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Synthesis and coordination chemistry of a 14-membered macrocyclic ligand containing one phosphorus, two sulfur and one ambidentate sulfoxide donor sets

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The macrocyclic ligand $PhP(CH_2CH_2SCH_2CH_2CH_2)_2SO$ (L) was obtained from the reaction between bis(3-chloropropyl) sulfoxide and bis(2-mercaptoethyl)phenylphosphine in the presence of caesium carbonate. The ligand is stable in the solid state but rearranges slowly into the isomeric phosphine oxide $S(CH_2CH_2CH_2SCH_2CH_2)_2P(O)Ph$ in solution. In the presence of molecular iodine, the oxygen migration process occurred spontaneously and the phosphine oxide was obtained quantitatively within several minutes. When treated with $[MCl_2(CH_3CN)_2]$ (where M = Pd, Pt), the sulfinyl-substituted macrocycle functions as a bidentate ligand *via* its phosphorus and one of the thioether sulfur donor atoms giving the corresponding neutral square-planar complexes *cis*-$[M(L\text{-}P,S)Cl_2]$. In both complexes, the sulfoxide group is not involved in metal complexation. However, when the dichloro complexes were treated with silver perchlorate, the corresponding tetradentate complexes $[M\{L\text{-}P,S,S,S\}][ClO_4]_2$ were formed. In both the perchlorate salts, the ambidentate sulfoxide functions are coordinated to the metal centre *via* their sulfur donor. In contrast to the previously reported acyclic analogues, the sulfoxide–metal bonds are kinetically stable.

Introduction

Currently, a great deal of attention is being focused on macrocylic ligands because they play an important role in many aspects of chemistry, medicine and the chemical industry.[1] As some examples of their applications we note the contrast-enhancing properties of their lanthanide complexes in NMR imaging,[2] their suitability as antibodies in radioimmunotherapy,[2] their high selectivity in the binding of metal ions[1,2] and nucleotide bases,[3] and their unique structural features as spacers for crystal engineering.[4] In seeking optimum efficiency in their existing and potential applications, numerous macrocyclic ligands with a wide spectrum of electronic and structural features have been designed and synthesised. To date, the majority of these synthetic cyclic ligands contain oxygen, sulfur, nitrogen or phosphorus donor atoms.

The coordination chemistry of these macrocycles and their mixed donor analogues is indeed an area of research that has flourished over the past three decades. Surprisingly, there is a paucity of information in the literature concerning the chemistry of macrocycles containing the sulfoxide functions that are borne within the macrocyclic ring despite the fact that coordination chemistry of these ambidentate ligands is well established.[5] Several polysulfinyl macrocycles have been shown to be excellent phase transfer catalysts[6] and are capable of forming complexes with selected alkali metal ions.[7] Certainly no macrocycle containing both tertiary phosphorus and sulfoxide donor atoms has been reported hitherto.

Such molecules should provide an interesting opportunity to compare the coordination chemistry of these ambidentate ligands in cyclic and acyclic systems, particularly when soft platinum metal ions are involved. For example, we have previously prepared some kinetically labile palladium(II) complexes in which the acyclic ligand (±)-$Ph_2PCH_2CH_2S(O)Me$ can behave as P–S, P–O or monodentate-P ligand.[8] The bonding mode of this acyclic ligand depends solely on the stereoelectronic environment of the metal centre. Interestingly, when this sulfinyl-substituted phosphine ligand is chelated to palladium and platinum ions the sulfoxide–metal bonds are readily displaced by other weak ligands, such as chloride anions to give the corresponding monodentate-P chloro complexes in an irreversible manner. Similar kinetic instabilities were also observed with a chiral sulfinyl-substituted phosphine ligand with a rigid carbon backbone.[9] However, we believe that the stability of the sulfoxide–metal bonds can be controlled by incorporating the ambidentate functional group inside a macrocyclic system. In this paper, we report the synthesis and the coordination chemistry of a novel 14-membered macrocycle containing one phosphorus, one sulfoxide and two thioether sulfur donor atoms in which the two similar sulfur atoms are located in the *trans* positions.

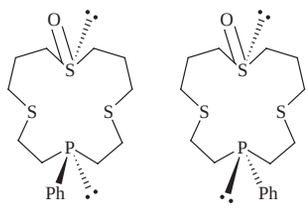
Results and discussion

Caesium carbonate promoted macrocyclization

A large number of phosphathia and polythia macrocycles have been prepared by either the high dilution or the metal template technique.[1,10] In principle, their sulfinyl-substituted analogues can be prepared directly from these known cyclic compounds by a chemoselective and partial oxidation reaction of the sulfur donor atoms. In practice, however, this synthetic approach is impeded by the presence of a highly oxygen-sensitive tertiary phosphorus atom in the macrocyclic ring. From a synthetic standpoint, therefore, it is more convenient to prepare phosphorus–sulfinyl macrocycles from their phospha- and sulfinyl-substituted precursors *via* a macrocyclization reaction. Accordingly, the 14-membered marcocyclic ligand $PhP(CH_2CH_2SCH_2CH_2CH_2)_2SO$, L, was prepared by a caesium carbonate promoted macrocyclization[11] between $PhP(CH_2CH_2SH)_2$ and $(ClCH_2CH_2CH_2)_2SO$. The reaction was carried out at 50 °C in dimethylformamide for 4 days. Following silica column

purification, the sulfinyl-substituted phospha-macrocycle was obtained as an air stable white solid in 60% yield. The IR(KBr) spectrum of the macrocycle exhibited a typical sharp ν(S=O) at 1026 cm^{-1} indicating that the sulfinyl function was not reduced by the tertiary phosphine during the macrocyclization.

