Oxidation of Alkylthio Substituted Tricarbonyl(η^6-arene)chromium(0) Complexes to Alkylsulfinyl Substituted Tricarbonyl(η^6-arene)chromium(0) Complexes

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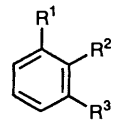
Dimethyldioxirane efficiently oxidises tricarbonylchromium(0) complexes of alkylthio substituted arenes to tricarbonylchromium(0) complexes of alkylsulfinyl substituted arenes. The diastereoselectivity of oxidation of *ortho* substituted complexes, which was determined by *inter alia* X-ray crystal structure analyses of tricarbonyl[η^6-1-methoxy-2-(methylsulfinyl)benzene]-chromium(0) **20**$_x$, [η^6-1-(*tert*-butylsulfinyl)-2-methoxybenzene]tricarbonylchromium(0) **23**$_x$ and tricarbonyl[η^6-1-(ethylsulfinyl)-2-methoxybenzene]chromium(0) **21**$_y$, is dependent on the alkylthio substituent and is reversed when this substituent is changed from methylthio to *tert*-butylthio.

The sulfinyl functional group is found in a range of natural products,[1] is widely used in organic chemistry to control the chemical and stereochemical outcome of organic reactions,[2] and is known to form coordination complexes with transition metals.[3] This latter property is as yet relatively unexploited although interesting studies of it are underway[4] and its considerable potential in the area of catalysis has been noted.[3]

We are interested in interactions between the sulfinyl functional group and metal carbonyl entities as a result of our observations that the sulfinyl substituted oxadienes [RS(O)CH=CHC(Me)=O; R=Bu^t, Ph] and the sulfinyl substituted alkene PhS(O)CH=CH$_2$ form diastereoisomerically pure iron carbonyl complexes when treated with sources of tricarbonyliron(0) and tetracarbonyliron(0), respectively.[5,6] In the latter case, an X-ray crystal structure analysis of the tetracarbonyliron(0) complex revealed evidence for a through-space interaction between the oxygen atom of the sulfinyl substituent and the carbon atom of one of the metal carbonyl ligands. In order to increase our knowledge of how sulfinyl substituted ligands interact with metal carbonyl groups, we wished to synthesize tricarbonylchromium(0) complexes of sulfinyl substituted arenes. We were considerably surprised, however, to find that despite the long standing interest in the application of tricarbonyl(η^6-arene)chromium(0) complexes to problems encountered in organic synthesis[7] and the current widespread interest in the stereochemical properties of these complexes,[8,9] tricarbonylchromium(0) complexes of sulfinyl substituted arenes had not been reported in the literature [although during the development of the use of dimethyldioxirane to remove the tricarbonylchromium(0) unit from arenes, a complex observed by ^{1}H NMR spectroscopy was postulated to be a sulfinyl substituted arene complex[10]]. We herein present an efficient method for oxidising tricarbonylchromium(0) complexes of alkylthio substituted arenes to tricarbonylchromium(0) complexes of alkylsulfinyl substituted arenes. In addition, experiments in which arene and alkylthio substituents were varied are described and the effect of these variations on the diastereoselectivity of the oxidation are discussed. Part of this work has been the subject of a preliminary publication.[11]

Results and Discussion

Our initial efforts to form a tricarbonylchromium(0) complex of an alkylsulfinyl substituted arene focussed on direct complexation of alkylsulfinyl substituted arenes. 1-Methoxy-2-(methylsulfinyl)benzene **1**[12] and 1-methoxy-3-(methylsulfinyl)-benzene **2**[13] were chosen as candidates for complexation for two reasons. Firstly, successful complexation of either of these arenes should give a mixture of two diastereoisomers, unless the complexation process is strongly controlled by the alkylsulfinyl substituent, in which case only one diastereoisomer may form. Secondly, it was reasoned that the electron-donating methoxy group would counteract any unfavourable electron-withdrawing effects of the alkylsulfinyl substituent.[14] Accordingly, 2-(methylthio)phenol **3** and 3-methoxybenzenethiol **4** were methylated to give 1-methoxy-2-(methylthio)-benzene **5**[15] and 1-methoxy-3-(methylthio)benzene[16] **12**, respectively. Subsequent oxidation of these alkylthio substi-



	R^1	R^2	R^3
1	MeS(O)	MeO	H
2	MeS(O)	H	MeO
3	MeS	HO	H
4	HS	H	MeO
5	MeS	MeO	H
6	EtS	MeO	H
7	Pr^{i}S	MeO	H
8	Bu^{t}S	MeO	H
9	MeS	Me	H
10	Bu^{t}S	Me	H
11	MeS	Bu^t	H
12	MeS	H	MeO
13	HS	MeO	H
14	HS	Me	H
15	HS	Bu^t	H

Table 1 Product distribution (%)[a] obtained on treating alkylsulfinyl substituted complex **1** with various sources of the $Cr(CO)_3$ unit

Reagent	Conditions	**1**	**5**	**16**	**20**	**34**	**35**
$[Cr(CO)_6]$	Refluxing Bu_2O–THF (10:1) 14.5 h	—	84	15	—	—	1
$[Cr(CO)_3(\eta^6\text{-naphthalene})]$	Refluxing EtOAc–THF (8:1) 5 h	38	45	7	4	—	6
$[Cr(CO)_3(MeCN)_3]$	Refluxing THF 5 h	50	9	2	2	13	24
$[Cr(CO)_3(pyridine)_3]$	$F_3B{\cdot}OEt_2$ Et_2O, room temp., 1.75 h	19	7	—	—	17	57

[a] Calculated from the 270 MHz ^1H NMR spectrum of the crude product

Table 2 Product distribution (%)[a] obtained on treating alkylsulfinyl substituted complex **2** with various sources of the $Cr(CO)_3$ unit

Reagent	Conditions	**2**	**12**	**29**	**32**	**36**	**37**
$[Cr(CO)_6]$	Refluxing Bu_2O–THF (10:1) 15 h	—	78	22	—	—	—
$[Cr(CO)_3(\eta^6\text{-naphthalene})]$	Refluxing EtOAc–THF (8:1) 5 h	32	42	22	—	—	4
$[Cr(CO)_3(MeCN)_3]$	Refluxing THF 4 h	4	7	—	—	19	70
$[Cr(CO)_3(pyridine)_3]$	$F_3B{\cdot}OEt_2$ Et_2O, room temp., 1 h	42	12	3	—	15	28

[a] Calculated from the 270 MHz ^1H NMR spectrum of the crude product

tuted arenes using purified[5,17] *m*CPBA efficiently gave the required alkylsulfinyl substituted arenes **1** and **2**.

The arenes **1** and **2** were allowed to react with a range of reagents routinely used for the formation of tricarbonyl(η^6-arene)chromium(0) complexes and the crude products obtained were examined by ^1H NMR spectroscopy. The results, which are summarised in Tables 1 and 2, were mostly disappointing. Treating the arene **1** with $[Cr(CO)_6]$[18] or $[Cr(CO)_3(pyridine)_3]$[19] gave none of the required sulfinyl complex **20**, whilst treating **1** with tricarbonyl(η^6-naphthalene)chromium(0)[20] or $[Cr(CO)_3(MeCN)_3]$[21] gave only trace amounts of it. With the arene **2**, none of the conditions tested produced any of the desired alkylsulfinyl complex **32**. The alkylsulfinyl substituted tricarbonylchromium(0) complex **20** and the alkylthio substituted tricarbonylchromium(0) complexes **16** and **29** were identified by comparison of their ^1H NMR data with data obtained from fully characterised compounds synthesised later (see below). The unstable alkylthio substituted pentacarbonylchromium(0) complexes **35** and **37** were isolated and fully characterised whereas the complexes assigned as alkylsulfinyl substituted pentacarbonylchromium(0) compounds **34** and **36** were extremely unstable and could not be fully characterised. They were, therefore, tentatively assigned their structures by comparison of their ^1H NMR data with the data obtained from complexes **16**, **20**, **29**, **32**, **35** and **37**.

Although the reactions between the arene **1** and tricarbonyl(η^6-naphthalene)chromium(0) and $[Cr(CO)_3(MeCN)_3]$ produced only traces of alkylsulfinyl substituted tricarbonylchromium(0) complex **20**, only one diastereoisomer of the complex was formed in each case. In order to determine its relative stereochemistry, the reaction between the arene **1** and $[Cr(CO)_3(MeCN)_3]$ was repeated and complex **20** was isolated, fully characterised and examined by X-ray crystallography (Fig. 1). This revealed that its relative stereochemistry was as indicated by structure X in Fig. 2 (R^1 = Me, R^2 = OMe).

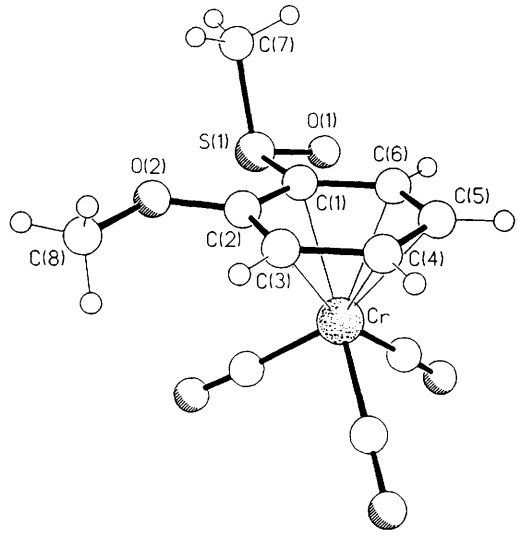
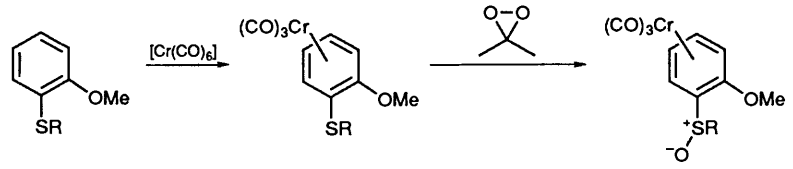


Fig. 1 Molecular structure of complex **20x** ($C_{11}H_{10}CrO_5S$). Selected bond lengths (Å) and bond angles (°); Cr–C(1) 2.206(4), Cr–C(2) 2.275(4), Cr–C(3) 2.241(4), Cr–C(4) 2.192(4), Cr–C(5) 2.218(4), Cr–C(6) 2.191(4), C(1)–C(2) 1.417(5), C(2)–C(3) 1.391(5), C(3)–C(4) 1.412(5), C(4)–C(5) 1.377(6), C(5)–C(6) 1.405(6), C(6)–C(1) 1.404(5), C(1)–S(1) 1.800(4), S(1)–O(1) 1.486(3), S(1)–C(7) 1.786(4), C(2)–O(2) 1.349(4), O(2)–C(8) 1.431(5); C(7)–S(1)–O(1) 106.0(2), C(7)–S(1)–C(1) 96.3(2), O(1)–S(1)–C(1) 106.1(2), S(1)–C(1)–C(2) 120.2(3), C(1)–C(2)–O(2) 115.2(3), C(2)–O(2)–C(8) 118.1(3).

Since the yield of alkylsulfinyl complex **20x** was both poor



R = Me **5**	R = Me **16** (89%)	R = Me **20** $20_X:20_Y$ = 7:93 20_Y (80%)
R = Et **6**	R = Et **17** (67%)	R = Et **21** $21_X:21_Y$ = 15:85 21_Y (39%)
R = Pr^i **7**	R = Pr^i **18** (52%)	R = Pr^i **22** $22_X:22_Y$ = 70:30 22_X (56%)
R = Bu^t **8**	R = Bu^t **19** (71%)	R = Bu^t **23** $23_X:23_Y$ = ≥98:2 23_X (77%)

Table 3 Selected ^{1}H NMR (δ)[a] data for diastereoisomers **X** and **Y** of alkylsulfinyl substituted complexes

Alkylsulfinyl substituted complex X	6-H[b]	Alkylsulfinyl substituted complex Y	6-H[b]
$\mathbf{20_X}$	6.19d	$\mathbf{20_Y}$	6.34d
$\mathbf{21_X}$	6.12d	$\mathbf{21_Y}$	6.31d
$\mathbf{22_X}$	6.09d	$\mathbf{22_Y}$	6.16d
$\mathbf{23_X}$	6.08d	$\mathbf{23_Y}$	Diastereoisomer not observed
$\mathbf{26_X}$	6.10d	$\mathbf{26_Y}$	6.17d
$\mathbf{27_X}$	5.98d	$\mathbf{27_Y}$	Diastereoisomer not observed
$\mathbf{31_X}$	5.91d	$\mathbf{31_Y}$	6.38d

[a] $CDCl_3$, 300 K, 270 MHz. [b] ^3J = 6–7 for all d. All signals displayed fine ^4J coupling.

