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Bis-sulfoxides as ligands for platinum complexes

Rocio Martinez Mallorquin, Saloua Chelli, Franck Brebion, Louis Fensterbank *, Jean-Philippe Goddard, Max Malacria *

Institut Parisien de Chimie Moléculaire (UMR CNRS 7201)—FR 2769 UPMC Univ Paris 06, C. 229, 4 place Jussieu, 75005 Paris, France

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Dedicated with admiration to Henri Kagan for his seminal and outstanding contributions in organic chemistry

ABSTRACT

In this article, we describe two new platinum(II) complexes incorporating C_2-symmetric enantiopure bis-sulfoxides ligands. The originality of these structures resides in the one-carbon tether between the two sulfoxide functions. X-ray structures show that coordination takes place through both sulfur atoms giving birth to intriguing platina-cyclobutane systems. We anticipate that these complexes should find uses in asymmetric catalysis.

1. Introduction

The coordination chemistry of sulfoxides is fascinating.[1] Thanks to their ambient character which promotes complexation via the oxygen or sulfur atom, sulfoxides have served as key stones for a lot of varied molecular assemblies.[1f] Moreover, their inherent chirality when dissymmetrically substituted makes them very attractive ligands for asymmetric transformations.[1e,2] All these features are reinforced, when we now deal with bis-sulfinyl structures[3,4] since different types of chelates can be envisioned and the chiral environment should be even better controlled.

While a large number of bis-sulfinyl complexes of transition metal have been reported as shown in Figure 1 with selected complexes **A**,[5] **B**,[6] **C**,[7] **D**,[8] **E** and **F**,[9] **G**,[4a] **I**,[10] and **J**,[11] and used, including very versatile applications in asymmetric catalysis,[12] our approach has focused on the design of new complexes based on a four-membered ring chelate and which involves geminal bis-sulfoxide ligands.

A source of inspiration for this has stemmed from the coordination chemistry of $R_2PCH_2PR_2$ ligands[13] and notably the work of Higgins[14] (complex **K**, Fig. 2). Further elaboration in this family came with the development of the C_2-symmetric Mini-Phos ligands **L** which incorporate stereogenic phosphorus atoms.[15]

While a complex of bis-phenylthiomethane with $PtCl_2$ **M** has been reported,[16] to the best of our knowledge, this mode of coordination has remained unexplored with the sulfoxide function and our preliminary findings are now reported.

2. Results and discussion

In order to pursue this goal, we synthesized bis-sulfinyl derivatives **1**–**4** as potential ligands. Bis-sulfinylmethane **1** was prepared according to our optimized procedure.[17] Its dimethyl bis-sulfinyl derivative **2** was prepared according to the procedure reported by Khiar[18] (Scheme 1). Thus, deprotonation of bis-sulfoxide **1** by LDA at −78 °C followed by the addition of methyl iodide allowed the formation of the mono-alkylated intermediate that was treated in a second step with KHMDS and methyl iodide to afford compound **2** in an overall improved yield of 90%. The preparation of ligand **3** was achieved in an efficient three-step synthesis inspired by Aggarwal's method.[19] Bis-sulfinyl derivative **1** was engaged in a Mannich reaction with formaldehyde and diethylamine in methanol. The resulting tertiary amine **5** was obtained in a quantitative yield. Then, a Hofmann-type elimination provided the known methylene **6** in 66% yield.[20] The cyclopropanation of such alkylidenes has already been reported with the use of the Corey-Chaykovsky reagent.[3b] Thus, trimethylsulfoxonium iodide was deprotonated with sodium hydride to generate the corresponding methylide derivative that can add onto the activated C–C double bond. The cyclopropane adduct **3** was obtained in 70% yield. Bis-mesityl **4** was prepared by conjugating two very versatile technologies. First, we prepared enantiopure sulfinate **9** based on Kagan's methodology[21] which involves the intermediate formation of cyclic sulfite **8**. The second component, methylmesitylsulfoxide **11**, was obtained from the diacetone-D-glucose-OH (DAG-OH) trick developed by Khiar.[22] Both components were then reacted in the presence of LDA delivering C_2-symmetric bis-sulfoxide **4** in good yield (87%).

