Short Communication

Palladium(II) and platinum(II) complexes with chelating sulfinyl functions

Simon Y. M. Chooi, Pak-hing Leung* and K. F. Mok*

Department of Chemistry, National University of Singapore, Kent Ridge 0511 (Singapore)

(Received August 24, 1992; revised October 26, 1992)

Abstract

The synthesis of palladium and platinum complexes of (±)-$Ph_2ECH_2CH_2S(O)Me$ (E = P, As) is described. A single crystal X-ray diffraction study of [(±)-$Ph_2PCH_2CH_2S(O)MePdCl_2$] reveals a square-planar geometry at the central atom which is attached by a chelate ring via the P–S donors of the sulfinyl-substituted ligand. Similar structures are assigned to all four complexes by ^1H NMR spectroscopy in d_3-acetonitrile solutions. Oxygen–metal bonds are not involved in these molecules.

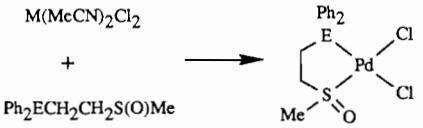
Introduction

Chiral sulfoxides have long been an important tool in the asymmetric synthesis of organic compounds [1]. Recently Ronan and Kagan published an asymmetric synthesis of chiral lactones using a Diels–Alder reaction between an optically active vinyl sulfoxide and a substituted cyclopentadiene [2]. Compared to the bewildering range of compounds known in organic chemistry, however, the number of well-defined hetero-chelating agents containing this ambidentate function is few [3, 4]. We were interested in the coordination chemistry of transition metal complexes with chelating chiral sulfinyl functions because of their potential use in homogenous asymmetric catalysis [3–5]. In this paper, we report the synthesis and properties of four model compounds [(±)-$Ph_2ECH_2CH_2S(O)MeMCl_2$] (where E = P, As; M = Pd, Pt). In subsequent work it will be shown that the information obtained in this preliminary study is crucial to the optical resolution of the chelating agents in which a metal complexation process [6] is involved.

*Authors to whom correspondence should be addressed.

Results and discussion

The sulfinyl-substituted ligands were prepared from a one-step reaction between $ClCH_2CH_2S(O)Me$ [7] and $LiEPh_2$ in THF at −78 °C. After column chromatography and subsequent recrystallizations, both compounds were obtained as white needles in high yields (E = P, 80%; E = As, 81%). In $CDCl_3$, the ^1H NMR spectra of both ligands exhibited sharp singlets for the S–Me groups: δ 2.53 (E = P) and 2.50 (E = As). The compounds are air-stable in the solid state although they can be slowly oxidized to the corresponding arsine and phosphine oxides in solution. The ligands are powerful sequesters for platinum metal ions. With $(CH_3CN)_2MCl_2$ [8], the acetonitrile ligands are readily replaced to give the corresponding square-planar complexes in high yields (83–85%). All the neutral complexes are stable in the solid state and in solution.



1 E = P, M = Pd
2 E = As, M = Pd
3 E = P, M = Pt
4 E = As, M = Pt

In the present series of compounds metal chelates were found to involve E–S donor atoms. Structural characterization of **1** was carried out by single-crystal X-ray diffraction (Fig. 1). The coordination geometry of Pd is shown to be square-planar. The Pd–S distance

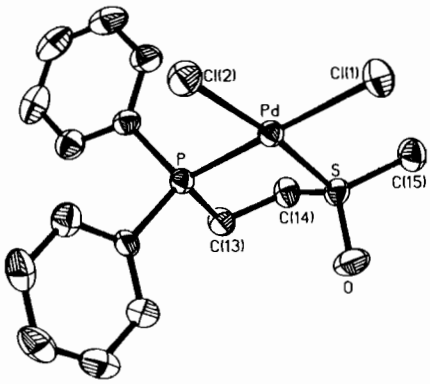


Fig. 1. Molecular structure and labeling scheme for [$PdCl_2(C_{15}H_{17}OS)$]. Selected bond distances and selected bond angles are: Pd–Cl(1) 2.369(1), Pd–Cl(2) 2.319(1), Pd–P 2.253(1), Pd–S 2.234(1), P–C(13) 1.837(4), C(13)–C(14) 1.517(6), C(14)–S 1.791(4), S–C(15) 1.758(5), S–O 1.469(2) Å; Cl(1)–P–Cl(2) 93.8(1), Cl(1)–Pd–P 176.2(1), Cl(2)–Pd–P 89.3(1), Cl(1)–Pd–S 91.6(1), Cl(2)–Pd–S 173.0(1), P–Pd–S 85.5(1), Pd–P–C(13) 106.5(1), Pd–S–O 114.1(1), C(14)–S–O 108.3(2), C(15)–S–O 109.1(2), Pd–S–C(14) 103.6(1), Pd–S–C(15) 117.3(1), C(14)–S–C(15) 103.4(2)°.

