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Optical resolution and the stereoelectronic properties of chelating (±)-[(methylsulfinyl)methyl]diphenylphosphine

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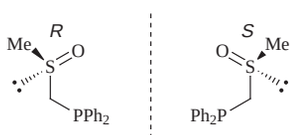
Optical resolution of the asymmetric chelating agent (±)-$Ph_2PCH_2S(O)Me$ has been achieved *via* fractional crystallization of a pair of diastereomeric palladium(II) cationic complexes containing the sulfinyl-substituted ligand and *ortho*-metallated (*S*)-[1-(dimethylamino)ethyl]naphthalene. The X-ray structural analysis of the perchlorate salt of the less-soluble diastereomer confirmed that the sulfinyl-substituted phosphine co-ordinated to the palladium *via* phosphorus and oxygen with the non-co-ordinated sulfur having an *R* absolute configuration. An unusual electronic repulsion is observed between palladium and the non-bonded sulfur lone pair thus directing the methyl substituent on sulfur to a sterically unfavored axial position. Furthermore, a two-dimensional rotating frame Overhauser enhancement ^{1}H NMR study of the complex in $CDCl_3$ confirmed that this intramolecular electronic interaction outweighs the general steric considerations in solution. Optically pure (*R*)-(+)-$Ph_2PCH_2S(O)Me$ was displaced from the resolving palladium complex with 1,2-bis(diphenylphosphino)ethane.

Transition-metal complexes of polydentate ligands containing sulfoxide functions have been studied extensively because of their catalytic, chemical and structural properties.[1] Continuing our studies concerning the stereochemistry of phosphines containing this important ambidentate functional group, we have resolved the asymmetric chelating agent (±)-$Ph_2PCH_2CH_2S(O)Me$ by using an organopalladium resolving agent.[2] Recently, we have also reported the asymmetric synthesis of a P-chiral phosphine ligand in which a resolved sulfinyl function is attached on the rigid phosphanorbornene skeleton.[3] These stereochemically well defined chelating agents have been shown to have a rich co-ordination chemistry.[4,5] For example, the P–S and the P–O bonding modes of the ambidentate sulfoxide donors in these metal chelates are governed by external factors such as the electronic effect of the *trans*-donor atom as well as the steric requirement of the neighboring *cis* ligands. Interestingly, in the presence of major stereoelectronic constraints these ligands are restricted to a monodentate co-ordination *via* phosphorus. Furthermore, we believe that the co-ordination chemistry of such ligands can be altered internally by controlling the size of the phosphorus–sulfoxide linkages. Here we present the optical resolution and some unusual stereoelectronic properties of the short-chain ligand $Ph_2PCH_2S(O)Me$, (±)-**1**.



(+)-**I** (–)-**I**

Results and Discussion

Formation and separation of diastereomers

The racemic ligand (±)-I was obtained as white prisms from the reaction between $NaPPh_2$ and $ClCH_2S(O)Me$ as described earlier.[6] It is air-stable in the solid state and in solution. However, in the presence of molecular iodine, (±)-I rearranged quantitatively into the corresponding isomeric methylthio-substituted phosphine oxide $Ph_2P(O)CH_2SMe$. In $CDCl_3$ the oxygen migration was completed within 5 min at room temperature.