With these ligands in hand, we next tackled the formation of complexes, focusing on the coordination of platinum(II) salts (Scheme 2). Applying the procedure reported by Cattalini for the preparation of complexes **A**,[5] a 4:3 water/methanol mixture of 1 equiv of (S_S,S_S)-**2** with 1.1 equiv of potassium tetrachloroplatinate(II) was heated at

* Corresponding authors.
E-mail addresses: louis.fensterbank@upmc.fr (L. Fensterbank), max.malacria@upmc.fr (M. Malacria).

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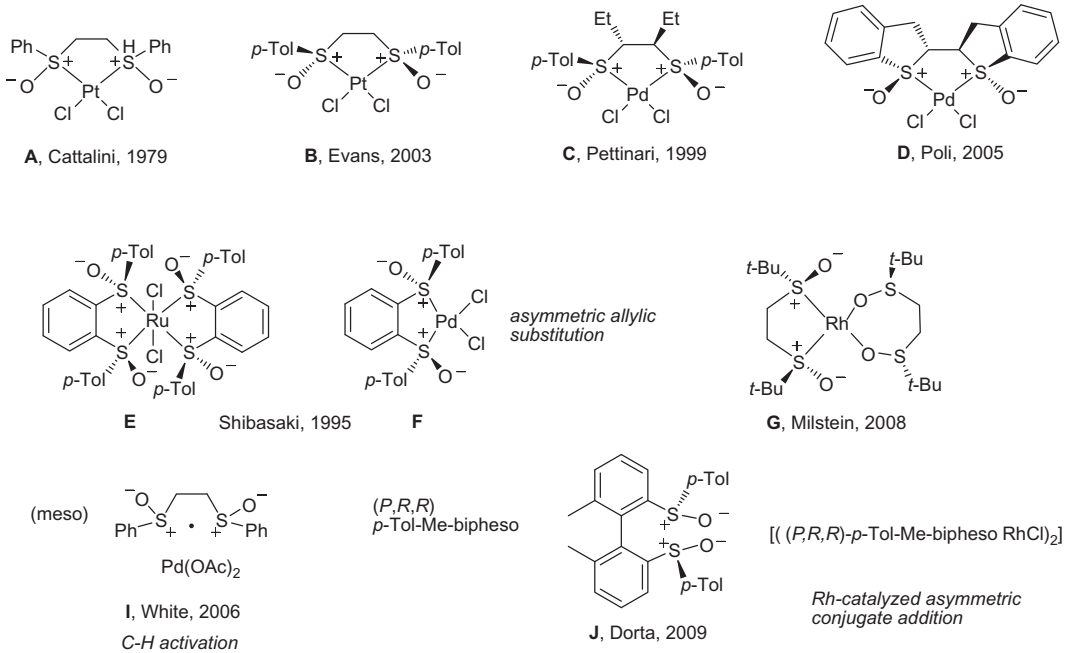


Figure 1.

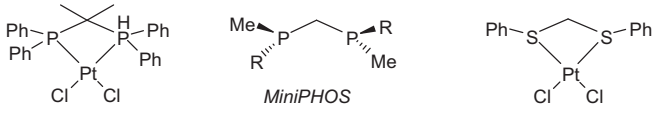


Figure 2.