0020-1693/93/$6.00

of 2.234(1) Å is very similar to data reported on other monodentate sulfoxide–S complexes [9]. Pd–P, Pd–Cl(1) and Pd–Cl(2) distances of 2.253(1), 2.369(1) and 2.319(1) Å, respectively, are also all within the range of literature values [10]. Clearly, no Pd–O bond is involved in the molecule.

^{1}H NMR studies of the complexes indicated that the metal–sulfur bonds remain unchanged in solution. In d_3-acetonitrile, each of the complexes **1–4** exhibited one sharp S–Me singlet in their 300 MHz ^{1}H NMR spectra at δ 3.53, 3.53, 3.61 (^3J(Pt–H) = 22.8 Hz) and 3.61 (^3J(Pt–H) = 21.2 Hz), respectively. The chemical shifts are consistent with sulfinyl–S complexation [9]. In addition, the metal–^{1}H coupling values for complexes **3** and **4** are typical for platinum complexes with such coordinated chiral donor atoms [9, 11].

In conclusion, we have isolated the first examples of sulfinyl-substituted tertiary arsine and phosphine metal chelates utilizing their E–S donor atoms. We are pursuing the optical resolution of both racemic ligands in an attempt to prepare a family of optically active heterochelating agents in which the sulfinyl–S centers are the only sources of chirality.

Experimental

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

Ligand syntheses

The sulfinyl-substituted arsine was prepared by treating a solution of diphenylarsine (11.1 g) in tetrahydrofuran (100 ml) with 1.6 M n-butyllithium (30.0 ml) at −78 °C followed by 2-chloroethyl methyl sulfoxide (6.1 g) in tetrahydrofuran (30 ml). After work up, the crude product was isolated as a white solid via column chromatography (silica gel 60 and 4:1 ethyl acetate:hexane as eluent). The solid was then recrystallized from ethyl acetate by addition of n-hexane: white needles; m.p. 97–98 °C, yield 12.4 g (81%). *Anal.* Calc. for $C_{15}H_{17}AsOS$: C, 56.2; H, 5.4. Found: C, 56.2; H, 5.4%. The phosphine ligand was prepared similarly using diphenylphosphine as starting material. White needles from dichloromethane–n-hexane: m.p. 106–107 °C, 80% yield. *Anal.* Calc. for $C_{15}H_{17}OPS$: C, 65.2; H, 6.2. Found: C, 64.8; H, 6.1%.

Palladium(II) complexes

Complex **1** was obtained from the reaction between $(CH_3CN)_2PdCl_2$ (1.0 g) and $Ph_2PCH_2CH_2S(O)Me$ (1.1 g) in acetonitrile at room temperature. The compound crystallized from acetonitrile–diethyl ether as yellow prisms; m.p. 230–231 °C, yield 1.5 g (83%). *Anal.* Calc. for $C_{15}H_{17}Cl_2OPPdS$: C, 39.7; H, 3.8. Found: C, 39.4; H, 3.7%. Complex **2** was prepared similarly using $Ph_2AsCH_2CH_2S(O)Me$ as ligand. Yellow prisms from acetonitrile–diethyl ether: m.p. 237–238 °C, 85% yield. *Anal.* Calc. for $C_{15}H_{17}AsCl_2OPdS$: C, 36.2; H, 3.5. Found: C, 36.4; H, 3.2%.

Platinum(II) complexes

Complex **3** was obtained by treating a solution of $(CH_3CN)_2PtCl_2$ (200 mg) with $Ph_2PCH_2CH_2S(O)Me$ (159 mg) in acetonitrile (30 ml) for 1 h. The compound was crystallized from acetonitrile–diethyl ether as white prisms; m.p. 237–238 °C, yield 252 mg (84%). *Anal.* Calc. for $C_{15}H_{17}Cl_2OPPtS$: C, 33.2; H, 3.2. Found: C, 33.4; H, 3.1%. Complex **4** was prepared similarly from $Ph_2AsCH_2CH_2S(O)Me$: white prisms, m.p. 251–252 °C, 83% yield. *Anal.* Calc. for $C_{15}H_{17}AsCl_2OPtS$: C, 30.7; H, 2.9. Found: C, 30.8; H, 2.9%.