The resolution procedure is summarized in Scheme 1. The initial mixture of cationic complexes was obtained in high yield (85%) from the reaction of stoichiometric quantities of the organopalladium resolving agent (S_c)-**1** and the sulfinyl-substituted ligand in dichloromethane. Prior to crystallization the ^{31}P NMR spectrum of the crude diastereomeric mixture in $CDCl_3$ exhibited two singlets of approximately equal intensities at δ 44.9 and 45.3. The less soluble (R_s,S_c) isomer was subsequently isolated by fractional crystallization of the mixture in dichloromethane–ethyl acetate. The pure epimer was obtained as pale yellow plates in 50% theoretical yield with α −165.8° (589 nm, dichloromethane). In both dichloromethane and acetone the complex behaves as a typical 1:1 electrolyte. In $CDCl_3$ the ^{31}P NMR spectrum of (R_s,S_c)-**2** exhibited only one sharp singlet at δ 45.3. The ^{31}P chemical shift indicates that the phosphorus donor atom is part of a five-membered chelate ring.[7] In addition, the ^{1}H NMR spectrum of the cationic complex in the same solvent showed a sharp S–Me resonance at δ 2.64. This chemical shift is consistent with sulfinyl-O complexation.[1] Collectively, the one-dimensional NMR studies indicated that in solution the sulfinyl-substituted phosphine ligand chelates to palladium *via* its phosphorus and oxygen donor atoms in (R_s,S_c)-**2**. Selected ^{1}H NMR data of the optically pure complex are given in Table 1. The spectroscopic assignments are based on a combination of selectively ^{31}P-decoupled proton spectra and proton COSY and ROESY (rotating frame Overhauser enhancement spectroscopy) experiments.

Interestingly, the physical properties of complex (R_s,S_c)-**2** are somewhat different from those of the analogous complex containing the longer-chain ligand $Ph_2PCH_2CH_2S(O)Me$. For example, the longer-chain complex is readily crystallized from acetone–diethyl ether and is stable upon isolation.[1] However, (R_s,S_c)-**2** could not be recrystallized from this particular solvent system and crystals of the complex obtained from other solvent systems generally suffer rapid desolvation, despite the cationic complex itself being intrinsically air-stable.

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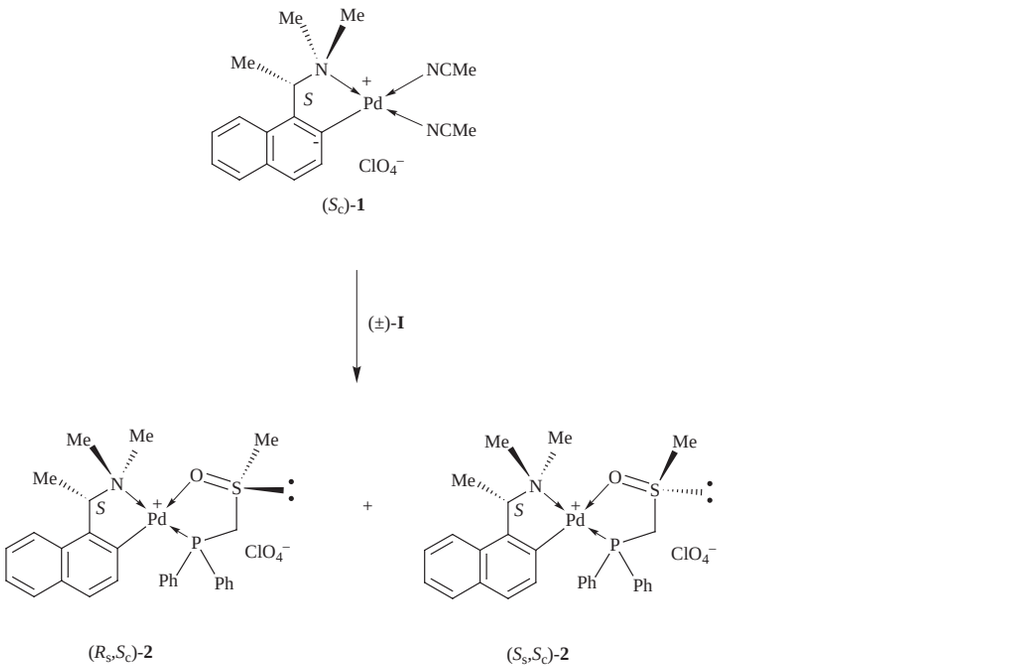


Scheme 1

Table 1 Selected ^{1}H chemical shifts δ (*J*/Hz) of complex (R_s,S_c)-**2** in $CDCl_3$ solution

