New Enantiopure Bis(thioether) and Bis(sulfoxide) Ligands from Benzothiophene

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The C_2-symmetric compound 2,3,2′,3′-tetrahydro-2,2′-bi(benzo[*b*]thiophenyl) and three diastereomeric bis(oxide) derivatives can be synthesized in a few steps from benzo[*b*]-thiophene by oxidative homocoupling of (*R*)-2,3-dihydrobenzo[*b*]thiophene 1-oxide. This new family of enantiopure bis(thioether) and bis(sulfoxide) ligands forms stable chelating Pd^{II} complexes. The fused pentacyclic structure of the complexes imparts a rigid chiral environment around the metal centre.

Introduction

The field of asymmetric catalysis is witnessing an ever-growing interest and several highly efficient catalytic methods are nowadays known in the literature. Despite these positive results, knowledge in this field is still limited and much work will be needed to make this methodology a comprehensive and well-established technique. In this context, the nature of the ancillary ligands used for a given metal-catalysed process is central, with chiral P- and N-based ligands occupying an incontestable leading position. Despite the vast knowledge on sulfur–metal interactions in coordination chemistry,[1] the use of S-based ligands in catalysis appears to be still rather underdeveloped. Indeed, bis(thioether)s have only been sporadically reported in the literature in the context of asymmetric catalysis, and are usually associated with modest enantioselectivities.[2,3] Such a drawback is often due to the loss of stereohomogeneity of the chelate complexes as a result of rapid epimerisation at the sulfur (stereogenic) centres. Nonetheless, stereocontrol at the sulfur atom can be forced in special cases, such as under stereoelectronic assistance, as recently demonstrated by Khiar et al.[4] Furthermore, related studies involving bis(sulfoxide)s, although of high potential interest, have so far been virtually neglected.[5]

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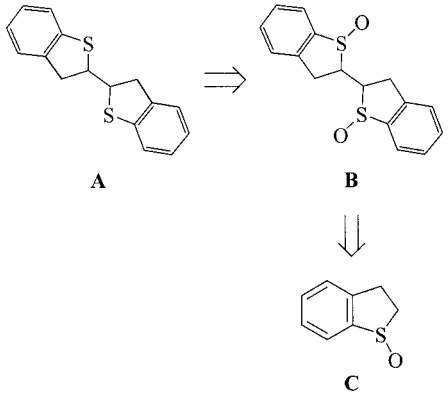

Scheme 1. New approach for the preparation of SCCS-type ligands

Results and Discussion

In this paper we describe our results in the development of a new family of enantiopure SCCS chiral ligands of potential interest for asymmetric catalysis. More specifically, we thought that homocoupling of 2,3-dihydrobenzo[*b*]thiophene 1-oxide (C → B), followed by sulfoxide reduction (B → A) might enable an easy entry to such a new class of enantiopure SCCS ligands (Scheme 1).[6]

Since this particular type of coupling involves the preservation of the pre-existing stereogenic centres at sulfur, as well as the concomitant generation of two new ones, the enantiomeric purity of the starting sulfoxide was expected to be central not only to obtain enantiopure products, but also to minimize the amount of possible homocoupled diastereomers.[7] Accordingly, commercially available benzo[*b*]-thiophene (**1**) was converted into the corresponding 2,3-dihydrobenzo[*b*]thiophene **4** by reproduction and/or optimi-

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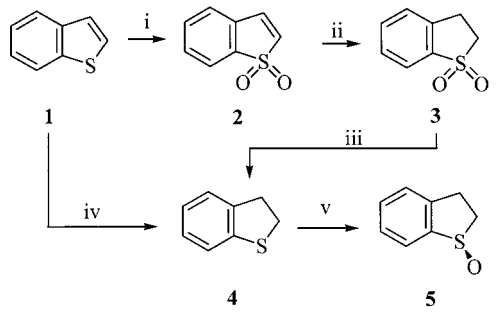
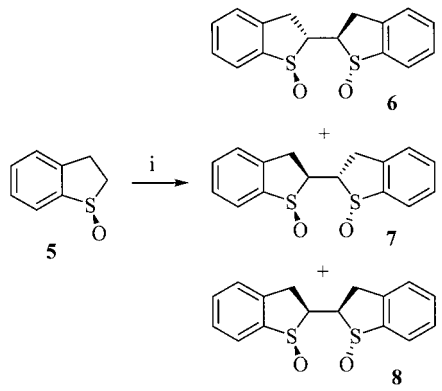


