The 20-Membered Ring Binuclear Complex Bis[μ-1,7-heptanediylbis(di-*tert*-butylphosphine)]-bis(dichloropalladium)

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Abstract. $C_{46}H_{100}Cl_4P_4Pd_2$, $[Pd_2(C_{23}H_{50}P_2)_2Cl_4]$, $M_r = 1131 \cdot 8$, monoclinic, $P2_1/n$, $a = 23 \cdot 009$ (6), $b = 15 \cdot 454$ (6), $c = 17 \cdot 944$ (5) Å, $\beta = 108 \cdot 98$ (3)°, $Z = 4$, $D_x = 1 \cdot 246$ Mg m^{-3}, $V = 6033$ (3) Å^3, μ(Mo $K\alpha$) $= 0 \cdot 898$ mm^{-1}. The compound contains a 20-membered ring of rectangular shape, with the bulky *tert*-Bu$_2$P groups in the four corner positions and the *trans* P—Pd—P linkages and extended —(CH$_2$)$_7$— chains forming the sides; the macrocycle has an elongated boat ('barge') conformation.

Introduction. Measurements were made on a Syntex $P2_1$ diffractometer using monochromatized Mo $K\alpha$ radiation ($\lambda = 0 \cdot 71069$ Å). Cell dimensions and their e.s.d.'s were obtained by least-squares treatment of the setting angles for 15 reflections with $35° < 2\theta < 40°$. Of the 5657 independent F_o's in the range $5° < 2\theta < 40°$ the 3720 having $I > 3\sigma(I)$ were used in the structure analysis. Lorentz, polarization, and absorption ($A^* = 1 \cdot 10–1 \cdot 30$) corrections were applied and the structure was solved from Patterson and electron density syntheses. Least-squares refinement with isotropic temperature factors converged at $R = 0 \cdot 087$, and inclusion of anisotropic temperature factors for Pd, P, and Cl led to a final R of $0 \cdot 064$ with $R' = 0 \cdot 085$; H atoms were not included. Modified variances $\sigma^2(I) = \sigma_c^2(I) + (QI)^2$ were used, where σ_c^2 is the variance calculated from counting statistics, and least-squares weights were calculated from the corresponding expression $w^{-1} = \sigma^2(F) + \frac{1}{4}(QF)^2$; a value of $Q = 0 \cdot 05$ was found to give a fairly uniform distribution of $w\Delta^2$ as a function of F_o. The final value of $[\sum w\Delta^2/(n - m)]^{1/2}$ was $2 \cdot 15$, a reasonable value for a model which does not include H atoms or anisotropic vibrations for C. Atomic scattering factors were calculated from the analytical approximation and coefficients given in *International Tables for X-ray Crystallography* (1974).

The atomic coordinates and their e.s.d.'s (by inversion of the block-diagonal least-squares matrix) are given in Table 1.*

Discussion. Shaw and co-workers have shown (Al Salem, Empsall, Markham, Shaw & Weeks, 1979) that the bulky *tert*-butyl substituents in diphosphines of the type Bu$_2^t$P(CH$_2$)$_n$PBu$_2^t$, with $n = 5–12$, promote cyclization and form macrocyclic binuclear complexes of the type [Pd$_2$Cl$_4${Bu$_2^t$P(CH$_2$)$_n$PBu$_2^t$}$_2$]. The present compound is one of this series and the analysis was carried out to confirm the structure and to establish details of the conformation of the ring.

As may be seen in Fig. 1, the ring is of rectangular shape, with sides formed by the extended —(CH$_2$)$_7$— chains and by the *trans* P—Pd—P linkages, while the *tert*-Bu$_2$P groups form the four corners. This latter feature is indicative of the role of the *tert*-Bu substituents in promoting cyclization, since the 'right-angle bend' at P is the preferred conformation. We have found that in the complexes [PdCl$_2$(PBu$_2^t$Pr^n)$_2$] and [PdCl$_2$(PBu$_2^t$Bu^n)$_2$] the same conformation at P occurs although the structures are acyclic; the angle between the P—Pd—P and *n*-alkyl chain directions is *ca* 90° (W. S. McDonald, unpublished results). There is a slight
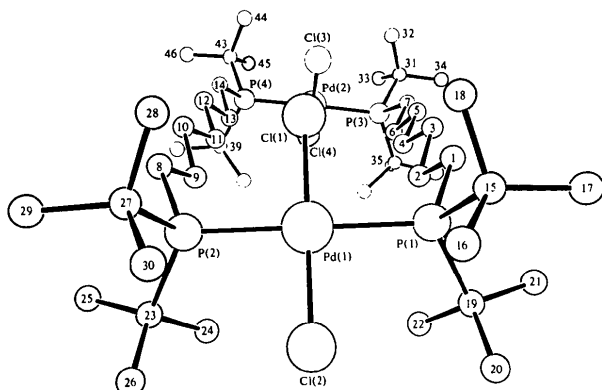

