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Note

Stereoelectronic properties of the sulfinyl-substituted phosphine ligands: synthesis and X-ray structure of the stable complex $[PdCl_2\{Ph_2PCH_2S(O)Me\}\{MeOH\}]$

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Abstract

The square-planar complex *trans*-$[PdCl_2\{Ph_2PCH_2S(O)Me\}\{MeOH\}]$ has been prepared. The compound crystallizes as orange–red prisms in the monoclinic space group $P2_1/n$, with $a=9.446(2)$, $b=14.858(3)$, $c=13.578(3)$ Å, $\beta=105.08(2)°$ and $Z=4$. The structure was determined by direct methods and refined to $R=0.027$ and $R_w=0.041$. All atoms including hydrogens were located directly from Fourier difference maps. The coordination geometry around palladium is square-planar. The metal is coordinated to the two chlorines, the oxygen of methanol and the phosphorus of the sulfinyl-substituted ligand. In solution, a similar structure is assigned to the complex by NMR studies. In contrast to the previously documented $Ph_2PCH_2CH_2S(O)Me$ analogue, the sulfoxide function in the $Ph_2PCH_2S(O)Me$ ligand is not involved in any coordination bondings with palladium, both in the solid state and in solution.

Keywords: Crystal structures; Palladium complexes; Methanol complexes; Phosphine sulfoxide complexes

1. Introduction

A significant number of chiral sulfoxides and their transition metal complexes have been reported in recent years for possible applications in biochemistry [1,2], asymmetric synthesis [3] and homogenous catalysis [4]. The use of such complexes as catalysts in asymmetric catalysis, however, is limited by their kinetic instability and the two interconvertible sulfoxide–metal connectivities [1,5]. In the effort to resolve these inherent problems, we have published several papers in the last two years describing the coordination chemistry and the optical resolution of a new family of sulfinyl-substituted chiral amine, arsine and phosphine ligands, $Ph_2E(CH_2)_2S(O)Me$ (where E = N, As, P). Hence, stable complexes with five-membered E-S and six-membered E-O chelates can be prepared controllably [6]. In this paper, we report the synthesis of the analogous ligand (±)-$Ph_2PCH_2S(O)Me$ and its coordination properties towards palladium(II).

2. Experimental

Routine ^1H and ^{31}P NMR spectra were recorded at 25 °C on a Bruker ACF 300 spectrometer. Chloromethylmethylsulfoxide was prepared by a literature method [7]. Elemental analyses were performed by the Microanalytical Laboratory staff of the Department of Chemistry.

2.1. Synthesis of $Ph_2PCH_2S(O)Me$

The sulfinyl-substituted phosphine was prepared by treating a solution of diphenylphosphine (12.7 g) in tetrahydrofuran (200 ml) with sodium metal (1.6 g) at room temperature followed by chloromethylmethylsulfoxide (9 g) in tetrahydrofuran at −78 °C. After work-up, the crude product was isolated as a white solid via column chromatography (silica gel 60 and 1:4 ethyl acetate:hexane as eluent). The product was then recrystallized as colourless prisms from ethyl acetate–hexane; m.p. 82–83 °C, yield 7.9 g (44%). *Anal.* Calc. for $C_{14}H_{15}OPS$: C, 64.1; H, 5.8; P, 11.8. Found: C, 64.1; H, 5.7; P, 11.6%.

2.2. Synthesis of trans-$[PdCl_2\{Ph_2PCH_2S(O)Me\}\{MeOH\}]$

The neutral complex was prepared by adding a solution of the sulfinyl-substituted phosphine ligand (0.62 g) in acetonitrile (15 ml) to $(CH_3CN)_2PdCl_2$ (0.61 g) in acetonitrile (40 ml). Methanol (40 ml) was then introduced and the

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Table 1
Summary of crystal data for $[PdCl_2\{Ph_2PCH_2S(O)Me\}\{MeOH\}]$

Chemical formula	$C_{15}H_{19}Cl_2O_2PPdS$
Formula weight	471.6
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	9.446(2)
b (Å)	14.858(3)
c (Å)	13.578(3)
β (°)	105.08(2)
Volume of unit cell (Å^3)	1839.9(6)
Z	4
D_c (g cm^{-3})	1.703
μ (cm^{-1})	15.02
$F(000)$	944
Temperature (°C)	25
R [a]	0.027
R_w [b]	0.041

[a] $R = \Sigma|F_o - F_c|/\Sigma(F_o)$.
[b] $R_w = \{[\Sigma_w|F_o - F_c|^2]/[\Sigma_w(F_o)^2]\}^{1/2}$.

reaction mixture was allowed to stir for 1 h at room temperature. The compound crystallized from methanol–diethyl ether as bright orange–red crystals; m.p. 200 °C (dec.), yield 0.83 g (80%). *Anal.* Calc. for $C_{15}H_{19}Cl_2O_2PPdS$: C, 38.2; H, 4.1; Cl, 15.0; P, 6.6. Found: C, 38.4; H, 4.2; Cl, 15.3; P, 6.7%.

