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THE CRYSTAL AND MOLECULAR STRUCTURE OF sym-*trans*-DI-μ-ACETATOBIS[*o*-(t-BUTYL-*o*-TOLYLPHOSPHINO)BENZYL]DIPALLADIUM-(II), A COMPLEX FORMED BY AN INTERNAL METALLATION REACTION

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Summary

The structure of $[Pd(OAc)\{CH_2C_6H_4P\text{-t-Bu}(o\text{-tolyl})\}]_2$ has been determined from three dimensional X-ray diffractometer data. The compound crystallizes in the space group $P\bar{1}$, $Z = 2$, with a reduced triclinic unit cell $a = 12.989$, $b = 15.643$, $c = 20.325$ Å, $\alpha = 130.85$, $\beta = 117.91$, $\gamma = 94.08°$. A least squares refinement of atomic positional and thermal parameters, based on 5436 observed reflections has converged to discrepancy indices, R_1 and R_2, of 0.044 and 0.058.

The structure consists of independent dimeric molecules packed with cyclohexane molecules of crystallization. [*o*-(t-butyl-*o*-tolylphosphino)benzyl]palladium(II) fragments are bridged by the two acetate groups so that each palladium has a slightly distorted planar coordination; the molecule has approximate C_2 symmetry with a Pd...Pd non-bonding distance of 3.413(1) Å. The mean Pd—P and Pd—C bond lengths are 2.204(2) and 2.033(5) Å respectively, other mean distances being Pd—O 2.13(1), C—C(methyl) 1.497(4), O—C(acetate) 1.247(6), C—C(benzyl) 1.497(7) Å. The solvated cyclohexane molecules are disordered.

Introduction

Much interest has been shown in the ability of a range of transition metal complexes to undergo intramolecular reactions to form metal—carbon bonds. The cleavage of aryl carbon—hydrogen bonds in, for example, Ir^I [1] complexes, is well characterized. More recently, reactions of phosphine complexes of palladium(II) and platinum(II) have been studied, in which intramolecular oxidative addition of the metal to primary, secondary and tertiary carbon—hydrogen bonds takes place [2, 3]. The title compound, prepared by the internal metallation at a tolyl-methyl carbon of the bis(*o*-tolyl)(t-butyl)phosphine ligand [3], is the first X-ray characterisation of this class of compounds and forms part of our general studies of the stereochemistries of *ortho*-metallation reactions in mononuclear, binuclear and polynuclear complexes [4-8].

Experimental

Crystal data

$[Pd(OAc)(CH_2C_6H_4P\text{-t-Bu})(o\text{-tolyl})]_2.C_6H_{12}$, $Pd_2P_2O_4C_{46}H_{62}$, $M = 953.7$, triclinic, the cell used was $a = 12.989(4)$, $b = 15.643(6)$, $c = 11.598(4)$ Å, $\alpha = 82.95(1)°$, $\beta = 101.75(1)°$, $\gamma = 85.92(1)°$, $U = 2278.4$ Å^3, D_m (by flotation in carbon tetrachloride and chlorobenzene) = 1.40(2) g cm^{-3}, $D_c = 1.39$ g cm^{-3} for $Z = 2$, $F(000) = 984$. The Delaunay reduced cell is: $a = 12.989$, $b = 15.643$, $c = 20.325$ Å, $\alpha = 130.85$, $\beta = 117.91$, $\gamma = 94.08°$. Space group (from structure solution), $P\bar{1}$. Cell data at ambient room temperature, with estimated standard deviations from the least squares refinement [9] of the setting angles for 12 reflections (average θ of 14.2°) automatically centred on a 4-circle diffractometer, λ (Mo-K_α) = 0.71069 Å. As a white powder formed on the surface of the pale cream crystals over several days exposure in air, the data crystal was coated with plastic spray.

Intensity data for reflections with $4° \leqslant 2\theta \leqslant 50°$ were collected on a Hilger—Watts Y290 4-circle diffractometer, using a standard $\omega/2\theta$ scan with background measurements at the extremities of each peak. The incident beam of Mo-K_α radiation was filtered through a zirconium foil. The diffracted rays were collected by a circular aperture of radius 3.5 mm placed 260 mm from the crystal. Each background measurement was made for 25 seconds and the peak intensity was accumulated over 50 steps, each of 0.01°, with a count time of one second at each point. No systematic variation in any of the three standard reflections was observed. The 5436 reflections with $I \geqslant 3\sigma(I)$, where I = Peak Count — Background (1) — Background (2), $\sigma(I)$ = (Peak Count + Background (1) + Background (2))$^{1/2}$ were corrected for Lorentz and polarization effects.