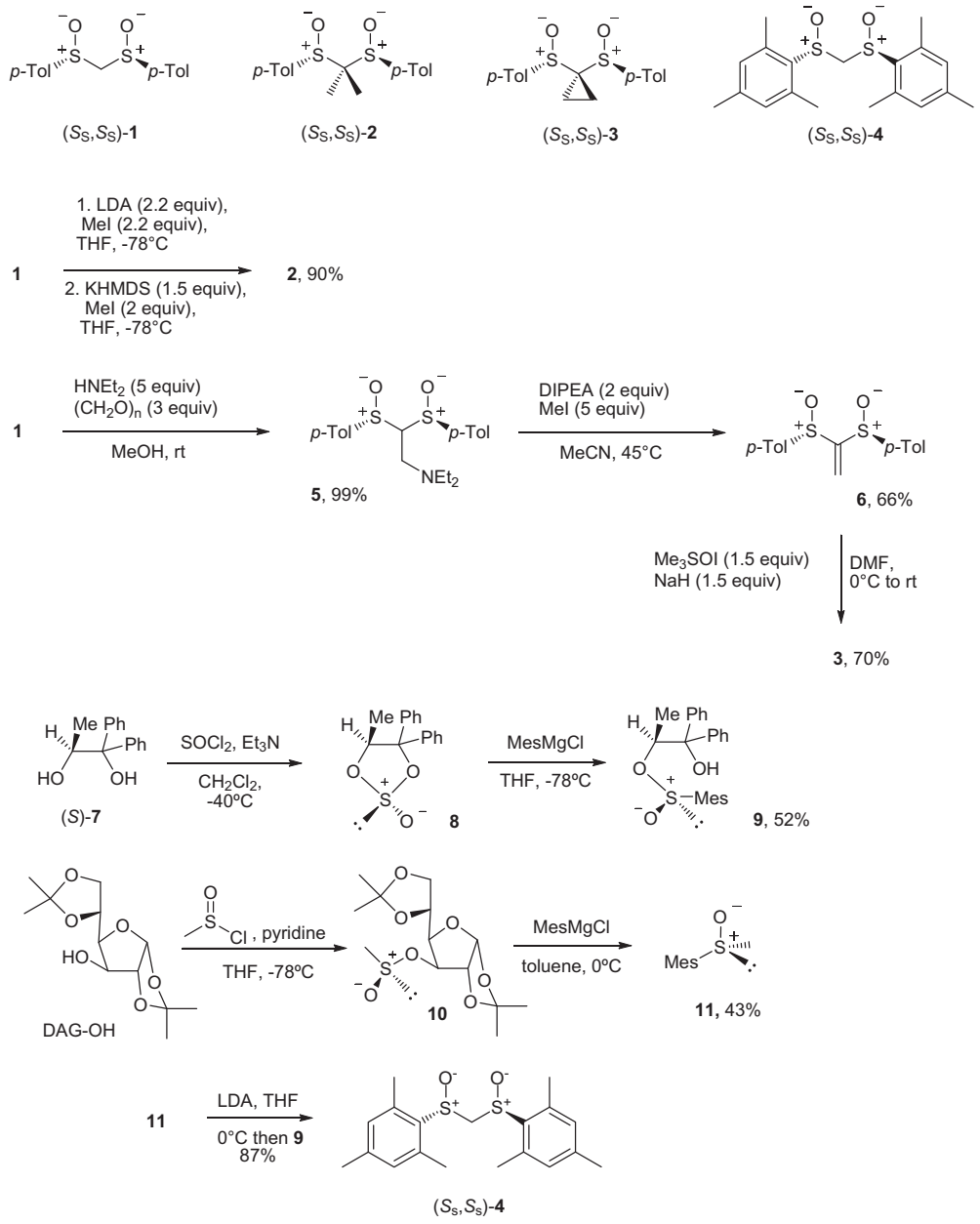
60 °C for 48 h. After that time, the complex [(S_S,S_S)-2,2-bis-(*p*-tolylsulfinyl)propane]dichloroplatinum(II) **2-Pt** was obtained as a pale brown solid in 72% yield after precipitation and washing with water and diethylether. The crude ^{1}H NMR showed traces of the free ligand. The crystallization of the complex was achieved by a slow evaporation of a dichloromethane complex solution. The X-ray crystal structure will be analyzed thereafter. Similar conditions allowed the formation of the [(S_S,S_S)-1,1-bis-(*p*-tolylsulfinyl)cyclopropane] dichloroplatinum(II) **3-Pt**. The monitoring of the reaction by ^{1}H NMR showed a shorter reaction time of 17 h versus 2 days for the formation of **2-Pt**. The complex **3-Pt** was obtained as an orange solid in 75% yield and the ^{1}H NMR of the crude did not show any traces of free ligand. The crystallization of the complex was accomplished through a slow evaporation of a diethylether/dichloromethane solution.

In sharp contrast, attempts to get an isolable complex with ligands **1**[23] and **4** failed and resulted in the formation of a dark suspension, presumably platinum(0) particles, and the free ligand was partially recovered. This illustrates the importance of the *gem*-disubstitution at the carbon center and is consistent with the literature.[14] Presumably, the *gem*-disubstitution forces the coordination and the stability of the corresponding complexes.[24]