According to its structural features, macrocycle L can exist as two stereochemically distinct regioisomers in which the sulfur and phosphorus lone pairs are located in either the *syn* or the *anti* relative positions with respect to the macrocyclic ring.[12]

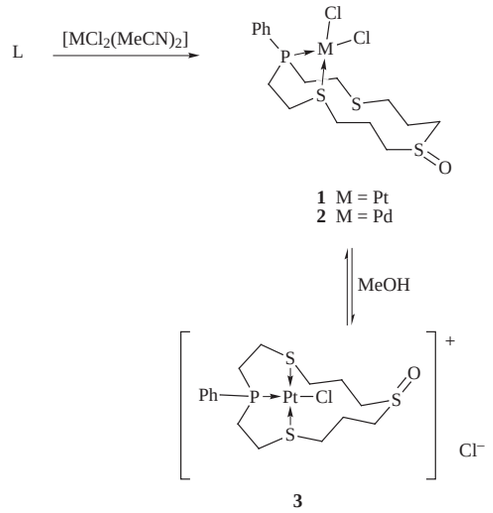


syn–**L** *anti*–**L**

Indeed, the ^{31}P NMR spectrum of the macrocyclic ligand in $CDCl_3$ exhibited two individual singlets of *ca*. equal intensities at δ −25.4 and −27.3. A small quantity of the less soluble isomer was isolated as white prisms by rapid recrystallization of the 1 : 1 isomeric mixture from dichloromethane–hexane. The ^{31}P NMR spectrum of the less soluble macrocycle ligand in $CDCl_3$ exhibited a sharp singlet at δ −25.4. However, both the isomers were found to be thermodynamically unstable and underwent an oxygen migration reaction in solution to give the corresponding phosphine oxide $S(CH_2CH_2CH_2SCH_2CH_2)_2$-P(O)Ph quantitatively. Hence when an NMR sample of the 1 : 1 regioisomers in $CDCl_3$ was kept under an inert atmosphere at room temperature, the original signals at δ −25.4 and −27.3 gradually disappeared and a lone sharp singlet was observed at δ 37.1 after 7 days. The observation of a single resonance for the oxygen migration product is in agreement with the structural considerations where the two stereochemically distinct regioisomers of L rearrange to give the same achiral phosphine oxide. Furthermore, NMR studies reveal that the rate of rearrangement for the two isomers is similar. The IR(KBr) spectrum of the oxygen migration product showed a strong ν(P=O) at 1156 cm^{-1} and the absence of ν(S=O). Interestingly, it was observed that the oxygen migration process could be accelerated significantly by the presence of iodine. Hence, when several crystals of molecular iodine were added to a dichloromethane solution of L, the phosphine oxide was formed quantitatively within 0.5 h. This oxygen migration process makes the separation of the two regioisomers of L *via* fractional crystallization or silica column chromatography difficult. Hence, the 1 : 1 mixture of the sulfinyl-substituted macrocylic ligand was used for metal complexation. It should be noted, however, that the 1 : 1 stereoisomeric ratio of the free macrocyclic ligand need not be retained in the corresponding macrocyclic metal complexes as it has been observed that phosphorus inversion can be induced by moderate heating.[13] Furthermore, in cases involving the macrocyclic phosphorus and arsenic ligands, the thermodynamic stabilities of different isomers are affected by metal complexation.[14] In addition, stereoisomeric transition metal complexes usually exhibit different solubilities that frequently lead to the preferential crystallization of only one particular isomer.[15]

Platinum(II) and palladium(II) complexes of 14-membered macrocycles

According to its structural features, the sulfinyl-substituted macrocycle L can behave as a potential tetradentate ligand to platinum metal ions *via* its phosphorus, the two thioether sulfur ligating sites and the ambidentate sulfinyl function, with which either the metal–sulfur or metal–oxygen bonding modes may be



Scheme 1

adopted. However, as shown in Scheme 1 the treatment of L with $[MCl_2(CH_3CN)_2]$ (where M = Pt, Pd) gave a pair each of regioisomers of the neutral square-planar complexes **1** and **2**. In these *cis*-$[M(L)Cl_2]$ complexes, the macrocycle behaves as a bidentate ligand *via* its phosphorus and one of its thioether sulfur donors. The IR(KBr) spectra of both the palladium and platinum complexes showed a characteristic ν(S=O) signal at 1026 cm^{-1}. This ν(S=O) signal is similar to that recorded for the free macrocyclic ligand and indeed is typical for sulfoxide functions that are not involved in metal complexation.[5,8]