H(2)	6.42 (dd, J_{HH} = 8.6, J_{PH} = 5.6)
H(3)	7.01 (d, J_{HH} = 8.6)
H(11)	4.43 (dd, J_{HH} = J_{PH} = 6.3)
Me(13)	1.88 (d, J_{HH} = 6.3)
Me(14) (eq)	2.79 (d, J_{PH} = 3.3)
Me(15) (ax)	2.85 (d, J_{PH} = 1.5)
H(28) (eq)	4.80 (dd, J_{HH} = 15.2, J_{PH} = 9.8)
H(28′) (ax)	4.14 (dd, J_{HH} = 15.2, J_{PH} = 4.5)
Me(29)	2.64 (s)
o-H of Ph (ax)	7.87 (m)
o-H of Ph′ (eq)	2.67 (m)

Table 2 Selected bond lengths (Å) and angles (°) for the four crystallographically independent molecules in complex (R_s,S_c)-**2**

	A	**B**	**C**	**D**
Pd–C(1)	1.98(2)	1.99(3)	1.98(3)	1.97(3)
Pd–N(12)	2.10(3)	2.09(3)	2.09(3)	2.11(4)
Pd–O	2.16(3)	2.17(3)	2.15(3)	2.16(3)
Pd–P	2.24(1)	2.25(1)	2.25(1)	2.25(1)
S–O	1.53(3)	1.53(3)	1.52(3)	1.51(4)
S–C(28)	1.74(5)	1.81(5)	1.76(4)	1.79(5)
S–C(29)	1.78(5)	1.75(5)	1.76(5)	1.75(6)
P–C(28)	1.80(4)	1.84(5)	1.86(5)	1.89(5)
C(1)–Pd–N(12)	81(1)	82(2)	82(1)	80(2)
C(1)–Pd–P	98.9(9)	100(1)	99(1)	99(1)
C(1)–Pd–O	173(1)	173(1)	174(1)	174(2)
N(12)–Pd–O	93(1)	91(1)	94(1)	94(2)
N(12)–Pd–P	172(1)	176(1)	175(1)	178(1)
O–Pd–P	87.2(9)	87.0(9)	85.8(9)	87(1)
O–S–C(28)	102(2)	103(2)	104(2)	105(2)
O–S–C(29)	105(2)	105(2)	106(2)	109(3)
S–O–Pd	116(2)	119(2)	118(2)	120(2)
S–C(28)–P	115(3)	111(2)	111(2)	109(3)
C(28)–S–C(29)	101(2)	101(2)	100(2)	99(3)
C(28)–P–Pd	102(2)	104(1)	104(1)	105(2)

Crystal and molecular structure of (R_s,S_c)-2. Absolute configuration and stereoelectronic properties of co-ordinated (R_s)-I

The X-ray analysis of complex (R_s,S_c)-**2** reveals the presence of four crystallographically independent molecules in the asymmetric unit (labelled **A** to **D**). All four molecules have the same absolute stereochemistry with an *R* configuration at sulfur and an *S* configuration at the C(11) centre of the naphthylamine ligand, Fig. 1. Their conformations are very similar (the methyl substituents on both chelate rings [C(13) and C(29)] occupying axial positions on the same side of the co-ordination plane), the only major difference being in the rotations of the C(22)–C(27) rings with respect to the co-ordination plane, which vary by up to 26°. Differences in the orientations of the C(16)–C(21) ring are small, varying by only *ca*. 5° between the four independent molecules, reflecting the hindered rotation of this ring due to the steric interaction with the axial S–Me group [C(29)]; this restriction is also observed in solution (see below). The co-ordination geometries at palladium for the four molecules are essentially the same, and each exhibits a small tetrahedral distortion (twist angles ranging between 2 and 10°) from square planar. Owing to the distinct electronic directing effects originating from the organometallic ring,[8] the P and O donor atoms are bound regiospecifically to the palladium centre, with the soft donor atom taking up the position *trans* to the NMe_2 group. The palladium co-ordination distances (Table 2) are very similar to those observed in related complexes.[2,9] The sulfur–oxygen distances, *ca*. 1.52 Å, are typical of O-bonded transition-metal sulfinyl systems,[1,8,10] being longer than the corresponding distances in unco-ordinated analogues, reflecting a loss of double-bond character.

