Notes

Access to Planar Chirality through Cycloplatination of ((Dimethylamino)methyl)ferrocene by *cis*-[PtCl₂(SOMeAr)₂] (Ar = Phenyl, *p*-Tolyl)

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*Summary: A reaction between ((dimethylamino)methyl)ferrocene and the enantiomerically pure complex cis-[PtCl₂(S-SOMeC₆H₄Me-p)₂] affords the two easily separable cycloplatinated S_SR_P and S_SS_P diastereoisomers **4** and **5**, respectively. The absolute configuration of **4** was established by an X-ray study. Diastereomers **4** and **5** react with PPh₃ to give enantiomers with the planar chirality only.*

Introduction

Cyclometalation has been so well refined¹⁻¹⁰ that a new but standard report in this area seems rather ordinary. However, the knowledge gained by numerous groups of workers is now being used in solving more advanced tasks compared with routine syntheses of new metallacycles. One such task includes the further development of the asymmetric cyclometalation pioneered by Sokolov and co-workers.¹¹ Surprisingly, after nearly 3 decades from the appearance of the first optically active cyclopalladated and cycloplatinated compounds, their number remains limited and, to our knowledge, only the Sokolov approach (palladium(II) salt with an N-protected amino acid) provides *direct* access to enantiomerically enriched metallacycles.¹² In addition to the recently emphasized virtue of planar chiral ferrocenes in various fields of chemistry,¹³ studies in this area are undoubtedly a great challenge. The recent progress in using the platinum(II) complex *cis*-[PtCl₂(dmso)₂] as a cyclometalating agent for sp² C−H bonds¹⁴⁻¹⁷ suggested a synthetic approach to asymmetrically cycloplatinated ferrocenes using Ptᴵᴵ coordinated to enantiomerically pure sulfoxides of the type SOMeAr. The fact that the sulfoxide remains bound to Ptᴵᴵ in the reaction product, unlike amino acid derivatives used as asymmetric inductors by Sokolov, gave hope for their utility in asymmetric cycloplatination and/or subsequent resolution of the planar chiral species formed. In this communication, we present evidence that a platinum(II) complex with enantiomerically pure sulfoxide reacts with a ferrocene derivative to afford a pair of cycloplatinated diastereomers which are extremely easy to separate and can be converted into individual enantiomers with planar chirality.

Results and Discussion

To ensure that Ptᴵᴵ complexes with sulfoxides bulkier than dmso are capable of cycloplatinating ((dimethy-

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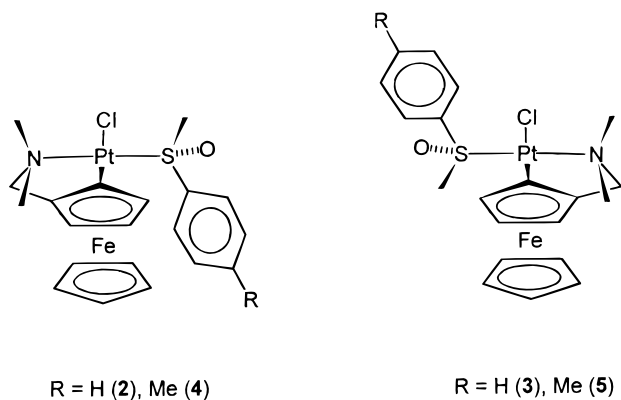(13) Togni, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1475.
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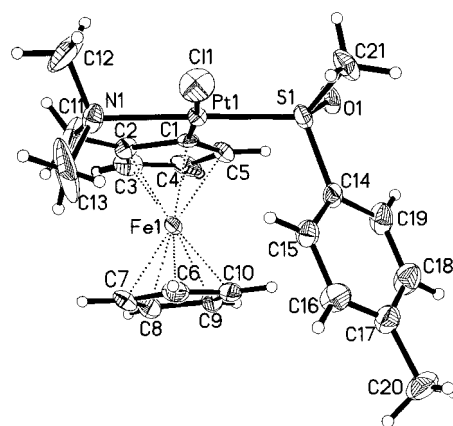(17) Ryabov, A. D.; Kazankov, G. M.; Panyashkina, I. M.; Grozovsky, O. V.; Dyachenko, O. G.; Polyakov, V. A.; Kuz'mina, L. G. *J. Chem. Soc., Dalton Trans.* **1997**, 4385.

