Asymmetric synthesis of sulfinyl-substituted arene chromium tricarbonyl complexes

Stephen G. Davies,*[a] Tracey Loveridge,[a] M. Fatima C. C. Teixeira[a] and John M. Clough[b]

[a] *Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QY*
[b] *ZENECA Agrochemicals, Jealott's Hill Research Station, Bracknell, Berkshire, UK RG12 6EY*

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The synthesis of (SRS_S)-[(phenylsulfinyl)benzene] chromium tricarbonyl **5** and (SRS_S)-[(*p*-tolylsulfinyl)benzene] chromium tricarbonyl **6** is achieved *via* a nucleophilic displacement reaction between the anion derived from (benzene) chromium tricarbonyl **9** and a suitable sulfinate ester. Replacing the sulfinate ester with a chiral sulfinyl-transfer reagent allows the isolation of the non-racemic sulfinyl-substituted complexes with good enantioselectivities (ee 80–89%) under optimised conditions. The use of Kagan's cyclic sulfite methodology for the synthesis of an enantiomerically pure *tert*-butylsulfinyl complex is unsuccessful, but results in the identification of a novel fragmentation–isomerisation process of the intermediate sulfinate.

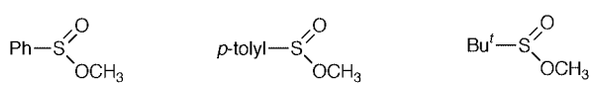
Introduction

The use of chiral arene chromium tricarbonyl complexes in asymmetric synthesis is well established. However, the relative paucity of methods for obtaining such complexes in homochiral form has reduced the scope of this methodology. In the past, homochiral complexes have been accessed *via* chemical[1] or enzymic kinetic resolutions[2] or by the diastereoselective complexation of a di- or tri-substituted benzene derivative carrying a stereogenic centre on one of the side-chains.[3] Since 1,2-differentially substituted arene chromium tricarbonyl complexes are chiral and have been shown to undergo highly stereoselective reactions, particular attention has recently been focused on their asymmetric synthesis, either by the attachment of a chiral auxiliary to the complexed arene ring in order to accomplish diastereoselective *ortho*-deprotonation,[4] or by the use of a homochiral base to achieve enantioselective *ortho*-deprotonation.[5] However, almost all the reported routes to enantiomerically pure arene chromium tricarbonyl complexes require the presence of a side-chain which cannot subsequently be cleaved, rendering them substrate specific. We envisaged that a novel combination of sulfoxide and arene chromium tricarbonyl chemistries, *via* the introduction of a sulfoxide substituent onto the complexed arene ring, would allow access to a homochiral complex. Furthermore, the sulfoxide functionality was anticipated to induce regio- and stereoselective *ortho*-deprotonation, whilst being a latent source of its *ipso* anion, thus being removable or replaceable at a subsequent stage.

In a series of excellent papers Thomas and co-workers have reported the diastereoselective oxidation of an *ortho*-substituted alkylthio complex using dimethyldioxirane to achieve the first documented synthesis of an alkylsulfinyl-substituted arene chromium tricarbonyl complex.[6] In an extension of this methodology these workers have recently published the direct asymmetric oxidation of (methylthiobenzene) chromium tricarbonyl, employing Kagan's modified Sharpless reagent, to give the required sulfoxide with 83% enantiomeric excess (ee). However, despite the efficacy of this methodology in achieving an asymmetric oxidation of this complex it is completely ineffective for other alkylthio or arylthio substituents.[7] We envisaged an alternative simple approach to the synthesis of homochiral sulfinyl-substituted arene chromium tricarbonyl complexes, *via* a nucleophilic displacement reaction between the anion derived by deprotonation of (benzene) chromium tricarbonyl and a suitable chiral sulfinyl-transfer reagent, and report herein our studies towards this goal. Part of this work has been the subject of a preliminary communication.[8]

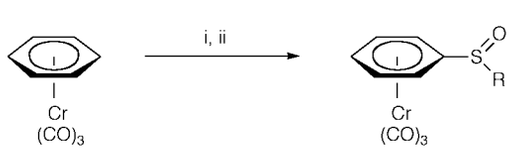
Results and discussion

The methyl benzene-, methyl toluene-*p*- and methyl 1,1-dimethylethanesulfinates **1**, **2**, and **3** were all prepared in reasonable to good yields according to literature procedures,[9] whilst (benzene) chromium tricarbonyl **4** was synthesised by the thermolysis of benzene with chromium hexacarbonyl in a mixture of dibutyl ether and THF (10:1).



1 **2** **3**

With these starting materials in hand the synthesis of a sulfinyl-substituted arene chromium tricarbonyl complex was attempted. Complex **4** was dissolved in THF and cooled to −78 °C before being treated with butyllithium and stirred for 2 h, in order to effect aryl deprotonation.[10] The resulting brown solution was then slowly added to a solution of **1** in THF at −78 °C and the reaction mixture stirred at this temperature for 14 h. Work-up and crystallisation led to the isolation of **5** as yellow–orange needles in good yield (71%), representing a significant improvement on the 55% yield achieved by Thomas and co-workers *via* dimethyldioxirane oxidation of the corresponding sulfide complex.[7] The synthesis of **6** was achieved in an analogous manner to give the novel complex as yellow–orange needle-like crystals in good yield (64%) (Scheme 1).

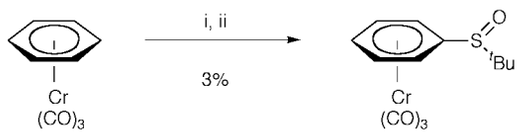


4 **5** R=Ph (71%)
6 R=*p*-tolyl (64%)

Scheme 1 *Reagents and conditions*: i, BuLi (1.1 equiv.), −78 °C; ii, **1** or **2** (1.3 equiv.), −78 °C.

In the synthesis of both **5** and **6**, the slow inverse addition protocol described was found to be vital in order to obtain good yields. Alternative procedures were found to afford significant quantities of a very polar by-product which appeared to account for the reduced yields observed.[11]

It was anticipated that this methodology could also be applied to the synthesis of the *tert*-butylsulfinyl complex **7**. Reaction of **4** with **3**, in an analogous manner to the synthesis of **5**, gave low conversion to the required product as indicated by TLC analysis of the crude reaction mixture. Hence, the reaction was allowed to warm to 0 °C over 2.5 h before work-up. Unfortunately, ^{1}H NMR spectroscopic analysis of the crude product showed the presence of only a trace of **7**. Column chromatography allowed isolation of returned starting material **4**, followed by **7** as a yellow oil in low yield (3%) which had an identical ^{1}H NMR spectrum to that described in the literature (Scheme 2).[7] This disappointing result has been attributed to



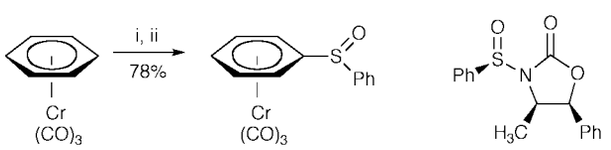
4 **7**

Scheme 2 *Reagents and conditions*: i, BuLi (1 equiv.), −78 °C; ii, **3** (1.4 equiv.), −78 to 0 °C.

the steric bulk of both **3** and the reacting anion of **4** which appears to prevent close approach of the anion to the sulfur centre precluding reaction. Increasing the reaction temperature did not improve this situation, resulting only in an increased amount of an unidentified, very polar by-product.