Initially, the most surprising feature of the conformation of the structure is the axial geometry observed for the methyl group attached to sulfur and the unusual near coplanarity of the O–Pd–P–C(28) atoms.[2,9] This appears to give a far more hindered geometry than for the alternative equatorial arrangement. However, in the former, the closest approach of a methyl hydrogen atom to the palladium centre is greater than 2.8 Å, providing no significant barrier to this conformation. On the other hand, an equatorial geometry would result in an aligning of the sulfur lone pair with the filled palladium non-bonding d_{z^2} orbital, an interaction that would be repulsive.

There is no evidence that packing effects play a significant role in determining the principal conformational features of the molecules, other than in the varying degrees of rotation of the C(22)–C(27) phenyl ring.

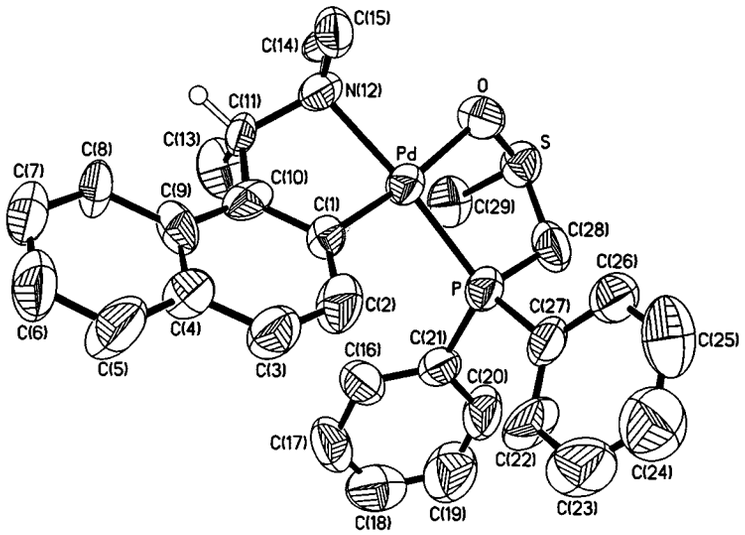


Fig. 1 Molecular structure of one of the independent cations (**A**) in complex (R_s,S_c)-**2**

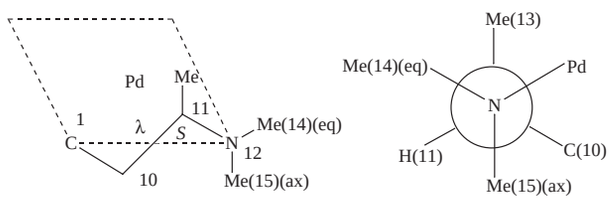


Fig. 2 Absolute conformation of the PdCN ring and the staggered orientation of its C(11) and N(12) substituents

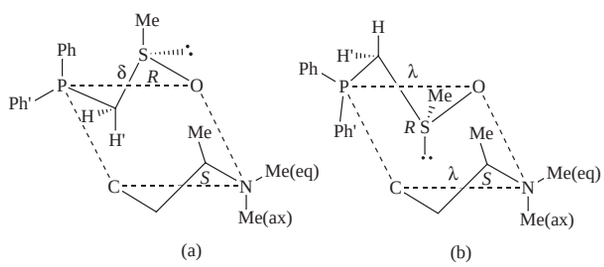


Fig. 3 Interchelate interactions in complex (R_s,S_c)-**2** in which the P–O ring adopts a (a) δ conformation in which the S-Me group is axial and (b) λ conformation in which the S-Me group is equatorial