The crystal was approximately a rectangular parallelepiped 0.30 × 0.25 × 0.35 mm. As test runs for an absorption correction ($\mu = 8.9$ cm^{-1}) using program ABSCOR [10] showed a maximum variation of 4 percent in transmission coefficients, no correction was applied.

Solution and refinement

The two independent palladium atoms were located from a three-dimensional unsharpened Patterson function [10]. The difference Fourier synthesis phased by these two atoms provided the positions of all the non-hydrogen atoms with the exception that the cyclohexane carbon atoms were poorly resolved (ρ_{max} 1.4 - 1.8 e Å^{-3} compared with the 2.1 e Å^{-3} of the next 'lowest' carbon atom).

Refinement was carried out using program CRYLSQ [10] in the free-blocking mode minimising the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes and w a weighting function. Unit weights were applied to all reflections in initial cycles. The final weights were the product of two quantities X and Y for each reflection: $X = 1.0$ for $\sin\theta \geqslant 0.34$, $X = \sin\theta/0.34$ for $\sin\theta < 0.34$, $Y = 1.0$ for $F_o < 65.0$ and $Y = 65.0/F_o$ for $F_o > 65.0$.

In all calculations of F_c, the atomic scattering factors for Pd, P, O and C were taken from Cromer and Waber [11], those for H from Stewart, Davidson and Simpson [12]. The effects of anomalous dispersion for Pd and P were included in the F_c calculations using the values of $\Delta f'$ and $\Delta f''$ given by Cromer [13]. Agreement factors quoted are $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (weighted residual) $= (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$.

The refinement of all positional parameters, anisotropic thermal parameters for the palladium and phosphorus atoms, and isotropic thermal parameters for the remaining fifty atoms converged to $R_1 = 0.094$. At this point, the isotropic thermal parameters for the cyclohexane carbon atoms were unrealistically high (average $U = 0.24$ Å^2). These six atoms were withdrawn to give converged indices, $R_1 = 0.070$ and $R_2 = 0.115$. Examination of the subsequent difference Fourier synthesis suggested that the cyclohexane ring was disordered. Attempts at refining occupancies for these six atoms were not completely successful, with neither significant improvement in R_2 nor physically reasonable parameters resulting from the refinement. A typical refinement gave between 25 and 45 percent occupancies for the six atoms. As the electron density contours approximated a (flattened) chair conformation undergoing rather extreme anisotropic thermal motion, this model was used in the remaining refinements. No physical meaning should be attached to the final geometry for the cyclohexane carbons, (C(71) - C(76)). The atoms of the acetate groups O(1), O(2), O(3), O(4), C(2), C(3), C(5) and C(6) also appeared to be vibrating anisotropically; however, their thermal parameters were reasonable being only slightly higher than the mean for the remaining carbon atoms.

After allocation of anisotropic thermal parameters to these fourteen atoms, the refinement converged to $R_1 = 0.056$ and $R_2 = 0.069$. Plots of R_2 against ranges of F_o and sin θ/λ led to the final weighting scheme above and the removal of 13 reflexions apparently suffering from extinction or other systematic errors. A difference Fourier indicated all the hydrogen atoms, ($\rho = 0.6$ - 1.0 e Å^{-3}) except those of the cyclohexane molecule. For the final cycles, hydrogen atoms (excluding those of cyclohexane placed in reasonable stereochemical positions) were included but not refined from their idealised positions (C—H 1.05 Å; tetrahedral or D_{6h} symmetry; $U_h = 0.07$ Å^2). The final converged R_1 and R_2 values were 0.044 and 0.058 respectively. The final difference Fourier synthesis had no excursions of magnitude greater than 0.5 e Å^{-3}, and these were all within 1 Å of the Pd atoms.

The final atomic positional and thermal parameters, together with their standard deviations as derived from the inverse matrix, are given in Table 1. A Table listing the final values of $10|F_o|$ and $10|F_c|$ (in electrons) may be obtained from the authors. Fig. 1 depicts atom labelling while Fig. 2 illustrates atomic thermal motions (50% probability ellipsoid surfaces). Fig. 3 shows details of the coordination of the two palladium atoms and some other significant bond lengths and bond angles.

