Acta Cryst. (1995). C**51**, 208–210

trans-Bromo(*o*-tolyl)bis(triphenylphosphine)palladium(II) Crystals With and Without Stacking Faults

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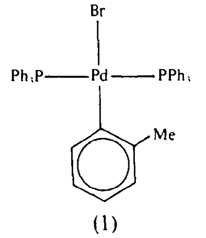
(*Received* 8 *July* 1994; *accepted* 3 *August* 1994)

Abstract

In *trans*-[$PdBr(C_7H_7)(C_{18}H_{15}P)_2$] the Pd atom has almost regular square-planar coordination geometry; the length of the Pd—Br bond [2.517 (2) Å] indicates that the σ-tolyl group exerts a strong *trans* influence. The molecular structure obtained from an ordered crystal is indistinguishable from that derived from a crystal with a stacking fault.

Comment

trans-[$PdBr(o\text{-}CH_3C_6H_4)(PPh_3)_2$] (1) was prepared as a precursor in the course of a study of complexes containing coordinated solvent. Colourless crystals were obtained from CH_2Cl_2/Et_2O solutions of the products of the reactions between either [$Pd(PPh_3)_4$] and *o*-bromotoluene or between *trans*-[$PdCl_2(PPh_3)_2$] and Li(*o*-tolyl) in the presence of LiBr. X-ray analysis of (1), using material derived from the first of these reactions, was undertaken for comparison with the structure of the chelate complex [$PdBr\{(Cy_2PCH_2)_2C_6H_3\}$] (2) [Cy = cyclohexyl (Cross, Kennedy & Muir, 1994)], in which the σ-aryl ring is held nearly coplanar with the Pd coordination plane. No Pd^{II}–tolyl complexes have been structurally characterized, although the structures of several Pt^{II}(*o*-tolyl) complexes have been reported (Rieger, Carpenter & Rieger, 1993; Terheijden, van Koten, Vinke & Spek, 1985; Hutton, Pringle & Shaw, 1985).



(1)

The molecular structure of (1), based on an ordered crystal (specimen *B*, see below), comprises a Pd atom with square-planar coordination geometry distorted only slightly by out-of-plane displacement of Br(1) and C(1) so that the Br(1)—Pd(1)—C(1) angle is 170.9 (3)° (see Fig. 1 and Tables 1 and 2). The two Pd—P distances agree well with each other and their mean [2.321 (2) Å] differs little from 2.308 Å, the mean length of 51 Pd—PPh_3 bonds in the compilation of Orpen, Brammer, Allen, Kennard, Watson & Taylor (1989) (OB89). The Pd—Br bond length [2.517 (2) Å] appears long compared with the value of 2.424 Å given by OB89, but is typical for such bonds *trans* to σ-C_{sp^2}, a donor atom of high *trans* influence: reported lengths for Pd—Br(*trans* to σ-C_{sp^2}) bonds range from 2.490 (4) to 2.563 (3) Å (Roe, Bailey, Moseley & Maitlis, 1972; Isobe, Kai, Nakamura, Nishimoto, Miwa, Kawaguchi, Kinoshita & Nakatsu, 1980); the value in (2) of 2.514 (2) Å is virtually identical to that found here. The Pd(1)—C(1) distance of 1.991 (8) Å is also typical of values for other σ-Pd—C_{sp^2} distances [*e.g.* 2.009 (8) Å in (2); see also Hursthouse, Sloan, Thornton & Walker (1986) and de Graaf, van Wegen, Boersma, Spek & van Koten (1989)]. The tolyl ring is almost normal to the metal coordination plane [P(2)—Pd(1)—C(1)—C(2) = −85.4 (8)°], whereas these planes almost coincide in (2) [P—Pd—C—C = 6.6 (5) and 0.9 (5)°]. The similarity of the Pd—C and Pd—Br bond lengths in (1) and (2) suggests that neither the Pd—C bonding nor the *trans* influence of the σ-aryl group is strongly influenced by the relative orientations of the σ-aryl and metal coordination planes. There is slight asymmetry in the Pd(1)—C(1)—C(2) and Pd(1)—C(1)—C(6) angles so that the methyl group is held clear of the Pd atom [Pd(1)···C(7) = 3.28 (1), Pd(1)···H(methyl) ≥ 2.99 Å]. The molecule as a whole has approximate $C_s(m)$ symmetry and the PPh_3 ligands almost eclipse each other when viewed along the P—Pd—P axis. The tolyl group is thus sandwiched between phenyl groups 2 and 5 [C(1)—Pd—P(1)—C(21) = −33.4 (4), C(1)—Pd—P(2)—C(51) = 24.8 (4)°].

