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Synthesis and X-ray structure of palladium dichloride complexed with THF and 2,6,7-trioxa-3,5,8-tris(trichloromethyl)-1,4-diphosphabicyclo[2.2.2]octane

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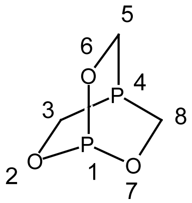
Abstract

Palladium(II) dichloride containing both THF and the title bicyclic diphosphorus ligand **2** {i.e. $P[OCH(CCl_3)]_3P$} has been synthesized and characterized by spectroscopic methods including X-ray crystallography. This compound is the first example of a metal complex containing the novel ligand **2**. The X-ray structure of the complex reveals a virtually square-planar geometry around the palladium with *trans* oriented chlorine atoms and with **2** ligated by the PO_3 terminus.

Keywords: Palladium(II) chloride; Difunctional phosphorus ligand; Bicyclic ligand; X-ray structure

1. Introduction

The chemistry of the bicyclic molecule $P(OCH_2)_3P$ (**1**), including some of its coordination properties, has received considerable attention in our laboratories [1–12]. Several more sterically hindered chiral 3,5,8-trialkyl derivatives of **1**, including the 3,5,8-*tris*(trichloromethyl) derivative **2** (see numbering scheme below), have also been described [13–16]. Difunctional bicyclic diphosphorus ligands of this type are interesting in that either or both phosphorus atoms can potentially engage in metal ligation, depending on the stereoelectronic properties of the metal moiety. No reports on the coordination chemistry of **2** have appeared, however, although several organic transformations of this molecule have been described along with its synthesis [13–16].



Several examples of zerovalent Fe, Cr, W and Mo complexes of **1** have been reported [10–12], but no examples of complexes of this ligand containing higher-valent metals have been described. Interesting in this regard is that the molecular library strategy [17] for supramolecular self-assembly chemistry using a non-chelating diligating ligand was first applied using $P(OCH_2)_3P$ by our group [12] and was later elaborated by Fujita and Stang using highly directional ligands containing monodentate units [17].

Herein is described the first report to the best of our knowledge of a coordination complex of **2**, namely, a monomeric Pd(II) dichloride compound containing **2** and also a THF molecule.

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2. Experimental

2.1. General considerations

All reactions were carried out under argon using standard Schlenk and glove box techniques [18] and chemicals were purchased from Aldrich and were used as supplied unless otherwise indicated. THF and toluene (Fisher HPLC grade) were dried and purified under nitrogen in a Grubbs-type non-hazardous two-column solvent purification system [19] (Innovative Technologies) and were stored over activated 3 Å molecular sieves. All deuterium solvents were dried over activated molecular sieves (3 Å) and were used after vacuum transfer to a Schlenk tube equipped with J. Young valve. ^{1}H, $^{13}C\{^{1}H\}$- and ^{31}P-NMR spectra were recorded at ambient temperature on a Varian VXR-400 NMR spectrometer using standard parameters. Chemical shifts are referenced to the residual peaks of $CDCl_3$ (7.24 ppm, ^{1}H-NMR; 77.0 ppm, $^{13}C\{^{1}H\}$-NMR). Elemental analysis was performed by Desert Analytics Laboratory.

2.2. Synthesis

$PdCl_2(PhCN)_2$ [20] and **2** [13] were synthesized by literature procedures and **4** was synthesized as follows. To a solution of $PdCl_2(PhCN)_2$ (500 mg, 1.31 mmol) in 30 ml of toluene was added a solution of **2** (617 mg, 1.31 mmol) in 20 ml of toluene at room temperature (r.t.) under an atmosphere of Ar. The reaction mixture was stirred for 12 h after which the volatiles were removed under reduced pressure to yield a yellow solid, which was recrystallized from THF–ether in a refrigerator (0.74 g, 75%).

