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Gas phase and crystal molecular structures of *cis*-$PdCl_2[P(CH_3)_3]_2$

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Abstract

The molecular structure of *cis*-dichloro-bis(trimethylphosphine)platinum has been determined by electron diffraction in the gas phase and by single crystal X-ray diffraction. The crystals of *cis*-$PdCl_2[P(CH_3)_3]_2$ are monoclinic, space group $P2_1$ with $a=6.350(4)$, $b=11.837(9)$, $c=8.813(7)$ Å, $\beta=109.85(6)°$ and $V=623.0(8)$ Å^3. In the crystal the bond configuration around the Pd atom is a distorted planar square, and the bond configurations around the P and C atoms depart from C_{3v} symmetry. One of the Pd–P bonds is nearly *syn* to one of the P–C bonds, and the other Pd–P bond is nearly *anti* to one of the P–C bonds, giving a nearly planar C–P–Pd–P–C chain. The following bond lengths (Å) and bond angles (°) were obtained: *r*(Pd–Cl) 2.359(3), 2.378(3); *r*(Pd–P) 2.256(2), 2.259(2); *r*(P–C) between 1.802 and 1.823 with maximal e.s.d. 0.008; <Cl–Pd–Cl 89.4(1); <P–Pd–P 94.7(1); <Pd–P–C between 110.0 and 123.2 with maximal e.s.d. 0.3. In the gas phase study the Pd bond configuration was constrained to C_2 symmetry and C_{3v} symmetry was assumed for the P and C configurations. The bond lengths of the same type were assumed to be equal, the bond configurations around the two P atoms as well as the bond configurations around the six C atoms were assumed to be identical. The gas-phase conformation is similar to that in the crystal. The following bond lengths (r_g, Å) and bond angle (°) are well determined: P–C 1.822±0.004, C–H 1.126±0.005, and Pd–P–C 116.4±0.7. The other parameters are determined with low precision mainly due to their sensitivity to the conditions of refinement, Pd–Cl 2.357±0.029, Pd–P 2.264±0.013, Cl–Pd–Cl 88.9±4.0, P–Pd–P 90.1±4.6, P–C–H 103.5±2.8, P–Pd–Cl_{cis} 91.3±4.0.

Introduction

Some years ago Messmer *et al.* [1] reported an X-ray crystallographic study on the molecular structure of *cis*-dichloro-bis(trimethylphosphine)platinum. Another study on this molecule was carried out by Del Pra and Zanotti [2]. Substantial deviations from the square-planar geometry around the Pt atom were revealed, in particular, a large P–Pt–P angle was found ascribed to steric interactions between the phosphine groups. The purpose of the present study was to determine the structure of the palladium analogue both in the solid and gas phases.

Experimental

General details

Trimethylphosphine and $PdCl_2$ were purchased from Strem Chemical Co. and used without further purification. The complex *cis*-$PdCl_2(PMe_3)_2$ was prepared by reaction of a benzene solution of $PdCl_2(NCPh)_2$ with equivalents of PMe_3 [3].

Electron diffraction study

The electron diffraction photographs were taken with a modified EG-100A apparatus [4] using a stainless steel nozzle system modified from a previous design [5]. The vapor flow was introduced into the nozzle through valve embedded in a graphite seal. The nozzle temperature was about 202 °C. Nozzle-to-plate distances

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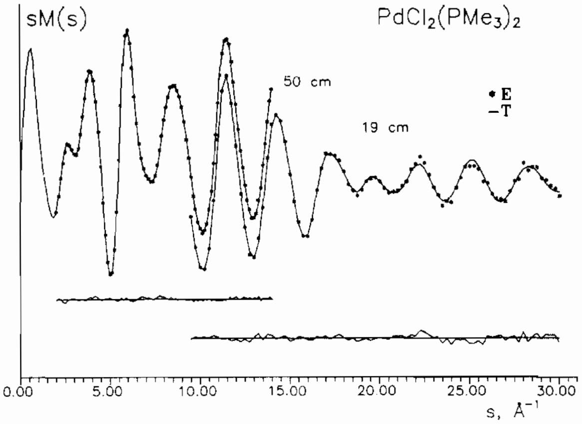

Fig. 1. Molecular intensity curves for the two camera distances (E, experimental; T, theoretical). Also shown are the difference curves (experimental - theoretical).

