Synthesis and Structural Investigations of Novel Palladium(II) and Rhodium(I) Complexes Containing Chiral Ligands with a Stereogenic Sulfur Donor, Such As *β*-Amino Sulfoxides and C_2-Symmetric Bis-Sulfoxides[1]

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Received October 13, 1998

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Published on January 26, 1999 on http://pubs.acs.org | doi: 10.1021/om9808460

Two kinds of new optically active chelating ligands bearing a chiral sulfinyl functionality, namely the 3,4-bis-(*p*-tolylsulfinyl)hexanes **4** and the N-mono- and N,N-disubstituted *β*-*p*-tolylsulfinyl ethylamines **5** and **2**, have been synthesized and their coordination chemistry with Pd(II) and Rh(I) metals has been studied in detail. Complexes formed with ligands **4** featured a homocoordination between the two sulfur donors and the metal atom, in solution as well as in the solid state, as demonstrated by X-ray diffraction of *cis*-dichloro[3,4-bis-(*p*-tolylsulfinyl)hexane]palladium(II) *((*3*R*,4*R*,R_S,R_S)-**7**), in which the ligand shows a C_2 symmetry. Complexes formed with ligands **2** and **5** showed a heterocoordination of the metal by the sulfur and the nitrogen donors, as confirmed by X-ray diffraction of *cis*-dichloro[*N*,*N*-dimethyl-2-(*p*-tolylsulfinyl)ethylamine]palladium(II) ((*R*)-**6**). All nine complexes **6**−**11**, displaying a monomeric structure, have been synthesized and completely characterized in the solid state (IR, MS-FAB) as well as in solution (^{1}H and ^{13}C NMR, $[\alpha]^{25}_D$).

Introduction

The synthesis of chiral catalysts carrying as ligands a bidentate phosphine framework or a mixed combination of heteroatoms such as phosphorus, nitrogen, oxygen, and sulfur,[2] with variable features and ratios, has been extensively investigated in recent years. However, only relatively few studies have explored the use of chiral nonracemic sulfoxides as ligands in coordination and organometallic chemistry,[3,4] for example in transition-metal catalysis, although some of the results obtained open interesting new perspectives.[5]

Optically pure sulfoxides are widely used in asymmetric synthesis, mainly as chiral auxiliaries in diastereoselective processes.[6,7] Their efficacy is due to the stereoelectronic differences between the substituents of

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(1) Preliminary results on the molecular structure of *cis*-dichloro-[3,4-bis(*p*-tolylsulfinyl)hexane]palladium(II) ((3*R*,4*R*,R_S,R_S)-**7**) in the crystal form were presented at the XXVII Congresso Nazionale della Associazione Italiana di Cristallografia, Perugia, Italy, Sept 12−14, 1997.

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Publication on Web 01/26/1999

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Published on January 26, 1999 on http://pubs.acs.org | doi: 10.1021/om9808460

the stereogenic sulfur atom, i.e., an electron lone pair, an oxygen atom, and two diverse carbon ligands, able to discriminate the diastereotopic sides of a proximal or remote reaction center.[6d] Moreover, the sulfinyl group is generally configurationally stable, since its pyramidal structure, whose inversion barrier has been estimated in the range of 45 kcal mol^{-1}, is well retained over room temperature. This allowed the isolation of many chiral sulfoxides[8] in nonracemic form.

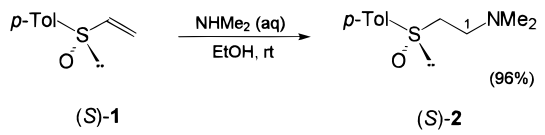
The versatility of sulfinyl-containing molecules in the synthesis of transition-metal complexes is due to the fact that the sulfoxide group can behave as a bidentate ligand. This feature has been analyzed in the light of a valence bond model and HSAB theory, also taking into account steric effects.[3a,5d,e] As a rule, in accordance with the relative hardness of oxygen and sulfur, hard metals give O-coordinated complexes, while soft metals (e.g. the platinum group) orient the coordination of sulfoxides by means of sulfur. However, in a recently reported diruthenium(II) complex,[9] both S and O atoms of the dimethyl sulfoxide ligand have been found to coordinate the metal, as a consequence of a delicate balance between electronic and steric factors.

Interestingly, bis-sulfoxide ligands having the two sulfinyl groups separated by two carbons have been reported to provide stable five-membered chelated complexes featuring homo-S-coordination of the metal.[3d,10]

Regarding their applications, it should be pointed out that chiral complexes of ruthenium(II) and rhodium(I) having sulfoxides as ligands have been used as catalysts in asymmetric hydrogenations. These complexes proved to be able to distinguish the prochiral faces of coordinated olefins, although the enantiomeric excesses were generally modest.[3f,11] A family of cationic complexes of formulas $[PtCl(RR'SO)(diene)]NO_3$[12] and $[PtCl(RR'SO)(diamine)]NO_3$[13] has been studied for their antitumor activity. It was found that their biological activity strongly depends on both the absolute configuration and the leaving-group ability of the chiral sulfoxide.[14]

This study was undertaken with the following purposes: (a) to investigate the effect of the simultaneous presence of a powerful donor atom such as the substituted nitrogen and the flexible bidentate sulfinyl function on the structure and stability of the resulting complexes and (b) to synthesize new chiral bis-sulfoxide ligands having a C_2 symmetry and the corresponding metal complexes which might be used efficiently in catalytic asymmetric synthesis. In fact, it is known that the presence of a C_2 symmetry axis diminishes the number of competing diastereomeric transition states,[15] often resulting in an improvement of the stereoselectivity of the corresponding asymmetric reactions.

Scheme 1



(*S*)-**1** (*S*)-**2**

To this end we decided to synthesize some chiral β-aminosulfoxides[16] such as **2** and **5** and C_2-symmetric bis-sulfoxides **4**, to investigate their coordination chemistry toward two transition metals in low oxidation states, i.e., palladium(II) and rhodium(I), and finally to obtain structural information on such species in both solution and the solid state.

As far as we are aware, only one paper has been published, by Shibasaki[17] and co-workers, describing the synthesis of a Pd(II) complex containing a C_2-symmetric chiral bis-sulfoxide as a bidentate ligand having two sulfur-donor atoms.

Results and Discussion

Synthesis of the Ligands. *N*,*N*-Dimethyl-2-(*p*-tolylsulfinyl)ethylamine ((*S*)-**2**) was prepared in high yield (96%) by Michael addition[16,18] (Scheme 1) of dimethylamine, in aqueous solution, to *p*-tolyl vinyl sulfoxide ((*S*)-**1**) dissolved in ethanol, at room temperature.

The three chiral diastereomers (3*S*,4*S*)-, (3*R*/*S*,4*S*/*R*)-, and (3*R*,4*R*)-bis[(*S*)-*p*-tolylsulfinyl]hexane (**4**) were obtained in moderate yield (51%; Scheme 2) by copper-promoted oxidative coupling[19] of the lithium derivative of *n*-propyl *p*-tolyl sulfoxide ((*S*)-**3**), as a 1.4:1.7:1.0 mixture easily separable by flash chromatography (FC). The fourth diastereomer was not detected in the reaction mixture.

Finally, *N*-(4-methoxyphenyl)-1-phenyl-2-(*p*-tolylsulfinyl)ethylamine ((1*S*,R_S)-**5**) was synthesized in good yield (88%) and stereoselectivity (85% diastereomeric excess (de)) by condensing the lithium derivative of (*R*)-methyl *p*-tolyl sulfoxide on benzylidene-*N*-(4-methoxyphenyl)aniline according to an improvement[20] of a published method[21] (Scheme 3).

