Photochemical Preparation of the *cis* Isomers of Dichlorobis(tri-n-alkylphosphine)palladium(II) (alkyl = Et, Pr^n, or Bu^n); the Crystal-structure Analysis of the Overcrowded n-Propyl Homologue

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Ultraviolet irradiation of the *trans* forms of the title compounds in nitromethane gives up to 70% of the labile *cis* isomers, which can be isolated in crystalline form. Irradiation of a 1 : 1 mixture of *trans*-$[Pd(PEt_3)_2Cl_2]$ and *trans*-$[Pd(PPr^n{}_3)_2Cl_2]$ gives almost entirely a 1 : 1 mixture of the corresponding *cis* isomers and only a few percent of *cis*-$[Pd(PEt_3)(PPr^n{}_3)Cl_2]$, indicating a predominantly intramolecular mechanism. Crystals of *cis*-$[Pd(PPr^n{}_3)_2Cl_2]$ are monoclinic, with space group $P2_1/m$, a = 9.729(1), b = 13.816(3), c = 9.614(1) Å, β = 100.77(1)°, and Z = 2. The structure has been refined to R = 0.029 for 1 873 reflections collected by a four-circle diffractometer. The *cis*-planar structure reveals considerable overcrowding [P–Pd–P 105.75(6)°, one Pd–P–C 121.1° (mean)]. The Pd–P distances are short (mean 2.322 Å) and the Pd–Cl distances long (mean 2.407 Å), attributable to the *trans* effect.

THE thermally and photochemically induced interconversions of the *cis* and *trans* isomers of the complexes $[Pt^{II}L_2X_2]$ (L = donor ligand, X = halide) have long been known [1,2] but still excite controversy.[3] In one case,[4] $[Pt(PPh_3)_2X_2]$, the *trans* form was first prepared by irradiating the *cis* form to give a photostationary-state mixture from which the *trans* isomer could be isolated. The quantum yields for isomerisation are typically *ca.* 10^{-2}, and the composition of the photostationary state is solvent-dependent,[5] with dipolar solvents enhancing the proportion of *cis* isomer. Six possible mechanisms have been discussed: (*i*) an intramolecular route involving a tetrahedral or 'twisted' intermediate (possibly an electronically excited state);[2,5,6] (*ii*) an associative mechanism involving a trigonal-bipyramidal intermediate $[PtL_2X_2S]$ (S = solvent);[2,4] (*iii*)—(*v*) dissociative mechanisms[2] involving either a co-ordinated unsaturated intermediate $[PtLX_2]$, its solvate,[5] $[PtLX_2S]$, or a 'caged' ion pair[5] $[PtL_2X^+ \cdots X^-]$; and, finally, (*vi*) a mechanism based on successive substitutions by excess of ligand.

Rather less attention has been paid to the palladium(II) analogues of these complexes. Grim and Keiter[7] demonstrated by ^{31}P n.m.r. spectroscopy that the behaviour of complexes $[PdL'_2X_2]$ (L' = a tertiary phosphine, PPh_nR_{3-n}) depends on the value of n; thus when $n = 0$ only the *trans* form is found in solution, whereas when $n = 1$ or 2 two ^{31}P resonances appear, corresponding to the two isomers. The isomers can be separated and isolated as solids but on dissolution in CH_2Cl_2 both yield the equilibrium mixture. The *cis* and *trans* forms of $[Pd(PMe_2Ph)_2Cl_2]$ achieve rapid equilibrium in solution, with the *cis* form favoured by lower temperatures and higher solvent polarity.[8] Traverso and co-workers[9,10] have demonstrated that irradiation of *trans*-$[Pd(PPr^n{}_3)_2Cl_2]$ yields a *cis–trans* mixture which reverts slowly in the dark to the pure *trans* form, although extended irradiation yields $[Pd_2(PPr^n{}_3)_2Cl_4]$.