lamino)methyl)ferrocene (**1**), the reaction of the latter with *cis*-[PtCl₂(*rac*-SOMePh)₂] was performed under the conditions elaborated by Ranatunge-Bandarage et al.[14] Among the other ferrocene derivatives tested, viz. acetylferrocene and (aminocarbonyl)ferrocene oximes, **1** provided the highest yield in the reaction with *cis*-[PtCl₂-(dmso)₂]. According to TLC, the interaction between **1** and *cis*-[PtCl₂(*rac*-SOMePh)₂] afforded two major products which were separated and thoroughly characterized. The ¹H NMR spectra were consistent with their formulation as a pair of racemic diastereomeric cycloplatinated compounds with different orientations of the sulfoxide ligand with respect to the iron and/or nonmetalated cyclopentadienyl ring; i.e., the sulfoxide phenyl ring was directed toward and opposite the C_5H_5 ring in the cases of **2** and **3**, respectively. The proof comes from the ¹H NMR spectra of **2** and **3**. A singlet from the C_5H_5 ring in **2** is seen at δ 3.60, which is 0.59 ppm upfield compared to that in **3**, due to the ring current effect from the sulfoxide phenyl group. There is no shielding for the corresponding singlet in **3**, since the C_5H_5 and phenyl rings are spatially separated. According to the ¹H NMR spectral data, compounds **2** and **3** have no tendency to rearrange into each other in a d_8-toluene solution in the temperature range 230−316 °C.
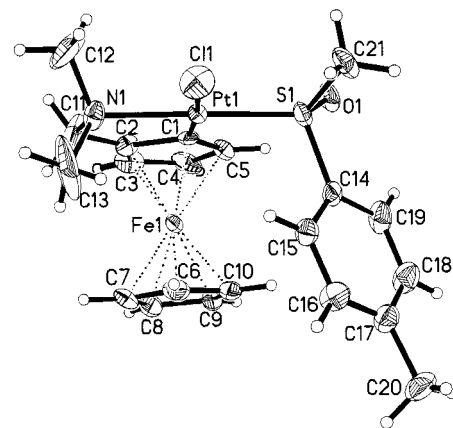

Figure 1. Crystal structure of complex **3**. Thermal ellipsoids are drawn at the 30% probability level.

Figure 2. Crystal structure of complex **4**. Thermal ellipsoids are drawn at the 30% probability level.

R = H (**2**), Me (**4**)   R = H (**3**), Me (**5**)

The cycloplatination of **1** by the enantiomerically pure complex *cis*-[PtCl₂(*S*-SOMeC₆H₄Me-*p*)₂] (the absolute configuration of sulfur is indicated for the *coordinated* ligand) was carried out in the same way as for the racemic complex to afford diastereomers **4** and **5** in 21 and 16.5% yields, respectively. Remarkably, the diastereomerically pure compound **4** crystallized from the reaction solution and no TLC was needed to isolate it. Its ¹H NMR spectrum, which had only one set of signals, indicated that complex **4** is structurally similar to **2**, since the singlet from the C_5H_5 ligand appeared at δ 3.62. In the mother liquor, diastereomer **5**, which is analogous to **3**, was found and recovered using preparative TLC. It should be pointed out that that the ¹H NMR spectrum of **5** consisted of two sets of signals. The material was presumably contaminated by either **4** and/or an analogue of **5** in which the tolyl group is directed at the C_5H_5 ring, provided the rotational barrier around the Pt−S bond is large at least for steric reasons in this case.

The geometry of the complexes discussed above was supported by X-ray structural studies of **3** and **4** (Figures 1 and 2, respectively). The key conclusions are as follows. (i) The absolute configuration of the sulfoxide sulfur remains unchanged during the course of cycloplatination. (ii) Whereas complex **3** is racemic, comprising of R_SR_P (as in Figure 1) and S_SS_P stereoisomers, complex **4** is stereochemically pure and only a S_SR_P stereoisomer is present. (iii) Diastereomers **2/3** and **4/5** have differently oriented sulfoxide aryl groups, and the X-ray and ¹H NMR data are in perfect agreement. (iv) The fact that the *p*-tolyl ring is directed at the C_5H_5 group, providing an H(10)···C(19) distance of 2.939 Å (a sum of the van der Waals radii) in **4**, accounts for a 20° staggered conformation of the Cp rings. The opposite orientation of the phenyl ring in **3** is accompanied by an eclipsed configuration, as observed for other cycloplatinated ferrocene derivatives.[14,16−19] The platinum center has a square-planar environment. The bond lengths and angles in molecules **3** and **4** are in the same range as recently reported.[14,16−19] The Pt−C bond distances equal 1.990(4) and 1.975(8) Å, and the Pt−Cl bond distances are 2.4061(9) and 2.395(2) Å for **3** and **4**, respectively. Structural features of the coordinated sulfoxide also seem to be normal.[20]