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecular structure showing the atom numbering.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34735 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates with e.s.d.'s and U_{eq} values for Pd, P and Cl, and U_{iso} for C*

E.s.d.'s for the original U_{ij} values for Pd, P and Cl are as follows: Pd 0·0007, P 0·003, Cl 0·003 Å².

	x	y	z	U_{eq} or U_{iso} (Å²)
Pd(1)	0·35098 (5)	0·64654 (8)	0·40733 (7)	0·0457
Pd(2)	0·63760 (5)	0·33771 (8)	0·11697 (7)	0·0457
P(1)	0·2649 (2)	0·5605 (3)	0·3372 (2)	0·048
P(2)	0·4364 (2)	0·7335 (3)	0·4781 (2)	0·047
P(3)	0·5470 (2)	0·2680 (3)	0·0360 (2)	0·048
P(4)	0·7237 (2)	0·4104 (3)	0·2041 (3)	0·053
Cl(1)	0·3668 (2)	0·6844 (3)	0·2905 (2)	0·065
Cl(2)	0·3287 (2)	0·6220 (3)	0·5208 (2)	0·078
Cl(3)	0·5860 (2)	0·4675 (3)	0·0887 (2)	0·060
Cl(4)	0·6943 (2)	0·2109 (3)	0·1285 (3)	0·077
C(1)	0·2688 (6)	0·5279 (9)	0·2388 (8)	0·053 (4)
C(2)	0·3287 (6)	0·4744 (10)	0·2456 (9)	0·055 (4)
C(3)	0·3348 (6)	0·4675 (10)	0·1633 (8)	0·054 (4)
C(4)	0·3964 (6)	0·4184 (9)	0·1736 (8)	0·053 (4)
C(5)	0·4042 (6)	0·3984 (9)	0·0919 (8)	0·051 (4)
C(6)	0·4655 (6)	0·3453 (9)	0·1075 (8)	0·052 (4)
C(7)	0·4755 (6)	0·3294 (9)	0·0270 (8)	0·045 (4)
C(8)	0·4922 (6)	0·7473 (9)	0·4239 (8)	0·049 (4)
C(9)	0·5193 (6)	0·6585 (9)	0·4074 (8)	0·054 (4)
C(10)	0·5602 (7)	0·6755 (10)	0·3557 (9)	0·062 (5)
C(11)	0·5831 (7)	0·5845 (10)	0·3372 (9)	0·062 (5)
C(12)	0·6300 (7)	0·5941 (10)	0·2954 (9)	0·064 (5)
C(13)	0·6548 (6)	0·5024 (10)	0·2849 (9)	0·056 (4)
C(14)	0·7007 (6)	0·5121 (10)	0·2394 (9)	0·060 (5)
C(15)	0·1932 (7)	0·6309 (10)	0·3104 (9)	0·064 (5)
C(16)	0·1871 (7)	0·6748 (11)	0·3847 (10)	0·079 (5)
C(17)	0·1330 (7)	0·5786 (11)	0·2659 (10)	0·078 (5)
C(18)	0·2037 (7)	0·7047 (11)	0·2552 (10)	0·078 (5)
C(19)	0·2520 (7)	0·4546 (10)	0·3854 (9)	0·064 (5)
C(20)	0·2185 (7)	0·4693 (11)	0·4479 (10)	0·079 (5)
C(21)	0·2163 (7)	0·3856 (11)	0·3242 (10)	0·073 (5)
C(22)	0·3202 (7)	0·4188 (11)	0·4310 (10)	0·069 (5)
C(23)	0·4841 (6)	0·6906 (10)	0·5788 (9)	0·057 (4)
C(24)	0·4875 (7)	0·5914 (10)	0·5731 (9)	0·066 (5)
C(25)	0·5526 (7)	0·7281 (10)	0·6040 (9)	0·068 (5)
C(26)	0·4583 (7)	0·7147 (11)	0·6463 (10)	0·074 (5)
C(27)	0·4102 (7)	0·8493 (10)	0·4856 (9)	0·068 (5)
C(28)	0·3860 (9)	0·8848 (13)	0·3978 (12)	0·101 (7)
C(29)	0·4599 (8)	0·9091 (11)	0·5350 (10)	0·082 (6)
C(30)	0·3546 (8)	0·8466 (12)	0·5160 (11)	0·086 (6)
C(31)	0·5451 (6)	0·2655 (10)	−0·0710 (9)	0·059 (4)
C(32)	0·5441 (7)	0·3597 (11)	−0·0969 (10)	0·072 (5)
C(33)	0·6065 (7)	0·2242 (12)	−0·0760 (10)	0·083 (6)
C(34)	0·4901 (8)	0·2144 (12)	−0·1252 (11)	0·088 (6)
C(35)	0·5319 (7)	0·1573 (10)	0·0743 (9)	0·061 (4)
C(36)	0·4621 (7)	0·1342 (11)	0·0465 (10)	0·078 (5)
C(37)	0·5557 (7)	0·1618 (11)	0·1671 (10)	0·073 (5)
C(38)	0·5661 (7)	0·0827 (11)	0·0474 (10)	0·074 (5)
C(39)	0·7662 (7)	0·3495 (10)	0·2973 (9)	0·066 (5)
C(40)	0·8142 (8)	0·2829 (12)	0·2846 (10)	0·083 (6)
C(41)	0·7991 (7)	0·4127 (11)	0·3680 (10)	0·081 (5)
C(42)	0·7164 (7)	0·2946 (11)	0·3189 (9)	0·068 (5)
C(43)	0·7768 (7)	0·4487 (11)	0·1480 (10)	0·075 (5)
C(44)	0·7962 (9)	0·3712 (13)	0·1073 (12)	0·107 (7)
C(45)	0·8336 (8)	0·4993 (13)	0·2028 (12)	0·100 (7)
C(46)	0·7388 (8)	0·5114 (12)	0·0858 (11)	0·095 (6)