We describe here the successful isolation of the *cis* isomer from the photostationary-state mixture (R = Et, Pr^n, or Bu^n), and its crystal structure when R = Pr^n. This fully confirms the crowding in the *cis* form which underlies its lability. A preliminary account of this work has appeared.[11]

EXPERIMENTAL

Materials.—The *trans* isomers of $[Pd(PR_3)_2Cl_2]$ (R = Et, Pr^n, Bu^n, or cyclohexyl) were prepared by a slight modification of the literature method.[12] A methanolic solution of PR_3 (2 mol) was added with stirring to aqueous $Na_2[PdCl_4]$ (1 mol) under N_2, giving a yellow precipitate of the *trans* isomer. Sometimes a red precipitate or oil would form initially, but this could be converted into the normal yellow product on prolonged stirring. The complexes were recrystallised from hot EtOH, sometimes with the addition of a little water. Attempts to prepare *trans*-$[Pd(PBu^t{}_3)_2Cl_2]$ resulted in a red-brown solid which was not characterised, although it appeared to be homogeneous on passage through a column of Al_2O_3.

N.M.R. Studies.—Phosphorus-31 n.m.r. measurements were carried out with a Bruker WH90 spectrometer equipped with thermostatting and a ^{31}P probe. Proton n.m.r. data at 220 MHz were obtained with a Perkin-Elmer R34 instrument. Spectra were recorded below room temperature to minimise isomerisation.

Photolyses of the trans *Isomers.*—These were carried out by exposing n.m.r. tubes containing solutions of the *trans* isomers to an unfiltered, focused 200-W Xe–Hg lamp point source, followed by comparison of the ^{31}P and ^1H resonances of the two isomers[7,9] (see Table 1). A variety of solvents (C^2HCl_3, $C^2H_3O^2H$, $C^2H_3NO_2$) was investigated to determine which yielded the highest photostationary concentration of the desired *cis* isomer, and, as expected, this was achieved with polar solvents. Nitromethane was selected as the routine solvent because the more polar MeCN might have introduced complications through its co-ordinating ability. Although the *cis* isomer might be expected to be better stabilised at lower temperatures, photolysis of nitromethane solutions at −10 °C enhanced the proportion of this isomer only marginally. When the solvent was chloroform, photolysis of cold solutions gave a higher percentage of the *cis* isomer (*ca.* 50%) compared with room temperature (*ca.* 25%). Addition of methanol also increased the amount of *cis* isomer. When irradiations were carried out as described, the n.m.r. intensities indicated *ca.* 75% conversion into the *cis* isomer in $C^2H_3NO_2$ solution when R = Et, Pr^n, or Bu^n. No conversion was detected with R = cyclohexyl.

Isolation of the cis *Isomers*.—Two procedures were employed. (*a*) Nitrogen-flushed solutions (0.08 mol dm^{-3}) of the *trans* isomer in CH_3NO_2 placed in a 4-cm silica spectrophotometer cell were irradiated overnight using the focused lamp. The cell was kept cool in a beaker of cold water. The solutions were then concentrated by evaporation with the stream of N_2, and the pale yellow *cis* isomer crystallised (50% yield) by gradual addition of diethyl ether (the *trans* form remaining in solution).

(*b*) (*For* R = Pr^n). Irradiation of a n-hexane solution of the *trans* isomer resulted in the precipitation of the *cis* isomer as it formed (25% yield). (When R = Bu^n, although crystals of the *cis* isomer formed on the surface at the entry point of the light beam, they dissolved rapidly on removal from the beam.)

Identification of the *cis* isomers was principally by ^{31}P n.m.r. spectroscopy. Thus, *cis*-$[Pd(PEt_3)_2Cl_2]$ shows a singlet at −34.1 p.p.m. in $C^2H_3NO_2$. Ultraviolet absorbances were exhibited at $\lambda_{max.}$ 332 (ε 2.8 × 10^3) and 256 nm (ε 1.3 × 10^4 dm^3 mol^{-1} cm^{-1}). Proton n.m.r. data are collected in Table 1.

TABLE 1

Proton n.m.r. data (p.p.m.) [a]

R	*cis*	*trans*
(*a*) For $[Pd(PR_3)_2Cl_2]$ [b]		
Et	1.26 (m), 2.10 (d of q) [c]	1.19 (p), 1.87 (m) [d]
Pr^n	1.11 (t), 1.69 (m), 2.02 (m) [e]	1.05 (t), 1.61 (m), 1.80 (m) [d]
Bu^n	0.97 (t), 1.50 (m), 1.62 (m), 2.07 (m) [c]	0.92 (t), 1.50 (m), 1.58 (m), 1.81 (m); [d] 0.96 (t), 1.52 (m), 1.61 (m), 1.84 (m) [c]
(*b*) For the ligands [f]		
PPr$^n_3$	0.96 (t), 1.26 (m), 1.42(m)	
PBu$^n_3$	0.90 (t), 1.37 (m)	

[a] t = Triplet, m = multiplet, p = pentet (possibly not a real pentet), d = doublet, q = quartet. [b] Although the resonances are described as multiplets due to coupling with both P and CH_2, the actual patterns are different for the *cis* and *trans* isomers. [c] In $C^2H_3NO_2$ solution. [d] In C^2HCl_3 solution. [e] In $C^2H_3O^2H$ solution. [f] In benzene solution.