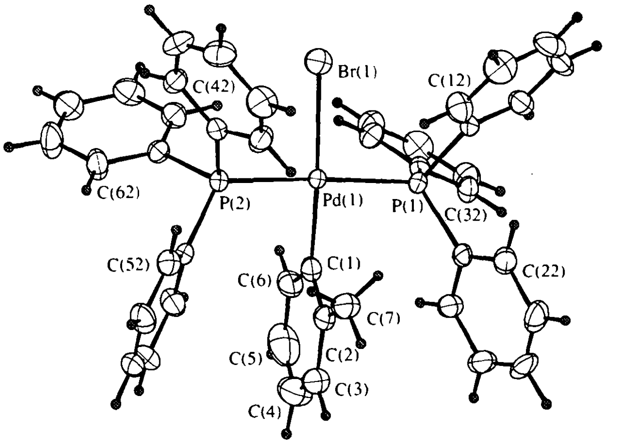


Fig. 1. Molecular structure of (1) with non-H atoms shown as 50% probability ellipsoids and H atoms represented as spheres of arbitrary radii. Triphenylphosphine phenyl rings are numbered cyclically as C(*n*1)–C(*n*6), *n* = 1–6, starting at the *ipso*-C atom. Only the labels of the C(*n*2) ring atoms are shown.

The analysis of (1) was initially undertaken with a crystal (specimen *A*) which came from a sample prepared and recrystallized separately, although in the same manner, as specimen *B*. Crystal *A* was also found to be triclinic, but with $a = 12.178\,(1)$, $b = 18.428\,(1)$, $c = 25.461\,(2)$ Å, $\alpha = 93.125\,(4)$, $\beta = 101.518\,(6)$, $\gamma = 95.019\,(5)^\circ$, $V = 5561.9\,(6)$ Å^3, $Z = 6$. Of 19684 reflections measured to θ(Mo $K\alpha$) = 24.6°, only 5231 were observed [$I > 3\sigma(I)$] and the presence of pseudo-origin peaks in P(uvw) at ±(1/3, −1/3, 1/3) led to the identification of a reduced sub-cell, also triclinic, with $Z = 2$ and dimensions substantially the same as those reported for crystal *B*. 4624 observed reflections could be re-indexed in this sub-cell [$h' = -1/3(h-k+l), k' = h, l' = -1/3(h+2k+l)$]. Subsequent averaging ($R_{\rm int}$ = 0.015) gave 4392 unique intensities. Structure solution and refinement in the same manner as for crystal *B* finally gave $R = 0.060$, $wR = 0.095$, $S = 3.6$. The results of this refinement, which have been deposited, are essentially the same as those reported for crystal *B*. However, the model fails to account for 607 observed reflections with $-h+k-l \neq 3n$ in the original indexing. Their existence implies that the true periodicity is three times the *a* axis of the sub-cell. An alternative description of the structure is that it appears to have a displacive commensurate modulation, such that the observed reciprocal lattice vectors, expressed in terms of the sub-cell, are $S = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m(\mathbf{a}^* + \mathbf{c}^*)/3$, where $m = 0$ for the 4392 reflections used to refine the structure and $m = 1$ or 2 for the 607 reflections not accounted for by the ordered structural model.

In order to verify that crystal *B* was not subject to a similar modulation, its cell was transformed to correspond with the super-cell of crystal *A* at the conclusion of the main data collection. A hemisphere of intensities out to θ(Mo $K\alpha$) = 15° was then collected. None of the 5293 reflections with $m = 1$ or 2 had $I > 3\sigma(I)$, confirming that crystal *B* did not display the modulation present in crystal *A*.

Experimental

Compound (1)

Crystal data

$[\mathrm{PdBr(C_7H_7)(C_{18}H_{15}P)_2}]$
$M_r = 802.04$
Triclinic
$P\overline{1}$
$a = 11.061$ (1) Å
$b = 12.171$ (1) Å
$c = 14.334$ (2) Å
$\alpha = 95.200$ (8)°
$\beta = 92.094$ (9)°
$\gamma = 105.191$ (8)°
$V = 1851.0$ (4) Å^3
$Z = 2$
$D_x = 1.439$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.7$–22.5°
$\mu = 1.68$ mm^{-1}
$T = 298$ K
Needle
0.30 × 0.10 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{\rm min} = 0.91$, $T_{\rm max} = 1.00$
9777 measured reflections
9347 independent reflections
4093 observed reflections [$I > 3.0\sigma(I)$]

