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Alkylthio Substituted Tricarbonyl(η^6-arene)chromium(0) Complexes as Substrates for Asymmetric Oxidation

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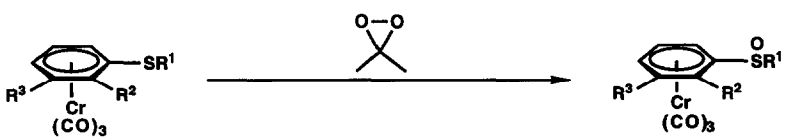
Abstract: Oxidation of methylthio substituted tricarbonyl(η^6-arene)chromium(0) complexes with $Ti(OPr^i)_4$ / diethyl tartrate / H_2O / cumene hydroperoxide (2:4:2:1.3) gives methylsulfinyl substituted tricarbonyl(η^6-arene)chromium(0) complexes in 60-73% yield and 81-86% e.e. (29-60% yield and 90-≥95% e.e. after crystallisation); diethyl tartrate gives higher optical and chemical yields than dimethyl or diisopropyl tartrates and the reaction conditions are ineffective for other alkylthio and arylthio substituents; diethyl L-(+)-tartrate and diethyl D-(-)-tartrate lead to complexes of *R* and *S* configuration respectively; although an attempted kinetic resolution of tricarbonyl[η^6-(methylsulfinyl)benzene]chromium(0) was unsuccessful, subjecting tricarbonyl[η^6-1-methyl-2-(methylthio)benzene]chromium(0) to kinetic resolution conditions led to the isolation of recovered starting material and the corresponding sulfinyl substituted complex with enantiomeric excesses of 59 and 60% respectively.

Asymmetric oxidation of sulfides is a conceptually simple approach to optically active sulfoxides.[1] To date, the most promising ways of achieving this transformation in a synthetically useful manner involve the use of chiral oxaziridines,[2] oxidation by hydroperoxides in the presence of optically active metal complexes[1] and enzymatic and microbial mediated oxidations.[3]

Recently we discovered that readily available alkylthio substituted tricarbonyl(η^6-arene)chromium(0) complexes **1** may be transformed efficiently into the hitherto unknown sulfinyl substituted tricarbonyl(η^6-arene)chromium(0) complexes **2** using the mild and selective achiral oxidising reagent dimethyldioxirane.[4,5]



1 R^1 = Me, Et, Pr^i, Bu^t; R^2 = H, Me, Bu^t, OMe; R^3 = H, OMe (±)-**2**

In view of current interest in the synthesis and reactivity of optically active tricarbonyl(η^6-arene)chromium(0) complexes,[6] we decided to embark upon a study designed to determine the feasibility of performing the oxidation of sulfide **1** to sulfoxide **2** stereoselectively. The results of this study are described herein.[7]

RESULTS AND DISCUSSION

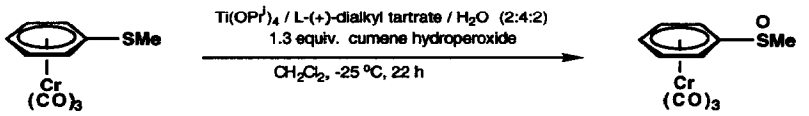
The air-stable and crystalline complex, tricarbonyl[η^6-(methylthio)benzene]chromium(0) **3**, was synthesised from (methylthio)benzene and hexacarbonylchromium(0) in 96% yield using a literature procedure.[5] Our initial attempts to oxidise sulfide **3** stereoselectively used [(8,8-dichlorocamphoryl)sulfonyl]oxaziridine, which has been reported to give enantioselectivities of 42-74% and isolated yields of 85-90% for the oxidation of organic sulfides to sulfoxides.[2] As these reactions led only to recovered starting material, an observation which is consistent with delocalisation of one of the sulfur lone pairs of **3** onto the tricarbonylchromium(0) moiety, our attention then turned to other oxidising systems and, in particular, Kagan's modified Sharpless reagent.

After some experimentation with the titanium-centred system, we were pleased to find conditions which led to minimal decomplexation and enantiomerically enriched sulfoxide complex **4**. Thus in an optimised oxidation of complex **3**, 4 equiv. diethyl L-(+)-tartrate in dichloromethane was cooled to 0 °C and 2 equiv. $Ti(OPr^i)_4$ was added. The solution was stirred vigorously for 20 min. at 0 °C after which 2 equiv. H_2O was added dropwise. After stirring the titanium reagent for 30 min. at 0 °C, it was added to 1 equiv. complex **3** in dichloromethane at room temperature. The catalyst/substrate mixture was then cooled to -25 °C and a mixture of dichloromethane and 1.3 equiv. cumene hydroperoxide was added dropwise to the cooled reaction mixture over 5 min. The reaction mixture was covered with aluminium foil and maintained at -25 °C for 22 h. (It is of note that using these conditions the asymmetric oxidation proved to be reliable and reproducible but that slight changes to the parameters defined, such as preparation of the catalyst at room temperature, gave capricious results.) After a work-up procedure which included washing with aqueous sodium metabisulfite, the product mixture was chromatographed to remove the diethyl L-(+)-tartrate, unreacted starting material and some sulfonyl substituted complex (see below). Every precaution possible was taken to ensure that all the sulfinyl substituted complex **4** was collected from the column. The resulting yellow solid [which represented essentially a 65% yield of **4** and contained only **4** and small amounts (<5%) of decomplexed material] was analysed by ^{1}H NMR spectroscopy using the chiral solvating reagent (-)-(*S*)-t-butylphenylphosphinothioic acid;[8] the solid was found to have an e.e. of 83%. Crystallisation of the yellow solid gave a 53% yield of pure crystals of **4** which were essentially optically pure {e.e. ≥95% by ^{1}H NMR spectroscopy; $[\alpha]_D^{25}$ = -208 (c 1, acetone)}.

It is worthy of note at this point that *S*-(-)-t-butylphenylphosphinothioic acid proved to be an invaluable analytical aid throughout this study. Addition of 1-2 equivalents of the reagent to a C_6D_6 solution of the complex gave differences in chemical shift of 0.1 - 0.2 ppm for one of the ring protons and up to 0.1 ppm for the methyl group of each of the complexes examined.

Having optimised conditions for the asymmetric oxidation of sulfide complex **3** to sulfoxide complex **4** with the diethyl L-(+)-tartrate titanium reagent, reagents formed from dimethyl L-(+)-tartrate and diisopropyl L-(+)-tartrate were prepared and used in the oxidation and the yields and enantiomeric excesses of the products obtained prior to crystallisation were measured. In the former case a 54% yield of material that had an e.e. of 69% was obtained, and in the latter case, a 57% yield of complex **4** with an e.e. of 70% was produced.

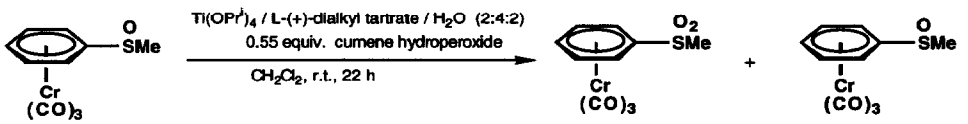
Thus, as is the case for oxidation of uncomplexed aromatic sulfides,[9] it was found that diethyl tartrate gave the best enantiomeric excess and this was the tartrate used in subsequent oxidations.



3 (-)-4

dialkyl tartrate:	before crystallisation:	after crystallisation:
dimethyl L-(+)-tartrate	54% yield, 69% e.e.	
diethyl L-(+)-tartrate	65% yield, 83% e.e.	53% yield, ≥95% e.e.
diisopropyl L-(+)-tartrate	57% yield, 70% e.e.	

We recently synthesised the first examples of sulfonyl substituted tricarbonyl(η^6-arene)chromium(0) complexes.[10] This was achieved by two methods one of which involved a titanium / tartrate / H_2O / hydroperoxide oxidation of alkylthio substituted complexes. In particular oxidation of complex **3** using 1 equiv. Ti(OPr^i)$_4$ / 2 equiv. diethyl L-(+)-tartrate / 1 equiv. H_2O / 2 equiv. cumene hydroperoxide gave a 56% yield of the corresponding sulfonyl complex **5**. Thus a second method of generating enantiomerically enriched sulfoxide complexes such as **4** was in principle available to us. Oxidation of racemic sulfoxide complexes with half an equivalent of cumene hydroperoxide and a homochiral titanium / tartrate / H_2O complex may lead to oxidation of only one enantiomer to the sulfone complex leaving the other enantiomer of the sulfoxide complex unreacted and relatively easy to isolate. In practise when racemic **4** (synthesised by dimethyldioxirane oxidation of complex **3**[5]) was oxidised with 0.55 equiv. of cumene hydroperoxide at the temperature used to oxidise the sulfide complexes to the sulfone complexes, sulfone **5** and sulfoxide **4** were isolated in 44 and 34% yield respectively. Disappointingly the sulfoxide complex was racemic.