All these ligands gave satisfactory elemental analyses and were completely characterized by NMR and IR spectroscopy, MS (FAB), and $[\alpha]^{25}_D$ determinations. ^1H

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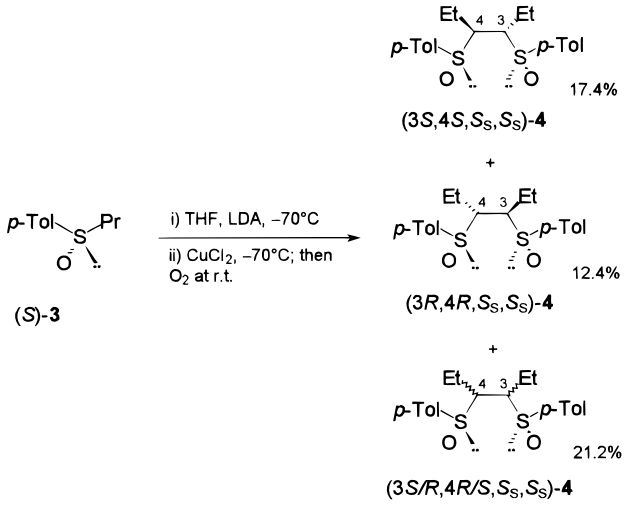
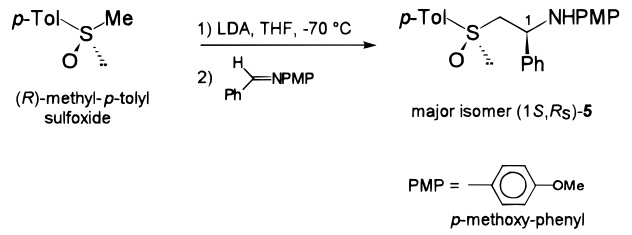
Scheme 2



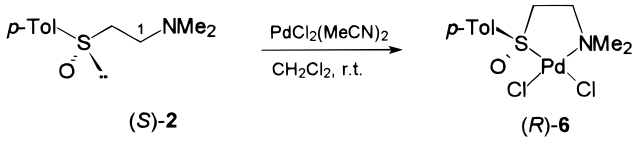
Scheme 3



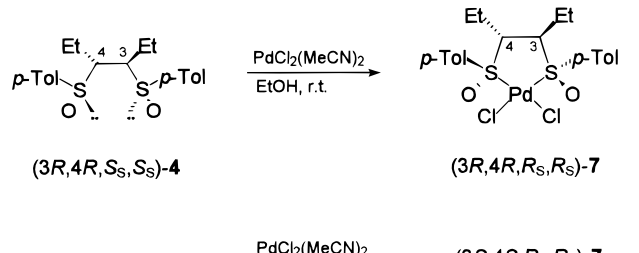
and ^{13}C NMR spectra fully agreed with proposed structures, and in the case of derivatives **4**, they each corresponded to a single diastereomer. The most noteworthy feature of the NMR spectra of bis-sulfoxides (3*S*,4*S*,S_S,S_S)-**4** and (3*R*,4*R*,S_S,S_S)-**4** was the presence of only one set of signals for the homotopic tolyl, ethyl, and SOCH groups, suggesting that these molecules should have C_2 symmetry. In contrast, the spectrum of (3*R*/*S*,4*S*/*R*,S_S,S_S)-**4** showed two different sets of signals, in accordance with the stereochemistry proposed in Scheme 2. The absolute configuration of the carbon atoms C-3 and C-4 of the latter ligand was not assigned, while in the case of the ligand (3*R*,4*R*,S_S,S_S)-**4**, the absolute configuration was assigned on the basis of the X-ray crystallographic data of the corresponding palladium complex (3*R*,4*R*,R_S,R_S)-**7** (see below). The main IR frequencies associated with the more characteristic functional groups (ν(S−O) and ν(N−H)) of the uncoordinated molecules **2**, **4**, and **5** are listed in the Experimental Section. As a general remark, we must emphasize that several vibrational modes are coupled, giving rise to spectra of great complexity[4b,22] with ν(S−O) centered at ca. 1010−1135 cm^{-1}, δ(S−C) at ca. 680 cm^{-1}, and δ(S−O) at ca. 390 cm^{-1}.

Synthesis of the Complexes. Reaction of (*S*)-**2** with bis(acetonitrile)dichloropalladium(II) in dichloromethane (Scheme 4) afforded the complex (*R*)-**6**[23] upon displacement of both CH_3CN ligands from the palladium environment. Analogously, the reaction between the three diastereomers of **4** and bis(acetonitrile)dichloropalladium(II), carried out in ethanol solution, gave the three optically active complexes (3*R*,4*R*,R_S,R_S)-**7**, (3*S*,4*S*,R_S,R_S)-**7**, and (3*S*/*R*,4*R*/*S*,R_S,R_S)-**7** as yellow precipitates (Scheme 5).

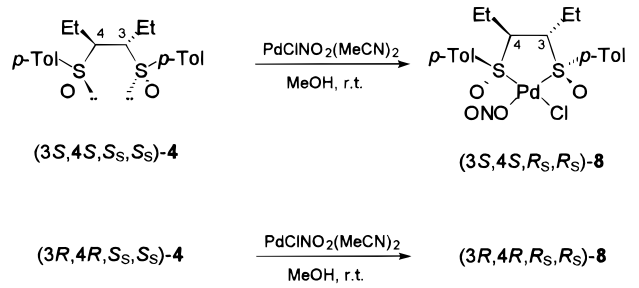
Scheme 4



Scheme 5



Scheme 6



Displacement of both CH_3CN molecules was also observed when the ligand (3*S*,4*S*,S_S,S_S)-**4** or (3*R*,4*R*,S_S,S_S)-**4** and bis(acetonitrile)chloronitropalladium(II) were reacted, providing the derivatives (3*S*,4*S*,R_S,R_S)-**8** and (3*R*,4*R*,R_S,R_S)-**8**, respectively (Scheme 6). In contrast, when the diastereomer (3*S*/*R*,4*R*/*S*,S_S,S_S)-**4** was used as starting material, we did not observe formation of any complex. In this case, only reduction of the Pd(II) derivative to metallic Pd occurred. Analogous reduction was observed when the donors (*S*)-**2** and (1*S*,R_S)-**5** were reacted with bis(acetonitrile)chloronitropalladium(II).

On the other hand, (1*S*,R_S)-**5** was able to displace CH_3CN ligands from bis(acetonitrile)dichloropalladium(II), giving the neutral complex (1*S*,S_S)-**9**, and also to coordinate the (1,5-cyclooctadiene)rhodium(I) cation, yielding the chelate ionic derivative (1*S*,S_S)-**10** (Scheme 7). The analogous rhodium(I) derivative (3*S*/*R*,4*R*/*S*,R_S,R_S)-**11** was synthesized by using the diastereomer (3*S*/*R*,4*R*/*S*,S_S,S_S)-**4** (Scheme 8).

The most important IR data of the free donors and their corresponding complexes are listed in the Experimental Section. In the IR spectra of all palladium(II) and rhodium(I) 1,5-cyclooctadiene complexes the ν(S−O) band is at higher frequencies than in the free

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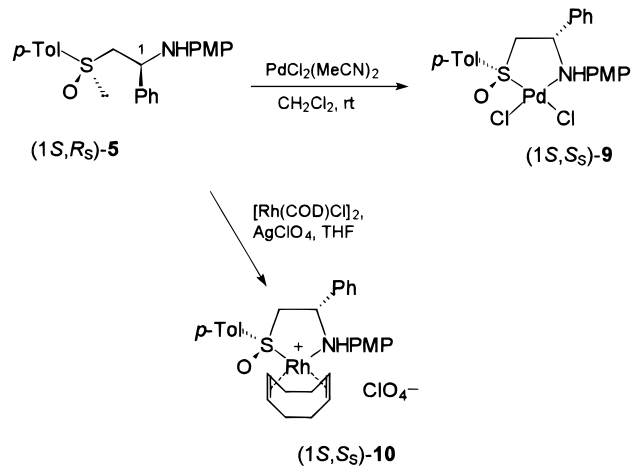
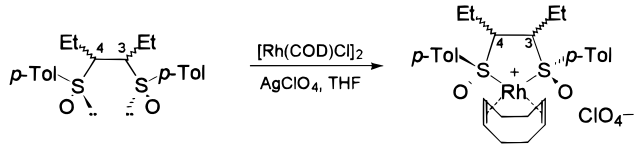
Scheme 7



(1*S*,R_S)-**5** (1*S*,S_S)-**9** (1*S*,S_S)-**10**

Scheme 8



(3*S*/*R*,4*R*/*S*,S_S,S_S)-**4** (3*S*/*R*,4*R*/*S*,R_S,R_S)-**11**

ligands.[4b,22] According to a simple diagnostic method for the determination of the coordination mode of sulfoxides[4b] and in light of the HSAB theory, we suggest S-complexation not only in palladium but also in rhodium derivatives. This is also confirmed by the presence of several weak to medium absorption bands, in the 270−230 cm^{-1} region of the palladium complexes, assignable on the basis of previous reports to Pd−S stretching vibrations. The rhodium(I) derivatives are ionic not only in solution but also in the solid state: in fact, in the IR spectra of **10** and **11** we found $\nu(ClO_4)$ as a strong broad band at ca. 1100 cm^{-1} which is typical of tetrahedral ionic ClO_4^- groups.[24] In the far-IR spectrum of (1*S*,S_S)-**10** the ν(Rh−C) stretching vibration appears as a doublet at ca. 495 cm^{-1} due to nonequivalence of the two Rh−C bonds caused by two different groups in trans positions,[25] whereas the ν(Rh−C) absorption in the derivative (3*S*/*R*,4*R*/*S*,R_S,R_S)-**11**, which is characterized by the presence of two equivalent S-donor groups in the square-planar rhodium environment, appears as a single strong broad absorption at ca. 490 cm^{-1}.

