Formation of Large Chelate Rings and Cyclometallated Complexes from $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$ and Platinum and Palladium Chlorides. Crystal Structure of $[Pd_2Cl_4\{Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2\}_2]$ †‡

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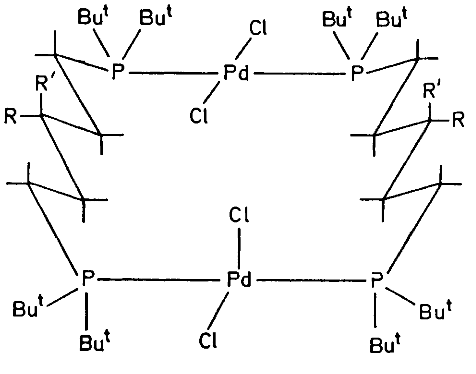
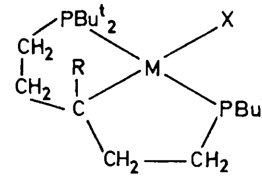
Treatment of $[PdCl_2(NCPh)_2]$ with $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$(Q) gives the binuclear complex $[Pd_2Cl_4(Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2)_2]$. The crystal structure of this 16-atom ring complex shows that the two methyl substituents on the ring occupy ' corner positions ' and the C_5 chains are not in the extended conformation. The crystals are monoclinic, space group *Pn*, with unit-cell dimensions a = 8.616(2), b = 28.485(5), c = 12.127(2) Å, β = 109.35(2)°, and Z = 2, final R = 0.07. A variable-temperature ^{31}P n.m.r. study shows the ring to be fluxional. With $[PtCl_2(NCPh)_2]$, Q gives a complex $[(PtCl_2Q)_x]$ (also fluxional) and a cyclometallated complex $[PtCl(Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2)]$ abbreviated to [PtCl(P–C–P)], $[PtCl_2Q]$ with CF_3COOH gives $[Pt(OOCCF_3)(P–C–P)]$, and [PtCl(P–C–P)] with $Na[BH_4]$ gives [PtH(P–C–P)]. Infrared and ^1H and ^{31}P n.m.r. data are given.

WE have described the products formed from bulky diphosphines $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 5—10 or 12) and palladium(II) or platinum(II) halides.[1-5] Several structures of the resultant large-ring chelates have been determined by *X*-ray crystallography. The pentamethylene diphosphine $Bu^t_2P(CH_2)_5PBu^t_2$ reacted with $[PdCl_2(NCPh)_2]$ to give the 16-atom ring chelate $[Pd_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ (1; R = R′ = H) and the mononuclear complex $[PdCl(Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2)]$ (2; R = H, M = Pd, X = Cl) in which the carbon atom of the central methylene had been metallated.[5] The complex $[PtCl_2(NCPh)_2]$ reacted similarly to give a large-ring chelate, probably analogous to (1), and a cyclometallated complex of type (2) (R = H, M = Pt, X = Cl). In addition, an unidentified product very similar to (2) was formed, which could not be separated from (2): possibly this minor product contained a π-allylic grouping.



(1)



(2)

In view of these results it was of interest to study the effect of introducing a methyl group into the middle of the polymethylene chain, *i.e.* to study the action of $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$ on palladium and platinum halides. We thought points of interest in this study would be: (*i*) whether the methyls would occupy pseudo-equatorial (R) or pseudo-axial (R′) positions in (1) or whether they would cause a conformational change on the C_5 chain; (*ii*) what would be the effect of the methyl substituent on the metallation since one might anticipate that a secondary carbon atom would metallate less readily than a primary one; (*iii*) a methyl substituent might help to isolate and identify the unknown type of product formed from platinum and the pentamethylene diphosphine (above).

RESULTS AND DISCUSSION

Palladium.—Treatment of $[PdCl_2(NCPh)_2]$ with $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$ in boiling ethanol for 18 h gave some metallic palladium and the hoped for yellow binuclear complex *trans*-$[Pd_2Cl_4(Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2)_2]$. Characterizing data are given in Tables 1 and 2. We were unable to detect any cyclometallated complex of type (2), however. This contrasts with the behaviour of $Bu^t_2P(CH_2)_5PBu^t_2$ which gave the cyclometallated complex (2; R = H, M = Pd, X = Cl) and exemplifies the difficulty of metallating secondary carbon atoms.