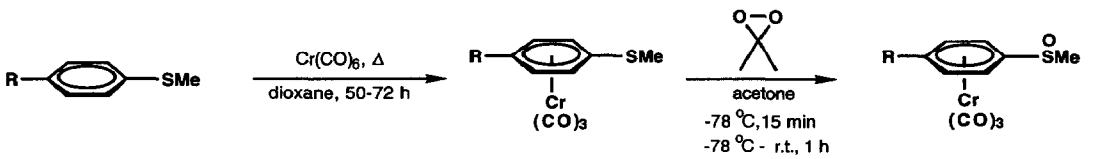


(±)-4 **5** (±)-4

44% 34%

Having established that an enantiomerically pure sulfinyl substituted tricarbonyl(η^6-arene)chromium(0) complex could be formed in acceptable yield by asymmetric oxidation of the corresponding alkylthio substituted complex, it was of interest to us to determine the scope and limitations of this oxidation. After checking that oxidation of complex **3** using D-(-)-diethyl tartrate instead of L-(+)-diethyl tartrate gave the opposite enantiomer of complex **4** in essentially the same yield (66% yield and 84% e.e. before crystallisation, 37% yield and ≥95% e.e., $[\alpha]_D^{25}$ = +202 after crystallisation), we initially examined the effect of introducing substituents *para* to the sulfide.

Complexation of commercially available sulfides **6** and **7** proceeded smoothly to give the known complexes **8**[11] and **9**.[10] In order to obtain samples of racemic sulfoxide complexes for the chiral solvating reagent studies, sulfides **8** and **9** were oxidised to the novel complexes **10** and **11** using dimethyldioxirane.

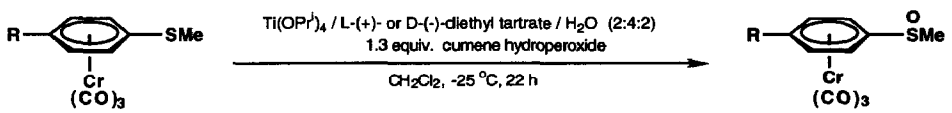


6 R = Me
7 R = MeO

8 R = Me (70%)
9 R = MeO (61%)

(±)-**10** R = Me (65%)
(±)-**11** R = MeO (70%)

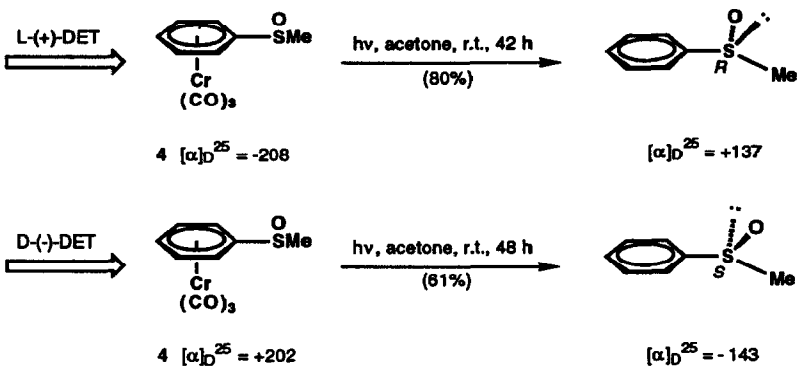
Oxidation of complexes **8** and **9** in the presence of either L-(+)- or D-(-)-diethyl tartrate gave very similar precrystallisation yields and e.e. values to those obtained on oxidation of the unsubstituted complex **3** (see Table below). Crystallisation again led to increased optical purity albeit at the expense of chemical yield.



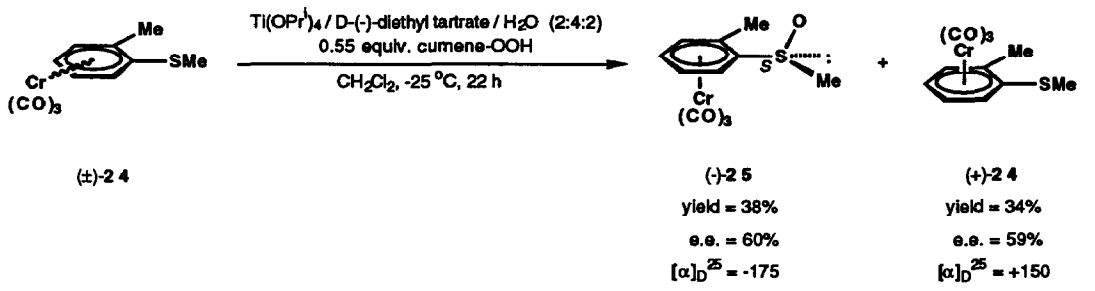
R	sulfenyl complex	diethyl tartrate	sulfinyl complex	before crystallisation		after crystallisation		
				yield(%)	e.e. (%)[a]	yield(%)	e.e.(%)[a]	$[\alpha]_D^{25}$[b]
H	**3**	L-(+)	(-)-**4**	65	83	53	≥95	-208
H	**3**	D-(-)	(+)-**4**	66	84	37	≥95	+202
Me	**8**	L-(+)	(-)-**10**	73	86	60	90	-170
Me	**8**	D-(-)	(+)-**10**	66	85	29	≥95	+179
MeO	**9**	L-(+)	(-)-**11**	60	81	46	≥95	-146
MeO	**9**	D-(-)	(+)-**11**	69	82	35	≥95	+147

[a] Measured by analysis of the ^{1}H NMR spectrum obtained by adding 1-2 equivalents of (-)-(*S*)-*t*-butylphosphinothioic acid to a C_6D_6 solution of the complex. [b] All measurements were taken at 25 °C in acetone (c =1)

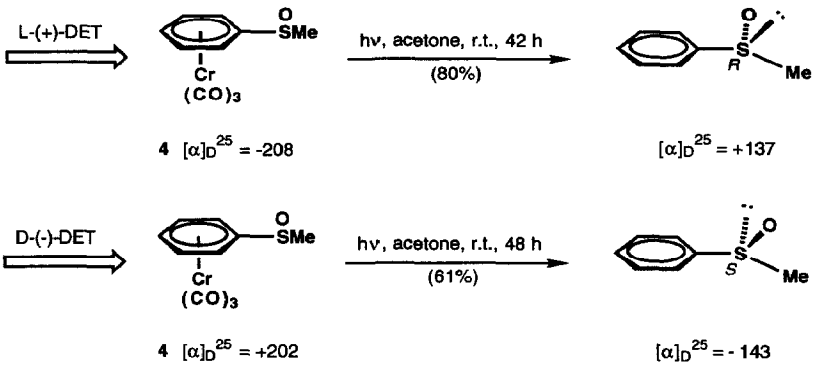
Having established that *para* substituents have little effect on the outcome of the asymmetric oxidation of alkylthio substituted tricarbonyl(η^6-arene)chromium(0) complexes, we turned our attention to the rôle of the sulfur substituent. Accordingly, the sulfides **12-15** were converted into the known sulfide complexes **16-19**[12,13] by thermolysis with $Cr(CO)_6$. [A small amount (6%) of the sulfide bearing two tricarbonylchromium(0) units was also isolated from the complexation of sulfide **15**. This novel complex was fully characterised.] As before, racemic sulfoxide complexes were generated from the sulfide complexes in order to obtain spectroscopic information on the potential products of asymmetric oxidation. Thus the novel racemic sulfoxide complexes **20-23** were synthesised from the sulfide complexes **16-19** in good yield using dimethyldioxirane.



The next complex to be examined had a substituent *ortho* to the sulfide undergoing oxidation. Substrates of this type are chiral and so interaction with a homochiral titanium / tartrate / H_2O complex may lead to preferential oxidation of one enantiomer of the substrate. Thus complex (±)-**24** was synthesised according to a literature method[5] and oxidised with only 0.55 equivalents of cumene hydroperoxide in the presence of the titanium reagent derived from diethyl D-(-)-tartrate. Work-up and careful column chromatography led to the isolation of the sulfinyl substituted complex **25** and unreacted starting material in 38 and 34% yield respectively. Pleasingly, examination of complex **25** by ^1H NMR spectroscopy in the presence of *S*-(-)-t-butylphenylphosphinothioic acid and HPLC analysis of the recovered starting material [CHIRALCEL OD-H, Daicel Chemical Industries; hexane-isopropanol (7:3), 0.6 ml min^{-1}] revealed that the former had an e.e. of 60% whilst the latter had an e.e. of 59%. Thus a partial chemical kinetic resolution of complex **24** had taken place. Complex **25** was formed as a single diastereoisomer. Knowing that the titanium-based reagent derived from diethyl D-(-)-tartrate preferentially forms the *S* sulfoxide and knowing the relative stereochemical outcome of the oxidation of complex **24** with dimethyldioxirane,[5] it is possible to deduce that the stereochemistry of the predominant enantiomer of complex **25** is that shown below. It is also possible to deduce that the recovered starting material is enriched in the enantiomer indicated. Studies are currently being undertaken to enhance the efficiency of this promising resolution procedure.