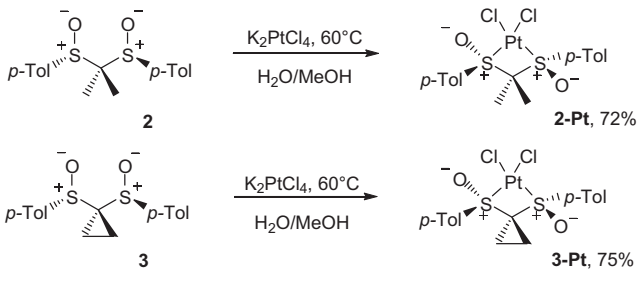
The X-ray crystallographic analysis of the complex **2-Pt**[25] provided an interesting structure where the platinum atom was coordinated by both sulfur centers, giving birth to a four-membered ring including the bis-sulfinyl core and the metal (Fig. 3). The average Pt–S distance of 2.2219 Å in this complex was slightly longer than the one reported for the corresponding bis-sulfinylethane complexes **A** with 2.217(2) and 2.209(2) Å for the meso one and 2.192(4) and 2.188(4) for the racemic one.[5,26] This can be explained by the modification of the steric interaction resulting in an elongation of the bond. The Pt–Cl average distance in the complex **2-Pt** is 2.3222 Å which is in agreement with the average bond length of 2.323(38) Å reported by Orpen from a compilation of different platinum complexes.[27] The coordination of the platinum by the sulfur atoms is generally evidenced by the shortening of the S–O distance bond length from a free sulfoxide (d_{S-O} = 1.492 Å) to an S-coordinated platinum–sulfoxide complex (d_{S-O} = 1.467 Å).[28] For the complex **2-Pt**, the distance is 1.466 Å which thus fits perfectly with such coordination.

Another interesting structural aspect of this complex is the relative position of the four platinum substituents. The square planar geometry was confirmed by measuring weak deviations (between 0.044 and 0.076 Å) from the mean plane comprising the four coordinated atoms and platinum.[29] The quaternary carbon center of the four-membered ring chelate lies 0.251 Å above that plane. The direct consequence of this deformation is the loss of the C_2-symmetry that was present in the free ligand and also illustrated by the deviation of the two oxygen atoms of 1.117 and 1.360 Å from the mean plane.

The structure analysis of the complex **3-Pt**[30] (Fig. 4) showed some differences related to the complex **2-Pt**. Some parameters were very consistent between the two structures. Thus, the average bond lengths for Pt–S (2.2268 Å), Pt–Cl (2.3183 Å), and S–O (1.4686 Å) were very similar. The main difference appeared with the coordination profile of the platinum and the shape of the four-membered ring formed by the ligand **3** and $PtCl_2$. The deviations of the ligands from the mean plane comprising the four coordinated atoms and the metal center are 0.086 and −0.076 Å for the two chlorine atoms, 0.102 and −0.095 Å for the two sulfur centers and 0.017 Å for the platinum atom. Therefore, the coordination of the platinum shows some distortion from the square planar geometry. A lower deviation of the quaternary carbon center of 0.084 Å in **3-Pt** compared to 0.251 Å for **2-Pt** is also suggestive of the tendency to get planarity for the four-membered ring. For typical cyclobutane derivatives, the puckered 'wing' conformation of the four-membered rings is more stable than the planar conformation. This is due to the unfavorable eclipsing interaction between the ring substituents in the latter. In our case, the higher steric demand of the *gem*-dimethyl group compared to the cyclopropyl group would intensify the 'wing-shaped' conformation of the complex **2-Pt** compared to **3-Pt**. The geometric



Scheme 1.



Scheme 2.

compensation is accomplished by the modification of the S–C–S angle from 96.65° for **2-Pt** to 100.05° for **3-Pt**.

In conclusion, we have described two new platinum(II) complexes incorporating C_2-symmetric enantiopure bis-sulfoxide ligands. The originality of these structures resides in the one-carbon tether between the two sulfoxide functions. Nevertheless, coordination takes place through both sulfur atoms giving birth to intriguing platina-cyclobutane systems. We anticipate that these complexes should find uses in asymmetric catalysis. One potential field of applications could be asymmetric cycloisomerizations of polyunsaturated substrates for which the platinum catalysis[31] has already given highly versatile results.[32] Results from our laboratory on this chemistry will be reported in due course.