The molecular structure of the binuclear complex $[Pd_2Cl_4(Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2)_2]$ was determined by *X*-ray diffraction and views of it are shown in Figures 1 and 2. Bond lengths and bond angles are normal or close to normal and selected ones are given in

† Di-μ-[1,5-bis(di-t-butylphosphino)-3-methylpentane-*PP*′]-bis[dichloropalladium(II)].

‡ No reprints available.

TABLE 1

Microanalytical (%) [a] and molecular-weight [a,b] data (Q = $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$ and P–C–P = $Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2$)

Complex	C	H	Halogen	*M*
trans-$[Pd_2Cl_4Q_2]$	47.65(47.9)	8.9(8.8)	13.0(12.8)	1 125(1 104)
trans-$[(PtCl_2Q)_x]$	41.7(41.3)	7.45(7.55)	11.25(11.1)	
[PtCl(P–C–P)]	43.45(43.75)	7.8(7.85)	6.2(5.85)	587(604)
$[Pt(OOCCF_3)$(P–C–P)]	42.8(42.3)	7.2(7.0)		699(682)
[PtH(P–C–P)]	45.65(45.4)	8.4(8.3)		536(555)

[a] Calculated values in parentheses. [b] Measured in chloroform.

Table 3. Torsion angles for the ring atoms are also given in Table 3. As can be seen the conformation of the 16-atom ring is different from that found for $[Pd_2Cl_4(Bu^t_2PCH_2CH_2CH_2CH_2CH_2PBu^t_2)_2]$.[4] The methyl substituent causes a conformational change. The torsion angle for C(1)–C(2)–C(3)–C(4) is *ca.* 60° and the carbon part of the structure can be considered as two fully staggered butane units in which two atoms are common to both, *i.e.* C(1)–C(2)–C(3)–C(30) and C(5)–C(4)–C(3)–C(2). Thus the methyl substituent C(3) is fully staggered with respect to the chain on one side of C(3) [*i.e.* on the side of C(1)] and *gauche* with respect to C(5). The methyls thus occupy 'corner positions'. This is a feature of methyl-substituted large carbocyclic rings and has been discussed by Dale and other workers.[6-8] The Cl–Pd–Cl moieties are arranged in a manner very similar to that found in all other crystal structures of compounds of this type, *viz.* with one chlorine *gauche* with respect to two sets of t-butyls (which are eclipsed) and the other lying above the two inward-pointing pseudo-equatorial hydrogens on the β-carbon atoms, C(2) and C(4). The non-linearity of the Cl–Pd–Cl moieties *viz. ca.* 171.5° is probably caused by non-bonding interactions.

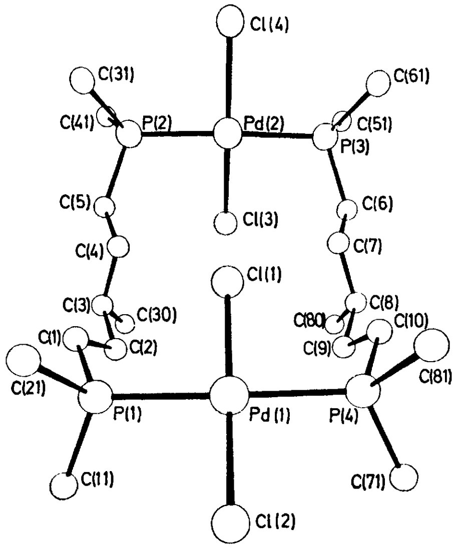


FIGURE 1 Molecular structure of $[Pd_2Cl_4(Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2)_2]$ showing atom numbering. For clarity the methyl carbon atoms of the t-butyl substituents have been omitted

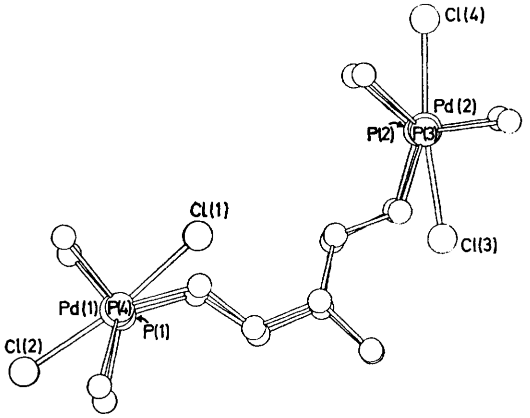


FIGURE 2 View of the molecular structure of $[Pd_2Cl_4\{Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2\}_2]$ showing the eclipsing of the two halves of the molecule, giving non-crystallographic symmetry C_s