Finally, it is noteworthy that a study of a $Ti(OPr^i)_4$ / diethyl tartrate / H_2O / cumene hydroperoxide oxidation of aryl and alkyl ferrocenyl sulfides has recently been reported. Under suitable conditions certain aryl ferrocenyl sulfoxides of high enantiomeric purity were produced.[16]



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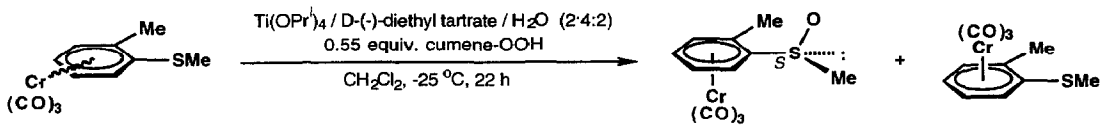

(±)-2 4

(-)-2 5
yield = 38%
e.e. = 60%
$[\alpha]_D^{25}$ = -175

(+)-2 4
yield = 34%
e.e. = 59%
$[\alpha]_D^{25}$ = +150

Finally, it is noteworthy that a study of a $Ti(OPr^i)_4$ / diethyl tartrate / H_2O / cumene hydroperoxide oxidation of aryl and alkyl ferrocenyl sulfides has recently been reported. Under suitable conditions certain aryl ferrocenyl sulfoxides of high enantiomeric purity were produced.[16]

EXPERIMENTAL

General Experimental

Reactions under nitrogen were performed using standard vacuum line and Schlenk tube techniques.[17] All thermolyses with hexacarbonylchromium(0) were carried out in the dark, under a nitrogen atmosphere, in a B 24 round-bottomed flask, equipped with a Liebig air condenser with a water condenser on top. Dioxane was distilled from sodium. Dichloromethane was distilled from CaH_2. *N,N*-Dimethylformamide was stored over molecular sieves (4Å). Diethyl and diisopropyl tartrate were distilled and stored over molecular sieves (4Å). All other chemicals were used as obtained from commercial sources. Dimethyldioxirane was prepared as a solution in acetone as described before.[5] Column chromatography and TLC were carried out using Sorbsil C60 silica and Kieselgel 60 F_{254} aluminium backed pre-coated plates respectively. M.p.s of organochromium complexes were measured in sealed capillaries under nitrogen on an Electrothermal IA9100 Digital Melting Point Apparatus and are uncorrected. Elemental analyses were performed by Imperial College Microanalytical Service. IR spectra were recorded on a Mattson 5000 FTIR spectrometer. NMR spectra were recorded in $CDCl_3$ (unless stated otherwise) on a JEOL GSX 270 spectrometer (270 MHz, ^1H; 67.9 MHz ^{13}C) and a Bruker AM 500 spectrometer (125.8 MHz, ^{13}C). For ease of comparison of all NMR assignments, in the NMR data given below, the aromatic carbon bearing the sulfur substituent is designated C-1. Mass spectra were recorded on VG Micromass 7070E and AutoSpec-Q instruments at Imperial College using EI and CI techniques. Optical rotations were recorded on a Perkin-Elmer 241 Polarimeter, using a 1 dm pathlength. Concentrations are given as g 100 ml^{-1} and all measurements were recorded at 25 °C. Except for (+)-**24**, enantiomeric excesses of complexes were measured by ^1H NMR spectroscopy with (*S*)-(-)-*tert*-butylphenylphosphinthoic acid (1-2 equivs.) in C_6D_6. The enantiomeric excess of (+)-**24** was measured by analytical HPLC using a Gilson 303 instrument, holochrome detector and a 250 mm x 4 mm Chiracel OD-H column (Daicel Chemical Industries). The flow rate was 0.6 ml $min^{-1}$and the solvent mixture hexane-isopropanol, 7:3.

Preparation of Thio Substituted Arenes

(Methylthio)benzene, 1-methyl-4-(methylthio)benzene **6**, 1-methoxy-4-(methylthio)benzene **7**, (ethylthio)-benzene **12** and (phenylthio)benzene **15** are commercially available.

(Isopropylthio)benzene **13**.[18] - In a 250 cm^3, two necked, round bottomed flask, equipped with a condenser and a nitrogen inlet, sodium hydride (60% dispersion in paraffin; 0.80 g, 20 mmol) was washed with DMF (2 x 25 cm^3). Further DMF (50 cm^3) was added to the flask and the resulting grey suspension was cooled to 0 °C and stirred vigorously. Thiophenol (2.0 g, 1.86 cm^3, 18.2 mmol) was added dropwise to the suspension, which was then stirred for a further 30 min at 0 °C by which time it had become yellow. 2-Bromopropane (2.46 g, 1.88 cm^3, 20 mmol) was added dropwise at 0 °C and the resulting mixture was stirred at this temperature for a further 15 min before being allowed to warm to room temperature overnight. 10%

Aqueous NaOH (50 cm^3) was added to the reaction mixture, which was then extracted with diethyl ether (6 x 40 cm^3). The combined organic layers were washed with water (6 x 50 cm^3), saturated brine (2 x 100 cm^3), dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave the title sulfide **13** as a pale yellow oil (2.31 g, 15.1 mmol, 82%); υ_{max}(neat)/cm^{-1} 3073vs, 3059vs, 2964vs, 2864vs, 1584s, 1468vs, 1441vs, 1382s, 1366s, 1243s, 1155s, 1091s, 1069s, 1050s, 1025s, 741vs and 693vs; δ_H($CDCl_3$) 7.37 (2H, m, 2-H), 7.22 (3H, m, 2 x 3-H, 4-H), 3.35 [1H, septet, *J* 6.8, C*H*(CH_3)$_2$], 1.27 [6H, d, *J* 6.8, CH(C*H*$_3$)$_2$]; δ_C($CDCl_3$) 135.5 (C-1), 131.7 (C-2/C-3), 128.7 (C-2/C-3), 126.5 (C-4), 38.0 [*C*H(CH_3)$_2$], 23.0 [CH(*C*H$_3$)$_2$]; *m/z* (EI, 70 eV) 152 (M^+, 31%), 137 (M - CH_3, 3), 110 (MH - C_3H_7, 100), 43 (C_3H_7, 18).

(tert-*Butylthio*)*benzene* **14**.[18] - To a 100 cm^3 round bottomed flask fitted with a reflux condenser was added acetic acid (6.8 cm^3). After cooling to 0 °C perchloric acid (60% solution; 1.8 cm^3) and acetic anhydride (6.8 cm^3) were added succesively and the solution was stirred for 10 min. Thiophenol (3 g, 27.2 mmol) and *tert*-butyl alcohol (2.42 g, 32.6 mmol, 1.2 equiv.) were then added to the mixture, the volume of which was made up to 40 cm^3 with acetic acid. The mixture was stirred for 24 h at room temperature and then diluted with cold saturated brine (75 cm^3) and extracted with diethyl ether (4 x 50 cm^3). The combined organic extracts were washed with cold aqueous sodium hydrogen carbonate solution (6 x 50 cm^3), water (3 x 100 cm^3), dried ($MgSO_4$) and filtered. After solvent removal under reduced pressure, column chromatography [SiO_2; light petroleum (b.p. 60-80 °C)] gave the title sulfide **14** as a colourless liquid (2.79 g, 16.8 mmol, 62%); υ_{max}(film)/cm^{-1} 3059s 3033s, 2962vs, 2942vs, 2898vs, 1582m, 1473vs, 1457vs, 1363s, 1168brs, 1067m, 1091m, 749vs, 695vs; δ_H ($CDCl_3$) 7.55 (2H, m, 2-H), 7.34 (3H, m, 2 x 3-H, 4-H), 1.20 [9H, s, (CH_3)$_3$]; δ_C ($CDCl_3$) 137.5 (C-2), 132.7 (C-1), 128.6 (C-4), 128.4 (C-3), 45.8 [*C*(CH_3)$_3$], 31.0 [C(*C*H$_3$)$_3$]; *m/z* (EI, 70 eV) 166 (M^+, 17.5%), 110 (MH - C_4H_9, 100), 57 (C_4H_9, 47).

Formation of Alkylthio Substituted Tricarbonyl(η^6-arene) chromium(0) Complexes

Tricarbonyl[η^6-(methylthio)benzene]chromium(0) **3** was prepared according to a literature procedure.[5]

General procedure for complexations. - A mixture of the aromatic sulfide and hexacarbonylchromium(0) in distilled 1,4-dioxane was heated under reflux for between 50 and 72 h. The resulting solution/suspension was cooled in an ice-bath and then filtered through a plug of Kieselguhr, eluting with diethyl ether. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography and/or recrystallisation.