With the racemic complexes **5**, **6** and **7** in hand it was anticipated that the above methodology could be extended to the synthesis of the corresponding homochiral complexes, by employing a suitable chiral sulfinyl-transfer reagent in place of the racemic sulfinate ester used previously.

For the preparation of (S_S)-**5** the Evans' sulfinyl transfer reagent (4*R*,5*S*,R_S)-**8** derived from (1*S*,2*R*)-norephedrine was identified as a candidate worthy of investigation due to its efficacy in the synthesis of homochiral sulfoxides, achieved *via* a clean S_N2 displacement reaction at the sulfur stereocentre on treatment with an appropriate nucleophile. Hence, (4R,5S,R_S)-**8** was synthesised in good yield according to the literature procedure.[12] Reaction of (phenyllithium) chromium tricarbonyl **9** with (4*R*,5*S*,R_S)-**8** (1.2 equiv.) in THF at −78 °C over a 19 h period led to isolation of "(S_S)"-**5** in 78% yield but with an ee of just 8% as determined by ^{1}H NMR spectroscopic studies employing the chiral solvating agent (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-methylbenzylamine[13] (Scheme 3).

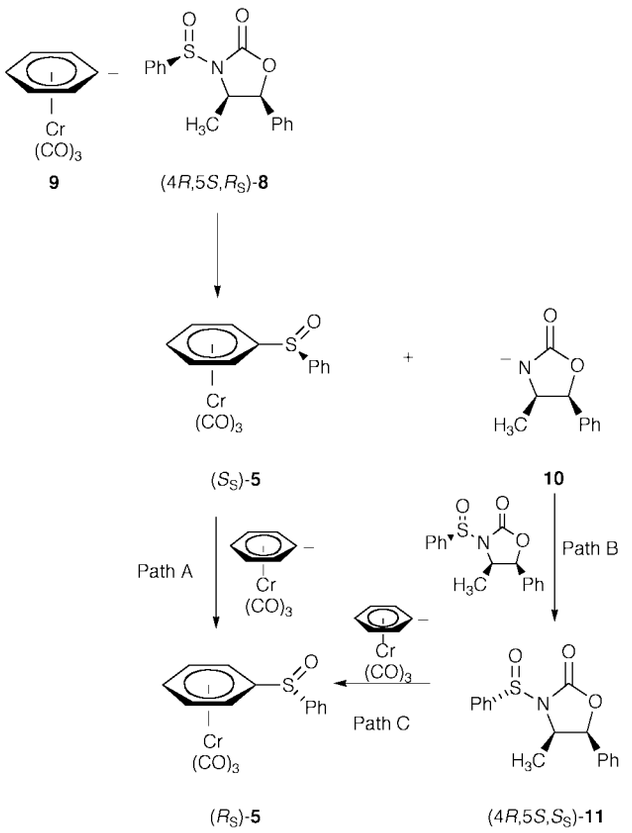


4 ee 8% (4*R*,5*S*,R_S)-**8**

5

Scheme 3 *Reagents and conditions*: i, BuLi (1 equiv.), −78 °C; ii, (4*R*,5*S*,R_S)-**8** (1.2 equiv.), −78 °C.

This unexpected and disappointing result focused attention on the identification of possible routes for the racemisation occurring in this reaction. Two such pathways were recognised as feasible, as illustrated in Scheme 4. Initial reaction between anion **9** and (4*R*,5*S*,R_S)-**8** must generate the homochiral complex (S_S)-**5**. However, any unchanged **9** may now react with

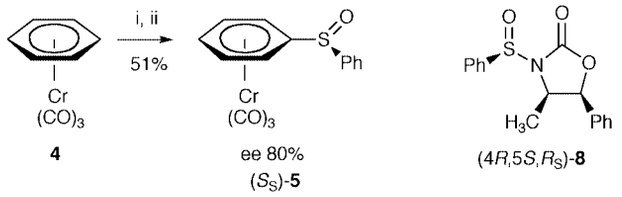


Scheme 4

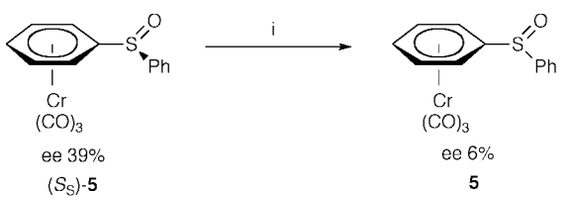
(S_S)-**5** in preference to the required reaction with (4*R*,5*S*,R_S)-**8**, resulting in racemisation at the sulfur centre of the newly formed complex (path A) and reflecting the stability of **9**. Furthermore, the initial step in this sequence generates an oxazolidinone anion **10**. This in turn may react with (4*R*,5*S*,R_S)-**8**, epimerising the sulfur centre of the sulfinyl-transfer reagent to give (4*R*,5*S*,S_S)-**11** (path B). Obviously, reaction of this with the anion of **4** will also form the unwanted enantiomer of **5** (path C). This path B/path C racemisation route was identified by Evans and used to explain the reduced enantiomeric purities of the sulfoxides obtained on reaction of the related sulfinyl-transfer reagent (4*S*)-4-benzyl-3-[(*S*)-*p*-tolylsulfinyl]-isoxazolidin-2-one with organolithium reagents.[12]

With these ideas in mind it was apparent that alteration of the reaction conditions should allow isolation of (S_S)-**5** of improved enantiomeric purity. Thus, a cooled (−100 °C) THF solution of the anion of **4** was added rapidly to (4*R*,5*S*,R_S)-**8** (10 equiv.) in THF at the same temperature. On completion of the addition the reaction was quenched immediately using saturated aq. ammonium chloride and worked up. ^{1}H NMR analysis of the crude material indicated 68% conversion to product and the diastereomeric purity of **8** to be eroded to 94%, validating path B and therefore path C as a route to racemisation in this synthesis. Column chromatography allowed the components of the mixture to be separated, the first fraction affording a white solid which on crystallisation gave (4*R*,5*S*,R_S)-**8** as white needles (72%). The second fraction yielded "(S_S)"-**5** (51%) with a much improved ee of 80% (Scheme 5). Unfortunately, this enantiomeric purity could not be reliably improved upon by crystallisation.[14]

