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Asymmetric syntheses, structures and reactions of palladium(II) complexes containing thiolato- and sulfinyl-substituted P chiral phosphines

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The palladium complex $(-)_{589}$-di-μ-chlorobis{(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,*N*}dipalladium(II) has been used successfully as the chiral template to promote the asymmetric [4 + 2] Diels–Alder reaction between 3,4-dimethyl-1-phenylphosphole and divinyl sulfoxide. A pair of diastereomeric *exo*-cycloadducts (1α,4α,5α,7*S*)-2,3-dimethyl-7-phenyl-5-(*R*/*S*-vinylsulfinyl)-7-phosphabicyclo[2.2.1]hept-2-ene were formed on the cationic palladium template with both behaving as bidentate ligands *via* their phosphorus and sulfinyl-oxygen donor atoms. Treatment of both diastereomeric template complexes with hydrochloric acid removed the chiral naphthylamine auxiliary from the template and resulted in the unexpected reductive cleavage of the S–O and the vinylic S–C bonds from the co-ordinating *exo*-cycloadducts to give a single optically pure thiolato-substituted phosphine P,S palladium chelate. In the absence of hydrochloric acid, the Pd–naphthylamine auxiliary and Pd–P bonds in both diastereomeric sulfinyl-substituted phosphine complexes are stable but their Pd–O bonds are easily displaced by any ionic chloride to give the corresponding neutral chloro complexes in which the sulfoxide functions are not involved in metal complexation. In these chloro complexes, the sulfinyl-substituted phosphines behave as monodentate ligands *via* their phosphorus donor and in contrast to their cationic counterparts the two neutral diastereomers could be separated efficiently by silica column chromatography.

A great deal of attention has been focused on chiral sulfoxides because they play important roles in many aspects of chemistry and medicine. As examples of their applications, we note the stereospecific antitumour activities of their platinum drugs,[1] the high stereoselectivity offered by their rhodium complexes in the homogeneous asymmetric hydrogenation of prochiral ketones,[2] the enhanced efficiency exhibited by the corresponding manganese complexes in the catalytic asymmetric oxidation of sulfides[3] and the large number of asymmetric induction organic reactions involving sulfoxides as synthetic chirons.[4] In terms of their co-ordination chemistry, polydentate ligands containing these ambidentate functionalities show interesting and facile bonding modes toward transition-metal ions.[5] For example, we have reported the optical resolution and the co-ordination properties of (±)-$Ph_2P(CH_2)_nS(O)Me$ (where $n = 1$ or 2).[6–11] It was observed that the metal–ligand bonds of these sulfinyl substituted phosphines are sensitive to the chelate ring sizes as well as the steric and electronic properties of the central metal ions. These ligands can adopt either the monodentate P[7,10] or the P,O[6,11] and P,S[8,9] chelation modes toward soft metal ions in a predictable manner. This series of studies also uncovered an interesting lone pair–lone pair electronic repulsion between palladium(II) and the sulfinyl-sulfur in a square-planar palladium(II) complex containing the P,O chelating (*R*)-$Ph_2PCH_2S(O)Me$.[11] With the same chiral ligand, we were also able to isolate the first stable palladium(II) complex containing an O-bonded molecular methanol ligand.[10] We now describe the asymmetric synthesis of a pair of diastereomeric palladium(II) complexes containing sulfinyl-substituted P-chiral phosphine ligands and the unprecedented chemical transformation of these optically active complexes into their thiolato analogues.

Results and Discussion

The enantiomerically pure forms of the organopalladium(II) complex **1** (see Scheme 1) have been successfully used as resolving agents for a larger number of chiral ligands.[12] Recently we found that these optically active complexes are also highly effective reaction promoters for the asymmetric Diels–Alder reaction between 3,4-dimethyl-1-phenylphosphole (DMPP) and various dienophiles such as substituted vinylphosphines, vinyl sulfides and *N*,*N*-dimethylacrylamide.[13] In general these chiral palladium complex promoted carbon–carbon bond formation reactions can be related to a common intermediate in which the cyclic diene and the dienophile are co-ordinated simultaneously to the chiral palladium template during the course of cycloaddition to give exclusively the *exo*-cycloadducts. The excellent stereoselectivities in these reactions have been attributed to the chiral inductive effects originating from the prochiral NMe groups and the protruding Hγ proton of the rigid five-membered metallated naphthylamine ring.[14] By using these superior chiral reaction promoters, we are now able to activate the asymmetric Diels–Alder reaction between DMPP and divinyl sulfoxide to give the corresponding sulfinyl-substituted P-chiral phosphines, as illustrated in Scheme 1. In the absence of the reaction promoter, no cycloaddition reaction was observed between the cyclic diene and the prochiral dienophile.

Preparation of diastereomeric complexes

Owing to the vast difference in the electronic *trans*-directing effects of the σ-donating nitrogen and π-accepting aromatic carbon atom in the five-membered organopalladium ring,[12,15] DMPP was co-ordinated regiospecifically to (R_C)-**1** to give the neutral monomer (R_C)-**2**.[16] Treatment of this chloro species in 1,2-dichloroethane with aqueous silver perchlorate generated the corresponding perchlorate analogue in quantitative yield.[17] We have recently reported the isolation and X-ray structural analysis of this rare perchlorate palladium complex.[17] In the present large scale synthesis of the sulfinyl-substituted phosphine ligands, however, this reactive intermediate was not isolated and the 1,2-dichloroethane solution containing the