Table 2. *Bond lengths (Å) and angles (°) with their e.s.d.'s*

Pd(1)–P(1)	2·378 (4)	P(1)–Pd(1)–P(2)	179·4 (2)
Pd(1)–P(2)	2·379 (4)	P(3)–Pd(2)–P(4)	175·7 (2)
Pd(2)–P(3)	2·376 (4)	Cl(1)–Pd(1)–Cl(2)	173·9 (2)
Pd(2)–P(4)	2·370 (4)	Cl(3)–Pd(2)–Cl(4)	171·1 (2)
Pd(1)–Cl(1)	2·316 (5)	P(1)–Pd(1)–Cl(1)	90·7 (1)
Pd(1)–Cl(2)	2·287 (5)	P(1)–Pd(1)–Cl(2)	89·3 (2)
Pd(2)–Cl(3)	2·302 (4)	P(2)–Pd(1)–Cl(1)	89·7 (1)
Pd(2)–Cl(4)	2·326 (4)	P(2)–Pd(1)–Cl(2)	90·2 (2)
P(1)–C(1)	1·87 (2)	P(3)–Pd(2)–Cl(3)	88·5 (1)
P(1)–C(15)	1·90 (2)	P(3)–Pd(2)–Cl(4)	91·6 (1)
P(1)–C(19)	1·92 (2)	P(4)–Pd(2)–Cl(3)	89·6 (1)
P(2)–C(8)	1·86 (2)	P(4)–Pd(2)–Cl(4)	91·0 (1)
P(2)–C(23)	1·90 (2)		
P(2)–C(27)	1·91 (2)	Pd–P–C	108·6–117·6 (5)
P(3)–C(7)	1·86 (2)	Average	112·5
P(3)–C(31)	1·91 (2)		
P(3)–C(35)	1·92 (2)		
P(4)–C(14)	1·84 (2)		
P(4)–C(39)	1·89 (2)		
P(4)–C(43)	1·91 (2)		

C–C   1·51–1·61 (3)
Average   1·560

twist of 7° between the two P–Pd–P linkages at the ends of the ring, a very small distortion when distributed over the seven methylene groups of the chain. The eclipsing of the *tert*-Bu₂P groups across the P–Pd–P linkage has been discussed in an earlier paper (Constable, McDonald & Shaw, 1979) and contrasts with the staggered conformation reported for the polymethylenediamine analogues in that paper. Bond lengths and angles listed in Table 2 show no abnormal values.

References

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