Despite the identification of path B as a route to racemisation the lower enantiomeric purity of the sulfoxide, compared with that of the sulfinyl-transfer reagent, indicated that a second racemisation pathway must also be in operation. Hence, a −100 °C solution of (phenyllithium) chromium tricarbonyl **9** was rapidly added to a solution of **5** (ee 39%) in THF at −100 °C. Immediate quenching furnished "(S_S)"-**5** of only



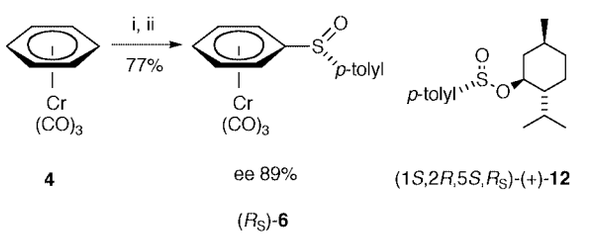
Scheme 5 *Reagents and conditions*: i, BuLi (1 equiv.), −78 °C; ii, (4*R*,5*S*,R_S)-**8** (10 equiv.), −100 °C.



Scheme 6 *Reagents and conditions*: i, **9** (0.6 equiv.), −100 °C.

6% enantiomeric excess, as determined by ^{1}H NMR chiral shift studies (Scheme 6). This result served to confirm the operation of path A in the racemisation process. Indeed, the rapid racemisation observed made the obtention of a scalemic sulfoxide by the above methodology all the more remarkable.

The synthesis of (R_S)-**6** was attempted in a manner analogous to that for (S_S)-**5**, employing (1*S*,2*R*,5*S*,R_S)-(+)-menthyl toluene-*p*-sulfinate **12** as the chiral sulfinyl-transfer reagent. As previously, duplication of the reaction conditions used for the synthesis of its racemic counterpart, replacing **2** with (1*S*,2*R*,5*S*,R_S)-(+)-**12**, afforded "(R_S)"-**6** with a low ee of 37%. However, rapid quenching of the reaction between (phenyllithium) chromium tricarbonyl **9** and (1*S*,2*R*,5*S*,R_S)-(+)-**12** (9.5 equiv.) at −100 °C afforded "(R_S)"-**6** in good yield (77%) and enantiomeric purity (ee 89%) (Scheme 7). (1*S*,2*R*,5*S*,R_S)-(+)-

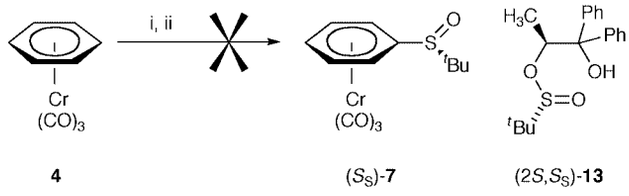


Scheme 7 *Reagents and conditions*: i, BuLi (1 equiv.), −78 °C; ii, (1*S*,2*R*,5*S*,R_S)-(+)-**12** (10 equiv.), −100 °C.

12 was isolated diastereomerically pure, indicating that in this instance the sulfinyl-transfer reagent is unlikely to be implicated in any racemisation pathway. A path A-type racemisation process is proposed as the only viable mechanism for the observed racemisation and was confirmed by the reaction of the anion of **4** with **6** (ee 68%) at −100 °C. Allowing reaction between these two substrates for 5 min before quenching and work-up afforded **6** in essentially racemic form (2% ee).

For the attempted synthesis of a homochiral *tert*-butylsulfinyl chromium tricarbonyl complex, the cyclic sulfite methodology developed by Kagan[15] was considered to be the most appealing, as simple alteration of the order of addition of the two nucleophilic reagents should allow access to both enantiomers of the required complex.

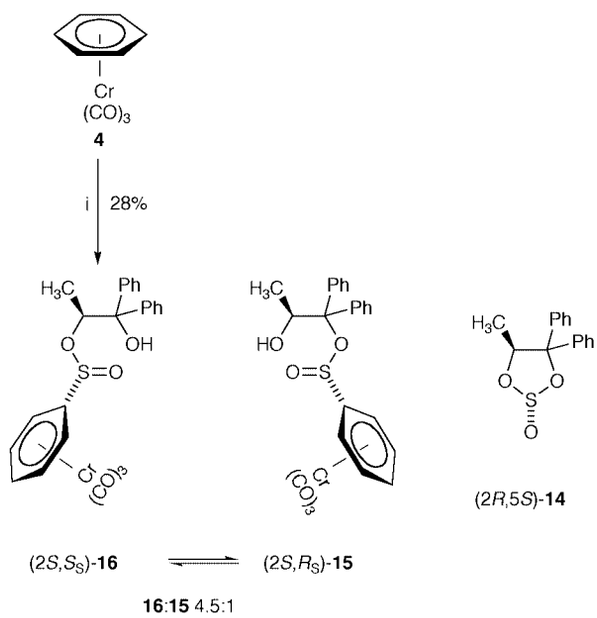
The route to (S_S)-**7** was anticipated to be straightforward, involving the intermediacy of the known compound (2*S*,S_S)-3-hydroxy-3,3-diphenylpropyl 1,1-dimethylethanesulfinate **13**.[15] Hence, a solution of the anion of **4** (2.3 equiv.) in THF at −78 °C was added over 40 min to (2*S*,S_S)-**13** in THF at the same temperature, and the resultant solution allowed to warm to ambient temperature over 16 h. However, inspection of the ^{1}H NMR spectrum of this crude material indicated only the presence of starting materials (Scheme 8). By analogy with the



Scheme 8 *Reagents and conditions*: i, BuLi (1.1 equiv.), −78 °C; ii, (2*S*,S_S)-**13** (0.4 equiv.), −78 °C to rt.

low yield achieved in the synthesis of *rac*-**7**, it was assumed that steric encumbrance once again accounted for the lack of reactivity seen.