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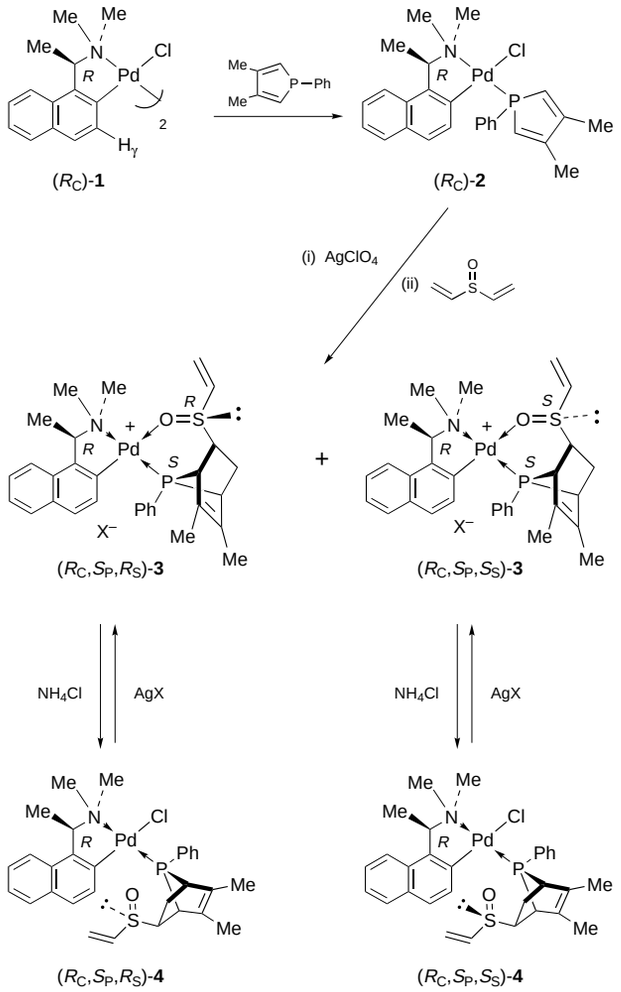


Scheme 1 $X = ClO_4^-$ or PF_6^-

perchlorate complex was directly treated with divinyl sulfoxide at 75 °C for 4 d to give a 1:1 mixture of the diastereomeric complexes (R_C,S_P,S_S)-**3** and (R_C,S_P,R_S)-**3**. The ^{31}P NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited two sharp singlets of similar intensities at δ 109.7 and 110.5. These diastereomeric cationic complexes, however, could not be isolated directly from the reaction mixture by crystallization or by column chromatography. Interestingly, however, when the crude product was chromatographed through a silica gel column, the chloro complex (R_C,S_P,R_S)-**4** was unexpectedly obtained. Presumably, the formation of this neutral species from (R_C,S_P,R_S)-**3** was due to the facile displacement of the kinetically labile Pd–O bond in the original perchlorate salt by the trace amount of chloride ion present in the silica gel. Indeed, the limited quantity of chloride present in the silica gel column was all taken up in the formation of the less polar (R_C,S_P,R_S) chloro complex and insufficient remained to form the more polar (R_C,S_P,S_S) isomer during the silica column separation. Thus (R_C,S_P,S_S)-**4** was not detected and reported in our preliminary communication.[16] This problem has only been identified recently but can be resolved by treating the crude cycloaddition reaction product with excess ammonium chloride prior to purification. Thus, both diastereomeric chloro complexes were separated chromatographically from the reaction mixture in 18–20% yield for each isomer, along with the recovery of the chloro starting material, (R_C)-**2** (30%). Pure (R_C,S_P,R_S)-**4** was subsequently recrystallized from benzene–diethyl ether as beautiful pale yellow prisms with α −80° (589 nm, benzene). The ^{31}P NMR spectrum of the complex in CD_3CN exhibited a sharp singlet at δ 119.0 and its IR spectrum (KBr) showed a characteristic ν(S=O) signal at 1042 cm^{-1}. On the other hand, its diastereomeric counterpart (R_C,S_P,S_S)-**4** was recrystallized from benzene–ethyl acetate as opaque microcrystals with α −14° (589 nm, benzene). The corresponding ^{31}P NMR spectrum obtained in CD_3CN showed a sharp singlet at δ 110.1 and a sharp ν(S=O) signal was observed at 1046 cm^{-1} in its IR spectrum. It is noteworthy that the low-field ^{31}P NMR chemical shifts of these complexes are typical for the bridgehead phosphorus in phosphanorbornenes with the *exo-syn* stereochemistry.[18] Similarly, the ν(S=O) signals of both complexes are consistent with the structural assignments in which the sulfinyl groups are not involved in either the sulfinyl-S or sulfinyl-O metal complexation.[5]

The regeneration of the original P,O chelating cycloadducts, (R_C,S_P,R_S)-**3** and (R_C,S_P,S_S)-**3** can be achieved efficiently by the treatment of the corresponding diastereomerically pure chloro complexes (R_C,S_P,R_S)-**4** and (R_C,S_P,S_S)-**4** with silver perchlorate. Thus, (R_C,S_P,R_S)-**3** was obtained as pale yellow needles with α −217° (589 nm, dichloromethane). The complex behaves as a typical 1:1 electrolyte in dichloromethane and in acetone. Its IR spectrum (KBr) showed a strong ν(S=O) signal at 979 cm^{-1} which is consistent with the sulfinyl–O complexation mode. The ^{31}P NMR spectrum of the perchlorate salt in $CDCl_3$ showed the diagnostic high field singlet at δ 109.7. The diastereomeric analogue (R_C,S_P,S_S)-**3**, with α −260° (589 nm, dichloromethane), showed a very similar ν(S=O) IR signal (981 cm^{-1}) and ^{31}P resonance pattern (δ 110.5) as well as conductivity under similar conditions. The crystals of both diastereomeric perchlorate salts, however, exhibited serious desolvation problems which prevented single-crystal X-ray structural analyses.

