Crystal structure of bis(triphenylphospine-κP)-dichloro-palladium(II) — acetonitrile (1:1), $[PdCl_2(C_{18}H_{15}P)_2] \cdot CH_3CN$

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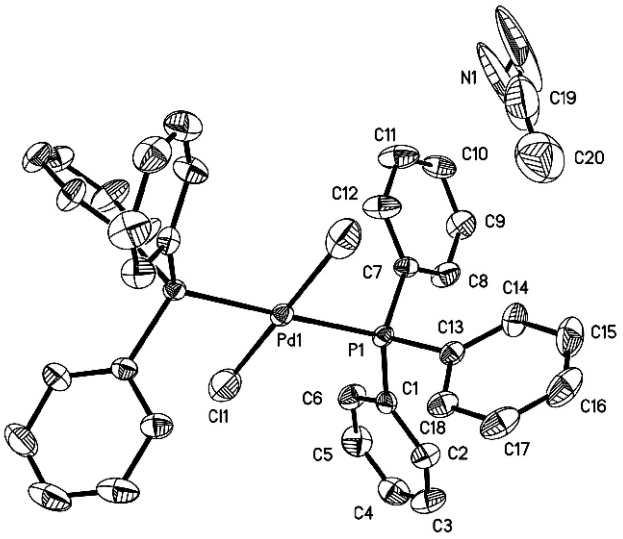

Abstract

$C_{38}H_{33}Cl_2NP_2Pd$, monoclinic, *C*12/*c*1 (no. 15), a = 12.056(1) Å, b = 14.393(1) Å, c = 20.002(2) Å, β = 92.372(1)°, V = 3467.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.070, $wR_{ref}(F^2)$ = 0.178, T = 298 K.

Source of material

The title crystal structure was unexpectedly obtained in an attempt to prepare palladium(II) complex of pyrazine and PPh_3. Triphenylphosphine (PPh_3) (0.2 mmol, 0.0525 g) and pyrazine (0.4 mmol, 0.0320 g) were added into the stirring solution of $PdCl_2$ (0.2 mmol, 0.0355 g) in a mixture of CH_3CN (5 ml) and CH_3OH (5 ml). After stirring for 7 h at room temperature, the yellow precipitate was filtered off. Subsequent slow evaporation of the filtrate resulted in the formation of yellow crystals of the title complex $[PdCl_2(PPh_3)_2] \cdot CH_3CN$. Crystals suitable for single crystal X-ray diffraction experiment were selected directly from the sample as prepared.

Discussion

The chemistry of palladium(II) complexes is of considerable interest. This field has become multidisciplinary in nature encompassing areas like organic synthesis, catalysis, materials science and photo-physical chemistry [1-4]. A range of crystal structures have been reported for *trans*-dichloro-bis(triphenylphosphine) palladium(II) complexes, with or without a solvent molecule [5-9].

The asymmetric unit of the title crystal structure consists of one neutral molecule $[PdCl_2(PPh_3)_2]$ and one solvent molecule CH_3CN. In the neutral molecule, the Pd(II) center is coordinated by two P atoms from PPh_3 and two Cl atoms. The two coordinated chloride ligands are in a *trans*-configuration. The molecule possesses a crystallographical centre of symmetry. The coordination sphere around the Pd(II) atom is a slightly distorted parallelogram, which is confirmed by ∠Cl–Pd–Cl = 179.66(12)°, ∠P–Pd–P = 178.45(8)°, ∠Cl–Pd–P = 92.04(7)° and 87.96(7)°. The important bond distances d(Pd—P) = 2.346(2) Å) and d(Pd—Cl) = 2.379(4) Å are similar to those in complex $[PdCl_2(PPh_3)_2] \cdot C_2H_4Cl_2$ (d(Pd—P) = 2.339(1) Å and d(Pd—Cl) = 2.326(1) Å) [10]. The Pd—P distance is longer than that in simlar complex $[PdCl_2(PPh_3)_2] \cdot 2CHCl_3$ (2.293(2) Å) [9]. No significant hydrogen bonding is observed. Related compounds are $[PdI_2(C_{18}H_{15}P)_2] \cdot 2CH_2Cl_2$ [11], *trans*-$[PdI_2(PPh_3)_2] \cdot CHCl_3$ [12], $[PdI_2(C_{18}H_{15}P)_2]$ [4], *trans*-$[PdI_2(PPhMe_2)_2]$ [13] and *trans*-$[PdCl_2(PPh_3)_2]$ [6].

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.30 × 0.33 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.09 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8090, 3044
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2129
$N(param)_{refined}$:	209
Programs:	SHELXS-97, SHELXL-97, SHELXTL [14]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2)	8*f*		0.4083	0.3992	0.0437	0.065
H(3)	8*f*		0.5018	0.4226	–0.0541	0.080
H(4)	8*f*		0.6292	0.3162	–0.0866	0.077
H(5)	8*f*		0.6665	0.1874	–0.0223	0.081
H(6)	8*f*		0.5775	0.1647	0.0761	0.065
H(8)	8*f*		0.3313	0.1518	0.0271	0.065
H(9)	8*f*		0.2530	0.0076	0.0068	0.074
H(10)	8*f*		0.2190	–0.0914	0.0937	0.070
H(11)	8*f*		0.2727	–0.0478	0.2007	0.085
H(12)	8*f*		0.3482	0.0973	0.2216	0.071
H(14)	8*f*		0.1674	0.2560	0.1077	0.070
H(15)	8*f*		0.0317	0.3709	0.1056	0.089
H(16)	8*f*		0.0742	0.5190	0.1384	0.088
H(17)	8*f*		0.2524	0.5589	0.1702	0.076
H(18)	8*f*		0.3906	0.4455	0.1770	0.060
H(20A)	8*f*	0.50	–0.0402	0.2725	0.2134	0.198
H(20B)	8*f*	0.50	0.0723	0.2704	0.2556	0.198
H(20C)	8*f*	0.50	–0.0396	0.2508	0.2903	0.198