TABLE 2

Hydrogen-1 [a] and ^{31}P n.m.r.[b] and i.r. (cm^{-1}) data (Q = $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$ and P–C–P = $Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2$)

	^1H			^{31}P		
Complex	$\delta(Bu^t)$	$\delta(CH_2)$	Other	$\delta(H_3PO_4)$	$^1J(Pt–P)$	i.r. (Nujol mull)
trans-$[Pd_2Cl_4Q_2]$	1.52(13) (t) 1.48(13) (t)	1.28—2.10	*ca.* 1.0 CH_3CH	39.0		343s ν(Pd–Cl)
$[(PtCl_2Q)_x]$	*c*	0.98—2.4	*d*	27.45	2 449	330s ν(Pt–Cl)
[PtCl(P–C–P)]	1.42(13) (t) 1.45(13) (t)	1.1—1.9	0.95 CH_3CPt $^3J(Pt–H) = 90$	73.3	3 223	263s ν(Pt–Cl)
$[Pt(OOCCF_3)$(P–C–P)]	1.37(14) (t)	1.2—2.0	1.05 $^3J(Pt–H) = 90$	76.5	3 296	1 200s ν(C–F) 1 690s, 1 710s ν(C–O)
[PtH(P–C–P)]	1.26(12) (t)	1.1—2.0	−3.10 (tt) HPt $^2J(P–H) = 18$ $^1J(Pt–H) = 748$	86.4	3 095	1 875s ν(Pt–H)

[a] In $CDCl_3$ at 60 MHz and 34 °C. Values of $^3J(P–H) + {^5J}(P–H)$ (Hz) for Bu^t resonances shown in parentheses. δ Values ±0.02, *J* values ±1 Hz. t = Triplet, tt = triplet of triplets. [b] In $CDCl_3$ at 36.43 MHz and 25 °C. δ Values ±0.05, *J* values ±1 Hz. [c] Multiplet. [d] Could not be observed, presumably obscured by other resonances.

As can be seen from Figures 1 and 2, P(1) and P(4) are not chemically equivalent to P(2) and P(3) although at 298 K only one ^{31}P resonance is observed (Table 2). We therefore did a variable-temperature ^{31}P n.m.r. study (in $\mathrm{CDCl_3}$) and found that on cooling the solution the resonance broadened, then separated. At or below 240 K the resonance pattern was two equally intense singlets at δ 38.3 and 38.8 p.p.m. together with a weak singlet at δ 39.4 p.p.m. This result is consistent with the presence of the conformer shown in Figures 1 and 2 together with a minor component, possibly of type (1) with equatorial methyls on the central carbons of the $\mathrm{C_5}$ chains. We suggest that at room temperature rotation around C–C and Pd–P bonds causes equivalence on the n.m.r. time scale.

TABLE 3

Selected bond lengths, bond angles, and torsion angles for $[\mathrm{Pd_2Cl_4(Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2)_2}]$

(*a*) Bond lengths (Å)			
Pd(1)–P(1)	2.388(6)	Pd(1)–Cl(1)	2.291(5)
Pd(1)–P(4)	2.380(6)	Pd(1)–Cl(2)	2.305(6)
Pd(2)–P(2)	2.372(6)	Pd(2)–Cl(3)	2.302(5)
Pd(2)–P(3)	2.374(7)	Pd(2)–Cl(4)	2.305(6)
P–C	1.75—1.96(3)	average = 1.88	
C–C	1.43—1.62(4)	average = 1.52	
(*b*) Bond angles (°)			
P(1)–Pd(1)–P(4)	175.9(2)	Cl(1)–Pd(1)–Cl(2)	171.5(2)
P(2)–Pd(2)–P(3)	175.9(2)	Cl(3)–Pd(2)–Cl(4)	171.4(2)
Pd–P–C	107.8—115.4(9)	average = 112.2	
(*c*) Torsion angles (°)			
Pd(1)–P(1)–C(1)–C(2)	56.9	Pd(1)–P(4)–C(10)–C(9)	–58.0
P(1)–C(1)–C(2)–C(3)	–173.3	P(4)–C(10)–C(9)–C(8)	174.7
C(1)–C(2)–C(3)–C(4)	60.3	C(10)–C(9)–C(8)–C(7)	–59.1
C(2)–C(3)–C(4)–C(5)	178.2	C(9)–C(8)–C(7)–C(6)	–176.5
C(3)–C(4)–C(5)–P(2)	–172.9	C(8)–C(7)–C(6)–P(3)	178.1
C(4)–C(5)–P(2)–Pd(2)	56.6	C(7)–C(6)–P(3)–Pd(2)	–59.4