Crystal structure of (R_C,S_P,S_S)-3

In order to confirm both the absolute stereochemistry of the sulfinyl-substituted phosphine ligands and its P,O chelation mode in the diastereomeric complexes, the hexafluorophosphate salts of **3** were prepared from the appropriate forms of **4** with $AgPF_6$. The optically pure hexafluorophosphate salts showed very similar physical and spectroscopic properties to their perchlorate counterparts except that their crystals were stable towards desolvation. In our preliminary communications we have reported the isolation and the X-ray structural analyses of the hexafluorophosphate salt of (R_C,S_P,S_S)-**3** and its chloro precursor (R_C,S_P,S_S)-**4**.[16,19] Similarly, pale yellow single crystals of the diastereomeric hexafluorophosphate salt of (R_C,S_P,S_S)-**3** that were suitable for structural analysis were obtained from acetone–benzene.[19] Crystallographic data for this more polar diastereomer are given in Table 1. The diastereomer crystallizes with two crystallographically independent molecules [molecules **A** and **B**] in the asymmetric unit. Both molecules, however, have identical configurations and virtually identical conformations. The only significant difference between the two crystallographically independent molecules being a small change in the relative orientations of the two vinyl groups [9° difference in the torsion angle about the S(14)–C(26) bond]. For clarity, only one molecule of (R_C,S_P,S_S)-**3** [molecule **A**] is depicted in Fig. 1. Selected bond lengths and angles of both molecules are given in Table 2. The X-ray analysis shows that the template directed synthesis of (R_C,S_P,S_S)-**3** has proceeded as intended with the controlled creation of *R*, *S*, *S* and *S* stereocentres at C(15), C(16), C(19) and P(21) respectively. A fifth asymmetric *S*-sulfur centre has also been formed at the S(14) position, though its chirality could not be controlled on the basis of the overall stereocontrol imposed by the naphthylamine chiral auxiliary. The geometries at palladium are slightly distorted square planar, there being a small pyramidal distortion in each molecule, the palladium atoms lying 0.07 and 0.04 Å out of the plane of their substituents in molecules **A** and **B** respectively. There is a characteristic reduction from 90° in the angle at palladium within the five-membered chelate ring [81.8(3) (**A**) and 81.7(3)° (**B**)]. There is also a small contraction in the angle at palladium

Table 1 Crystallographic data for complexes (R_C,S_P,S_S)-**3** and (S_P)-**6**

	(R_C,S_p,S_S)-**3**	(S_P)-**6**
Formula	$C_{30}H_{35}F_6NOP_2PdS\cdot0.5Me_2CO$	$C_{64}H_{62}As_2Cl_2O_8P_2Pd_2S_2\cdot1.25CHCl_3\cdot0.25CCl_4$
M	769.0	1706.4
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1$
a/Å	8.727(1)	13.994(2)
b/Å	12.561(1)	19.241(6)
c/Å	16.962(2)	16.348(3)
α/°	99.45(1)	—
β/°	100.81(1)	114.03(1)
γ/°	106.63(1)	—
U/Å^3	1702.5(3)	4020(2)
Z	2[a]	2
T/K	293	293
D_c/g cm^{-3}	1.500	1.410
λ(Mo-Kα)/Å	0.710 73	0.710 73
μ/cm^{-1}	7.61	16.3
$R1$ (obs. data)[b]	0.037	0.067
$wR2$ (obs. data)[c]	0.088	0.175

[a] There are two crystallographically independent molecules in the asymmetric unit. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Table 2 Selected bond lengths (Å) and angles (°) for complex (R_C,S_P,S_S)-**3** *

Pd–C(1)	1.985(7)	Pd–N(12)	2.117(6)
Pd–O(13)	2.165(6)	Pd–P(21)	2.220(2)
O(13)–S(14)	1.514(6)	S(14)–C(26)	1.755(10)
S(14)–C(15)	1.844(8)	P(21)–C(34)	1.792(4)
C(25)–C(26)	1.290(14)	Pd′–C(1′)	1.984(7)
Pd′–N(12′)	2.125(6)	Pd′–O(13′)	2.159(6)
Pd′–P(21′)	2.223(2)	O(13′)–S(14′)	1.522(6)
S(14′)–C(26′)	1.756(9)	S(14′)–C(15′)	1.847(7)
C(1)–Pd–N(12)	81.8(3)	C(1)–Pd–O(13)	172.3(3)
N(12)–Pd–O(13)	93.1(2)	C(1)–Pd–P(21)	96.6(2)
N(12)–Pd–P(21)	177.6(2)	O(13)–Pd–P(21)	88.2(2)
S(14)–O(13)–Pd	119.9(3)	O(13)–S(14)–C(26)	104.8(4)
O(13)–S(14)–C(15)	107.6(3)	C(26)–S(14)–C(15)	97.6(4)
C(1′)–Pd′–O(13′)	174.4(3)	C(1′)–Pd′–N(12′)	81.7(3)
C(1′)–Pd′–P(21′)	96.7(2)	N(12′)–Pd′–O(13′)	93.6(2)
O(13′)–Pd′–P(21′)	87.9(2)	N(12′)–Pd′–P(21′)	178.0(2)
O(13′)–S(14′)–C(26′)	103.6(4)	S(14′)–O(13′)–Pd′	118.2(3)
C(26′)–S(14′)–C(15′)	98.6(4)	O(13′)–S(14′)–C(15′)	107.2(3)

* Unprimed atoms relate to molecule **A** and primed atoms to molecule **B**.

