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cis-Dichloro[1,2-bis(dicyclohexylphosphino)ethane]palladium(II)

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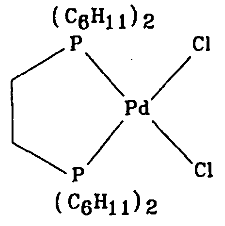
Abstract

The structure of *cis*-$PdCl_2$(dcpe), where dcpe is 1,2-bis(dicyclohexylphosphino)ethane, $[PdCl_2(C_{26}H_{48}P_2)]$, consists of an approximately square planar Pd^{II} ion coordinated by a chelating dcpe ligand and two Cl^- ions. The coordination sphere of the Pd shows a slight tetrahedral distortion. A significant *trans* influence of the dcpe ligand on the Pd—Cl distances is evident.

Comment

Recently, we have employed hydroxy-bridged dinuclear Pd^{II} complexes such as $[Pd(\mu\text{-}OH)(dppe)]_2(BF_4)_2$ [dppe is 1,2-bis(diphenylphosphino)ethane] as catalysts for the homogeneous hydration of alkenes (Ganguly & Roundhill, 1991). As part of continuing studies to assess the effect of changes in the electronic and steric properties of the phosphine ligand(s) on the catalysis, the related species $[Pd(\mu\text{-}OH)(dcpe)]_2(BF_4)_2$ was prepared from *cis*-$PdCl_2$(dcpe) (Ganguly, Mague & Roundhill, 1992). Recent studies have indicated that the analogous platinum complex *cis*-$PtCl_2$(dcpe) is a precursor to a wide variety of species containing the [Pt(dcpe)] moiety (Mague, Fink & Recatto, 1993) and suggest that *cis*-$PdCl_2$(dcpe) can similarly be the source of a broad range of palladium complexes containing the chelated dcpe ligand. Therefore, we have determined the structure of $PdCl_2$(dcpe) (I).



(I)

The coordination sphere of the Pd atom is approximately square planar but with a small tetrahedral distortion, as can be seen from the dihedral angle of 5.3 (2)° between the plane defined by Pd, P(1) and P(2), and that defined by Pd, Cl(1) and Cl(2). A similar distortion [dihedral angle of 5.9 (5)°] was found in the Pt analogue (Mague, Fink & Recatto, 1993). The Pd—P distances are equal, within experimental error, and essentially the same as found in *cis*-$PdCl_2$(dppe) [2.226 (2) and 2.233 (2) Å (Steffen & Palenik, 1976)] and in *cis*-$PdCl_2$(DH), where DH is 1,2-bis(diisopropylphosphino)benzene [2.233 (1) and 2.234 (1) Å (Liu, Cheu, Peng, Hsiao & Cheng, 1990)]. The contraction of the P(1)—Pd—P(2) angle from the ideal value of 90° is greater than that found in the Pt analogue but not as great as that found in *cis*-$PdCl_2$(dppe). The Pd—Cl distances in (I) differ by an amount which is possibly significant; an even greater difference [2.398 (2) *versus* 2.417 (2) Å] is seen in *cis*-$PdCl_2(P^nPr_3)_2$ (Alcock, Kemp & Wimmer, 1981). By contrast, the Pd—Cl distances in *cis*-$PdCl_2$(dppe) and *cis*-$PdCl_2$(DH) are equal within experimental error. The inequality seen in the triisopropylphos-

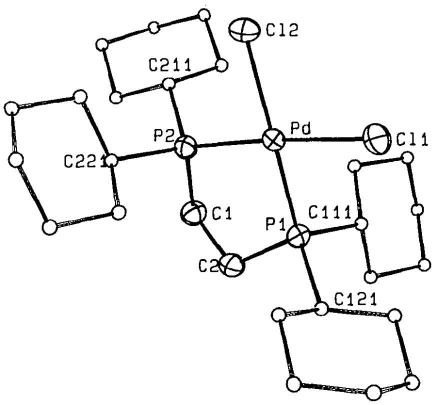


Fig. 1. A perspective view of $PdCl_2$(dcpe); displacement ellipsoids are drawn at the 50% contour level, cyclohexyl C atoms are drawn arbitrarily small and H atoms are omitted for clarity.

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phine complex was attributed to steric effects (but a detailed analysis was not performed); it is possible that this is also the case with the present structure, although there are no obviously short intermolecular contacts involving these ligands. The Pd—Cl distances are longer than most such distances of Cl *trans* to P but shorter than those in the triisopropylphosphine complex, indicating that a significant *trans* influence is exerted by the dcpe ligand.