Mechanistic Studies.—Attempts were made to assess the roles of inter- and intra-molecular pathways in the photochemically induced *cis–trans* isomerisation as follows. Photolysis in $C^2H_3NO_2$ of a 1 : 1 (molar) mixture of *trans*-$[Pd(PEt_3)_2Cl_2]$ and *trans*-$[Pd(PPr^n_3)_2Cl_2]$ gave a ^{31}P n.m.r. spectrum indicating 70—75% conversion into *cis*-$[Pd(PEt_3)_2Cl_2]$ and *cis*-$[Pd(PPr^n_3)_2Cl_2]$ together with minor resonances consistent with formation of the mixed complexes. Essentially the same result was obtained in C^2HCl_3 except that the overall conversion into the two *cis* isomers was only *ca.* 40%. Thermolysis of the mixture of *trans* complexes was also examined by ^{31}P n.m.r. spectroscopy in nitromethane solution; on heating, small quantities of the *cis* isomers were formed, *i.e.* *cis*-$[Pd(PEt_3)_2Cl_2]$, *cis*-$[Pd(PPr^n_3)_2Cl_2]$, and *cis*-$[Pd(PEt_3)(PPr^n_3)Cl_2]$, while the major new product was *trans*-$[Pd(PEt_3)(PPr^n_3)Cl_2]$.

TABLE 2

Atomic co-ordinates (× 10^4) with standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Pd	534.9(4)	2 500.0	−1 225.6(4)
P(1)	1 101(2)	3 238(1)	877(1)
P(2)	1 451(2)	3 408(1)	−2 736(2)
Cl(1)	−779(2)	1 466(1)	44(2)
Cl(2)	51(2)	1 361(1)	−3 164(2)
C(1)	1 880(7)	2 348(13)	2 223(6)
C(2)	3 231(9)	1 899(6)	1 922(9)
C(3)	3 834(11)	1 132(7)	2 948(11)
C(4)	−467(7)	3 727(5)	1 420(7)
C(5)	−1 499(8)	4 186(6)	243(8)
C(6)	−2 851(8)	4 528(8)	752(9)
C(7)	2 374(7)	4 229(4)	1 166(6)
C(8)	2 868(7)	4 545(5)	2 710(7)
C(9)	3 726(8)	5 481(6)	2 798(8)
C(10)	2 118(6)	4 628(4)	−2 237(6)
C(11)	2 381(8)	5 283(5)	−3 474(8)
C(12)	3 029(10)	6 243(6)	−2 922(10)
C(13)	99(7)	3 614(5)	−4 285(6)
C(14)	−1 224(7)	4 082(6)	−3 952(8)
C(15)	−2 358(8)	4 226(8)	−5 272(8)
C(16)	2 884(6)	2 795(4)	−3 384(6)
C(17)	4 018(6)	2 347(9)	−2 224(6)
C(18)	5 189(7)	1 862(6)	−2 808(9)
H(11)	2 084(38)	2 687(41)	3 143(40)
H(12)	1 441(46)	1 972(32)	2 206(47)
H(21)	3 179(53)	1 591(36)	1 070(54)
H(22)	3 928(36)	2 329(47)	1 896(37)
H(31)	4 502(49)	523(37)	2 635(48)
H(32)	4 435(48)	1 640(34)	3 950(48)
H(33)	3 002(54)	786(44)	3 363(64)
H(41)	−792(46)	3 234(33)	1 746(47)
H(42)	−197(46)	4 206(35)	2 154(47)
H(51)	−1 159(47)	4 668(36)	−67(49)
H(52)	−1 779(47)	3 698(34)	−592(48)
H(61)	−3 548(47)	4 810(35)	−107(49)
H(62)	−3 482(48)	3 837(35)	846(51)
H(63)	−2 641(55)	5 037(37)	1 400(56)
H(71)	3 204(55)	3 998(36)	854(53)
H(72)	2 030(50)	4 708(36)	729(48)
H(81)	2 153(51)	4 688(36)	2 918(48)
H(82)	3 412(55)	3 894(41)	3 082(63)
H(91)	4 507(48)	5 513(36)	2 116(48)
H(92)	4 006(47)	5 600(34)	3 736(50)
H(93)	3 181(48)	5 980(34)	2 346(48)
H(101)	1 569(52)	4 844(35)	−1 880(48)
H(102)	3 126(50)	4 477(36)	−1 440(53)
H(111)	3 163(52)	4 970(37)	−3 835(51)
H(112)	1 673(53)	5 432(41)	−3 765(56)
H(121)	3 054(51)	6 357(36)	−2 005(57)
H(122)	4 240(50)	6 100(34)	−2 425(47)
H(123)	2 699(52)	6 654(36)	−3 224(57)
H(131)	379(45)	4 007(34)	−4 967(48)
H(132)	−140(46)	3 022(30)	−4 705(45)
H(141)	−1 563(46)	3 632(34)	−3 353(47)
H(142)	−930(47)	4 717(34)	−3 488(47)
H(151)	−3 323(47)	4 385(36)	−4 882(50)
H(152)	−2 012(57)	4 849(45)	−5 631(59)
H(153)	−2 767(51)	3 582(38)	−5 802(51)
H(161)	2 573(39)	2 288(38)	−3 853(38)
H(162)	3 356(49)	3 260(35)	−3 960(49)
H(171)	3 952(47)	2 177(35)	−1 517(48)
H(172)	4 208(56)	1 908(39)	−1 928(54)
H(181)	5 588(50)	3 184(33)	−1 857(48)
H(182)	5 655(41)	2 855(29)	−3 478(42)
H(183)	4 683(48)	3 745(35)	−3 274(48)