The isolated platinum complex **1** is insoluble in non-polar solvents. However it can be dissolved in dimethylformamide and dimethyl sulfoxide and is sparingly soluble in methanol and acetonitrile. In dimethylformamide, the complex behaves as a typical non-electrolyte. Prior to crystallization, the ^{31}P NMR spectrum of the platinum complex in d_7-dimethylformamide exhibited two distinct singlets of *ca*. equal intensities at δ 47.1 (J_{Pt-P} = 3574 Hz) and δ 47.7 (J_{Pt-P} = 3562 Hz). The corresponding ^{31}P coordination shifts (*ca.* 73–75 ppm) are typical of P–Pt(II) species involving 5-membered chelate rings.[16] Interestingly, only one singlet at δ 47.7 was observed in the ^{31}P NMR spectrum of recrystallized **1** thus indicating that the complex regioisomers could be separated *via* fractional crystallization. The molecular structure of the less soluble isomer was confirmed by X-ray crystallography. Crystallographic data for this platinum complex are given in Table 1. The structural analysis establishes unambiguously the coordination chemistry of the platinum which is coordinated to two *cis* chlorines, the phosphorus and a sulfur two carbon atoms from the phosphorus. There are two molecules in the crystal structure arising from the flexible conformation of the 14-membered macrocyclic ring. Fig. 1 shows the molecular structures of the two conformers. In both molecules, the P–phenyl ring and the S–oxygen are located on opposite sides of the macrocyclic ring and hence both molecules are of the *anti*-orientation. neither conformer exhibits sulfoxide–platinum coordination, through the oxygen or sulfur. Despite the conformational isomerism, the immediate environment about the platinum in both isomers is almost the same; the Pt–Cl, Pt–P and Pt–S distances are not significantly different (Table 2). It should be noted that when the stereoisomerically pure dichloroplatinum complex was treated with aqueous cyanide, the ^{31}P NMR spectrum of the crude macrocyclic ligand in $CDCl_3$ exhibited a sharp singlet at δ −25.4, thus revealing that the less soluble free macrocyclic ligand is the *anti*-isomer.

An interesting dynamic process was observed when the recrystallized platinum complex **1** was dissolved in d_4-methanol (Scheme 1). Its ^{31}P NMR spectrum in this solvent shows two individual singlets of approximately equal intensities at δ 49.3

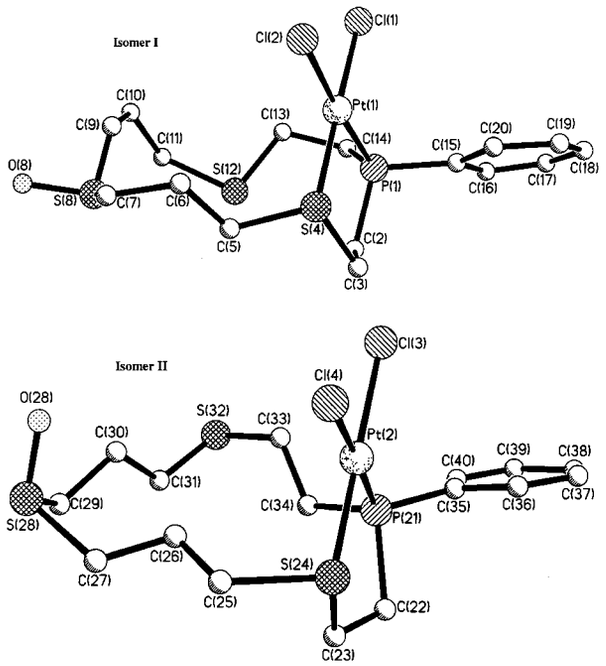


Fig. 1 The molecular structures and labelling scheme for the two conformers of **1**.

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

	1	**4**
Formula	$C_{16}H_{25}Cl_2OPS_3Pt\cdot 0.5MeCN$	$[C_{16}H_{25}OPS_3Pt][ClO_4]_2\cdot 2MeCN$
M	647.03	836.6
Space group	$P\bar{1}$	$P2_1/c$ (no. 14)
a/Å	12.473(1)	11.799(1)
b/Å	13.855(1)	19.561(3)
c/Å	15.131(1)	13.014(2)
α/°	67.05(1)	90.00
β/°	71.16(1)	103.15(1)
γ/°	80.11(1)	90.00
V/Å^3	2276(1)	2925(1)
Z	4	4
T/K	293(2)	203(2)
D_c/g cm^{-3}	1.888	1.900
λ/Å	0.71073 (Mo)	1.54178 (Cu)
μ/cm^{-1}	6.75	13.62
R_1 (obs. data)[a]	0.050	0.043
wR_2 (obs. data)[b]	0.136	0.121