Stereoelectronic properties of complex (R_s,S_c)-2 in solution

It is well established that C-methyl substituted five-membered chelate rings always adopt a single static chiral conformation with the C-methyl group occupying the sterically favorable equatorial position.[11] On another hand, it has been reported that, both in the solid state and in solution, the five-membered (*S*)-metallated naphthylamine ring adopts only the averaged preferred λ conformation with the methyl substituent on the stereogenic carbon invariably taking up the axial position (Fig. 2).[2–4,8,9,12,13] In this exceptional organometallated ring the axial rather than equatorial geometry for the methyl group is attributed to the unfavorable steric interaction that would otherwise be present with the proximal naphthylene proton C(8).[14] Such dominating repulsive intrachelate interactions, however, are not observed around the S-methyl group within the five-membered P–O ring. We were therefore surprised to observe that this ring adopts a distorted δ conformation in the solid state with the S-methyl group of (R_s,S_c)-**2** located in the sterically unfavored axial position. Indeed, the crystallographic study clearly revealed that there is a classic 1,3-diaxial repulsion between this axially disposed S-methyl group and the C(16)–C(21) P-phenyl ring. In order to confirm that this axial disposition is indeed due to the intrinsic metal–sulfur lone pair–lone pair repulsion and not simply due to crystal-packing forces, a two-dimensional ROESY ^{1}H NMR study was carried out to determine the absolute stereochemistry of (R_s,S_c)-**2** in solution. Since the torsional barrier of five-membered chelate rings is usually small in the absence of major steric factors,[15] rearrangement in solution of the chiral (R_s)-P–O ring from the distorted δ form seen in the crystal structure to the λ form would be relative facile. This would permit the S-methyl group to adopt the more sterically favorable equatorial position provided that the electronic factors are not the dominant controlling force determining the conformation of the P–O ring. We have previously applied similar ROESY NMR experiments to assign the absolute stereochemistry of several P-chiral diphosphines in solution.[13]

Figs. 3(a) and 3(b) show the two possible conformations that compound (R_s)-**I** may adopt in (R_s,S_c)-**2**. In this spectroscopic determination the characteristic orientation of the chiral organopalladium–naphthylamine unit is used as the internal stereochemical reference. Owing to the well established λ absolute conformation of this (*S*)-metallated naphthylamine ring, the prochiral N–Me groups are locked into non-interconvertible axial and equatorial positions. Hence, the aromatic proton at C(2) protrudes invariably toward the region somewhat below the phosphorus donor. Fig. 4 shows the ROESY NMR spectrum of the cationic complex in $CDCl_3$. The characteristic intrachelate NOE interactions within the organometallic rings are prominently reflected in the spectrum (signals A–F). The interchelate interactions between H(2)···*o*-H of Ph (signal G) and H(2)···*o*-H of Ph′ (H) are consistent with the *cis* relationship between C(1) and the PPh_2 group. Similarly the long-range NOE contacts for Me(13)···*o*-H of Ph (I) and Me(13)···Me(29) (J) establish that these substituents are located on the same side above the square plane. Furthermore the Me(13)···Me(29) (J) long-range signal clearly indicates the axial disposition of the S–Me group, as shown in Fig. 3(a). Consistent with this structural assignment, the 1,3-diaxial repulsive interaction between Me(29) and Ph is clearly reflected in the spectrum (signal K). As expected, within the five-membered P–O ring, the two prochiral protons attached to C(28) interact strongly with each other (signal L). However, each prochiral proton interacts with only one neighboring PPh ring, *i.e.* H(28)···Ph (M), H(28′)···Ph′ (N). The lack of H(28)···Ph′ and H(28′)···Ph interactions suggest that, in solution, the P–O ring preferentially adopts the more stable δ conformation, as in the solid state. The S-Me group therefore does not occupy the sterically favored equatorial position in solution. Consistently, while a relatively strong interaction is observed between H(28) and Me(29) (signal O), only a weak signal for the H(28′)···Me(29) interaction (P) is detected. The

