Br_{eq}—Te—C_{eq} 97·1 (3)°]. The molecules are held together by a single intermolecular secondary bond [3·713 (1) Å] between the Te atoms and the axial bromine atoms of adjacent pairs of molecules to give loose dimers.

The remaining tribromides all attain square-based pyramidal geometry at the tellurium atom by means of bridging bromine atoms. The geometries of the CTeBr₄ units are closely comparable in the three compounds but whereas the title compound adopts a polymeric chain structure, the presence of an ethoxy substituent on the phenyl ring in tribromo(4-ethoxyphenyl)-tellurium apparently leads to a dimeric structure (although the corresponding trichloride is polymeric). This structure is also adopted by the cyclohexene compound. None of these square-based pyramidal structures show significant secondary bonding because the 'vacant' coordination site at the tellurium atom is occupied by the lone pair. In the biphenylyl compound a secondary Te···Br bond can be formed as a vacant site remains in the tellurium coordination sphere. In this case the bulky biphenylyl group {with the second phenyl ring, not directly attached to the Te atom, making a close approach to the Te atom [Te···C = 2·945 (9) Å]} would appear to prevent a fourth bromine atom fully entering the tellurium coordination sphere, but it allows very asymmetric bridging by a bromine atom, with one primary Te—Br bond [2·675 (1) Å] and one secondary Te···Br bond [3·713 (1) Å]. The other examples all have almost symmetrical μ-bromo bridges with a mean Te—μ-Br = 2·90 Å.

On the evidence so far gathered (Table 3), the preferred structure for $RTeBr_3$ compounds appears to be that with bridging halogen atoms giving rise to square-based pyramidal geometry with oligomeric or dimeric structures. However, when a bulky organic group is present the trigonal bipyramidal geometry predicted by simple VSEPR is adopted.

References

ALCOCK, N. W. (1970). In *Crystallographic Computing*, edited by F. R. AHMED. Copenhagen: Munksgaard.
ALCOCK, N. W. & HARRISON, W. D. (1982*a*). *Acta Cryst.* B38, 1809–1811.
ALCOCK, N. W. & HARRISON, W. D. (1982*b*). *J. Chem. Soc. Dalton Trans.* pp. 251–254.
ALCOCK, N. W. & HARRISON, W. D. (1982*c*). Unpublished work.
BIRD, P. H., KUMAR, V. & PANT, B. C. (1980). *Inorg. Chem.* 19, 2487–2493.
HAZELL, A. C. (1972). *Acta Chem. Scand.* 26, 1510–1516.
KNOBLER, C. & McCULLOUGH, J. D. (1977). *Inorg. Chem.* 16, 612–615.
KOBELT, D. & PAULUS, E. F. (1971). *Angew. Chem. Int. Ed. Engl.* 10, 74–75.
McCULLOUGH, J. D. & KNOBLER, C. (1976). *Inorg. Chem.* 15, 2728–2731.
STEWART, J. M. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

---

trans-Dichlorobis(triphenylphosphine)palladium(II)

By George Ferguson, Robert McCrindle, Alan J. McAlees and Masood Parvez

The Chemistry Department, The University of Guelph, Guelph, Ontario, Canada N1G 2W1

Abstract. $C_{36}H_{30}Cl_2P_2Pd$, $M_r = 701·19$, triclinic, $P\bar{1}$, $a = 9·690$ (2), $b = 10·325$ (2), $c = 9·194$ (1) Å, $\alpha = 91·38$ (1), $\beta = 111·94$ (1), $\gamma = 72·51$ (1)°, $V = 809·71$ Å³, $Z = 1$, $D_c = 1·44$ g cm⁻³, $F(000) = 356$, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, μ(Mo $K\alpha$) = 8·5 cm⁻¹. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to a final R of 0·024 for 4343 independent observed reflections [$I > 3\sigma(I)$]. The crystal structure contains centrosymmetric, square-planar $PdCl_2(PPh_3)_2$ molecules with Pd—Cl 2·290 (1), Pd—P 2·337 (1) Å, and Cl—Pd—P 92·0 (1)°.

Introduction. In the course of studies of solvates of *trans*-Pd(Cl)(CH₂CN)(PPh₃)₂ (Ferguson, McAlees, McCrindle, Parvez & Roberts, 1982) we were surprised on interrogating the Cambridge Crystallographic Database to find no structure determination for *trans*-PdCl₂(PPh₃)₂ (1). As we had available a plentiful supply of crystals of (1) grown from acetonitrile, we undertook its X-ray analysis to determine precise values for the Pd—P and Pd—Cl bond lengths.