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \sqrt{\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

(J_{Pt-P} = 3591 Hz) and δ 91.6 (J_{Pt-P} = 3083 Hz). The large difference in the chemical shifts suggested that these resonance signals are not due to conformational isomerism. Instead, the distinct large coordination shift (*ca.* 116 ppm) and the low field position are diagnostic of the phosphorus donor being involved as the central donor atom of a tridentate ligand in which two conjoined 5-membered metal chelate rings are formed.[16] Based on this NMR evidence, we believe that the macrocyclic ligand adopts both the P–S bidentate and S–P–S tridentate bonding modes with platinum(II) and hence complexes **1** and **3** (Scheme 1) co-exist as an equilibrium mixture in methanol. Presumably, in methanol, the high affinity of platinum(II) for sulfur causes the macrocycle to displace a chloro ligand with its non-coordinating thioether-sulfur donor to adopt the sterically imposing conjoined 5-membered rings system. Owing to the ring strain, however, one of the thioether donors is displaced readily by the chloride anion to regenerate the neutral dichloro species. Consistent with the formation of this neutral–ionic equilibrium mixture, conductivity measurements indicated that a conducting electrolyte was obtained when the neutral platinum complex **3** was dissolved in methanol. Owing to the dual presence of the neutral and the cationic complex species the molar conductance of this methanol–complex solution (Λ_M = 61 cm^2 Ω^{-1} mol^{-1}) is somewhat below the range of a standard 1:1 electrolyte (80–115 cm^2 Ω^{-1} mol^{-1}).[17] However, attempts to isolate the cationic complex **3** by crystallization of the equilibrium mixture from methanol were not successful. The original neutral complex **1** was always being recovered in quantitative yields, presumably due to the favorable crystal packing forces of **1**. Furthermore, when a 1:1 *syn*:*anti* stereoisomeric mixture of the platinum complex **1** was dissolved in d_4-methanol, the ^{31}P NMR spectrum of this sample exhibited four singlets of *ca.* equal intensities at δ 48.5 (J_{Pt-P} = 3573 Hz), 49.3 (J_{Pt-P} = 3591 Hz), 91.6 (J_{Pt-P} = 3083 Hz) and 92.0 (J_{Pt-P} = 3065 Hz). Accordingly, we assigned the NMR signal at δ 92.0 to the *syn* analogue of the tridentate complex **3**.

Table 2 Selected bond lengths (Å) and angles (°) for the two conformers of **1**

Isomer **I**		Isomer **II**	
Pt(1)–P(1)	2.213(2)	Pt(2)–P(21)	2.198(3)
Pt(1)–S(4)	2.275(2)	Pt(2)–S(24)	2.265(3)
Pt(1)–Cl(1)	2.333(2)	Pt(2)–Cl(3)	2.322(3)
Pt(1)–Cl(2)	2.363(2)	Pt(2)–Cl(4)	2.354(3)
P(1)–C(2)	1.817(8)	P(21)–C(22)	1.903(13)
P(1)–C(14)	1.826(10)	P(21)–C(34)	1.774(11)
P(1)–C(15)	1.810(10)	P(21)–C(35)	1.811(9)
S(4)–C(3)	1.828(9)	S(24)–C(23)	1.789(13)
S(4)–C(5)	1.829(9)	S(24)–C(25)	1.975(17)
S(8)–O(8)	1.528(12)	S(28)–O(28)	1.472(10)
P(1)–Pt(1)–S(4)	88.52(8)	P(21)–Pt(2)–S(24)	88.13(11)
P(1)–Pt(1)–Cl(1)	89.26(8)	P(21)–Pt(2)–Cl(3)	92.53(10)
S(4)–Pt(1)–Cl(1)	177.76(8)	S(24)–Pt(2)–Cl(3)	179.13(10)
P(1)–Pt(1)–Cl(2)	175.35(9)	P(21)–Pt(2)–Cl(4)	175.58(12)
S(4)–Pt(1)–Cl(2)	91.91(9)	S(24)–Pt(2)–Cl(4)	87.45(12)
Cl(1)–Pt(1)–Cl(2)	91.32(9)	Cl(3)–Pt(2)–Cl(4)	91.89(12)
C(2)–P(1)–Pt(1)	108.0(3)	C(22)–P(21)–Pt(2)	103.1(5)
C(14)–P(1)–Pt(1)	116.4(3)	C(34)–P(21)–Pt(2)	114.7(4)
C(15)–P(1)–Pt(1)	110.2(3)	C(35)–P(21)–Pt(2)	117.2(3)
C(3)–S(4)–Pt(1)	104.3(3)	C(23)–S(24)–Pt(2)	106.6(4)
C(5)–S(4)–Pt(1)	106.8(3)	C(25)–S(24)–Pt(2)	107.3(4)