The ^1H and ^{13}C NMR spectra of the chiral ligands and their derivatives **1**−**11** have been recorded in deuterated chloroform or DMSO-d_6. The choice of the solvent was dictated by the solubility of the compounds. In the ^1H NMR spectra of complexes **6**−**11**, with the exception of the signals due to CH_2CH_3 groups in derivatives **7** and **8**, all the signals have been found shifted to lower field upon complexation. Deshielding is attenuated at positions remote from the metal. The $\Delta\delta$ value observed for the chemical shifts is likely due to a σ-charge donation from sulfur−sulfur or sulfur−nitrogen donors to palladium(II) or rhodium(I) acceptors and is clear evidence of the formation of the complexes. As previously indicated,[4b] the α-protons can be used as probes for the coordination mode, in terms of variations of the deshielding level and methylene proton nonequivalence. In fact, *S*-bonding deshields α-protons from ca. 0.20 ppm in (3*S*/*R*,4*R*/*S*,R_S,R_S)-**11** to ca. 1.0 ppm in (*R*)-**6** and at the same time, in derivatives such as (1*S*,S_S)-**9** and (1*S*,S_S)-**10**, increases the methylene proton nonequivalence. The $\Delta\delta$ value is greater in derivatives of palladium than in those of rhodium(I), suggesting a stronger bonding interaction in the former. The $\Delta\delta$ value is also slightly greater in dichloropalladium(II) complexes than in nitrochloropalladium ones. The methylene proton chemical shift seems to be independent of the presence of a NO_2 or a Cl group in a trans position. Analogously, N-bonding gives rise to a remarkable deshielding of groups directly attached to the nitrogen atom. In the complex **6** the methyl groups of the aminic function move up to lower fields with $\Delta\delta$ of ca. 0.7−0.8 ppm, along with the α-amino methylene protons. In the same way, the aminic proton in the complexes **9** and **10** moves up to lower fields upon complexation, with a $\Delta\delta$ value up to ca. 3 ppm. Differently from the latter complexes, the α-amino methyne proton shows lower values of $\Delta\delta$, in the range of ca. 0.05 ppm, due to the presence of the phenyl group.

The positive fast atom bombardment (FAB^+) mass spectrometric investigations of the sulfoxide donors (**2**, **4**, and **5**) and their palladium(II) (**6**−**9**) and rhodium(I) (**10** and **11**) complexes (some selected data are reported in the Experimental Section) gave valuable information on the stability and structural properties of these compounds. *m*-Nitrobenzyl alcohol was always used as a matrix for recording the positive-ion mass spectra.

The predominant pathway for the ligand ion fragmentation is the dissociation or the complete loss of the $[p\text{-TolSO}]^+$ group. In the case of compound **2** also a fragment corresponding to $[NHMe_2]^+$ has been identified. The protonated molecular ion is also present in all the spectra.

In the FAB spectra of the palladium complexes **6**−**9** the fragment ions containing palladium and chloride atoms are identified by the presence of the characteristic clusters of isotopic peaks, corresponding to the relative abundance of palladium and chlorine isotopes. It can be immediately noted that in all the spectra of palladium complexes the relative abundance of the protonated molecular ions is very small or totally absent and that the highest mass ion originates from the loss of the chloride (derivatives **6**, **7**, and **9**) or of NO_2 (derivatives **8**) from the parent molecular ion. The fact that when Cl and NO_2 are simultaneously coordinated to Pd loss of the NO_2 group always occurred likely means that the Pd−Cl bond is stronger than the Pd−ONO one. Loss of both chloride groups is observed only in the spectrum of compound **9**.

The results related to the decomposition behavior of the free sulfoxide ligands provide a basis for interpreting their neutral palladium and ionic rhodium complexes: in fact, the decomposition of the metal derivatives goes also under a fragmentation route in which the parent molecular ion sequentially loses the sulfoxide ligands or its fragments. It should be noted that there are not significant differences in the FAB-MS spectra of the diastereomeric compounds **4** and also of their derivative palladium complexes **7**.

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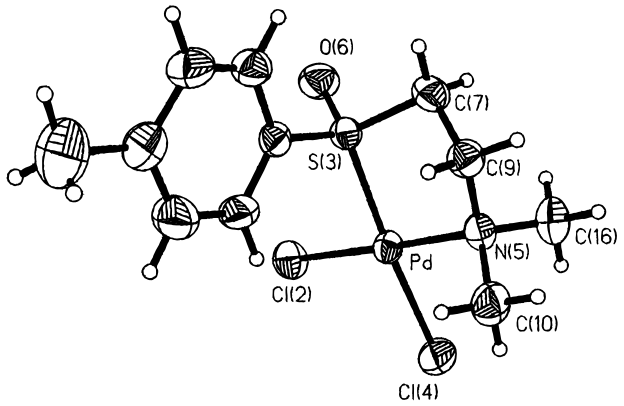

Figure 1.

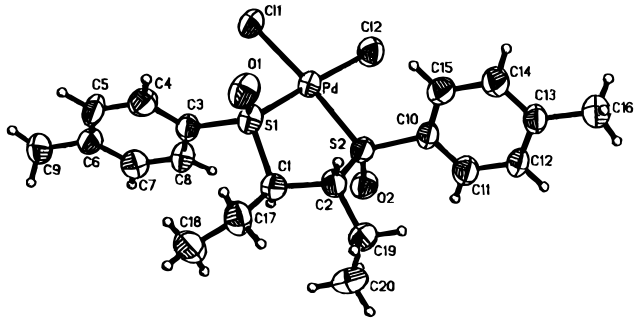

Figure 2.

In general when FAB is used in the analysis of ionic analytes of the form $[A]^+[B]^-$, the intact cation $[A]^+$ and possibly its fragment ions will dominate the positive-ion mass spectrum. In the FAB^+-MS analysis of our ionic rhodium(I) complexes (**10** and **11**) the intact cation is the major fragment ion and, with the exception of the protonated ligand molecule, the other diagnostic fragments are generally very poor. In some cases in the high-mass region of the ligands and their complexes there are also few characteristic peaks obtained by interaction with the *m*-nitrobenzyl alcohol matrix.

The optical rotation measurements ($[\alpha]^{25}_D$) showed a general trend (with the exception of the cationic rhodium(I) complex **10**), in which the free ligands and their corresponding complexes exhibit a different sign of the optical rotation value: that is, if the sign of $[\alpha]^{25}_D$ in the ligand is negative, the corresponding complex shows a positive optical rotation value, in the same solvent. The concentrations of the samples used for the analyses of the complexes range from 0.09 to 0.38 g/100 mL, due mainly to the generally poor solubility showed by the complexes.

The crystal structures of *cis*-dichloro[*N*,*N*-dimethyl-2-(*p*-tolylsulfinyl)ethylamine]palladium(II) ((*R*)-**6**) and *cis*-dichloro[3,4-bis-(*p*-tolylsulfinyl)hexane]palladium-(II) ((3*R*,4*R*,R_S,R_S)-**7**) are shown in Figures 1 and 2, respectively, together with the numbering scheme. Selected bond distances and angles are reported in Table 1.

In both complexes under examination, the sulfoxide ligands coordinate the Pd atom in a bidentate fashion, giving rise to slightly distorted square-planar adducts. The maximum deviations from the least-squares planes are −0.074(2) Å for N(5) in the derivative (*R*)-**6** and 0.073(3) Å for the S(3) in the derivative (3*R*,4*R*,R_S,R_S)-**7**. The chelate ring of (3*R*,4*R*,R_S,R_S)-**7** exhibits a C_2 pseudosymmetry axis which passes through the Pd atom and the midpoint of the C(1)−C(2) bond. In the adduct (*R*)-**6** this axis is clearly missing, due to the intrinsically asymmetric ligand. The interaction between the Pd atom and the sulfinyl groups occurs through the S atoms in both adducts, in accord with HSAB theory. This observation is, in any case, of some interest due to the scarcity of data about the Pd adducts with sulfinyl-bearing ligands. In their extensive review about metal−sulfoxide complexes[26] Calligaris and Carugo reported only 8 X-ray structures (against a body of 76 structures for Pt) of DMSO-like complexes with Pd (in addition, 16 independent structures have been found in the April 1997 version of the CSD[27] and two new α-sulfinyl−palladium complexes in 1998 have been reported by Leung et al.[28]). The occurrence of interaction through the sulfur atom in (3*R*,4*R*,R_S,R_S)-**7** and (*R*)-**6**, analogously to DMSO-like Pt complexes, confirms the prediction based on the HSAB theory, even if the different hardness of the ligand cannot be in general the only explanation when describing the palladium−sulfinyl interaction.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compounds (*R*)-6 and (3*R*,4*R*,R_S,R_S)-7