Experimental

Crystal data

$[PdCl_2(C_{26}H_{48}P_2)]$
$M_r = 600.01$
Triclinic
$P1$
$a = 7.3983\ (7)$ Å
$b = 9.433\ (1)$ Å
$c = 10.825\ (1)$ Å
$\alpha = 93.231\ (8)°$
$\beta = 107.931\ (7)°$
$\gamma = 99.920\ (8)°$
$V = 703.2\ (3)$ Å^3
$Z = 1$
$D_x = 1.42$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.05\text{-}16.80°$
$\mu = 0.97$ mm^{-1}
$T = 298$ K
Plate
0.33 × 0.30 × 0.04 mm
Light yellow
Crystal source: evaporation of acetone solution in air

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.84$, $T_{\max} = 0.99$
3292 measured reflections
3292 independent reflections
3114 observed reflections $[I \geq 3\sigma(I)]$

$\theta_{\max} = 27°$
$h = 0 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity variation: −2.1%

Refinement

Refinement on F
$R = 0.022$
$wR = 0.030$
$S = 1.068$
3114 reflections
277 parameters
H-atom parameters not refined
$w = 4F/[\sigma^2(I) + (0.04F^2)^2]$

$(\Delta/\sigma)_{\max} = 0.05$
$\Delta\rho_{\max} = 0.371$ e Å^{-3}
$\Delta\rho_{\min} = -0.105$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Pd	0.210	0.230	0.320	1.807 (3)
Cl(1)	−0.0093 (1)	0.3645 (1)	0.19382 (9)	3.32 (2)
Cl(2)	0.0607 (1)	0.2053 (1)	0.48442 (8)	3.24 (2)
P(1)	0.3464 (1)	0.22583 (8)	0.16277 (7)	2.01 (1)
P(2)	0.4272 (1)	0.10535 (8)	0.42837 (7)	1.95 (1)
C(1)	0.5537 (5)	0.0441 (3)	0.3187 (3)	2.38 (6)
C(2)	0.5672 (5)	0.1493 (4)	0.2198 (3)	2.56 (6)
C(111)	0.1736 (5)	0.1113 (3)	0.0175 (3)	2.38 (6)
C(112)	0.2625 (6)	0.0715 (5)	−0.0872 (4)	3.69 (8)
C(113)	0.0998 (7)	−0.0077 (5)	−0.2102 (4)	4.2 (1)
C(114)	−0.0126 (7)	−0.1419 (5)	−0.1801 (4)	3.90 (9)
C(115)	−0.0964 (7)	−0.1073 (5)	−0.0738 (4)	4.3 (1)
C(116)	0.0605 (6)	−0.0255 (4)	0.0500 (4)	3.34 (8)
C(121)	0.4367 (5)	0.3948 (4)	0.1031 (3)	2.55 (6)
C(122)	0.2890 (6)	0.4462 (4)	−0.0076 (4)	3.52 (8)
C(123)	0.3804 (7)	0.5832 (4)	−0.0512 (4)	4.08 (9)
C(124)	0.4723 (8)	0.7017 (4)	0.0592 (5)	4.5 (1)
C(125)	0.6211 (8)	0.6541 (5)	0.1732 (5)	4.4 (1)
C(126)	0.5330 (6)	0.5157 (4)	0.2179 (4)	3.34 (8)
C(211)	0.3347 (5)	−0.0603 (3)	0.4897 (3)	2.40 (6)
C(212)	0.4956 (7)	−0.1417 (4)	0.5528 (4)	3.64 (8)
C(213)	0.4170 (7)	−0.2694 (4)	0.6157 (4)	4.4 (1)
C(214)	0.2469 (7)	−0.3719 (4)	0.5134 (5)	4.4 (1)
C(215)	0.0906 (7)	−0.2919 (4)	0.4478 (5)	4.2 (1)
C(216)	0.1647 (6)	−0.1636 (4)	0.3856 (4)	3.25 (8)
C(221)	0.6153 (5)	0.2139 (3)	0.5730 (3)	2.18 (6)
C(222)	0.5515 (6)	0.2206 (5)	0.6945 (3)	3.21 (8)
C(223)	0.7126 (6)	0.3078 (4)	0.8117 (4)	3.34 (8)
C(224)	0.7810 (6)	0.4594 (4)	0.7823 (4)	3.33 (8)
C(225)	0.8452 (6)	0.4536 (4)	0.6625 (4)	3.39 (8)
C(226)	0.6856 (6)	0.3663 (4)	0.5440 (3)	2.69 (7)

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

Pd—Cl(1)	2.376 (1)	Pd—P(1)	2.232 (1)
Pd—Cl(2)	2.369 (1)	Pd—P(2)	2.233 (1)
Cl(1)—Pd—Cl(2)	94.88 (5)	Cl(2)—Pd—P(1)	173.47 (6)
Cl(1)—Pd—P(1)	88.93 (5)	Cl(2)—Pd—P(2)	89.15 (5)
Cl(1)—Pd—P(2)	175.97 (6)	P(1)—Pd—P(2)	87.05 (5)