Description and discussion of the molecular structure

The figures illustrate the crystal structure as being built up from bis(μ-acetato)palladium(II) complexes with solvated cyclohexane molecules; contrary to

(continued on p. 401)

TABLE 1a

ATOMIC PARAMETERS (X 10^4) AND THEIR ESTIMATED STANDARD DEVIATIONS FOR NON-HYDROGEN ATOMS

Atom	X	Y	Z	U^a
Pd(1)	1934 0(3)	1020 4(2)	3529.8(3)	See below
Pd(2)	541.5(3)	3015 5(2)	2831.1(3)	"
P(1)	2466(1)	362 0(8)	2152(1)	"
P(2)	−1179(1)	3257 4(8)	2690(1)	"
O(1)	3102(3)	1919(2)	3650(4)	"
O(2)	2144(3)	3150(3)	2759(4)	"
O(3)	1547(4)	1380(3)	5105(3)	"
O(4)	1012(3)	2786(3)	4728(3)	"
C(71)	5107(18)	2892(14)	7041(22)	"
C(72)	5036(25)	2440(16)	8205(26)	"
C(73)	4839(27)	2859(15)	9042(23)	"
C(74)	4559(25)	3802(20)	8812(23)	"
C(75)	4534(25)	4258(15)	7647(20)	"
C(76)	4804(25)	3825(15)	6767(25)	"
C(2)	3004(4)	2701(4)	3230(5)	"
C(3)	3987(6)	3143(5)	3255(9)	"
C(5)	1433(4)	2113(3)	5400(4)	"
C(6)	1843(6)	2213(4)	6681(5)	"
C(1)	894(5)	108(4)	3495(5)	631(14)
C(4)	142(5)	3357(4)	1037(5)	588(13)
C(11)	1132(4)	− 675(4)	2922(5)	550(12)
C(12)	648(5)	−1430(4)	3091(6)	683(15)
C(13)	924(6)	−2145(5)	2570(6)	760(17)
C(14)	1651(5)	−2123(4)	1885(6)	704(16)
C(15)	2144(5)	−1376(4)	1698(5)	610(13)
C(16)	1884(4)	− 658(3)	2225(5)	520(11)
C(21)	3895(4)	77(4)	2459(5)	555(13)
C(22)	4504(6)	453(5)	1701(6)	756(17)
C(23)	5607(7)	278(5)	1970(8)	933(22)
C(24)	6069(7)	− 259(6)	2975(8)	961(23)
C(25)	5506(6)	− 632(5)	3720(7)	837(19)
C(26)	4401(5)	− 479(4)	3497(5)	613(14)
C(27)	3834(6)	− 909(5)	4386(6)	753(17)
C(30)	1950(4)	913(4)	597(5)	567(13)
C(31)	2294(5)	1827(4)	433(6)	684(15)
C(32)	2216(6)	378(5)	− 348(7)	870(20)
C(33)	735(6)	994(5)	467(6)	751(17)
C(41)	− 894(4)	3881(3)	547(5)	520(12)
C(42)	−1139(5)	4366(4)	− 588(6)	681(15)
C(43)	−2095(6)	4857(5)	− 990(7)	793(18)
C(44)	−2828(6)	4872(5)	− 305(7)	802(18)
C(45)	−2616(5)	4385(4)	829(6)	665(15)
C(46)	−1654(4)	3895(3)	1232(5)	512(12)
C(51)	−1527(4)	3934(3)	3757(5)	520(12)
C(52)	−2034(5)	3619(4)	4643(6)	701(16)
C(53)	−2285(6)	4134(5)	5464(7)	800(18)
C(54)	−2022(6)	4961(5)	5403( )	828(19)
C(55)	−1481(6)	5283(5)	4572(6)	753(17)
C(56)	−1224(5)	4786(4)	3728(5)	593(13)
C(57)	− 632(5)	5191(4)	2866(6)	732(16)
C(60)	−1964(4)	2295(4)	2665(5)	569(13)
C(61)	−1522(5)	1632(4)	3783(6)	700(16)
C(62)	−1760(5)	1877(4)	1583(6)	741(17)
C(63)	−3164(6)	2530(5)	2492(6)	775(18)

TABLE 1b

ANISOTROPIC[a] TEMPERATURE FACTORS AND THEIR ESTIMATED STANDARD DEVIATIONS ($\times 10^4$) FOR ATOMS Pd(1)—C(6)