(*R*)-**6**		(3*R*,4*R*,R_S,R_S)-**7**	
Pd(1)−Cl(2)	2.299(1)	Pd(1)−Cl(1)	2.326(2)
Pd(1)−Cl(4)	2.315(2)	Pd(1)−Cl(2)	2.320(2)
Pd(1)−S(3)	2.213(1)	Pd(1)−S(1)	2.257(2)
Pd(1)−N(5)	2.105(2)	Pd(1)−S(2)	2.252(2)
S(3)−O(6)	1.458(5)	S(1)−O(1)	1.482(5)
S(3)−C(7)	1.783(6)	S(2)−O(2)	1.482(5)
S(3)−C(8)	1.780(6)	S(1)−C(1)	1.845(7)
N(5)−C(9)	1.494(7)	S(1)−C(3)	1.789(6)
N(5)−C(10)	1.483(8)	S(2)−C(2)	1.845(7)
N(5)−C(16)	1.493(8)	S(2)−C(10)	1.780(6)
S(3)−Pd(1)−N(5)	86.9(1)	S(1)−Pd(1)−S(2)	87.02(6)
S(3)−Pd(1)−Cl(2)	89.97(6)	S(1)−Pd(1)−Cl(1)	89.73(7)
N(5)−Pd(1)−Cl(2)	175.3(1)	S(2)−Pd(1)−Cl(1)	174.42(8)
S(3)−Pd(1)−Cl(4)	175.83(7)	S(1)−Pd(1)−Cl(2)	176.63(7)
N(5)−Pd(1)−Cl(4)	91.5(1)	S(2)−Pd(1)−Cl(2)	90.37(7)
Cl(2)−Pd(1)−Cl(4)	91.84(7)	Cl(2)−Pd(1)−Cl(1)	93.04(7)
Pd(1)−S(3)−O(6)	123.7(2)	Pd(1)−S(1)−O(1)	113.7(2)
Pd(1)−N(5)−C(9)	109.5(3)	Pd(1)−S(2)−O(2)	113.3(2)
Pd(1)−N(5)−C(10)	110.0(4)	Pd(1)−S(1)−C(1)	105.4(2)
Pd(1)−S(3)−C(7)	99.7(2)	Pd(1)−S(1)−C(3)	114.6(2)
Pd(1)−S(3)−C(8)	110.2(2)	Pd(1)−S(2)−C(2)	105.4(2)
Pd(1)−N(5)−C(16)	110.4(4)	Pd(1)−S(2)−C(10)	116.9(2)

Bond lengths and angles well agree with data reported in the literature for similar compounds.[29] The Pd−S(=O) bond length shows the usual strengthening with respect to a Pd−S bond where S is not oxidized. This effect has been described in terms of π back-bonding from the metal atom to sulfoxide orbitals having a marked S−O antibonding character, in agreement with the observed lengthening of the S−O bond with respect to the free DMSO.[26]

The Pd−S bond lengths in (3*R*,4*R*,R_S,R_S)-**7** are significantly longer than the Pd−S ones in (*R*)-**6**. This effect

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has already been noticed in platinum−sulfinyl adducts,[26] and it has been ascribed to a π cis influence of the ligand on the Pt−S bond. It has been described that sulfoxide ligands have the greatest effect on a vicinal Pd−S bond, whereas ammonia ligands have the smallest effect,[30] in agreement with our observations. In the adduct (*R*)-**6** the possibility of a trans effect, due to the different nature of the ligand atoms, was also taken into account. However, only a small difference was found between the two Pd−Cl bond lengths, which is not significant in order to establish the real occurrence of such an effect. The same general conclusions were reached from Calligaris and Carugo[26] on the basis of a statistical analysis.

The different natures of the ligands seem to play a key role in the geometry of the chelate ring, as indicated from the analysis of the pseudorotation parameters.[31,32] The two adducts exhibit different extents of the total puckering of the chelate ring, as indicated from the pseudoration amplitude τ_m, which is 54.1(4)° in (*R*)-**6** against a value of 57.1(4)° in (3*R*,4*R*,R_S,R_S)-**7**. The effect of the different ligand nature is also evident in the conformation assumed by the chelate ring.[33] In (3*R*,4*R*,R_S,R_S)-**7** the chelate ring assumes an almost ideal twisted conformation, which can be described as a linear combination of 92% of the twisted form and only 8% of the envelope form.[33] The situation is rather different in (*R*)-**6**, where the conformation appears to be an almost equally populated combination of twisted (44%) and envelope (56%) ring conformations. Moreover, comparison of S−O groups inside the two ligands shows that in (3*R*,4*R*,R_S,R_S)-**7** the S−O bonds can both be described as axial, whereas in (*R*)-**6** the S−O bond is in a borderline situation between a bisecting position and an equatorial one. The same situation has been observed for both N−C bonds. The differences on the arrangement of the chelate ring are obviously due to the differences in the two ligands, i.e. the substitution of one sulfinyl group with a (dimethylamino)ethyl group and the presence of ethyl substituents bound to the chiral carbons in the bis-sulfinyl complex. Our opinion is that the presence of equatorial substituents bound to chiral carbons of (3*R*,4*R*,R_S,R_S)-**7** in the chelate ring is the most important factor, even if, on the basis of data reported in the literature, we could not make any clear-cut distinction.

We have examined the nine structures[3d,5g,34−38] found in the CSD[27] that have a five-membered chelate ring involving Pt or Pd atoms and contain at least one sulfinyl group. We have drawn qualitative conclusions taking into account the effects due to (a) different metal atoms, (b) substitution on the sulfinyl group, (c) the nature of the group bound to S=O, and (d) substituents bound to the bridging carbons of the ligand. The percentage of the twisted (or envelope) form seems to be independent of the substitution of one sulfinyl group with a different heteroatomic group. Nonetheless, when a diphenylphosphino group substitutes a sulfinyl group, we have observed the greater twisted form percentage. The different nature of the metal may have a certain influence on the overall geometry: the Pd adducts show in general a greater twisted form percentage with respect to the Pt ones. The configuration of chiral sulfoxide also seems to play an interesting role, favoring a twisted conformation when the S=O bonds are arranged trans to each other. The effects due to substituents bound to the bridging ethyl groups are ambiguous: they seem not to play a relevant role in the overall conformation of the ring, as shown in the very similar adducts[36,37] dichloro((*S*-methyl-L-cysteine) sulfoxide)−M(II) hydrate (M = Pt, Pd), which are 52% twisted when M = Pd but only 5% twisted when M = Pt. In these compounds the intermolecular interactions and the packing forces likely play a greater role in the chelate ring conformation. Nonetheless, the presence of equatorial substituents seems to influence the geometry of the S=O group, favoring the axial orientation instead of the most commonly adopted equatorial one. Comparison of the structure of (3*R*,4*R*,R_S,R_S)-**7** with that of *cis*-dichloro[*rac*-1,2-bis(phenylsulfinyl)ethane]platinum(II)[3d] seems to reinforce our view. In fact, in (3*R*,4*R*,R_S,R_S)-**7** the two S=O bonds adopt a marked axial orientation, with respect to the platinum(II) complex, and in general (3*R*,4*R*,R_S,R_S)-**7** is the only compound which shows the presence of two axially oriented S=O bonds.

Conclusions

We have reported the synthesis of novel chiral nonracemic sulfinyl-containing complexes of palladium and rhodium starting from the optically active free ligands with high diastereomeric purity. A full characterization of the resulting complexes has been accomplished by physical measurements and X-ray diffraction. The spectroscopic and analytical investigations in both the solid state and solution suggest that our palladium(II) and rhodium(I) complexes are sufficiently stable to allow a full characterization. Studies are in progress to evaluate the possible applications of these complexes as catalysts in asymmetric synthesis.

Experimental Section

General Comments. Palladium(II) chloride, bis(acetonitrile)dichloropalladium(II), and bis(acetonitrile)chloronitropalladium(II) were purchased from Aldrich (Milwaukee) and used as received. Solvent evaporations were always carried out under vacuum by using a rotavaporator. The samples for microanalysis were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). All syntheses were carried out under a nitrogen atmosphere. Hydrocarbon solvents were dried by distillation from sodium−potassium; dichloromethane was distilled from calcium hydride and tetrahydrofuran from sodium and benzophenone. All solvents were degassed with dry nitrogen prior to use.

Elemental analyses (C,H,N,S) were performed in-house with a Carlo-Erba Model 1106 instrument. IR spectra were recorded

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from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^1H and ^{13}C NMR spectra were recorded on a VXR-300 Varian instrument and on Bruker ARX 400, AC250L, or AC 200 spectrometers operating at room temperature (respectively at 400, 300, 250, and 200 MHz for ^1H and 100, 75, 62.8, and 50 MHz for ^{13}C). The chemical shifts (δ) are reported in parts per million (ppm) from $SiMe_4$ (^1H and ^{13}C, calibration by internal deuterium solvent lock). Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; multiplet, m. Optical rotations were measured in the specified solvents (concentrations *c* are reported in g/100 mL) in a 1 dm cell at 25 °C, on a W. Kernchen Propol polarimeter. FAB mass spectra were obtained on a Finnigan-MAT TSQ70 triple-stage quadrupole instrument equipped with an Ion Tech (Teddington, U.K.) atom gun using Xe as bombarding gas. The emission current was typically set at 2 mA with an accelerating voltage of 8 keV. For all the experiments the source was kept at room temperature, using CsI for mass calibration. Samples were directly dissolved in the matrix *m*-nitrobenzyl alcohol. Melting points are uncorrected and were taken on an IA 8100 Electrothermal instrument and on a capillary apparatus.