$R_{\rm int} = 0.029$
$\theta_{\rm max} = 28.5°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 16$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity decay: −0.8%

Refinement

Refinement on F
$R = 0.051$
$wR = 0.054$
$S = 1.7$
4093 reflections
424 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.00023F^2]$

$(\Delta/\sigma)_{\rm max} = 0.02$
$\Delta\rho_{\rm max} = 0.64$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.08$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Pd(1)	−0.18522 (6)	0.04221 (5)	0.22486 (5)	0.033
Br(1)	0.04025 (10)	0.06242 (9)	0.18914 (9)	0.084
P(1)	−0.21766 (18)	−0.14797 (16)	0.25299 (14)	0.036
P(2)	−0.15958 (18)	0.23427 (16)	0.20676 (14)	0.036
C(1)	−0.3696 (7)	0.0188 (6)	0.2313 (6)	0.047
C(2)	−0.4289 (8)	0.0379 (7)	0.3111 (8)	0.058
C(3)	−0.5628 (10)	0.0231 (8)	0.3081 (9)	0.076
C(4)	−0.6267 (11)	−0.0115 (11)	0.2231 (12)	0.099
C(5)	−0.5717 (13)	−0.0353 (10)	0.1434 (10)	0.103
C(6)	−0.4433 (8)	−0.0183 (7)	0.1461 (8)	0.068
C(7)	−0.3594 (9)	0.0752 (8)	0.3996 (7)	0.070
C(11)	−0.0832 (7)	−0.1794 (6)	0.3108 (5)	0.039
C(12)	−0.0028 (9)	−0.0962 (7)	0.3719 (6)	0.061
C(13)	0.0948 (9)	−0.1211 (10)	0.4205 (7)	0.076
C(14)	0.1151 (9)	−0.2243 (11)	0.4097 (7)	0.076
C(15)	0.0377 (10)	−0.3070 (9)	0.3506 (7)	0.073
C(16)	−0.0622 (8)	−0.2871 (7)	0.3003 (6)	0.054
C(21)	−0.3431 (7)	−0.2093 (6)	0.3286 (5)	0.041
C(22)	−0.3164 (8)	−0.2211 (7)	0.4207 (6)	0.056
C(23)	−0.4123 (11)	−0.2619 (8)	0.4798 (6)	0.076
C(24)	−0.5330 (11)	−0.2888 (8)	0.4457 (8)	0.075
C(25)	−0.5627 (8)	−0.2781 (7)	0.3546 (8)	0.069
C(26)	−0.4661 (8)	−0.2365 (7)	0.2952 (6)	0.055
C(31)	−0.2534 (6)	−0.2406 (6)	0.1438 (5)	0.037
C(32)	−0.3214 (7)	−0.3556 (6)	0.1399 (6)	0.046
C(33)	−0.3477 (8)	−0.4217 (7)	0.0549 (7)	0.059
C(34)	−0.3115 (9)	−0.3759 (8)	−0.0261 (6)	0.062
C(35)	−0.2449 (9)	−0.2642 (8)	−0.0237 (6)	0.065
C(36)	−0.2160 (7)	−0.1963 (7)	0.0611 (6)	0.047
C(41)	−0.0116 (7)	0.3166 (6)	0.2688 (5)	0.039
C(42)	0.0822 (8)	0.3902 (6)	0.2274 (6)	0.048
C(43)	0.1919 (8)	0.4461 (7)	0.2783 (7)	0.057
C(44)	0.2088 (8)	0.4347 (8)	0.3708 (7)	0.063
C(45)	0.1152 (9)	0.3607 (9)	0.4133 (6)	0.069
C(46)	0.0059 (8)	0.3005 (7)	0.3618 (6)	0.057
C(51)	−0.2734 (7)	0.3096 (6)	0.2498 (5)	0.038
C(52)	−0.2425 (8)	0.4007 (7)	0.3207 (6)	0.052
C(53)	−0.3321 (10)	0.4546 (8)	0.3489 (6)	0.069
C(54)	−0.4509 (9)	0.4197 (9)	0.3100 (7)	0.072
C(55)	−0.4836 (8)	0.3318 (8)	0.2404 (7)	0.068
C(56)	−0.3955 (8)	0.2766 (7)	0.2100 (6)	0.055