Atom	*U*(1,1)	*U*(2,2)	*U*(3,3)	*U*(1,2)	*U*(1,3)	*U*(2,3)
Pd(1)	571(2)	419(2)	392(2)	41(2)	133(2)	−20(2)
Pd(2)	502(2)	416(2)	454(2)	18(2)	96(2)	−13(2)
P(1)	526(7)	417(6)	393(6)	31(5)	126(5)	−24(5)
P(2)	500(7)	434(6)	395(6)	8(5)	113(5)	−33(5)
O(1)	610(23)	536(20)	679(23)	21(17)	56(18)	−33(17)
O(2)	543(22)	589(23)	890(29)	17(18)	148(20)	86(20)
O(3)	1026(32)	568(22)	523(20)	54(21)	317(21)	−63(17)
O(4)	841(28)	588(22)	501(20)	92(20)	−6(19)	−110(17)
C(71)	2555(215)	2123(182)	2014(195)	574(159)	611(176)	−854(158)
C(72)	3239(344)	1863(193)	2490(243)	478(198)	563(245)	−878(181)
C(73)	4462(420)	2073(180)	2351(241)	−183(222)	1103(256)	−688(170)
C(74)	3658(363)	2810(290)	2970(247)	505(261)	1342(240)	−1617(225)
C(75)	3498(348)	2180(214)	2376(193)	1022(223)	104(203)	−1034(167)
C(76)	3585(361)	2199(204)	2976(258)	1000(225)	1440(252)	112(184)
C(2)	528(30)	543(30)	640(32)	−30(24)	175(25)	−54(24)
C(3)	559(39)	883(51)	1435(74)	−69(35)	157(43)	80(48)
C(4)	570(31)	573(29)	454(26)	15(24)	157(23)	−55(22)
C(6)	948(47)	741(39)	463(30)	38(34)	41(30)	−53(27)

TABLE 1c

HYDROGEN ATOMIC COORDINATES ($\times 10^4$)[b]

Atom	*X*	*Y*	*Z*
H(101)[c]	153	407	3035
H(102)[c]	865	−111	4380
H(401)[c]	127	2785	647
H(402)[c]	732	3718	786
H(31)	4532	2937	4066
H(32)	4292	2971	2550
H(33)	3811	3818	3161
H(61)	1435	1848	7232
H(62)	1755	2866	6800
H(63)	2635	1979	6857
H(271)	3248	−463	4548
H(272)	4377	−1139	5179
H(273)	3471	−1431	4035
H(311)	3122	1772	607
H(312)	2008	2182	−420
H(313)	2024	2169	1054
H(321)	1631	−48	−537
H(322)	2246	773	−1141
H(323)	2952	17	−12
H(331)	474	391	709
H(332)	498	1442	988
H(333)	446	1211	−437
H(571)	−123	4703	2671
H(572)	−1173	5469	2093
H(573)	−170	5677	3193
H(611)	−1823	1056	3581
H(612)	−1783	1827	4522
H(613)	−694	1559	3968

(continued)

TABLE 1c (continued)

Atom	*X*	*Y*	*Z*
H(621)	−1933	2342	821
H(622)	− 965	1628	1744
H(623)	−2246	1373	1450
H(631)	−3229	2753	3299
H(632)	−3446	3017	1768
H(633)	−3581	1984	2373
H(12)	73	−1465	3610
H(13)	558	−2716	2714
H(14)	1838	−2668	1495
H(15)	2706	−1355	1162
H(22)	4128	870	925
H(23)	6061	563	1401
H(24)	6894	− 396	3174
H(25)	5906	−1043	4489
H(42)	− 594	4350	−1140
H(43)	−2255	5231	−1832
H(44)	−3555	5247	− 628
H(45)	−3179	4393	1361
H(52)	−2230	2977	4695
H(53)	−2680	3888	6117
H(54)	−2235	5359	6000
H(55)	−1256	5914	4570

[a] Temperature factors are of the form: $T = \exp{-2\pi^2[U(1,1)h^2a^{*2} + ... 2U(1,2)hka^*b^*....]}$. [b] H atom numbers for the phenyl groups are the same number as the carbon to which they are bound; H atom numbers for methylene and methyl carbons are of the form H *nm* where *n* is the carbon atom number and *m* is 1,2 or 3 distinguishing up to 3 H's. [c] Exceptions to the general numbering system: H(101), H(102) are bound to C(1); H(401), H(402) are bound to C(4)

