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# COMMUNICATION

## $^1$H NMR STUDIES OF PALLADIUM COMPLEXES WITH TRIDENTATE CHELATES, E—S(O)—E (E = P, As) AND THEIR NOVEL ASYMMETRIC ANALOGUE

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**Abstract**—Three stable palladium(II) complexes, $[Pd\{Ph_2ECH_2CH_2S(O)CH_2CH_2E'Ph_2\}Cl]ClO_4$ (where E, E′ = As, **1**; E, E′ = P, **2**; E = As, E′ = P, **3**), were prepared. The $^1$H NMR studies on these square-planar complexes revealed the stereochemically favoured ring conformations adopted by the tridentate ligands in solution. Copyright © 1996 Elsevier Science Ltd

Currently, the development of chiral coordination complexes in asymmetric synthesis has received considerable attention.[1] In order to prepare effective metal systems for different asymmetric transformations, much research interest has been targeted in the design and synthesis of new chiral ligands.[2] Recently, a number of papers has emerged as a result toward understanding the chiral discrimination of certain promising ligands.[3] This apparently highlights the importance of establishing defined stereochemistry for the chiral auxiliaries employed.[4]

While we were examining the possibility of utilizing sulfinyl-substituted polydentate in asymmetric catalysis, we have resolved four novel sulfinyl-substituted bidentates, $Z(CH_2)_nS(O)Me$ ($Z = AsPh_2$, $n = 1, 2$; $Z = PPh_2$, $n = 1, 2$; $Z = NH_2$, $n = 2$).[5–7] As an extension to the systems, we have synthesized the novel asymmetric sulfinyl-substituted tridentate, As—S(O)—P, and its palladium complex **3**. In order to explore the potential of this asymmetric ligand in exerting chiral induction in homogenous asymmetric synthesis, we have undertaken the preliminary efforts in studying the solution properties of this ligand in **3** by using both its symmetrical phosphine and arsine analogues as electronic resembling templates. We have previously reported on the synthesis of the symmetrical trifunctional phosphine, P—S(O)—P, and the solid-state structural characterization of its platinum complex, $[Pt\{P—S(O)—P\}Cl]ClO_4$.[8] In this paper we report the $^1$H NMR analyses of **1–3**, which are considered useful in studying and predicting the stereochemistry manifested by the asymmetric tridentate As—S(O)—P in solution.

## EXPERIMENTAL

All syntheses involving air-sensitive compounds were performed under a positive pressure of purified nitrogen.

### $(Ph_2AsCH_2CH_2)_2SO$

A solution of bis(2-chloroethyl)sulfoxide (1.73 g, 10 mmol) in THF (25 cm$^3$) was introduced slowly to a $LiAsPh_2$ solution (−78°C) generated *in situ* from diphenylarsine (4.55 g, 20 mmol) and *n*-Bu-Li (1.6 M, 20 mmol). The mixture was stirred overnight. The crude compound was obtained as a white solid by extraction and purification by silica column chromatography. The pure product crystallized as colourless needles from a dichloromethane–hexane system: m. pt 124–126°C; yield 3.00 g (54%); IR (KBr, cm$^{-1}$): 1032 (S=O); $^1$H NMR (300 MHz,

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$CDCl_3$): $\delta$ 2.11–2.34 (m, 4H, $AsCH_2$), 2.63–2.73 (m, 4H, $SCH_2$), 7.31–7.41 (m, 20H, aromatics). Found: C, 59.8; H, 5.1. Calc. for $C_{28}H_{28}As_2OS$: C, 59.8; H, 5.0%.

$Ph_2AsCH_2CH_2S(O)CH_2CH_2PPh_2$

A mixture of diphenylphosphine (0.52 g, 3 mmol) and *n*-Bu-Li (1.6 M, 3 mmol) at −78°C was added to a cooled solution of $Ph_2AsCH_2CH_2S(O)CH_2CH_2Cl$ (1.04 g, 3 mmol) in THF (50 $cm^3$). The mixture was stirred overnight. The crude product was obtained as a white solid after extraction and purification by silica column chromatography. The pure ligand crystallized as colourless needles from a dichloromethane–diethyl ether system: m. pt 126–128°C; yield 0.72 g (49%); IR (KBr, $cm^{-1}$): 1033 (S=O); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 2.13–2.45 (m, 4H, $AsCH_2+PCH_2$), 2.60–2.73 (m, 4H, $SCH_2$), 7.31–7.42 (m, 20H, aromatics). Found: C, 64.6; H, 5.2. Calc. for $C_{28}H_{28}AsOPS$: C, 64.9; H, 5.5%.