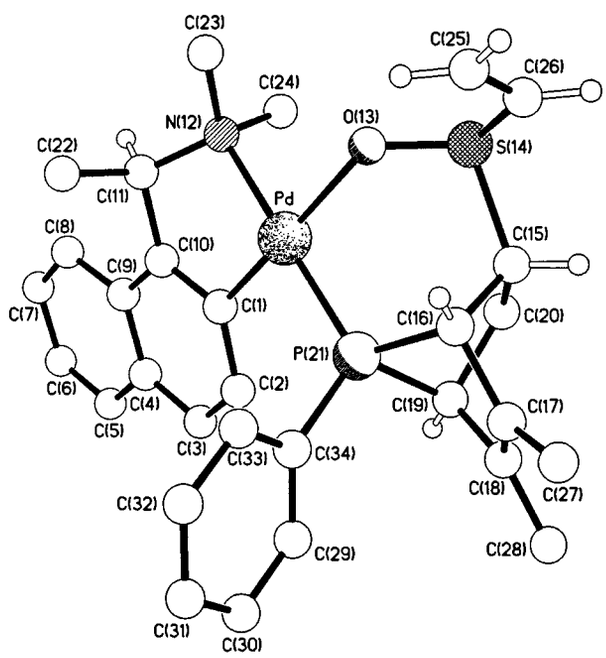


Fig. 1 The molecular structure and absolute stereochemistry of the cation in complex (R_C,S_P,S_S)-**3**

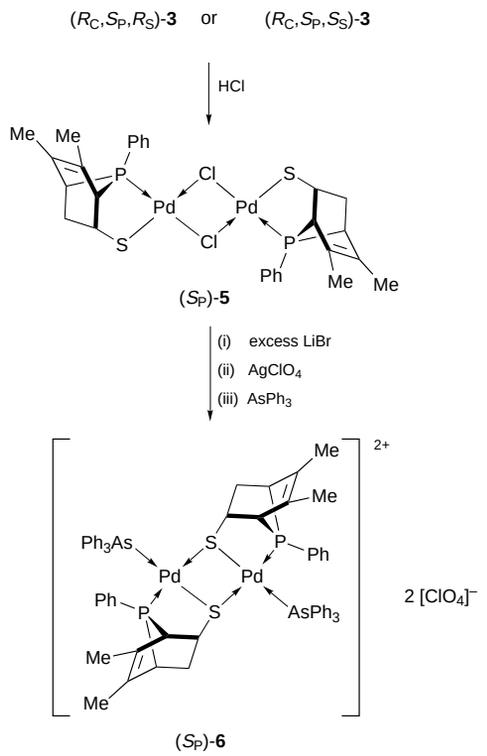
within the six-membered chelate ring, the bite angles being 88.2(2) (in molecule **A**) and 87.9(2)° (molecule **B**). The Pd–C, Pd–N and Pd–P bond lengths do not differ significantly from those observed in the related amidophosphine analogues[13] and the Pd–O distance is the same as that observed in (R_C,S_P,S_S)-**3** and in a corresponding sulfinylphosphine counterpart.[19]

The geometry at sulfur is distorted tetrahedral, with angles in the range of 97.6(4) to 107.6(3)° (**A**) and 98.6(4) to 107.2(3)° (**B**). The S–O bond [1.514(6) (**A**), 1.522(6) Å (**B**)] is significantly lengthened from that of a free sulfoxide, demonstrating a typical loss of double bond character for an O-bonded sulfoxide function.[6] There is a near coplanarity of the sulfinyl and vinyl groups, probably due to an intramolecular C–H···O hydrogen bond between one of the β-vinylic hydrogen atoms [attached to C(25)] and the sulfinyl oxygen atom [O(13)]. The associated C···O, H···O, C–H···O distances and angles are 2.82, 2.37 Å, 108° and 2.79, 2.35 Å, 108°, respectively. The six-membered chelate ring has a slightly twisted boat conformation with the prow and stern atoms O(13) and C(16) both lying above the plane. The geometry of the phosphanorbornene skeleton is typical, with the angle at phosphorus being acute [80.2(4) (**A**) and 80.9(3)° (**B**)].

An inspection of the packing of the molecules reveals edge-to-face aromatic–aromatic interactions between the naphthyl rings of molecules of type **A** and those of type **B** and *vice versa.* For molecules of type **B** there are in addition pairs of C–H···π interactions with a vinylic α-C–H in one molecule and a naphthyl C(7)–H in another being directed into opposite faces of the P–Ph ring of a third molecule (the H···π distances being 2.75 and 3.06 Å, respectively). For molecules of type **A** only the equivalent (though much weaker) vinylic α-C–H interaction (3.02 Å) is present.

Formation of chiral thiolato complexes

It is well established that optically active S-chiral sulfoxides racemize readily in acidic solution.[4,20] Mislow and co-workers have correlated the rate of racemization of various sulfoxides in concentrated hydrochloric acid with the steric demands of the sulfinyl functions.[21] Their findings showed an inverse relationship between steric effects and the rate of racemization. We