Platinum.—When we treated $[\mathrm{PtCl_2(NCPh)_2}]$ with the diphosphine a yellow crystalline complex $[\{\mathrm{PtCl_2(Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2)}\}_x]$ was obtained. This was insufficiently soluble in chloroform or benzene for a molecular-weight measurement although it seems most likely that the complex is binuclear ($x = 2$). Characterizing data are in Tables 1 and 2. Like the palladium analogue it was fluxional, thus at 297 K the ^{31}P n.m.r. pattern (in $\mathrm{CDCl_3}$) consists of a singlet with satellites δ(P) = 27.6 p.p.m., and ^1J(Pt–P) = 2 445 Hz. When the solution is cooled, the resonance broadens and at $\leqslant$250 K it consists of two equally intense singlets with satellites δ = 26.9 p.p.m., ^1J(Pt–P) = 2 432 Hz and δ = 27.2 p.p.m., ^1J(Pt–P) = 2 427 Hz. This result could correspond to the ' freezing out ' of the conformer analogous to that shown in Figures 1 and 2 for palladium.

In addition to this very sparingly soluble yellow complex, a white, volatile, and very soluble cyclometallated complex $[\mathrm{PtCl(Bu^t{}_2PCH_2CH_2CMeCH_2CH_2PBu^t{}_2)}]$ (2; R = Me, M = Pt, X = Cl) was formed. Characterizing data are given in Tables 1 and 2, these are similar to those found for the analogous complex without the methyl group (2; R = H).[5] Thus platinum(II) cyclometallates the secondary carbon atom whereas palladium(II) does not. This is yet another example of platinum(II) cyclometallating a tertiary phosphine ligand more readily than palladium(II), the reverse seems to apply with nitrogen donor ligands.[9,10]

The yellow complex $[\{\mathrm{PtCl_2(Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2)}\}_x]$ when heated with trifluoroacetic acid–chloroform (ethanol free) gave the cyclometallated complex $[\mathrm{Pt(OOCCF_3)(Bu^t{}_2PCH_2CH_2CMeCH_2CH_2PBu^t{}_2)}]$ (2; R = Me, M = Pt, X = $\mathrm{OOCCF_3}$), see Tables 1 and 2 for characterizing data. We also reduced the chloro-complex (2; R = Me, M = Pt, X = Cl) to the corresponding hydride (X = H) by treatment with sodium tetrahydroborate. The hydrido- and trifluoroacetato-complexes have similar characterizing n.m.r. data to those of the corresponding complexes without the methyl group (2; R = H). In none of the preparations and reactions discussed above did we find evidence for the formation of the unidentified cyclometallated minor components we previously reported from the pentamethylene diphosphine.[5] We do not know why the methyl group should have this effect.

EXPERIMENTAL

The general preparative and spectroscopic techniques, *etc.* were the same as those described in other recent papers from this laboratory.[11]

1,5-*Bis(di-t-butylphosphino)*-3-*methylpentane*.— This was prepared from 1,5-dilithio-3-methylpentane and $\mathrm{PBu^t{}_2Cl}$ in an exactly analogous manner to 1,5-bis(di-t-butylphosphino)pentane.[5] The product is a colourless liquid, b.p. 130—140 °C (bath temperature) (0.05 mmHg).* Yield 32%.

Action of $\mathrm{Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2}$ *on* $[\mathrm{PdCl_2(NCPh)_2}]$.—A suspension of $[\mathrm{PdCl_2(NCPh)_2}]$ (0.84 g, 2.18 mmol) was heated under reflux with the diphosphine (0.79 g, 2.18 mmol) in ethanol (25 cm^3) for 18 h. The resulting precipitate when recrystallized from dichloromethane–methanol gave *trans*-$[\mathrm{Pd_2Cl_4(Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2)_2}]$ (0.53 g, 0.95 mmol, 44%) as yellow needles, m.p. 267—284 °C (decomp.).