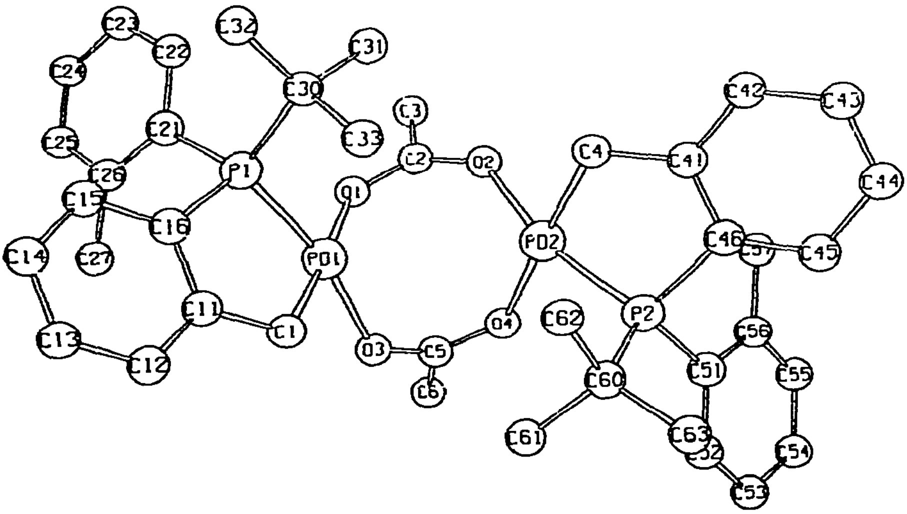

Fig. 1. $[Pd(OAc)(CH_2C_6H_4P\text{-t-Bu}(o\text{-tolyl}))]_2$. A projection of the molecule down its approximate two-fold axis and atom labelling.

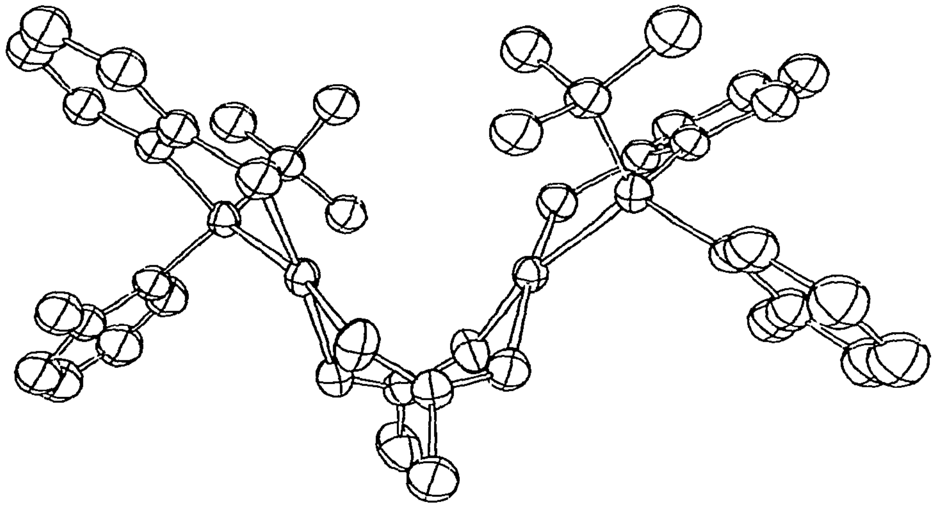

Fig. 2. $[Pd(OAc)(CH_2C_6H_4P\text{-t-Bu}(o\text{-tolyl}))]_2$. Atomic thermal motions depicted by 50% probability surfaces

our expectation, the 'basket' of the binuclear complex is not sufficiently large to semi-clathrate the solvated cyclohexane.

The formation of two palladium—carbon bonds of mean length 2.033(5) Å has followed intramolecular palladation of the tolyl-methyl carbon—hydrogen bond. The μ-acetato ligands span the internally metallated species so as to provide approximate C_2 symmetry to the complex; this symmetry axis is normal to the plane of Fig. 1 and the close similarity of chemically equivalent bonds is brought out in the listings of Table 2.

In contrast to bis(π-allylpalladium acetate) [14] where acetate bridging provides a palladium—palladium bonding distance of 2.944(2) Å, (cf. 2.95 Å in bis(dimethylphenylphosphine)chloropalladium acetate [15]), the metal—metal separation of 3.413(1) Å in the present complex is held to be non-bonding.

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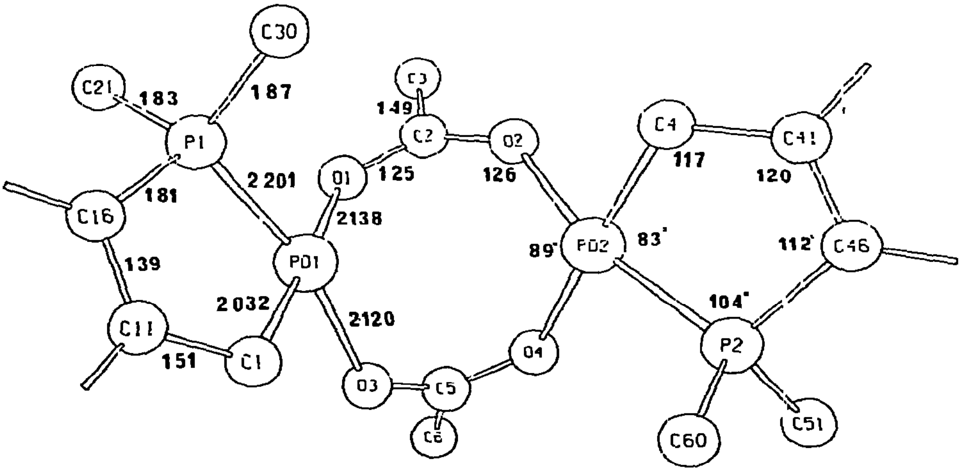