It was considered that reversing the order of addition of the two nucleophilic reagents should circumvent this problem. Thus, treatment of a cooled (−78 °C) THF solution of (2*R*,5*S*)-*trans*-5-methyl-4,4-diphenyl-1,3,2-dioxathiolane 2-oxide **14** with the anion of **4** (0.9 equiv.) gave a yellow solid shown to comprise a mixture of the regioisomers (2*S*,R_S)-**15** and (2*S*,S_S)-**16** in the ratio 1:4.5, together with 50% unchanged starting material by ^{1}H NMR spectroscopy (Scheme 9). Attempted



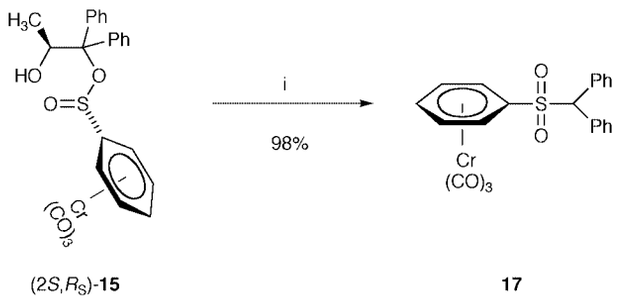
Scheme 9 *Reagents and conditions*: i, BuLi (1.1 equiv.), −78 °C; ii, (2*R*,5*S*)-**14** (1.1 equiv.), −78 °C.

crystallisation from hexane–dichloromethane (2:1) led to the isolation of the minor diastereomer (2*S*,R_S)-**15** as a yellow powder (15% yield). Further crystallisation of the mother liquors afforded a second crystalline fraction as orange rods (13% yield) shown to be a 1.3:1 mixture of (2*S*,R_S)-**15** and (2*S*,S_S)-**16** by ^{1}H NMR spectroscopic analysis. Calculation of the combined yield of compound **15** showed it to have been isolated in greater than 100% mass balance from the original mixture, consistent with an *in situ* regioisomerisation to the more stable regioisomer (2*S*,R_S)-**15**. This is particularly surprising in the light of the observation by Kagan that the corresponding (2*S*,R_S)-1,1-dimethylethanesulfinate analogue decomposed at room temperature to give diphenylacetone.

The regioisomeric assignment was confirmed by the ^{1}H NMR spectra of (2*S*,R_S)-**15** and (2*S*,S_S)-**16**. That of (2*S*,R_S)-**15** demonstrated a distinctive multiplet at δ 5.18–5.15 [HOC*H*-(CH_3)] due to coupling of this hydrogen with both the adjacent methyl and hydroxy hydrogens, which is only possible in this regioisomer. By contrast, a simple quartet (δ 5.59, 1H, q, *J* 6.4, CH_3C*H*) was observed for the corresponding proton in the spectrum for (2*S*,S_S)-**16**. It is reasonable to assume that the anion of **4** can be regarded as a bulky nucleophile; hence,

the sense of regioselectivity observed in the cleavage of the cyclic sulfite is in agreement with the model proposed by Kagan.[15]

With the pure complex (2*S*,R_S)-**15** in hand the preparation of (S_S)-**7** was attempted. Treatment of a THF solution of (2*S*,R_S)-**15** with *tert*-butylmagnesium chloride (2.2 equiv.) furnished a yellow crystalline solid shown to comprise a single compound (98% yield) by ^{1}H NMR spectroscopy (Scheme 10). However,

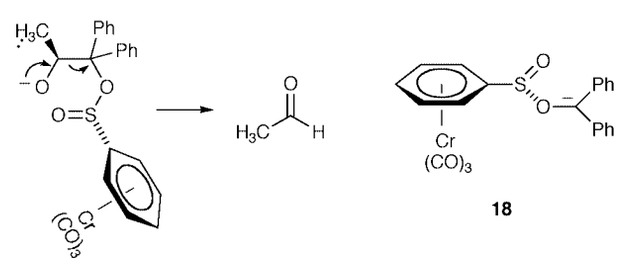


Scheme 10 *Reagent*: i, ^{t}BuMgCl (2.2 equiv.).

none of the observed signals corresponded to those seen in the ^{1}H NMR spectrum of *rac*-**7**. Instead, two triplets and a doublet were observed in the region δ 5.56–4.94. In addition, a distinctive one-proton singlet at δ 5.33 and two aromatic multiplets [δ 7.61–7.57 (4H, m, Ph), 7.39–7.36 (6H, m, Ph)] were noted. IR spectroscopy showed two strong absorptions at 1329 and 1145 cm^{-1}, indicative of a sulfone functional group, in addition to the two very strong absorption bands at 1996 and 1937 cm^{-1} corresponding to the stretching modes of the CO ligands.[16] On this basis the compound was tentatively assigned as benzhydryl (phenyl) chromium tricarbonyl sulfone **17** although the alternative [(benzhydrylsulfinyl)benzene] chromium tricarbonyl structure could not be discounted.

Confirmation of the structure of **17** was achieved by subjecting this complex to standard oxidative decomplexation conditions to give benzhydryl phenyl sulfone, shown to be identical to an independently synthesised, authentic sample by ^{1}H and ^{13}C NMR spectroscopy.

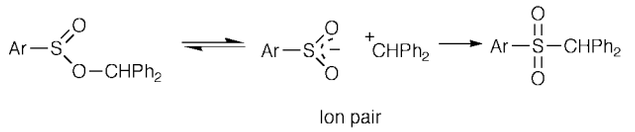
The generation of **17** is postulated to occur *via* a fragmentation of the initially generated alkoxide anion as illustrated (Scheme 11), facilitated by the ability of the benzhydryl group



Scheme 11

to stabilise the negative charge in the resultant carbanion **18**. It is noteworthy that Kagan and co-workers did not witness this fragmentation process, as in all cases they reported quantitative conversion of the intermediate sulfinate to the required sulfoxide. It is possible that the steric bulk at the sulfur centre in (2*S*,R_S)-**15**, due to the presence of the (benzene) chromium tricarbonyl fragment, reduces the propensity for reaction between the sulfinate and the second equivalent of the Grignard reagent present, resulting in the alternative reaction pathway observed being favoured.