Action of $\mathrm{Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2}$ *on* $[\mathrm{PtCl_2(NCPh)_2}]$.—A suspension of $[\mathrm{PtCl_2(NCPh)_2}]$ (0.94 g, 2.0 mmol) in 2-methoxyethanol (20 cm^3) was treated with the diphosphine (0.79 g, 2.1 mmol) and the mixture heated under reflux for 16 h. The resulting precipitate when recrystallized from dichloromethane–methanol gave $[\{\mathrm{PtCl_2(Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2)}\}_x]$ (0.45 g, 35%) as yellow prisms. The 2-methoxyethanol mother liquor was evaporated to dryness and the residue recrystallized from light petroleum (b.p. 60—80 °C) to give white plates of $[\mathrm{PtCl(Bu^t{}_2PCH_2CH_2CMeCH_2CH_2PBu^t{}_2)}]$ (0.17 g, 0.28 mmol, 14%), m.p. 253—265 °C with sublimation. The mass spectrum showed a cluster of peaks around m/e = 604 with the intensity ratios expected for the molecular ion.

$[\mathrm{Pt(OOCCF_3)(Bu^t{}_2PCH_2CH_2CMeCH_2CH_2PBu^t{}_2)}]$.—A suspension of $[\{\mathrm{PtCl_2(Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2)}\}_x]$ (0.20 g) in a mixture of ethanol-free chloroform (1 cm^3) and trifluoroacetic acid (2 cm^3) was heated under reflux for 2 d. The resulting yellow solution was evaporated to dryness.

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

The required product formed colourless microcrystals, m.p. 253—260 °C (decomp.) from acetone. Yield 0.097 g (46%).

$[\mathrm{PtH(Bu^t{}_2PCH_2CH_2CMeCH_2CH_2PBu^t{}_2)}]$.—A suspension of the corresponding chloro-complex (0.116 g, 0.193 mmol) in ethanol (5 cm^3) was treated with sodium tetrahydroborate (0.16 g) and the mixture heated under reflux for 1 h. The resulting suspension was evaporated to dryness, the residue washed with water, and the required hydrido-complex recrystallized from ethanol. Yield 0.90 g (0.158 mmol, 82%) of colourless needles, m.p. 173—177 °C (decomp.).

TABLE 4

Fractional co-ordinates x, y, z with estimated standard deviations in parentheses

Atom	x	y	z
Pd(1)	−0.029 76	0.127 52(5)	0.076 58
Pd(2)	0.031 20(21)	−0.123 63(5)	−0.076 47(15)
Cl(1)	−0.070 2(8)	0.050 9(2)	0.016 2(5)
Cl(2)	−0.031 1(10)	0.205 4(2)	0.127 9(6)
Cl(3)	0.287 3(7)	−0.092 6(2)	0.018 8(5)
Cl(4)	−0.204 4(8)	−0.165 1(2)	−0.173 3(6)
P(1)	−0.030 4(7)	0.103 7(2)	0.265 2(4)
P(2)	0.006 6(6)	−0.142 0(2)	0.107 8(4)
P(3)	0.054 5(7)	−0.099 5(2)	−0.257.7(5)
P(4)	−0.012 6(7)	0.147 7(2)	−0.109 5(5)
C(1)	0.027(3)	0.045 1(7)	0.297(2)
C(2)	0.204(3)	0.028 8(7)	0.291(2)
C(3)	0.236(2)	−0.023 6(6)	0.306(2)
C(30)	0.405(4)	−0.033 3(11)	0.319(4)
C(4)	0.114(2)	−0.050 8(6)	0.214(2)
C(5)	0.136(2)	−0.104 4(7)	0.226(2)
C(6)	0.193(3)	−0.048 4(7)	−0.238(2)
C(7)	0.146(3)	−0.005 1(6)	−0.187(2)
C(8)	0.267(3)	0.034 2(7)	−0.170(2)
C(80)	0.442(3)	0.020 5(9)	−0.110(3)
C(9)	0.224(3)	0.078 6(7)	−0.110(2)
C(10)	0.061(3)	0.098 6(7)	−0.177(2)
C(11)	0.121(4)	0.139 1(8)	0.392(2)
C(12)	0.173(4)	0.108 2(9)	0.506(2)
C(13)	0.037(3)	0.182 9(7)	0.418(2)
C(14)	0.274(3)	0.147 5(9)	0.355(2)
C(21)	−0.240(3)	0.103 6(7)	0.272(2)
C(22)	−0.253(3)	0.090 7(10)	0.390(2)
C(23)	−0.320(4)	0.151 3(9)	0.230(3)
C(24)	−0.340(4)	0.066 9(11)	0.187(3)
C(31)	−0.208(3)	−0.131 9(6)	0.115(2)
C(32)	−0.209(3)	−0.122 4(9)	0.238(2)
C(33)	−0.272(3)	−0.086 9(7)	0.039(2)
C(34)	−0.321(3)	−0.174 3(8)	0.071(2)
C(41)	0.089(2)	−0.202 5(6)	0.159(2)
C(42)	0.057(4)	−0.217 8(8)	0.272(2)
C(43)	0.264(3)	−0.203 1(7)	0.168(3)
C(44)	−0.001(3)	−0.239 4(6)	0.070(3)
C(51)	0.157(3)	−0.146 5(8)	−0.321(2)
C(52)	0.335(4)	−0.154 7(9)	−0.229(2)
C(53)	0.071(4)	−0.193 5(8)	−0.334(3)
C(54)	0.181(3)	−0.133 0(10)	−0.430(2)
C(61)	−0.148(3)	−0.077 3(8)	−0.370(2)
C(62)	−0.249(3)	−0.054 3(8)	−0.306(2)
C(63)	−0.252(3)	−0.118 5(10)	−0.442(2)
C(64)	−0.114(4)	−0.042 8(10)	−0.456(2)
C(71)	0.132(3)	0.198 1(7)	−0.109(2)
C(72)	0.285(3)	0.193 1(8)	0.001(2)
C(73)	0.050(3)	0.246 1(7)	−0.112(2)
C(74)	0.191(3)	0.195 0(7)	−0.216(2)
C(81)	−0.236(3)	0.160 0(8)	−0.215(2)
C(82)	−0.321(3)	0.193 0(10)	−0.164(3)
C(83)	−0.327(3)	0.111 4(8)	−0.234(3)
C(84)	−0.227(4)	0.177 3(9)	−0.334(2)