3. Experimental section

3.1. General informations

Reactions were carried out under argon, with magnetic stirring and distilled solvents. THF was distilled from Na/benzophenone. DMF, toluene, and CH_2Cl_2 were distilled from CaH_2. MeOH was distilled from sodium. Thin layer chromatography (TLC) was

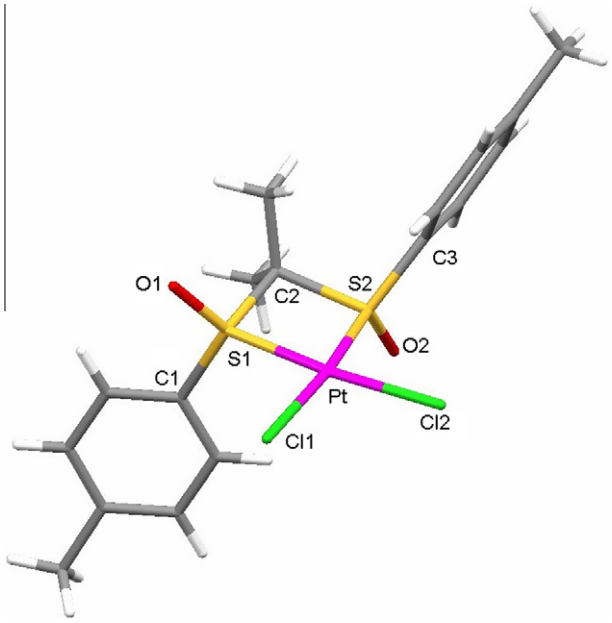


Figure 3.

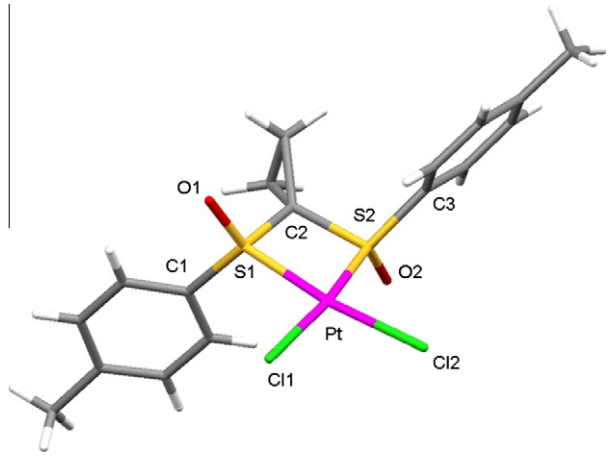
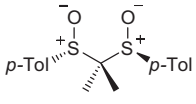


Figure 4.

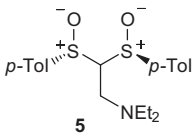
performed on Merck 60 F254 silica gel. Merck Geduran SI 60 A silica gel (35−70 mm) was used for column chromatography. The reported melting points were measured with a Reichert hot stage apparatus and are uncorrected. IR spectra were recorded with a Bruker Tensor 27 ATR diamant PIKE spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, using a Bruker AVANCE spectrometer fitted with a BBFO probehead. Chemical shifts are given in ppm using the $CDCl_3$ signal as reference (^{1}H = 7.26 ppm, ^{13}C = 77.16 ppm). Unless noted, NMR spectra were recorded in $CDCl_3$ at 300 K. The terms m, s, d, t, q, quint., and sept. stand for multiplet, singlet, doublet, triplet, quadruplet, quintuplet, and septet, respectively, and the term br s means a broad signal. Exact masses were recorded by the plateforme de spectrométrie de masse (IPCM UMR7201) of Université Pierre et Marie Curie (electrospray source).



(S_S,S_S)-**2**

3.1.1. (S_s,S_s)-2,2-Bis-(*p*-tolylsulfinyl)propane 2

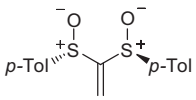
Following the procedure reported by Khiar,[18] (S_s,S_s)-1,1-bis-(*p*-tolylsulfinyl)methane **1** was converted into (S_s,S_s)-2,2-bis-(*p*-tolylsulfinyl)propane **2**, purified by column chromatography (AcOEt/petroleum ether 7:3), and isolated as a white solid (1.4 g, 85%). $[\alpha]_D^{20} = +337$ (*c* 0.14, $CHCl_3$); IR (neat) ν = 2965, 1596, 1491, 1451, 1379, 1178, 1081, 1047, 806 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 4H, arom.), 7.33 (d, *J* = 7.9 Hz, 4H, arom.), 2.42 (s, 6H, *p*-Tol), 1.07 (s, 6H, $(CH_3)_2$–C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7 (2C arom.), 135.5 (2C arom.), 129.6 (4CH arom.), 126.6 (4CH arom.), 82.6 ($C(CH_3)_2(SOp\text{-}tol)_2$), 21.5 (2 *p*-tol), 13.0 ($2CH_3$–$C(SOp\text{-}tol)_2$); HRMS calcd for $C_{17}H_{20}NaO_2S_2$ ($[M+Na]^+$): 343.0797, found: 343.0800. Spectral data are in agreement with the literature.[18]



