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An alkyl–palladium(II) complex with a bidentate phosphine ligand: [1,3-bis(diphenylphosphino)propane-*P*,*P*′]dimethylpalladium(II) toluene hemisolvate

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Adnan S. Abu-Surrah,[a]* Tony Debaerdemaeker,[b] Wolfgang Huhn,[c] Bernhard Rieger,[c] Martti Klinga,[a] Timo Repo[a] and Markku Leskelä[a]

[a]Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, PO Box 55, FIN-00014 Helsinki, Finland, [b]Sektion Röntgen-und Elektronenbeugung, Universität Ulm, D-89069 Ulm, Germany, and [c]Anorganische Chemie II, Universität Ulm, D-89081 Ulm, Germany
Correspondence e-mail: adnan.surrah@helsinki.fi

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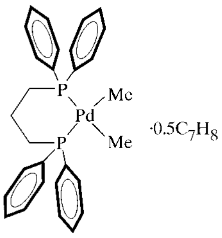
In the title compound, [Pd(CH_3)$_2$($C_{27}H_{26}P_2$)]·0.5C_7H_8, the Pd atom is at the centre of an approximately square-planar arrangement of two P atoms and two methyl groups. The P—Pd—P angle [93.19 (3)°] is significantly larger than that in the corresponding dichloride complex [Pd(dppp)Cl_2]. The toluene molecule is disordered across an inversion centre.

Comment

The solvated dicationic palladium(II) complex [Pd(dppp)($NCCH_3$)$_2$](BF_4)$_2$, bis(acetonitrile)[1,3-bis(diphenylphosphino)propane]palladium(II) bis(tetrafluoroborate), has been successfully used as catalyst precursor in the perfectly alternating copolymerization of alkenes with carbon monoxide (Abu-Surrah & Rieger, 1999). The two alternating propagation steps in this reaction are migratory insertion of carbon monoxide in the Pd–alkyl bond and subsequent migratory insertion of olefin in the resulting Pd–acyl bond. Since alkyl–palladium compounds with bidentate phosphines are of low stability, thermodynamically and kinetically, few of them have been structurally characterized (Wisner *et al.*, 1986). Here we report on the X-ray structure of the dimethylpalladium complex [Pd(dppp)(CH_3)$_2$]·0.5C_7H_8, (I).



(I)

The bond lengths of the two Pd—CH_3 distances [2.084 (2) and 2.087 (3) Å] are typical for Pd—C bonds (Crociani *et al.*, 1980) and in close agreement with the values found in [Pd(dmpe)(CH_3)$_2$] [2.087 (4) Å; de Graaf *et al.*, 1989; dmpe is 1,2-bis(dimethylphosphino)ethane], but they are significantly longer than those in [Pd(tmeda)(CH_3)$_2$] [2.026 (3) and 2.029 (3) Å; tmeda is *N*,*N*,*N*′,*N*′-tetramethylethylendiamine; de Graaf *et al.*, 1989]; this is an indication to the larger *trans* influence of the diphosphine ligand (Abu-Surrah *et al.*, 1999).

The lengths of the Pd—P bonds in the title compound (I) are 2.2999 (7) and 2.3038 (7) Å, which are longer than in the monomeric compound [Pd(dppp)Cl_2] [Steffen & Palenik, 1976; 2.244 (2) and 2.249 (2) Å]. Phosphines *trans* to alkyl groups in square-planar complexes tend to have longer M—P bond distances because alkyl groups are believed to weaken the *trans* bond by inductive effect (Appleton *et al.*, 1973; Saleem & Hodali, 1991).

The P—Pd—P angle of 93.19 (3)° in the dimethyl complex is significantly larger than that reported for the corresponding dichloride complex [89.32 (3)°], despite that both square-planar complexes contain the same diphosphine ligand. This indicate that the P—Pd—P angle is dependent not only on the ligand (Steffen & Palenik, 1976), but also on the influence of the alkyl groups occupying the two other coordinating positions. Upon formation of the Pd—C bond, believed to be the intermediate in catalytic processes forming C—C bonds, the steric constrains imposed by chelation of the dppp ligand decreases, thus leading to greater flexibility in the catalytically active palladium–alkyl species.

Experimental

The title compound (I) was prepared following a previously published procedure (Saleem & Hodali, 1990). A suspension of the dichloride complex [Pd(dppp)Cl_2] (2.0 g, 3.39 mmol) in dry diethyl ether (50 ml) was cooled to 273 K. Methyl lithium solution (1.6 M, 17 mmol) was added dropwise within 30 min. The mixture was then allowed to warm up to room temperature, and treated at 273 K with saturated aqueous NH_4Cl (50 ml). The ether layer was separated and dried over $MgSO_4$. The filtrate was evaporated to dryness to give a white microcrystalline solid. Recrystallization from toluene yielded colourless crystals suitable for X-ray analysis (total yield 1.50 g, 81%).

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Crystal data

$[Pd(CH_3)_2(C_{27}H_{26}P_2)]\cdot 0.5C_7H_8$
$M_r = 594.95$
Monoclinic, $P2_1/n$
$a = 12.260$ (3) Å
$b = 15.025$ (2) Å
$c = 16.347$ (3) Å
$\beta = 99.00$ (2)°
$V = 2974.2$ (10) Å^3
$Z = 4$

$D_x = 1.329$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4521 reflections
$\theta = 2.16$–24.10°
$\mu = 0.750$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.45 × 0.40 × 0.35 mm

Data collection

Stoe–IPDS image-plate diffractometer
Rotation scans
22466 measured reflections
4521 independent reflections
3825 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.034$
$\theta_{\rm max} = 24.10°$
$h = -13 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -18 \rightarrow 18$
Intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.062$
$S = 1.036$
4521 reflections
355 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 0.2200P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—C28	2.084 (2)	Pd1—P1	2.2999 (7)
Pd1—C29	2.087 (3)	Pd1—P2	2.3038 (7)
C28—Pd1—C29	85.05 (11)	C28—Pd1—P2	92.00 (8)
C28—Pd1—P1	174.63 (8)	C29—Pd1—P2	176.49 (7)
C29—Pd1—P1	89.72 (8)	P1—Pd1—P2	93.19 (3)

The measured intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *XMY* program package (Debaerdemaeker, 1993). All non-H atoms were refined anisotropically. H atoms were positioned geometrically and their displacement factors were set at 1.2 times the isotropic factor for the host atom.

Data collection: *IPDS* (Stoe & Cie, 1997)); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *XMY*93 (Debaerdemaeker, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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