Fig. 2 Relative orientations of the two chiral elements in the alkylsulfinyl substituted complexes looking down the S–C bond in the plane of the arene ring

and capricious, an alternative route to tricarbonylchromium(0) complexes of alkylsulfinyl substituted arenes was sought. It has been known for some time that alkylthio substituted arenes readily form tricarbonylchromium(0) complexes,[22] and so oxidation of alkylthio substituents was proposed as a potentially much more efficient route to tricarbonylchromium(0) complexes of sulfinyl substituted arenes. Thus, the sulfide **5** was converted into its tricarbonylchromium(0) complex **16** in 89% yield by heating it with $[Cr(CO)_6]$. Oxidation of complex **16** with 1.1 equiv. of either *m*CPBA, *tert*-butyl hydroperoxide[23] or 2-hydroperoxy-2-methoxypropane[24] gave, in the former two cases, a mixture of the sulfide ligand **5** and the organic sulfoxide **1** or, in the latter case, a mixture of the starting sulfide complex **16** and decomplexed ligand **5**. Attention then turned to dimethyldioxirane,[25] a reagent which has rapidly been accepted as a useful mild oxidant for many organic transformations,[26] including the oxidation of sulfides to sulfoxides,[27] and which is beginning to prove very useful for organometallic transformations.[26,28] Pleasingly, oxidation of the sulfide complex **16** with 1.1 equiv. of dimethyldioxirane led to the formation of the required sulfoxide complex **20** in good yield. Examination of the crude product by ^{1}H NMR spectroscopy indicated that the two possible diastereoisomers of **20** had been formed in a ratio of 93:7. Comparison of this spectrum with the ^{1}H NMR data of the complex obtained by direct complexation revealed that the complex obtained previously was the minor diastereoisomer in the product mixture obtained by oxidation (see Table 3). Thus, the major diastereoisomer obtained by oxidation was assigned the relative stereochemistry indicated by structure Y in Fig. 2 (R^1 = Me, R^2 = OMe). Crystallisation of the crude product mixture from acetone–hexane gave diastereoisomerically and analytically pure sulfoxide complex $\mathbf{20_Y}$ in 80% yield.

In order to determine whether or not the diastereoisomeric ratio of 93:7 observed in the oxidation of the alkylthio substituted complex **16** to the sulfinyl substituted complex **20** could be improved significantly, the size of the alkyl group of the alkythio substituent was increased. The thiol **13** was converted into the *tert*-butyl sulfide **8** and thence to the *tert*-butylthio complex **19** which was subsequently oxidised with dimethyldioxirane. The ^{1}H NMR spectrum of the crude product contained signals for only one diastereoisomeric sulfoxide complex. Subsequent crystallisation gave pure sulfinyl substituted complex **23** in 77% yield. Interestingly, an X-ray crystal structure analysis of the yellow crystals (Fig. 3) revealed that the relative stereochemistry of the major diastereoisomer obtained by oxidation of complex **19** corresponded with stereochemistry X in Fig. 2 (R^1 = Bu^t, R^2 = OMe). Therefore, oxidation of the methylthio substituted complex **16** and the *tert*-butylthio substituted complex **19** had proceeded with complementary selectivity to give predominantly diastereoisomers Y and X, respectively.

To investigate this interesting reversal of stereochemistry in more detail, the thiol **13** was converted into the ethylthio- and isopropylthio- complexes **17** and **18** *via* the corresponding sulfides **6** and **7**. Dimethyldioxirane oxidation of the ethylthio substituted complex **17** gave a product dominated by diastereoisomer Y ($\mathbf{21_X}:\mathbf{21_Y}$ = 15:85) whilst oxidation of the isopropylthio substituted complex **18** gave a product dominated by diastereoisomer X ($\mathbf{22_X}:\mathbf{22_Y}$ = 70:30). Complexes $\mathbf{21_Y}$ and $\mathbf{22_X}$ were isolated and characterised and an X-ray crystal structure analysis was performed on $\mathbf{21_Y}$ (Fig. 4). Examination of the ^{1}H NMR spectra of the diastereoisomers of complexes **20–23** revealed that 6-H showed a relatively large variation in its δ value between diastereoisomers **X** and **Y** (see Table 3). Correlation with the X-ray crystal structures of $\mathbf{20_X}$ and $\mathbf{21_Y}$ and to a lesser extent $\mathbf{23_X}$ led to the working

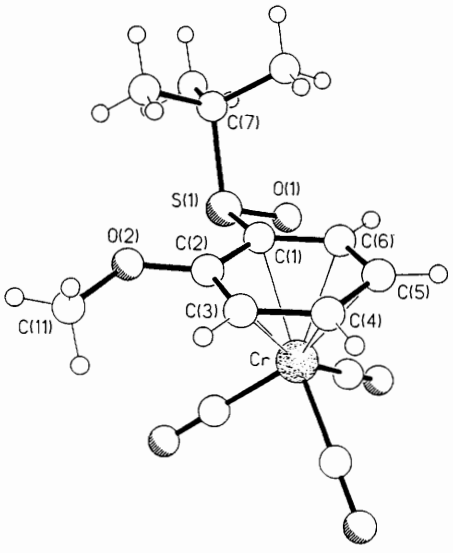


Fig. 3 Molecular structure of one of the pair of crystallographically independent molecules of complex $\mathbf{23_X}$ ($C_{14}H_{16}CrO_5S$). Selected bond lengths (Å) and bond angles (°) (values in [] refer to the second independent molecule: Cr–C(1) 2.210(5) [2.218(5)], Cr–C(2), 2.255(5) [2.273(5)], Cr–C(3) 2.232(5) [2.240(5)], Cr–C(4) 2.180(6) [2.183(6)], Cr–C(5) 2.217(5) [2.209(6)], Cr–C(6) 2.174(5) [2.180(5)], C(1)–C(2) 1.421(7) [1.414(7)], C(2)–C(3) 1.400(7) [1.406(7)], C(3)–C(4) 1.396(8) [1.389(8)], C(4)–C(5) 1.398(8) [1.400(8)], C(5)–C(6) 1.400(8)[1.391(8)], C(6)–C(1) 1.389(7) [1.399(7)], C(1)–S(1) 1.813(5) [1.811(5)], S(1)–O(1) 1.479(4) [1.493(4)], S(1)–C(7) 1.850(5) [1.847(5)], C(2)–O(2) 1.347(6) [1.343(7)], O(2)–C(8) 1.454(6) [1.432(7)]; C(7)–S(1)–O(1) 105.4(2) [105.4(2)], C(7)–S(1)–C(1) 101.7(2) [102.6(2)], O(1)–S(1)–C(1) 104.6(2) [104.6(2)], S(1)–C(1)–C(2) 121.8(4) [121.7(4)], C(1)–C(2)–O(2) 116.1(4) [116.4(4)], C(2)–O(2)–C(8) 117.2(4) [118.0(4)].

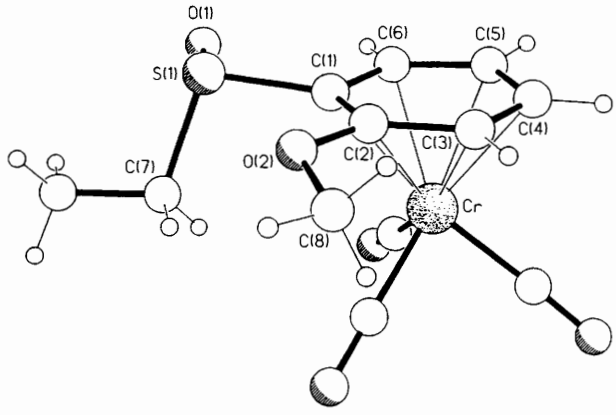


Fig. 4 Molecular structure of one of the pair of crystallographically independent molecules of complex $\mathbf{21_Y}$ ($C_{12}H_{12}CrO_5S$). Selected bond lengths (Å) and bond angles (°) (values in [] refer to the second independent molecule): Cr–C(1) 2.223(4) [2.225(5)], Cr–C(2) 2.276(4) [2.280(5)], Cr–C(3) 2.242(4) [2.234(5)], Cr–C(4) 2.200(5) [2.188(6)], Cr–C(5) 2.229(5) [2.220(5)], Cr–C(6) 2.200(5) [2.193(5)], C(1)–C(2) 1.413(5) [1.418(6)], C(2)–C(3) 1.399(6) [1.399(7)], C(3)–C(4) 1.400(7) [1.393(8)], C(4)–C(5) 1.387(7) [1.373(10)], C(5)–C(6) 1.393(7) [1.419(8)], C(6)–C(1) 1.407(6) [1.396(7)], C(1)–S(1) 1.803(4) [1.797(5)], S(1)–O(1) 1.493(3) [1.491(4)], S(1)–C(7) 1.800(5) [1.790(5)], C(2)–O(2) 1.349(5) [1.342(6)], O(2)–C(8) 1.445(6) [1.434(7)]; C(7)–S(1)–O(1) 105.5(2) [105.3(2)], C(7)–S(1)–C(1) 100.3(2) [99.8(2)], O(1)–S(1)–C(1) 105.1(2) [105.3(2)], S(1)–C(1)–C(2) 122.0(3) [122.5(4)], C(1)–C(2)–O(2) 115.7(3) [115.9(4)], C(2)–O(2)–C(8) 117.8(3) [118.5(4)].

hypothesis that 6-H of diastereoisomer **X** has a lower δ value than 6-H of the corresponding diastereoisomer **Y**.

Next, the methoxy substituent (R^2 = OMe) was replaced by a methyl group (R^2 = Me) in order to gain some insight into whether or not the observed change in diastereoselectivity was electronic or steric in nature. Thus, the thiol **14** was converted into the methylthio- and *tert*-butylthio substituted complexes **24** and **25** *via* the methyl and *tert*-butyl sulfides **9** and **10**. Dimethyldioxirane oxidation of the methylthio substituted complex **24** gave a product dominated by diastereoisomer **Y** ($\mathbf{26_X}$:$\mathbf{26_Y}$ = 10:90) whilst oxidation of the *tert*-butylthio substituted complex **25** gave a product dominated by diastereoisomer **X** ($\mathbf{27_X}$:$\mathbf{27_Y}$ ≥ 98:2). Complexes $\mathbf{26_Y}$ and $\mathbf{27_X}$ were isolated in 78 and 92% yield, respectively, and fully characterised.

An explanation for the dramatic difference in diastereoselectivity between the methylthio substituted complexes and the *tert*-butylthio substituted complexes is illustrated in Fig. 5. When R^1 = Me, eclipsing interactions between R^1 and the hydrogen *ortho* to the alkylthio group are inconsequential and so the methylthio substituted complex can adopt conformation **A** in which one of the sulfur lone pairs is exposed on the *exo* face of the complex. Oxidation of this lone pair leads to the diastereoisomer **Y**. When R^1 = Bu^t, however, eclipsing interactions between the *tert*-butyl group and the *ortho* hydrogen, the R^2 substituent and the tricarbonylchromium(0) fragment, restrict the *tert*-butylthio substituent to conformation **B** in which neither of the sulfur lone pairs are on the *exo* face of the complex. Consequently, the dioxirane is forced to approach the *endo* face of the complex past the least sterically demanding *ortho* substituent to give the diastereoisomer **X**. The cases where R^1 = Et and Pr^i represent intermediate situations in which the energy differences between the transition states leading to diastereoisomers **X** and **Y** are less pronounced.

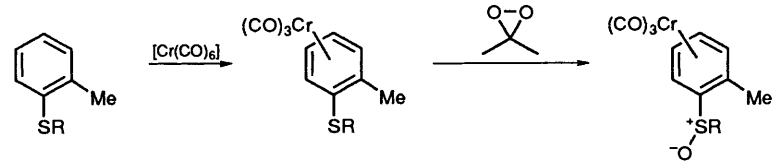
The effect of increasing the size of the *ortho* substituent R^2 was examined next. Thus, the thiol **15** was converted into its methyl sulfide **11** and thence into complex **28** (R^1 = Me and R^2 = Bu^t). Oxidation of complex **28** under conditions identical with those used for all the other oxidations gave a crude product containing not only the required alkylsulfinyl substituted complex, dominated by diastereoisomer **Y** ($\mathbf{31_X}$:$\mathbf{31_Y}$ = 7:93), but also significant quantities of starting complex **28** (**28**:**31** = 33:67). Complex $\mathbf{31_Y}$ was subsequently isolated in 45% yield. Repetition of this experiment gave a similar result ($\mathbf{31_X}$:$\mathbf{31_Y}$ = 7:93; **28**:**31** = 32:68). Thus, when R^2 = Bu^t rather than MeO or Me, the rate of oxidation is significantly retarded and this is attributed to the increased energy required for the dimethyldioxirane to approach the *exo* lone pair of conformation **A** past the relatively sterically demanding *tert*-butyl group.

Finally, oxidation of the *meta* substituted alkylthio complex **29** was found to proceed unselectively ($\mathbf{32_X}$:$\mathbf{32_Y}$ = 50:50), and oxidation of tricarbonyl(η^6-thioanisole)chromium(0) **30**[22] proceeded efficiently to give a 93% yield of the alkylsulfinyl substituted complex **33**.