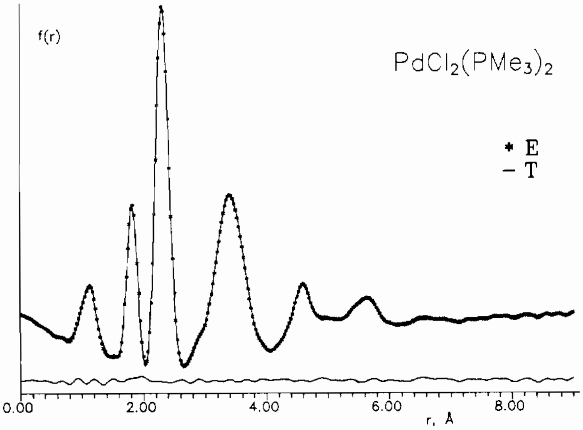

Fig. 2. Radial distribution curves (E, experimental; T, theoretical). The functions were calculated with an artificial damping factor equal to $\exp(-0.002^2s^2)$; theoretical values were used in the $0.00 \leqslant s \leqslant 2.00$ $Å^{-1}$. The difference curve is also shown (experimental - theoretical).

of about 50 and 19 cm were used. The nominal accelerating voltage of the electron beam was 60 kV. The electron wavelength (λ) was calibrated with a TlCl powder pattern [6]. Eight and seven plates were used for analysis from the 50 and 19 cm camera distances, respectively. The ranges of intensity data used were $2.0 \leqslant s \leqslant 14.0$ $Å^{-1}$ and $9.5 \leqslant s \leqslant 30.0$ $Å^{-1}$ with data intervals of 0.125 and 0.25 $Å^{-1}$, respectively ($s = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle). See also 'Supplementary material'. Experimental and calculated molecular intensities and radial distributions are presented in Figs. 1 and 2, respectively. Figure 3 shows the numbering of the non-hydrogen atoms.

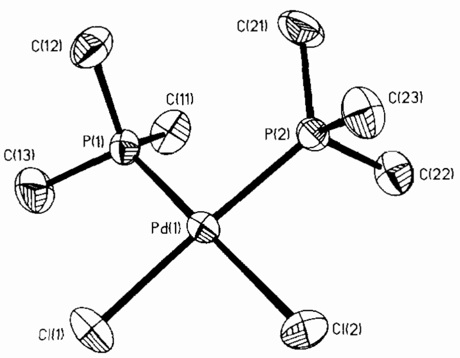

Fig. 3. ORTEP projection of *cis*-$PdCl_2[P(CH_3)_3]_2$. Thermal ellipsoids are at 50% probability. Hydrogen atoms have been omitted for clarity.

TABLE 1. Crystal, data collection and refinement parameters for *cis*-$PdCl_2[P(CH_3)_3]_2$

Formula weight	329.4
Color, habit	yellow, wedge
Crystal size (mm)	0.3×0.4×0.7
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	6.350(4)
b (Å)	11.837(9)
c (Å)	8.813(7)
β (°)	109.85(6)
V ($Å^3$)	623.0(8)
Z	2
Density (calc.)	1.756 (g/cm^3)
Radiation	monochromated by highly oriented graphite crystal Mo Kα ($\lambda = 0.71073$ Å)
Temperature (K)	273
Scan type	2θ–θ
Scan range (°)	4–60
Diffractometer	Nicolet P3
T(max.)/T(min.)	0.987/0.778
Reflections collected	2113
Independent reflections	1904
Observed reflections	1788 ($F > 6.0\sigma(F)$)
Standard reflections	three standards for every 97 reflections
Observed reflections/ least-squares parameters	17.7
Goodness-of-fit	1.47
R_F (%)	2.88
R_{wF} (%)	3.80
Weighting scheme	$w = (\sigma^2(F) + 0.0004F^2)^{-1}$

X-ray crystallographic study

Crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution of *cis*-$PdCl_2(PMe_3)_2$. The crystal was mounted on a glass fiber with epoxy and centered on a Nicolet P3 automated diffractometer. The unit-cell parameters were obtained by least-squares refinement of the setting angles of 20 reflections. Crystal and instrument stability was monitored with a set of three standard reflections measured every 97 reflections. No significant variations of the intensities were observed. Details of other crystal data and relevant information are summarized in Table 1.

Structure analysis

Electron diffraction data

The analysis of electron diffraction data was carried out by applying the least-squares method to molecular intensities using a modified version of the program of Seip and co-workers [7]. The atomic inelastic and elastic scattering factors and phase shifts were taken from refs. 8 and 9.