Tricarbonyl[η^6-1-*methyl*-4-(*methylthio*)*benzene*]*chromium*(0) **8**.[11] - Following the general procedure described above 1-methyl-4-(methylthio)benzene **6** (1.0 g, 7.23 mmol) was treated with hexacarbonylchromium(0) (3.98 g, 18.0 mmol) in 1,4-dioxane (40 cm^3) for 68 h to give a brown cloudy solution. Filtration, then column chromatography [SiO_2; light petroleum (b.p. 60-80 °C)], followed by crystallisation of the resulting yellow solid from diethyl ether-light petroleum (b.p.60-80 °C) yielded the title complex **8** as yellow crystals (1.387 g, 5.06 mmol, 70%), m.p. 64-65 °C (lit.,[11] 62-63 °C) (Found: C, 48.41; H, 3.55.

$C_{11}H_{10}CrO_3S$ requires C, 48.17; H, 3.68%); υ_{max}/cm^{-1} 1966s and 1889s (CO); δ_H ($CDCl_3$) 5.43 (2H, d, *J* 6.6, 2 x 2-H), 5.23 (2H, d, *J* 6.6, 2 x 3-H), 2.43 (3H, s, SCH_3), 2.14 (3H, s, CH_3); δ_C ($CDCl_3$) 233.0 (3CO), 110.1 (C-1), 106.4 (C-4), 92.97 (C-2/C-3), 92.9 (C-2/C-3), 20.2 (CH_3), 17.1 (SCH_3); *m/z* (CI, NH_3) 292 [$(M + NH_3)^+$, 16%], (MH, 100), 52 (Cr, 4).

Tricarbonyl[η^6-1-*methoxy*-4-(*methylthio*)*benzene*]*chromium*(0) **9**.[10] - Following the general procedure described above, 1-methoxy-4-(methylthio)benzene **9** (0.5 g, 3.24 mmol) was treated with hexacarbonylchromium(0) (1.78 g, 8.1 mmol) in 1,4-dioxane (20 cm^3) for 67 h to give a black solution. Filtration followed by crystallisation from dichloromethane-light petroleum (b.p. 60-80 °C) yielded the title complex **9** as yellow crystals (0.571 g, 1.97 mmol, 61%), m.p. 80.5-81.5 °C (Found: C, 45.37; H, 3.19. $C_{11}H_{10}CrO_4S$ requires C, 45.52; H, 3.47%); $\upsilon_{max}(CH_2Cl_2)/cm^{-1}$ 1967s and 1890s (CO); δ_H ($CDCl_3$) 5.63 (2H, d, *J* 7.1, 2 x 3-H), 5.11 (2H, d, *J* 7.1, 2 x 2-H), 3.69 (3H, s, OCH_3), 2.42 (3H, s, SCH_3); δ_C ($CDCl_3$) 232.7 (3CO), 141.7 (C-4), 103.2 (C-1), 95.7 (C-2), 77.6 (C-3), 55.8 (OCH_3), 19.2 (SCH_3); *m/z* (EI, 70 eV, 220°C) 290(M^+, 8.6%), 262 (M - CO, 0.7), 234 (M - 2CO, 17.6), 206 (M - 3CO, 51.2), 191 (M - 3CO - CH_3, 57.7), 176 [M - 3CO - 2(CH_3), 13.6], 154 [M - $Cr(CO)_3$, 10.6], 52 (Cr, 100).

Tricarbonyl[η^6-(*ethylthio*)*benzene*]*chromium*(0) **16**.[13] - Following the general procedure described above (ethylthio)benzene **12** (0.75 g, 5.43 mmol) was treated with hexacarbonylchromium(0) (2.98 g, 13.56 mmol) in 1,4-dioxane (30 cm^3) for 72 h to give a cloudy orange solution. Filtration, column chromatography [SiO_2; light petroleum (b.p. 60-80 °C)-diethyl ether, 9:1] followed by crystallisation of the resulting orange solid from dichloromethane-light petroleum (b.p. 60-80 °C) yielded *the title complex* **16** as yellow crystals (0.8 g, 1.92 mmol, 54%), m.p. 39.0-39.5 °C (lit.,[13] 34 °C) (Found: C, 47.95; H 3.69. $C_{11}H_{10}CrO_3S$ requires C, 48.17; H, 3.68%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1970m and 1894m (CO); δ_H ($CDCl_3$) 5.24 (4H, m, 2 x 2-H, 2 x 3-H), 5.21 (1H, m, 4-H), 2.98 (2H, q, *J* 7.4, CH_2H_3), 1.43 (3H, t, *J* 7.4, CH_2CH_3); δ_C($CDCl_3$) 232.4 (3CO), 111.6 (C-1), 92.8 (C-2/C-3), 92.6 (C-2/C-3), 89.5 (C-4), 28.5 (CH_2CH_3), 14.0 (CH_2CH_3); *m/z* (EI, 70 eV) 274 (M^+, 47), 246 (M - CO, 3), 218 (M - 2CO, 45), 190 (M - 3CO, 77), 162 (MH - 3CO - C_2H_5, 90), 52 (Cr, 100).

Tricarbonyl[η^6-(*isopropylthio*)*benzene*]*chromium*(0) **17**.[12] - Following the general procedure described above (isopropylthio)benzene **13** (0.5 g, 3.28 mmol) was treated with hexacarbonylchromium(0) (1.81 g, 8.21 mmol) in 1,4-dioxane (20 cm^3) for 50 h to give a black solution. Two filtrations, followed by crystallisation of the resulting solid from diethyl ether-light petroleum (b.p. 60-80 °C) yielded the title complex **12** as yellow flakes (0.528g, 1.83 mmol, 56%), m.p. 48.5-50.0 °C (lit.,[12] m.p. 50 °C) (Found: C, 49.26; H, 4.21. $C_{12}H_{12}CrO_3S$ requires C, 49.0; H, 4.20%); $\upsilon_{max}(CH_2Cl_2)/cm^{-1}$ 1972s and 1897s(CO); δ_H($CDCl_3$) 5.43 (2H, d, *J* 6.2, 2 x 2-H), 5.33 (2H, m, 2 x 3-H), 5.12 (1H, t, *J* 6.2, 4-H), 3.24 [1H, septet, *J* 6.7, $CH(CH_3)_2$], 1.34 [6H, d, *J* 6.7, $(CH_3)_2$]; δ_C ($CDCl_3$) 232.1 (3CO), 107.1 (C-1), 96.2 (C-2/C-3), 92.4 (C-2/C-3), 90.4 (C-4), 39.8 [$CH(CH_3)_2$], 23.2 [$CH(CH_3)_2$]; *m/z* (EI, 70 eV, 220 °C) 288 (M^+, 0.1%), 260 (M - CO, 0.5), 232 (M - 2CO, 3.6), 204 (M - 3CO, 24), 162 (MH - 3CO - C_3H_7, 97), 152 [M - $Cr(CO)_3$, 7.3], 52 (Cr, 100).

[η^6-(tert-*Butylthio)benzene]tricarbonylchromium*(0) **18**.[12,19] - Following the general procedure described above (*tert*-butylthio)benzene **14** (0.5 g, 3.01 mmol) was treated with hexacarbonylchromium(0) (1.65 g, 7.52 mmol) in 1,4-dioxane (20 cm^3) for 68 h to give a cloudy orange solution. Two filtrations, followed by crystallisation of the resulting yellow solid from dichloromethane-light petroleum (b.p. 60-80 °C) gave the title compound **18** as yellow flakes (0.664 g, 2.20 mmol, 73%), m.p. 93-95 °C (lit.,[19] m.p. 94-95 °C) (Found: *m/z* 302.0058. $C_{13}H_{14}CrO_3S$ requires 302.0068); $\upsilon_{max}(CH_2Cl_2)/cm^{-1}$ 1974s and 1900s (CO); δ_H ($CDCl_3$) 5.61 (2H, d, *J* 6.4, 2 x 2-H), 5.36 (3H, m, 2 x 3-H, 4-H) 1.41 [9H, s, $(CH_3)_3$]; δ_C ($CDCl_3$) 231.6 (3CO), 101.9 (C-2), 100.1 (C-1), 92.1 (C-4), 91.4 (C-3), 47.3 [*C*$(CH_3)_3$], 30.7 [C(*C*$H_3)_3$]; *m/z* (EI, 70 eV, 220 °C) 302 (M^+, 4.8%), 274 (M - CO, 0.2), 246 (M - 2CO, 7.2), 218 (M - 3CO, 11.6), 162 (MH - 3CO - C_4H_9, 50), 110 [MH - $Cr(CO)_3$ - C_4H_9, 18.8], 52 (Cr, 100).