C(61)	−0.1465 (7)	0.2684 (6)	0.0860 (5)	0.040
C(62)	−0.1637 (9)	0.3702 (7)	0.0603 (6)	0.071
C(63)	−0.1502 (11)	0.3965 (9)	−0.0323 (7)	0.097
C(64)	−0.1239 (10)	0.3191 (10)	−0.0987 (6)	0.083
C(65)	−0.1056 (8)	0.2195 (8)	−0.0740 (6)	0.064
C(66)	−0.1173 (7)	0.1939 (7)	0.0189 (6)	0.050

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

Pd(1)—Br(1)	2.517 (2)	P(1)—C(21)	1.836 (8)
Pd(1)—P(1)	2.322 (2)	P(1)—C(31)	1.811 (8)
Pd(1)—P(2)	2.319 (2)	P(2)—C(41)	1.829 (8)
Pd(1)—C(1)	1.991 (8)	P(2)—C(51)	1.834 (8)
P(1)—C(11)	1.820 (8)	P(2)—C(61)	1.818 (7)
Br(1)—Pd(1)—P(1)	92.9 (1)	C(21)—P(1)—C(31)	104.8 (4)
Br(1)—Pd(1)—P(2)	89.9 (1)	Pd(1)—P(2)—C(41)	108.4 (3)
Br(1)—Pd(1)—C(1)	170.9 (3)	Pd(1)—P(2)—C(51)	121.2 (3)
P(1)—Pd(1)—P(2)	175.9 (1)	Pd(1)—P(2)—C(61)	114.3 (3)
P(1)—Pd(1)—C(1)	87.2 (3)	C(41)—P(2)—C(51)	103.5 (4)
P(2)—Pd(1)—C(1)	90.6 (3)	C(41)—P(2)—C(61)	105.3 (4)
Pd(1)—P(1)—C(11)	114.1 (3)	C(51)—P(2)—C(61)	102.6 (4)
Pd(1)—P(1)—C(21)	118.6 (3)	Pd(1)—C(1)—C(2)	125.0 (7)
Pd(1)—P(1)—C(31)	110.5 (3)	Pd(1)—C(1)—C(6)	116.6 (7)
C(11)—P(1)—C(21)	101.3 (4)	C(2)—C(1)—C(6)	118.4 (9)
C(11)—P(1)—C(31)	106.4 (4)		
C(1)—Pd(1)—P(1)—C(11)	−152.6 (4)	C(1)—Pd(1)—P(2)—C(41)	144.1 (4)
C(1)—Pd(1)—P(1)—C(21)	−33.4 (4)	C(1)—Pd(1)—P(2)—C(51)	24.8 (4)
C(1)—Pd(1)—P(1)—C(31)	87.6 (4)	C(1)—Pd(1)—P(2)—C(61)	−98.8 (4)

The orientation of the methyl group was determined from a difference synthesis. All H atoms rode on their parent C atoms with C—H = 0.96 Å and $U(H) \simeq 1.2\,U(C)$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *GX* (Mallinson & Muir, 1985). Program(s) used to refine structure: *GX*. Molecular graphics: *CAMERON* (Pierce & Watkin, 1994). Software used to prepare material for publication: *GX*.

We wish to thank the SERC for an equipment grant and for a studentship (to ARK) and Dr D. J. Watkin for making *CAMERON* available to us.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 210–213

Bis(dimethylglyoximato)(phenylacetylido)(triphenylphosphine)rhodium(III) Dichloromethane, [$Rh(C_4H_7N_2O_2)_2(C_8H_5)(C_{18}H_{15}P)$].$CH_2Cl_2$

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(*Received* 21 *December* 1993; *accepted* 25 *May* 1994)

Abstract

The title structure {alternative name: bis[2,3-butanedial dioximato(1 −)-N,N'](phenylethynyl)(triphenylphosphine-P)rhodium(III) dichloromethane solvate} consists of discrete complexes [$Rh(dmgH)_2(PPh_3)R$] ($R = C{\equiv}CPh$ and dmgH = dimethylglyoximato, $C_4H_7N_2O_2^-$) in which the Rh atom displays distorted octahedral coordination with the two dimethylglyoximato ligands in the equatorial plane and the phenylacetylide and triphenylphosphine groups in axial positions. The Rh atom is displaced by 0.073 (1) Å from the mean plane through the four oxime N-atom donors. The average Rh—N distance is 1.971 (2) Å, while the axial Rh—P and Rh—C distances are 2.409 (1) and 1.991 (3) Å, respectively.

Acta Crystallographica Section C
ISSN 0108-2701 ©1995