^{1}H-NMR ($CDCl_3$, 400.147 MHz): δ 5.96 (d, $J = 6.7$ Hz, 3H, $C\mathit{H}P$), 3.74 (m, 4H, $C\mathit{H_2}O$), 1.84 (m, 4H, $C\mathit{H_2}CH_2O$).

$^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 100.626 MHz): δ 85.9 (d, $J = 7.8$ Hz, $P\mathit{C}H$), 85.4 (d, $J = 8.1$ Hz, $\mathit{C}Cl_3$), 68.1 ($O\mathit{C}H_2$), 25.6 ($OCH_2\mathit{C}H_2$).

^{31}P-NMR ($CDCl_3$, 81.01 MHz): δ 77.7 (br, $\mathit{P}O$), -13.2 (d, $J = 12.2$ Hz, $\mathit{P}CH$).

Elemental analysis: Anal. Calc. for $C_{10}H_{11}Cl_{11}P_2O_4Pd$: C, 15.94; H, 1.47; P, 8.22. Found: C, 15.88; H, 1.71; P, 7.86%.

2.3. X-ray structure determination

A yellow single crystal selected under ambient conditions was mounted and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed at 173 K on a Bruker CCD-1000 diffractometer with Mo–K_α ($\lambda = 0.71073$ Å) radiation with a detector-to-crystal distance of 5.03 cm. The initial cell constants were obtained from three series of ω-scans at different starting angles. Each series consisted of 30 frames collected at intervals of 0.3° in a 10° range about ω with an exposure time of 10 s per frame. A total of 189 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built into the SMART program. The final cell constants were calculated from a set of 4352 strong reflections from the actual data collection. The data were collected using the full sphere routine. A total of 10 069 data were harvested by collecting four sets of frames with 0.3° scans in ω with an exposure time 10 s per frame. This dataset was corrected for Lorentz and polarization effects. The absorption correction was based on a function fitted to the empirical transmission surface as sampled by multiple equivalent measurements [21] using SADABS software [22]. The compound crystallized in the triclinic system and the space group $P\bar{1}$ was confirmed [22]. The position of the heavy atom was found by the Patterson method. The remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in a full-matrix anisotropic approximation. All hydrogen atoms were placed in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Final least-squares refinement of 253 parameters against 4877 independent reflections converged to an R (based on F for $I \geq 2\sigma$) and a wR (based on F for $I \geq 2\sigma$) of 0.0255 and 0.0587, respectively. The detailed data are given in Table 1.

3. Results and discussion

Ligand **2** was easily synthesized by a modification of a literature method whose last step is the reaction of $P[CH(CCl_3)OH]_3$ with PCl_3 in THF, giving a 32% yield [13]. We used $P(OMe)_3$, which in our hands worked more conveniently than PCl_3, although the yield (ca. 30%) was similar. Compound **2** was purified before use by sublimation per 70 °C per 7 µm. When ligand **2** was allowed to react with one equivalent of $PdCl_2(PhCN)_2$ (Scheme 1) a yellow powder **3** was obtained in 86% yield after evaporation. According to its ^{1}H-NMR spectrum, this complex contains a coordinated PhCN molecule. However, recrystallization from THF–diethyl ether caused the replacement of the PhCN by THF, affording **4** in 75% yield. Complex **4** is soluble in polar organic solvents and in toluene, but it is insoluble in alkanes such as n-hexane. In the solid state, **4** is air-stable for extended periods and is also quite thermally stable, resisting decomposition, even upon heating to 100 °C under vacuum.