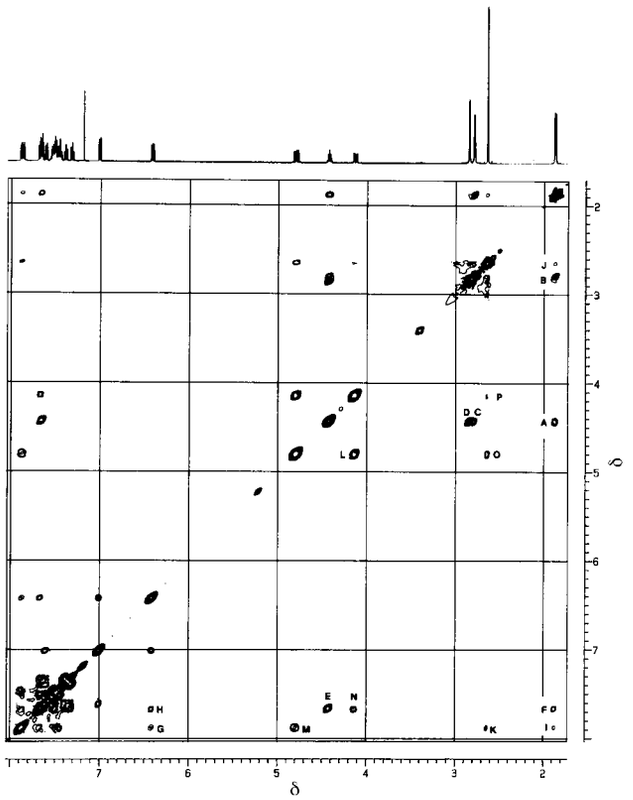


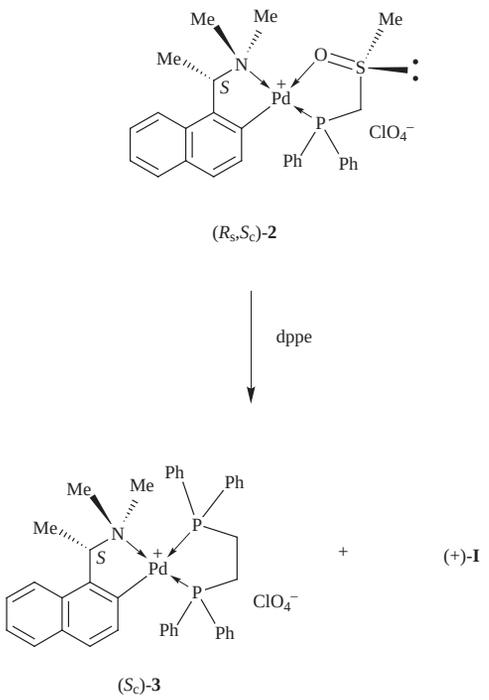
Fig. 4 Two-dimensional ^{1}H ROESY NMR spectrum of complex (R_s,S_c)-**2** in $CDCl_3$. All off-diagonal peaks are of negative intensity. Selected NOE contacts: A, H(11)···Me(13); B, Me(13)···Me(14); C, H(11)···Me(14); D, H(11)···Me(15); E, H(8)···H(11); F, H(8)···Me(13); G, H(2)···*o*-H of Ph; H, H(2)···*o*-H of Ph′; I, Me(13)···*o*-H of Ph; J, Me(13)···Me(29); K, Me(29)···*o*-H of Ph; L, H(28)···H(28′); M, H(28)···*o*-H of Ph; N, H(28′)···*o*-H of Ph′; O, H(28)···Me(29).

NMR studies therefore confirm that the electronic properties in (R_s,S_c)-**2** do indeed overrule the steric contributions in the P–O ring. It is noteworthy that such electronic properties were not observed in the analogous cationic complex containing the more extended ligand, $Ph_2PCH_2CH_2S(O)Me$; in this complex the ambidentate ligand has a larger six-membered P–O ring and hence the sulfur lone pair does not interact directly with the filled d_{z^2} palladium orbital.