Crystal orientation, unit-cell determination and refinement, and data collection were performed using *CAD*-4 *Software* (Enraf-Nonius, 1989). Data reduction, structure solution and refinement were obtained with *MolEN* (Fair, 1990) and the molecular graphics package used was *ORTEP*II (Johnson, 1976). Assuming a density comparable to that for the Pt analogue (Mague, Fink & Recatto, 1993), $Z = 1$ suggests $P1$ as the space group. This was also indicated by intensity statistics being consistent with a non-centrosymmetric space group. The Pd atom was placed in an arbitrarily fixed location and subsequent cycles of structure-factor calculations and calculation of $\Delta\rho$ maps allowed location of the remaining non-H atoms. Following full-matrix least-squares refinement of all non-H atoms with anisotropic displacement parameters, a $\Delta\rho$ map showed the locations of the H atoms. These were placed in calculated positions (C—H = 0.95 Å) with isotropic displacement parameters 20% larger than those of the attached C atoms and updated periodically. As a check on the absolute configuration of the molecule, the opposite enantiomer was also refined to convergence yielding significantly (95% confidence level) higher values of R and wR. Thus the original choice was retained. All calculations were performed on a VAXStation 3100.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71501 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1038]

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3,3′-Dimethyl-4,4′-diphenyl-2,2′,5,5′-tetrathiafulvalenium Hexamolybdate, $2(C_{20}H_{16}S_4^{+})[Mo_6O_{19}]^{2-}$

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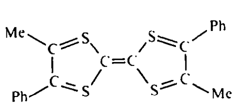
Abstract

The central C=C bond length [1.391 (9) Å] and the two types of C—S bond lengths [average 1.712 (6) and 1.735 (7) Å] of the DMDPh-TTF ($C_{20}H_{16}S_4$) molecule compare well with those observed for the fully oxidized species. This organic molecule has a *trans* configuration. The phenyl rings are not coplanar with the central TTF fragment. The dihedral angles observed between the phenyl rings and the central TTF core are 38.1 (2) and 50.9 (2)°. There are no interactions between the organic molecules since the intermolecular S···S contacts are greater than 4 Å. The shortest S···O contacts observed are: S(1)···O(6) 3.217 (5), S(2)···O(4) 3.296 (5) and S(3)···O(3) 3.298 (5) Å.

Comment

The crystal structure represented in Fig. 1 is built from one independent organic molecule (DMDPh-TTF) and one inorganic anion, $[Mo_6O_{19}]^{2-}$, having a Lindquist type of structure (Lindquist, 1953). This anion is located at the origin of the lattice, with bond distances and bond angles within $[Mo_6O_{19}]^{2-}$ close to those observed previously for such a unit (Triki *et al.*, 1992; Allcock, Bissell & Shawl, 1973). The organic molecule has a *trans* configuration. The phenyl rings do not assume a coplanar configuration with respect to the central TTF fragment. The dihedral angle observed between the two phenyl rings is 91.4 (3)°, while those observed between the phenyl rings and the central TTF core are 38.1 (2) and 50.9 (2)°. These values are different from those (33.3 and 37.0°) observed in $(DMDPh\text{-}TTF)_2[Re_2Cl_8].2CH_2Cl_2$ (Fettouhi, Ouahab, Perrin, Grandjean & Fabre, 1991). The charge on the DMDPh-TTF moiety is assumed to be + 1 as there are only two molecules per anionic unit. The central C=C bond length [1.391 (9) Å] and the two types of C—S bond lengths [average: 1.712 (6) and 1.735 (7) Å] of the organic molecule compare well with those observed for the fully oxidized species in $[(DMDPh\text{-}TTF)_2Re_2Cl_8].2CH_2Cl_2$ (Fettouhi *et al.*, 1991).



DMDPh-TTF

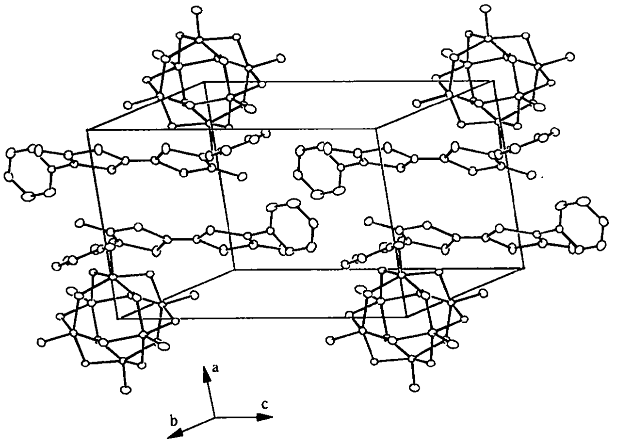


Fig. 1. Perspective view of the crystal structure, with four Mo_6O_{19} units omitted for clarity.