2.3. X-ray data collection and structure refinement

Cell dimensions of $[PdCl_2\{Ph_2PCH_2S(O)Me\}\{MeOH\}]$ were determined by least-squares calculation from 24 reflections at $2\theta > 15°$. The reflections were obtained by an automated random search routine at room temperature on a Siemens R3m/V four-circle diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). An orange–red crystal of approximate dimensions 0.45 × 0.30 × 0.30 mm was used. Data were collected for $3.0 \leq 2\theta \leq 50°$ and index range $0 \leq h \leq 11$, $0 \leq k \leq 17$, $-16 \leq l \leq 15$ with a variable scan rate of 3.00–33.48° min^{-1}. Table 1 gives a summary of the crystallographic data. A total of 3610 reflections was collected and 3007 observed reflections ($F > 3\sigma(F)$) were used in the refinement. Semiempirical absorption corrections were applied. The structure was solved by direct methods. All atoms were located from Fourier difference maps but only the non-hydrogen atoms were refined anisotropically. The function minimized during full-matrix least-squares refinement was $\Sigma w|F_o - F_c|^2$ where $w^{-1} = \sigma^2(F) + 0.0011F^2$ giving $R = 0.027$, $R_w = 0.041$ and $S = 1.09$. All calculations were performed on a Digital Equipment Corp. MicroVax II computer using the Siemens SHELXTL PLUS package.

3. Results and discussion

The sulfinyl-substituted ligand was prepared from the reaction between $NaPPh_2$ and $MeS(O)CH_2Cl$ [7] in THF at −78 °C. The compound was crystallized from ethyl acetate–hexane as air-stable colourless prisms. In $CDCl_3$, the ^{31}P NMR spectrum of the ligand exhibited a sharp singlet at δ −29.01. The 300 MHz ^1H NMR spectrum of the same sample showed a characteristic sharp SMe singlet at δ 2.69. A four line NMR resonance pattern at δ 3.51 was assigned to one of the non-equivalent CH_2 protons ($^2J(HH) = 13.2$ Hz, $^2J(PH) = 2.86$ Hz). Interestingly, the second prochiral proton exhibited only a simple doublet at δ 3.69 ($^2J(HH) = 13.2$ Hz); no phosphorus coupling was detected for this nucleus. The sulfoxide ligand is stable in the solid state and in solution. In contact with iodide or molecular iodine, however, it rearranges immediately to the isomeric methylthio-substituted phosphine oxide, $Ph_2P(O)CH_2SMe$ [6].

Similar to its $Ph_2E(CH_2)_2S(O)Me$ analogues, the shorter chain compound $Ph_2PCH_2S(O)Me$ is also a powerful ligand for the palladium(II) ion. It reacts immediately with $[PdCl_2(CH_3CN)_2]$ in acetonitrile–methanol to give the stable neutral complex $[PdCl_2\{Ph_2PCH_2S(O)Me\}\{MeOH\}]$ as orange–red prisms in 80% isolated yield. The ^{31}P NMR spectrum of the complex in $CDCl_3$ shows a sharp peak at δ 24.12. The chemical shift of the NMR signal, however, indicates that the sulfinyl-sustituted ligand does not adopt a five-membered P–O chelate ring [8], and coordinates to palladium only with its phosphorus atom. The ^1H NMR spectrum of the same sample exhibits two sharp singlets at δ 2.68 and 3.48 for the SMe and OMe resonances, respectively. The chemical shift of the sulfoxide SMe signal is typical for palladium complexes with uncoordinated sulfoxide functions [1,9]. For comparision, the ^{31}P and SMe resonances of the analogous compound $[PdCl_2\{Ph_2PCH_2CH_2S(O)Me\}]$ in CD_3CN both occurred at significantly higher chemical shifts, i.e. δ 70.50 and δ 3.53, respectively [6]. Based on these NMR data, a five-membered P–S ring has been assigned to the structure of the complex in solution. In another resolving complex, $[Pd\{(S)\text{-}CH_3CH(1\text{-}C_{10}H_6)NMe_2\}\{(S)\text{-}\{Ph_2P\text{-}CH_2CH_2S(O)Me\}\}]ClO_4$, in which the sulfoxide ligand adopted a six-membered P–O ring [6], the ^{31}P and SMe signals were observed at δ 33.23 and 3.12 (in $CDCl_3$).

In the solid state, structural characterization of the palladium complex was carried out by single crystal X-ray diffraction (Fig. 1). Selected bond lengths and angles are listed in Table 2. Table 3 gives the fractional atomic coordinates

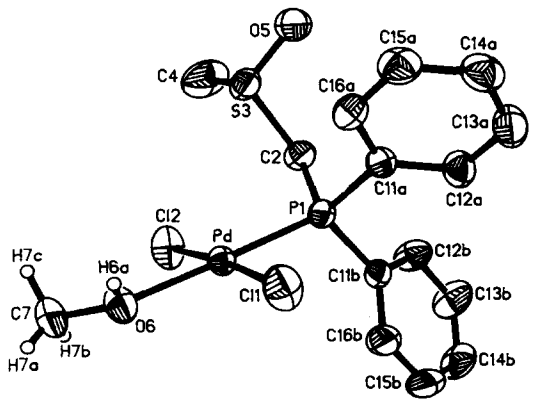

Fig. 1. Molecular structure and atomic numbering scheme for $[PdCl_2\{Ph_2PCH_2S(O)Me\}\{MeOH\}]$.