Scheme 2. Preparation of (*R*)-2,3-dihydrobenzo[*b*]thiophene 1-oxide (**5**); reagents and conditions: (i) *m*-CPBA, $CHCl_3$, room temp., 19 h (90%); (ii) H_2, 1 atm, 10% Pd/C (quant.); (iii) $LiAlH_4$, Et_2O, reflux, 4 h (77%); (iv) H_2, 30 atm, $[Ru^{II}(triphos)(MeCN)_3(OTf)_2]$, THF, 100 °C (96%); (v) CPO, H_2O_2, pH 5 buffer, room temp., 22 h (90%, 98% *ee*)



Scheme 3. Synthesis of bis(sulfoxide)s **6**–**8**; reagents and conditions: (i) a: LDA, THF, –78 °C. b: $CuCl_2$, –78 °C → room temp. c: O_2, 76%, 1:1:1 diastereomeric ratio

sation of known synthetic routes (Scheme 2). Oxidation of **1** with *m*-chloroperbenzoic acid (*m*-CPBA) afforded the corresponding sulfone **2**, which was quantitatively hydrogenated to give 2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (**3**). Treatment of the latter with an excess of $LiAlH_4$ gave the desired 2,3-dihydrobenzo[*b*]thiophene **4**.[8] Alternatively, hydrogenation of **1** in the presence of $[Ru^{II}(triphos)(MeCN)_3(OTf)_2]$, according to Bianchini's protocol,[9] gave the desired thioether **4** directly.[10]

A synthetically useful conversion of thioether **4** into its corresponding sulfoxide **5** was then necessary. After a few disappointing hydroperoxide/Ti^{IV} oxidations in the presence of various chiral ligands, we turned our attention to chloroperoxidases (CPOs). Indeed, Allenmark[11] has reported that, on the micromolar scale, the CPO isolated from *Caldariomyces fumago* affords the desired sulfoxide (*R*)-**5** with a 99% *ee*. Remarkably, the method could be easily transposed from an analytical to a preparative scale (1500-fold scale-up) simply by using a commercially available CPO. Accordingly, multigram oxidation of **4** gave the desired sulfoxide (*R*)-**5** in 90% yield and 98% *ee*.

Homocoupling of (*R*)-**5** turned out be very tricky. Indeed, we soon realized that the lithium anion of **5**, generated by deprotonation with LDA in THF at –78 °C, suffers ring opening above –50 °C. Furthermore, treatment of the above anion at –78 °C with $CuCl_2$, and subsequent warming,[12] gave only tiny amounts of the homocoupled product along with some α-chlorinated and α,β-unsaturated sulfoxides in a very irreproducible way. Bubbling oxygen through the mixture after $CuCl_2$ addition[13] did not improve these results. After much effort we finally discovered that careful warming of the reaction mixture to room temperature after $CuCl_2$ addition, followed by oxygen bubbling, gave the three expected diastereomers **6**, **7** and **8** in a 1:1:1 ratio and with a reproducible yield of 76% (Scheme 3).

Diastereomer **8** could be easily detected on the basis of its (more complex) ^{13}C NMR spectrum; the two remaining dissymmetric isomers show only half the number of signals. Additionally, a single-crystal X-ray diffraction structure of the more polar diastereomer **6** (Figure 1) unveiled its absolute stereochemistry, and, by extension, that of the remaining one.