When excess of PEt_3 was added to *trans*-$[Pd(PPr^n_3)_2Cl_2]$ in $C^2H_3O^2H$ the yellow colour faded and it was clear from the ^{31}P n.m.r. spectrum that not only had both PPr^n_3 groups been substituted but further reaction had yielded $[Pd(PEt_3)_3Cl]^+$, since the spectrum consisted of a triplet at −31.9 p.p.m. (J_{PP} 19.1 Hz) and a doublet at −25.1 p.p.m. (J_{PP} 19.1 Hz).

Crystal Data.—$C_{18}H_{42}Cl_2P_2Pd$, *M* = 498, Monoclinic, space group $P2_1/m$, *a* = 9.729(1), *b* = 13.816(3), *c* = 9.614(1) Å, β = 100.77(1)°, *U* = 1 269.4(3) Å^3, *F*(000) = 520, *Z* = 2, D_c = 1.30 g cm^{-3}, λ = 0.710 69 Å, μ = 10.65 cm^{-1}.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. The maximum value of 2θ was 55°, with a scan range of ±0.75° (2θ) around the $K\alpha_1$ — $K\alpha_2$ angles and a scan speed of 2—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time.

Three standard reflections were monitored every 200 reflections, and showed slight changes during data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. 1 873 Observed reflections $[I/\sigma(I) > 3.0]$ were used in refinement, and corrected for Lorentz, polarisation, and absorption effects, the last with ABSCOR; [13] maximum and minimum transmission factors were 0.95 and 0.77.

Systematic absences $0k0$ with $k \neq 2n$ indicated space group $P2_1$ or $P2_1/m$. With the Pd positioned from a Patterson synthesis, two independent medium-weight peaks could be seen on a Fourier synthesis in space group $P2_1/m$. These should be P and Cl, but both had lesser peaks within bonding distance of them. It therefore appeared that $P2_1$ was the correct space group. Using this, light atoms were located and refined to $R = 0.12$, with anisotropic temperature factors for Pd, P, and Cl. However, there were a large number of residual peaks, and the temperature factors of many atoms seemed implausible. It was then noted that the largest residual peaks were m-related to the P atoms. The structure was therefore returned to space group $P2_1/m$, with a complete disordered molecule lying across the mirror plane. Refinement with all atoms isotropic now gave $R = 0.10$. After anisotropic refinement, the hydrogen atoms could be seen on a Fourier-difference synthesis and refined with fixed temperature factors. Final refinement by least squares (in large blocks) gave $R = 0.029$ (using unit weights which were found to be satisfactory). There were no significant residual peaks on a Fourier-difference synthesis.