Preparation of Chiral Nonracemic Ligands. *N*,*N*-Dimethyl-2-(*p*-tolylsulfinyl)ethylamine ((*S*)-2). The ligand (*S*)-**2** (96% yield) was obtained according to published methods:[18] mp (*n*-pentane) 39−40 °C; $[\alpha]^{25}_D$ −193° (*c* 1.48, DMSO-d_6); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 6H, N−CH_3), 2.40 (s, 3H, Ar−CH_3), 2.47−2.53 (m, 1H, CH_2), 2.79−2.86 (m, 1H, CH_2), 2.88−2.99 (m, 2H, CH_2), 7.31 (d, 2H, CH_{arom}, ^3J = 8 Hz), 7.53 (d, 2H, CH_{arom}, ^3J = 8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ 21.43 (Ar−*C*H_3), 45.32 (N−*C*H_3), 52.36, 55.86 (*C*H_2), 124.14, 129.94, 140.79, 141.49 (C_{arom}); MS (FAB) *m*/*z* 212 ([M + H]$^+$, 100%); IR (cm^{-1}) 1043 s br [ν(S−O)]. Anal. Calcd for $C_{11}H_{17}NOS$: C, 62.5; H, 8.1; N, 6.6; S, 15.2. Found: 62.7; H, 8.1; N, 6.5; S, 15.0.

3,4-Bis(*p*-tolylsulfinyl)hexane (4). A stirred solution containing 4.4 mL (6.6 mmol) of a 1.5 M cyclohexane solution of lithium diisopropylamide and 20 mL of dry THF, cooled to −70 °C, was treated with a solution of *n*-propyl *p*-tolyl sulfoxide[39]((*S*)-**3**; 1 g, 5.5 mmol) dissolved in 10 mL of dry THF, added drop by drop under nitrogen. After 5 min to the mixture was added 0.96 g (7.14 mmol) of dry cupric chloride powder at the same temperature, and after 20 min this mixture was warmed to room temperature. Then a dried oxygen stream was bubbled into the flask, in place of nitrogen, and the reaction was run at room temperature until the disappearance of starting material (ca. 45 min) as revealed by TLC analysis (*n*-hexane/ethyl acetate 1/1). A solution of 1 M HCl was added afterwards to the reaction mixture and the aqueous layer extracted with chloroform (3 × 5 mL). The collected organic layers were washed with dilute aqueous ammonia solution and brine and dried over anhydrous sodium sulfate. The crude product was purified by flash chromatography (*n*-hexane/ethyl acetate from 55/45 to 10/90), giving 1.014 g (51% overall yield) of product **4** as a 1.4:1.7:1.0 mixture of the following diastereomers. (3*S*,4*S*,S_S,S_S)-**4**: mp (*i*-Pr_2O) 116−117 °C; $[\alpha]^{25}_D$ −77.6° (*c* 0.33, $CHCl_3$); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.12 (t, 6H, CH_2CH_3, ^3J = 7.3 Hz), 1.94−2.06 (m, 2H, CH_2CH$_3$), 2.19−2.29 (m, 2H, CH_2CH$_3$), 2.42 (s, 6H, Ar−CH_3), 2.56 (dd, 2H, SOC*H*, ^3J = 10.2 and 2.8 Hz), 7.04 (d, 4H, CH_{arom}, ^3J = 8 Hz), 7.12 (d, 4H, CH_{arom}, ^3J = 8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ 12.33 (*C*1, *C*6), 19.59 (*C*2, *C*5), 21.23 (Ar−*C*H_3), 63.24 (*C*3, *C*4), 123.92, 129.53, 138.26, 140.56 (C_{arom}); MS (FAB): *m*/*z* 363 ([M + H]$^+$, 63%), 223 ([M + H − C_7H_8OS]$^+$, 100%); IR (cm^{-1}) 1082 s, 1055 s, 1016 s [ν(S−O)]. Anal. Calcd for $C_{20}H_{26}O_2S_2$: C, 66.3; H, 7.2; S, 17.7. Found: C, 66.6; H, 7.5; S, 17.6. (3*R*/*S*,4*S*/*R*,S_S,S_S)-**4**: oil; $[\alpha]^{25}_D$ −242.7° (*c* 1.56, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.47 (t, 3H, CH_2CH_3, ^3J = 7.4 Hz), 1.03 (t, 3H, CH_2CH_3, ^3J = 7.4 Hz), 1.49−1.58 (m, 1H, CH_2CH$_3$), 1.70−1.77 (m, 1H, CH_2CH$_3$), 2.08−2.18 (m, 1H, CH_2CH$_3$), 2.22−2.29 (m, 1H, CH_2CH$_3$), 2.40 (s, 3H, Ar−CH_3), 2.41 (s, 3H, Ar−CH_3), 2.72−2.76 (m, 1H, SOC*H*), 3.03−3.07 (m, 1H, SOC*H*), 7.30−7.33 (m, 4H, CH_{arom}), 7.53 (d, 2H, CH_{arom}, ^3J = 8 Hz), 7.69 (d, 2H, CH_{arom}, ^3J = 8 Hz);$^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ 10.86, 13.38 (*C*1, *C*6), 14.57, 19.25 (*C*2, *C*5), 21.15, 21.19 (Ar−*C*H_3), 62.00, 67.60 (*C*3, *C*4), 124.29, 124.55, 129.37, 129.83, 139.36, 140.09, 140.40, 141.68 (C_{arom}); MS (FAB): *m*/*z* 363 ([M + H]$^+$, 20%), 223 ([M + H − C_7H_8OS]$^+$, 60%). IR (cm^{-1}) 1084 s, 1043 s, 1015 s [ν(S−O)]. Anal. Calcd for $C_{20}H_{26}O_2S_2$: C, 66.3; H, 7.2; S, 17.7. Found: C, 66.4; H, 7.3; S, 17.8. (3*R*,4*R*,S_S,S_S)-**4**: mp (*i*-Pr_2O) 165−169 °C (subl); $[\alpha]^{25}_D$ −134.5° (*c* 0.22, $CHCl_3$); ^1H NMR ($CDCl_3$, 250 MHz) δ 0.91 (t, 6H, CH_2CH_3, ^3J = 7.3 Hz), 1.25−1.37 (m, 2H, CH_2CH$_3$), 1.78−1.90 (m, 2H, CH_2CH$_3$), 2.43 (s, 6H, Ar−CH_3), 3.04 (t, 2H, SOC*H*, ^3J = 5.6 Hz), 7.25 (d, 4H, CH_{arom}, ^3J = 8 Hz), 7.38 (d, 4H, CH_{arom}, ^3J = 8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ 12.99 (*C*1, *C*6), 17.43 (*C*2, *C*5), 21.29 (Ar−*C*H_3), 64.64 (*C*3, *C*4), 124.73, 129.64, 138.28, 141.68 (C_{arom}); MS (FAB) *m*/*z* 363 ([M + H]$^+$, 40%), 223 ([M + H − C_7H_8OS]$^+$, 63%); IR (cm^{-1}) 1079 s, 1050 s, 1035 s [ν(S−O)]. Anal. Calcd for $C_{20}H_{26}O_2S_2$: C, 66.3; H, 7.2; S, 17.7. Found: C, 66.5; H, 7.3; S, 17.4.

***N*-(4-Methoxyphenyl)-1-phenyl-2-(*p*-tolylsulfinyl)ethylamine ((1*S*,R_S)-5)**. The ligand (1*S*,R_S)-**5** (88% yield, 85% de) was obtained using an improved procedure[20] of a published method:[21] mp (ethyl acetate) 208−209 °C; $[\alpha]^{25}_D$ +166.6° (*c* 0.43, acetone); ^1H NMR ($CDCl_3$, 250 MHz) δ 2.40 (s, 3H, Ar−CH_3), 3.07−3.13 (m, 2H, SOCH_2), 3.69 (s, 3H, Ar−OCH_3), 4.72−4.80 (pseudo-t, 1H, C*H*NH), 4.95 (br signal, 1H, N*H*), 6.50 (d, 2H, CH_{arom}, ^3J = 8.8 Hz), 6.68 (d, 2H, CH_{arom}, ^3J = 8.8 Hz), 7.25−7.35 (m, 7H, CH_{arom}), 7.50 (d, 2H, CH_{arom}, ^3J = 8 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 63 MHz) δ 21.41 (Ar−*C*H_3), 55.62, 55.73 (SO*C*H_2, Ar−O*C*H_3), 63.59 (SOCH_2*C*H), 114.64, 115.91, 124.05, 126.52, 127.79, 128.96, 130.08, 139.79, 140.93, 141.73, 152.79 (C_{arom}); MS (FAB): *m*/*z* 366 ([M + H]$^+$, 56%), 225 ([M + H − C_7H_8OS]$^+$, 100%); IR (cm^{-1}) 3302 w [ν(N−H)], 1025 s, 1010 s [ν(S−O)]. Anal. Calcd for $C_{22}H_{23}NO_2S$: C, 72.3; H, 6.3; N, 3.8; S, 8.8. Found: C, 72.5; H, 6.5; N, 3.7; S, 8.6.