In conclusion, it has been demonstrated that dimethyldioxirane chemoselectively oxidises the sulfur of alkylthio substituted tricarbonyl(η^6-arene)chromium(0) complexes to produce alkylsulfinyl substituted tricarbonyl(η^6-arene)chromium(0) complexes for the first time. The diastereoselectivity of oxidation of *ortho* substituted complexes is dependent on the alkylthio substituent and is reversed when this substituent is changed from methyl to *tert*-butyl.

Experimental

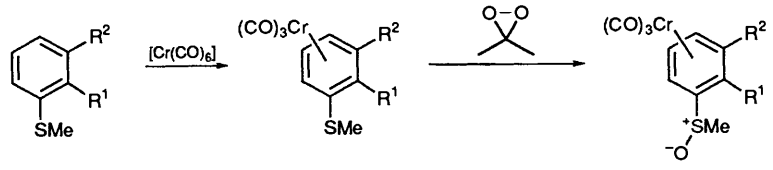
Reactions under nitrogen were performed using standard vacuum line and Schlenk tube techniques.[29] All thermolyses with hexacarbonylchromium were carried out in the dark, under a nitrogen atmosphere, in a B24 neck round-bottom



R = Me **9**
R = Bu^t **10**

R = Me **24** (75%)
R = Bu^t **25** (78%)

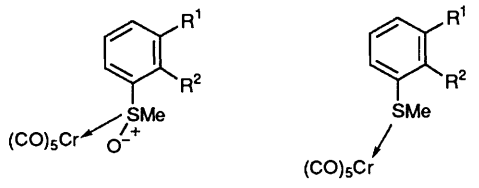
R = Me **26** 26_X:26_Y = 10:90 26_Y (78%)
R = Bu^t **27** 27_X:27_Y = ≥98:2 27_X (92%)



R^1 = Bu^t, R^2 = H **11**
R^1 = H, R^2 = OMe **12**

R^1 = Bu^t, R^2 = H **28** (50%)
R^1 = H, R^2 = OMe **29** (92%)
R^1 = H, R^2 = H **30** (96%)

R^1 = Bu^t, R^2 = H **31** 31_X:31_Y = 6:94 31_Y (45%)
R^1 = H, R^2 = OMe **32** 32_X:32_Y = 50:50 $32_{X/Y}$ (65%)
R^1 = H, R^2 = H **33** **33** (93%)



34 R^1 = H, R^2 = MeO
36 R^1 = MeO, R^2 = H

35 R^1 = H, R^2 = MeO
37 R^1 = MeO, R^2 = H

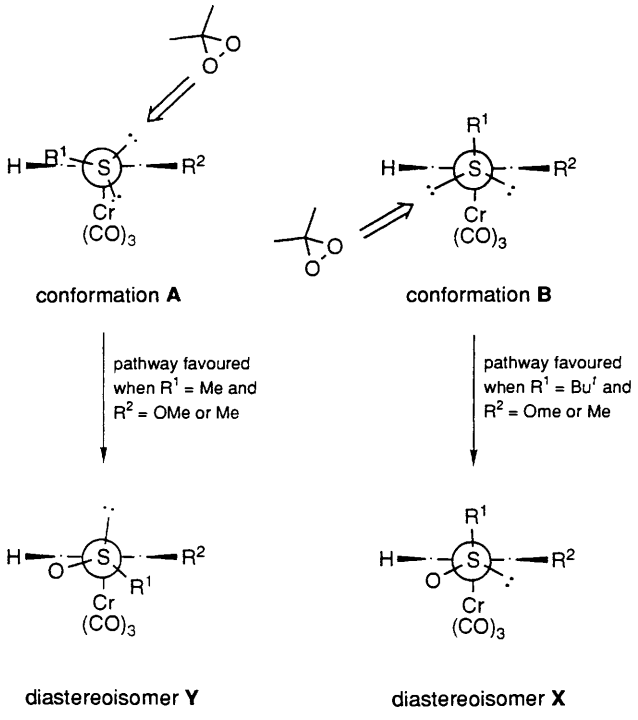


Fig. 5 Proposed origin of the complementary diastereoselectivity observed for oxidation of the methylthio and *tert*-butylthio substituted complexes

flask, equipped with a long Liebig air condenser with a water condenser on top. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Diethyl ether was dried over Na wire. 1,4-Dioxane and acetonitrile were distilled from CaH_2 and stored over molecular sieves (4 Å). Dibutyl ether was distilled from CaH_2. *N*,*N*-Dimethylformamide was stored over molecular sieves (4 Å). Ethyl acetate was distilled from P_4O_{10}. Pyridine was distilled from KOH and stored over KOH. $F_3B{\cdot}OEt_2$ was purified according to a literature procedure.[30] Commercially available *m*CPBA (50–60%) was purified according to a literature procedure.[6] All other chemicals were used as obtained from commercial sources. M.p.s of organochromium complexes were measured in sealed capillaries under nitrogen on a Gallenkamp capillary m.p. apparatus and are uncorrected. Elementary analyses were performed by Imperial College Microanalytical Service. IR spectra were obtained on a Perkin-Elmer 1710 FTIR instrument. NMR spectra were recorded in $CDCl_3$ on a JEOL GSX 270 spectrometer (270 MHz ^{1}H, 67.9 MHz ^{13}C) and a Bruker AM 500 spectrometer (125.8 MHz ^{13}C). Mass spectra were recorded on VG Mass Lab 12/1250 and VG analytical ZAB/E instruments at the SERC Mass Spectrometry Service Centre, Swansea, and on VG Micromass 7070E and AutoSpec-Q instruments at Imperial College using EI and CI techniques. The X-ray crystal structure of the sulfinyl substituted complex $\mathbf{23_X}$ has been reported previously.[11] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Preparation of a Dimethyldioxirane Solution in Acetone.[25]—A 500 cm^3, three-necked, round-bottom flask, equipped with a large and efficient magnetic stirrer bar and connected by means of an U tube to a Schlenk tube cooled at −78 °C, was charged with distilled water (53 cm^3), acetone (40 cm^3) and sodium hydrogen carbonate (12 g). The resulting white suspension was cooled to 5–10 °C and vigorously stirred. Oxone® (25 g) was then added in five portions at 3-min intervals and the

temperature of the reaction mixture carefully maintained below 10 °C. 3 Min after the last addition, a moderate vacuum (80–100 mmHg) was applied and the cooling bath (5–10 °C) removed from the reaction flask. The effluent dimethyldioxirane–acetone solution (20–25 cm^3, 0.08–0.1 mol) was collected in the cooled Schlenk tube (the distillation took more than 1.5 h), dried over K_2CO_3, transferred under nitrogen into a bottle containing molecular sieves (4 Å) and stored in the freezer for a few days without any dramatic decomposition.

The concentration of dimethyldioxirane was determined, before each experiment, by partial oxidation of a known amount of methylthiobenzene to its sulfoxide. One drop of methylthiobenzene was weighed accurately and washed into a Schlenk tube with dry diethyl ether. The solution was stirred at room temperature under nitrogen and dimethyldioxirane (0.5 cm^3) was added to it. After the mixture had been stirred for 30 min, the solvent was removed and the product analysed by ^1H NMR spectroscopy. Comparison of the integrals of the methyl singlets of the sulfide (δ = 2.5 ppm) and sulfoxide (δ = 2.7 ppm) led to an estimate of the concentration.

1-Methoxy-2-methylthiobenzene **5**.[15]—2-(Methylthio)phenol (4 g, 28.5 mmol) was treated with sodium hydride (60% dispersion in paraffin; 1.24 g, 31 mmol) and iodomethane (8 g, 57 mmol), according to the procedure described for the synthesis of the sulfide **12** (see below). (After the addition of iodomethane, however, the solution was heated at 38 °C for 24 h.) After work-up and distillation, the title sulfide **5** was isolated as a colourless oil (3.8 g, 24.7 mmol, 86%), b.p. 111–113 °C (8 mmHg) [lit.,[15] b.p. 86–89 °C (1 mmHg)]; ν_{max}(neat)/cm^{-1} 3003s, 2960s, 2936s, 2920s, 2835s, 1578vs, 1479vs, 1434vs, 1307s, 1274vs, 1240vs, 1182s, 1134s, 1074vs and 1026vs; *m/z* (EI, 70 eV, 180 °C) 154 (M^+, 100%), 139 (M − CH_3, 34), 77 (C_6H_5, 17) and 45 (CHS, 53). See Tables 4 and 5 for ^1H and ^{13}C NMR spectroscopic data.

1-Methoxy-3-methylthiobenzene **12**.[16]—In a 500 cm^3, two-necked, round-bottom flask, equipped with a condenser and a gas inlet, sodium hydride (60% dispersion in paraffin; 1.57 g, 39.3 mmol) was washed with DMF (4 × 20 cm^3). Further DMF (150 cm^3) was added to the flask and the resulting grey suspension was stirred vigorously at 0 °C. 3-Methoxybenzenethiol **4** (5 g, 36 mmol) was added dropwise to the reaction mixture which was then stirred at 0 °C for 15 min during which time it turned yellow. Iodomethane (5.59 g, 39.3 mmol) was then added dropwise to the solution after which it was stirred at 0 °C for 15 min and then allowed to warm to room temperature and stirred for a further 45 min. 10% Aqueous NaOH (100 cm^3) as added to the reaction mixture which was then extracted with diethyl ether (20 cm^3). After separation of the ethereal layer, the aqueous phase was extracted with diethyl ether (3 × 20 cm^3). The organic extracts were combined, washed successively with 10% aqueous NaOH (3 × 50 cm^3), water (3 × 50 cm^3) and saturated brine (3 × 50 cm^3), dried ($MgSO_4$) and filtered. Solvent removal from the mixture and distillation of the residue under reduced pressure gave the title sulfide **12** (4.96 g, 32.2 mmol, 90%) as a colourless oil, b.p. 118–119 °C (9 mmHg) [lit.,[16] b.p. 118–119 °C (10 mmHg)]; ν_{max}(neat)/cm^{-1} 2970vs, 1592vs, 1578vs, 1467vs, 1379vs, 1284vs, 1249vs, 1231s and 1052s; *m/z* (EI, 70 eV, 210 °C) 154 (M^+, 100%), 139 (M − CH_3, 4), 121 (M − SH, 52), 77 (C_6H_5, 12) and 45 (CHS, 11). See Tables 4 and 5 for ^1H and ^{13}C NMR spectroscopic data.

1-Methoxy-2-methylsulfinylbenzene **1**.[12]—1-Methoxy-2-methylthiobenzene **5** (1.1 g, 7 mmol) was dissolved in dichloromethane (10 cm^3) and the solution cooled to 0 °C. The solution was then rapidly stirred whilst a solution of purified *m*CPBA (1.33 g, 7.7 mmol) in dichloromethane (15 cm^3) was added dropwise to it over 15 min. After the reaction mixture had been stirred at 0 °C for 2 h, it was allowed to warm to room temperature and then stirred for a further 2 h. The resulting white slurry was washed with 10% aqueous NaOH (30 cm^3) after which the organic layer was separated and the aqueous layer extracted with dichloromethane (3 × 20 cm^3). The combined organic extracts were then washed with 10% aqueous NaOH (3 × 20 cm^3), water (3 × 30 cm^3) and saturated brine (3 × 30 cm^3), dried ($MgSO_4$), and concentrated under reduced pressure to give a colourless oil. Column chromatography (SiO_2; ethyl acetate–dichloromethane, 3:7) of this gave the title sulfoxide **1** (1.11 g, 6.53 mmol, 94%) as a colourless oil; ν_{max}(neat)/cm^{-1} 3068m, 3009m, 2970m, 2941m, 2918m, 2840m, 1587s, 1478vs, 1436s, 1273vs and 1240vs; δ_H 2.50 (3 H, s, $SOCH_3$), 3.62 (3 H, s, OCH_3), 6.68 (1 H, dd, *J* 1.0, 8.3, 3-H or 6-H), 6.90 (1 H, dt, *J* 1.0, 7.6, 4-H or 5-H), 7.18 (1 H, ddd, *J* 1.7, 7.6, 8.3, 4-H or 5-H) and 7.55 (1 H, dd, *J* 1.7, 7.6, 3-H or 6-H); $\delta_C\{^1H\}$ (67.5 MHz) 40.6 ($SOCH_3$), 55.1 (OCH_3), 110.1 (C-3), 120.9 (C-5), 123.7 (C-6), 131.4 (C-4), 132.5 (C-1) and 154.2 (C-2); *m/z* (EI, 70 eV, 200 °C) 170 (M^+, 17%), 155 (M − CH_3, 48) 154 (M − O, 82), 153 (M − OH, 100), and 139 (M − OCH_3, 30).