5

3.1.2. (*S*,*S*)-1,1-Bis-(*p*-tolyl-sulfinyl)-2-(dimethylaminomethyl)-ethane

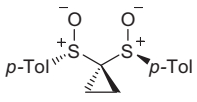
To the bis-(*p*-tolylsulfinyl)-methane **1** (3.7 g, 12.7 mmol, 1 equiv) was added paraformaldehyde (1.1 g, 38.1 mmol, 3 equiv) followed by $NHEt_2$ (26.6 mL of a 25% solution in MeOH, 63.5 mmol, 5 equiv) and the reaction mixture was stirred under nitrogen at room temperature for 17 h. The solvents were removed under reduced pressure to give a yellow solid (4.7 g, 12.6 mmol, 99%) that was engaged in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H, arom.), 7.39 (d, *J* = 7.9 Hz, 2H, arom.), 7.19 (d, *J* = 8.3 Hz, 2H, arom.), 7.03 (d, *J* = 8.2 Hz, 2H, arom.), 3.45 (dd, *J* = 9.6, 4.5 Hz, 1H, CH–C*H*H–N), 3.28 (dd, *J* = 14.5, 9.6 Hz, 1H, S–C*H*–S), 2.97 (dd, *J* = 14.5, 4.5 Hz, 1H, CH–CH*H*–N), 2.46 (s, 3H, *p*-tol), 2.41 (dd, *J* = 11.6, 7.1 Hz, 4H, CH_3CH_2–N), 2.35 (s, 3H, *p*-tol), 0.87 (t, *J* = 7.1 Hz, 6H, CH_2–CH_3).



6

3.1.3. (S_s,S_s)-1,1-Bis-(*p*-tolylsulfinyl)-ethene 6

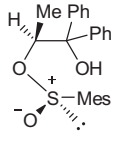
The amino derivative **5** (4.73 g, 12.5 mmol, 1 equiv) was dissolved in acetonitrile (31 mL) and stirred at room temperature under nitrogen. *N*,*N*-Diisopropylethylamine (3.24 g, 25 mmol, 2 equiv) was added dropwise to the reaction mixture followed by the addition of methyl iodide (8.87 g, 62.5 mmol, 5 equiv). After a few minutes the reaction mixture turned cloudy. After 17 h no amine **5** was detected by TLC. Dry ethyl acetate (10 mL) was added to the solution and the precipitate was filtered and washed with AcOEt (4 × 5 mL). The filtrate was evaporated in vacuo and the residue was subjected to flash chromatography (ethyl acetate/petroleum ether 7:3) to afford **6** as a brown solid (2.31 g, 66%). $[\alpha]_D^{20} = +111$ (*c* 0.11, $CHCl_3$) lit. $[\alpha]_D^{24} = +83.9$ (*c* 0.65, $CHCl_3$); IR (neat) ν = 2920, 1595, 1492, 1304, 1179, 1082, 1050 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 4H, arom.), 7.24 (d, *J* = 8.0 Hz, 4H, arom.), 6.75 (s, 2H, CH_2), 2.41 (s, 6H, *p*-tol); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6 (2C arom.), 138.2 (2C arom.), 130.4 (4CH arom.), 126.6 (4CH arom.), 120.4 (CH_2), 21.7 ($2CH_3$ *p*-tol), the C1 was not observed. Spectral data are in agreement with the literature.[20]