Synthesis of the Complexes. *cis*-Dichloro[*N*,*N*-dimethyl-2-(*p*-tolylsulfinyl)ethylamine]palladium(II) ((*R*)-6). To a stirred dichloromethane suspension (3 mL) of bis(acetonitrile)dichloropalladium(II) (221 mg, 0.853 mmol), at room temperature and under nitrogen, was added dropwise a dichloromethane solution (1.2 mL) of (*S*)-**2** (180 mg, 0.853 mmol). After ca. 15 min (no more substrate was revealed by TLC control) the yellow precipitate was filtered off and washed with diethyl ether to give 290 mg (88% yield) of the analytical sample (*R*)-**6**: mp ($CHCl_3$, diethyl ether) 214−217 °C; $[\alpha]^{25}_D$ +123.2° (*c* 0.37, DMSO-d_6); ^1H NMR ($CDCl_3$, 200 MHz) δ 2.50 (s, 3H, Ar−CH_3), 3.01 (s, 3H, N−CH_3), 3.13 (s, 3H, N−CH_3), 3.4−3.7 (m, 4H, CH_2), 7.50 (d, 2H, CH_{arom}, ^3J = 8 Hz), 8.17 (d, 2H, CH_{arom}, ^3J = 8 Hz); ^1H NMR (DMSO-d_6, 250 MHz) δ 2.48 (s, 3H, Ar−CH_3), 2.89 (s, 3H, N−CH_3), 2.98 (s, 3H, N−CH_3), 3.34 (m, 2H, CH_2), 4.06 (m, 2H, CH_2), 7.57 (d, 2H, CH_{arom}, ^3J = 8 Hz), 8.17 (d, 2H, CH_{arom}, ^3J = 8 Hz); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 63 MHz) δ 21.14 (Ar-*C*H_3), 51.26 (N−*C*H_3), 51.79 (N−*C*H_3), 59.38, 60.92 (*C*H_2), 127.03, 130.22, 135.72, 144.97 (C_{arom}); MS (FAB) *m*/*z* 354 ([M − Cl]$^+$, center of isotopic cluster); IR (cm^{-1}) 1135 s [ν(S−O)], 351 s, 330 s [ν(Pd−Cl)], 264 m, 253 w, 239 m [δ(Cl−Pd−Cl) and ν(Pd−S)]. Anal. Calcd for $C_{11}H_{17}Cl_2NOSPd$: C, 34.0; H, 4.4; N, 3.6; S, 8.2. Found: C, 33.6; H, 4.6; N, 3.6; S, 8.0.

***cis*-Dichloro[3,4-bis(*p*-tolylsulfinyl)hexane]palladium(II) (7).** To a stirred ethanol suspension (3 mL) of bis(acetonitrile)dichloropalladium(II) (38 mg, 0.146 mmol), at room temperature and under nitrogen, was added dropwise an ethanol solution (3 mL) of (3*R*,4*R*,S_S,S_S)-**4** (53 mg, 0.146 mmol). After ca. 15 min (no more substrate was revealed by TLC control) the yellow precipitate was filtered off and washed with diethyl ether to give 59 mg (75% yield) of the analytical

(39) The starting material *n*-propyl *p*-tolyl sulfoxide ((*S*)-**3**) ($[\alpha]^{25}_D$ −213 (*c* 1.1, $CHCl_3$)) has been synthesized by starting from (+)-menthyl *p*-toluenesulfinate according to: Bickart, P.; Carson, F. W.; Jacobus, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869.

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Published on January 26, 1999 on http://pubs.acs.org | doi: 10.1021/om9808460

sample (3*R*,4*R*,R_S,R_S)-**7**: mp ($CHCl_3$) 180−182 °C; $[\alpha]^{25}_D$ +375.8° (*c* 0.13, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.80 (t, 6H, CH_2CH_3, ^3J = 7.5 Hz), 1.70−1.95 (m, 2H, CH_2CH_3), 2.05−2.30 (m, 2H, CH_2CH_3), 2.47 (s, 6H, Ar−CH_3), 3.64 (br signal, 2H, SOC*H*), 7.52 (d, 4H, CH_{arom}, ^3J = 8 Hz), 7.93 (d, 4H, CH_{arom}, ^3J = 8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz) δ 11.94 (*C*1, *C*6), 17.95 (*C*2, *C*5), 21.77 (Ar−CH_3), 72.82 (*C*3, *C*4), 126.20, 130.72, 134.81, 145.58 (C_{arom}); MS (FAB) *m*/*z* 505 ([M − Cl]$^+$, center of isotopic cluster); IR (cm^{-1}) 1142 s, 1120 m [ν(S−O)], 334 s, 325 s [ν(Pd−Cl)], 303 w, 279 m, 253 m [δ(Cl−Pd−Cl) and ν(Pd−S)]. Anal. Calcd for $C_{20}H_{26}Cl_2O_2S_2Pd$: C, 44.5; H, 4.8; S, 11.9. Found: C, 43.7; H, 5.0; S, 11.3. The diastereomeric complexes (3*S*,4*S*,R_S,R_S)-**7** and (3*R*/*S*,4*S*/*R*,R_S,R_S)-**7** have been obtained by a similar procedure, starting respectively from the substrates (3*S*,4*S*,S_S,S_S)-**4** and (3*R*/*S*,4*S*/*R*,S_S,S_S)-**4**. (3*S*,4*S*,-R_S,R_S)-**7** (69% yield): mp ($CHCl_3$, Et_2O) 169−170 °C; $[\alpha]^{25}_D$ +236.4° (*c* 0.11, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.86 (t, 6H, CH_2CH_3, ^3J = 7.3 Hz), 1.30−1.55 (m, 2H, CH_2CH_3), 1.65−1.90 (m, 2H, CH_2CH_3), 2.52 (s, 6H, Ar−CH_3), 3.30 (t, 2H, SOC*H*, ^3J = 4.6 Hz), 7.53 (d, 4H, CH_{arom}, ^3J = 8.2 Hz), 8.11 (d, 4H, CH_{arom}, ^3J = 8.2 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz) δ 11.74 (*C*1, *C*6), 21.36, 21.90 (*C*2, *C*5, and Ar−CH_3), 74.76 (*C*3, *C*4), 127.99, 130.63, 132.50, 146.77 (C_{arom}); MS (FAB) *m*/*z* 505 ([M − Cl]$^+$, center of isotopic cluster); IR (cm^{-1}) 1135 s, 1120 m [ν(S−O)], 318 s [ν(Pd−Cl)], 294 w, 278 m, 247 w, 229 w [δ(Cl−Pd−Cl) and ν(Pd−S)]. Anal. Calcd for $C_{20}H_{26}Cl_2O_2S_2$-Pd: C, 44.5; H, 4.8; S, 11.9. Found: C, 44.1; H, 5.0; S, 11.7. (3*R*/*S*,4*S*/*R*,R_S,R_S)-**7** (52% yield): mp ($CHCl_3$) 183−186 °C dec; $[\alpha]^{25}_D$ +318.9° (*c* 0.18, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.33 (t, 3H, CH_2CH_3, ^3J = 7.4 Hz), 0.96 (t, 3H, CH_2CH_3, ^3J = 7.4 Hz) 1.68−1.76 (m, 1H, CH_2CH_3), 1.82−2.07 (m, 3H, CH_2-CH_3), 2.48 (s, 3H, Ar− CH_3), 2.52 (s, 3H, Ar−CH_3), 3.28−3.31 (m, 1H, SOC*H*), 3.91−3.96 (m, 1H, SOC*H*), 7.46−7.52 (m, 4H, CH_{arom}), 7.94 (d, 2H, CH_{arom}, ^3J = 8.5 Hz), 8.20 (d, 2H, CH_{arom}, ^3J = 8.5 Hz): ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 12.67, 13.11 (*C*1, *C*6), 14.80, 17.03 (*C*2, *C*5), 21.78, 21.90 (Ar−CH_3), 73.57, 77.86 (*C*3, *C*4), 126.26, 128.83, 130.26, 130.67, 131.36, 135.91, 145.59, 146.82 (C_{arom}); MS (FAB) *m*/*z* 505 ([M − Cl]$^+$, center of isotopic cluster); IR (cm^{-1}) 1143 m, 1128 m [ν(S−O)], 337 s, 326 s [ν(Pd−Cl)], 289 w, 250 sh, 247 m [δ(Cl−Pd−Cl) and ν(Pd−S)]. Anal. Calcd for $C_{20}H_{26}Cl_2O_2S_2Pd$: C, 44.5; H, 4.8; S, 11.9. Found: C, 44.6; H, 4.9; S, 11.7.