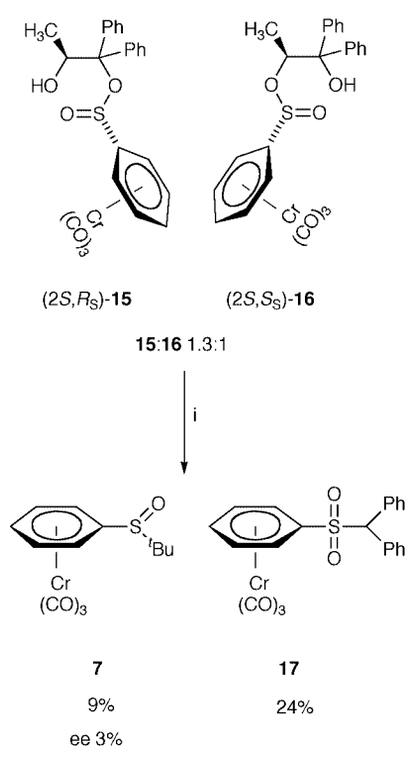
The rearrangement of sulfinate esters to sulfones has been the subject of extensive investigation.[18] Darwish and McLaren have studied the rearrangement of benzhydryl 2,6-dimethylbenzenesulfinate to the corresponding sulfone under a range of conditions and propose an ion-pair mechanism to account



Scheme 12

for their observations (Scheme 12).[19] The driving force for this isomerisation process is obviously the formation of the strong sulfur–oxygen bond in the sulfonyl group. Rearrangement of the intermediate anion **18** to the sulfone **17** may occur *via* homolytic fission of the C–O bond, followed by a novel radical–radical anion-pair isomerisation, in an analogous fashion to the Wittig rearrangement of ethers with alkyllithium reagents. Alternatively, protonation of the anion on work-up may be followed by the standard sulfinate ester–sulfone rearrangement which, if this is correct, would appear to proceed more rapidly for the complexed sulfinate than for its uncomplexed counterpart (benzhydryl toluene-*p*-sulfinate undergoes isomerisation only at elevated temperatures in acetic acid[20]). However, the precise course of this rearrangement remains open to speculation.

It was predicted that (2*S*,S_S)-**16** would not undergo an analogous fragmentation reaction on treatment with *tert*-butylmagnesium chloride due to the inability of a methyl group to stabilise an adjacent carbanion. Hence, reaction of a mixture of (2*S*,R_S)-**15** and (2*S*,S_S)-**16** with *tert*-butylmagnesium chloride was expected to afford the required homochiral complex (R_S)-**7** together with the sulfone **17** and to obviate the need to separate (2*S*,R_S)-**15** and (2*S*,S_S)-**16**. Thus, a solution of (2*S*,R_S)-**15** and (2*S*,S_S)-**16** (1.3 : 1) in THF was treated with *tert*-butylmagnesium chloride (2.4 equiv.) to give a yellow oil shown to comprise **7** and **17** in the ratio 1 : 2.7. Column chromatography on silica gel allowed separation of these two components, which were both isolated in low yield (**17** 24% yield; **7** 9% yield). However, ^{1}H NMR spectroscopic analysis of "(S_S)"-**7** using the chiral solvating agent (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-methylbenzylamine showed it to have an ee of just 3% (Scheme 13).



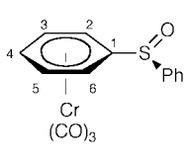
Scheme 13 *Reagent*: i, ^{t}BuMgCl (2.4 equiv.).

In conclusion, it has been shown that the synthesis of the sulfinyl-substituted chromium tricarbonyl complexes **5** and **6** can be readily achieved in good yield by a simple nucleophilic displacement reaction between the anion of **4** and a suitable sulfinate ester. However, the synthesis of the *tert*-butyl analogue **7** using this methodology was much less successful. Synthesis of the non-racemic material (S_S)-**5** and (R_S)-**6** was achieved with reasonable success employing (4*R*,5*S*)-4-methyl-5-phenyl-3-[(*R*)-phenylsulfinyl]isoxazolidin-2-one and (1*S*,2*R*,5*S*,R_S)-(+)-menthyl toluene-*p*-sulfinate as the chiral sulfinyl transfer reagents [(S_S)-**5** ee 80%; (R_S)-**6** ee 89%]. Identification of the racemisation pathways in operation enabled rational experimental design in order to optimise the ees obtained. In contrast, all attempts to achieve an asymmetric synthesis of **7** using Kagan's cyclic sulfite methodology failed. Instead a novel fragmentation–isomerisation process was observed.

Experimental

General

All reactions involving air- or moisture-sensitive reagents were carried out under an atmosphere of dry nitrogen unless stated otherwise. All experiments and purifications involving (arene) chromium tricarbonyl complexes were performed using standard vacuum line and Schlenk tube techniques,[21] with all solvents being deoxygenated prior to use. THF and diethyl ether were distilled, under an atmosphere of nitrogen, from sodium benzophenone ketyl, and dichloromethane from calcium hydride, also under nitrogen. Dibutyl ether was passed through a short plug of alumina (Grade I) prior to distillation from calcium hydride under a nitrogen atmosphere. 'Petroleum ether' (petrol) refers to that fraction which boils in the range 40–60 °C and was re-distilled before use. Chromium hexacarbonyl was sublimed under reduced pressure before use. Butyllithium was used as a 1.3–2.1 M solution in hexane, and *tert*-butylmagnesium chloride as a 2 M solution in diethyl ether. Silica gel column chromatography was performed on Kieselgel 60 according to the guidelines of Still *et al.*[22] TLC was carried out using Camlab Polygram SIL G/UV_{254}, with a 0.25 mm coating of silica gel containing fluorescent indicator UV_{254}. Visualisation was effected by UV and palladium(II) chloride in acidic methanol. ^{1}H NMR spectra were measured in deuteriochloroform unless otherwise stated, using residual chloroform as an internal standard (δ 7.27), on either a Bruker WH 300 (300 MHz) or AM 500 (500 MHz) instrument. Coupling constants (J) are all given in Hertz and first-order approximations are used throughout. A Bruker AMX 500 (125 MHz) machine was used to record ^{13}C NMR spectra, which were obtained in deuteriochloroform unless specified otherwise. The following numbering system has been utilised for the complexed arene ring proton and carbon resonances, and Ar′ used to designate resonances due to previously complexed aryl rings.



Mass spectra were recorded by the Dyson Perrins Laboratory analytical department on either a VG MICROMASS ZAB-1F or VG MASSLAB VG 20–250 machine, employing either chemical impact, electron impact or fast atom bombardment techniques. Elemental microanalyses were performed by the Dyson Perrins Laboratory analytical department. Unless otherwise stated, all IR spectra were recorded for samples as chloroform solutions in 0.1 mm sodium chloride cells on a Perkin-Elmer 1750 FT spectrophotometer. Optical rotations were recorded using a Perkin-Elmer 241 polarimeter with a thermally jacketed 10 cm cell. $[\alpha]_D$-Values are given in units of 10^{-1} deg cm^2 g^{-1}. Mp were recorded on a Gallenkamp hot-stage apparatus and are uncorrected.

Preparation of (benzene) chromium tricarbonyl 4[23]

A solution of benzene (17.5 ml, 0.196 mol) and chromium hexacarbonyl (4.02 g, 18.3 mmol) in dibutyl ether (120 ml)–THF (10 ml) was rigorously degassed and heated at reflux under nitrogen for 48 h. After cooling, the resulting yellow solution was filtered through alumina (Grade I), washing initially with petrol (100 ml) to remove the dibutyl ether, followed by dichloromethane (200 ml) to yield a yellow solution. Evaporation of the solvents *in vacuo* gave the title compound **4** as a yellow solid (2.35 g, 60%); δ_H (300 MHz) 5.33 (6H, s, ArH).