The composition of **4** was established by ^{1}H-, $^{13}C\{^{1}H\}$- and ^{31}P-NMR spectroscopy and by elemental

Table 1
Crystallographic data and parameters for **4**

Empirical formula	$C_{10}H_{11}Cl_{11}O_4P_2Pd$
Formula weight	753.48
Temperature (K)	173
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.082(2)
b (Å)	11.698(3)
c (Å)	12.381(3)
α (°)	114.186(4)
β (°)	97.094(4)
γ (°)	108.638(4)
Volume (Å^3)	1206.2(5)
Z	2
D_{calc} (mg m^{-3})	2.075
Absorption coefficient (mm^{-1})	2.137
F(000)	732
Crystal size (mm^3)	0.2 × 0.2 × 0.1
θ Range for data collection (°)	2.04–26.39
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-14 \le l \le 15$
Reflections collected	10 069
Independent reflections	4877 [$R_{int} = 0.0263$]
Completeness to $\theta = 26.39°$ (%)	98.6
Absorption correction	Empirical
Max/min transmission	0.86 and 0.70
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4877/0/253
Goodness-of-fit on F^2	0.963
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0255$, $wR_2 = 0.0587$
R indices (all data)	$R_1 = 0.0340$, $wR_2 = 0.0613$
Largest difference peak and hole (e Å^{-3})	0.653 and −0.518

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

analysis, and its structure was determined by X-ray means. The ^{1}H-NMR spectrum of **4** displays well-defined resonances with expected integrations. Compared with **2**, all signals in the ^{1}H- and $^{13}C\{^1H\}$-NMR spectra of **4** are shifted downfield. The ^{31}P-NMR signal for the PO_3 phosphorus of **4** is broadened and shifted substantially upfield (from 109.3 in **2** to 77.7 ppm in **4**) but the PC_3 resonance shifted only slightly downfield (from −15.7 to −13.2 ppm). These results accord with the presence of a ligated PO_3 phosphorus in **4** and a free PC_3 phosphorus, and hence the complex is mononuclear, as is confirmed by the X-ray crystallographic results. We were unable to obtain $Cl_2Pd(\mathbf{2})_2$ by reacting two equivalents of **2** with $PdCl_2(PhCN)_2$. The proton NMR spectrum of the product mixture in this case was complicated, although a small amount of **3** did seem to be present.

Deep yellow single crystals of **4** suitable for X-ray crystallographic studies were obtained from a refrigerated (−15 °C) THF–diethyl ether solution of **3**. Complex **4** crystallizes as discrete mononuclear species in the triclinic space group $P\bar{1}$. The ORTEP diagram presented in Fig. 1 shows an almost square-planar geometry around the palladium atom with two Cl atoms in mutually *trans* positions. Selected bond lengths and angles are listed in Table 2.

Interestingly, the Pd1 atom is very slightly distorted toward a tetrahedron with a deviation (outside of 3 × estimated S.D. value) of about 0.058 Å from the near planarity of the O1, Cl1, P1 and Cl11 atoms. The structure of **4** also displays deviations from square angles at the palladium atoms (e.g. O1–Pd1–P1 =

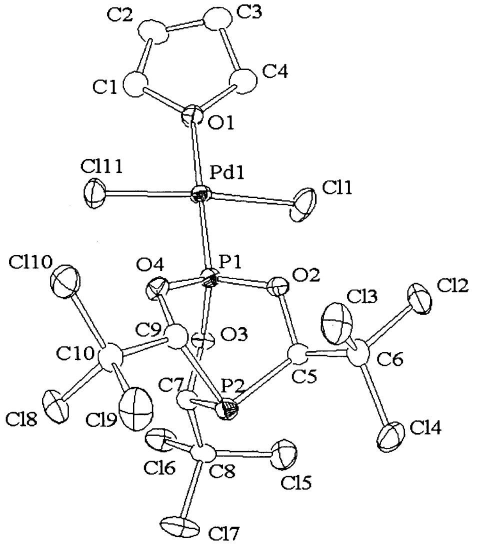
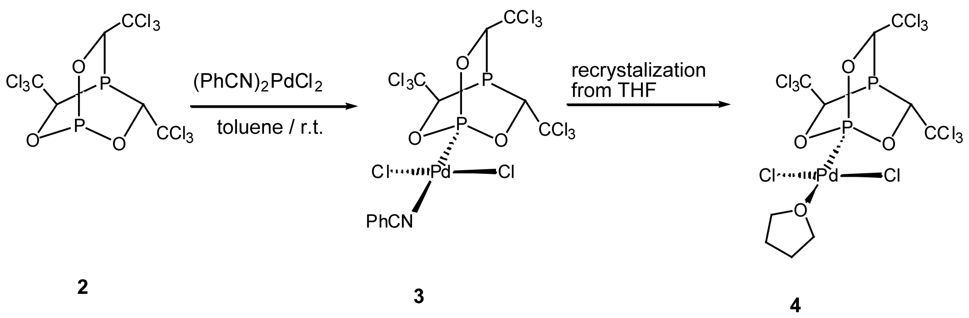