1-Methoxy-3-methylsulfinylbenzene **2**.[13]—Following the procedure described above for the synthesis of the sulfoxide **1**, 1-methoxy-3-methylthiobenzene **12** (1.1 g, 7 mmol), dissolved in dichloromethane (10 cm^3) was oxidised using a solution of purified *m*CPBA (1.33 g, 7.7 mmol) in dichloromethane (15 cm^3). Purification by column chromatography (SiO_2, ethyl acetate–dichloromethane, 3:7) gave the title sulfoxide **2** (1.06 g, 6.23 mmol, 89%) as a colourless oil; ν_{max}(neat)/cm^{-1} 3063m, 3002m, 2963m, 2941m, 2913m, 2837m, 1595vs, 1482vs, 1250vs and 1040vs; δ_H 2.60 (3 H, s, $SOCH_3$), 3.74 (3 H, s, OCH_3), 6.86–6.91 (1 H, m, 4-H or 6-H), 7.00–7.03 (1 H, dd, *J* 1.7, 2.2, 2-H) and 7.26–7.32 (1 H, m, 5-H); $\delta_C\{^1H\}$ (67.5 MHz) 43.9 ($SOCH_3$), 55.4 (OCH_3), 107.8 (C-2), 115.4 (C-6), 117.2 (C-4), 130.2 (C-5), 147.1 (C-1) and 160.4 (C-3); *m/z* (EI, 70 eV, 200 °C) 170 (M^+, 57%), 155 (M − CH_3, 100), 124 (M − CH_3 − OCH_3, 20) and 107 (M − $SOCH_3$, 9).

Reaction of 1-*Methoxy*-2-*methylsulfinylbenzene* **1** *with Hexacarbonylchromium*.—Following procedure E (see below), 1-methoxy-2-(methylsulfinyl)benzene **1** (0.085 g, 0.5 mmol) was heated with hexacarbonylchromium (0.121 g, 0.55 mmol) at 130 °C in dibutyl ether–THF (10:1, 11 cm^3) for 14.5 h, giving a cloudy green mixture. Filtration and removal of the solvent gave a yellow oil (0.11 g), which was analysed by ^1H NMR spectroscopy (see Table 1).

Procedure A

Reaction of 1-*Methoxy*-2-(*methylsulfinyl*)*benzene* **1** *with Tricarbonyl*(η^6-*naphthalene*)*chromium*(0).—*Tricarbonyl*(η^6-*naphthalene*)*chromium*(0). Naphthalene (3.08 g, 24 mmol) and hexacarbonylchromium (2.79 g, 12.7 mmol) were refluxed in dibutyl ether–THF (10:1; 93.5 cm^3), in the dark under a nitrogen atmosphere for 36 h. After the resulting red solution had been allowed to cool in an ice bath it was filtered through Kieselguhr, eluting with diethyl ether, and then concentrated under reduced pressure. Purification of the residue by column chromatography [SiO_2; light petroleum (b.p. 40–60 °C)–diethyl ether, 100:0 to 50:50, gradient elution] gave the title compound (1.33 g, 5 mmol, 40%) as a red crystalline solid, m.p. 123 °C (decomp.), (lit.,[31] m.p. 134–136 °C); ν_{max}(CH_2Cl_2)/cm^{-1} 1965vs and 1888vs (C≡O); δ_H 5.51 (2 H, dd, *J* 2.7, 5.1, 2-H and 3-H), 6.12 (2 H, dd, *J* 2.7, 5.1, 1-H and 4-H), 7.4 (2 H, dd, *J* 3.2, 6.6, 6-H and 7-H) and 7.57 (2 H, dd, *J* 3.2, 6.6, 5-H and 8-H);

$\delta_C\{^1H\}$ (125.8 MHz) 90.7 (C-1 and C-4), 92.3 (C-2 and C-3), 105.7 (C-4a and C-8a), 128.8 (C-6 and C-7), 128.7 (C-5 and C-8) and 232.0 (C≡O); *m/z* (EI, 70 eV, 120 °C) 264 (M^+, 4.5%), 236 (M − CO, 0.2), 208 (M − 2CO, 3.1), 180 (M − 3CO, 17.6), 128 [M − $Cr(CO)_3$, 41.2] and 52 (Cr, 100).

Reaction of 1-*Methoxy*-2-(*methylsulfinyl*)*benzene* **1** *with Tricarbonyl*(η^6-*naphthalene*)*chromium*(0).—A 50 cm^3, two-necked, round-bottom flask fitted with a condenser and a gas inlet, was charged under a nitrogen atmosphere with 1-methoxy-2-(methylsulfinyl)benzene **1** (0.153 g, 0.9 mmol) and tricarbonyl(η^6-naphthalene)chromium(0) (0.27 g, 1 mmol). A nitrogen saturated ethyl acetate–THF solution (8 : 1, 9 cm^3) was then added *via* a cannula to the mixture. The resulting deep red solution was saturated with nitrogen and allowed to reflux under nitrogen in the dark. The progress of the reaction was monitored by TLC. After 5 h, all the naphthalene complex had reacted. The resulting brown solution was allowed to cool in an ice-bath and was then filtered through Kieselguhr, eluting with diethyl ether. Subsequent solvent removal under reduced pressure afforded a yellow powder (0.35 g), which was analysed by ^1H NMR spectroscopy (see Table 1).

Procedure B

Reaction of 1-*Methoxy*-2-(*methylsulfinyl*)*benzene* **1** *with Tris*(*acetonitrile*)*tricarbonylchromium*(0).—*Tris*(*acetonitrile*)*tricarbonylchromium*(0).[32] A suspension of hexacarbonylchromium (0.6 g, 2.75 mmol) in acetonitrile (15 cm^3) was saturated with nitrogen and refluxed in the dark under a nitrogen atmosphere for 18 h. The resulting orange solution was cooled in an ice bath and transferred under nitrogen into a Schlenk tube *via* a filter cannula. Removal of the solvent afforded the title complex as yellow crystals (0.71 g, 2.7 mmol, 99%). This complex is unstable and consequently was used directly.

Reaction of 1-*Methoxy*-2-(*methylsulfinyl*)*benzene* **1** *with Tris*(*acetonitrile*)*tricarbonylchromium*(0).—A 100 cm^3, two-necked, round-bottom flask, fitted with a condenser and a gas inlet, was charged under a nitrogen atmosphere with a solution of 1-methoxy-2-(methylsulfinyl)benzene **1** (0.42 g, 2.5 mmol) in THF (1 cm^3). A red nitrogen-saturated solution of tris(acetonitrile)tricarbonylchromium(0) (0.7 g, 2.75 mmol) in the minimum amount of THF was then added to the mixture *via* a cannula. The resulting red solution was saturated with nitrogen and allowed to reflux under nitrogen in the dark for 5 h. The resulting green–black solution was cooled in an ice bath and filtered through Kieselguhr, eluting with diethyl ether. Solvent removal from the filtrate under reduced pressure afforded a green solid which was treated with diethyl ether and filtered through Kieselguhr to give a yellow solution. Concentration under reduced pressure yielded a yellow powder (0.53 g) which was analysed by ^1H NMR spectroscopy (see Table 1) and subjected to column chromatography (SiO_2).

Initial elution with light petroleum (b.p. 40–60 °C)–dichloromethane (9 : 1) allowed collection of a deep yellow fraction, concentration of which under reduced pressure afforded a yellow powder which was recrystallised from dichloromethane–pentane to give *pentacarbonyl*[1-*methoxy*-2-(*methylthio*)*benzene*-S]*chromium*(0) **35** as yellow crystals (0.14 g, 0.4 mmol, 16%), m.p. 70–71 °C (Found: *m/z* 345.9603. $C_{13}H_{10}CrO_6S$ requires 345.9603); ν_{max}(hexane)/cm^{-1} 1945vs and 1930s (C≡O); δ_H 2.63 [3 H, s, $SCH_3Cr(CO)_5$], 3.97 (3 H, s, OCH_3), 6.92–7.03 (2 H, m, 3-H, 4-H, 5-H or 6-H) and 7.29–7.39 (2 H, m, 3-H, 4-H, 5-H or 6-H); $\delta_C\{^1H\}$ (125.8 MHz) 24.1 [$SCH_3Cr(CO)_5$], 55.4 (OCH_3), 111.1 (C-3), 121.4 (C-4 or C-5 or C-6), 124.0 (C-1), 127.9 and 130.3 (C-4 or C-5 or C-6), 156.8 (C-2), 214.8 (4 × C≡O *cis*) and 221.9 (1 × C≡O *trans*); *m/z* (EI, 70 eV, 100 °C) 346 (M^+, 0.1%), 290 (M − 2CO, 0.1), 262 (M − 3CO, 0.1), 234 (M − 4CO, 0.2), 206 (M − 5CO, 0.2) and 154 [M − $Cr(CO)_5$, 70.6].

Further elution with light petroleum (b.p. 40–60 °C)–dichloromethane (1 : 1) allowed collection of a second deep yellow fraction but subsequent concentration of this under reduced pressure led to decomposition of the complex. However, from the ^1H NMR spectrum of the crude mixture, this very unstable complex was assigned as *pentacarbonyl*[1-*methoxy*-2-(*methylsulfinyl*)*benzene*-*S*']*chromium*(0) **34**; δ_H 3.33 [3 H, s, $SOCH_3Cr(CO)_5$], 3.99 (3 H, s, OCH_3) and 6.9–7.45 (4 H, m, 3-H, 4-H, 5-H and 6-H).

Procedure C

Reaction of 1-*Methoxy*-2-(*methylsulfinyl*)*benzene* **1** *with Tricarbonyltris*(*pyridine*)*chromium*(0).—*Tricarbonyl*(η^6-*methoxybenzene*)*chromium*(0).[33] Hexacarbonylchromium (6.16 g, 28 mmol) and methoxybenzene (40 g, 370 mmol) were heated under reflux in a mixture of dibutyl ether–THF (5 : 1; 120 cm^3) for 40 h. The resulting yellow solution was cooled in an ice-bath and then filtered through Kieselguhr, eluting with diethyl ether. Concentration of the filtrate under reduced pressure afforded the title complex as a yellow crystalline solid (6.59 g, 27 mmol, 97%), m.p. 83–84 °C (lit.,[33] m.p. 84–85 °C) which was pure enough to be used without any further purification; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 1967vs and 1885vs (C≡O); δ_H 3.72 (3 H, s, OCH_3), 4.85–4.90 (1 H, m, 4-H), 5.11 (2 H, d, *J* 6.3, 2-H and 6-H) and 5.52–5.57 (2 H, m, 3-H and 5-H); $\delta_C\{^1H\}$ (125.8 MHz) 55.5 (OCH_3), 78.1 (C-2 and C-6), 85.4 (C-4), 95.0 (C-3 and C-5), 143.3 (C-1) and 233.1 (C≡O); *m/z* (EI, 70 eV, 120 °C) 244 (M^+, 12%), 216 (M − CO, 0.5), 188 (M − 2CO, 4.4), 160 (M − 3CO, 31.4), 145 (M − 3CO − CH_3, 4.4), 108 [M − $Cr(CO)_3$, 31] and 52 (Cr, 100).

Tricarbonyltris(*pyridine*)*chromium*(0).—A 50 cm^3, two-necked, round-bottom flask, fitted with a condenser and a gas inlet, was charged with tricarbonyl(η^6-methoxybenzene)-chromium(0) (0.48 g, 1.97 mmol) under a nitrogen atmosphere and nitrogen-saturated pyridine (8 cm^3) was then added to it *via* a cannula. The resulting yellow solution was heated under reflux in the dark, upon which it turned red immediately. After 3 h, the resulting deep red solution was allowed to cool in an ice-bath and cold nitrogen-saturated diethyl ether was added to it until red crystals appeared. These were filtered off under nitrogen and washed with cold nitrogen-saturated diethyl ether (3 × 5 cm^3) to afford the title complex as red crystals (0.7 g, 1.94 mmol, 98%). Since this complex is unstable it was kept under a nitrogen atmosphere and used directly in the same flask.

Reaction of 1-*Methoxy*-2-(*methylsulfinyl*)*benzene* **1** *with Tricarbonyltris*(*pyridine*)*chromium*(0).—To a 50 cm^3, two-necked, round-bottom flask, fitted with a condenser and a gas inlet, and containing freshly prepared tricarbonyltris(pyridine)-chromium(0) (0.72 g, 1.94 mmol), a nitrogen-saturated solution of 1-methoxy-2-(methylsulfinyl)benzene **1** (0.3 g, 1.76 mmol) in diethyl ether (10 cm^3) was transferred *via* a cannula. Boron trifluoride–diethyl ether (0.7 cm^3, 0.79 g, 5.6 mmol) was then added to the reaction mixture which turned orange–yellow immediately. After the mixture had been stirred at room temperature for 1.75 h, nitrogen-saturated water (15 cm^3) was added to it. The organic layer was extracted with diethyl ether and the extract dried ($MgSO_4$) and concentrated under reduced pressure to afford a yellow–orange solid (0.5 g) which was analysed by ^1H NMR spectroscopy (see Table 1). An unspecified amount of pentacarbonyl(pyridine)chromium(0)[34] was detected as a by-product in the crude mixture (see Table 1).