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	4*e*		½	0.25723(5)	¼	0.0441(5)	0.0264(4)	0.0353(4)	0	–0.0030(3)	0
Cl(1)	8*f*		0.6761(3)	0.2567(2)	0.2005(1)	0.115(2)	0.067(2)	0.078(2)	–0.007(2)	–0.022(2)	0.007(1)
P(1)	8*f*		0.4055(1)	0.2550(1)	0.14507(8)	0.0374(9)	0.0256(8)	0.0325(9)	0.0035(8)	–0.0009(7)	0.0003(6)
N(1)	8*f*	0.50	0.019(3)	0.069(2)	0.215(1)	0.12(2)	0.12(2)	0.15(2)	–0.01(2)	0.00(2)	0.00(2)
C(1)	8*f*		0.4822(6)	0.2782(5)	0.0695(3)	0.042(4)	0.042(4)	0.035(4)	–0.004(3)	–0.003(3)	0.000(3)
C(2)	8*f*		0.4605(8)	0.3560(6)	0.0306(4)	0.061(6)	0.050(5)	0.051(5)	0.003(4)	0.008(4)	0.006(3)
C(3)	8*f*		0.5165(9)	0.3701(7)	–0.0282(4)	0.084(7)	0.062(5)	0.055(5)	–0.003(6)	0.012(5)	0.013(4)
C(4)	8*f*		0.5922(8)	0.3072(7)	–0.0473(4)	0.065(6)	0.075(6)	0.054(5)	–0.009(5)	0.017(4)	–0.003(4)
C(5)	8*f*		0.6145(8)	0.2305(7)	–0.0088(5)	0.064(6)	0.071(6)	0.068(6)	0.008(5)	0.016(5)	–0.007(5)
C(6)	8*f*		0.5605(7)	0.2165(6)	0.0498(4)	0.058(5)	0.048(4)	0.057(5)	0.011(4)	0.011(4)	0.006(4)
C(7)	8*f*		0.3462(6)	0.1396(4)	0.1264(3)	0.048(4)	0.028(3)	0.040(4)	0.000(3)	0.006(3)	–0.001(3)
C(8)	8*f*		0.3186(8)	0.1121(5)	0.0627(4)	0.077(6)	0.044(4)	0.042(4)	–0.010(4)	–0.005(4)	0.000(3)
C(9)	8*f*		0.2716(9)	0.0254(6)	0.0505(4)	0.085(7)	0.049(5)	0.051(5)	–0.011(5)	–0.007(5)	–0.012(4)
C(10)	8*f*		0.2523(8)	–0.0340(6)	0.1018(4)	0.076(6)	0.040(4)	0.061(5)	–0.018(4)	0.015(5)	–0.011(4)
C(11)	8*f*		0.2828(9)	–0.0073(6)	0.1653(5)	0.103(8)	0.052(5)	0.059(6)	–0.023(6)	0.015(5)	–0.004(4)
C(12)	8*f*		0.3290(8)	0.0798(5)	0.1779(4)	0.091(7)	0.045(4)	0.043(4)	–0.025(5)	0.011(4)	–0.012(3)
C(13)	8*f*		0.2938(7)	0.3384(5)	0.1417(3)	0.047(5)	0.036(4)	0.036(4)	0.007(4)	0.004(3)	0.002(3)
C(14)	8*f*		0.1854(7)	0.3163(6)	0.1208(4)	0.059(6)	0.055(5)	0.060(5)	0.015(5)	–0.003(4)	0.000(4)
C(15)	8*f*		0.1041(9)	0.3854(7)	0.1196(5)	0.063(6)	0.082(7)	0.078(6)	0.024(6)	–0.001(5)	0.005(5)
C(16)	8*f*		0.130(1)	0.4741(7)	0.1388(5)	0.084(8)	0.067(6)	0.072(6)	0.037(6)	0.014(5)	0.014(5)
C(17)	8*f*		0.2356(9)	0.4977(6)	0.1587(4)	0.084(7)	0.048(5)	0.059(5)	0.021(5)	0.022(5)	0.007(4)
C(18)	8*f*		0.3190(8)	0.4301(5)	0.1618(4)	0.061(5)	0.039(4)	0.049(5)	0.007(4)	0.008(4)	0.002(3)
C(19)	8*f*	0.50	0.01(1)	0.143(2)	0.236(4)	0.10(5)	0.11(2)	0.13(7)	–0.01(3)	–0.01(5)	0.02(3)
C(20)	4*e*		0	0.243(2)	¼	0.12(2)	0.14(2)	0.14(2)	0	0.01(1)	0

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