Tricarbonyl[η^6-*(phenylthio)benzene]chromium*(0) **19**.[13] - Following the general procedure described above (phenylthio)benzene **15** (0.5 g, 2.68 mmol) was treated with hexacarbonylchromium(0) (1.18 g, 5.37 mmol) in 1,4-dioxane (20 cm^3) for 65 h to give a cloudy orange solution. Filtration followed by column chromatography [SiO_2; light petroleum (b.p. 60-80 °C)-diethyl ether, 4:1] allowed collection of a deep yellow fraction which when evaporated under reduced pressure gave a yellow solid which was recrystallised from diethyl ether-light petroleum (b.p. 60-80 °C) to yield the title complex **19** as yellow crystals (0.318 g, 0.99 mmol, 37%), m.p. 71.5-72.5 °C (lit.,[13] 70.5-71.5 °C) (Found: C, 56.10; H, 2.93. $C_{15}H_{10}CrO_3S$ requires C, 55.90; H, 3.13%); $\upsilon_{max}(CH_2Cl_2)/cm^{-1}$ 1970m and 1896m (CO); δ_H ($CDCl_3$) 7.53 (2H, m, 2 x 2'-H), 7.42 (3H, m, 2 x 3'-H, 4'-H), 5.34 (2H, t, *J* 6.5, 2 x 3-H), 5.23 (2H, d, *J* 6.5, 2 x 2-H), 5.14 (1H, t, *J* 6.5, 4-H); δ_C ($CDCl_3$) 232.3 (3CO), 133.6 (C-2'/C-3'), 131.5 (C-1'), 129.7 (C-2'/C-3'), 129.2 (C-4'), 111.5 (C-1), 92.7 (C-2/C-3), 92.5 (C-2/C-3), 89.8 (C-4); *m/z* (EI, 70 eV, 220 °C) 322 (M^+, 5%), 294 (M - CO, 0.1), 266 (M - 2CO, 5), 238 (M - 3CO, 62), 186 [M - $Cr(CO)_3$, 27.4], 52 (Cr, 100). Further elution with the same solvent mixture led to the collection of a second yellow fraction which was evaporated under reduced pressure and recrystallised from dichloromethane-light petroleum (b.p. 60-80 °C) to give η^6,η^6-*[(phenylthio)benzene]bistricarbonylchromium(0)* as yellow crystals (0.0754 g, 0.165 mmol, 6%), m.p. 147-148.5 °C (Found: C, 46.89; H, 2.21. $C_{18}H_{10}Cr_2O_6S$ requires C, 47.17; H, 2.20%); $\upsilon_{max}(CH_2Cl_2)/cm^{-1}$ 1983sh, 1971m and 1906br (CO); δ_H ($CDCl_3$) 5.48 (4H, m, 4 x 2-H), 5.32 (6H, m, 4 x 3-H, 2 x 4-H); δ_C ($CDCl_3$) 231.2 (6CO), 104.1 (C-1), 95.8 (C-2/C-3), 91.6 (C-4), 91.4 (C-2/C-3); *m/z* (EI, 70 eV, 220 °C) 458 (M^+, 3.7%), 374 (M - 3CO, 5.0), 346 (M - 4CO, 3.5), 322 [M - $Cr(CO)_3$, 6.0], 318 (M - 5CO, 0.4), 290 (M - 6CO, 26.2), 238 [M - $Cr(CO)_3$ - 3CO, 72.1], 186 {M - 2[$Cr(CO)_3$], 50.7}, 52 (Cr, 100).

Dimethyldioxirane Oxidation of Alkylthio Substituted Tricarbonyl(arene)chromium(0) Complexes

Tricarbonyl[η^6-(methylsulfinyl)benzene]chromium(0) (±)-**4** was oxidised according to a published procedure.[5]

General procedure for racemic oxidations. - The sulfide complex was dissolved in nitrogen saturated degassed acetone, and the resulting yellow solution was cooled to -78 °C under a nitrogen atmosphere.

Dimethyldioxirane (solution in acetone; known concentration) was diluted with nitrogen saturated acetone, cooled to -78 °C and added very slowly to the complex solution *via* a cannula. When the addition was complete, the reaction mixture was stirred at -78 °C for a further 15 min, and then at room temperature for 1 h. After solvent removal the crude mixture was analysed by ^{1}H NMR spectroscopy. Filtration through a short plug of Kieselguhr and then purification by column chromatography and/or crystallisation yielded the sulfinyl substituted complex.

Tricarbonyl[η^6-1-*methyl*-4-(*methylsulfinyl*)*benzene*]*chromium*(0) (±)-**10**. - Following the general racemic oxidation procedure described above tricarbonyl[η^6-1-methyl-4-(methylthio)benzene]chromium(0) **8** (110 mg, 0.4 mmol) in acetone (10 cm^3) was treated with dimethyldioxirane (0.087 mol dm^{-3} acetone solution; 5.52 cm^3, 0.48 mmol, 1.2 equiv.) diluted with acetone (5 cm^3). Work-up followed by crystallisation of the resulting yellow solid from dichloromethane-light petroleum (b.p. 60-80 °C) yielded the *title complex* (±)-**10** as yellow crystals (75.8 mg, 0.261 mmol, 65%), m.p. 64.5-65.0 °C (Found: C, 48.41; H, 3.55. $C_{11}H_{10}CrO_3S$ requires C, 48.17; H, 3.68%); $\upsilon_{max}(CH_2Cl_2)$/cm^{-1} 1978m and 1907m (CO); $\delta_H(CDCl_3)$ 5.90 (1H, dd, *J* 6.6, 1.5, 2-H/6-H), 5.63 (1H, dd, *J* 6.6, 1.5, 2-H/6-H), 5.19 (1H, dd, *J* 6.6, 1.5, 3-H/5-H), 5.10 (1H, dd, *J* 6.6, 1.5, 3-H/5-H); $\delta_C(CDCl_3)$ 230.7 (3CO), 110.7 (C-1/C-4), 110.3 (C-1/C-4), 90.3, 89.6, 89.3 and 88.6 (C-2, C-3, C-5 and C-6), 44.6 [S(O)CH_3], 20.6 (CH_3); *m/z* (CI, NH_3) 292 [(M + NH_4)$^+$,16%], 275 (MH, 100), 52 (Cr, 4).

Tricarbonyl[η^6-1-*methoxy*-4-(*methylsulfinyl*)*benzene*]*chromium*(0) (±)-**11**. - Following the general racemic oxidation procedure described above tricarbonyl[η^6-1-methoxy-4-(methylthio)benzene]chromium(0) **9** (100 mg, 0.345 mmol) in acetone (10 cm^3) was treated with dimethyldioxirane (0.1 mol dm^{-3} acetone solution; 4.14 cm^3, 0.414 mmol, 1.2 equiv.) diluted in acetone (5 cm^3). Work-up followed by crystallisation of the resulting yellow solid from dichloromethane-light petroleum (b.p. 60-80 °C) yielded the *title complex* (±)-**11** as yellow crystals (74 mg, 0.242 mmol, 70%), m.p. 135-137 °C (decomp.) (Found: C, 42.88; H, 3.29. $C_{11}H_{10}CrO_5S$ requires C, 43.14; H, 3.23%); $\upsilon_{max}(CH_2Cl_2)$/cm^{-1} 1978s and 1905s (CO); $\delta_H(CDCl_3)$ 5.99 (1H, dd, *J* 6.8, 1.7, 2-H/6-H), 5.79 (1H, dd, *J* 6.8, 1.7, 2-H/6-H), 5.17 (1H, dd, *J* 6.8, 2.2, 3-H/5-H), 5.10 (1H, dd, *J* 6.8, 2.2, 3-H/5-H), 3.76 (3H, s, OCH_3), 2.80 [3H, s, S(O)CH_3]; $\delta_C(CDCl_3)$ 230.6 (3CO), 143.9 (C-4), 106.7 (C-1), 90.7 (C-2/C-6), 89.3 (C-2/C-6), 75.3 (C-3/C-5), 75.2 (C-3/C-5), 55.9 (OCH_3), 44.7 [S(O)CH_3]; *m/z* (EI, 70 eV) 306 (M$^+$, 17%), 291 (MH - O, 100), 275 (M - OCH_3, 90), 243 [M - S(O)CH_3, 28].