General procedure A: Synthesis of (SR_S)-sulfinyl-substituted arene chromium tricarbonyl complexes

To a solution of (benzene) chromium tricarbonyl **4** in THF at −78 °C was added butyllithium dropwise. The resultant brown solution was stirred for 2 h before its addition over 40 min, *via* cannula, to a solution of the required sulfinyl-transfer reagent in THF at −78 °C. The mixture was stirred at this temperature for 14 h and then quenched by the addition of saturated aq. ammonium chloride (20 ml) and warmed to room temperature. The product was extracted with ethyl acetate (3 × 20 ml), filtered through a plug of magnesium sulfate and silica, and the solvent removed *in vacuo*.

Preparation of (SR_S)-[(phenylsulfinyl)benzene] chromium tricarbonyl 5. A solution of **4** (879 mg, 4.10 mmol) in THF (30 ml) was treated with butyllithium (3.47 ml, 4.51 mmol) and **1** (860 mg, 5.53 mol) in THF (10 ml) according to General Procedure A to give a yellow–orange oil. Crystallisation from hexane–ethyl acetate (1:1) yielded the *title compound* **5** as yellow–orange needles (978 mg, 71%), mp 86–89 °C (Found: C, 52.98; H, 2.67. $C_{15}H_{10}CrO_4S$ requires C, 53.26; H, 2.98%); ν_{max} ($CHCl_3$)/cm^{-1} 1986, 1921 vs (C≡O), 1040 w (S=O); δ_H (300 MHz) 7.75–7.73 (2H, m, Ph), 7.56–7.53 (3H, m, Ph), 5.88 (1H, d, *J* 6.5, ArH^2), 5.43 (1H, d, *J* 6.4, ArH^6), 5.39 (1H, t, *J* 6.2, ArH^4), 5.30 (1H, t, *J* 6.4, ArH^3), 5.17 (1H, t, *J* 6.3, ArH^5); δ_C (125 MHz) 230.4 [$Cr(CO)_3$], 144.4 (Ph C^i), 132.0 (Ph C^p), 129.6, 124.4 (Ph C^o, C^m), 113.9 (Ar C^1), 93.4, 89.9, 89.0, 88.7, 87.8 (Ar C$^{2–6}$); *m*/*z* (CI, NH_3) 356 (MNH_4^+, 6%), 339 (10), 323 (7), 203 (100).

Preparation of (SR_S)-[(*p*-tolylsulfinyl)benzene] chromium tricarbonyl 6. A solution of **4** (200 mg, 0.93 mmol) in THF (5 ml) was treated with butyllithium (642 μl, 1.03 mmol) and **2** (196 mg, 1.16 mmol) in THF (10 ml) according to General Procedure A to give a yellow–orange oil. Crystallisation from petrol–ethyl acetate (2:1) yielded the *title compound* **6** as yellow–orange needles (210 mg, 64%); mp 133–136 °C (Found: C, 54.42; H, 3.56. $C_{16}H_{12}CrO_4S$ requires C, 54.54; H, 3.43%); ν_{max} ($CHCl_3$)/cm^{-1} 1985, 1921 vs (C≡O); δ_H (300 MHz) 7.63 (2H, d, *J* 8.1, Ph), 7.35 (2H, d, *J* 8.1, Ph), 5.90 (1H, d, *J* 6.5, ArH^2), 5.40–5.36 (2H, m, ArH^4, H^6), 5.31 (1H, t, *J* 6.0, ArH^3), 5.16 (1H, t, *J* 6.3, ArH^5), 2.42 (3H, s, CH_3); δ_C (125 MHz) 230.9 [$Cr(CO)_3$], 143.3, 141.6 (Ph C^i, C^p), 130.7, 125.1 (Ph C^o, C^m), 114.7 (Ar C^1), 93.7, 90.2, 89.5, 89.2, 88.4 (Ar C$^{2–6}$), 21.9 (CH_3); *m*/*z* (CI, NH_3) 353 (MH^+, 13%), 337 (50), 217 (100).

Preparation of (SR_S)-[(*tert*-butylsulfinyl)benzene] chromium tricarbonyl 7. A solution of **4** (119 mg, 0.56 mmol) in THF (5 ml) was treated with butyllithium (350 μl, 0.56 mmol) and **3** (0.104 g, 0.77 mmol) in THF (10 ml) according to General Procedure A except that the solution was allowed to warm to 0 °C over 2.5 h before quenching with saturated aq. ammonium chloride and reaction work-up under standard conditions to yield a yellow oil. Purification by column chromatography on silica gel [EtOAc–petrol (1:1)] yielded initially returned starting

material **4** (28 mg, 24% recovery), followed by the title compound **7** as a yellow oil (5 mg, 3%); δ_H (300 MHz) 5.88 (1H, d, *J* 6.3, ArH^2), 5.45–5.40 (2H, m, ArH^4, H^6), 5.34 (1H, t, *J* 6.2, ArH^3), 5.20 (1H, t, *J* 6.2, ArH^5), 1.25 [9H, s, $C(CH_3)_3$].

Attempted preparation of (S_S)-[(phenylsulfinyl)benzene] chromium tricarbonyl 5. A solution of **4** (598 mg, 2.79 mmol) in THF (15 ml) was treated with butyllithium (1.75 ml, 2.80 mmol) and a solution of (4*R*,5*S*,R_S)-**8** (965 mg, 3.34 mol) in THF (25 ml) according to General Procedure A except that the solution was stirred at −78 °C for 19 h before quenching with saturated aq. ammonium chloride (40 ml). The product was extracted with diethyl ether (3 × 20 ml), filtered through a plug of magnesium sulfate and silica, and the solvent removed *in vacuo* to yield a yellow–orange oil. Purification by column chromatography on silica gel [petrol–EtOAc (2:1)] gave an orange solid, which was recrystallised from diethyl ether to give **5** as orange crystals (733 mg, 78%). ^{1}H NMR spectroscopic studies using (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-methylbenzylamine as a chiral solvating agent showed the product (S_S)-**5** to have an ee of 8%.

The above procedure was repeated with the following modifications.