A crystal 0·50 × 0·35 × 0·25 mm was used for data collection with an Enraf–Nonius CAD-4 diffractometer. Following preliminary photographic studies, ac-

curate unit-cell data and the crystal-orientation matrix were determined from a least-squares refinement of the setting angles of 25 reflexions with $10 < \theta < 15°$. Intensity data were collected by the $\theta/2\theta$ scan method using monochromatic Mo $K\alpha$ radiation. The intensities of three reflexions, chosen as standards, were monitored every hour of exposure time and showed no significant variation. Intensities for 4493 reflexions were measured of which 4343 had $I > 3\sigma(I)$ and were used in structure solution and refinement. Data were corrected for Lorentz–polarization factors and for absorption. Maximum and minimum values of the transmission coefficients are 0·831 and 0·723 respectively.

The structure was solved by the heavy-atom method. Initial refinement (Sheldrick, 1976) by full-matrix least-squares calculations with isotropic temperature factors lowered R to 0·095 which then dropped to 0·032 after four rounds of full-matrix refinement with anisotropic vibration parameters. The top 15 peaks (0·3–0·6 e Å^{-3}) of a difference map computed at this stage corresponded to the 15 H atoms in the asymmetric unit; these were then included but not refined in subsequent refinement cycles in geometrically idealized positions (C–H 0·95 Å) and an overall isotropic thermal parameter was refined for H. In the final rounds of calculations a weighting scheme of the form $w = 1/(\sigma^2 F + pF^2)$ was employed where the final p parameter refined to 0·0025. Scattering factors used in the calculations were taken from

Table 1. $PdCl_2(PPh_3)_2$: *final fractional coordinates* (P and Cl $\times 10^5$, C $\times 10^4$) *and* $\bar{U}$ (Å^2; Pd, Cl *and* P $\times 10^4$, C $\times 10^3$), *with estimated standard deviations in parentheses*

	x	y	z	$\bar{U}^*$
Pd	0	0	0	293 (1)
Cl	15473 (5)	8668 (5)	20630 (5)	504 (2)
P	21012 (4)	−19362 (3)	2080 (4)	325 (2)
C(11)	4075 (2)	−1893 (2)	1348 (2)	41 (1)
C(12)	5094 (2)	−1862 (3)	613 (3)	74 (1)
C(13)	6581 (3)	−1789 (3)	1551 (5)	103 (2)
C(14)	7060 (3)	−1775 (3)	3114 (5)	90 (2)
C(15)	6030 (3)	−1763 (3)	3858 (3)	68 (1)
C(16)	4549 (2)	−1829 (2)	2967 (2)	53 (1)
C(21)	1979 (2)	−3409 (1)	1144 (2)	39 (1)
C(22)	558 (2)	−3368 (2)	1195 (2)	51 (1)
C(23)	436 (3)	−4476 (3)	1912 (3)	73 (1)
C(24)	1713 (3)	−5640 (2)	2523 (2)	76 (1)
C(25)	3101 (3)	−5676 (2)	2478 (3)	75 (1)
C(26)	3273 (3)	−4561 (2)	1817 (3)	62 (1)
C(31)	2117 (2)	−2390 (2)	−1701 (2)	41 (1)
C(32)	2426 (2)	−3724 (2)	−2090 (2)	55 (1)
C(33)	2433 (3)	−4011 (2)	−3574 (3)	76 (1)
C(34)	2194 (3)	−2961 (3)	−4642 (2)	80 (1)
C(35)	1884 (3)	−1648 (3)	−4282 (2)	79 (1)
C(36)	1845 (3)	−1345 (2)	−2799 (2)	64 (1)

$^* \bar{U} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* $PdCl_2(PPh_3)_2$