Tricarbonyl[η^6-(*ethylsulfinyl*)*benzene*]*chromium*(0) (±)-**20**. - Following the general racemic oxidation procedure described above tricarbonyl[η^6-(ethylthio)benzene]chromium(0) **16** (109.7 mg, 0.4 mmol) in acetone (10 cm^3) was treated with dimethyldioxirane (0.073 mol dm^{-3} acetone solution; 6.03 cm^3, 0.44 mmol, 1.1 equiv.) diluted in acetone (5 cm^3). After work-up and filtration of the resulting yellow solid crystallisation from dichloromethane-light petroleum (b.p. 60-80 °C) gave the *title complex* (±)-**20** as yellow crystals (92.9 mg, 0.32 mmol, 80%), m.p. 80-82 °C (Found: C, 45.29; H, 3.46. $C_{11}H_{10}CrO_4S$ requires C, 45.52; H, 3.47%); $\upsilon_{max}(CH_2Cl_2)$/cm^{-1} 1982s and 1912s (CO); $\delta_H(CDCl_3)$ 5.85 (1H, m, 2-H/6-H), 5.40 (3H, m, 2-H/6-

H and two of 3-H, 4-H and 5-H), 5.27 (1H, m, 3-H/4-H/5-H), 2.90 (2H, m, CH_2CH_3), 1.32 (3H, t, *J* 7.4, CH_2CH_3); $\delta_C(CDCl_3)$ 230.4 (3CO), 111.3 (C-1), 93.0 (C-2/C-6), 89.4, 89.2 and 88.8 (C-3, C-4 and C-5), 86.73 (C-2/C-6); *m/z* (CI, NH_3) 581 (2M + H, 10%), 308 [$(M + NH_4)^+$, 64], 291 (MH, 100), 275 (MH - O, 27), 207 (MH - 3CO, 13), 155 [MH - $Cr(CO)_3$, 77].

Tricarbonyl[η^6-(*isopropylsulfinyl*)*benzene*]*chromium*(0) (±)-**21**. - Following the general racemic oxidation procedure described above, tricarbonyl[η^6-(isopropylthio)benzene]chromium(0) **17** (100 mg, 0.34 mmol) in acetone (10 cm^3) was treated with dimethyldioxirane (0.07 mol dm^{-3} acetone solution; 5.94 cm^3, 0.416 mmol, 1.2 equiv.) diluted in acetone (5 cm^3). After work-up, crystallisation of the resulting yellow solid from diethyl ether-pentane yielded the *title complex* (±)-**21** as yellow crystals (53 mg, 0.17 mmol, 50%), m.p. 89.5-90.5 °C [Found: *m/z* $(M + NH_4)^+$; 322.020513. $C_{12}H_{16}CrNO_4S$ requires 322.020515); $\upsilon_{max}(CH_2Cl_2)/cm^{-1}$ 1981s and 1911s (CO); $\delta_H(CDCl_3)$ 5.86 (1H, m, 2-H/6-H) 5.38 (3H, m, 3-H, 4-H and 5-H), 5.25 (1H, m, 2-H/6-H), 2.86 [1H, septet, *J* 6.9, $CH(CH_3)_2$], 1.32 [3H, d, *J* 6.9, one of $CH(CH_3)_2$], 1.23[3H, d, *J* 6.9, one of $CH(CH_3)_2$]; $\delta_C(CDCl_3)$ 230.4 (3CO), 109.3 (C-1), 93.0 (C-2/C-6) 88.8, 89.2 and 89.7 (C-3, C-4 and C-5), 86.9 (C-2/C-6), 55.5 [$CH(CH_3)_2$], 13.9 and 15.7 [$CH(CH_3)_2$]; *m/z* (CI, NH_3) 322 [$(M + NH_4)^+$, 57%], 305 (MH, 96), 289 (MH - O, 36), 221 (MH- 3CO, 10.5), 169 [MH - $Cr(CO)_3$, 100], 153 [MH - O - $Cr(CO)_3$, 18].

[η^6-(tert-*Butylsulfinyl*)*benzene*]*tricarbonylchromium*(0) (±)-**22**. - Following the general racemic oxidation procedure described above, [η^6-(*tert*-butylthio)benzene]tricarbonylchromium(0) **18** (100 mg, 0.33 mmol) in acetone (10 cm^3) was treated with dimethyldioxirane (0.095 mol dm^{-3} acetone solution; 4.18 cm^3, 0.397 mmol, 1.2 equiv.) diluted in acetone (5 cm^3). Work-up, filtration and then crystallisation of the yellow solid from dichloromethane-light petroleum (b.p. 60-80 °C) yielded the *title complex* (±)-**22** as yellow crystals (75.8 mg, 0. 238 mmol, 72%), m.p. 102.5-103.5 °C [Found C, 48.77; H, 4.49. $C_{13}H_{15}CrO_4S$ requires C, 49.05; H, 4.43); $\upsilon_{max}(CH_2Cl_2)/cm^{-1}$ 1981s and 1908s (CO); δ_H ($CDCl_3$) 5.87 (1H, d, *J* 6.3, 2-H/6-H), 5.42 (1H, t, *J* 6.1, 6.3, 3-H/4-H/5-H), 5.40 (1H, d, *J* 6.4, 2-H/6-H), 5.33 (1H, t, *J* 6.1, 6.3, 3-H/4-H/5-H), 5.19 (1H, t, *J* 6.1, 6.3, 3-H/4-H/5-H), 1.24 [9H, s, $C(CH_3)_3$]; $\delta_C(CDCl_3)$ 230.4 (3CO), 107.2 (C-1), 93.7, 91.9, 88.6, 88.0 and 87.8 (C-2, C-3, C-4, C-5 and C-6), 57.0 [$C(CH_3)_3$], 22.8 [$C(CH_3)_3$]; *m/z* (CI, NH_3) 336 [$(M + NH_4)^+$, 43%], 319 (MH, 100), 303 (MH - O, 24), 263 (MH - 2CO, 10), 183 [MH - $Cr(CO)_3$].

Tricarbonyl[η^6-(*phenylsulfinyl*)*benzene*]*chromium*(0) (±)-**23**. - Following the general experimental procedure described above (except that the reaction was allowed to stir at -78 °C for an extra half hour) tricarbonyl[η^6-(phenylthio)benzene]chromium(0) **19** (200 mg, 0.62 mmol) in acetone (18 cm^3) was treated with dimethyldioxirane (0.079 mol dm^{-3} solution in acetone; 8.63 cm^3, 0.682 mmol, 1.1 equiv.) diluted in acetone (8 cm^3). Work-up, followed by column chromatography (SiO_2; diethyl ether-light petroleum, 1:1, followed by diethyl ether) yielded the *title complex* (±)-**23** (115.8 mg, 0.342 mmol, 55%) as a yellow oil. A sample was recrystallised from dichloromethane-light petroleum (b.p. 60-80 °C) to give yellow crystals for analysis, m.p. 92.5-93 °C (Found: C, 52.99; H, 3.01. $C_{15}H_{10}CrO_4S$ requires C, 53.26; H, 2.98%); $\upsilon_{max}(CH_2Cl_2)/cm^{-1}$ 1982s and 1913s (CO); $\delta_H(CDCl_3)$, 7.73 (2H, m, 2'-H and 6'-H), 7.53 (3H, m, 3'-H,

4'-H and 5'-H), 5.88 (1H, d, *J* 6.4, 2-H/6-H), 5.41 (1H, t, *J* 7.2, 3-H/4-H/5-H) overlapping with 5.37 (1H, d, *J* 6.2 2-H/6-H), 5.29 (1H, t, *J* 7.4, 3-H/4-H/5-H), 5.16 (1H, t, *J* 7.4, 3-H/4-H/5-H); $\delta_C(CDCl_3)$ 230.4 (CO), 144.5 (C-1'), 132.0 (C-4'), 129.6 (C-2'/C-3'), 124.5 (C-2'/C-3'), 114.0 (C-1), 93.3 (C-2/C-6), 89.9, 89.0, 88.7 and 87.9 (C-2/C-6, C-3, C-4 and C-5); *m/z* (CI, NH_3) 356 [$(M + NH_4)^+$, 9%], 339 (MH, 64), 323 (MH - O, 65), 255 (MH - 3CO, 28), 203 [MH- $Cr(CO)_3$, 100], 186 [M - O - $Cr(CO)_3$, 47], 52 (Cr, 45).