Platinacycles **2**, **4**, and **5** were treated with a 5% excess of PPh₃ in benzene at 70 °C for 1 h to afford the

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complexes (R_P,S_P)-**6**, (R_P)-**6**, and (S_P)-**6** with $[\alpha]_D$ (*c* 0.4, CHCl$_3$) equal to 0, +43.7, and −23.7°, respectively, with the coordinated achiral phosphine instead of asymmetric sulfoxides (eq 1). The structure of **6** was established
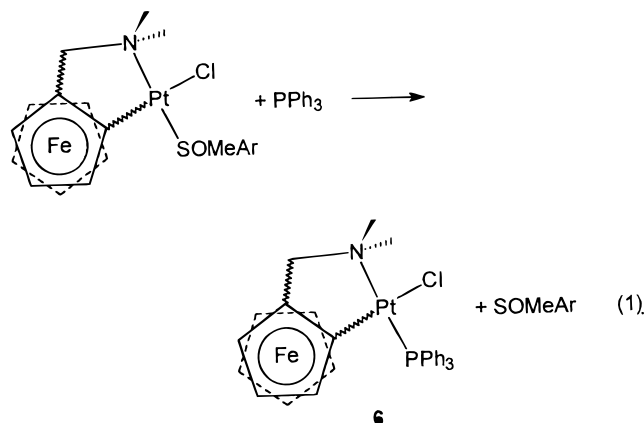
on the basis of the ^{1}H NMR and IR data. No sulfoxides were coordinated to platinum in **6** (abscence of strong S=O bands in the region 1140−1130 cm^{-1}), whereas the Pt−N bond was preserved ($^4J_{PH}$ = 2.3 Hz at the NCH$_3$ signals). The CD spectra of **6** showed that a sample derived from **2** is racemic, as expected, whereas those from **4** and **5** are enantiomerically enriched. The spectra of the last two mirror each other, and in the case of (R_P)-**6**, in particular, the strongly positive and negative CD effects are observed around 470 and 335 nm, respectively, together with a crossover point at 357 nm. A comparison of the $[\alpha]_D$ values for (R_P)-**6** and (S_P)-**6** allows us to estimate the enantiomeric purity of (S_P)-**6**. Taking into account that (R_P)-**6** was derived from a diastereomerically homogeneous material and assuming that the optical purity of the "planar chiral" center is unaffected by reaction 1, it follows that the enantiomeric purity of (S_P)-**6** equals 54% ee.

The X-ray data reported here and elsewhere[17] together with the CD measurements allow us to understand the origin of different orientations of the aryl groups of the coordinated sulfoxide with respect to the C$_5$H$_5$ ring observed by ^{1}H NMR. It has recently been indicated[17] that the oxygen atom of dmso is involved in hydrogen bonding with the hydrogen of the C−H bond of the platinated Cp ring (O(1) and H(5) atoms in Figure 2). This bonding should retard an easy rotation around the Pt−S bond, implying that the *p*-tolyl group must be directed toward and opposite the C$_5$H$_5$ ring in the cases of **4** and **5**, respectively.

There is an interesting observation that throws light on the mechanism of the cycloplatination. It should first be indicated that **4** and **5** are isolated in similar yields, viz. 21 and 16.5%, respectively. Second, the X-ray data reveal that platination by *cis*-[PtCl$_2$(*rac*-SOMePh)$_2$] and *cis*-[PtCl$_2$(*S*-SOMeC$_6$H$_4$Me-*p*)$_2$] affords species with different planar chirality, the central sulfur chirality being the same. In particular, **4** is a S_SR_P compound (Figure 2) and, if the cycloplatination were in fact distereospecific, the product with the same "planar" configuration (R_P) should be S_S configured at sulfur. As seen in Figure 1, one of the enantiomers of racemic complex **3** is, however, a R_SR_P diastereomer rather than the expected S_SR_P one. Therefore, it seems likely that the

cycloplatination is not very stereoselective by itself and the process reported is a successful combination of less stereoselective cyclometalation and much more efficient resolution of enantiomers.