The solubility of the palladium complex **2** is rather different from its platinum analogue, **1**. The neutral palladium complex readily dissolves in dichloromethane but is sparingly soluble in chloroform and acetonitrile. Although it is soluble in some polar solvents such as dimethylformamide and dimethyl sulfoxide, the dichloropalladium complex is insoluble in methanol. In dichloromethane, the complex behaves as a typical non-electrolyte. Prior to crystallization, the ^{31}P NMR spectrum of the palladium complex in d_2-dichloromethane exhibited two distinct singlets of *ca.* equal intensities at δ 72.0 and δ 72.3. However, the ^{31}P NMR spectrum of recrystallized **2** in d_2-dichloromethane exhibited only one sharp singlet at δ 72.3. Single crystal X-ray analysis revealed that a pair of conformers with the same *anti*-stereochemical relationship were present in the crystal structure of the dichloropalladium complex **2** which were isostructural with their platinum analogue **1**. Since no unusual features separate the structures of **1** and **2**, however, the X-ray structural analysis of **2** will not be discussed further. In order to test if the aforementioned P–S and S–P–S equilibrium process occurs with the palladium complex **2** in a methanolic environment, an NMR experiment was conducted in which a d_2-dichloromethane solution of the complex was diluted with an equal volume of d_4-methanol. The ^{31}P NMR spectrum of the complex remain unchanged, *i.e.* no additional NMR resonance signal was detected in this mixed solvent sample. Therefore, we believe that the macrocyclic ligand adopts only the P–S bidentate bonding modes in the methanol–dichloromethane solution. Compared with the platinum analogue, it is likely that the lower affinity of palladium toward sulfur precluded the

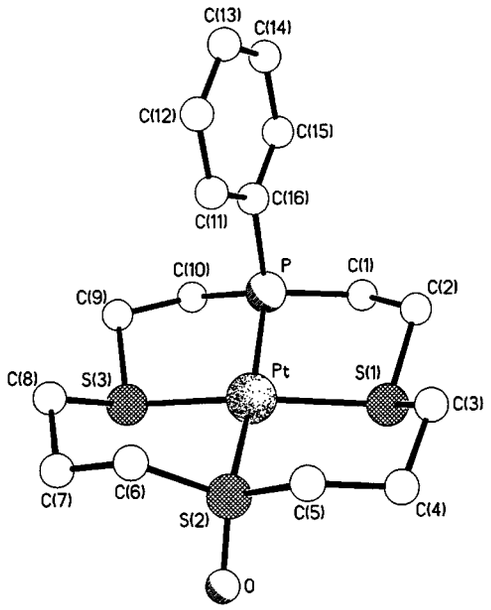
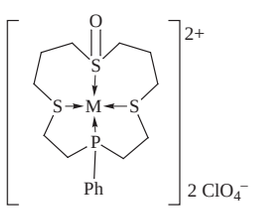


Fig. 2 The molecular structure of the complex cation in **4**.

formation of the strained conjoined S–P–S rings in the methanolic environment. Furthermore, it is noteworthy that in all three chloro species **1**–**3**, the sulfoxide functions are not involved in any metal complexation, both in the solid state and in solution.

The conversion of the bidentate *cis*-[M(L-*P*,*S*)Cl_2] complexes **1** and **2** into their respective tetradentate analogues [M{L-*P*,*S*,*S*,*S*}]$^{2+}$ could be achieved by the chloro abstraction reaction of the corresponding recrystallized dichloro species with silver perchlorate. Thus, the platinum complex **4** and its palladium counterpart **5** were obtained in 38 and 33% isolated



4 M = Pt
5 M = Pd

yields, respectively. In contrast to the dichloro complexes, these tetradentate complexes readily dissolved in acetonitrile to give the corresponding 1:2 conducting electrolytes. In d_3-acetonitrile, the ^{31}P NMR spectra of each complex showed only one sharp singlet resonance (δ 99.5 with J_{Pt-P} = 2683 Hz for **4** and δ 115.3 for **5**).

The X-ray analysis of **4** reaffirms that, as desired, the tetradentate platinum complex has been formed (Fig. 2). The P–phenyl and the S–oxygen are located at the *anti* positions with respect to the macrocyclic ring. Platinum is coordinated to the phosphorus and all three sulfur donors of the macrocyclic ligand. The coordination geometry at platinum is square planar with angles at platinum in the ranges 86.7(1)–95.7(1) and 160.3(1)–167.1(1)° (Table 3). The sulfoxide-oxygen is not bonded to platinum and the S–O distance (1.47 Å) is typical for sulfoxide complexes involved in S-complexation. The two thioether S–Pt bonds are of similar distances [2.275(2) and 2.285(2) Å]. Comparatively, the P–Pt bond [2.246(2) Å] does not seem to lengthen the *trans* Pt–S(O) distance [2.299(2) Å] significantly. As expected from the different ring sizes, the P–Pt–S angles [86.7(1) and 86.9(1)°] of the two 5-membered chelate rings are clearly smaller than those involved in the 6-membered S–Pt–S(O) rings [94.7(1) and 95.7(1)°]. The differences in the