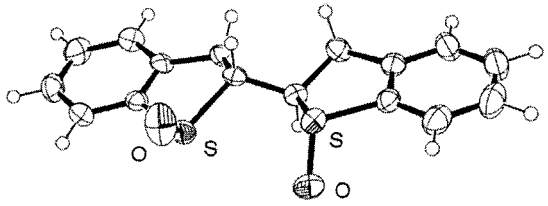
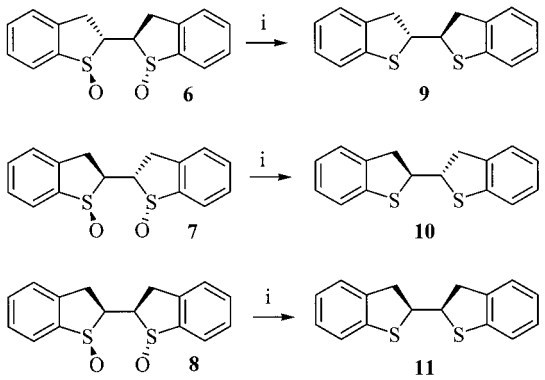


Figure 1. ORTEP diagram of bis(sulfoxide) **6**

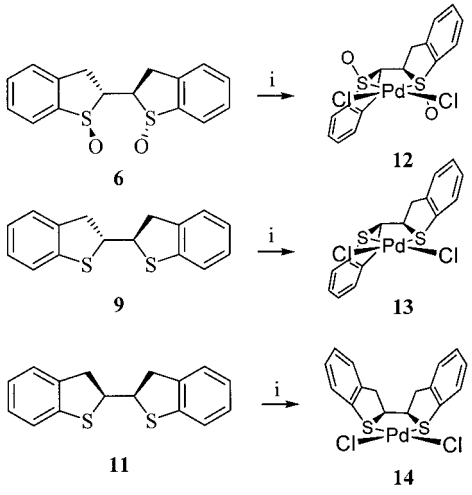
The sulfoxide functions of **6**–**8** are incorporated into five-membered ring structures. As a consequence, assuming metal coordination through the sulfur atom, only the diastereomer **6** has the proper geometry for chelation. Tests of metal complexation confirmed the above speculation. Indeed, addition of an equimolar amount of $PdCl_2$ to **6** in CH_2Cl_2 afforded a new complex, which could be easily monitored by TLC analysis and isolated as a yellow-orange solid. Unfortunately, all attempts to obtain crystals suitable for an X-ray diffraction analysis failed. However, comparison of the SO absorption bands in the IR spectrum of **6** (1020 cm^{-1}) with those of its palladium(II) complex **12** (1150 cm^{-1}) clearly indicated coordination through sulfur.[5] As expected, treatment of diastereomer **7** under identical conditions did not afford results consistent with the discrete formation of a chelated palladium(II) complex.

BH_3 ·THF reduction of bis(sulfoxide)s **6**–**8** gave the corresponding bis(thioether)s **9**–**11** (Scheme 4). Analysis of their optical rotatory power clearly evidenced the enantiomeric relationship between **9** and **10**, as well as the *meso* structure of **11**.[14]

A check of the coordinating/chelating abilities of the bis(thioether)s was performed next. Separate treatment of **9** and **11** with $PdCl_2$ in CH_2Cl_2 at room temperature afforded the corresponding chelated complexes **13** and **14** (Scheme 5), whose structures were determined by X-ray diffraction analysis (Figure 2 and Figure 3, respectively). Interestingly, no epimerisation at the stereogenic sulfur centres appears to be possible in complex **13**.



Scheme 4. Synthesis of bis(thioether)s **9**–**11**; reagents and conditions: (i) BH_3 ·THF, THF, 0 °C → room temp. (quant.)



Scheme 5. Preparation of complexes **12**–**14**; reagents and conditions: (i) $PdCl_2$, CH_2Cl_2, room temp. (quant.)

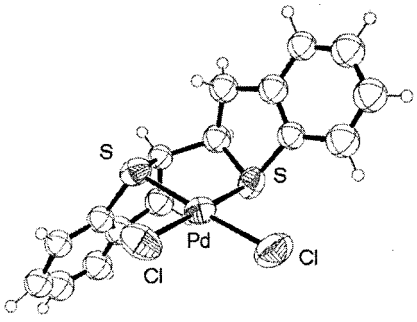


Figure 2. ORTEP diagram of complex **13**

Conclusions

In conclusion, we have presented an easy preparation of a new family of practically enantiopure SCCS-type ligands [bis(sulfoxide)s and bis(thioether)s] starting from commercially available benzo[*b*]thiophene. The key steps in the synthesis are the successful microgram-to-multigram scale-up of a highly enantioselective CPO-catalysed thioether-to-sulfoxide oxidation, and the Cu^{II}-mediated homocoupling reaction of an α-lithiosulfoxide. The bis(sulfoxide)s and bis(thioether)s thus obtained afford rigid pentacyclic metal-chelated structures, which can create a well-defined asymmetric or dissymmetric "chiral space" around a metal, a feature that is of obvious potential interest for asymmetric catalysis. Extension of the present method to the homocoupling of additional enantiopure sulfoxides and studies of asymmetric catalysis are planned for the future.