$[Pd\{(Ph_2AsCH_2CH_2)_2SO\}Cl]ClO_4$ (**1**)

A solution of $[Pd(CH_3CN)_2Cl_2]$, prepared by refluxing $PdCl_2$ (0.10 g, 0.6 mmol) in acetonitrile (25 $cm^3$), was treated with $AgClO_4$ (117 mg, 0.6 mmol) for 4 h in the dark. The resulting solution was filtered through celite. The filtrate was treated with $(Ph_2AsCH_2CH_2)_2SO$ (0.32 g, 0.6 mmol) and stirred for 30 min. The solution was then concentrated. With slow introduction of diethyl ether, **1** was afforded as bright yellow prisms from the mother liquor: m. pt 249–251°C (dec.); yield 0.27 g (60%); $^1H$ NMR (500 MHz, $CD_3CN$): $\delta$ 3.19 (dt, 2H, $^3J_{H2H4} = 5.50$ Hz, $^3J_{H1H4} = {}^2J_{H3H4} = 14.47$ Hz, H4), 3.63 (dd, 2H, $^3J_{H1H3} = 5.94$ Hz, $^2J_{H3H4} = 14.13$ Hz, H3), 3.73 (dt, 2H, $^3J_{H1H3} = 5.90$ Hz, $^3J_{H1H4} = {}^2J_{H1H2} = 14.19$ Hz, H1), 4.54 (dd, 2H, $^3J_{H2H4} = 5.26$ Hz, $^2J_{H1H2} = 13.64$ Hz, H2), 7.55–7.95 (m, 20H, aromatics). Found: C, 41.9; H, 3.7. Calc. for $C_{28}H_{28}As_2Cl_2O_5PdS$: C, 41.8; H, 3.5%.

$[Pd\{Ph_2PCH_2CH_2)_2SO\}Cl]ClO_4$ (**2**)

Compound **2** was obtained as yellow needles by the published method:[8] $^1H$ NMR (500 MHz, $CD_3CN$): $\delta$ 3.22 (dddt, 2H, $^3J_{PH} = {}^4J_{P'H} = 2.85$ Hz, $^3J_{H2H4} = 5.47$ Hz, $^3J_{H1H4} = {}^2J_{H3H4} = 15.44$ Hz, H4), 3.61 (dddd, 2H, $^3J_{PH} = {}^4J_{P'H} = 4.58$ Hz, $^3J_{H1H3} = 4.58$ Hz, $^2J_{H3H4} = 15.77$ Hz, H3), 3.88 (dddt, 2H, $^2J_{PH} = {}^4J_{P'H} = 1.86$ Hz, $^3J_{H1H3} = 5.22$ Hz, $^3J_{H1H4} = {}^2J_{H1H2} = 14.27$ Hz, H1), 4.27 (dddd + "virtually coupled" bd, 2H, $^4J_{P'H} = 1.42$ Hz, $^3J_{H2H4} = 5.50$ Hz, $^2J_{H1H2} = 13.57$ Hz, $^2J_{PH} = 52.32$ Hz, H2), 7.54–7.93 (m, 20H, aromatics). Found: C, 46.8; H, 3.8 Calc. for $C_{28}H_{28}Cl_2O_5P_2PdS$: C, 47.0; H, 4.0%.

$[Pd\{Ph_2AsCH_2CH_2S(O)CH_2CH_2PPh_2\}Cl]ClO_4$ (**3**)

Compound **3** was prepared similarly as for **1** from the starting materials, $PdCl_2$ (0.17 g, 1.0 mmol), $AgClO_4$ (200 mg, 1.0 mmol) and $Ph_2AsCH_2CH_2S(O)CH_2CH_2PPh_2$ (0.50 g, 1.0 mmol). The complex crystallized as yellow prisms from an acetonitrile–diethyl ether solvent system: m. pt 252–254°C (dec.); yield 0.55 g (75%); $^1H$ NMR (500 MHz, $CD_3CN$): $\delta$ 3.27 (dt, 1H, $^3J_{H2H4} = 5.50$ Hz, $^3J_{H1H4} = {}^2J_{H3H4} = 14.48$ Hz, H4[As]), 3.33–3.43 (m, 1H, H4[P]), 3.68–3.76 (m, 2H, H3[As]+H3[P]), 3.81–3.99 (m, 2H, H1[As]+H1[P]), 4.40 (br dd, 1H, $|^3J_{H2[P]H4[P]} + {}^2J_{H1[P]H2[P]}| = 9.91$ Hz, $^2J_{PH} = 52.75$ Hz, H2[P]), 4.62–4.66 (m, 1H, H2[As]), 7.55–8.00 (m, 20H, aromatics). Found: C, 44.2; H, 4.0. Calc. for $C_{28}H_{28}AsCl_2O_5PPdS$: C, 44.3; H, 3.7%.