Fig. 3. $[Pd(OAc)(CH_2C_6H_4P\text{-t-Bu}(o\text{-tolyl}))]_2$. Some important intramolecular dimensions.

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°)

(i) Around the palladium atoms			
Pd(1)—P(1)	2.201(2)	Pd(2)—P(2)	2.208(2)
Pd(1)—C(1)	2.032(7)	Pd(2)—C(4)	2.033(6)
Pd(1)—O(1)	2.137(4)	Pd(2)—O(4)	2.138(4)
Pd(1)—O(3)	2.120(4)	Pd(2)—O(2)	2.125(4)
P(1)—Pd(1)—O(1)	95.9(1)	P(2)—Pd(2)—O(4)	98.0(1)
P(1)—Pd(1)—C(1)	83.8(2)	P(2)—Pd(2)—C(4)	83.2(2)
P(1)—Pd(1)—O(3)	166.9(1)	P(2)—Pd(2)—O(2)	164.1(1)
O(1)—Pd(1)—O(3)	89.2(2)	O(2)—Pd(2)—O(4)	88.6(2)
O(3)—Pd(1)—C(1)	90.3(2)	O(2)—Pd(2)—C(4)	88.8(2)
O(1)—Pd(1)—C(1)	176.2(2)	O(3)—Pd(2)—C(4)	174.2(2)
(ii) Around the phosphorus atoms			
P(1)—C(16)	1.814(6)	P(2)—C(46)	1.819(5)
P(1)—C(21)	1.829(6)	P(2)—C(51)	1.827(6)
P(1)—C(30)	1.868(5)	P(2)—C(60)	1.878(6)
Pd(1)—P(1)—C(16)	104.6(2)	Pd(2)—P(2)—C(46)	104.0(2)
Pd(1)—P(1)—C(21)	113.6(2)	Pd(2)—P(2)—C(51)	113.6(2)
Pd(1)—P(1)—C(30)	114.7(2)	Pd(2)—P(2)—C(60)	117.4(2)
C(16)—P(1)—C(21)	105.8(3)	C(46)—P(2)—C(51)	105.8(2)
C(16)—P(1)—C(30)	105.3(3)	C(46)—P(2)—C(60)	104.8(2)
C(21)—P(1)—C(30)	111.8(3)	C(51)—P(2)—C(60)	110.0(3)
(iii) The acetate ligands			
O(1)—C(2)	1.247(6)	O(4)—C(5)	1.247(6)
O(3)—C(5)	1.244(8)	O(2)—C(2)	1.259(6)
C(2)—C(3)	1.492(10)	C(5)—C(6)	1.504(8)
Pd(1)—O(1)—C(2)	123.7(3)	Pd(2)—O(2)—C(2)	133.8(4)
Pd(1)—O(3)—C(5)	129.2(4)	Pd(2)—O(4)—C(5)	129.8(4)
O(1)—C(2)—C(3)	117.7(5)	O(2)—C(2)—C(3)	116.6(5)
O(3)—C(5)—C(6)	117.8(5)	O(4)—C(5)—C(6)	116.0(5)
O(1)—C(2)—O(2)	125.7(7)	O(3)—C(5)—O(4)	126.2(5)

(iv) The benzyl ligands

	Min.	Max.	Range	Number	Weighted mean
C—C(methylene)	1.491(7)	1.506(9)	0.015	2	1.479(6)
C—C(phenyl)	1.352(11)	1.401(9)	0.049	12	1.385(3)
o tolyl group					
C—C(phenyl)	1.351(11)	1.415(8)	0.064	12	1.388(3)
C—C(methyl)	1.489(10)	1.505(10)	0.016	2	1.497(7)
t-butyl group					
C—C	1.529(9)	1.549(9)	0.020	6	1.540(4)
P—C—C	103.9(4)	113.9(4)	10.0	6	109.5(2)
C—C—C	107.9(5)	112.1(6)	4.2	6	109.3(2)
(v) The cyclohexane[a] solvated molecule					
C—C	1.29	1.47	0.18	6	1.42

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[a] See text about disorder.