Table 3 Selected bond lengths (Å) and angles (°) for **4**

Pt–P	2.246(2)	Pt–S(1)	2.275(2)
Pt–S(2)	2.299(2)	Pt–S(3)	2.285(2)
P–C(1)	1.81(1)	C(1)–C(2)	1.51(1)
C(2)–S(1)	1.84(1)	S(1)–C(3)	1.82(1)
C(3)–C(4)	1.52(1)	C(4)–C(5)	1.54(1)
C(5)–S(2)	1.78(1)	S(2)–C(6)	1.78(1)
C(6)–C(7)	1.53(1)	C(7)–C(8)	1.54(1)
C(8)–S(3)	1.81(1)	S(3)–C(9)	1.83(1)
C(9)–C(10)	1.55(1)	C(10)–P	1.81(1)
P–C(16)	1.81(1)	S(2)–O	1.47(1)
P–Pt–S(1)	86.9(1)	P–Pt–S(2)	167.1(1)
P–Pt–S(3)	86.7(1)	S(1)–Pt–S(2)	95.7(1)
S(1)–Pt–S(3)	160.3(1)	S(2)–Pt–S(3)	94.7(1)
C(1)–P–Pt	105.9(2)	C(10)–P–Pt	107.2(2)
C(16)–P–Pt	111.4(2)	C(2)–S(1)–Pt	104.0(2)
C(3)–S(1)–Pt	109.7(2)	C(5)–S(2)–Pt	109.2(2)
C(6)–S(2)–Pt	104.1(2)	O–S(2)–Pt	119.8(2)
O–S(2)–C(5)	110.5(3)	O–S(2)–C(6)	110.1(3)
C(9)–S(3)–Pt	105.0(2)	C(8)–S(3)–Pt	109.7(2)
P–C(1)–C(2)	106.2(5)	C(1)–C(2)–S(1)	108.4(5)
C(2)–S(1)–C(3)	105.6(3)	S(1)–C(3)–C(4)	109.1(5)
C(3)–C(4)–C(5)	115.4(6)	C(4)–C(5)–S(2)	113.7(5)
C(5)–S(2)–C(6)	101.5(3)	S(2)–C(6)–C(7)	112.7(5)
C(6)–C(7)–C(8)	115.5(6)	C(7)–C(8)–S(3)	110.5(5)
C(8)–S(3)–C(9)	104.2(3)	S(3)–C(9)–C(10)	109.8(4)
C(9)–C(10)–P	106.0(4)	C(10)–P–C(1)	118.6(3)
C(10)–P–C(16)	106.1(3)	C(1)–P–C(16)	107.7(3)

ring strain are also reflected by the larger Pt–S(1)–C(3) and Pt–S(3)–C(8) angles [both 109.7(2)°] in the 6-membered chelates as compared with their neighbouring 5-membered counterparts [104.0(2)° for Pt–S(1)–C(2) and 105.0(2)° for Pt–S(3)–C(9)]. Furthermore, a drastic bond angle [118.6(3)°] enlargement is observed at the sterically imposing C(1)–P–C(10) fragment of the coordinated 14-membered macrocyclic ligand. The other two C–P–C angles are 106.1(3) and 107.7(3)° only. The three C–S–C angles are 101.5(3), 104.2(3) and 105.6(3)°, of which, the smallest angle is C–S(O)–C. Another interesting observation being the considerably large bond angle oberved for Pt–S–O [119.8(2)°]. In the analogous acyclic complex [$PdCl_2${(±)-$Ph_2PCH_2CH_2S(O)Me$-*P*,*S*}], the Pd–S–O angle is only 114.1(1)°. Clearly, in the present platinum complex, the sulfinyl-oxygen is kept further away from the metal centre by the macrocyclic ligand.

In solution, the kinetic stabilities of the tetradentate macrocyclic ring in both complexes **4** and **5** were investigated by treating the acetonitrile solutions of the complexes with a large excess of ammonium chloride and aqueous lithium chloride. Under such reaction conditions, the corresponding chloro complexes **1** and **2** can be generated in an irreversible manner if the macrocyclic complexes or the metal–sulfoxide bonds are labile.[8,9] However, the ^{31}P NMR spectra of the crude reaction product showed that both **4** and **5** remained unchanged throughout the chloride treatment. Hence, both the macrocyclic palladium and platinum complexes are kinetically stable. Clearly, the macrocyclic effect which is operating in the tetradentate complexes **4** and **5** stablizes the otherwise highly labile and weak metal–sulfoxide bonds.