***cis*-Chloronitro[3,4-bis(*p*-tolylsulfinyl)hexane]palladium(II) (8).** To a stirred methanol solution (3 mL) of bis(acetonitrile)chloronitropalladium(II) (60 mg, 0.22 mmol), at room temperature and under nitrogen, was added (3*S*,4*S*,S_S,-S_S)-**4** (105 mg, 0.29 mmol). After ca. 15 min the orange-red precipitate was filtered off and washed with methanol, to give 72 mg (60% yield) of the analytical sample (3*S*,4*S*,R_S,R_S)-**8**: mp (CH_2Cl_2) 160 °C dec; $[\alpha]^{25}_D$ +53.3°(*c* 0.38, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.86 (t, 6H, CH_2CH_3, ^3J = 7.3 Hz), 1.30−1.55 (m, 2H, CH_2CH_3), 1.70−1.90 (m, 2H, CH_2CH_3), 2.53 (s, 6H, Ar−CH_3), 3.32 (pseudo-t, 2H, SOC*H*), 7.53 (d, 4H, CH_{arom}, ^3J = 8 Hz), 8.11 (d, 4H, CH_{arom}, ^3J = 8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz) δ 11.70, 12.53 (*C*1, *C*6), 19.77, 21.31, 21.46, 21.88 (*C*2, *C*5 and Ar−CH_3), 63.52, 74.69 (*C*3, *C*4), 124.21, 127.94, 129.74, 130.62, 138.54, 140.79, 142.72, 146.77 (C_{arom}); MS (FAB) *m*/*z* 505 ([M − NO_2]$^+$, center of isotopic cluster); IR (cm^{-1}) 1132 m, 1118 m [ν(S−O)], 480 br [ν(Pd−O)], 317 s [ν(Pd−Cl)], 298 sh, 278 m, 248 w, 230 w [δ(Cl−Pd−Cl) and ν(Pd−S)]. Anal. Calcd for $C_{20}H_{26}ClNO_4S_2Pd$: C, 43.6; H, 4.8; N, 2.5; S, 11.6. Found: C, 43.4; H, 4.9; N, 2.3; S, 11.2. The same procedure performed on diastereomer (3*R*,4*R*,S_S,S_S)-**4** gave the diastereomeric complex (3*R*,4*R*,R_S,R_S)-**8** in 50% yield: mp (CH_2Cl_2) 117−122 °C dec; $[\alpha]^{25}_D$ +20.4° (*c* 0.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.82 (t, 6H, CH_2CH_3, ^3J = 7.3 Hz), 1.90 (m, 2H, CH_2CH_3), 2.10 (br, 2H, CH_2CH_3), 2.51 (s, 6H, Ar−CH_3), 3.50 (br, 2H, SOC*H*), 7.51 (d, 4H, CH_{arom},^3J = 8 Hz), 7.94 (d, 4H, CH_{arom}, ^3J = 8 Hz); MS (FAB) *m*/*z* 551 ([M + H]$^+$, center of isotopic cluster); IR (cm^{-1}) 1150 br [ν(S−O)], 350 br [ν(Pd−Cl)], 280 m, 250 w, 246 m [δ(Cl−Pd−Cl) and ν(Pd−S)]. Anal. Calcd for $C_{20}H_{26}ClNO_4S_2Pd$: C, 43.6; H, 4.8; N, 2.5; S, 11.6. Found: C, 43.8; H, 4.9; N, 2.3; S, 11.3.

***cis*-Dichloro[*N*-(4-methoxyphenyl)-1-phenyl-2-(*p*-tolylsulfinyl)ethylamine]palladium(II) ((1*S*,S_S)-9).** To a stirred dichloromethane suspension (3 mL) of bis(acetonitrile)dichloropalladium(II) (29 mg, 0.112 mmol), at room temperature and under nitrogen, was added dropwise a dichloromethane solution (1.2 mL) of (1*S*,R_S)-**5** (41 mg, 0.112 mmol). After ca. 1 h the TLC control revealed that the substrate was completely consumed. The solvent was removed under reduced pressure, and diethyl ether was added until an orange precipitate was formed; the latter was filtered off and washed with diethyl ether to give 42 mg (70% yield) of the analytical sample (1*S*,S_S)-**9**: mp ($CHCl_3$) 199−200 °C; $[\alpha]^{25}_D$ −202.3° (*c* 0.09, acetone); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.34 (s, 3H, Ar−CH_3), 3.40−3.50 (m, 1H, SOCH_2), 3.78 (s, 3H, OCH_3), 4.34 (t, 1H, SOCH_2, ^3J = 13.6 Hz), 4.8 (t, 1H, NC*H*, ^3J = 12.1 Hz), 6.7 (br signal, 2H, CH_{arom}), 7.12−7.28 (m, 9H, CH_{arom}), 8.06 (d, 1H, N*H*, ^3J = 10.4 Hz), 8.28 (d, 2H, CH_{arom}, ^3J = 8 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz) δ 22.10 (Ar−CH_3), 55.85 (OCH_3), 68.66 (CH_2), 69.84 (*C*H), 114.23, 126.39, 127.46, 129.11, 129.48, 130.27, 130.77, 131.3, 134.46, 138.08, 145.13, 158.73 (C_{arom}); MS (FAB): *m*/*z* 470 ([M − Cl_2]$^+$, center of isotopic cluster); IR (cm^{-1}) 1150 br [ν(S−O)], 340 s, 318 s [ν(Pd−Cl)], 290 br, 254 w, 248 w [δ(Cl−Pd−Cl) and ν(Pd−S)]. Anal. Calcd for $C_{22}H_{23}$-Cl_2NO_2SPd: C, 48.7; H, 4.3; N, 2.6; S, 5.9. Found: C, 48.4; H, 4.5; N, 3.0; S, 5.7.

[*N*-(4-Methoxyphenyl)-1-phenyl-2-(*p*-tolylsulfinyl)ethylamine](1,5-cyclooctadiene)rhodium(I) Perchlorate ((1*S*,-S_S)-10). To a stirred THF solution (10 mL) of $[Rh(COD)Cl]_2$ (30 mg, 0.060 mmol) at room temperature, under nitrogen in the dark, was added $AgClO_4 \cdot H_2O$ (27 mg, 0.120 mmol). After ca. 20 min the colorless precipitate (AgCl) was filtered off and washed with THF (3 × 5 mL). The yellow solution was then added to a THF solution of (1*S*,R_S)-**5** (44 mg, 0.120 mmol). The reaction was carried out at room temperature under nitrogen for 24 h. The solvent was removed under reduced pressure, and the residue was washed with diethyl ether to give 65 mg (80% yield) of the analytical sample (1*S*,S_S)-**10**: mp ($CHCl_3$) 216−219 °C; $[\alpha]^{25}_D$ +108.7° (*c* 0.09, acetone); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.5−2.4 (m br, 6H, CH_2−COD), 2.47 (s, 3H, Ar−CH_3), 2.9 (m br, 2H, CH_2−COD), 3.38 (m, 1H, SOCH_2), 3.72 (s, 5H, OCH_3 and C*H*−COD), 4.14 (m, 1H, SOCH_2), 4.70−5.00 (m br, 3H, NC*H* and C*H*−COD), 6.40−7.60 (m br, 10H, N*H* and CH_{arom}), 7.51 (d, 2H, CH_{arom}, ^3J = 8 Hz), 8.11 (d, 2H, CH_{arom}, ^3J = 8 Hz); MS (FAB) *m*/*z* 576 ([$C_{30}H_{35}NO_2SRh$]$^+$, 100%); IR (cm^{-1}) 1115 br, 1069 br [ν(S−O)], 500 m, 490 m [ν(Rh−C)]. Anal. Calcd for $C_{30}H_{35}ClNO_6RhS$: C, 53.3; H, 5.2; N, 2.1; S, 4.7. Found: C, 53.0; H, 5.4; N, 2.2; S, 4.4.