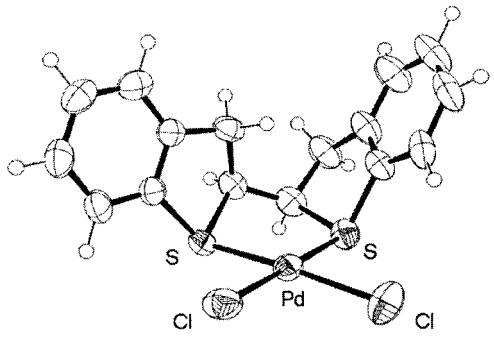


Figure 3. ORTEP diagram of complex **14**

Experimental Section

General Remarks: Diethyl ether and THF were distilled from sodium benzophenone ketyl; dichloromethane and diispropylamine were distilled from CaH_2. All other reagents and solvents were used without further purification. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded with a Bruker ARX-400 spectrometer using the residual peak of deuterated chloroform (δ = 7.27 ppm for ^1H and = 77.14 ppm for ^{13}C) as internal standard. IR spectra were recorded with a Bruker Tensor 27 (pike) instrument and only the strongest or structurally most important peaks are listed. Optical rotations were measured with a Perkin–Elmer 343 polarimeter. Analytical HPLC was performed with a Waters liquid chromatograph using Chiralcel OJ column. Chromatographic purifications were conducted using 40–63 μm or 15–40 μm silica gel and analytical TLC was performed on Merck precoated silica 60-F_{254} plates.

Benzo[*b*]thiophene 1,1-Dioxide (2): [8,15] *m*-Chloroperbenzoic acid (70%, 31.4 g, 0.127 mol, 2.5 equiv.) was added portionwise to a solution of benzo[*b*]thiophene (6.83 g, 0.051 mol) in chloroform (350 mL) at room temperature with vigorous stirring. The mixture was allowed to stir overnight at the same temperature. Then, a saturated aqueous $NaHCO_3$ solution (1 L) was added and the aqueous layer was extracted with dichloromethane (3 × 200 mL). The collected organic layers were dried, and the solvent was removed in vacuo. Crystallization from ethanol afforded white crystals (7.60 g, 90% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.73 (d, *J* = 7.1 Hz, 1 H), 7.23 (d, *J* = 7.1 Hz, 1 H), 7.38 (dd, *J* = 6.6, *J* = 1.5 Hz, 1 H), 7.51–7.60 (m, 2 H), 7.73 (d, *J* = 7.1 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 121.3, 125.5, 130.6, 130.8, 131.2, 132.5, 133.7, 136.7 ppm. MS (CI/NH_3): *m*/*z* = 201 [$MN_2H_7^+$], 184 [MNH_4^+], 137. IR (powder): $\tilde{\nu}$ = 3115, 3060, 1550, 1450, 1445, 1280, 1265, 1190, 1145, 1120, 865, 765, 750 cm^{-1}. M.p. 141–143 °C.

2,3-Dihydrobenzo[*b*]thiophene 1,1-Dioxide (3): [8,15b] Hydrogenation of benzo[*b*]thiophene 1,1-dioxide (**2**) (7.30 g, 0.044 mol) was accomplished under a pressure of 1 atm of hydrogen over 24 h in 500 mL of ethanol as the solvent and with 0.1 g of 10% palladium-on-charcoal catalyst. Evaporation of the solvent, after filtration of the catalyst through a Celite pad, gave white crystals of **3** (7.30 g, quant.). ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.40 (t, *J* = 7.1 Hz, 2 H), 3.51 (t, *J* = 7.1 Hz, 2 H), 7.39 (d, *J* = 7.6 Hz, 1 H), 7.48 (t, *J*

= 7.6 Hz, 1 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.75 (d, *J* = 7.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 25.5, 50.7, 121.6, 127.4, 128.9, 133.6, 137.3, 139.0 ppm. MS (CI/NH_3): *m*/*z* = 186 [MNH_4^+], 104. IR ($CHCl_3$): $\tilde{\nu}$ = 3120, 3060, 1280, 1150, 705 cm^{-1}. M.p. 88–89 °C.