Unfortunately, due to the limitations of the electron diffraction method, a complete determination of geometrical parameters of this relatively complicated system was not possible. It was assumed that the bond configuration around the Pd atom has C_2 symmetry, and the phosphine and methyl bond configurations were all assumed to have C_{3v} symmetry. Only one mean parameter was refined for each bond length type and bond angle type.

The following parameters were used to characterize the geometry of the molecule: bond lengths C–H, P–C, Pd–P; the difference between the Pd–P and Pd–Cl bond lengths; bond angles Cl–Pd–Cl, P–Pd–P, Pd–P–C, P–C–H; dihedral angles Ω1 = C(21)–P(2)–Pd–P(1), Ω2 = C(13)–P(1)–Pd–P(2); the angle between the PPdP and ClPdCl planes (Φ); and six angles of torsion describing the rotation of the methyl groups.

The radial distribution displays six distinct maxima (Fig. 2). The calculated radial distribution contains the contributions of more than 200 different internuclear distances even if the rotation-dependent H...H distances are ignored. The first three peaks correspond mainly to bond distances. The first one is due to C–H, the second to P–C, and the third to Pd–P and Pd–Cl. The remaining peaks are more complicated. In addition to the above-mentioned geometrical parameters, seven independent amplitudes were also refined. One of these, *l*(C–H), was refined individually, while the remaining ones were coupled in groups with fixed differences. The amplitudes giving contributions to the same peak were coupled.

At the early stages of the analysis it was seen that: (i) the bond configuration around the Pd atom is nearly planar and the two chlorine atoms are *cis* oriented, and (ii) the C(13)–P(1)–Pd–P(2)–C(21) chain is nearly planar with *syn* orientation for C(21)–P(2)–Pd–P(1) and *anti* orientation for C(13)–P(1)–Pd–P(2). Methyl rotation has only a limited influence on the calculated distributions. It was assumed that one of the hydrogen atoms attached to each of C(13), C(22) and C(23) assumes an *anti* position with respect to the corresponding P–Pd bond. The hydrogens attached to the methyl carbons, C(11), C(12) and C(21) were assumed to take an orientation maximizing the shortest rotation-dependent H...H distance. The difference between the amplitudes, *l*(Pd–Cl) − *l*(Pd–P), appeared to influence various parameters considerably. Since this difference is not known, it was fixed at various values in a wide range. A shallow minimum was obtained at about 0.02 Å. The changes in the other parameters in the interval of 0.00–0.04 Å for this difference, were taken into account in estimating the total errors.

The results of the least-squares refinements for model A are presented in Table 2. In this model the torsional angles Ω1 and Ω2 were fixed at 0 and 180°, respectively. In model B, Ω1 and Ω2 were varied, and the *R* factor decreased considerably but an unacceptable small value was obtained for rotation-dependent H...H distances. Introduction of methyl rotation could not remedy this situation, while increasing the Pd–P–C angle in the *syn* arrangement worsened the agreement. Further analysis was based on model A, while the results for model B were taken into account in the error estimation (*vide infra*). The reported least-squares standard deviations are strongly underestimated due to the restrictions of

TABLE 2. Selected molecular parameters of *cis*-$Cl_2[P(CH_3)_3]_2$ as obtained from electron diffraction least-squares refinement[a]

Bond lengths (r_a, Å) and mean amplitudes of vibration (l, Å)

Atom pair	r_a	$\sigma_{tot}(r)$	l	$\sigma_{tot}(l)$
C–H	1.121(3)	0.005	0.079(3)	0.005
P–C	1.8207(9)	0.004	0.047(1)	0.002
Pd–P	2.263(4)	0.013	0.047(4)	0.012
Pd–Cl[b]	2.354(4)	0.029	0.067[c]	
r[d]	2.308(1)	0.008		
Δ[e]	−0.091(6)	0.024		

Angles (°)

Angle	Value	σ_{tot}
Cl–Pd–Cl	88.9(26)	4.0
P–Pd–P	90.1(5)	4.6
Pd–P–C	116.4(2)	0.7
P–C–H	103.5(8)	2.8
Ω1[f]	0.0 (fixed)	
Ω2[g]	180.0 (fixed)	
Φ[h]	13.9(13)	2.0
P(1)–Pd–Cl(1)[b]	91.3(13)	4.0
C–P–C[b]	101.7(2)	0.8
R factor (%)	4.98	