Crystal Data.—$\mathrm{C_{44}H_{96}Cl_4P_4Pd_2}$, M = 1 104, Monoclinic, a = 8.616(2), b = 28.485(5), c = 12.127(2) Å, β = 109.35(2)°, U = 2 808 Å^3, D_m = 1.29 g cm^{-3}, Z = 2, D_c = 1.306 g cm^{-3}, $F(000)$ = 1 160, space group Pn (equivalent positions, x, y, z and $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$), Cu-$K_\alpha$ radiation, λ = 1.541 8 Å, μ(Cu-K_α) = 83.9 cm^{-1}.

Crystal-structure Determination.—Measurements were made on a Nonius CAD4 diffractometer using monochromatized Cu-K_α radiation. Cell dimensions and their standard deviations were obtained by least-squares fit of sin θ values for 26 reflections. Intensities of the 5 150 independent reflections to θ = 70° were measured by θ—2θ scans and the structure analysis used the 3 235 having $I > 3\sigma(I)$. Corrections were applied for Lorentz and polarization factors, and for the 8% decay shown by a control reflection during the course of data collection.

The structure was solved from Patterson and difference syntheses, and refined by least squares, using programs in the '*X*-ray' system.[12] The initial approximate positions for Pd and P obtained from the Patterson synthesis conform to the centrosymmetric space group $P2_1/n$, but not to $P2/n$ which is consistent with the systematic absences. Lowering of the symmetry to the true space group of Pn was achieved by inclusion of the chlorine atoms, and location of the carbon atoms was then straightforward. Because of this pseudo $P2_1/n$ symmetry we describe the structure in terms of a setting with the n glide plane at $y = \frac{1}{4}$ and a false symmetry centre [relating Pd(1) and Pd(2) in the same molecule] at the origin; the equivalent positions are therefore x, y, z, and $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$. Block-diagonal refinement with anisotropic temperature factors converged at R = 0.077, while reconvergence with the polarity reversed [13] gave R = 0.076, with a significant lowering of R' from 0.090 to 0.088. All hydrogen atoms were then located from a difference synthesis, and their inclusion as fixed contributions led to a final R of 0.071. A final difference map showed no features >0.3 e Å^{-3} except in the immediate vicinity of the Pd atoms. The least-squares weights $w = 1/\sigma^2(F)$ were derived from modified values for $\sigma^2(I) = \sigma_c{}^2(I) + (0.05I)^2$, $\sigma_c{}^2(I)$ being the value from counting statistics. Atomic scattering factors, including $\Delta f'$ and $\Delta f''$ were taken from ref. 14. Atomic co-ordinates and estimated standard deviations are given in Table 4.

The anisotropic vibration parameters, hydrogen-atom co-ordinates, and the observed and calculated structure factors are listed in Supplementary Publication No. SUP 22650 (30 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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