TABLE 3

Selected bond lengths (Å) and angles (°) with standard deviations in parentheses

Pd–P(1)	2.239(2)	P(1)–Pd–P(2)	105.75(6)
Pd–P(2)	2.227(2)	P(1)–Pd–Cl(1)	82.91(6)
Pd–Cl(1)	2.398(2)	P(2)–Pd–Cl(2)	84.72(6)
Pd–Cl(2)	2.417(2)	Cl(1)–Pd–Cl(2)	87.64(6)
P(1)–C(1)	1.842(13)	Pd–P(1)–C(1)	109.3(4)
P(1)–C(4)	1.832(7)	Pd–P(1)–C(4)	110.3(2)
P(1)–C(7)	1.833(6)	Pd–P(1)–C(7)	121.5(2)
		C(1)–P(1)–C(4)	107.5(3)
		C(1)–P(1)–C(7)	102.4(4)
		C(4)–P(1)–C(7)	104.9(3)
P(2)–C(10)	1.838(6)	Pd–P(2)–C(10)	120.7(2)
P(2)–C(13)	1.816(6)	Pd–P(2)–C(13)	107.8(2)
P(2)–C(16)	1.836(7)	Pd–P(2)–C(16)	112.5(2)
		C(10)–P(2)–C(13)	103.7(3)
		C(10)–P(2)–C(16)	104.9(3)
		C(13)–P(2)–C(16)	105.9(3)
C(1)–C(2)	1.529(13)	P(1)–C(1)–C(2)	113.1(6)
C(2)–C(3)	1.492(13)	C(1)–C(2)–C(3)	114.1(9)
C(4)–C(5)	1.505(9)	P(1)–C(4)–C(5)	114.5(5)
C(5)–C(6)	1.560(12)	C(4)–C(5)–C(6)	112.0(6)
C(7)–C(8)	1.536(9)	P(1)–C(7)–C(8)	116.1(5)
C(8)–C(9)	1.532(11)	C(7)–C(8)–C(9)	111.2(6)
C(10)–C(11)	1.554(10)	P(2)–C(10)–C(11)	115.8(4)
C(11)–C(12)	1.520(10)	C(10)–C(11)–C(12)	111.0(6)
C(13)–C(14)	1.527(10)	P(2)–C(13)–C(14)	113.8(4)
C(14)–C(15)	1.531(10)	C(13)–C(14)–C(15)	112.7(6)
C(16)–C(17)	1.544(9)	P(2)–C(16)–C(17)	115.2(5)
C(17)–C(18)	1.516(11)	C(16)–C(17)–C(18)	113.2(5)

Final atomic co-ordinates are in Table 2 and bond lengths and angles in Table 3. Thermal parameters and final structure factors are listed in Supplementary Publication No. SUP 22955 (17 pp.).* All computing was done with the 'X-RAY '76' system [14] on a Burroughs B6700 computer, and scattering factors in the analytical form were taken from ref. 15.

RESULTS AND DISCUSSION

Production of the cis *Isomers*.—The ^{31}P n.m.r. results give the general evidence that the *cis* isomers are produced in yields of only a few percent when *trans*-[Pd$(PR_3)_2Cl_2$] is dissolved in polar solvents which are expected to favour the *cis* form. However, under the stimulation of light, a photostationary state is set up which consists of up to 70% *cis* isomer when the temperature and solvent are optimised, and from which the *cis* isomers can be isolated as crystalline solids. Irradiation of alkane solutions of the *trans* isomer leads to deposition of the pure *cis* isomer, albeit in rather lower yields.