Reaction of 1-*Methoxy*-3-(*methylsulfinyl*)*benzene* **2** *with Hexacarbonylchromium*.—Following procedure E (see below), 1-methoxy-3-(methylsulfinyl)benzene **2** (0.085 g, 0.5 mmol) was treated with hexacarbonylchromium (0.121 g, 0.55 mmol) at 130 °C in dibutyl ether–THF (10:1; 11 cm^3) for 15 h, to give a cloudy green mixture. Filtration of this followed by solvent evaporation gave a yellow oil (0.13 g), which was analysed by ^1H NMR spectroscopy (see Table 2).

Reaction of 1-*Methoxy*-3-(*methylsulfinyl*)*benzene* **2** *with Tricarbonyl*(η^6-*naphthalene*)*chromium*(0).—Following procedure A described above, 1-methoxy-3-(methylsulfinyl)benzene **2** (0.153 g, 0.9 mmol) was treated for 5 h with tricarbonyl(η^6-naphthalene)chromium(0) (0.27 g, 1 mmol) in ethyl acetate–THF (8:1; 13.5 cm^3) to give a green–brown solution. Filtration of this followed by solvent evaporation gave a yellow powder (0.35 g) which was analysed by ^1H NMR spectroscopy (see Table 2).

Reaction of 1-*Methoxy*-3-(*methylsulfinyl*)*benzene* **2** *with Tris*(*acetonitrile*)*tricarbonylchromium*(0).—Following procedure B described above, 1-methoxy-3-(methylsulfinyl)benzene **2** (0.46 g, 2.7 mmol) was treated for 4 h in THF with tris-(acetonitrile)tricarbonylchromium(0) (0.76 g, 2.9 mmol), freshly prepared by thermolysis of hexacarbonylchromium (0.6 g, 2.75 mmol) in acetonitrile (20 cm^3). After standard work-up and analysis by ^1H NMR spectroscopy (see Table 2), the yellow residue was subjected to column chromatography (SiO_2).

Initial elution with light petroleum (b.p. 40–60 °C)–dichloromethane (7:3) gave a deep yellow fraction which when concentrated under reduced pessure gave a yellow powder and was recrystallised from dichloromethane–light petroleum (b.p. 40–60 °C) to give *pentacarbonyl*[1-*methoxy*-3-(*methylsulfenyl*)-*benzene*-S]*chromium*(0) **37** as yellow crystals (0.44 g, 1.27 mmol, 48%), m.p. 47–48 °C (Found: *m/z* 345.9603. $C_{13}H_{10}CrO_6S$ requires 345.9603); ν_{max}(hexane)/cm^{-1} 1947vs and 1934vs (C≡O); δ_H 2.66 [3 H, s, $SCH_3Cr(CO)_5$], 3.84 (3 H, s, OCH_3), 6.88 (1 H, d, *J* 7.8, 4-H or 6-H), 5.95 (1 H, s, 2-H), 7.00 (1 H, d, *J* 7.8, 4-H or 6-H) and 7.33 (1 H, t, *J* 7.8, 5-H); δ_C (125.8 MHz) 26.2 [$SCH_3Cr(CO)_5$], 55.4 (OCH_3), 113.6, 114.7, 120.1 and 130.5 (C-2, C-4, C-5 and C-6), 138.4 (C-1), 160.1 (C-3), 214.5 (4 × C≡O *cis*) and 221.5 (1 × C≡O *trans*); *m/z* (EI, 70 eV, 80 °C) 346 (M^+, 0.1%), 290 (M − 2CO, 0.1), 244 (M − 2CO − CH_3 − OCH_3, 0.1), 234 (M − 4CO, 0.2), 206 (M − 5CO, 1.1), 154 [M − $Cr(CO)_5$, 69.3] and 52 (Cr, 5.6).

Further elution with light petroleum (b.p. 40–60 °C)–dichloromethane (1:1) gave a second deep yellow fraction, the subsequent concentration of which under reduced pressure led to decomposition of the complex. However, from the ^1H NMR spectrum of the crude mixture, this very unstable complex was assigned as *pentacarbonyl*[1-*methoxy*-3-(*methylsulfinyl*)-*benzene*-*S*]*chromium*(0) **36**; δ_H 3.29 [3 H, s, $SOCH_3Cr(CO)_5$], 3.87 (3 H, s, OCH_3), 6.8–7.4 (3 H, m, 2-H, 4-H and 6-H) and 7.5 (1 H, t, *J* 8, 5-H).

Reaction of 1-*Methoxy*-3-(*methylsulfinyl*)*benzene* **2** *with Tricarbonyltris*(*pyridine*)*chromium*(0).—Following procedure C described above, 1-methoxy-3-(methylsulfinyl)benzene **2** (0.22 g, 1.3 mmol) was treated for 1 h with boron trifluoride—diethyl ether (0.59 g, 0.5 cm^3, 4.16 mmol) and tricarbonyltris-(pyridine)chromium(0) (0.54 g, 1.43 mmol), freshly prepared from tricarbonyl(η^6-methoxybenzene)chromium(0) (0.35 g, 1.43 mmol) and pyridine (8 cm^3). Work-up gave a yellow–orange powder (0.4 g) which was analysed by ^1H NMR spectroscopy (see Table 2). An unspecified amount of pentacarbonyl(pyridine)chromium(0)[34] was detected as a by-product in the crude mixture (see Table 2).

Synthesis of Tricarbonyl[η^6-1-*methoxy*-2-(*methylsulfinyl*)-*benzene*]*chromium*(0) $\mathbf{20_X}$ *from* 2-*methoxy*-1-(*methylsulfinyl*)-*benzene* **1**.—Tris(acetonitrile)tricarbonylchromium(0), synthesised from hexacarbonylchromium (0.88 g, 3.99 mmol) and acetonitrile (9 cm^3), was treated with 1-methoxy-2-(methylsulfinyl)benzene **1** (0.4 g, 2.35 mmol) according to procedure B. After work-up, column chromatography [SiO_2; light petroleum (b.p. 40–60 °C)–ethyl acetate, 20:1] of the resulting yellow–green solid gave the *title complex* $\mathbf{20_X}$ (0.106 g, 15%) as a yellow solid, m.p. 128–129 °C (Found: C, 43.3; H, 3.1. $C_{11}H_{10}CrO_5S$ requires C, 43.14; H, 3.29%); *m/z* (FAB, NOBA) 306 (M^+, 16%), 250 (M − 2CO, 100) and 222 (M − 3CO, 82). See Tables 6, 7, and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

Procedure D

Tricarbonyl[η^6-1-*methoxy*-2-(*methylthio*)*benzene*]*chromium*(0) **16**.—A mixture of 1-methoxy-2-(methylthio)benzene **5** (0.2 g, 1.3 mmol) and hexacarbonylchromium (0.72 g, 3.27 mmol) in nitrogen-saturated 1,4-dioxane (15 cm^3) was heated under reflux for 40 h. The resulting orange solution was cooled in an ice-bath and filtered through Kieselguhr, eluting with diethyl ether. Solvent removal from the filtrate under reduced pressure gave a yellow solid, recrystallisation of which from diethyl ether yielded the *title complex* **16** as orange needles (0.33 g, 1.16 mmol, 89%), m.p. 103–104 °C (Found: C, 45.4; H, 3.5. $C_{11}H_{10}CrO_4S$ requires C, 45.52; H, 3.48%); *m/z* (EI, 70 eV, 220 °C) 290 (M^+, 18%), 262 (M − CO, 1), 234 (M − 2CO, 39), 206 (M − 3CO, 67), 191 (M − 3CO − CH_3, 70), 176 (M − 3CO − $2CH_3$, 100), 160 (M − 3CO − CH_3 − OCH_3, 51), 154 [M − $Cr(CO)_3$, 6] and 52 (Cr, 85). See Tables 6, 7 and 8 for IR ^1H and ^{13}C NMR spectroscopic data.

Tricarbonyl[η^6-1-*methoxy*-2-(*methylsulfinyl*)*benzene*]-*chromium*(0) $\mathbf{20_Y}$.—Tricarbonyl[η^6-1-methoxy-2-(methylthio)benzene]chromium(0) **16** (92 mg, 0.32 mmol) was dissolved in nitrogen-saturated acetone (10 cm^3) and the solution cooled to −78 °C under a nitrogen atmosphere. Dimethyldioxirane (0.08 mol dm^{-3} solution in acetone; 3.18 cm^3, 1.1 equiv.) was diluted with nitrogen-saturated acetone (5 cm^3), cooled to −78 °C and added very slowly dropwise *via* a cannula to the yellow solution of **16**. After the addition was complete, the reaction mixture was stirred for 15 min at −78 °C and then for 1 h at room temperature. Solvent removal from the resulting slightly cloudy yellow product mixture gave a yellow–pale green solid which was analysed by ^1H NMR spectroscopy. Dichloromethane was added to the solid and the mixture was filtered through Kieselguhr and concentrated. Recrystallisation of the residue from acetone–hexane gave the *title complex* $\mathbf{20_Y}$ as yellow crystals (78 mg, 0.256 mmol, 80%), m.p. 122–124 °C (decomp.) (Found: C, 43.2; H, 3.2. $C_{11}H_{10}CrO_5S$ requires C, 43.14; H, 3.29%); *m/z* (EI, 70 eV, 240 °C) 306 (M^+, 1.0%), 290 (M − CO, 2.2) 250 (M − 2CO, 8.4), 234 (M − 2CO − O, 3.4), 222 (M − 3CO, 14.3), 207 (M − 3CO − CH_3, 12.0), 206 (M − 3CO − O, 12.3), 192 (M − 3CO − $2CH_3$, 16.9), 176 (M − 3CO − $2CH_3$ − O, 20.7), 170 [M − $Cr(CO)_3$, 1.9], 52 (Cr, 100) and 28 (CO, 95.5). See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

1-(*tert*-*Butylthio*)-2-*methoxybenzene* **8**.[35,36]—To a 100 cm^3 round-bottom flask fitted with a magnetic stirrer and a reflux condenser and cooled in an ice-bath, acetic acid (5 cm^3), perchloric acid (72% solution; 0.7 cm^3) and acetic anhydride (1.85 cm^3) were successively added and the solution stirred for 15 min. 2-Methoxybenzenethiol **13** (2.34 g, 17 mmol) and *tert*-butyl alcohol (1.48 g, 20 mmol, 1.2 equiv.) were added to the mixture, the volume of which was made up to 20 cm^3 with acetic acid. The mixture was stirred for 2 days at room

temperature, and then diluted with saturated brine (20 cm^3) and extracted with diethyl ether (5 × 10 cm^3). The combined extracts were washed with saturated aqueous sodium hydrogencarbonate (3 × 50 cm^3) and water (50 cm^3) and dried ($MgSO_4$). Column chromatography (SiO_2; diethyl ether) gave the title sulfide **8** as a colourless liquid (2.66 g, 13.6 mmol, 81%); ν_{max}(neat)/cm^{-1} 2960vs, 2939s, 2921s, 2896s, 1583s, 1475vs, 1432vs, 1363s, 1271vs, 1246vs, 1161s, 1069s, 1027s and 754vs; *m/z* (EI, 70 eV, 220 °C), 196 (M^+, 9%), 140 (MH − C_4H_9, 100) and 125 (MH − C_4H_9 − CH_3, 19). See Tables 4 and 5 for ^1H and ^{13}C NMR spectroscopic data.

[η⁶-1-(tert-*Butylthio*)-2-*methoxybenzene*]*tricarbonylchromium*(0) **19**.—Following procedure D, 1-(*tert*-butylthio)-2-methoxybenzene **8** (0.5 g, 2.55 mmol) was treated with hexacarbonylchromium (1.42 g, 6.37 mmol) in 1,4-dioxane (20 cm^3) for 67 h to give a black mixture. Filtration of this followed by column chromatography [SiO_2; light petroleum (b.p. 60–80 °C)–diethyl ether, 7:3] and recrystallisation of the product from dichloromethane–light petroleum (b.p. 60–80 °C) yielded the *title complex* **19** as yellow crystals (0.6 g, 1.8 mmol, 71%), m.p. 100–102 °C (Found: C, 50.6; H, 4.8. $C_{14}H_{16}CrO_4S$ requires C, 50.60; H, 4.85%); *m/z* (EI, 70 eV, 240 °C) 332 (M^+, 4.6%), 276 (M − 2CO, 8.4), 248 (M − 3CO, 15.2), 192 (MH − 3CO − C_4H_9, 61.7), 140 [M − C_4H_9 − $Cr(CO)_3$, 100], 52 (Cr, 69) and 28 (CO, 94.3). See Tables 6, 7, and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

[η⁶-1-(tert-*Butylsulfinyl*)-2-*methoxybenzene*]*tricarbonylchromium*(0) **23**$_X$.—Following the general oxidation procedure described above for the synthesis of complex **20**$_Y$, [η⁶-1-(*tert*-butylthio)-2-methoxybenzene]tricarbonylchromium(0) **19** (133 mg, 0.4 mmol) was treated in acetone (10 cm^3) with dimethyldioxirane (0.094 mol dm^{-3} solution in acetone; 5.1 cm^3, 0.48 mmol, 1.2 equiv.), diluted in acetone (5 cm^3). Work-up, followed by recrystallisation from dichloromethane–light petroleum (b.p. 60–80 °C) of the resulting yellow solid gave the *title complex* **23**$_X$ as yellow crystals (108 mg, 0.31 mmol, 77%), m.p. 134–138 °C (decomp.) (Found: C, 48.0; H, 4.5. $C_{14}H_{16}CrO_5S$ requires C, 48.27; H, 4.63%); *m/z* (CI, NH_3) 366 [(M + NH_4)$^+$, 7%], 349 (MH, 100), 333 (MH − O, 10) 293 (MH − 2CO, 11) 277 (MH − Cr − 2CO − O, 79), 213 [MH − $Cr(CO)_3$, 51], 197 [MH − $Cr(CO)_3$ − O, 59], 155 [M − $Cr(CO)_3$ − C_4H_9, 72] and 140 [MH − $Cr(CO)_3$ − O − C_4H_9, 44]. See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

1-(*Ethylthio*)-2-*methoxybenzene* **6**.[37]—2-Methoxybenzenethiol **13** (2.8 g, 20 mmol) was treated with sodium hydride (60%; 0.88 g, 22 mmol) and ethyl iodide (3.43 g, 22 mmol) according to the procedure described above for the synthesis of the sulfide **12**. Work-up gave the title sulfide **6** as a pale yellow oil (3.06 g, 18 mmol, 91%); ν_{max}(neat)/cm^{-1} 2965s, 2928s, 1578s, 1478vs, 1433vs, 1262vs, 1240vs, 1075vs, 1045s, 1026vs and 747vs; *m/z* (EI, 70 eV, 200 °C), 168 (M^+, 100%), 153 (M − CH_3, 30), 140 (MH − C_2H_5, 25), 138 (MH − OCH_3, 24) and 125 (MH − CH_3 − C_2H_5, 31). See Tables 4 and 5 for ^1H and ^{13}C NMR spectroscopic data.