[3,4-Bis(*p*-tolylsulfinyl)hexane](1,5-cyclooctadiene)-rhodium(I) Perchlorate ((3*R*/*S*,4*S*/*R*,R_S,R_S)-11). To a stirred THF solution (10 mL) of $[Rh(COD)Cl]_2$ (100 mg, 0.203 mmol) at room temperature, under nitrogen in the dark, was added $AgClO_4 \cdot H_2O$ (92 mg, 0.406 mmol). After ca. 20 min the colorless precipitate (AgCl) was filtered off and washed with THF (3 × 5 mL). The solution was then added to a THF solution of (3*R*/*S*,4*S*/*R*,S_S,S_S)-**4** (147 mg, 0.406 mmol). The reaction was carried out at room temperature under nitrogen for 20 h. The solvent was removed under reduced pressure and the yellow residue was washed with diethyl ether to give 200 mg (73% yield) of the analytical sample (3*R*/*S*,4*S*/*R*,R_S,R_S)-**11**: mp ($CHCl_3$) 150−151 °C; $[\alpha]^{25}_D$ +17.1° (*c* 0.28, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.78 (t, 3H, CH_2CH_3), 1.04 (t, 3H, CH_2CH_3), 1.50−2.71 (m br, 12H, CH_2CH_3 and CH_2−COD), 2.45 (s, 3H, Ar−CH_3), 2.50 (s, 3H, Ar−CH_3), 2.98 (m, 1H, SOC*H*), 3.20 (m, 1H, SOC*H*), 4.4 (m br, 2H, C*H*−COD), 4.8 (m br, 2H, C*H*−COD), 7.30−7.70 (m, 4H, CH_{arom}), 7.76 (d, 2H, CH_{arom}, ^3J = 8 Hz), 8.03 (d, 2H, CH_{arom}, ^3J = 8 Hz); MS (FAB) *m*/*z* 573 ([$C_{28}H_{38}O_2S_2Rh$]$^+$, 69%); IR (cm^{-1}) 1090 br [ν(S−O)], 515 sh, 491 m [ν(Rh−C)]. Anal. Calcd for $C_{28}H_{38}ClO_6RhS_2$: C, 50.0; H, 5.7; S, 9.5. Found: C, 49.8; H, 5.9; S, 9.3.

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Published on January 26, 1999 on http://pubs.acs.org | doi: 10.1021/om9808460

Table 2. Data Collection Parameters for Compounds (*R*)-6 and (3*R*,4*R*,R_S,R_S)-7

	(*R*)-**6**	(3*R*,4*R*,R_S,R_S)-**7**
formula	$C_{11}H_{17}Cl_2NOSPd$	$C_{20}H_{26}Cl_2O_2S_2Pd$
fw	388.6	539.9
space group	$P2_12_12_1$	$P2_1$
a, Å	8.556(6)	7.558(2)
b, Å	8.638(3)	14.156(3)
c, Å	19.77(6)	10.780(2)
β, deg		91.25(3)
V_c, Å^3	1463.1(7)	1153.1(6)
Z	4	2
D_c, g cm^{-3}	1.764	1.555
μ(Mo Kα), mm^{-1}	1.760	1.230
F(000)	776	548
radiation (monochromated)	Mo Kα	Mo Kα
T of data collecn, K	293	293
scan mode	$\omega/2\theta$	$\omega/2\theta$
scan width, deg	1.2	1.2
scan speed, deg min^{-1} (min, max)	3, 30	3, 30
data collecn range, deg	$4 \le \theta \le 60$	$4 \le \theta \le 60$
hkl ranges	0−12, 0−12, 0−27	0−10, 0−18, −15 to +15
no. of unique rflns measd	1911	3660
no. of obsd rflns ($\|F_o\| \ge 3\sigma(\|F_o\|)$)	1875	1761
refinement	full matrix on $\|F_o\|$	full matrix on $\|F_o\|$
no. of params refined	155	244
R^a	0.037	0.027
$R_w{}^b$	0.039	0.030
S^c (goodness of fit)	1.19	1.17

[a] $R = (\sum||F_o| - k|F_c||)/\sum|F_o|$. [b] $R_w = [(\sum_w(|F_o| - k|F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $S = [(\sum w(|F_o| - k|F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

X-ray Structure Determinations. A summary of the experimental conditions and refinement details for both (*R*)-**6** and (3*R*,4*R*,R_S,R_S)-**7** is reported in Table 2.

***cis*-Dichloro[*N*,*N*-dimethyl-2-(*p*-tolylsulfinyl)ethylamine]palladium(II) ((*R*)-6).** Pale yellow crystals were grown from slow evaporation of a dichloromethane/diethyl ether (1/1) solution. The data were collected on a Huber diffractometer driven by in-house software,[40] using a crystal of approximate dimensions 0.2 × 0.2 × 0.2 mm. The cell parameters and orientation matrix were determined by least-squares refinement of 15 well-centered reflections, in the range $5.0° < 2\theta < 25°$. The crystal system was found to be orthorhombic; the space group was then assigned as $P2_12_12_1$. A total of 1971 reflections were collected with $4° \le 2\theta \le 60°$. The data were then corrected for Lorentz and polarization effects. No decay was observed for (*R*)-**6** (3 standard reflections collected every 97 measurements), and no absorption correction was applied in this case. The data were merged together, sorted, and then purged for systematic absences, giving in the end 1911 independent reflections (1875 observed).

The structure was solved by using the Patterson method, giving the position of the palladium and chlorine atoms. The complete structure was then obtained after several difference Fourier maps followed by refinement. The complete structure was then refined isotropically ($R = 0.074$) and then anisotropically ($R = 0.051$). Hydrogen atoms were introduced by a model ($d = 1.06$ Å) with U_{iso} being 30% greater than the value of the bonded atom. The structure was refined by treating the hydrogen as riding (the hydrogen positions were recalculated after every refinement stage), giving an *R* factor of 0.045. At this stage the inspection of the strongest reflections showed that $|F_o|$ values were systematically weaker than the $|F_c|$ values. This observation led us to introduce and refine an extinction parameter[41] (47(8) cm^{-6} at the end of the refinement); the *R* factor dropped to 0.038, and most important, for the strongest reflections, we did not observe the previous trend any more. Finally, a better weighting scheme was adopted, on the basis of $w\Delta^2$ distribution as a function of both $|F_o|$ and $(\sin\theta)/\lambda$. A robust-resistant weighting scheme based on three-term Chebyshev polynomials[42−44] ($a_1 = 2.09$, $a_2 = -0.337$, $a_3 = 1.24$) was used. The final *R* value was 0.037. The minimum and maximum $\Delta\rho$ values were −0.53 and 0.6 e Å^{-3}, both near the metal atom. No attempt was made to determine the absolute structure of (*R*)-**6**.

***cis*-Dichloro[3,4-bis-(*p*-tolylsulfinyl)hexane]palladium(II) ((3*R*,4*R*,R_S,R_S)-7).** Pale yellow crystals were grown by slow evaporation of a dichloromethane/diethyl ether (1/1) solution. A crystal of approximate dimensions 0.15 × 0.1 × 0.1 was mounted on a Huber diffractometer, as for the (*R*)-**6** structure. The orientation matrix and cell were obtained by following the same procedure as for (*R*)-**6**; the crystal system was found to be monoclinic, and the space group was then identified as $P2_1$. We collected 3791 reflections, using the same range of 2θ as in the previous structure, obtaining in the end 3660 independent reflections (1761 observed). No decay was observed for (3*R*,4*R*,R_S,R_S)-**7** (3 reflections monitored as for (*R*)-**6**). No absorption correction was applied.

The structure was solved by using the Patterson method together with difference Fourier maps, giving in the end the complete structure of the adduct. The structure was refined isotropically ($R = 0.078$) and then anisotropically ($R = 0.036$). Hydrogen atoms were then introduced by a model and the whole structure was refined, following the same criteria as for (*R*)-**6** ($R = 0.028$). In the case of (3*R*,4*R*,R_S,R_S)-**7** we did not find any need to introduce an extinction parameter. We then introduced a more appropriate weighting scheme, as was done for (*R*)-**6** ($a_1 = 2.84$, $a_2 = -1.45$, $a_3 = 1.67$). The final *R* value was 0.0276; the minimum and maximum $\Delta\rho$ values were −0.5 and 0.39 e Å^{-3}, both near the palladium atom.

All the refinement stages converged without difficulty. Anomalous scattering was taken into account at every refinement level. Scattering factors and anomalous scattering coefficients were taken from ref 45. Calculations were carried out on a personal computer, using the crystallographic program suite CRYSTALS.[46] Additional calculations were done by using the program Platon[47] (Windows95 version from Dr. L. J. Farrugia).

Acknowledgment. We are grateful to the Universities of Camerino and L'Aquila and to Politecnico of Milano, Milano, Italy, and the Consiglio Nazionale delle Ricerche for financial support.

Supporting Information Available: Details about the X-ray crystal structures, including tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for (*R*)-**6** and (3*R*,4*R*,R_S,R_S)-**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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