TABLE 3

PLANES CONTAINING SELECTED GROUPS OF ATOMS: DISTANCES (Å × 10^3) OF ATOMS FROM MEAN PLANE ARE GIVEN IN PARENTHESES

Plane	Atoms defining plane						Other atoms		Equation of planes expressed as $Px + Qy + Rz - S = 0$			
1	Pd(1)(46)	C(1)(−24)	O(1)(−22)	O(3)(0)			P(1)(−362)		−7.101	9.015	−4.090	−1.943
2	Pd(2)(−64)	C(4)(33)	O(2)(1)	O(4)(32)			P(2)(410)		−0.791	15.462	2.674	5.412
3	O(1)(72)	O(3)(−79)	C(1)(83)	P(1)(−76)			Pd(1)(147)		−6.648	8.470	−1.997	−2.332
4	O(2)(−85)	O(4)(−75)	C(4)(90)	P(2)(80)			Pd(2)(−183)		0.471	12 589	2.341	5.573
5	Pd(1)(149)	P(1)(−70)	O(1)(7)	O(3)(−72)			C(1)(163)		−6.264	8 896	−5.024	−2.226
6	Pd(2)(−177)	P(2)(82)	O(2)(84)	O(4)(12)			C(4)(−162)		0.451	15.533	2.766	5.669
7	Pd(1)(118)	P(1)(−105)	C(1)(55)	O(1)(42)	O(3)(109)				−6.650	8.465	−5.000	−2.304
8	Pd(2)(−146)	P(2)(116)	C(4)(55)	O(2)(122)	O(4)(−37)				0 470	15 588	2.350	5 537
9	C(11)(−1)	C(12)(−4)	C(13)(4)	C(14)(1)	C(15)(−4)	C(16)(4)	P(1)(73)	Pd(1)(541)	7 509	− 2 822	7.474	3 174
10	C(41)(9)	C(42)(−7)	C(43)(1)	C(44)(3)	C(45)(−1)	C(46)(−5)	P(2)(73)	Pd(2)(644)	4.823	13.541	4.882	5 082
11	C(21)(0)	C(22)(0)	C(23)(−1)	C(24)(2)	C(25)(2)	C(26)(1)	P(1)(108)	C(27)(20)	0.422	13.460	7.015	1.993
12	C(51)(−17)	C(52)(12)	C(53)(6)	C(54)(−18)	C(55)(11)	C(56)(6)	P(1)(13)	C(57)(45)	9.694	− 3.018	4.794	−0.850

TABLE 4

INTERMOLECULAR (NON-BONDED) DISTANCES (Å)

Atoms		D	Atoms		D
(i) Between dimers[a]					
Pd(1)	H(25)[b]	3.25	H(33)	H(54)	2.75
O(1)	C(25)	3.52	H(61)	H(12)	2.16
O(1)	H(25)	2.47	H(62)	H(55)	2.29
O(2)	C(43)	3.50	H(63)	H(24)	2.51
O(2)	H(43)	2.65	H(321)	H(623)	2.59
O(3)	H(24)	2.76	H(323)	H(23)	2.47
O(4)	H(55)	2.30	H(331)	H(331)	2.37
C(5)	H(12)	2.66	H(42)	H(571)	2.54
C(6)	C(12)	3.59	H(572)	H(42)	2.76
C(12)	H(12)	2.80	H(573)	H(42)	2.76
C(12)	H(612)	2.83	H(612)	H(12)	2.74
H(102)	H(611)	2.65	H(613)	H(12)	2.74
H(402)	H(43)	2.84	H(621)	H(14)	2.70
H(33)	H(43)	2.53	H(24)	H(63)	2.51
(ii) Between dimers and "cyclohexane"					
C(71)	H(273)	3.35			
C(72)	H(15)	3.18			
C(74)	H(44)	3.16			
C(74)	H(45)	3.20			
H(75)	H(45)	3.12			
(iii) Selected intramolecular distances					
Pd(1)	Pd(2)	3.413			
Pd(1)	H(102)	2.55	Pd(2)	H(401)	2.56
Pd(1)	H(101)	2.55	Pd(2)	H(402)	2.56
Pd(1)	H(271)	2.76	Pd(2)	H(571)	2.69
Pd(1)	H(313)	3.22	Pd(2)	H(613)	3.19

[a] All non-hydrogen contacts to 3.6 Å; all C..H, H..H and O..H to 2.8 Å. [b] Second atom coordinates generated by transformation $-x$, $-y$, $-z$ on those in Table 2