(S_S,S_S)-**3**

3.1.4. (S_s,S_s)-1,1-Bis-(*p*-tolylsulfinyl)-cyclopropane 3

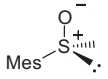
According to the procedure reported by Yoshimatsu,[33] NaH (0.1 g, 2.5 mmol, 1.5 equiv, 60% w/w suspension in oil) was added to a solution of trimethylsulfoxonium iodide (0.55 g, 2.5 mmol, 1.5 equiv) in dry DMF (5 mL) and the reaction mixture was allowed to stir for 1 h. A solution of **6** (0.5 g, 1.64 mmol, 1 equiv) in dry DMF (15 mL) was added dropwise to the mixture at 0 °C and the resulting solution was stirred for 2 h at room temperature. It was then poured into an aqueous saturated NH_4Cl solution (50 mL) and extracted with AcOEt (3 × 30 mL). The combined extracts were dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (AcOEt/pentane 8:2) to afford **3** as colorless crystals (0.26 g, 70%). $[\alpha]_D^{20} = +30$ (*c* 0.12, $CHCl_3$); mp: 101 °C; IR (neat) ν = 2923, 1596, 1493, 1398, 1231, 1085, 1049 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.30 (m, 4H, arom.), 7.30–7.23 (m, 4H, arom.), 2.38 (s, 6H, *p*-tol), 1.48–1.41 (m, 2H, 2CH*H*-C(SO*p*-tol)$_2$), 1.39–1.33 (m, 2H, 2*CH*H–C(SO*p*-tol)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6 (2C arom.), 138.2 (2C arom.), 130.0 (4CH arom.), 125.1 (4CH arom.), 61.2 (*C*(CH$_2$)$_2$(SO*p*-tol)$_2$), 21.5 (2 *p*-tol), 9.2 (2*C*H$_2$–C(SO*p*-tol)$_2$); HRMS calcd for $C_{17}H_{19}O_2S_2$ ([M+H]$^+$): 319.0821, found: 319.0820.



9

3.1.5. Mesityl sulfinate 9

According to the procedure reported by Kagan,[21] the sulfinate **9** was obtained as a white solid (2.18 g, 52%) after flash chromatography on silica gel (petroleum ether/ethyl acetate 7:3). ^1H NMR (200 MHz, $CDCl_3$) δ 7.64–7.46 (m, 4H, H arom. phenyl), 7.35–7.15 (m, 6H, H arom. phenyl), 6.77 (bs, 2H, H arom. mesityl), 5.45 (q, *J* = 6.4 Hz, 1H, C*H*Me), 3.20 (br s, 1H, O*H*), 2.27 (s, 9H, Me mesityl), 1.43 (d, *J* = 6.4 Hz, 3H, Me). Spectral data are in agreement with the literature.[21]



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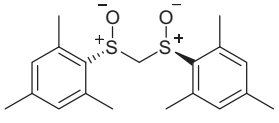
3.1.6. (R_s)-Mesitylmethylsulfoxide 11

According to the procedure reported by Khiar,[22] the sulfinate derivative **10** (4.0 g, 12.3 mmol) was converted to the enantiomerically pure sulfoxide **11** (963 mg, 43%) as a colorless oil. $[\alpha]_D^{20} = +100.6$ (*c* 1.06, EtOH) lit. $[\alpha]_D^{20} = +45$ (*c* unknown EtOH);[21] ^1H NMR (400 MHz, $CDCl_3$) δ 6.86 (br s, 2H, H arom. mesityl), 2.84 (s, 3H, *S-Me*), 2.55 (s, 6H, *o-Me*), 2.28 (s, 3H, *p-Me*); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2 (Cq mesityl), 138.0 (2Cq mesityl), 136.2 (Cq mesityl), 131.1 (2CH mesityl), 38.6 (*C*H$_3$–S), 21.1 (*p*-*C*H$_3$), 19.1 (2 *o*-*C*H$_3$). Spectral data are in agreement with the literature.[21,34]