Asymmetric Oxidation of Alkylthio Substituted Tricarbonyl(arene)chromium(0) Complexes

Typical asymmetric oxidation procedure. - A solution of diethyl tartrate (0.825 g, 0.68 cm^3, 4 mmol) in distilled dichloromethane (8 cm^3) was cooled to 0 °C and $Ti(OPr^i)_4$ (0.569 g, 0.60 cm^3, 2 mmol) was added. The solution was stirred vigorously for 20 min at 0 °C, after which H_2O (0.036 g, 36 mm^3, 2 mmol) was added dropwise. After stirring for a further 30 min at 0 °C the catalyst was ready to use. A degassed solution of the complex (1.0 mmol) in distilled dichloromethane (35 cm^3) was stirred at room temperature whilst the catalyst solution was added to it. The resulting mixture was then cooled to -25 °C, and cumene hydroperoxide (80%, 0.247 g, 0.240 cm^3, 1.3 mmol) diluted in dichloromethane (5 cm^3) was added dropwise to the reaction mixture over 5 min *via* cannula. After being thoroughly degassed, the reaction mixture was covered with aluminium foil and maintained at -25 °C for 22 h. Sodium metabisulfite solution (20% w/v, 85 cm^3) was subsequently added to the product mixture at <-20 °C and the mixture was stirred vigorously for 30 min whilst warming up to room temperature. The aqueous layer was then removed and the remaining yellow gel was transferred *via* cannula onto a short pad of Kieselguhr in a fritted column. The aqueous layer was extracted with dichloromethane (20 cm^3) and the extract was added to the filtration column. The column was further eluted with dichloromethane until all the yellow coloured material had been collected. After drying ($MgSO_4$), and removal of the solvent under reduced pressure, the resulting yellow residue was purified by column chromatography to give a yellow solid which was analysed by ^1H NMR spectroscopy, and then further purified by crystallisation.

R-(-)-*Tricarbonyl*[η^6-(*methylsulfinyl*)*benzene*]*chromium*(0) (-)-**4**. Using L-(+)-diethyl tartrate and following the general asymmetric oxidation procedure described above, tricarbonyl[η^6-(methylthio)benzene]chromium(0) **3** (0.260 g, 1.0 mmol) gave a yellow residue after work-up. Column chromatography (SiO_2; column loaded using diethyl ether-dichloromethane, 1:1 and eluted with diethyl ether followed by diethyl ether-acetone 9:1) gave a yellow solid (0.178 g, 0.64 mmol, 65%, 83% e.e.). Crystallisation from dichloromethane-light petroleum (b.p. 60-80 °C) gave the *title complex* (-)-**4** as yellow crystals (0.145 g, 0.525 mmol, 53%, ≥ 95% e.e.); $[\alpha]_D$ = -208 (c = 1 g 100 ml^{-1}, acetone).

Reaction of tricarbonyl[η^6-(*methylthio*)*benzene*]*chromium*(0) **3** *with catalyst prepared from L-(+)-dimethyl tartrate.* - The catalyst was prepared using L-(+)-dimethyl tartrate (0.713 g, 4 mmol), distilled dichloromethane (8 cm^3), $Ti(OPr^i)_4$ (0.569 g, 0.60 cm^3, 2.0 mmol) and H_2O (0.036 g, 36 mm^3, 2 mmol). Then following the general asymmetric oxidation procedure described above tricarbonyl[η^6-methylthio)benzene]chromium(0) **3** gave a yellow residue after work-up. Purification by column

chromatography (SiO_2; column loaded using diethyl ether-dichloromethane, then eluted with diethyl ether, followed by diethyl ether-acetone, 9:1) gave (-)-**4** as a yellow solid (0.149 g, 0.539 mmol, 54%, 69% e.e.).

Reaction of tricarbonyl[η^6-(*methylthio*)*benzene*]*chromium*(0) **3** *with catalyst prepared from L-(+)-diisopropyltartrate.* - The catalyst was prepared using L-(+)-diisopropyl tartrate (0.937 g, 0.822 cm^3, 4 mmol), distilled dichloromethane (8 cm^3), $Ti(OPr^i)_4$ (0.569 g, 0.60 cm^3, 2.0 mmol) and H_2O (0.036 g, 36 mm^3, 2 mmol). Then following the general asymmetric oxidation procedure described above tricarbonyl[η^6-methylthio)benzene]chromium(0) **3** gave a yellow residue after work-up. Purification by column chromatography (SiO_2; column loaded using diethyl ether-dichloromethane, then eluted with diethyl ether, followed by diethyl ether-acetone, 9:1) gave (-)-**4** as a yellow solid (0.157 g, 0.568 mmol, 57%, 70% e.e.).

S-(+)-*Tricarbonyl*[η^6-(*methylsulfinyl*)*benzene*]*chromium*(0) (+)-**4**. Using D-(-)-diethyl tartrate and following the general asymmetric oxidation procedure described above, tricarbonyl[η^6-(methylthio)benzene]chromium(0) **3** (0.260 g, 1.0 mmol) gave a yellow residue after work-up. Column chromatography (SiO_2: column loaded using diethyl ether-dichloromethane, and eluted with diethyl ether, followed by diethyl ether:acetone, 9:1) gave a yellow solid (0.182 g, 0.659 mmol, 66%, 84% e.e.). Crystallisation from dichloromethane-light petroleum (b.p. 60-80 °C) gave the *title complex* (+)-**4** as yellow crystals (0.102 g, 0.369 mmol, 37%, $\geq$ 95% e.e.); $[\alpha]_D$ = +202 (c = 1 g 100 ml^{-1}, acetone).

R-(-)-*Tricarbonyl*[η^6-1-*methyl*-4-(*methylsulfinyl*)*benzene*]*chromium*(0) (-)-**10**. Using L-(+)-diethyl tartrate and following the general asymmetric oxidation procedure described above tricarbonyl[η^6-1-methyl-4-(methylthio)benzene]chromium(0) **8** (0.274 g, 1.0 mmol) gave a yellow residue after work-up. Column chromatography (SiO_2; column loaded using diethyl ether:dichloromethane, 1:1 and eluted with diethyl ether followed by diethyl ether-acetone, 4:1) gave a yellow solid (0.211 g, 0.727 mmol, 73%, 86% e.e.). Crystallisation from dichloromethane-light petroleum (b.p. 68-80 °C) gave the *title complex* (-)-**10** as yellow crystals (0.175 g, 0.604 mmol, 60%, 90% e.e.); $[\alpha]_D$ = -170 (c = 1 g 100 ml^{-1}, acetone).

S-(+)-*Tricarbonyl*[η^6-1-*methyl*-4-(*methylsulfinyl*)*benzene*]*chromium*(0) (+)-**10**. Using D-(-)-diethyl tartrate and following the general asymmetric oxidation procedure described above tricarbonyl[η^6-1-methoxy-4-(methylthio)benzene]chromium(0) **8** (0.290 g, 1 mmol) gave a yellow residue after work-up. Column chromatography (SiO_2; column loaded diethyl ether-dichloromethane, 1:1, and eluted with diethyl ether, followed by diethyl ether-acetone, 4:1) gave a yellow solid (0.192 g, 0.661 mmol, 66%, 85% e.e.). Crystallisation from dichloromethane-light petroleum (b.p. 60-80 °C) gave the *title complex* (+)-**10** as yellow crystals (0.0842 g, 0.29 mmol, 29%, $\geq$ 95% e.e.); $[\alpha]_D$ = +179 (c = 1 g 100 ml^{-1}, acetone).

R-(-)-*tricarbonyl*[η^6-1-*methoxy*-4-*methylsulfinyl*)*benzene*]*chromium*(0) (-)-**11**. - Using L-(+)-diethyl tartrate and following the general asymmetric oxidation procedure described above tricarbonyl[η^6-1-methoxy-4-(methylthio)benzene]chromium(0) **9** (0.290 g, 1 mmol) gave a yellow residue after work-up. Column chromatography (SiO_2; column loaded using diethyl ether-dichloromethane, 1:1, and eluted with diethyl ether,

followed by diethyl ether-acetone, 9:1) gave a yellow solid (0.183 g, 0.598 mmol, 60%, 81% e.e.). Crystallisation from dichloromethane-light petroleum (b.p. 60-80 °C) gave the *title complex* (-)-**11** as yellow crystals (0.140 g, 0.455 mmol, 46%, ≥ 95% e.e.); $[\alpha_D = -146$ (c = 1 g 100 ml^{-1}, acetone).

S-(+)-*tricarbonyl*[η^6-1-*methoxy*-4-(*methylsulfinyl*)*benzene*]*chromium*(0) (+)-**11**. - Using D-(-)-diethyl tartrate and following the general asymmetric oxidation procedure described above with tricarbonyl[η^6-1-methoxy-4-(methylthio)benzene]chromium(0) **9** (0.203 g, 0.7 mmol), catalyst solution (6.50 cm^3, 1.4 mmol) and cumene hydroperoxide (80%, 0.173 g, 0.168 cm^3, 0.91 mmol) diluted in dichloromethane (4 cm^3) gave a yellow residue after work-up. Column chromatography (SiO_2; column loaded using diethyl ether-dichloromethane, 1:1, and eluted with diethyl ether followed by diethyl ether-acetone, 9:1) gave a yellow solid (0.148 g, 0.483 mmol, 69%, 82% e.e.). Crystallisation from dichloromethane-light petroleum (b.p. 60-80 °C) yielded the *title complex* (+)-**11** as yellow crystals (0.075 g, 0.245 mmol, 35%, ≥95% e.e.); $[\alpha]_D = +147$ (c = 1 g 100 ml^{-1}, acetone).