Liberation of resolved sulfoxide

As illustrated in Scheme 2, treatment of complex (R_s,S_c)-**2** with $Ph_2PCH_2CH_2PPh_2$ liberated the optically pure (R_s)-**I** as a colorless viscous oil with α +22.7° (589 nm, dichloromethane). Stereospecific displacement of the resolved sulfoxide ligand from palladium was confirmed by the quantitative repreparation of (R_s,S_c)-**2** from liberated (R_s)-**I** and (S_c)-**1**: the 202 MHz ^{31}P NMR spectrum of the crude product indicated the presence of diastereomer (R_s,S_c)-**2** only. In a further test of optical purity, the soluble diastereomer (R_s,R_c)-**2** was prepared from (R_s)-**I** and the equally accessible (R_c)-**1**: only the singlet at δ 44.9 due to the (R_s,R_c) isomer was observed. Finally, it should be noted that optically pure (S_s)-**I** was obtained similarly by using (S_c)-**1** as the resolving agent.

By using (±)-**I** as the supporting ligand, we have recently isolated the first stable palladium(II) complex containing a molecular methanol ligand: *trans*-[$PdCl_2${$Ph_2PCH_2S(O)Me$-*P*}(MeOH-*O*)].[6] In this structurally characterized neutral complex (±)-**I** behaves as a monodentate phosphine ligand and the sulfoxide function is not involved in any co-ordinative bonding, either in the solid state or in solution. Under similar conditions, interestingly, the corresponding longer-chain ligand forms a stable five-membered P–S chelate producing *cis*-[$PdCl_2${$Ph_2PCH_2CH_2S(O)Me$-*P*,*S*}] exclusively. We are currently comparing the stereoelectronic properties of the various forms of **I** with those of the corresponding longer-chain analogue.



Scheme 2

Experimental

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. Proton and ^{31}P NMR spectra were measured on a Bruker AMX 500 spectrometer with samples in 5 mm outside diameter tubes at frequencies of 500.14 and 202.46 MHz respectively. Phase-sensitive ROESY spectra were obtained using the pulse sequence 90°–t_1 spin-lock – acquire (t_2) with a spin-locking field given by $\gamma B_1/2\pi = 5000$ Hz and a spin-locking (mixing) time of 250 ms. Typically, 32 free induction decays were acquired into 1024 data points for each of 512 values of t_1 and a shifted sine-bell weighting function was used in each dimension prior to transformation into a 1K × 1K data matrix. Optical rotations were measured on the specified solutions in a 1 dm cell at 25 °C with a Perkin-Elmer model 341 polarimeter. The racemic form of **I**[6] and the enantiomerically pure form of bis(acetonitrile){(*S*)-1-[1-(dimethylamino)ethyl]naphthalen-2-yl-*C*,*N*}palladium(II) perchlorate (±)-**1**[2] were prepared as previously described. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry at the National University of Singapore.

Resolution of compound (±)-I: formation and isolation of [*SP*-4-3(*R*),(*S*)]-{1-[1-(dimethylamino)ethyl]naphthalen-2-yl-*C*,*N*}-{[(methylsulfinyl)methyl]diphenylphosphine-*P*,*O*}palladium(II) perchlorate (R_s,S_c)-2

A mixture of compound (±)-**I** (2.1 g) and (S_c)-**1** (3.9 g) in dichloromethane (100 cm^3) was stirred at room temperature for 30 min. The solvent was removed from the reaction mixture and the residue recrystallized twice from dichloromethane–ethyl acetate, forming bright yellow prisms which rapidly turned opaque upon isolation (1.1 g, 50%); m.p. 178–180 °C (decomp.) (Found: C, 50.2; H, 4.9; Cl, 5.4; N, 1.9; P, 4.7. Calc. for $C_{28}H_{31}ClNO_5PPdS$: C, 50.5; H, 4.7; Cl, 5.3; N, 2.1; P, 4.7%). α −165.8° (589 nm, *c* 1.0 g per 100 cm^3, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.88 (d, 3 H, $^3J_{HH} = 6.3$, CH*Me*), 2.64 (s, 3 H, SMe), 2.79 (d, 3 H, $^4J_{PH} = 3.3$, NMe), 2.85 (d, 3 H,