Finally, it should be noted that **4** and **5** could be obtained in similar isolated yields from the reaction between [$M(MeCN)_4$]-[ClO_4]$_2$ (where M = Pt, Pd) and the 1:1 *syn*:*anti* isomeric mixture of the free macrocycle L. In these direct syntheses, 1:1 *syn*:*anti* mixtures of the corresponding tetradentate complexes were obtained. Thus, prior to crystallization, the ^{31}P NMR spectra of the platinum complex in d_3-acetonitrile showed two singlets of *ca*. equal intensities at δ 88.4 (J_{Pt-P} = 2549 Hz) and 99.5 (J_{Pt-P} = 2688 Hz). Similarly, the ^{31}P NMR spectra of the crude palladium complex in the same solvent exhibited two sharp singlets at δ 115.3 and 127.5. Upon crystallization, however, only the *anti*-isomer of the platinum and palladium

complexes were obtained. Clearly, the *syn*-isomers of complexes **4** and **5** are significantly more soluble than their counterparts with the *anti*-orientation.

Experimental

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. For NMR, all samples were dissolved in *ca*. 0.6 mL selected deuterated solvents in 5 mm outer diameter NMR tubes and examined at 25 °C. Proton spectra were recorded at 500.14 MHz and ^{31}P spectra at 202.46 MHz on Bruker ACF 300 and AMX500 NMR spectrometers. Molar conductivities were measured with a Horiba ES-12 conductivity meter for 10^{-3} M solutions of the complexes at 25 °C. Elemental analyses were performed by the microanalytical Laboratory of the Department of Chemistry at the National University of Singapore.

Synthesis of 1-phenyl-1-phospha-4,8,12-trithiacyclotetradecane-8-oxide L

A suspension of caesium carbonate (6.08 g, 18.7 mmol) in dried dimethylformamide (120 cm^3) was stirred vigorously in a 500 mL three-neck flask which was fitted with a pressure equalising dropping funnel and a condenser. The suspension was then heated in an oil bath at 100 °C for 3 h before the bath temperature was lowered to 50 °C. A solution of bis(3-chloropropyl) sulfoxide (3.79 g, 18.7 mmol) and bis(2-mercaptoethyl)-phenylphosphine (4.30 g, 18.7 mmol) in dimethylformamide (120 cm^3) was added dropwise into the vigorously stirred suspension from the dropping funnel over a period of 4 h at 50 °C. The mixture was then stirred at 50 °C for 4 d. The solvent was removed by distillation under reduced pressure. The residue was dissolved in dichloromethane (300 cm^3) and then filtered. The organic filtrate was washed with aqueous sodium hydroxide (1 M, 200 cm^3) and water and then dried ($MgSO_4$). The dichloromethane solution was then evaporated to *ca*. 20 cm^3 and chromatographed over silica gel. The fraction eluted with ethyl acetate–hexane (1 : 1) was collected and evaporated to dryness to give the crude product as a 1 : 1 stereoisomeric mixture in 60% yield. The stereoisomerically pure ligand could be recrystallized as colorless micro-crystals from dichloromethane–hexane (1.7 g, 26%) (Found: C, 53.4; H, 7.0; S, 26.9. Calc. for $C_{16}H_{25}OPS_3$: C, 53.3; H, 7.0; S, 26.7%). ^{31}P NMR ($CDCl_3$) δ −25.4 (s, 1P). ^{1}H NMR ($CDCl_3$) δ 1.95–3.04 (m, CH_2, 20H), 7.28–7.48 (m, 5H, aromatics). IR (KBr, cm^{-1}) 1026 (S=O).

[*SP*-4-3]-Dichloro[1-phenyl-1-phospha-4,8,12-trithiacyclotetradecane-8-oxide-*P*^{1},*S*^{4}]platinum(II) 1

A solution of $[PtCl_2(MeCN)_2]$ (96.5 mg, 0.28 mmol) in acetonitrile (20 cm^3) was slowly added to a solution of the macrocycle (100.0 mg, 0.28 mmol) in dichloromethane (10 cm^3). After the reaction mixture was refluxed for 2 h, the solvent was removed and the white residue was dissolved in methanol (100 cm^3). The resulting solution was filtered and subsequently concentrated to a small volume (*ca*. 30 cm^3). Upon standing, the pure compound crystallized as white prisms (74.6 mg, 43%), mp 214–217 °C (decomp.) (Found: C, 30.6; H, 4.6; S, 15.1. Calc. for $C_{16}H_{25}Cl_2OPS_3Pt$: C, 30.7; H, 4.0; S, 15.3%). ^{31}P NMR (d_7-DMF) δ 47.7 (s, 1P, J_{Pt-P} = 3562 Hz). IR (KBr, cm^{-1}) 1026 (S=O).