2,3-Dihydrobenzo[*b*]thiophene (4). Method A: [8] A suspension of 2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (**3**) (1 g, 5.95 mmol) in dry diethyl ether (45 mL) was added to a suspension of $LiAlH_4$ (2.03 g, 53.49 mmol, 9 equiv.) in dry diethyl ether (45 mL) at room temperature. The reaction mixture was refluxed for 4 h, then cooled to 0 °C. The excess of hydride was decomposed by dropwise addition of water (10 mL), and the resultant white precipitate dissolved in dilute hydrochloric acid (4 M, 250 mL). The aqueous layer was extracted with diethyl ether (3 × 100 mL). The collected organic layers were dried, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (pentane) to afford 2,3-dihydrobenzo[*b*]thiophene as a colorless oil (0.622 g, 77% yield).

Method B: [9] A solution of [Ru(triphos)(CH_3CN)$_3$](OTf)$_2$ (100 mg, 0.2 mol%) and benzo[*b*]thiophene (6 g, 44.7 mmol) in THF (45 mL) was placed in a 60 mL Parr reactor under nitrogen. After pressurizing with hydrogen to 30 bar at room temperature, the mixture was heated to 100 °C with stirring (750 rpm). After 24 h the reactor was cooled to room temperature, depressurised, and the contents of the reactor were transferred into a flask. The solvent was evaporated under reduced pressure and then the residue was washed with pentane (50 mL) and filtered through a cotton pad. The solvent was evaporated under reduced pressure to afford **4** as a colourless oil (5.87 g, 96% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.31–3.44 (m, 4 H), 7.08 (td, *J* = 7.6, *J* = 1.0 Hz, 1 H), 7.19 (td, *J* = 7.6, *J* = 1.0 Hz, 1 H), 7.28 (dd, *J* = 7.6, *J* = 1.0 Hz, 1 H), 7.31 (d, *J* = 7.1 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 33.4, 36.3, 122.2, 124.2, 124.5, 127.4, 140.1, 141.6 ppm. MS (CI/NH_3): *m*/*z* = 137 [MH^+], 136 [M^+], 135, 121, 108, 91. IR (neat): $\tilde{\nu}$ = 3070, 2950, 1590, 1465, 1450, 1430, 1260, 1125, 1065, 750 cm^{-1}.

(*R*)-2,3-Dihydrobenzo[*b*]thiophene 1-Oxide (5): [11,16] An aqueous H_2O_2 solution (6.30 mL of 35% v/v H_2O_2 in 43.70 mL of distilled water, 73.6 mmol, 2 equiv.) was added dropwise by means of a syringe pump (flow rate: 3.2 mL h^{-1}) to an emulsion of 2,3-dihydrobenzo[*b*]thiophene (**4**) (5 g, 36.8 mmol) and CPO (540 μL, 22314 u mL^{-1}, 12064 u) in 0.1 M citrate buffer (pH 5.0, 1 L) at room temperature, with vigorous stirring. Six hours after the end of the addition, the reaction was treated with a saturated Na_2SO_3 aqueous solution (300 mL), and the aqueous layer was extracted with ethyl acetate (4 × 300 mL) and then with chloroform (2 × 300 mL). The collected organic layers were dried, and the solvent was removed in vacuo. The residue was purified by flash chromatography (gradient of elution: ethyl acetate → ethyl acetate/methanol, 95:5) to afford **5** as a pure, white solid (5.035 g, 90% yield). ^{1}H NMR ($CDCl_3$ 400 MHz): δ = 3.23–3.42 (m, 3 H), 3.83–3.95 (m, 1 H), 7.40–7.56 (m, 3 H), 7.85 (d, *J* = 7.6 Hz, 1 H) ppm. ^{1}H NMR (C_6D_6, 400 MHz): δ = 2.25–2.39 (m, 2 H), 2.57–2.64 (m, 1 H), 3.07–3.14 (m, 1 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 6.85 (t, *J* = 7.6 Hz, 1 H), 6.95 (td, *J* = 7.6, *J* = 1.0 Hz, 1 H), 7.50 (d, *J* = 7.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.6, 52.9, 126.1, 126.9, 128.4, 132.4, 143.3, 145.0 ppm. MS (CI/NH_3): *m*/*z* = 170 [MNH_4^+], 153 [MH^+], 136. IR (powder): $\tilde{\nu}$ = 1465, 1440, 1410, 1120, 1025, 790, 770 cm^{-1}. M.p. 54 °C. *ee*: 98% [determination by HPLC, column Chiralcel OJ^{TM}; temperature column: 35 °C. UV detection λ = 220 nm; eluent: hexane/ethanol, 85:15, flow rate: 1 mL/ min; t_R 7.40 min (*S*) 9.25 min (*R*)]. $[\alpha]_D^{25}$ = –310 (*c* = 1.5, acetone).