Scheme 2

were interested in extending such investigations to our present series of sulfoxide complexes. Since (R_C,S_P,R_S)-**3** and (R_C,S_P,S_S)-**3** have the same absolute stereochemistry at all the carbon and phosphorus stereogenic centres and as the diastereoisomerism is due solely to the difference in the absolute chirality at their sulfinyl-S stereogenic centres, it would be interesting to measure the inter-conversion between these two optically active isomers under acidic conditions. Such a study might reveal the effect of metal complexation on the sulfoxide inversion process and also provide an estimate of the relative thermodynamic stabilities of the two diastereomeric complexes. We were, however, surprised to find that both (R_C,S_P,R_S)-**3** and (R_C,S_P,S_S)-**3** underwent a quantitative conversion into (S_P)-**5** upon brief treatment with concentrated hydrochloric acid in acetone (Scheme 2). Interestingly, the reductive cleavages of the S–O and the vinylic C–S bonds also resulted in the loss of chirality at sulfur and hence, regardless of whether (R_C,S_P,R_S)-**3** or (R_C,S_P,S_S)-**3** was used as the starting material, the ligand stereochemistry in the resulting thiolato complex was identical. The transformation of the sulfoxide function in **3** to the thiolato moiety in (S_P)-**5** was established by IR and elemental analyses, although its high insolubility in all common polar and non-polar solvent systems precluded any further structural characterization. It is noteworthy, however, that (S_P)-**5**, might adopt the μ-dichloro structure as depicted in Scheme 2, or an alternative isomeric structure in which the dipalladium units are linked by two thiolato bridges together with a terminal chloro ligand co-ordinated to each metal centre. In the absence of adequate spectroscopic information we were unable to unequivocally deduce the absolute co-ordination chemistry of this highly insoluble complex. The chloro ligands in (S_P)-**5** however, could be replaced by bromide ions by treatment with potassium bromide in hot methanol to give the somewhat more soluble bromo analogue. This bromo species was successfully converted into the soluble μ-thiolato dimer (S_P)-**6** by the halide displacement reaction using silver perchlorate in acetonitrile followed by the addition of triphenylarsine to the acetonitrile–complex solution. The introduction of the bulky arsenic ligand into the dimeric complex was to facilitate crystallization of the complex as well as to improve its solubility in organic solvents. Thus the perchlorate salt was obtained as yellow prisms with α −240°

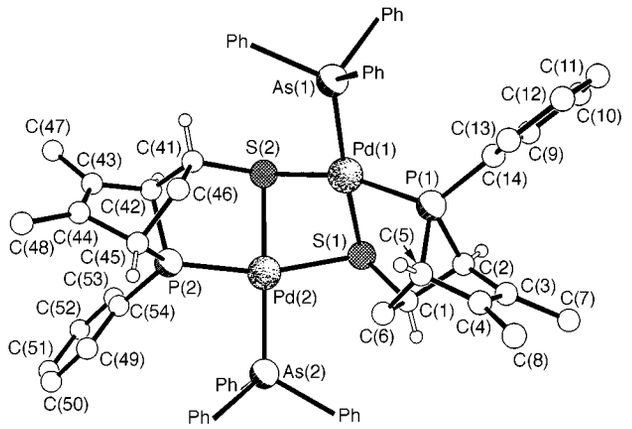


Fig. 2 The molecular structure and absolute stereochemistry of the cation in complex (S_P)-**6** (the As–Ph rings have been omitted for clarity)

Table 3 Selected bond lengths (Å) and angles (°) for complex (S_P)-**6**

Pd(1)–P(1)	2.266(4)	Pd(1)–S(1)	2.344(4)
Pd(1)–S(2)	2.374(4)	Pd(1)–As(1)	2.414(2)
S(1)–C(1)	1.85(2)	S(1)–Pd(2)	2.359(4)
P(1)–Pd(1)–S(1)	83.1(2)	P(1)–Pd(1)–S(2)	162.6(2)
S(1)–Pd(1)–S(2)	80.0(2)	P(1)–Pd(1)–As(1)	97.01(12)
S(1)–Pd(1)–As(1)	174.75(13)	S(2)–Pd(1)–As(1)	100.19(12)
C(1)–S(1)–Pd(1)	98.5(6)	C(1)–S(1)–Pd(2)	116.3(7)
Pd(1)–S(1)–Pd(2)	87.83(13)		

(589 nm, dichloromethane). The ^{31}P NMR spectrum of (S_P)-**6** in $CDCl_3$ showed the high field singlet at δ 122.6 and there was no ν(S=O) signal detected in its IR spectrum. This μ-thiolato dimer is stable toward concentrated hydrochloric acid and is chemically inert toward S-alkylation reactions.

Crystal structure of (S_P)-6

The X-ray analysis shows that after treatment of (S_P)-**5** with HCl followed by $AgClO_4$–$AsPh_3$ the product formed has the dimeric structure (S_P)-**6** (depicted in Fig. 2, selected bond lengths and angles are given in Table 3) in which the stereochemistries at the four chiral centres in the phosphanorbornene skeleton have retained intact, *i.e.* *R*, *S*, *S* and *S* at C(1)/C(41), C(2)/C(42), C(5)/C(45) and P(1)/P(2) respectively. The molecule has non-crystallographic C_2 symmetry about an axis passing through the centre of, and perpendicular to, the Pd_2S_2 ring plane.

Both palladium centres have distorted square-planar geometries, the deformations taking the form of (*i*) small tetrahedral distortions [6 and 7° twists at Pd(1) and Pd(2) respectively], (*ii*) contractions from 90° of the S–Pd–P angles of the five-membered chelates [83.1(2) and 83.5(2)°] and (*iii*) slightly larger contractions, to 80.0(2) and 80.4(2)°, within the Pd_2S_2 ring. The Pd–P, Pd–S and Pd–As bond lengths are typical,[6] there being no significant difference between the two co-ordination centres. The Pd_2S_2 ring is substantially folded, the two Pd_2S planes being inclined by 53°. The associated transannular Pd···Pd and S···S distances are 3.26 and 3.03 Å respectively. There are marked deviations from tetrahedral geometry at the two sulfur centres, with angles of 87.8(1), 98.5(6) and 116.3(7)° at S(1) and 87.6(1), 98.3(5) and 115.5(6)° at S(2). Both five-membered chelate rings have conventional skewed (δ) conformations. The geometries of the phosphanorbornene rings do not differ significantly, and exhibit a characteristic acute angular geometry at the phosphorus bridgehead [79(1) and 82(1)° for P(1) and P(2) respectively].