[*SP*-4-3]-Dichloro[1-phenyl-1-phospha-4,8,12-trithiacyclotetradecane-8-oxide-*P*^{1},*S*^{4}]palladium(II) 2

A solution of $[PdCl_2(MeCN)_2]$ (71.9 mg, 0.28 mmol) in acetonitrile (20 cm^3) was slowly added to a solution of the macrocycle (100.0 mg, 0.28 mmol) in dichloromethane (10 cm^3). After the reaction mixture was refluxed for 2 h, the solvent was removed, the yellow residue was dissolved in dichloromethane (100 cm^3), the resulting solution filtered and concentrated to a small volume (*ca*. 30 cm^3). Upon slow addition of ethyl acetate, the pure compound crystallized as pale yellow needles (62.6 mg, 42%), mp 210–212 °C (decomp.) (Found: C, 34.1; H, 4.7; S, 16.7. Calc. for $C_{16}H_{25}Cl_2OPS_3Pd\cdot0.5CH_2Cl_2$: C, 34.1; H, 4.5; S, 16.6%). ^{31}P NMR (CD_2Cl_2) δ 72.3 (s, 1P). IR (KBr, cm^{-1}) 1026 (S=O).

[*SP*-4-4]-[1-Phenyl-1-phospha-4,8,12-trithiacyclotetradecane-8-oxide-*P*^{1},*S*^{4},*S*^{8},*S*^{12}]platinum(II) perchlorate 4

Tetrakis(acetonitrile)platinum(II) perchlorate was generated by refluxing a mixture of $[PtCl_2(MeCN)_2]$ (96.5 mg, 0.28 mmol) and silver perchlorate (114.8 mg, 0.56 mmol) in acetonitrile (50 cm^3) for 16 h in the dark. The AgCl was filtered off, and the filtrate was slowly added to a solution of the macrocycle (100 mg, 0.28 mmol) in dichloromethane (15 cm^3). After the reaction mixture was stirred at 40 °C for 4 h, the solvent was removed. The white residue was dissolved in acetonitrile (60 cm^3), and the resulting solution was filtered and concentrated to a small volume (*ca*. 30 cm^3). Upon slow addition of diethyl ether, the pure compound crystallized as white prisms (79.3 mg, 38%), mp >300 °C (decomp.) (Found: C, 25.3; H, 3.4; S, 12.5. Calc. for $[C_{16}H_{25}OPS_3Pt][ClO_4]_2$: C, 25.5; H, 3.3; S, 12.8%). ^{31}P NMR (CD_3CN) δ 99.5 (s, 1P, J_{Pt-P} = 2683 Hz). IR (KBr, cm^{-1}) 1146 (S=O). Λ_M = 230 cm^2 Ω^{-1} mol^{-1} (CH_3CN). Alternatively, the platinum complex can be prepared by treating an acetonitrile solution of the dichloro complex **1** with a stoichiometric amount of aqueous silver perchlorate (38%) yield.

[*SP*-4-4]-[1-Phenyl-1-phospha-4,8,12-trithiacyclotetradecane-8-oxide-*P*^{1},*S*^{4},*S*^{8},*S*^{12}]palladium(II) perchlorate 5

The tetradentate platinum complex was prepared similarly either from L with $[PdCl_2(MeCN)_2]$ (33% yield) or from **2** with silver perchlorate (36% yield), mp >300 °C (decomp.) (Found: C, 28.8; H, 3.7; S, 14.6. Calc. for $[C_{16}H_{25}OPS_3Pd][ClO_4]_2$: C, 28.9; H, 3.8; S, 14.4.) ^{31}P NMR (CD_3CN) δ 115.3 (s, 1P). IR (KBr, cm^{-1}) 1135 (S=O). Λ_M = 250 cm^2 Ω^{-1} mol^{-1} (CH_3CN). Alternatively, the palladium complex could be prepared by treating a dichloromethane solution of the dichloro complex **1** with a stoichiometric quantity of aqueous silver perchlorate (45% yield).

Crystal structure determination of 1 and 4

Crystal data for complexes **1** and **4** and a summary of the crystallographic analyses are given in Table 1. The dichloro complex **1** was analysed at the National University of Singapore using a Siemens CCD diffractometer using graphite monochromated Mo-Kα radiation. Among the collected data, 9033 had [$F > 4\sigma(F)$] and were considered to be observed. Semi-empirical absorption corrections were applied. The structures were solved by Patterson methods and non-hydrogen atoms were located from Fourier difference maps and were refined anisotropically, except for the solvent molecule. Hydrogen atoms were introduced at fixed distance from carbon atoms and were assigned fixed thermal parameters. All calculations were performed on a Silicon Graphics workstation using programs provided by Siemens.

Complex **4** and its molecular formula were structurally characterized at Imperial College. Although the tetradentate platinum complex is chemically stable and readily recrystallized from acetonitrile–diethyl ether, the crystals of the complex suffer from serious problems of rapid desolvation. At room temperature, the crystals deformed instantly upon isolation from the mother liquor. Thus, the entire data collection process was carried out at −70 °C using a Siemens P4 diffractometer using Cu-Kα radiation. 4828 Unique reflections were measured ($2\theta \leq 128°$) using ω-scans of which 4716 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The structure was solved by

direct methods and all the non-hydrogen atoms were refined anisotropically. One of the two perchlorate anions was disordered and two partial occupancy orientations were identified. The hydrogen atoms were placed in calculated positions. Computations were carried out using the SHELXTL PC program system.[18]

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