Tricarbonyl[η^6-(*ethylsulfinyl*)*benzene*]*chromium*(0) **20**. - Using L-(+)-diethyl tartrate and following the general asymmetric procedure described above tricarbonyl[η^6-(ethylthio)benzene)chromium(0) **16** (0.274 g, 1 mmol) gave a yellow residue after work-up. Column chromatography (SiO_2; column loaded using diethyl ether-dichloromethane, 1:1, then eluted with diethyl ether followed by diethyl ether-acetone, 4:1) gave the *title complex* as a yellow solid (0.0358 g, 0.123 mmol, 12%).

Attempted asymmetric oxidation of tricarbonyl[η^6-(*isopropylthio*)*benzene*]*chromium*(0) **17**. - The catalyst was prepared using L-(+)-diisopropyl tartrate (0.937g, 0.841 cm^3, 4.0 mmol), distilled dichloromethane (8 cm^3), $Ti(OPr^i)_4$ (0.569 g, 0.60 cm^3, 2.0 mmol) and H_2O (0.036 g, 36 mm^3, 2.0 mmol). Then following the general asymmetric oxidation procedure described above tricarbonyl[η^6-(isopropylthio)benzene]chromium(0) **17** (0.075 g, 0.260 mmol) in distilled dichloromethane (8 cm^3) was treated with catalyst solution (1.04 cm^3, 0.260 mmol) at room temperature, cooled to -25 °C and cumene hydroperoxide (80%; 0.049 g, 48 mm^3, 0.260 mmol) diluted in dichloromethane (2.6 cm^3) was added dropwise. The reaction mixture was covered with aluminium foil and kept at -25 °C for 24 h. After work-up the crude yellow residue was examined by ^1H NMR spectroscopy and found to contain only a trace of the desired oxidised product. .

Attempted asymmetric oxidation of [η^6-(tert-*butylthio*)*benzene*]*tricarbonylchromium*(0) **18**. - The catalyst was prepared using L-(+)-diisopropyl tartrate (0.469 g, 0.42 cm^3, 2.0 mmol), distilled dichloromethane (4 cm^3), $Ti(OPr^i)_4$ (0.284 g, 0.30 cm^3, 1.0 mmol) and H_2O (0.018 g, 18 mm^3, 1.0 mmol). Then following the general asymmetric oxidation procedure described above [η^6-(*tert*-butylthio)benzene]tricarbonylchromium(0) **18** (0.075 g, 0.248 mmol) in distilled dichloromethane (8 cm^3) was treated with catalyst solution (0.992 cm^3, 0.248 mmol) at room temperature. After cooling to -25 °C cumene hydroperoxide (80%; 0.047 g, 46 mm^3, 0.248 mmol) diluted in dichloromethane (2.5 cm^3) was added dropwise. The reaction mixture was covered with aluminium foil and maintained at -25 °C for 23 h. After work-up the crude yellow residue was examined by ^1H NMR spectroscopy and found to contain starting material and decomplexed products.

Attempted asymmetric oxidation of tricarbonyl[η⁶-(phenylthio)benzene]chromium(0) **19**. - Following the general asymmetric oxidation procedure described above the catalyst was prepared using L-(+)-diethyl tartrate. Then tricarbonyl[η⁶-(phenylthio)benzene]chromium(0) **19** (0.064 g, 0.2 mmol) in dichloromethane (8 cm^3) was treated with catalyst solution (1.86 cm^3, 0.4 mmol), cooled to -25 °C and cumene hydroperoxide (80%; 0.049 g, 48 mm^3, 0.26 mmol, 1.3 equiv.) was added. The reaction mixture was covered with aluminium foil and maintained at -25 °C for 22 h. After work-up the crude yellow residue was examined by ^1H NMR spectroscopy and found to contain a trace of the desired oxidised product.

Decomplexation Experiments

R-(+)-(Methylsulfinyl)benzene.[14] - (-)-Tricarbonyl[η⁶-(methylsulfinyl)benzene]chromium(0) (-)-**4** (≥95% e.e.; 50 mg, 0.181 mmol) was dissolved in acetone (20 cm^3) in a 50 cm^3 round-bottomed flask fitted with a water condenser. The resulting yellow solution was stirred open to the air for 42 h whilst being irradiated with a lamp containing a 100W household light bulb. The cloudy solution was then filtered through a short plug of Kieselguhr and the solvent removed to leave the title compound as a colourless oil (20.2 mg, 0.144 mmol, 80%), $[\alpha]_D$ = + 137 (c = 0.945 g 100 ml^{-1}, absolute EtOH).

S-(-)-Methylsulfinylbenzene.[14] - (+)-Tricarbonyl[η⁶-(methylsulfinyl)benzene]chromium(0) (+)-**4** (≥95% e.e.; 50 mg, 0.181 mmol) was dissolved in acetone (20 cm^3) in a 50 cm^3 round-bottomed flask fitted with a water condenser. The resulting yellow solution was stirred open to the air for 48 h whilst being irradiated with a lamp containing a 100W household light bulb. The cloudy solution was then filtered twice through a short plug of Kieselguhr and the solvent removed to leave the title compound as a colourless oil (15.4 mg, 0.110 mmol, 61%), $[\alpha]_D$ = - 143 (c = 0.69 g 100 ml^{-1}, absolute EtOH).

Kinetic Resolution Experiments

Tricarbonyl[η⁶-(methylsulfinyl)benzene]chromium(0) **4** and *tricarbonyl[η⁶-(methylsulfonyl)-benzene]chromium*(0) **5**. - Tricarbonyl[η⁶-(methylsulfinyl)benzene]chromium(0) (±)-**4** (41.4 mg, 0.15 mmol) in distilled dichloromethane (10 cm^3) was treated with the catalyst solution (prepared from L-(+)-diethyl tartrate as described above; 1.39 cm^3, 0.3 mmol). Then cumene hydroperoxide (80% solution; 15.7 mg, 15.2 mm^3, 0.083 mmol, 0.55 equiv.) was added undiluted with vigorous stirring at room temperature. The flask was covered with aluminium foil and maintained at room temperature for 22 h. Work up as described above gave a yellow residue which was examined by ^1H NMR spectroscopy. Column chromatography (SiO_2; column loaded using dichloromethane-diethyl ether, then eluted with diethyl ether) yielded, after solvent removal tricarbonyl[η⁶-(methylsulfonyl)benzene]chromium(0) **5**[10] as a yellow powder (18.4 mg, 0.063 mmol, 44%). Further elution with diethyl ether-acetone, 9:1, yielded after solvent removal tricarbonyl[η⁶-(methylsulfinyl)benzene]chromium(0) (±)-**4** as a yellow solid (14.0 mg, 0.051 mmol, 34%, 0% e.e.).

(+)-*Tricarbonyl*[η^6-1-*methyl*-2-(*methylthio*)*benzene*]*chromium*(0) (+)-**24** and (-)-*tricarbonyl*[η^6-1-*methyl*-2-(*methylsulfinyl*)*benzene*]*chromium*(0) (-)-**25**. - (±)-Tricarbonyl[η^6-1-methyl-2-(methylthio)benzene]-chromium(0)[5] (±)-**24** (55 mg, 0.2 mmol) in distilled dichloromethane (7 cm^3) was treated with catalyst solution (prepared from L-(+)-diethyl tartrate as described above; 1.86 cm^3, 0.4 mmol) at room temperature. The resulting mixture was cooled to -25 °C and cumene hydroperoxide (80% solution; 20.9 mg, 20.3 mm^3, 0.11 mmol, 0.55 equiv.) diluted in dichloromethane (3 cm^3) was added dropwise *via* cannula. The flask was covered with aluminium foil and maintained at -25 °C for 22 h. After work up the yellow residue was examined by ^1H NMR spectroscopy. Purification by column chromatography (SiO_2; column loaded using dichloromethane-diethyl ether; 1:1, then eluted with diethyl ether) allowed collection of a yellow fraction which after solvent evaporation was found to also contain some tartrate residues by ^1H NMR spectroscopy. Further elution with diethyl ether-acetone, 9:1, allowed collection of a second yellow fraction which after solvent evaporation yielded (-)-tricarbonyl[η^6-1-methyl-2-(methylsulfinyl)benzene]chromium(0) (-)-**25** as a single diastereoisomer (22 mg, 0.08 mmol, 38%, 60% e.e.); $[\alpha]_D$ = -175 (c = 0.095 g 100 ml^{-1}, absolute EtOH). The first impure yellow fraction was recolumned (SiO_2; light petroleum-diethyl ether, 4:1) and after solvent removal (+)-tricarbonyl[η^6-1-methyl-2-(methylthio)benzene]chromium(0) (+)-**24** was isolated as a yellow powder (18.4 mg, 0.07 mmol, 34%, 59% e.e.); $[\alpha]_D$ = +150 (c = 0.09 g 100ml^{-1}, absolute EtOH).

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