There is evidence for a degree of intramolecular conformational stabilization involving C–H···π interactions between

the C(1) and C(41) methine hydrogen atoms and their proximal As–Ph rings [H···π 2.67 and 2.69 Å respectively]. The molecules are loosely packed, the interstitial spaces being filled by perchlorate anions and chlorinated solvent molecules.

Conclusion

The transformation of (R_C,S_P,R_S)-**3** and (R_C,S_P,S_S)-**3** into (S_P)-**5** involved the liberation of the naphthylamine ligand and the cleavage of a sulfur–carbon bond. Although it has been observed frequently that the five-membered metallated naphthylamine rings in similar phosphine complexes can be displaced from palladium by treatment with concentrated hydrochloric acid, no examples of mineral acid promoted reductive cleavage of the sulfur-vinylic or sulfur-alkyl substituents from sulfoxide metal chelates have been reported hitherto. Although not proven, the transformation could involve firstly, the cleavage of the Pd–O bond by a chloride to release the sulfoxide function from metal complexation; secondly, the protonation of the non-co-ordinated sulfinyl-oxygen to form a recipient positive charge on the sulfinyl-sulfur; thirdly, an electrophilic addition of an acidic proton to the vinylic double bond *via* an anti-Markownikoff mechanism to generate a carbocation with the positive charge residing on the terminal carbon of the formerly vinyl group;[22] fourthly, the hydrolysis of the carbocation to form the corresponding β-hydroxyalkyl sulfoxide; fifthly, a mineral acid catalysed elimination of the hydroxyalkyl group to generate the corresponding thiolate[23] and lastly, the reco-ordination of the thiolato donor to two palladium ions to form the μ-thiolato dimer.

Finally, we believe that the lack of stereochemical control at the stereogenic sulfur centre during the course of the cycloaddition reaction is due to the fact that the sulfinyl group adopts the O-complexation mode in the transition state of the reaction. In all analogous reactions, the prochiral NMe groups of the metallated naphthylamine auxiliary control the stereochemistry of their neighbouring co-ordination and hence the template site *via* the substituents attached to the incoming donor atoms, for example, the P–Ph groups in the reactions between substituted-phenyldivinylphosphines and DMPP. However, such chirality receivers were not available on the co-ordinating sulfoxide-oxygen donor and hence the chirality of the naphthylamine auxiliary could not be transmitted efficiently to the relative remote sulfur stereogenic centre. Further investigations on the chemical reactivities and the catalytic properties of transition-metal complexes containing these new optically active sulfinyl- and thiolato-substituted phosphine ligands are currently in progress.

Experimental

Reactions involving air-sensitive compounds were performed under purified nitrogen using the Schlenk technique. The NMR spectra were recorded at 25 °C on Bruker ACF 300 and AMX 500 spectrometers. Optical rotations were measured on the specified solution in a 1 dm^3 cell at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry at the National University of Singapore.

The compounds $(-)_{589}$-di-μ-chloro-bis{(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,*N*}dipalladium(II) (R_C)-**1**,[24] chloro{(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,*N*}[3,4-dimethyl-1-phenylphosphole-*P*]palladium(II) (R_C)-**2**,[16] {(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,*N*}{(1α,4α,5α,7*S*)-2,3-dimethyl-7-phenyl-5-(*R*-vinylsulfinyl)-7-phosphabicyclo[2.2.1]-hept-2-ene-O^5,P^7}palladium(II) hexafluorophosphate, (R_C,S_P,R_S)-**3**[19] and chloro{(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,*N*}{(1α,4α,5α,7*S*)-2,3-dimethyl-7-phenyl-5-(*R*-vinylsulfinyl)-7-phosphabicyclo[2.2.1]hept-2-ene-P^7}palladium(II) (R_C,S_P,R_S)-**4**,[16] were prepared according to literature methods.

Syntheses

Chloro{(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,*N*}-{(1α,4α,5α,7*S*)-2,3-dimethyl-7-phenyl-5-(*S*-vinylsulfinyl)-7-phosphabicyclo[2.2.1]hept-2-ene-P^7}palladium(II) (R_C,S_P,S_S)-4. A mixture of the chloro complex (R_C)-**2** (3.10 g, 5.7 mmol) and divinyl sulfoxide (0.6 g, 5.9 mmol) in 1,2-dichloroethane (35 cm^3) was treated with silver perchlorate (1.19 g, 5.7 mmol) in water (1 cm^3) for 30 min. The resulting mixture was filtered through a layer of Celite to remove silver chloride and the organic layer was dried over anhydrous $MgSO_4$. The dried reaction mixture was stirred for 4 d at 75 °C. The solution was treated with ammonium chloride (1 g, 18.7 mmol) in water (10 cm^3). The organic layer was separated, washed with water and then dried over $MgSO_4$. The solvent was removed under reduced pressure to give a black residue. This material was chromatographed on a silica column (50 g, Merck, 40–63 μm) giving the diastereomeric neutral complexes (R_C,S_P,R_S)-**4** and (R_C,S_P,S_S)-**4** in 20 and 18% yield, respectively. In addition, 30% of the chloro starting material, (R_C)-**2**, was recovered from the silica column. The spectroscopic properties and the structural analysis of (R_C,S_P,R_S)-**4** have been reported previously.[16] The diastereomeric chloro complex (R_C,S_P,S_S)-**4** could be crystallized from benzene–ethyl acetate as opaque microcrystals, m.p. 212–214 °C (decomp.) (Found: C, 57.3; H, 5.8; N, 2.5. Calc. for $C_{30}H_{35}ClNOPPdS$: C, 57.1; H, 5.6; N, 2.2%). α −74.0° (589 nm, *c* 1 g per 100 cm^3, CH_2Cl_2); α −14.0° (589 nm, *c* 1 g per 100 cm^3, C_6H_6). ^{1}H NMR (CD_3CN): δ 1.45 (s, 3 H, C=CMe), 1.81 (s, 3 H, C=CMe), 1.86 (d, 3 H, $^3J_{HH}$ = 6.0, CH*Me*), 2.11–2.31 (m, 1 H, $CH_{exo}H_{endo}$), 2.57 (s, 3 H, NMe), 2.80–2.95 (m, 1 H, SCH), 2.94 (s, 3 H, NMe), 3.30–3.40 (m, 2 H, $CH_{exo}H_{endo}$ + PCH), 3.66 (br s, 1 H, PCH), 4.38 (qnt, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.1 Hz, C*H*Me), 4.95–5.03 (m, 1 H, *Z*-SC=CH), 5.43–5.49 (m, 1 H, *E*-SC=CH), 6.20–6.30 (m, 1 H, SCH=C), 7.05–7.98 (m, 11 H, aromatics). ^{31}P-{H} NMR (CD_3CN): δ 110.1 (s, 1 P).