1-(*Isopropylthio*)-2-*methoxybenzene* **7**.[38]—2-Methoxybenzenethiol **13** (1.68 g, 12 mmol) was treated with sodium hydride (60%; 0.53 g, 13.2 mmol) and 2-bromopropane (1.62 g, 13.2 mmol) according to the procedure described above for the synthesis of the sulfide **12**. Work-up gave the title sulfide **7** as a pale yellow oil (1.94 g, 10.6 mmol, 89%); ν_{max}(neat)/cm^{-1} 2962s, 2926s, 1477vs, 1433s, 1271s, 1248vs, 1073s, 1026s and 750s; *m/z* (EI, 70 eV, 200 °C), 182 (M^+, 46%), 140 (MH − C_3H_7, 100) and 125 (MH − CH_3 − C_3H_7, 46). See Tables 4 and 5 for ^1H and ^{13}C NMR spectroscopic data.

Tricarbonyl[η⁶-1-(*ethylthio*)-2-*methoxybenzene*]*chromium*(0) **17**.—Following procedure D, 1-(ethylthio)-2-methoxybenzene **6** (0.505 g, 3.0 mmol) was treated with hexacarbonylchromium (1.65 g, 7.5 mmol) in 1,4-dioxane (20 cm^3) for 67 h to give a black solution. Filtration of this followed by column chromatography [SiO_2; light petroleum (b.p. 60–80 °C)–diethyl ether, 8:2] and subsequent recrystallisation of the product from dichloromethane–light petroleum (b.p. 60–80 °C) yielded the *title complex* **17** as orange crystals (0.613 g, 2.0 mmol, 67%), m.p. 45.5–46 °C (Found: C, 47.4; H, 3.7. $C_{11}H_{10}CrO_4S$ requires C, 47.37; H, 3.98%); *m/z* (EI, 70 eV, 180 °C) 304 (M^+, 4%), 248 (M − 2CO, 10), 220 (M − 3CO, 19), 192 (MH − 3CO − C_2H_5, 65), 176 (M − 3CO − C_2H_5 − CH_3, 41), 168 [MH − $Cr(CO)_3$, 30] and 52 (Cr, 100). See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

Tricarbonyl[η⁶-1-(*isopropylthio*)-2-*methoxybenzene*]*chromium*(0) **18**.—Following procedure D, 1-(isopropylthio)-2-methoxybenzene **7** (0.46 g, 2.5 mmol) was treated with hexacarbonylchromium (1.38 g, 6.25 mmol) in 1,4-dioxane (20 cm^3) for 65 h to give a black solution. Filtration, followed by column chromatography [SiO_2; light petroleum (b.p. 60–80 °C)–diethyl ether, 8:2] and subsequent recrystallisation from dichloromethane–light petroleum (b.p. 60–80 °C) yielded the *title complex* **18** as yellow crystals (0.416 g, 1.3 mmol, 52%), m.p. 56–57 °C (Found: C, 49.1; H, 4.4. $C_{11}H_{10}CrO_4S$ requires C, 49.05; H, 4.43%); *m/z* (EI, 70 eV, 140 °C) 318 (M^+, 5%), 262 (M − 2CO, 12), 234 (M − 3CO, 20), 206 (M − 3CO − C_2H_4, 21), 192 (MH − 3CO − C_3H_7, 60), 182 [M − $Cr(CO)_3$, 13], 176 (M − 3CO − CH_3 − C_3H_7, 48) and 52 (Cr, 100). See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

Tricarbonyl[η⁶-1-(*ethylsulfinyl*)-2-*methoxybenzene*]*chromium*(0) **21**$_Y$.—Following the general oxidation procedure described above for the synthesis of complex **20**$_Y$, tricarbonyl[η⁶-1-(ethylthio)-2-methoxybenzene]chromium(0) **17** (456 mg, 1.5 mmol) dissolved in acetone (20 cm^3) was treated with dimethydioxirane (0.12 mol dm^{-3} solution in acetone; 5 cm^3, 1.8 mmol, 1.2 equiv.), diluted in acetone (15 cm^3). After work-up, recrystallisation from dichloromethane–light petroleum (b.p. 60–80 °C) of the resulting yellow solid gave the *title complex* **21**$_Y$ as orange–yellow crystals (185 mg, 0.58 mmol, 39%), m.p. 109–115 °C (decomp.) (Found: C, 44.8; H, 3.5. $C_{14}H_{16}CrO_4S$ requires C, 45.00; H, 3.78%); *m/z* (EI) 320 (M^+, 18%), 304 (M − O, 6), 264 (M − 2CO, 48), 248 (M − 2CO − O, 6), 236 (M − 3CO, 74), 220 (M − 3CO − O, 11), 207 (M − 3CO − C_2H_5, 24), 192 (MH − 3CO − O − C_2H_5, 100), 177 (MH − 3CO − O − C_2H_5 − CH_3, 47), 168 [M − $Cr(CO)_3$ − O, 41] and 52 (Cr, 48). See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

Tricarbonyl[η⁶-1-(*isopropylsulfinyl*) 2-*methoxybenzene*]*chromium*(0) **22**$_X$.—Following the general oxidation procedure described above for the synthesis of complex **20**$_Y$, tricarbonyl[η⁶-1-(isopropylthio)-2-methoxybenzene]chromium(0) **18** (80 mg, 0.25 mmol) dissolved in acetone (10 cm^3) was treated with dimethyldioxirane (0.063 mol dm^{-3} solution in acetone; 4.8 cm^3, 0.3 mmol, 1.2 equiv.), diluted in acetone (5 cm^3). After work-up, recrystallisation from dichloromethane–light petroleum (b.p. 60–80 °C) of the resulting yellow solid gave the *title complex* **22**$_X$ as yellow crystals (47 mg, 0.14 mmol, 56%), m.p. 129–136 °C (decomp.) (Found: C, 46.6; H, 4.2. $C_{14}H_{16}CrO_4S$ requires C, 46.71; H, 4.22%); *m/z* (EI, 70 eV, 260 °C) 334 (M^+, 0.5%), 318 (M − O, 0.7), 290 (M − O − CO, 0.1), 278 (M − 2CO, 16.8), 262 (M − O − 2CO, 3.0), 250 (M − 3CO, 27.0), 234 (M − O − 3CO, 5.5), 182 [M − O − $Cr(CO)_3$, 27.8], 156 [MH − $Cr(CO)_3$ − C_3H_7, 35.2], 140 [MH − O − $Cr(CO)_3$ − C_3H_7, 100.0], 125 [MH − O −

Table 4 1H NMR (δ)[a] data for alkylthio substituted arenes

Arene	ArH[b]	SR	Other substituent
5	6.84 (1 H, d, 3-H), 6.96 (1 H, t, 5-H) and 7.12–7.19 (2 H, m, 4-H and 6-H)	2.43 (3 H, s, SCH_3)	3.90 (3 H, s, OCH_3)
6	6.85 (1 H, d, 3-H), 6.93 (1 H, t, 5-H), 7.17 (1 H, t, 4-H) and 7.26 (1 H, d, 6-H)	1.32 (3 H, t, *J* 7.3, SCH_2CH_3) and 2.92 (2 H, q, *J* 7.3, SCH_2Me)	3.89 (3 H, s, OCH_3)
7	6.84–6.94 (2 H, m, 3-H and 5-H), 7.21 (1 H, t, 4-H) and 7.35 (1 H, d, 6-H)	1.29 [6 H, d, *J* 6.6, $SCH(CH_3)_2$] and 3.48 (1 H, sept, *J* 6.6, $SCHMe_2$)	3.88 (3 H, s, OCH_3)
8	6.86–6.92 (2 H, m, 3-H and 5-H), 7.32 (1 H, t, 4-H) and 7.49 (1 H, d, 6-H)	1.27 [9 H, s, $C(CH_3)_3$]	3.82 (3 H, s, OCH_3)
9	7.13–7.27 (4 H, m, 3-H, 4-H, 5-H and 6-H)	2.43 (3 H, s, SCH_3)	2.51 (3 H, s, CH_3)
10	7.15–7.28 (3 H, m, 3-H, 4-H and 5-H) and 7.53 (1 H, d, 6-H)	1.31 [9 H, s, $C(CH_3)_3$]	2.54 (3 H, s, CH_3)
11	7.12–7.23 (2 H, m, 4-H and 5-H) and 7.35–7.42 (2 H, m, 3-H and 6-H)	2.52 (3 H, s, SCH_3)	1.55 [9 H, s, $C(CH_3)_3$]
12	6.69 (1 H, d, 4-H), 6.82–6.88 (2 H, m, 2-H and 6-H) and 7.21 (1 H, t, 5-H)	2.49 (3 H, s, SCH_3)	3.80 (3 H, s, OCH_3)

[a] $CDCl_3$, 300 K, 270 MHz. [b] ^3J = 6–7 for all d and t. All signals displayed fine ^4J coupling.

Table 5 $^{13}C\{^1H\}$ NMR (δ)[a] data for alkylthio substituted arenes

Arene	C-1	C-2	C-3	C-4	C-5	C-6	Others
5	126.7	156.1	109.9	125.96/125.78	121.1	125.96/125.78	14.6 (SCH_3) 55.6 (OCH_3)
6	124.6	156.8	110.1	126.4	120.7	128.5	13.8 (SCH_2CH_3), 25.6 (SCH_2Me) 55.4 (OCH_3)
7	123.7	158.2	110.6	127.8	120.8	132.2	22.9 [$SCH(CH_3)_2$], 35.9 ($SCHMe_2$) 55.6 (OCH_3)
8	120.4	161.1	110.9	130.5	120.2	140.1	30.8 [$SC(CH_3)_3$], 46.6 ($SCMe_3$) 55.4 (OCH_3)
9	137.5	135.6	129.7	124.5	124.5	126.4	15.1 (SCH_3) 19.8 (CH_3)
10	132.2	143.6	130.3	128.8	125.7	138.9	31.1 [$SC(CH_3)_3$], 46.8 ($SCMe_3$) 21.8 (CH_3)
11	137.3	148.5	126.3	125.4	126.5	129.6	18.4 (SCH_3) 30.2 [$C(CH_3)_2$], 36.5 (CMe_3)
12	140.3	111.0	160.3	112.5	130.1	119.1	16.1 (SCH_3) 55.6 (OCH_3)

[a] $CDCl_3$, 300 K, 67.9 MHz.

$Cr(CO)_3 - C_3H_7 - CH_3$, 45.6] and 52 (Cr, 5.1). See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

1-Methyl-2-(methylthio)benzene **9**.[39]—2-Methylbenzenethiol **14** (3.0 g, 24 mmol) was treated with sodium hydride (60%; 1.06 g, 26.6 mmol) and methyl iodide (3.77 g, 26.6 mmol) according to the procedure described above for the synthesis of the sulfide **12**. Work-up gave the title sulfide **9** as a very pale yellow liquid (3.23 g, 23 mmol, 97%); ν_{max}(neat)/cm^{-1} 3061s, 3011s, 2976s, 2921vs, 2854s, 1590s, 1470vs, 1436vs, 1380s, 1068vs, 1049vs and 742vs; *m/z* (EI, 70 eV, 260 °C), 138 (M^+, 100%) and 123 (M − CH_3, 61). See Tables 4 and 5 for ^1H and ^{13}C NMR spectroscopic data.