[a] Least-squares standard deviations are given in parentheses as units in the last digit; σ_{tot} are estimated total errors as error limits. [b] Dependent parameter. [c] Coupled with *l*(Pd–P). [d] The mean value of Pd–Cl and Pd–P bond lengths. [e] Δ = *r*(Pd–P) − *r*(Pd–Cl). [f] Dihedral angle C(21)–P(2)–Pd–P(1). [g] Dihedral angle C(13)–P(1)–Pd–P(2). [h] Dihedral angle between planes PPdP and ClPdCl.

the applied model. Nevertheless, some of the parameters, including the mean C–H and mean P–C bond distances and the Pd–P–C bond angle are well determined. The refined values of Ω1 and Ω2 dihedral angles in model B were close to 0 and 180°, namely −3.7(30) and 166.0(19)°, respectively. The positive sign corresponds to anticlockwise torsion. The changes in the other parameters were taken into account in estimating the total errors. This was yet another term in the error estimation in addition to the above already mentioned term arising from the uncertainty of the difference l(Pd–Cl) − l(Pd–P). The two standard terms of error estimation, viz. the systematic experimental error and the least-squares standard deviations, were also included [10]. The following bond lengths (r_g, Å) and bond angles (°) with estimated total errors were obtained: C–H 1.126 ± 0.005, P–C 1.822 ± 0.004, Pd–P 2.264 ± 0.013, Pd–Cl 2.357 ± 0.029, Pd–P–C 116.4 ± 0.7, Cl–Pd–Cl 88.9 ± 4.0, P–Pd–P 90.1 ± 4.6, P–Pd–Cl_{cis} 91.3 ± 4.0, P–C–H 103.5 ± 2.8.

The molecular geometry determined from X-ray crystallography contained asymmetries, all of which could not be introduced in the electron diffraction model because it would increase the number of variables beyond reasonable limit for an electron diffraction study. Instead, a test was carried out in which the bond angles and the angles of torsion were assumed from the crystallographic geometry. The bond lengths were allowed to vary in this test. The electron and X-ray diffraction bond lengths have different physical meaning and by allowing the bond lengths to vary we tried to diminish any systematic error due to such a difference in this test. The amplitudes of vibration were also refined applying the coupling scheme as before. The agreement was by a factor of two worse than before, accordingly, this model was discarded.

X-ray data

The structure of *cis*-$\mathrm{PdCl_2[P(CH_3)_3]_2}$ was solved by direct methods using SHELX PLUS computer programs (Nicolet Instrument Corp.) and refined by full-matrix least-squares procedures. The function minimized was $\Sigma w(F_o - F_c)^2$. Weights were given according to the function $w = (\sigma^2(F) + 0.0004F^2)^{-1}$. All non-hydrogen atoms were refined with anisotropic temperature coefficients. The hydrogen atoms were introduced in fixed calculated positions and their coordinates were allowed to vary in the final cycles of full-matrix least-squares refinement. The final R and R_w were 2.88% and 3.80%, respectively. The number of observations per refined parameter was 17.7. The final atomic coordinates and equivalent isotropic displacement coefficients for non-hydrogen atoms are given in Table 3. Bond lengths and bond angles are given in Table 4.

TABLE 3. Atomic coordinates and equivalent isotropic displacement coefficients for *cis*-$\mathrm{PdCl_2[P(CH_3)_3]_2}$

	x	y	z	U_{eq}
Pd(1)	0.2048(1)	0	0.8149(1)	0.027(1)
Cl(1)	0.1892(3)	−0.0344(1)	1.0745(2)	0.049(1)
Cl(2)	−0.0550(3)	−0.1494(2)	0.7118(2)	0.052(1)
P(1)	0.4148(2)	0.1561(1)	0.9022(1)	0.032(1)
P(2)	0.2263(2)	0.0062(2)	0.5643(1)	0.030(1)
C(11)	0.288(1)	0.2815(5)	0.7879(8)	0.052(2)
C(12)	0.7033(9)	0.1500(7)	0.9084(8)	0.052(2)
C(13)	0.445(1)	0.2006(8)	1.1040(7)	0.065(3)
C(21)	0.422(1)	0.0968(7)	0.5100(8)	0.057(3)
C(22)	−0.0397(9)	0.0417(5)	0.4133(6)	0.045(2)
C(23)	0.304(1)	−0.1308(5)	0.5102(7)	0.044(2)