A solution of **4** (61 mg, 0.29 mmol) in THF (10 ml) was treated with butyllithium (182 μl, 0.29 mmol) according to General Procedure A before cooling to −100 °C and fast addition *via* cannula of the resultant anion to a solution of (4*R*,5*S*,R_S)-**8** (824 mg, 2.85 mmol) in THF (30 ml) at −100 °C. The reaction mixture was quenched by the addition of saturated aq. ammonium chloride (30 ml) as soon as the addition of the anion was complete. Reaction work-up according to General Procedure A afforded a mixture of a yellow oil and a white solid comprising 68% of **5** and the sulfinyl-transfer reagent **8** (de 94%) as determined by ^{1}H NMR spectroscopic analysis. Column chromatography on silica gel [petrol–EtOAc (2:1)] led to the isolation of two fractions, the first a white solid which, on recrystallisation, yielded (4*R*,5*S*,R_S)-**8** as white needles (592 mg, 72% recovery). The second fraction gave the title compound **5** as a yellow solid (49 mg, 51%). ^{1}H NMR spectroscopic studies using (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-methylbenzylamine as a chiral solvating agent showed the product (S_S)-**5** to have an ee of 80%.

Treatment of (S_S)-[(phenylsulfinyl)benzene] chromium tricarbonyl 5 with (phenyllithium) chromium tricarbonyl 9. A solution of **4** (71 mg, 0.332 mmol) in THF (2 ml) was treated with butyllithium (186 μl, 0.30 mmol) according to General Procedure A before cooling to −100 °C and fast addition of the resultant anion **9** to a solution of (S_S)-**5** (65 mg, 0.19 mmol, ee 39%) in THF (2 ml) at −100 °C. The reaction mixture was stirred for 30 s before being quenched by the addition of saturated aq. ammonium chloride (5 ml) and work-up according to General Procedure A. ^{1}H NMR spectroscopic studies using (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-methylbenzylamine as a chiral solvating agent on the crude reaction mixture showed the ee of **5** to have been reduced to 6%.

Attempted preparation of (R_S)-[(*p*-tolylsulfinyl)benzene] chromium tricarbonyl 6. In an analogous manner to the preparation of (S_S)-**5** a solution of **4** (251 mg, 1.17 mmol) in THF (10 ml) was treated with butyllithium (730 μl, 1.17 mmol) and (1*S*,2*R*,5*S*,R_S)-(+)-menthyl toluene-*p*-sulfinate **12** (407 mg, 1.38 mmol) in THF (10 ml) at −78 °C. Work-up and column chromatography on silica gel [petrol–EtOAc (2:1)], followed by crystallisation from diethyl ether, afforded the title compound **6** as yellow crystals (230 mg, 56%). ^{1}H NMR spectroscopic studies using (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-methylbenzylamine as a chiral solvating agent showed the product (R_S)-**6** to have an ee of 37%.

The above procedure was repeated with the following modifications.

A solution of **4** (39 mg, 0.18 mmol) in THF (2 ml) was treated with butyllithium (137 μl, 0.19 mmol) according to General Procedure A before cooling to −100 °C and fast addition of the resultant anion to a solution of (1*S*,2*R*,5*S*,R_S)-(+)-**12** (507 mg, 1.72 mmol) in THF (20 ml) at −100 °C. The reaction mixture was stirred for 5 min before being quenched by the addition of saturated aq. ammonium chloride (20 ml). Reaction work-up according to General Procedure A afforded a mixture of a yellow oil and a white solid comprising 77% of **6** as determined by ^{1}H NMR spectroscopic analysis. Column chromatography on silica gel [petrol–EtOAc (2:1)] led to the isolation of two fractions, the first (1*S*,2*R*,5*S*,R_S)-(+)-**12** as white needles (413 mg, 82% recovery); $[\alpha]_D^{23}$ +203 (*c* 1.05, CH_3COCH_3) {lit.,[24] (−)-menthyl toluene-*p*-sulfinate $[\alpha]_D^{21}$ −201 (*c* 2.0, CH_3COCH_3)}. The second fraction gave the title compound **6** as a yellow solid (50 mg, 77%). ^{1}H NMR spectroscopic studies using (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-methylbenzylamine as a chiral solvating agent showed the product (R_S)-**6** to have an ee of 89%.

Treatment of (R_S)-[(*p*-tolylsulfinyl)benzene] chromium tricarbonyl 6 with (phenyllithium) chromium tricarbonyl 9. In an analogous manner to the treatment of **5** with (phenyllithium) chromium tricarbonyl **9** a solution of **4** (17 mg, 0.079 mmol) in THF (5 ml) was treated with butyllithium (43 μl, 0.069 mmol) and (R_S)-**6** (10 mg, 0.028 mmol, ee 68%) in THF (2 ml) at −100 °C. The reaction mixture was stirred for 5 min before being quenched by the addition of saturated aq. ammonium chloride (10 ml) and work-up according to General Procedure A to afford a yellow oil. ^{1}H NMR spectroscopic studies using (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-methylbenzylamine as a chiral solvating agent on the crude reaction mixture showed the ee of **5** to have been reduced to 2%.

Attempted preparation of (S_S)-[(*tert*-butylsulfinyl)benzene] chromium tricarbonyl 7. A solution of **4** (50 mg, 0.23 mmol) in THF (2 ml) was treated with butyllithium (153 μl, 0.25 mmol) and a solution of **13** (34 mg, 0.10 mmol) in THF (5 ml) according to General Procedure A except that the resultant solution was allowed to warm to ambient temperature over 16 h before being quenched to give, after standard work-up, a mixture of a yellow oil and white crystals. Analysis of the ^{1}H NMR spectrum of the crude product indicated only the presence of starting materials.

Preparation of (2*S*,R_S)-2-hydroxy-1,1-diphenylpropyl(benzene) chromium tricarbonyl sulfinate 15 and (2*S*,S_S)-1-hydroxy-1,1-diphenylpropan-2-yl(benzene) chromium tricarbonyl sulfinate 16

A solution of **4** (255 mg, 1.19 mmol) in THF (5 ml) was treated with butyllithium (818 μl, 1.31 mmol) and a solution of (2*R*,5*S*)-*trans*-5-methyl-4,4-diphenyl-1,3,2-dioxathiolane 2-oxide **14** (346 mg, 1.26 mmol) in THF (15 ml) according to General Procedure A except that the solution was stirred at −78 °C for 20 h before quenching. Standard work-up led to the isolation of a yellow solid, which was shown to comprise a mixture of (2*S*,R_S)-**15** and (2*S*,S_S)-**16** in the ratio 1:4.5, together with 50% unchanged starting material by ^{1}H NMR spectroscopy. Crystallisation from hexane–dichloromethane (2:1) yielded (2*S*,R_S)-**15** as a yellow powder (86 mg, 15%). Further crystallisation of the mother liquors afforded a second crystalline fraction as orange rods (77 mg, 13%) shown to be a 1.3:1 mixture of **15** and **16** by ^{1}H NMR spectroscopic analysis.