In conclusion, we have shown an easy entry to both enantiomers of a planar chiral compound which is based on *cycloplatination* of ferrocenes with a chelate arm by enantiomerically pure platinum(II) sulfoxide complexes of the type *cis*-[PtCl$_2$(SOMeAr)$_2$]. Unfortunately, neither we nor other workers[14,16,19] have been able yet to develop a successful functionalization procedure for cycloplatinated ferrocenes. However, our first preliminary results show that the chemistry reported here can be extended to palladium(II) compounds, which are recognized starting materials in fine organic synthesis.[5,21]

Experimental Section

The starting complexes were prepared according to Price et al.[22] A 3-fold excess of the sulfoxide (*R*)-methyl *p*-tolyl sulfoxide or methyl phenyl sulfoxide (Aldrich) was added to a solution of K$_2$PtCl$_4$ in 5 mL of water and the mixture stirred for 48 h to form a white precipitate (90%). (Note that the sign of the sulfoxide changes upon complexation.) Satisfactory C, H, S anaylsis was obtained. IR (KBr, cm^{-1}): *cis*-[PtCl$_2$(*rac*-SOMePh)$_2$] 1145 and 1155; *cis*-[PtCl$_2$(*S*-SOMeC$_6$H$_4$Me-*p*)$_2$] 1150 (s, sh, S=O). $[\alpha]_D^{25}$ = −160° (*c* = 0.283, acetone). *cis*-[PtCl$_2$(*rac*-SOMePh)$_2$] was a mixture of *meso* and *RR/SS* stereoisomers in a 0.33:1 ratio (^{1}H NMR); *cis*-[PtCl$_2$(*S*-SOMeC$_6$H$_4$Me-*p*)$_2$] was a single stereoisomer.

Complexes 2 and 3. **1** (99 mg, 0.4 mmol) and [PtCl$_2$(*rac*-SOMePh)$_2$] (231.5 mg, 0.42 mmol) were mixed in 16 mL of absolute MeOH and refluxed for 4 h. The yellow heterogeneous mixture turned into a crimson solution after 1 h, from which an orange material began to precipitate. Two products were observed by TLC (Silufol) with R_f 0.7 and 0.5 (C$_6$H$_6$/acetone 9.5:0.5). After the reaction was completed, the precipitate was filtered off and dried to give 80.7 mg of mostly the product with R_f 0.5. The mother liquor contained mostly the product with R_f 0.7. Both fractions were purified by preparative TLC on SiO$_2$ with benzene/acetone (9:1) as eluent. The products with R_f 0.7 and 0.5 were washed off from SiO$_2$ with acetone and CHCl$_3$, respectively; with solvents removed, 50.2 (25%) and 31.5 mg (16%) of the compounds with R_f 0.5 and 0.7, respectively, were obtained. Analytically pure samples were obtained on recrystallization from C$_6$H$_6$/petroleum ether and MeOH, respectively. **2** (R_f 0.5): mp 193 °C; ^{1}H NMR (CDCl$_3$, δ, *J* in Hz) 3.03 (s, NCH$_3$, *J* 33), 3.27 (s, NCH$_3$, *J* 31), 3.60 (bs, NCH$_2$, *J* 29.2), 3.60 (s, C$_5$H$_5$), 3.64 (s, SCH$_3$, *J* 21.2), 4.01 and 4.02 (s, H(3) and H(4)), 4.41 (s, H(5)), 7.60−7.66 (m, 3H, Ph), 8.28−8.32 (m, 2H, Ph). Anal. Found: C, 39.04, 38.81; H, 4.07, 4.04; N, 2.24. Calcd for C$_{20}$H$_{24}$NSOClFePt: C, 39.20; H, 3.95; N, 2.29. **3** (R_f = 0.7): mp 183 °C; ^{1}H NMR (CDCl$_3$, δ, *J* in Hz) 2.91 (s, NCH$_3$, *J* 33.6), 3.28 (s, NCH$_3$, *J* 31.8), 3.65 (s, SCH$_3$, *J* 20.5), 4.01 (bs, NCH$_2$), 4.19 (s, C$_5$H$_5$), 4.41 (s, H(5)), 7.49−7.50 (m, 3H, Ph), 8.10−8.16 (m, 2H, Ph).