Crystal data

Complex **1** (298 K): $C_{15}H_{17}Cl_2OPPdS$, monoclinic, $P2_1/C$, $a = 8.728(2)$, $b = 14.684(3)$, $c = 13.655(2)$ Å, $\beta = 107.32(2)°$, $V = 1670.8(5)$ Å^3, $Z = 4$, $D_{calc} = 1.803$ g cm^{-3}, $D_{meas} = 1.79$ g cm^{-3}, $\mu = 1.65$ mm^{-1}. A pale yellow prism approximately $0.15 \times 0.25 \times 0.30$ mm in size was used for data collection (Siemens R3m/V, $2.5° < 2\theta < 50.0°$, Mo Kα, $0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 17$, $-16 \leqslant l \leqslant 16$). A total of 2963 out of 3311 reflections

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$)

Atom	x	y	z	U_{eq}[a]
Pd	−247(1)	9894(1)	1737(1)	25(1)
Cl(1)	627(1)	11141(1)	940(1)	41(1)
Cl(2)	−2667(1)	10577(1)	1683(1)	42(1)
P	−997(1)	8647(1)	2440(1)	26(1)
C(1)	−2778(4)	8081(2)	1634(3)	30(1)
C(2)	−3506(5)	7407(3)	2056(3)	39(1)
C(3)	−4776(5)	6900(3)	1437(4)	50(2)
C(4)	−5301(5)	7084(3)	391(4)	54(2)
C(5)	−4585(5)	7743(3)	−29(3)	51(2)
C(6)	−3320(5)	8261(3)	592(3)	40(1)
C(7)	−1289(4)	8832(2)	3677(3)	28(1)
C(8)	−2770(5)	9175(3)	3714(3)	38(1)
C(9)	−2976(5)	9387(3)	4645(3)	47(2)
C(10)	−1751(6)	9275(3)	5545(3)	46(2)
C(11)	−299(6)	8946(3)	5512(3)	45(1)
C(12)	−53(5)	8722(3)	4573(3)	36(1)
C(13)	616(4)	7806(3)	2594(3)	35(1)
C(14)	1540(4)	7998(3)	1835(3)	34(1)
S	2094(1)	9176(1)	1981(1)	29(1)
C(15)	3104(5)	9344(3)	1057(3)	44(1)
O	3229(3)	9307(2)	3008(2)	45(1)

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

collected was independent, of which 2614 were considered observed ($F_o > 3.0\ \sigma\ (F)$). Semi-empirical absorption correction and extinction correction were used. The structure was solved by direct methods and all non-hydrogen atoms were refined by full-matrix least-squares. Hydrogen atoms were calculated and refined by riding model with fixed isotropic U:$R = 3.08\%$, $R_w = 4.40\%$ ($R = \Sigma|F_o - F_c|/\Sigma(F_o)$; $R_w = \{[\Sigma w|F_o - F_c|^2]/[\Sigma w(F_o)^2]\}^{1/2}$), all data $R = 3.64\%$, $GOF = 0.85$. All calculations were performed on a Digital Equipment Corporation MicroVax II computer using the Siemens SHELXTL PLUS package (G. M. Sheldrick, a program for crystal-structure determination, version 4.21/V (1990), Siemens Analytical X-ray Instruments, Madison WI). Atomic coordinates are listed in Table 1.

Supplementary material

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

Acknowledgements

We acknowledge the financial support from the Shaw Foundation, the National University of Singapore for this project (Grant No. RP900604 to P.H.L.) and a research scholarship to S.Y.M.C.

References

1 F. Rebiere, O. Samuel, L. Ricard and H. B. Kagan, *J. Org. Chem., 56* (1991) 5991, and refs. therein.
2 B. Ronan and H. B. Kagan, *Tetrahedron: Asymmetry, 3* (1992) 115.
3 K. U. Baldenius and H. B. Kagan, *Tetrahedron: Asymmetry, 1* (1990) 597.
4 N. W. Alcock, J. M. Brown and P. L. Evans, *J. Organomet. Chem., 356* (1988) 233.
5 B. R. James and R. S. McMillan, *Can. J. Chem., 55* (1977) 3927.
6 P. G. Kerr, P. H. Leung and S. B. Wild, *J. Am. Chem. Soc., 109* (1987) 4321.
7 F. L. Hsu, L. L. Szafraniec, W. T. Beaudry and Y. C. Yang, *J. Org. Chem., 55* (1990) 4153.
8 F. R. Hartley, S. G. Murray and C. A. McAuliffe, *Inorg. Chem., 18* (1979) 1394.
9 J. A. Davies, *Adv. Inorg. Radiochem., 24* (1981) 115.
10 S. Y. M. Chooi, T. S. A. Hor, P. H. Leung and K. F. Mok, *Inorg. Chem., 31* (1992) 1494, and refs. therein.
11 P. H. Leung, J. W. L. Martin and S. B. Wild, *Inorg. Chem., 25* (1986) 3396.