(S_S,S_S)-**4**

3.1.7. (S_s,S_s)-1,1-Bis-(mesitylsulfinyl)-methane 4

In a two-necked flask, a solution of DIPA (0.74 mL, 5.2 mmol, 3.1 equiv) in THF (5 mL) was cooled to 0 °C and *n*-BuLi (2.26 mL, 5.2 mmol, 3.1 equiv, 2.3 M in hexanes) was added dropwise. After 15 min, a solution of sulfoxide **11** (900 mg, 4.9 mmol, 3 equiv) in THF (5 mL) was cannulated over a period of 15 min. The reaction mixture was warmed to room temperature and stirred for 45 min. The solution was cooled to 0 °C and a solution of sulfinate **9** (676 mg, 1.63 mmol, 1 equiv) in THF (5 mL) was cannulated over a period of 25 min and monitored by TLC. The reaction was quenched at 0 °C with an aqueous saturated solution of NH_4Cl (30 mL) and the reaction mixture was extracted with Et_2O (3 × 40 mL). The combined organic layers were successively washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The product was purified by column chromatography on silica gel (AcOEt/petroleum ether = 7:3) affording **4** as a white solid (495 mg, 87%). $[\alpha]_D^{20} = +484$ (*c* 0.125, $CHCl_3$); IR (neat) ν = 2924, 1601, 1570, 1447, 1380, 1336, 1294, 1087, 1066, 1028, 857, 823 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 4H, arom.), 4.49 (s, 2H, S–C*H*$_2$–S), 2.54 (s, 12H, *o*-C*H*$_3$), 2.28 (s, 6H, *p*-C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0 (2C arom.), 138.4 (4C arom.), 134.1 (2C arom.), 131.2 (4CH arom.), 74.5 (CH$_2$), 21.1 (2 *p*-C*H*$_3$), 19.1 (4 *o*-C*H*$_3$); HRMS calcd for $C_{19}H_{25}O_2S_2$ ([M+H]$^+$): 349.1290, found: 349.1289.

3.1.8. [(R_s,R_s)-2,2-Bis-(*p*-tolylsulfinyl)-propane]-dichloroplatine(II) 2-Pt

According to the procedure reported by Cattalini,[5] a mixture of the free ligand **2** (96 mg, 0.3 mmol, 1 equiv) and K_2PtCl_4 (137 mg, 0.33 mmol, 1.1 equiv) was heated in H_2O/MeOH (4 mL/3 mL) at 60 °C for 48 h to obtain the crude **2-Pt** that precipitates from the reaction mixture. It was washed with H_2O (2 × 5 mL) and Et_2O (3 × 10 mL) to afford **2-Pt** as a brown solid (127 mg, 72%) accompanied by 12% of free ligand **2**. $[\alpha]_D^{20} = -80$ (*c* 0.11, $CHCl_3$); mp 176 °C; IR (neat) ν = 3075, 2927, 1588, 1489, 1447, 1158, 1070, 810 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.23 (d, 4H, *J* = 8.3 Hz, arom.), 7.53 (d, 4H, *J* = 8.3 Hz, arom.), 2.54 (s, 6H, *p*-tol), 1.36 (s, 6H, C*H*$_3$-C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7 (2C arom.), 130.0 (4CH arom.), 128.9 (2C arom.), 128.3 (4CH arom.), 21.0 (2 *p*-tol), 20.0 (2CH$_3$-C(SO*p*-tol)$_2$) the C1 was not observed; HRMS calcd for $C_{17}H_{20}O_2Cl_2NaPtS_2$ ([M+Na]$^+$): 606.9800, found: 606.9809.

3.1.9. [(R_s,R_s)-1,1-Bis-(*p*-tolylsulfinyl)-cyclopropane]-dichloroplatine(II) 3-Pt

According to the procedure reported by Cattalini,[5] a mixture of the free ligand **3** (60 mg, 0.19 mmol, 1 equiv) and K_2PtCl_4 (86 mg, 0.20 mmol, 1.1 equiv) was heated in H_2O/MeOH (2.7 mL/2 mL) at 60 °C for 17 h to obtain the crude **3-Pt** that precipitates from the reaction mixture. It was washed with H_2O (2 × 5 mL) and Et_2O (10 mL) to afford **3-Pt** as an orange solid (83 mg, 75%). $[\alpha]_D^{20} = -25$ (*c* 0.10, $CHCl_3$); mp 206 °C decomposition; IR (neat) ν = 3079, 2145, 1588, 1487, 1401, 1171, 1071, 910, 875 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 4H, arom.), 7.55 (d, *J* = 8.5 Hz, 4H, arom.), 2.53 (s, 6H, *p*-tol), 1.85 (td, *J* = 7.6, 5.8 Hz, 2H, 2C*H*H–C(SO*p*-tol)$_2$), 1.11 (td, *J* = 7.6, 5.8 Hz, 2H, 2CH*H*–C(SO*p*-tol)$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2 (2C arom.), 131.9 (2C arom.), 131.4 (4CH arom.), 127.5 (4CH arom.), 102.5 (*C*(CH$_2$)$_2$(SO*p*-tol)$_2$), 22.3 (2CH$_2$-C(SO*p*-tol)$_2$), 21.9 (2 *p*-tol); HRMS calcd for $C_{17}H_{18}O_2Cl_2NaPtS_2$ ([M+Na]$^+$): 606.9639, found: 606.9661.

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