(1*R*,2*R*,1′*R*,2′*R*)-2,3,2′,3′-Tetrahydro-2,2′-bi(benzo[*b*]thiophenyl) 1,1′-Dioxide (6), (1*R*,2*S*,1′ *R*,2′*S*)-2,3,2′,3′-Tetrahydro-2,2′-bi(benzo[*b*]thiophenyl) 1,1′-Dioxide (7) and (1*R*,2*S*,1′ *R*,2′*R*)-2,3,2′,3′-Tetrahydro-2,2′-bi(benzo[*b*]thiophenyl) 1,1′-Dioxide (8): A THF (2 mL) solution of the sulfoxide **5** (100 mg, 0.664 mmol) was added dropwise to a stirred solution of lithium diisopropylamide (0.723 mmol, 1.1 equiv.) in THF (2 mL) at –78 °C. After 5 min at the same temperature dry, powdered cupric chloride (115 mg, 0.855 mmol, 1.3 equiv.) was added to the yellow solution and, after 25 min, the resulting brown mixture was warmed to room temperature. A dry oxygen stream was then bubbled through the green solution over 90 min. An aqueous 1.0 M HCl solution (5 mL) was then added to the resulting green suspension and the aqueous layer was extracted with chloroform (3 × 5 mL). The collected organic layers were washed with an NH_4Cl/NH_3 (2:1) aqueous solution (3 × 5 mL) and brine (5 mL), then dried with anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was purified by flash chromatography (gradient of elution: ethyl acetate/cyclohexane, 80:20 → ethyl acetate → ethyl acetate/methanol, 95:5) to afford, in order of elution, **7** (25 mg, 25% yield), **8** (25 mg, 25% yield) and **6** (26 mg, 26%).

6: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.35 (dd, *J* = 16.4, *J* = 6.3 Hz, 2 H), 3.87 (dd, *J* = 16.4, *J* = 6.8 Hz, 2 H), 3.99 (m, 2 H), 7.39–7.56 (m, 6 H), 7.78 (d, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.1, 70.9, 126.3, 126.9, 129.1, 132.6, 140.5, 143.2 ppm. MS (CI/NH_3): *m*/*z* = 320 [MNH_4^+], 303 [MH^+], 287, 271. HRMS: *m*/*z* calculated for $C_{16}H_{15}O_2S_2$ 303.0513 [MH^+]; found 303.0515. IR (powder): $\tilde{\nu}$ = 1470, 1450, 1065, 1020, 750 cm^{-1}. $[\alpha]_D^{25}$ = –140.3 (*c* = 0.7, $CHCl_3$). M.p. 180–182 °C.

7: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.51 (dd, *J* = 15.2, *J* = 4.6 Hz, 2 H), 3.80–3.98 (m, 4 H), 7.42–7.58 (m, 6 H), 7.91 (d, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.2, 58.7, 126.0, 127.5, 128.6, 132.9, 143.6, 144.2 ppm. MS (CI/NH_3): *m*/*z* = 320 [MNH_4^+], 303 [MH^+], 285, 267. IR (powder): $\tilde{\nu}$ = 1460, 1070, 1010, 750 cm^{-1}. $[\alpha]_D^{25}$ = +53.4 (*c* = 0.5, $CHCl_3$). M.p. 156–160 °C.