Fig. 1. ORTEP drawing of **4** showing 50% probability thermal ellipsoids, with H atoms omitted for clarity.



Scheme 1.

Table 2
Selected bond distances (Å) and bond angles (°) for **4**

Bond distances	
Pd1–O1	2.1119(18)
Pd1–Cl11	2.2790(8)
P1–O2	1.5936(18)
P1–O4	1.5967(18)
P2–C7	1.895(2)
O1–C1	1.451(3)
P1···P2	3.065
Pd1–Cl1	2.2789(9)
Pd1–P1	2.1383(8)
P1–O3	1.5967(18)
P2–C5	1.888(3)
P2–C9	1.893(3)
O1–C4	1.448(3)
Bond angles	
O1–Pd1–P1	179.42(6)
O1–Pd1–Cl1	91.36(6)
P1–Pd1–Cl1	88.32(3)
Pd1–O1–C1	124.33(16)
Pd1–P1–O2	115.76(7)
Pd1–P1–O4	112.84(7)
C1–C2–C3	103.8(2)
C3–C4–O1	104.8(2)
Pd1–P1–P2	177.52
Cl1–Pd1–Cl11	174.75(3)
O1–Pd1–Cl11	92.04(6)
P1–Pd1–Cl11	88.24(3)
Pd1–O1–C4	124.80(17)
Pd1–P1–O3	117.08(7)
O1–C1–C2	105.3(2)
C2–C3–C4	103.2(3)
C4–O1–C1	109.9(2)

179.42(6)°, Cl1–Pd1–Cl11 = 174.75(3)°). The Pd–Cl [2.2790 Å], Pd–O [2.1119(18) Å] and Pd–P [2.1383(8) Å] bond distances are similar to the average of such bonds present in other structurally characterized palladium(II) complexes [23–25]. A novel feature of **4** is the presence of a coordinated THF molecule, despite the well-known tendency of this molecule to solvate rather than to ligate palladium(II) [26–28]. Although some Pd complexes containing a coordinated THF molecule have been reported, their structural characterization was limited to the interpretation of NMR and IR spectra, and elemental analysis [29–33]. Only one example of a structurally characterized Pd complex ligated by THF has to our knowledge been reported [namely, [{(*S*)-MeO-BIPHEP}Pd(H_2O)(THF)]$(OTf)_2$ [wherein MeO-BIPHEP is (6,6′-dimethoxy-biphenyl-2,2′diyl)*bis*(diphenylphosphine)] [25]. The P1–P2 non-bonding distance and the Pd1–P1–P2 bond angle is 3.065 Å and 177.52°, respectively.

To investigate the possibility of forming a molecular square with **2** and palladium(II), a solution of one equivalent of $PdCl_2(PhCN)_2$ in toluene was added to a solution of **4** in the same solvent at room temperature under an argon atmosphere. However, only unreacted **4** and $PdCl_2(PhCN)_2$ were recovered. Similarly, the reaction between one equivalent of $PdCl_2(PhCN)_2$ and two equivalents of **2** in toluene gave a mixture of **4** and uncharacterized compounds. We surmise from these results that although coordination of the PO_3 phosphorus is relatively easy, the PC_3 phosphorus is sterically encumbered by the CCl_3 groups, and is therefore prevented from forming a square array of palladium atoms bonded in *cis* positions by **2**.

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC 197572 for **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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