trans to the cis configuration.

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(13) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(14) M. J. Bennett, F. A. Cotton, and D. L. Weaver, *Acta Crystallogr.*, **23**, 788 (1967).

(15) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955).

(16) G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967).