8: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.29–3.39 (m, 1 H), 3.43 (dd, *J* = 16.3, *J* = 6.6 Hz, 1 H), 3.74 (dd, *J* = 16.3, *J* = 6.6 Hz, 1 H), 4.01–4.15 (m, 2 H), 4.20 (dd, *J* = 16.3, *J* = 7.1 Hz, 1 H) 7.42–7.60 (m, 6 H), 7.84 (d, *J* = 7.1 Hz, 1 H), 7.90 (d, *J* = 7.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 35.9, 37.0, 63.1, 69.5, 126.4, 126.6, 126.8, 127.5, 128.6, 128.9, 132.5, 133.3, 140.5, 143.5, 143.7, 144.7 ppm. MS (CI/NH_3): *m*/*z* = 320 [MNH_4^+], 303 [MH^+], 285, 267. IR (powder): $\tilde{\nu}$ = 1465, 1445, 1060, 1015, 760 cm^{-1}. $[\alpha]_D^{25}$ = –17.4 (*c* = 0.9, $CHCl_3$). M.p. 172–174 °C.

General Procedure for the Preparation of Bis(thioether) Ligands: BH_3·THF (0.8 mL, 1.0 M in THF, 0.8 mmol, 6 equiv.) was added to a dry THF (3 mL) solution of bis(sulfoxide) (40 mg, 0.13 mmol) at room temperature. After 15 h stirring the mixture was cooled to 0 °C and a saturated aqueous NH_4Cl solution (4 mL) was added slowly. The aqueous layer was then extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with an aqueous saturated $NaHCO_3$ solution (5 mL) and brine (5 mL), dried with anhydrous magnesium sulfate and evaporated under reduced pressure. Flash chromatography (cyclohexane/dichloromethane, 95:5) of the resulting crude product afforded the pure bis(thioether) ligand as a white solid.

(2*R*,2′*R*)-2,3,2′,3′-Tetrahydro-2,2′-bi(benzo[*b*]thiophenyl) (9): Synthesised from **6** in quantitative yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.21 (dd, *J* = 15.9, *J* = 3.9 Hz, 2 H), 3.42 (dd, *J* = 15.9, *J* = 7.1 Hz, 2 H), 4.06–4.15 (m, 2 H), 7.03 (td, *J* = 7.3, *J* = 1.3 Hz, 2 H), 7.09–7.23 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 39.4, 55.0, 122.1, 124.5, 124.7, 127.7, 138.5, 140.1 ppm. MS (CI/NH_3): *m*/*z* = 288 [MNH_4^+], 271 [MH^+]. HRMS: *m*/*z* calculated for $C_{16}H_{15}S_2$ 271.0615 [MH^+]; found 271.0614. IR (powder): $\tilde{\nu}$ = 3060,

Table 1. Crystallographic data and structure refinement for **6**, **13** and **14**