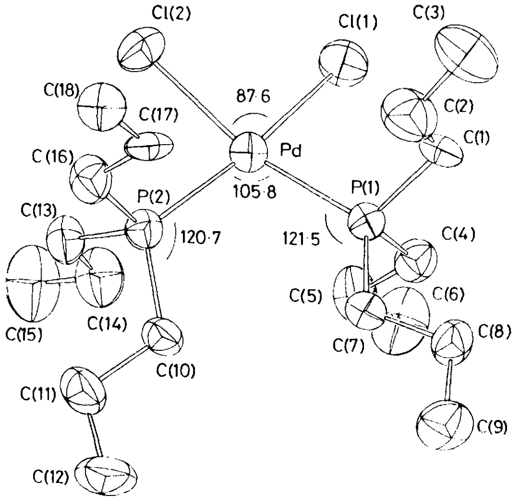

FIGURE 1 View of the molecule, showing the atomic numbering and some principal bond angles

Mechanism of the Isomerisation.—The most significant result is that irradiation of the mixture of *trans*-[Pd$(PEt_3)_2Cl_2$] and *trans*-[Pd$(PPr^n_3)_2Cl_2$] indicates a predominantly intramolecular process, involving presumably a tetrahedral intermediate which collapses to either square-planar form. However, small quantities of the cross-products were visible in the ^{31}P spectrum. A concurrent dissociative pathway must therefore be present. It was also observed that, in polar solvents, a small percentage of *cis* isomer is formed even in the dark, especially when the solution is heated. Taking a rather arbitrary figure of 1% conversion into the *cis* form at 298 K yields a free-energy difference between the two forms of only 11.4 kJ mol^{-1}. This figure contrasts with the measured activation energy for the *cis* ⟶ *trans* conversion in $CHCl_3$ of 124.4 kJ mol^{-1}, which must refer to the difficulty of attaining the tetrahedral transition state.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

Crystallographic Confirmation of the Crowding in the cis *Isomer of* $[Pd(PPr^n_3)_2Cl_2]$.—The crystal-structure determination unequivocally confirms the *cis* geometry (Figure 1); the molecular dimensions show the effects of overcrowding very clearly. This is apparent first in the P–Pd–P angle [105.75(6)], rather than the 90° expected for square-planar geometry. There is one very large C–P–Pd angle at each phosphorus [121.5, 120.7°], involving the two carbon chains that face inwards. It follows from this that all the C–P–C angles are small (102.4—107.5°). It is also noticeable that the P–C–C and C–C–C angles are relatively large (111.0—116.1°), *i.e.* the carbon chains are somewhat stretched. This may also be a consequence of the overcrowding. The plane around Pt is also slightly distorted with P(1) and Cl(2) being buckled up by 0.15 Å each, and P(2) and Cl(1) down by the same amount, from the mean plane.

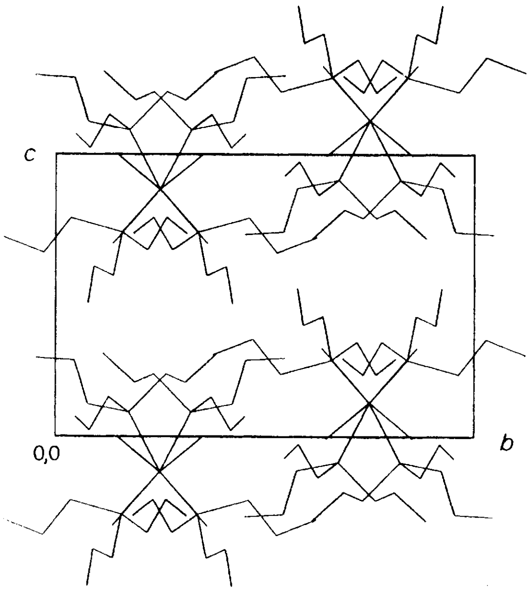

FIGURE 2 Packing diagram, viewed down *a*, showing both alternative positions of the molecules

Considering the full range of Pd–P and Pd–Cl distances that have been observed,[16,17] the Pd–P distance (mean 2.233 Å) is short and the Pd–Cl distance (mean 2.407 Å) long. However, this is presumably due to *trans* effects. The shortest Pd–P distances collected by Palenik *et al.*[16] all have Cl *trans* to P. The distances observed here are also similar to those in *cis*-$[Pd(PMe_2Ph)_2Cl_2]$ [17] [Pd–P 2.260(2), Pd–Cl 2.362(3) Å]. It seems that steric factors are principally responsible for the minor variations in bond lengths,[16] although it is not possible to rationalise these in detail.

The packing diagram (Figure 2) shows that the intermolecular interactions are between the terminal methyl groups only (no C–C <2.4 Å). It is presumably for this reason that the observed disorder arises.

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