1-(tert-Butylthio)-2-methylbenzene **10**.[40]—2-Methylbenzenethiol **14** (3.1 g, 25 mmol) was treated with *tert*-butyl alcohol (1.85 g, 25 mmol) in the presence of perchloric acid (72% solution; 1.05 cm^3) and acetic anhydride (2.78 g) in acetic acid (25 cm^3) using the procedure described for the synthesis of the sulfide **8**. Work-up gave the title sulfide **10** as a pale yellow liquid (4.39 g, 24 mmol, 98%); ν_{max}(neat)/cm^{-1} 2961vs, 2922vs, 1898vs, 1862vs, 1471vs, 1456vs, 1363vs, 1170vs, 1063s, 754vs and 717s; *m/z* (EI, 70 eV, 260 °C), 180 (M^+, 11%), 165 (M − CH_3, 2) and 124 (MH − C_4H_9, 100). See Tables 4 and 5 for ^1H and ^{13}C NMR spectroscopic data.

Tricarbonyl[η⁶-1-methyl-2-(methylthio)benzene]chromium(0) **24**.—Following procedure D, 1-methyl-2-(methylthio)benzene **9** (0.55 g, 4 mmol) was treated with hexacarbonylchromium (2.2 g, 10 mmol) in 1,4-dioxane (20 cm^3) for 44 h to give a green mixture. After filtration and removal of the solvent, the resulting yellow solid was recrystallised from dichloromethane–light petroleum (b.p. 60–80 °C) to afford the *title complex* **24** as yellow crystals (0.82 g, 3 mmol, 75%), m.p. 83–84 °C (Found: C, 48.1; H, 3.5. $C_{11}H_{10}CrO_3S$ requires C, 48.17; H, 3.68%); *m/z* (EI, 70 eV, 220 °C) 274 (M^+, 2.6%), 218 (M − 2CO, 3.6), 190 (M − 3CO, 7.5), 175 (M − 3CO − CH_3, 7.4), 138 [M − $Cr(CO)_3$, 65.2], 52 (Cr, 19.1) and 28 (CO, 100). See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

[η⁶-1-(tert-Butylthio)-2-methylbenzene]tricarbonylchromium(0) **25**.—Following procedure D, 1-(*tert*-butylthio)-2-methylbenzene **10** (0.51 g, 2.8 mmol) was treated with hexacarbonylchromium (1.54 g, 7 mmol) in 1,4-dioxane (20 cm^3) for 40 h to give an orange–yellow solution. Filtration followed by recrystallisation from dichloromethane–light petroleum (b.p. 60–80 °C) yielded the *title complex* **25** as yellow crystals (0.67 g, 2.2 mmol, 78%), m.p. 128–130 °C (Found: C, 52.9; H, 4.9. $C_{14}H_{16}CrO_3S$ requires C, 53.16; H, 5.10%); *m/z* (EI, 70 eV, 220 °C) 316 (M^+, 12.9%), 260 (M − 2CO, 12.8), 232 (M − 3CO, 21.3), 176 (MH − 3CO − C_4H_9, 100) and 52

Table 6 IR data (ν/cm^{-1})[a,b] for alkylthio and alkylsulfinyl substituted complexes

Alkylthio substituted complex	C≡O	Alkylsulfinyl substituted complex	C≡O
16	1965, 1886	**20$_X$**	1981, 1913[c]
		20$_Y$	1973, 1898
17	1966, 1887	**21$_Y$**	1976, 1900
18	1969, 1890	**22$_X$**	1976, 1902
19	1970, 1893	**23$_X$**	1977, 1904
24	1964, 1887	**26$_Y$**	1976, 1904
25	1971, 1896	**27$_X$**	1979, 1909
28	1963, 1885	**31$_Y$**	1972, 1899
29	1965, 1886	**32$_{X/Y}$**	1977, 1904
30	1969, 1893	**33**	1983, 1913

[a] CH_2Cl_2 solution. [b] All recorded absorptions are very strong. [c] $CHCl_3$ solution.

(Cr, 69.7). See Tables 6, 7 and 8 for IR, ^{1}H and ^{13}C NMR spectroscopic data.

Tricarbonyl[η^6-*1-methyl-2-(methylsulfinyl)benzene*]-*chromium*(0) **26$_Y$**.—Following the general oxidation procedure described above for the synthesis of complex **20$_Y$**, tricarbonyl[η^6-1-methyl-2-(methylthio)benzene]chromium(0) **24** (100 mg, 0.35 mmol) was treated in acetone (10 cm^3) with dimethyldioxirane (0.078 mol dm^{-3} acetone solution; 5.6 cm^3, 0.44 mmol, 1.2 equiv.), diluted in acetone (5 cm^3). After work-up, recrystallisation of the resulting yellow solid from dichloromethane–light petroleum (b.p. 60–80 °C) gave the *title complex* **26$_Y$** as yellow crystals (83 mg, 0.29 mmol, 78%), m.p. 105–107 °C (Found: C, 45.7; H, 3.2. $C_{11}H_{10}CrO_4S$ requires C, 45.52; H, 3.47%); *m/z* (EI, 70 eV, 260 °C) 290 (M^+, 1.6%), 274 (M − O, 4.7), 234 (M − 2CO, 9.3), 218 (M − 2CO − O, 8.5), 206 (M − 3CO, 17.4), 190 (M − 3CO − O, 18.9), 174 (M −

Table 7 ^{1}H NMR (δ)[a,b] data for alkylthio and alkylsulfinyl substituted complexes

Complex	2-H	3-H	4-H	5-H	6-H	C-1 substituent	C-2/C-3 substituent
16		5.12d	5.45t	4.90t	5.71d	2.44 (3 H, s, SCH_3)	3.84 (3 H, s, OCH_3)
17		5.10d	5.46t	4.89t	5.75d	1.34 (3 H, m, SCH_2CH_3), 2.85–2.91 (2 H, m, SCH_2Me)	3.82 (3 H, s, OCH_3)
18		5.07d	5.49t	4.89t	5.77d	1.31 [3 H, d, *J* 6.8, $SCH(CH_3)_2$] 1.32 [3 H, d, *J* 6.6, $SCH(CH_3)_2$] 3.27 [1 H, m, $SCH(CH_3)_2$]	3.81 (3 H, s, OCH_3)
19		5.05d	5.58t	4.88t	5.85d	1.31 [9 H, s, $SC(CH_3)_3$]	3.78 (3 H, s, OCH_3)
24		5.31d	5.22t	5.26t	5.43d	2.44 (3 H, s, SCH_3)	2.28 (3 H, s, CH_3)
25		5.12–5.20m	5.42t	5.12–5.20m	5.73d	1.34 [9 H, s, $SC(CH_3)_3$]	2.40 (3 H, s, CH_3)
28		5.17d	4.95t	5.54t	5.75d	2.49 (3 H, s, SCH_3)	1.49 [9 H, s, $C(CH_3)_3$]
29	5.21s		4.93d	5.59t	4.89d	2.46 (3 H, s, SCH_3)	3.74 (3 H, s, OCH_3)
30	5.31d	5.42t	5.11t			2.45 (3 H, s, SCH_3)	
20$_X$		5.02d	5.57t	5.01t	6.19d	2.79 (3 H, s, $SOCH_3$)	3.82 (3 H, s, OCH_3)
20$_Y$		5.01d	5.75t	4.90t	6.34d	2.93 (3 H, s, $SOCH_3$)	3.83 (3 H, s, OCH_3)
21$_Y$		5.01d	5.74t	4.90t	6.31d	1.55 (3 H, t, *J* 7.6, $SOCH_2CH_3$), 2.76 (1 H, dq, *J* 12.9, 7.6, $SOCH_2Me$) 3.18 (1 H, dq, *J* 12.9, 7.6, $SOCH_2Me$)	3.82 (3 H, s, OCH_3)
22$_X$		5.00d	5.57t	4.99t	6.09d	1.11 [3 H, d, *J* 6.8, $SOCH(CH_3)_2$], 1.39 [3 H, d, *J* 7.1, $SOCH(CH_3)_2$], 3.01 (1 H, m, $SOCHMe_2$)	3.80 (3 H, s, OCH_3)
23$_X$		4.99d	5.61t	4.94t	6.08d	1.23 [9 H, s, $SOC(CH_3)_3$]	3.79 (3 H, s, OCH_3)
26$_Y$		5.01d	5.65t	5.17t	6.17d	2.94 (3 H, s, $SOCH_3$)	2.37 (3 H, s, CH_3)
27$_X$		4.95d	5.50t	5.20t	5.98d	1.24 [9 H, s, $SOC(CH_3)_3$]	2.32 (3 H, s, CH_3)
31$_Y$		5.30d	----5.39t/5.58t----		6.38d	2.99 (3 H, s, $SOCH_3$)	1.46 [9 H, s, $C(CH_3)_3$]
32$_{X/Y}$	5.13s/5.60s		---4.87d/5.14 2 × d/5.37d/5.57t/5.67t--			2.85 (3 H, s, $SOCH_3$) 2.87 (3 H, s, $SOCH_3$)	3.75 (3 H, s, OCH_3) 3.79 (3 H, s, OCH_3)
33	5.49d/5.85d	-------	5.28t/5.39t/5.43t	-------	5.49d/5.85d	2.82 (3 H, s, $SOCH_3$)	

[a] $CDCl_3$, 300 K, 270 MHz. [b] ^3J = 6–7 for all d and t. All signals displayed fine ^4J coupling.

Table 8 $^{13}C\{^1H\}$ NMR (δ)[a] data for alkylthio and alkylsulfinyl substituted complexes

Complex	C-1	C-2	C-3, C-4, C-5 and C-6	$Cr(CO)_3$	C-1 substituent	C-2/C-3 substituent
16	100.5	141.5	73.7, 85.1, 92.5, 96.2	232.9	18.3 (SCH_3)	56.3 (OCH_3)
17	97.6	142.1	73.8, 85.2, 92.9, 98.4	232.8	13.9 (SCH_2CH_3), 29.7 (SCH_2Me)	56.3 (OCH_3)
18	94.1	143.3	73.7, 85.3, 93.3, 101.0	232.5	23.1, 22.9 [$SCH(CH_3)_2$], 39.2 ($SCHMe_2$)	56.2 (OCH_3)
19	88.9	145.6	73.3, 85.1, 94.5, 105.6	232.0	30.8 [$SC(CH_3)_3$], 48.3 ($SCMe_3$)	55.9 (OCH_3)
24	112.3	108.6	90.6, 91.2, 91.3, 93.9	233.1	16.7 (SCH_3)	19.5 (CH_3)
25	100.3/115.1		89.5, 92.1, 94.5, 104.3	232.1	30.9 [$SC(CH_3)_3$], 48.6 ($SCMe_3$)	21.1 (CH_3)
28	116.3	119.4	86.4, 88.5, 94.9, 95.0	233.3	17.7 (SCH_3)	30.8 [$C(CH_3)_3$], 36.0 (CMe_3)
29	117.1	77.4	74.7, 83.2, 93.8, 143.0	232.9	15.3 (SCH_3)	55.7 (OCH_3)
30	114.6	90.1	88.9, 93.1	232.6	15.9 (SCH_3)	
20$_X$	101.5	140.2	71.6, 83.8, 88.1, 93.8	230.8	42.7 ($SOCH_3$)	56.3 (OCH_3)
20$_Y$	106.6	139.8	70.9, 81.4, 94.3, 95.6	231.4	46.9 ($SOCH_3$)	56.3 (OCH_3)
21$_Y$	105.0	139.8	71.0, 81.6, 94.5, 95.6	231.5	8.6 ($SOCH_2CH_3$), 55.4 ($SOCH_2Me$)	56.2 (OCH_3)
22$_X$	98.5	141.0	71.6, 83.5, 89.4, 94.1	231.0	12.4, 17.0 [$SOCH(CH_3)_2$], 52.1 ($SOCHMe_2$)	56.2 (OCH_3)
23$_X$	97.1	143.1	71.0, 82.9, 90.0, 94.6	230.9	22.9 [$SOC(CH_3)_3$], 58.6 ($SOCMe_3$)	55.8 (OCH_3)
26$_Y$	109.4/112.3		85.8, 89.2, 92.7, 96.4	231.0	43.4 ($SOCH_3$)	18.0 (CH_3)
27$_X$	107.5/110.1		86.0, 89.2, 89.3, 95.3	230.8	23.0 [$SOC(CH_3)_3$], 58.8 ($SOCMe_3$)	19.6 (CH_3)
31$_Y$	117.8/123.8		86.8, 88.3, 93.2, 95.2	231.5	44.7 ($SOCH_3$)	31.9 [$C(CH_3)_3$], 36.4 (CMe_3)
32$_{X/Y}$	116.9, 117.2	69.2, 72.7	77.7, 78.8, 79.1, 80.3, 92.4, 92.9, 141.4, 142.2	231.0	44.3, 46.6 ($SOCH_3$)	56.0, 56.1 (OCH_3)
33	113.5	86.7	88.8, 89.1, 89.5, 93.3	230.4	44.5 ($SOCH_3$)	

[a] $CDCl_3$, 300 K, 125.8 MHz.