	6	**13**	**14**
Empirical formula	$C_{16}H_{14}O_2S_2$	$C_{16}H_{14}Cl_2PdS_2$	$C_{16}H_{14}Cl_2PdS_2$, CH_2Cl_2
Formula mass	302.42	447.72	532.66
Crystal color	colourless	colourless	orange
Crystal system	monoclinic	trigonal	monoclinic
Space group	$P2_1$ (no. 4)	$P3_2$ (no. 145)	$P2_1/c$ (no. 14)
a [Å]	8.003(1)	14.710(7)	11.3275(6)
b [Å]	7.9984(8)	14.710(7)	12.673(3)
c [Å]	11.212(2)	19.617(9)	13.416(2)
β [°]	102.94(1)	–	95.74(1)
Volume [Å^3]	699.4(2)	3676(3)	1916.3(5)
Z	2	9	4
Radiation type	Mo-K_α	Mo-K_α	Mo-K_α
Wavelength [Å]	0.710730	0.710730	0.710730
Density [g cm^{-1}]	1.44	1.82	1.85
μ [mm^{-1}]	0.378	1.707	1.741
Temperature [K]	295	295	295
Size [mm]	0.04 × 0.12 × 0.5	0.04 × 0.04 × 0.25	0.20 × 0.20 × 0.30
Shape	plate	stick	block
Reflections measured	4469	9314	17994
Independent reflections	2729	6442	3758
R_{int}	0.11	0.16	0.11
θ_{min}, θ_{max}	1, 27.48	1, 25.02	2, 26.00
h_{min}, h_{max}	–10, 6	–16, 15	–13, 13
k_{min}, k_{max}	–10, 6	–17, 16	–15, 14
l_{min}, l_{max}	–11, 14	–23, 21	–16, 16
Refinement	on F	on F	on F
R-factor	0.0448	0.141[17]	0.0440
Weighted R-factor	0.0445	0.131	0.0498
$\Delta\rho_{min}$	–0.40	–2.23	–1.11
$\Delta\rho_{max}$	0.57	1.93	0.89
Reflections used	1809	5240	2032
$\sigma(I)$ limit	1.80	3.00	2.00
Number of parameters	183	329	204
Goodness-of-fit	1.099	1.103	1.094
Flack parameter	0.05(12)	0.04(13)	–

2930, 2870, 1585, 1460, 1445, 1120, 1090, 1060, 945, 730 cm^{-1}. $[\alpha]_D^{25}$ = –160 (c = 1.0, $CHCl_3$). M.p. 129–131 °C.

(2*S*,2′*S*)-2,3,2′,3′-Tetrahydro-2,2′-bi(benzo[*b*]thiophenyl) (10): Synthesised from **7** in quantitative yield. Spectroscopic data were identical to those of **9** except for the specific rotation. $[\alpha]_D^{25}$ = +159 (c = 1.0, $CHCl_3$).

***meso*-2,3,2′,3′-Tetrahydro-2,2′-bi(benzo[*b*]thiophenyl) (11):** Synthesised from **8** in quantitative yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.33 (dd, J = 15.9, J = 3.3 Hz, 2 H), 3.44–3.54 (m, 2 H), 3.81–3.90 (m, 2 H), 7.07 (td, J = 7.6, J = 1.2 Hz, 2 H), 7.13–7.25 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 41.5, 54.4, 122.3, 124.6, 125.0, 127.6, 138.4, 139.6 ppm. MS (CI/NH_3): m/z = 288 [MNH_4^+], 271 [MH^+]. HRMS: m/z calculated for $C_{16}H_{15}S_2$ 271.0615 [MH^+]; found 271.0618. IR (powder): $\tilde{\nu}$ = 3055, 2945, 2895, 1583, 1460, 1445, 1210, 1115, 1060, 945, 735 cm^{-1}. M.p. 150–153 °C.

General Procedure for the Preparation of Palladium(II) Complexes 12, 13 and 14: An equimolar (0.5 M) mixture of either the bis(sulfoxide) **6** or bis(thioether)s **9** or **11** and palladium(II) chloride was stirred at room temperature in dichloromethane for 18 h. The solvent was removed in vacuo to leave an orange solid. Crystallisation of the crude product by slow evaporation of a saturated dichloromethane solution afforded the four desired palladium(II) complexes. Suitable crystals of complexes **13** and **14** could be used for X-ray analyses. M.p. of **13**: 262 °C (dec.); **14**: 168–170 °C.

X-ray Crystallographic Study: Single crystal X-ray data were collected at room temperature on a Nonius KappaCCD diffractometer with graphite monochromated Mo-K_α radiation. A summary of the crystal data, data collection for **6**, **13**, and **14**, and refinement techniques is given in Table 1. The diffraction data were reduced using the EvalCCD[18] program package. Absorption corrections were applied using DIFABS.[19] The structures were solved with SIR92[20] and refined by full-matrix least-squares on F using the programs of the PC version of CRYSTALS[21] with anisotropic thermal parameters for non-hydrogen atoms, when sufficient data were available. Hydrogen atoms were introduced in calculated positions, and only one overall isotropic displacement parameter was refined. CCDC-234009 (for **6**), -234175 (for **13**) and -234010 (for **14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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