TABLE 4. Bond lengths (Å) and bond angles (°) of *cis*-$\mathrm{PdCl_2[P(CH_3)_3]_2}$ as obtained from X-ray study[a]

Bond lengths			
Pd–Cl(1)	2.359(3)	Pd–Cl(2)	2.378(3)
Pd–P(1)	2.256(2)	Pd–P(2)	2.259(2)
P(1)–C(11)	1.821(7)	P(2)–C(21)	1.823(8)
P(1)–C(12)	1.815(6)	P(2)–C(22)	1.810(5)
P(1)–C(13)	1.802(7)	P(2)–C(23)	1.806(7)
Bond angles			
Cl(1)–Pd–Cl(2)	89.4(1)	Cl(1)–Pd–P(1)	91.4(1)
Cl(2)–Pd–P(1)	173.0(1)	Cl(1)–Pd–P(2)	171.9(1)
Cl(2)–Pd–P(2)	85.1(1)	P(1)–Pd–P(2)	94.7(1)
Pd–P(1)–C(11)	112.3(2)	Pd–P(1)–C(12)	116.8(3)
C(11)–P(1)–C(12)	107.5(3)	Pd–P(1)–C(13)	115.4(3)
C(11)–P(1)–C(13)	100.8(4)	C(12)–P(1)–C(13)	102.3(3)
Pd–P(2)–C(21)	123.2(2)	Pd–P(2)–C(22)	112.0(2)
C(21)–P(2)–C(22)	102.6(3)	Pd–P(2)–C(23)	110.0(2)
C(21)–P(2)–C(23)	100.8(3)	C(22)–P(2)–C(23)	106.6(3)

[a] Standard deviations in parentheses as units in the last digit.

Discussion

The most remarkable structural feature of *cis*-$\mathrm{PdCl_2[P(CH_3)_3]_2}$ is the planarity of the C(21)–P(2)–Pd–P(1)–C(13) chain with *syn* orientation for C(21)–P(2)–Pd–P(1) and *anti* orientation for C(13)–P(1)–Pd–P(2), both in the gas phase and in the crystal. The bond configuration around the Pd atom departs from local C_2 symmetry, and around the P and C atoms from local C_{3v} symmetry in the crystal. The deviation from C_2 symmetry is indicated by a 6° difference between the bond angles Cl(1)–Pd–P(1) and Cl(2)–Pd–P(2). The deviation from C_{3v} symmetry around the two P atoms is characterized by the different Pd–P–C bond angles: for P(1) 112.3(2)°, 116.8(3)°, 115.4(3)°; for P(2) 123.2(2)°, 112.0(2)°, 110.0(2)°. The lack of local C_2 and C_{3v} symmetries may be interpreted as a consequence of strong steric interactions between the C(21)$\mathrm{H_3}$ methyl group of one phosphorus atom and

TABLE 5. Geometrical parameters of *cis*-$PdCl_2[P(CH_3)_3]_2$ from electron diffraction and the corresponding mean parameters from X-ray crystallography (distances in Å, angles in degrees). The electron diffraction data are given with estimated total errors, the X-ray data are given with maximal standard deviations

Parameter	ED study	XD study
Pd–P	2.263 ± 0.013	2.257(3)
Pd–Cl	2.354 ± 0.029	2.368(2)
r^a	2.308 ± 0.008	2.317(3)
P–C	1.821 ± 0.004	1.812(8)
C–H	1.121 ± 0.005	
Cl(1)–Pd–Cl(2)	88.9 ± 4.0	89.4(1)
P(1)–Pd–P(2)	90.1 ± 4.6	94.7(1)
P(1)–Pd–Cl(1)	91.3 ± 4.0	88.3(1)[b]
Pd–P–C	116.4 ± 0.7	114.9
C–P–C	101.7 ± 0.8	103.6(4)

[a]The mean value of Pd–Cl and Pd–P bond lengths. [b]The mean value of P(1)–Pd–Cl(1) and P(2)–Pd–Cl(2) angles.