{(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthyl-C^2,*N*}{(1α,4α,-5α,7*S*)-2,3-dimethyl-7-phenyl-5-(*S*-vinylsulfinyl)-7-phosphabicyclo[2.2.1]hept-2-ene-O^5,P^7}palladium(II) perchlorate (R_C,S_P,S_S)-3 and its hexafluorophosphate analogue. A solution of the chloro complex (R_C,S_P,S_S)-**4** (0.2 g, 0.3 mmol) in dichloromethane (50 cm^3) was treated with silver perchlorate (0.064 g, 0.3 mmol) in water (1 cm^3) for 30 min. The resulting mixture was filtered through a layer of Celite to remove silver chloride and the pale yellow organic layer was dried over anhydrous $MgSO_4$. Removal of solvent left a yellow glass. Pure (R_C,S_P,S_S)-**3** was subsequently obtained from acetone–benzene as pale yellow needles (0.19 g, 85%), m.p. 203–205 °C (decomp.) (Found: C, 51.8; H, 4.9; N, 2.0. Calc. for $C_{30}H_{35}ClNO_5PPdS$: C, 51.8; H, 5.1; N, 2.0%). α −260° (589 nm, *c* 0.5 g per 100 cm^3, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 3 H, C=CMe), 1.86 (d, 3 H, $^3J_{HH}$ = 6.3, CH*Me*), 1.95 (s, 3 H, C=CMe), 2.70–2.88 (m, 1 H, $CH_{exo}H_{endo}$), 2.70 (s, 3 H, NMe), 2.78 (d, 3 H, $^4J_{PH}$ = 3.2, NMe), 3.01 (br s, 1 H, PCH), 3.33 (dd, 1 H, $^2J_{HH}$ = 14.0, $^3J_{HH}$ = 4.8, $CH_{exo}H_{endo}$), 3.63 (br s, 1 H, PCH), 3.81 (ddd, 1 H, $^3J_{HH}$ = 4.8, $^3J_{HH}$ = 10.3, $^3J_{PH}$ = 21.9, SCH), 4.32 (qnt, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.1, C*H*Me), 6.27 (d, 1 H, $^3J_{HH}$ = 16.2, *Z*-SC=CH), 6.32 (d, 1 H, $^3J_{HH}$ = 9.8 Hz, *E*-SC=CH), 6.75–7.65 (m, 12 H, aromatics + SCH=C). ^{31}P-{H} NMR ($CDCl_3$): δ 110.5 (s, 1 P). The corresponding hexafluorophosphate salt of the cationic complex was prepared similarly from (R_C,S_P,S_S)-**4** and silver hexafluorophosphate. The complex was obtained as pale yellow needles from acetone. One acetone solvate was found in every two complex molecules, m.p. 208–209 °C (decomp.) (Found: C, 49.3; H, 4.6; N, 1.6. Calc. for $C_{31.5}H_{38}F_6NO_{1.5}P_2PdS$: C, 49.0; H, 4.9; N, 1.9%). α −264° (589 nm, *c* 0.5 g per 100 cm^3, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 3 H, C=CMe), 1.87 (d, 3 H, $^3J_{HH}$ = 6.4, CH*Me*), 1.95 (s, 3 H, C=CMe), 2.70–2.79 (m, 1 H, $CH_{exo}H_{endo}$), 2.70 (s, 3 H, NMe), 2.78 (d, 3 H, $^4J_{PH}$ = 3.3, NMe), 3.01 (br s, 1 H, PCH), 3.30 (dd, 1 H, $^2J_{HH}$ = 13.4, $^3J_{HH}$ = 4.9,

CH_{exo}H$_{endo}$), 3.61 (ddd, 1 H, $^3J_{HH}$ = 4.9, $^3J_{HH}$ = 10.3, $^3J_{PH}$ = 21.9, SCH), 3.62 (br s, 1 H, PCH), 4.32 (qnt, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.1, C*H*Me), 6.27 (d, 1 H, $^3J_{HH}$ = 16.3, *Z*-SC=CH), 6.34 (d, 1 H, $^3J_{HH}$ = 9.8 Hz, *E*-SC=CH), 6.73–7.66 (m, 12 H, aromatics + SCH=C). ^{31}P-{H} NMR ($CDCl_3$): δ 109.9 (s, 1 P, PPd), −144.2 (spt, $^1J_{PF}$ = 713.2 Hz, 1 P, PF).