3CO − S, 23.1), 154 [M − $Cr(CO)_3$, 19.0] and 52 (Cr, 100). See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

[η^6-1-(tert-*Butylsulfinyl*)-2-*methylbenzene*]*tricarbonyl chromium*(0) **27$_X$**.—Following the general oxidation procedure described above for the synthesis of complex **20$_Y$**, [η^6-1-(*tert*-butylthio)-2-methylbenzene]tricarbonylchromium(0) **25** (127 mg, 0.4 mmol) was treated in acetone (10 cm^3) with dimethyldioxirane (0.075 mol dm^{-3} solution in acetone; 6.4 cm^3, 0.48 mmol, 1.2 equiv.), diluted in acetone (5 cm^3). Work-up and recrystallisation from dichloromethane–light petroleum (b.p. 60–80 °C) of the resulting yellow solid gave the *title complex* **27** as yellow crystals (122 mg, 0.37 mmol, 92%), m.p. 136–140 °C (decomp.) (Found: C, 50.5; H, 4.8. $C_{14}H_{16}CrO_4S$ requires C, 50.60; H, 4.85%); *m/z* (EI, 70 eV, 240 °C) 332 (M^+, 0.8%), 316 (M − O, 0.9), 276 (M − 2CO, 4.4), 260 (M − 2CO − O, 1.4), 248 (M − 3CO, 7.3), 232 (M − 3CO − O, 2.1), 192 (MH − 3CO − C_4H_9, 4.9), 52 (Cr, 30.1) and 28 (CO, 100). See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

1-tert-*Butyl*-2-(*methylthio*)*benzene* **11**.[41]—2-*tert*-Butylbenzenethiol **15** (3.0 g, 18 mmol) was treated with sodium hydride (60%; 0.79 g, 19.8 mmol) and methyl iodide (2.82 g, 19.8 mmol) according to the procedure described above for the synthesis of the sulfide **12**. Work-up gave the title sulfide **11** as a pale yellow oil (3.10 g, 17 mmol, 95%); ν_{max}(neat)/cm^{-1} 2956vs, 2920vs, 2870s, 1481s, 1467vs, 1430vs, 1363s, 1247s, 1050vs, 753vs and 735s; *m/z* (EI, 70 eV, 260 °C), 180 (M^+, 61%), 165 (M − CH_3, 100) and 150 (M − $2CH_3$, 31). See Tables 4 and 5 for ^1H and ^{13}C NMR spectroscopic data.

[η^6-1-tert-*Butyl*-2-(*methylthio*)*benzene*]*tricarbonyl-chromium*(0) **28**.—Following procedure D, 1-*tert*-butyl-2-(methylthio)benzene **11** (0.5 g, 2.76 mmol) was treated with hexacarbonylchromium (1.52 g, 6.9 mmol) in 1,4-dioxane (20 cm^3) for 70 h to give a green solution, filtration of which followed by column chromatography [SiO_2; light petroleum (b.p. 60–80 °C)–diethyl ether, 4:1] and recrystallisation from dichloromethane–light petroleum (b.p. 60–80 °C) yielded the *title complex* **28** as yellow crystals (0.44 g, 1.4 mmol, 50%), m.p. 72–74 °C (Found: C, 53.3; H, 4.9. $C_{11}H_{10}CrO_4S$ requires C, 53.16, H, 5.1%); *m/z* (EI, 70 eV, 240 °C) 316 (M^+, 5%), 260 (M −2CO, 10), 232 (M − 3CO, 22), 216 (M − 3CO − CH_4, 6), 184 (M − 3CO − CH_4 − S, 16), 180 [M − $Cr(CO)_3$, 9], 165 [M − $Cr(CO)_3$ − CH_3, 19] and 52 (Cr, 100). See Tables 6, 7 and 8 for IR ^1H and ^{13}C NMR spectroscopic data.

[η^6-1-tert-*Butyl*-2-(*methylsulfinyl*)*benzene*]*tricarbonyl-chromium*(0) **31$_Y$**.—Following the general oxidation procedure described above for the synthesis of complex **20$_Y$**, [η^6-1-*tert*-butyl-2-(methylthio)benzene]tricarbonylchromium(0) **28** (127 mg, 0.4 mmol) dissolved in acetone (10 cm^3) was treated with dimethyldioxirane (0.099 mol dm^{-3} solution in acetone; 4.85 cm^3, 0.48 mmol, 1.2 equiv.), diluted in acetone (5 cm^3). After filtration, column chromatography (SiO_2) using diethyl ether as the eluent gave the starting sulfide complex; further elution with acetone gave the title sulfoxide complex. Recrystallisation of this second fraction from dichloromethane–light petroleum (b.p. 60–80 °C) gave the *title complex* **31$_Y$** as orange–yellow crystals (60 mg, 0.18 mmol, 45%), m.p. 100–102 °C (Found: C, 50.5; H, 4.85. $C_{14}H_{16}CrO_4S$ requires C, 50.60; H, 4.85%); *m/z* (EI, 70 eV, 240 °C) 332 (M^+, 2%), 316 (M − O, 5), 276 (M −2CO, 2), 260 (M − O − 2CO, 8), 248 (M − 3CO, 10), 232 (M − O − 3CO, 22), 180 [M − O − $Cr(CO)_3$, 40], 165 [M − O − $Cr(CO)_3$ − CH_3, 79], 150 [M − O − $Cr(CO)_3$ − $2CH_3$, 35] and 52 (Cr, 100). See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

Procedure E

Tricarbonyl[η^6-3-*methoxy*-1-(*methylthio*)*benzene*]-*chromium*(0) **29**.—A solution of 1-methoxy-3-(methylthio)benzene **12** (0.077 g, 0.5 mmol) and hexacarbonylchromium (0.26 g, 1.19 mmol) in a mixture of dibutyl ether–THF (10:1, 11 cm^3) was degassed and heated in the dark at 135 °C under a nitrogen-saturated atmosphere. After 14 h, the resulting orange solution was cooled in an ice-bath and filtered through Kieselguhr, eluting with diethyl ether. The solvent was removed under reduced pressure to afford a yellow powder, which was subsequently recrystallised from diethyl ether–hexane to give the *title complex* **29** as yellow crystals (0.13 g, 0.46 mmol, 92%), m.p. 59.5–60 °C (Found: C, 45.2; H, 3.3. $C_{11}H_{10}CrO_4S$ requires C, 45.52; H, 3.48%); *m/z* (EI, 70 eV, 200 °C) 290 (M^+, 26%), 262 (M − CO, 1), 234 (M − 2CO, 32), 206 (M − 3CO, 100), 191 (M − 3CO − CH_3, 74), 176 (M − 3CO − $2CH_3$, 23), 160 (M − 3CO − CH_3 − OCH_3, 6), 154 [M − $Cr(CO)_3$, 6] and 52 (Cr, 74). See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

Tricarbonyl[η^6-1-*methoxy*-3-(*methylsulfinyl*)*benzene*]-*chromium*(0) **32$_{X/Y}$**.—Following the general oxidation procedure described above for the synthesis of complex **20$_Y$**, tricarbonyl[η^6-1-methoxy-3-(methylthio)benzene]chromium-(0) **29** (110 mg, 0.38 mmol) was treated in acetone (10 cm^3) with dimethyldioxirane (0.1 mol dm^{-3} acetone solution; 4.2 cm^3, 0.42 mmol, 1.1 equiv.), diluted in acetone (5 cm^3). After work-up, column chromatography [SiO_2; dichloromethane–ethyl acetate, 9:1] and subsequent recrystallisation from dichloromethane–hexane gave an inseparable 1:1 mixture of both diastereoisomers of the *title complex* **32$_{X/Y}$** as yellow crystals (76 mg, 0.25 mmol, 65%) [Found: *m/z* 306.9732. $C_{11}H_{11}CrO_5S$ (MH^+) requires 306.9732]; *m/z* (CI, NH_3) 324 [$(M + NH_4)^+$, 52%], 307 (MH, 30), 291 (MH − O, 63) and 171 [MH −$Cr(CO)_3$, 100]. See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

Tricarbonyl[η^6-(*methylthio*)*benzene*]*chromium*(0) **30**.[22]—Following procedure D, (methylthio)benzene (0.5 g, 4 mmol) was treated with hexacarbonylchromium (2.21 g, 10 mmol) in 1,4-dioxane (20 cm^3) for 64 h to give an orange solution. Filtration and removal of solvent from this gave a yellow solid which upon crystallisation from dichloromethane–light petroleum (b.p. 60–80 °C) yielded the title complex **30** as yellow crystals (1.01 g, 3.88 mmol, 96%), m.p. 101–102 °C (lit.,[42] m.p. 101–102 °C) (Found: C, 45.9; H, 2.9. $C_{10}H_8CrO_3S$ requires C, 46.16; H, 3.1%); *m/z* (EI, 70 eV, 220 °C) 260 (M^+, 2.7%), 232 (M − CO, 0.4), 204 (M − 2CO, 3.9), 176 (M − 3CO, 9.1), 161 (M − 3CO − CH_3, 7.6), 124 [M − $Cr(CO)_3$, 83.3], 52 (Cr, 33.3) and 28 (CO, 100). See Tables 6, 7 and 8 for IR, ^1H and ^{13}C NMR spectroscopic data.

Tricarbonyl[η^6-(*methylsulfinyl*)*benzene*]*chromium*(0) **33**.—Following the general oxidation procedure described above for the synthesis of complex **20$_Y$**, tricarbonyl[η^6-(methylthio)-benzene]chromium(0) **30** (89 mg, 0.34 mmol) was treated in acetone (10 cm^3) with dimethyldioxirane (0.095 mol dm^{-3} acetone solution; 4.3 cm^3, 0.41 mmol, 1.2 equiv.), diluted in acetone (5 cm^3). Work-up and crystallisation of the resulting yellow solid from dichloromethane–light petroleum (b.p. 60–80 °C) gave the *title complex* **33** as yellow crystals (87.5 mg, 0.32 mmol, 93%), m.p. 82–83 °C (Found: C, 43.2; H, 2.6. $C_{10}H_8CrO_4S$ requires C, 43.48; H, 2.92%); *m/z* (CI, NH_3) 294 [$(M + NH_4)^+$, 22%], 277 (MH, 40), 261 (MH − O, 18) and 141 [MH − $Cr(CO)_3$, 100]. See Tables 6, 7 and 8 for IR ^1H and ^{13}C NMR spectroscopic data.

X-Ray Crystallographic Analysis of **20$_X$**.—*Crystal data.* Single crystals of **20$_X$**, suitable for X-ray crystallography were

grown from diethyl ether–pentane. $C_{11}H_{10}CrO_5S$, $M = 306.3$, monoclinic, $a = 8.571(2)$, $b = 14.581(4)$, $c = 10.432(4)$ Å, $\beta = 94.62(2)°$, $U = 1299.6(7)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 1.57$ g cm^{-3}, μ(Mo-Kα) = 10.5 cm^{-1}, $F(000) = 624$. Data were measured on a Siemens P4/PC diffractometer ($2\theta < 50°$) with Mo-Kα radiation (graphite monochromator) using ω-scans. 2295 Independent reflections were measured and of these 1702 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; no absorption correction was applied. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised C–H = 0.96 Å, assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares to give $R = 0.039$, $R_w = 0.041$ [$w^{-1} = \sigma^2(F) + 0.0004F^2$]. The maximum residual electron density in the final ΔF map was 0.25 eÅ^{-3}. Computations were carried out on a 486 PC using the SHELXTL-PC program system.[42] Atomic coordinates, bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Cata Centre.

X-Ray Crystallographic Analysis of **21$_Y$**.—*Crystal data.* Single crystals of **21$_Y$**, suitable for X-ray crystallography were grown from dichloromethane–light petroleum (b.p. 60–80 °C). $C_{12}H_{12}CrO_5S$, $M = 320.3$, monoclinic, $a = 11.097(4)$, $b = 15.729(6)$, $c = 15.695(6)$ Å, $\beta = 97.72(2)°$, $U = 2715(2)$ Å^3, space group $P2_1/c$, $Z = 8$ (2 crystallographic independent molecules), $D_c = 1.57$ g cm^{-3}, μ(Mo-Kα) = 10.1 cm^{-1}, $F(000) = 1312$. Data were measured on a Siemens P4/PC diffractometer ($2\theta < 50°$) with Mo-Kα radiation (graphite monochromator) using ω-scans. 4789 Independent reflections were measured and of these 3836 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; no absorption correction was applied. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised C–H = 0.96 Å, assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares to give $R = 0.050$, $R_w = 0.054$ ($w^{-1} = \sigma^2(F) + 0.0006F^2$). The maximum residual electron density in the final ΔF map was 0.63 eÅ^{-3}. Computations were carried out on a 486 PC using the SHELXTL-PC program system.[42] Atomic coordinates, bond lengths, angles and thermal parameters have been deposited as the Cambridge Crystallographic Data Centre.

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