It is presumably the oxygen—oxygen chelate bite distance that requires the coordination planes around the metal atoms in both π-allylpalladium acetate and the present complex to have quite accurately the eclipsed conformation. In the π-allyl complex, the dihedral angle between the two planes containing the relevant palladium and acetato-oxygen atoms is 29° whereas it is 48° in this complex. We imagine that this difference, which is reflected, of course, in the changing metal—metal bond distance, is largely due to intramolecular steric overcrowding between the bulky phosphine ligands. There are other data which relate directly to this suggestion, and which can be summarised by the view that the coordination stereochemistry of each palladium atom is a compromise between its normal planar arrangement and a required planar stereochemistry of the phosphino-benzyl moiety of the [2-(t-butyl-*o*-tolylphosphino)benzyl] ligand. Some planes, calculated by least squares methods, through various groups of atoms are collected in Table 3. Both phosphorus atoms are displaced 0.4 Å from the coordination planes of the palladium atoms defined by the acetate ligands. The five-membered chelate rings (Pd(1)—C(1)—C(11)—C(16)—P(1);

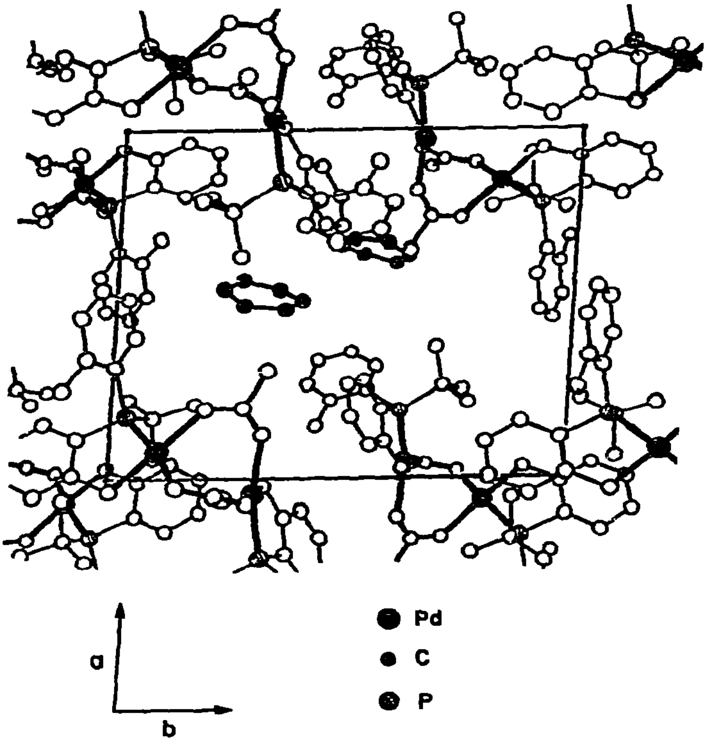

Fig. 4. $[Pd(OAc)(CH_2C_6H_4P\text{-}t\ Bu(o\text{-}tolyl))]_2$. The crystal packing viewed down the 'c' axis

Pd(2)—C(4)—C(41)—C(46)—P(2)) are respectively quite planar with the r.m.s. deviations of the atoms being 0.09 and 0.10 Å, respectively; they impose a competition via the phosphorus atoms between the preferred planar geometries of the benzyl ring and palladium atoms. The resultant strain may be reflected in the metal—phosphorus bond lengths, which are somewhat shorter than those found in $(Me_2PhP)_2PdCl_2$ [16] and, for example, in $(C_{12}H_9N_2)(PEt_3)_2PdCl$ [17], but this may simply reflect differing *trans* influences of the ligands in these complexes; one is on more certain ground to associate distortions in the bond angles about the phosphorus and benzyl-carbon atoms with the strain effects imposed by chelation and substituent-group repulsions.

The Pd—O bond lengths are entirely comparable with those in π-allylpalladium acetate and in the trimers $[Pd(OAc)(ONCMe_2)]_3$ [18] and $[Pd(OAc)_3]$ [19]. They are demonstrative of the benzyl-carbon atom having a comparable *trans* influence to the phosphorus of a tertiary phosphine, which is compatible with earlier comments and explanations [20, 21].

There are no close contacts between the solvated cyclohexane and the palladium complex; rather the solvated molecules fit into rather large holes (Fig. 4; Table 4) with few translational constraints. It is hardly surprising, therefore, that so much uncertainty attaches to our definition of the molecular parameters. The final atomic coordinates correspond to a near-planar conformation and we have no reason to believe that this is anything but a poor space-averaged description of the several alternative chain conformations. Fortunately, this uncertainty has not prevented an accurate analysis of the geometry of the binuclear complex.

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