Bis[triphenylarsine{μ-(1α,4α,5α,7*S*)-2,3-dimethyl-7-phenyl-5-thiolato-7-phosphabicyclo[2.2.1]hept-2-ene-*S*^{5},*P*^{7}}]dipalladium(II) (*S*$_P$)-6. A solution of (*R*$_C$,*S*$_P$,*R*$_S$)-**3** (0.5 g, 0.7 mmol) in acetone (50 cm^3) was treated with hydrochloric acid (10 M, 5 cm^3) at 40 °C for 5 min. Yellow microcrystals of (*S*$_P$)-**5** precipitated during this period (0.2 g, 85%), m.p. 203–205 °C (decomp.) (Found: C, 43.8; H, 4.7; S, 7.5. Calc. for $C_{28}H_{32}Cl_2P_2Pd_2S_2\cdot Me_2CO\cdot H_2O$: C, 43.6; H, 4.7; S, 7.5%). This material was suspended in methanol (100 cm^3) and treated with lithium bromide (20 g) at reflux temperature for 16 h. The solvent was removed under reduced pressure and the residue was washed with water to remove excess halides. The dark brown residue was then suspended in acetonitrile and treated with silver perchlorate (0.14 g, 0.7 mmol) at room temperature for 2 h in the dark. The resulting mixture was filtered through a layer of Celite. The filtrate was then treated with a solution of triphenylarsine (0.2 g, 0.7 mmol) in dichloromethane (10 cm^3) for 30 min. The solvent mixture was removed and pure (*S*$_P$)-**6** was subsequently obtained as yellow squarish blades by crystallization from acetonitrile–hexane (0.2 g, 53%), m.p. 223–224 °C (decomp.) (Found: C, 49.5; H, 4.5; S, 4.3. Calc. for $C_{64}H_{62}As_2Cl_2O_8P_2Pd_2S_2\cdot 2H_2O$: C, 49.4; H, 4.3; S, 4.1%). α −240° (589 nm, *c* 0.1 g per 100 cm^3, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 1.17 (s, 3 H, C=CMe), 1.32 (ddd, 1 H, $^3J_{HH}$ = 2.3, $^3J_{HH}$ = 7.2, $^3J_{PH}$ = 47.7, SCH), 1.44 (s, 3 H, C=CMe), 1.67 (ddd, 1 H, $^2J_{HH}$ = 13.7, $^3J_{HH}$ = 7.2, $^3J_{PH}$ = 29.6, CH$_{exo}$*H*$_{endo}$), 2.75 (dd, 1 H, $^2J_{HH}$ = 13.6, $^3J_{HH}$ = 3.1, C*H*$_{exo}$H$_{endo}$), 3.56 (br s, 1 H, PCH), 3.62 (br s, 1 H, PCH), 6.58–7.56 (m, 20 H, aromatics + SCH=C). ^{31}P-{H} NMR ($CDCl_3$): δ 122.6 (s, 1 P). These crystals exhibited desolvation problems and it was necessary to recrystallize the complex from chloroform–carbon tetrachloride prior to X-ray structural determination.

X-Ray crystallography

Crystal data for (*R*$_C$,*S*$_P$,*S*$_S$)-**3** and (*S*$_P$)-**6** and a summary of the crystallographic analyses are given in Table 1. 6378 and 7234 Independent reflections were measured on a Siemens P4 diffractometer using ω-scans for (*R*$_C$,*S*$_P$,*S*$_S$)-**3** and (*S*$_P$)-**6** respectively (2θ ≤ 50° in each case) of which 5650 and 5126 respectively had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors, and in the case of (*S*$_P$)-**6**, for absorption (semiempirical based on ψ-scans, maximum and minimum transmission factors 0.59 and 0.50 respectively). The complex (*R*$_C$,*S*$_P$,*S*$_S$)-**3** was solved by direct methods and (*S*$_P$)-**6** by the heavy atom method. In (*R*$_C$,*S*$_P$,*S*$_S$)-**3** all the major occupancy non-hydrogen atoms were refined anisotropically (the minor occupancy fluorine atoms of the 67:33 disordered PF_6 anion were refined isotropically). In (*S*$_P$)-**6** the perchlorate anions were found to be disordered, though alternate, discrete, partial occupancy orientations could not be identified; the oxygen atoms were refined isotropically. All the other major occupancy non-hydrogen atoms in (*S*$_P$)-**6** were refined anisotropically, including those of the chloroform and carbon tetrachloride solvent molecules, which were disordered over four partial occupancy sites. In both structures the phenyl rings were treated as idealized rigid bodies, and the hydrogen atoms of the methyl groups attached to sp^2 centres were located from Δ*F* maps and subsequently optimized. In (*R*$_C$,*S*$_P$,*S*$_S$)-**3** the hydrogen atoms of the vinyl group were also located and optimized. The remaining hydrogen atoms throughout both structures were placed in calculated positions. All the H atoms were assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}$(C–Me)], and allowed to ride on their parent carbon atoms. Refinements were by full-matrix least squares based on F^2. The absolute stereochemistries were determined unambiguously by both *R*-factor tests and by use of the Flack parameter [for (*R*$_C$,*R*$_P$,*S*$_S$)-**3**: $R^+ = 0.0372$, $R^- = 0.0386$, $x^+ = -0.01(5)$, $x^- = +1.01(5)$ and for (*S*$_P$)-**6**: $R^+ = 0.0673$, $R^- = 0.0687$, $x^+ = -0.00(6)$, $x^- = +1.03(6)$].[25]

For both structures, computations were carried out using the SHELXTL PC program system.[26]

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