Table 3 Crystallographic data for complex (R_s,S_c)-**2**

Formula	$[C_{28}H_{31}NOPPdS][ClO_4]\cdot 0.75CHCl_3\cdot 0.5CH_2Cl_2$
M	777.2
Crystal system	Triclinic
Space group	$P1$
a/Å	12.966(4)
b/Å	16.015(4)
c/Å	17.670(4)
α/°	76.32(2)
β/°	89.08(2)
γ/°	88.54(2)
U/Å^3	3564(2)
Z	4[a]
D_c/g cm^{-3}	1.45
F(000)	1576
Crystal size/mm	0.83 × 0.67 × 0.06
μ(Mo-Kα)/cm^{-1}	9.4
$R1$[b]	0.083
$wR2$[c]	0.188

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

$^4J_{PH}$ = 1.5, NMe), 4.14 [dd, 1 H, $^2J_{HH}$ = 15.2, $^2J_{PH}$ = 4.5, H(28′)], 4.43 (qnt, 1 H, $^3J_{HH} = {}^4J_{PH}$ = 6.3, C*H*Me), 4.80 [dd, 1 H, $^2J_{HH}$ = 15.2, $^2J_{PH}$ = 9.8, H(28)], 6.42 [dd, 1 H, $^3J_{HH}$ = 8.6, $^4J_{PH}$ = 5.6, H(2)], 7.01 [d, 1 H, $^3J_{HH}$ = 8.6 Hz, H(3)], 7.30–7.69 (m, 12 H, aromatics) and 7.84–7.90 (m, 2 H, *o*-Ph). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 45.3 (s, 1P).

(*R*)-[(Methylsulfinyl)methyl]diphenylphosphine (+)-I

A solution of complex (R_s,S_c)-**2** (3.0 g) in dichloromethane (50 cm^3) was treated with 1,2-bis(diphenylphosphino)ethane (1.8 g) in the same solvent (20 cm^3) for 15 min. Ethyl acetate was then added intermittently to crystallize out (S_c)-**3**. The filtrate was subjected to silica column chromatography affording (+)-**I** as an air-sensitive colorless viscous oil (0.85 g, 67.5%). α +22.7° (589 nm, *c* 1.0 g per 100 cm^3, CH_2Cl_2). Proton and ^{31}P NMR ($CDCl_3$) spectra identical with those of its racemic counterpart.[6]

Crystallography

A clear plate of dimensions 0.83 × 0.67 × 0.06 mm obtained from a dichloromethane–chloroform–carbon tetrachloride solution of complex (R_s,S_c)-**2** was used. Crystallographic details are given in Table 3. Data were measured on a Siemens P4/PC diffractometer with Mo-Kα radiation (λ = 0.710 73 Å) (graphite monochromator) using ω scans. The structure was solved by direct methods and all the major occupancy non-hydrogen atoms were refined anisotropically. The chlorinated solvent molecules were found to be disordered over eight partial-occupancy sites; the minor occupancy atoms were refined isotropically. The phenyl rings were refined as idealized rigid bodies. The bond lengths within the naphthalene rings were constrained to those values normally found in naphthylene residues.[2–4] All of the hydrogen atoms were placed in calculated positions, 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. Refinement was blocked by full-matrix least squares based on F^2 using absorption-corrected data to give $R1 = 0.083$, $wR2 = 0.188$ for 7597 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 50°$] and 1456 parameters. The S configuration at C(11) in the naphthylamine ligand was used as the internal stereochemical marker. In addition, both the R-factor test ($R^+ = 0.0877$, $R^- = 0.0880$) and the Flack parameter [$x^+ = 0.16(6)$, $x^- = 0.84(6)$] are consistent with the stereochemical assignment.

Computations were carried out on a Pentium PC computer using the SHELXTL PC program system.[16]

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