## RESULTS AND DISCUSSION

From the X-ray structural study of $[Pt\{P—S(O)—P\}Cl]ClO_4$, it is found that the two P—S five-membered chelate rings of P—S(O)—P adopt a pair of enantiomeric $\delta$–$\lambda$ conformations. As indicated by the Dreiding models, such a $\delta$–$\lambda$ conformational pair is required in order to form a stable bischelate [Fig. 1(a)]. Vibrational changes may allow slight relaxation from the strictly $\delta$–$\lambda$ pair, but the formation of an "envelope" conformation is unfavourable due to the steric interaction between H3 and the S=O [Fig. 1(b)]. Model studies also revealed that in an "envelope" conformation, the torsional angle H3—C—S—O is close to 10° compared with that obtained with a $\delta$ or $\lambda$ conformation (which is *ca* 40°). The central S=O function therefore locks the conformations of the two rings. Due to such conformational "interlocking",[4a,9,10] the two rings cannot undergo $\delta \leftrightarrow \lambda$ interconversions as freely as for a simple monochelate. For such conversions to occur, the M—S and/or M—E linkages would have to be cleaved in order to allow the free rotation along the chelate skeleton. Hence, with the model structure as shown in Fig. 1(a), it can be assumed that H1–H4 protons on one chelate ring share identical stereochemical environments as their respective counterparts on the other enantiomeric ring.

The assignment of the four different protons, H1–H4, in the NMR spectrum of the arsenic complex **1** can be reached by a first-order treatment [Fig. 2(a)]. On the first order basis and with the appropriate approximations made, the resonance pat-

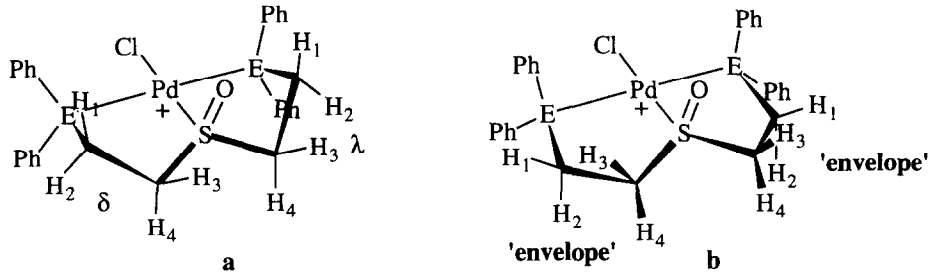


Fig. 1. Ring conformations of E—S(O)—E in $[Pd\{E—S(O)—E\}Cl]^+$, (a) a $\delta$–$\lambda$ pair; (b) an "envelope"–"envelope" pair.

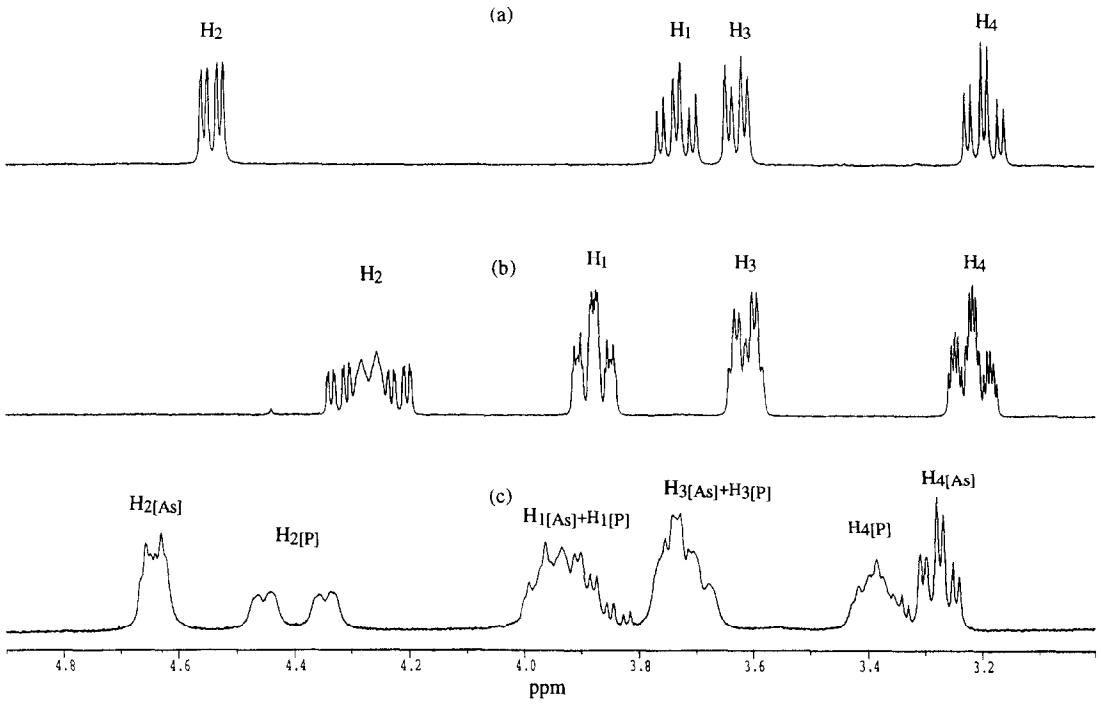


Fig. 2. 500 MHz $^1H$ NMR spectra of (a) **1**, (b) **2** and (c) **3**, which were recorded in $CD_3CN$ at 27 °C. Only the methylene resonances are shown.