Table 2
Selected bond distances (Å) and angles (°) of $[PdCl_2\{Ph_2PCH_2S(O)Me\}\{MeOH\}]$ with e.s.d.s in parentheses

Pd–Cl(1)	2.275(1)
Pd–Cl(2)	2.291(1)
Pd–P(1)	2.213(1)
Pd–O(6)	2.148(2)
P(1)–C(2)	1.838(3)
C(2)–S(3)	1.819(4)
S(3)–C(4)	1.791(5)
S(3)–O(5)	1.497(2)
O(6)–C(7)	1.424(5)
Cl(1)–Pd–Cl(2)	174.3(1)
Cl(1)–Pd–P(1)	90.8(1)
Cl(1)–Pd–O(6)	84.9(1)
Cl(2)–Pd–P(1)	91.8(1)
Cl(2)–Pd–O(6)	92.9(1)
P(1)–Pd–O(6)	174.4(1)
Pd–P(1)–C(2)	112.0(1)
Pd–O(6)–C(7)	127.8(2)
C(2)–S(3)–C(4)	97.8(2)
C(2)–S(3)–O(5)	104.7(1)
C(4)–S(3)–O(5)	104.9(2)

for the non-hydrogen atoms. The study confirms that $Ph_2PCH_2S(O)Me$ coordinates to the metal as a mondentate via solely its phosphorus donor atom. Methanol is coordinated to the metal via its oxygen in the position *trans* to phosphorus and the Pd–O distance (2.148 Å) is the shortest among the four metal–donor bondings. The large Pd–O(6)–C(7) angle of 127.8° is noteworthy and probably suggests the presence of π-bond character. The oxygen and sulfur atoms of the sulfoxide function are not located within the bonding distance to palladium; they are about 5.04 and 3.85 Å from Pd, respectively. Interestingly, the S–O bond length of 1.497(2) Å is in between those involved in palladium complexes with sulfoxide–O (1.52–1.56 Å) and sulfoxide–S (1.46–1.49) bonds [1,6,9,10].

Table 3
Fractional atomic coordinates ($\times 10^4$) and equivalent thermal parameters ($Å^2 \times 10^3$) with e.s.d.s in parentheses for the non-hydrogen atoms of $[PdCl_2\{Ph_2PCH_2S(O)Me\}\{MeOH\}]$

Atom	x	y	z	U_{eq} [a]
Pd	10716(1)	5212(1)	2233(1)	30(1)
Cl(1)	11763(1)	3825(1)	2513(1)	55(1)
Cl(2)	9778(1)	6641(1)	2116(1)	52(1)
P(1)	8503(1)	4610(1)	1942(1)	30(1)
C(2)	7091(3)	5342(2)	1146(2)	38(1)
S(3)	7418(1)	5588(1)	−89(1)	41(1)
C(4)	6614(7)	6687(3)	−260(4)	81(2)
O(5)	6357(3)	5001(2)	−824(2)	50(1)
O(6)	12922(3)	5686(2)	2437(2)	43(1)
C(7)	13420(5)	6594(3)	2505(3)	55(1)
C(11A)	8291(3)	3530(2)	1288(2)	33(1)
C(12A)	7518(3)	2831(2)	1592(2)	44(1)
C(13A)	7369(4)	2015(2)	1076(3)	52(1)
C(14A)	7957(4)	1895(2)	262(3)	51(1)
C(15A)	8727(4)	2588(2)	−36(3)	49(1)
C(16A)	8905(3)	3396(2)	473(2)	43(1)
C(11B)	7870(3)	4458(2)	3084(2)	33(1)
C(12B)	6399(4)	4518(3)	3058(3)	49(1)
C(13B)	5945(4)	4378(3)	3947(3)	60(1)
C(14B)	6953(4)	4181(3)	4842(3)	56(1)
C(15B)	8390(4)	4120(3)	4872(3)	57(1)
C(16B)	8880(4)	4251(3)	3998(3)	48(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

It is noteworthy that the isolation and the remarkable stability of this methanol–palladium(II) complex are somewhat unexpected. Although it is long known that methanol coordinates to palladium(II) in solution [11,12], previous attempts to isolate such complexes in solid state have not been successful [12]. Our experimental observations clearly indicate that the α-sulfinyl-substituted phosphine ligand is a more efficient supporting ligand for coordinating methanol than other tertiary phosphines, such as dppe [12]. Although not proven, it is likely that the well known π-acid character of the phosphorus donor atom is further strengthened by the electron withdrawing sulfoxide function in $Ph_2PCH_2S(O)Me$. When methanol was not introduced during the complex synthesis, however, only small quantities of $[PdCl_2\{Ph_2PCH_2S(O)Me\}_2]$ could be isolated from a mixture of yet unidentified products.

4. Supplementary material

Synthetic and spectroscopic data, tables of thermal parameters, and bond distances and angles are available from the authors on request.

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