Complexes 4 and 5. **1** (81.5 mg, 0.335 mmol) and [PtCl$_2$(*S*-OSMeC$_6$H$_4$Me-*p*)$_2$] (206 mg, 0.358 mmol) were refluxed in 15 mL of MeOH as above. Brownish red crystals started to form after 1 h. The TLC analysis (benzene/acetone 9:1) showed two products with R_f 0.65 and 0.45. The reaction mixture was kept at +5 °C for 3 days to afford brownish red crystals, which were washed with hexane and dried; R_f 0.45 (43.8 mg, 21%). The product **5** with R_f 0.65 (34.8 mg, 16.5%) was recovered from the mother liquor by TLC. **4** (R_f 0.45): mp 103 °C; ^{1}H NMR

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(CDCl$_3$, δ, J in Hz) 2.45 (s, CH$_3$), 3.02 (s, NCH$_3$, J 34), 3.25 (s, NCH$_3$, J 31), 3.50 (bs, NCH$_2$, J 30.6), 3.62 (s, C$_5$H$_5$), 3.61 (s, SCH$_3$, J 20.2), 4.01 and 4.06 (s, H(3) and H(4)), 4.45 (s, H(5)), 7.41, 7.45, 8.14, and 8.18 (AA′BB′, C$_6$H$_4$). Found: C, 39.95, 39.93; H, 4.31; N, 2.23. Calcd for C$_{21}$H$_{26}$NSOClFePt: C, 40.24; H, 4.18, N, 2.23.

Crystal Structure Analyses. A Siemens SMART diffractometer was used, with Mo Kα radiation (graphite monochromator, $\lambda = 0.710\ 73$ Å, $T = 150$ K). **3**: light brown crystals, crystal dimensions $0.56 \times 0.10 \times 0.08$ mm, C$_{20}$H$_{24}$ClFeNOPtS, $M_r = 612.85$, $a = 30.5504(6)$ Å, $b = 30.5504(6)$ Å, $c = 11.1282$-(6) Å, $V = 8994.8(2)$ Å^3; hexagonal, space group $R\bar{3}$, $Z = 18$, $\rho_{calcd} = 2.037$ g cm^{-3}, $\mu = 7.964$ mm^{-1}, 4247 independent reflections with $1.33 \leq \theta \leq 26.75°$. The structure was solved by full-matrix least squares on F^2 (SHELXL-93).[23] All H atoms were found from difference Fourier synthesis and refined with isotropic thermal parameters. Final R indices ($I > 2\sigma(I)$) R1 $= 0.0228$ and wR2 $= 0.0484$. Selected bond distances: (Å): Pt−C(1), 1.990(4); Pt−N, 2.136(3); Pt−S, 2.1973(9), Pt−Cl, 2.4061(9); S−O, 1.473(3). Selected bond angles (deg): C(1)−Pt−N, 82.35(14); C(1)−Pt−S 93.12(11); N−Pt−S, 175.25(9); N−Pt−Cl, 90.72(9); S−Pt−Cl, 93.89(4). **4**: brownish red crystals, crystal dimensions $0.55 \times 0.16 \times 0.07$ mm; C$_{21}$H$_{26}$-ClFeNOPtS, $M_r = 626.88$, $a = 10.4742(2)$ Å, $b = 9.5587(2)$ Å, $c = 10{,}8507(2)$ Å, $\beta = 101.3693(3)°$, $V = 1065.07(4)$ Å^3; monoclinic, space group $P2_1$, $Z = 2$, $\rho_{calcd} = 1.955$ g cm^{-3}, $\mu =$

7.476 mm^{-1}, 4553 independent reflections with $1.91 \leq \theta \leq 25.57°$. The structure was solved by full-matrix least squares on F^2 (SHELXL-93).[23] All H atoms were calculated in ideal positions and refined using the riding model with B(iso) $=$ $1.5B$(eq) of the parent carbon atom. Final R indices ($I > 2\sigma$-(I)) R1 $=0.0424$ and wR2 $= 0.1055$. Selected bond distances: (Å): Pt−C(1), 1.975(8); Pt−N, 2.141(7); Pt−S, 2.197(2); Pt−Cl, 2.395(2); S−O, 1.473(6). Selected bond angles (deg): C(1)−Pt−N, 82.9(3); C(1)−Pt−S, 92.9(2); N−Pt−S, 175.8(2); N−Pt−Cl, 91.2(2); S−Pt−Cl, 92.95(8). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-100667.

Supporting Information Available: Tables of X-ray experimental details, positional and thermal parameters, bond lengths, and bond angles for the crystal structures of **3** and **4** (14 pages). Ordering information is given on any current masthead page.

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