terns of the four protons can be predicted. Taking $^3J_{trans} \approx {}^2J_{gem}$ and $^3J_{gauge}$ ($\phi \approx 70°$) $\approx 0$ Hz ($\phi$ = dihedral angle),[11,12] a doublet of doublet and a triplet of doublet are predicted for the pairs of H2, H3 and H1, H4, respectively (Fig. 3). The assignment of H2 was facilitated by the observable $^2J_{PH}$ in the NMR spectrum of **2** [Fig. 2(b)]. Irradiation of H2 ($^1H$ homonuclear decoupling) in **1** led to unambiguous assignment of H1 and H4. Using the NMR spectrum of **1** as an analogy, the full assignments of the different protons in the spectra of **2** and **3** [Fig. 2(c)] can be obtained accordingly.

Interestingly virtually coupled[13] features were observed for H2 in the spectrum of **2**. The outer sharp, discernible resonance patterns which are

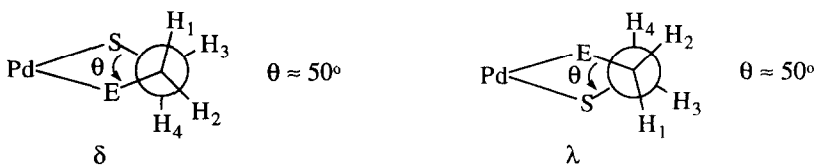


Fig. 3. $^3J_{trans} \approx {}^2J_{gem} > {}^3J_{gauge}$ ($\phi \approx 50°$) $> J_{gauge}$ ($\phi \approx 70°$) $\approx 0$ Hz; the torsional angle E—C—C—S ($\theta$) was taken as 50° with reference to the crystal structural information of $[Pt\{P—E(O)—E\}Cl]ClO_4$.[8]

centred at $\delta$ 4.27 represent the expected *dddd* involving geminal and long range $^{31}P$–$^{1}H$ couplings arising from the two magnetically non-equivalent phosphorus nuclei. The invariant sharp lines are characteristic, in this case, of either a "locked" conformation or a mutual $\delta \leftrightarrow \lambda$ conformational exchange process,[14] which is fast on the NMR timescale. The central broad doublet is probably due to the loss of geminal phosphorus–proton coupling. A "virtual coupling" pattern as such is commonly found in an $X_nAA'X_n$ system in which the magnetically non-equivalent A and A′ couple to each other strongly. It is well documented that when $J_{AA'} \gg |J_{AX} - J_{A'X}|$,[15] virtual coupling will occur. A few causal mechanisms have been discussed by Fackler *et al.* to account for the observations made on different systems.[16] In our system, there are two plausible mechanisms, namely (i) the phosphorus spin–spin exchange which transmits through the P—M—P′ bonding and (ii) the fast exchange of P and P′ coordination sites followed by the rapid realignment of the spins along P—M—P′. The relaxation of $^{2}J_{PH}$ clearly indicates that the *cis* positioning of the two phosphorus nuclei is not involved in our system as in the *cis* isomer the $^{2}J_{PP'}$ value will be much weaker.

The full assignment of the solution $^{1}H$ NMR of H1–H4 on the bischelate carbon backbone is based on the assumption that **1–3** adopt the same well-defined conformational preferences as in the solid state.[17] The hypothesis is supported by the good compliance of the experimental data with the well-established $^{1}H$ NMR analysis method utilizing coupling constants (*vide supra*). No changes were observed for the methylene resonance signals from −40 to 60°C. The fact that the NMR patterns remain invariant over a temperature range of 100°C suggests the absence of phosphorus nuclei exchange, although such an exchange is not ruled out. This implies the spin-spin exchange is likely the cause for the virtual coupling,[16] despite the high *trans*-labilizing effect of the phosphorus nuclei.

In summary, our findings suggest the preferred conformations for our tridentates in the palladium systems. The information forms the basis of our research in the stereochemical environment and asymmetric induction manifested by the As—S(O)—P system. Currently, investigations on the resolution of the asymmetric tridentate are underway.

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