Bond	Distance		Bond	Distance
Pd–Cl	2·290 (1)		C(21)–C(22)	1·383 (3)
Pd–P	2·337 (1)		C(21)–C(26)	1·388 (2)
			C(22)–C(23)	1·390 (2)
P–C(11)	1·819 (2)		C(23)–C(24)	1·382 (4)
P–C(21)	1·820 (1)		C(24)–C(25)	1·351 (4)
P–C(31)	1·810 (1)		C(25)–C(26)	1·395 (3)
C(11)–C(12)	1·397 (2)		C(31)–C(32)	1·386 (2)
C(11)–C(16)	1·390 (2)		C(31)–C(36)	1·391 (2)
C(12)–C(13)	1·399 (3)		C(32)–C(33)	1·391 (2)
C(13)–C(14)	1·336 (5)		C(33)–C(34)	1·387 (3)
C(14)–C(15)	1·403 (5)		C(34)–C(35)	1·359 (4)
C(15)–C(16)	1·383 (3)		C(35)–C(36)	1·403 (3)
Cl–Pd–P	92·0 (1)		C(12)–C(11)–C(16)	119·5 (2)
			C(11)–C(12)–C(13)	118·3 (2)
Pd–P–C(11)	118·1 (1)		C(12)–C(13)–C(14)	122·3 (3)
Pd–P–C(21)	110·7 (1)		C(13)–C(14)–C(15)	119·9 (2)
Pd–P–C(31)	112·1 (1)		C(14)–C(15)–C(16)	119·2 (2)
C(11)–P–C(21)	104·0 (1)		C(11)–C(16)–C(15)	120·7 (2)
C(11)–P–C(31)	104·8 (1)		C(22)–C(21)–C(26)	119·4 (1)
C(21)–P–C(31)	106·3 (1)		C(21)–C(22)–C(23)	119·9 (2)
			C(22)–C(23)–C(24)	120·4 (2)
P–C(11)–C(12)	121·0 (1)		C(23)–C(24)–C(25)	119·5 (2)
P–C(11)–C(16)	119·3 (1)		C(24)–C(25)–C(26)	121·3 (2)
P–C(21)–C(22)	118·8 (1)		C(21)–C(26)–C(25)	119·4 (2)
P–C(21)–C(26)	121·8 (1)		C(32)–C(31)–C(36)	119·3 (1)
P–C(31)–C(32)	123·0 (1)		C(31)–C(32)–C(33)	120·3 (2)
P–C(31)–C(36)	117·7 (1)		C(32)–C(33)–C(34)	119·6 (2)
			C(33)–C(34)–C(35)	120·7 (2)
			C(34)–C(35)–C(36)	120·1 (2)
			C(31)–C(36)–C(35)	119·9 (2)

Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) and allowance was made for anomalous dispersion (Cromer & Liberman, 1970). Refinement converged with $R = 0·024$ and $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2} = 0·032.^*$ A final difference map was devoid of significant features. The final fractional coordinates and their standard deviations are in Table 1 and details of molecular dimensions are in Table 2.

Discussion. The crystal structure consists of discrete molecules (Fig. 1) separated by normal van der Waals distances. The $PdCl_2(PPh_3)_2$ molecule lies on a crystallographic inversion centre and the PdP_2Cl_2 moiety is consequently *trans* and planar.

The Pd–P and Pd–Cl bond lengths are compared in Table 3 with dimensions from other $PdCl_2(L)_2$ systems ($L =$ phosphine ligand) obtained *via* the Cambridge Database. The Pd–Cl [2·290 (1) Å] and Pd–P [2·337 (1) Å] distances in (1) are in the middle of the ranges of values 2·267 (9)–2·326 (4) Å and 2·310 (5)–2·388 (6) Å given in Table 3 for Pd–Cl and Pd–P distances respectively.
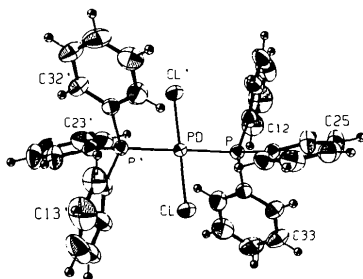
Fig. 1. A molecule of *trans*-PdCl₂(PPh₃)₂. The phenyl-ring C atoms are numbered sequentially C(*i*1)–C(*i*6) (*i* = 1, 2, 3). For clarity only one atom in each ring is numbered. C(*i*1) is bonded to P.