(2*S*,R_S)-**15** mp 167 °C (decomp.) (Found: C, 58.80; H, 3.83. $C_{24}H_{20}CrO_6S$ requires C, 59.01; H, 4.13%); $[\alpha]_D^{23}$ −43.0 (*c* 0.47, CH_3COCH_3); ν_{max} ($CHCl_3$)/cm^{-1} 1996, 1932 vs (C≡O); δ_H (300 MHz) 7.68–7.66 (2H, m, Ph), 7.45–7.29 (8H, m, Ph), 5.49 (1H, d, *J* 6.3, ArH), 5.44 (1H, t, *J* 6.2, ArH) 5.18–5.15 [1H, m,

HOC*H*(CH_3)], 5.10 (1H, d, *J* 6.6, ArH), 4.88 (1H, t, *J* 6.3, ArH), 4.70 (1H, t, *J* 6.2, ArH), 3.71 (1H, br s, OH), 1.21 [3H, d, *J* 6.2, HOCH(C*H*$_3$)]; δ_C (125 MHz) 228.9 [Cr(CO)$_3$], 135.9, 133.1 (Ph C^i), 132.2, 131.9, 129.0, 128.6, 127.9, 127.6 (Ph C^o, C^m, C^p), 101.4 (Ar C^1), 95.1, 94.7, 94.6, 84.8, 84.7, (Ar C$^{2-6}$), obscured (*C*Ph$_2$), 69.7 [HO*C*H(CH$_3$)], 19.2 (CH$_3$); *m*/*z* (FAB$^+$) 489 (MH$^+$, 46%), 405 (100).

(2*S*,*S*$_S$)-**16** δ_H (300 MHz) 7.69 (2H, d, *J* 7.7, Ph H^o), 7.54 (2H, d, *J* 7.6, Ph H^o), 7.44 (2H, t, *J* 7.6, Ph H^m), 7.36–7.30 (3H, m, Ph H^m, H^p) 7.24 (1H, obs t, Ph H^p), 5.59 (1H, q, *J* 6.4, CH_3CH), 5.41–5.37 (2H, m, ArH), 5.11 (1H, t, *J* 6.4, ArH), 4.93 (1H, t, *J* 6.4, ArH), 4.46 (1H, d, *J* 6.5, ArH^2 or H^6), 2.81 (1H, s, OH), 1.43 (3H, d, *J* 6.4, CH$_3$).

Treatment of (2*S*,*R*$_S$)-2-hydroxy-1,1-diphenylpropyl(benzene) chromium tricarbonyl sulfinate 15 with *tert*-butylmagnesium chloride

To a solution of (2*S*,*R*$_S$)-**15** (44 mg, 0.09 mmol) in THF (5 ml) at ambient temperature was added *tert*-butylmagnesium chloride (100 μl, 0.20 mmol) dropwise. The solution was stirred for 14 h at room temperature before quenching of the reaction with saturated aq. ammonium chloride (10 ml). The product was extracted using ethyl acetate (2 × 10 ml), filtered through a plug of magnesium sulfate and silica, and the solvent evaporated to yield a yellow crystalline solid tentatively assigned as *benzhydryl* (*phenyl*) *chromium tricarbonyl sulfone* **17** (39 mg, 98%). A portion was recrystallised from hexane–dichloromethane (2:1) to give an analytically pure sample as fine yellow needles, mp 186 °C (Found: C, 59.48; H, 3.42. $C_{22}H_{16}CrO_5S$ requires C, 59.46; H, 3.63%); $[\alpha]_D^{25}$ 0.0 (*c* 0.47, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1996, 1937 vs (C≡O), 1329, 1145 s (O=S=O); δ_H (300 MHz) 7.61–7.57 (4H, m, Ph), 7.39–7.36 (6H, m, Ph), 5.56 (2H, d, *J* 6.5, ArH^2, H^6), 5.47 (1H, t, *J* 6.2, ArH^4), 5.33 (1H, s, Ph$_2$C*H*), 4.94 (2H, t, *J* 6.4, ArH^3, H^5); δ_C (125 MHz) 228.9 [Cr(CO)$_3$], 132.5 (Ph C^i), 130.1, 128.9 (Ph C^o, C^m), 129.1 (Ph C^p), 101.9 (Ar C^1), 94.1 (Ar C^4), 93.8, 85.7 (Ar C^{2,6}, C^{3,5}), 76.7 (Ph$_2$*C*H); *m*/*z* (CI, NH$_3$) 462 (MNH$_4^+$, 51%), 326 (20), 167 (100).

Decomplexation of benzhydryl (phenyl) chromium tricarbonyl sulfone 17

A solution of **17** (5 mg, 0.011 mmol) in diethyl ether (5 ml) was exposed to atmospheric oxygen and sunlight for 3 days. Filtration through alumina (Grade V) and removal of the solvent *in vacuo* gave a pale yellow solid. Crystallisation from ethyl acetate–hexane (2:1) led to the isolation of white, needle-like crystals (3 mg, 86%) shown to be benzhydryl phenyl sulfone by comparison with an authentic sample; ν_{max} ($CHCl_3$)/cm^{-1} 1309, 1148 s (O=S=O); δ_H (300 MHz) 7.63 (2H, d, *J* 7.8, Ph H^o), 7.56–7.31 (13H, m, Ph), 5.29 (1H, s, C*H*Ph$_2$); selected data for δ_C (125 MHz; CD_2Cl_2) 76.5 (*C*HPh$_2$); *m*/*z* (CI, NH$_3$) 326 (MNH$_4^+$, 27%), 167 (100).

Attempted preparation of (*S*$_S$)-[(*tert*-butylsulfinyl)benzene] chromium tricarbonyl 7 from 15/16

To a solution of **15/16** (33 mg, 0.068 mmol, 1.3:1) in THF (2 ml) at room temperature was added *tert*-butylmagnesium chloride (80 μl, 0.16 mmol) dropwise. The reaction mixture was stirred for 45 min before quenching by the addition of saturated aq. ammonium chloride (5 ml). The product was extracted with ethyl acetate (2 × 5 ml), filtered through a plug of magnesium sulfate and silica, and the solvent evaporated to give a yellow oil. Analysis of the ^{1}H NMR spectrum of the crude material indicated the presence of **7** and **17** in the ratio 1:2.7. Column chromatography on silica gel [petrol–EtOAc (1.5:1)] led to the isolation of 2 fractions; the first a yellow solid comprising **17** (7 mg, 24%). The second fraction afforded the title compound **7** as a yellow oil (2 mg, 9%). ^{1}H NMR spectroscopic studies using (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-methylbenzylamine as a chiral solvating agent showed the product **7** to have an ee of 3%.

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