TABLE 6. The geometrical parameters of *cis*-$PdCl_2[P(CH_3)_3]_2$ and *cis*-$PtCl_2[P(CH_3)_3]_2$ from X-ray crystallography. Bond lengths in Å, angles in degrees with standard deviations in parentheses

Parameter	Pt	Pd
Bond lengths		
X–Cl(1)	2.368(3)	2.359(3)
X–Cl(2)	2.377(3)	2.378(3)
X–P(1)	2.233(3)	2.256(2)
X–P(2)	2.243(3)	2.259(2)
P(1)–C(11)	1.81(1)	1.821(7)
P(1)–C(12)	1.81(1)	1.815(6)
P(1)–C(13)	1.82(1)	1.802(7)
P(2)–C(21)	1.79(1)	1.823(8)
P(2)–C(22)	1.82(2)	1.810(5)
P(2)–C(23)	1.81(1)	1.806(7)
Bond angles		
P(1)–X–P(2)	96.2(1)	94.7(1)
Cl(1)–X–Cl(2)	87.9(1)	89.4(1)
P(1)–X–Cl(1)	91.1(1)	91.4(1)
P(1)–X–Cl(2)	174.2(1)	173.0(1)
P(2)–X–Cl(1)	171.6(1)	171.9(1)
P(2)–X–Cl(2)	85.3(1)	85.1(1)
X–P(1)–C(11)	112.8(4)	112.3(2)
X–P(1)–C(12)	116.6(4)	116.8(3)
X–P(1)–C(13)	115.8(4)	115.4(3)
X–P(2)–C(21)	122.6(4)	123.2(2)
X–P(2)–C(22)	112.7(4)	112.0(2)
X–P(2)–C(23)	111.3(4)	110.0(2)
C(11)–P(1)–C(12)	106.7(5)	107.5(3)
C(11)–P(1)–C(13)	101.4(7)	100.8(4)
C(12)–P(1)–C(13)	101.9(5)	102.3(3)
C(21)–P(2)–C(22)	102.3(5)	102.6(3)
C(22)–P(2)–C(23)	104.8(5)	106.6(3)
C(21)–P(2)–C(23)	101.1(6)	100.8(3)

the $C(12)H_3$ and $C(11)H_3$ methyl groups of the other phosphorus atom. The C(21) methyl is practically enveloped by the other two methyl groups, like a cogwheel.

Due to the steric restrictions of the molecular model used for the analysis of electron diffraction data a direct comparison of electron and X-ray diffraction results is not possible. The refined electron diffraction parameters are mean values which fit the experimental data. They can be compared at best with the mean values of the corresponding X-ray parameters. The electron diffraction geometrical parameters and the corresponding mean X-ray parameters are given in Table 5. Here the mean value of the Pd–P and Pd–Cl bond lengths is also given as it is believed to be better determined than the individual lengths in the electron diffraction work. The largest discrepancy between the electron diffraction geometry and the mean X-ray diffraction geometry is observed for the P–Pd–P and P–Pd–Cl_{cis} angles. This discrepancy may or may not be a consequence of the assumed C_2 symmetry of the Pd bond configuration in the electron diffraction analysis. The other geometrical parameters obtained from electron diffraction and X-ray diffraction are in satisfactory agreement.

The geometrical parameters obtained for *cis*-$PdCl_2[P(CH_3)_3]_2$ by X-ray study can be compared with the results of the X-ray study on *cis*-$PtCl_2[P(CH_3)_3]_2$ [2]. The corresponding data are presented in Table 6. There is good agreement between the corresponding parameters indicating the similarity of bonding properties of the Pt and Pd atoms.

Supplementary material

Total electron diffraction experimental intensities (3 pages) may be obtained from G. Sch. or I.H. Tables of anisotropic thermal parameters, bond distances, bond angles, hydrogen atom coordinates, isotropic thermal parameters and structure factors for *cis*-$PdCl_2(PMe_3)_2$ (12 pages) may be obtained from C.M.J.

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References

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

2 A. Del Pra and G. Zanotti, *Cryst. Struct. Commun.*, *8* (1979) 737.

3 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 4th edn., 1980, p. 952.

4 I. Hargittai, J. Tremmel and M. Kolonits, *Hung. Sci. Instrum.*, *50* (1980) 31.

5 J. Tremmel and I. Hargittai, *J. Phys. E*, *18* (1985) 148.

6 W. Witt, *Z. Naturforsch.*, *19* (1964) 1363.

7 B. Andersen, H. M. Seip, T. G. Strand and R. Stølevik, *Acta Chem. Scand.*, *23* (1969) 3224.

8 C. Tavard, D. Nicolas and M. Roault, *J. Chim. Phys. Phys.-Chim. Biol.*, *64* (1967) 540.

9 R. A. Bonham and L. Schäfer, *International Tables for X-ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, Ch. 2.5.

10 M. Hargittai and I. Hargittai, *J. Chem. Phys.*, *59* (1973) 2513.