Table 3. *Bond lengths (Å) in trans-dichlorobis(phosphine)palladium complexes*

L in *trans*-PdCl₂L₂	Pd–Cl	Pd–P	Reference
PPh₃	2·290 (1)	2·337 (1)	This work
(Buⁱ)₂P(CH₂)₂CHMe(CH₂)₂P(Buⁱ)₂	2·291 (5)	2·388 (6)	(1)
	2·305 (6)	2·380 (6)	
	2·302 (5)	2·372 (6)	
	2·305 (6)	2·374 (6)	
Ph₂PCH=CClCF₃	2·291 (1)	2·322 (1)	(2)
PMe₂(*neo*-menthyl)	2·304 (5)	2·344 (4)	(3)
	2·297 (5)	2·361 (5)	
PMe₂(menthyl)	2·296 (9)	2·310 (5)	(3)
	2·267 (9)		
(Buⁱ)₂P(CH₂)₅P(Buⁱ)₂	2·316 (5)	2·379 (4)	(4)
	2·287 (5)	2·376 (4)	
	2·302 (4)	2·370 (4)	
	2·326 (4)	2·378 (4)	
Ph₂PCH₂C₁₈H₁₀CH₂PPh₂	2·311 (2)	2·326	(5)
	2·293 (2)	2·322	

References: (1) Al-Salem, McDonald, Markham, Norton & Shaw (1980); (2) Taylor, Jacobson & Carty (1975); (3) Kan, Miki, Kai, Yasuoka & Kasai (1978); (4) McDonald (1979); (5) Bachechi, Zambonelli & Venanzi (1977).

The small distortion of the Cl–Pd–P angle from 90° [to 92·0 (1)°] is undoubtedly a consequence of intramolecular crowding effects. Thus, the phenyl-ring C atom (C11) comes close to eclipsing the Cl atom

[torsion angle Cl–Pd–P–C(11) 16·0 (2)°] and Pd–P–C(11) [118·1 (1)°] is considerablly larger than the other Pd–P–C angles [110·7 and 112·1 (1)°]. As is commonly found in PPh₃ complexes, the C–P–C angles are all less than tetrahedral [104·0–106·3 (1)°]. The orientations adopted by the phenyl rings C(21)–C(26) and C(31)–C(36) are such that an *ortho* proton on each ring is directed towards the Pd atom but the distances [Pd···H(22) 2·92, Pd···H(36) 3·22 Å] are too great for any significant interaction. The remaining dimensions [mean P–C 1·816 (1), C–C 1·384 (4) Å] are normal and in accord with accepted values.

References

AL-SALEM, N. A., McDONALD, W. S., MARKHAM, R., NORTON, M. C. & SHAW, B. L. (1980). *J. Chem. Soc. Dalton Trans.* pp. 59–63.

BACHECHI, F., ZAMBONELLI, L. & VENANZI, L. M. (1977). *Helv. Chim. Acta*, **60**, 2815–2823.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

FERGUSON, G., McALEES, A. J., McCRINDLE, R., PARVEZ, M. & ROBERTS, P. J. (1982). In preparation.

KAN, K., MIKI, K., KAI, Y., YASUOKA, N. & KASAI, N. (1978). *Bull. Chem. Soc. Jpn*, **51**, 733–740.

McDONALD, W. S. (1979). *Acta Cryst.* B**35**, 3051–3052.

SHELDRICK, G. M. (1976). *SHELX.* A program for crystal structure determination. Univ. of Cambridge, England.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TAYLOR, N. J., JACOBSON, S. E. & CARTY, A. J. (1975). *Inorg. Chem.* **14**, 2648–2653.

Structure of Bis[hydroxolead(II)] 5,5'-Azotetrazolediide

By MELANIE A. PIERCE-BUTLER

Propellants, Explosives and Rocket Motor Establishment (PERME),* Waltham Abbey, Essex EN9 1BP, England

Abstract. 2[PbOH]⁺.C₂N₁₀²⁻, triclinic, P1̄, a = 4·3604 (4), b = 7·4214 (6), c = 7·5016 (9) Å, α = 101·31 (1), β = 96·97 (2), γ = 109·19 (1)°, V = 220·24 Å³, Mᵣ = 612·484, Z = 1, Dₑ = 4·62 Mg m⁻³. Mo Kα radiation, λ = 0·71069 Å, μ(Mo Kα) = 38·53 mm⁻¹. Final R = 0·055 for 959 unique reflections. In the [Pb(OH)]⁺ complex ion each lead atom is coordinated to three oxygen atoms, and each oxygen atom to three lead atoms, thus forming an infinite ladder-like chain. The azotetrazolide anion adopts a *trans* conformation about the N=N bond.

* Formerly ERDE.