First Synthesis of Sulfinyl Substituted Tricarbonyl(η⁶-arene)chromium(0) Complexes

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Dimethyldioxirane efficiently oxidises tricarbonylchromium(0) complexes of sulfenyl substituted arenes to tricarbonylchromium(0) complexes of sulfinyl substituted arenes: *ortho* substituted complexes are oxidised with high diastereoselectivity and determination of the relative stereochemistry of the oxidation products by *inter alia* an X-ray crystal structure analysis of tricarbonyl[η⁶-1-(*tert*-butylsulfinyl)-2-methoxybenzene]chromium(0) (**2b$_X$**) revealed that oxidations of methylsulfenyl and *tert*-butylsulfenyl substituted complexes proceed to give complementary diastereoisomers.

For over two decades, there has been considerable interest in the application of tricarbonyl(η⁶-arene)chromium(0) complexes to problems encountered in organic synthesis.[1] Recently, a substantial proportion of research in this area has been directed towards the discovery and exploitation of reactions of tricarbonyl(η⁶-arene)chromium(0) complexes that proceed with high diastereoselectivity,[2] and the design and implementation of efficient routes to enantiomerically pure complexes.[3] We are currently interested in the synthesis of transition metal complexes of sulfinyl substituted ligands as a result of our recent observations that the sulfinyl substituted oxoalkenes [RS(O)CH=CHC(Me)=O; R = Bu^t, Ph] and the sulfinyl substituted alkene PhS(O)CH=CH$_2$ form diastereomerically pure iron carbonyl complexes when treated with sources of tricarbonyliron(0) and tetracarbonyliron(0) respectively.[4,5] In order to increase our knowledge of how sulfinyl substituted ligands interact with metal carbonyl groups, we wished to synthesise tricarbonylchromium(0) complexes of sulfinyl substituted arenes. In view of the considerable interest in the stereochemical properties of tricarbonyl(η⁶-arene)chromium(0) complexes referred to above, and the widespread use of sulfinyl substituents to control the chemical and stereochemical outcome of organic reactions,[6] we were somewhat surprised to find that, to the

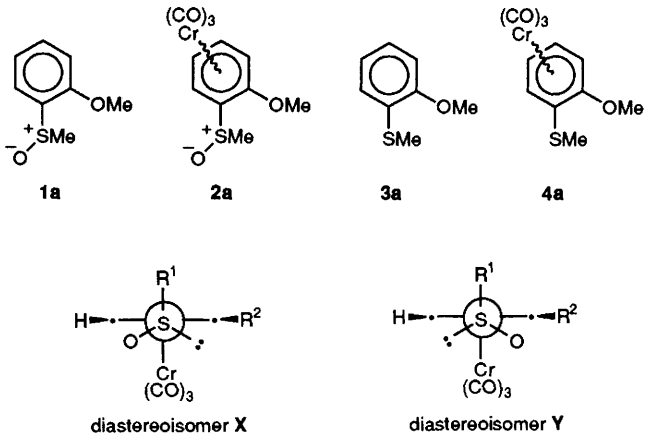


Fig. 1 Relative orientations of the two chiral elements in sulfinyl substituted complexes **2** looking down the S–C bond in the plane of the arene ring

best of our knowledge, tricarbonylchromium(0) complexes of sulfinyl substituted arenes are to date unknown.† We thus report herein that tricarbonylchromium(0) complexes of sulfenyl substituted arenes may be oxidised efficiently and diastereoselectively to tricarbonylchromium(0) complexes of sulfinyl substituted arenes.

Initial efforts to form a tricarbonylchromium(0) complex of a sulfinyl substituted arene focused on direct complexation of 2-methoxy-1-(methylsulfinyl)benzene **1a** under a range of conditions used routinely for the formation of tricarbonyl(η^6-arene)chromium(0) complexes. The results were mostly disappointing; reacting arene **1a** with $[Cr(CO)_6]$[8] or $[Cr(CO)_3(pyridine)_3]$[9] gave none of the required complex, whilst treating **1a** with tricarbonyl(η^6-naphthalene)chromium(0)[10] or $[Cr(CO)_3(MeCN)_3]$[11] gave only trace amounts of the sulfinyl complex **2a**. When the reaction using $[Cr(CO)_3(MeCN)_3]$ was performed on a relatively large scale, however, it did prove possible to isolate and characterise‡ fully the required sulfinyl complex **2a**. Examination of the ^1H NMR spectrum of the crude product mixture indicated that only one diastereoisomer had formed in the reaction and an X-ray crystal structure analysis of the isolated complex revealed that its relative stereochemistry was as indicated by structure **X** in Fig. 1 (R^1 = Me, R^2 = OMe).

As the yield of sulfinyl complex **2a** was both poor and capricious, an alternative route to tricarbonylchromium(0) complexes of sulfinyl substituted arenes was sought. It has been known for some time that sulfenyl substituted arenes readily form tricarbonylchromium(0) complexes,[12] and so oxidation of sulfenyl substituents was proposed as a potentially much more efficient route to tricarbonylchromium(0) complexes of sulfinyl substituted arenes. Thus sulfide **3a** was converted to its tricarbonylchromium(0) complex **4a** in 89% yield by heating it with $[Cr(CO)_6]$.§ Oxidation of complex **4a** with 1.1 equiv. of either *m*-chloroperbenzoic acid (*m*CPBA), *tert*-butyl hydroperoxide[13] or 2-hydroperoxy-2-methoxypropane[14] gave, in the former two cases, a mixture of sulfide ligand **3a** and the organic sulfoxide **1a**, or in the latter case, a mixture of starting sulfide complex **4a** and decomplexed ligand **3a**. Attention then turned to dimethyldioxirane,[15] a reagent which has rapidly been accepted as a useful mild oxidant for many organic transformations,[16] including the oxidation of sulfides to sulfoxides,[17] and which is beginning to prove useful for organometallic transformations.[18] Pleasingly, oxidation of sulfide complex **4a** with 1.1 equiv. of dimethyldioxirane led to the formation of the required sulfoxide complex **2a** in good yield. Examination of the crude product by ^1H NMR spectroscopy indicated that the two possible diastereoisomers of **2a** had been formed in a ratio of 93 : 7. Comparison of this spectrum with the ^1H 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.¶ Thus the major diastereoisomer obtained by oxidation was assigned the relative stereochemistry indicated by structure **Y** in Fig. 1 (R^1 = Me, R^2 = OMe). Crystallisation of the crude product mixture from acetone–hexane gave diastereoisomerically and analytically pure sulfoxide complex ($\mathbf{2a_Y}$) in 80% yield (Table 1, Entry 1).

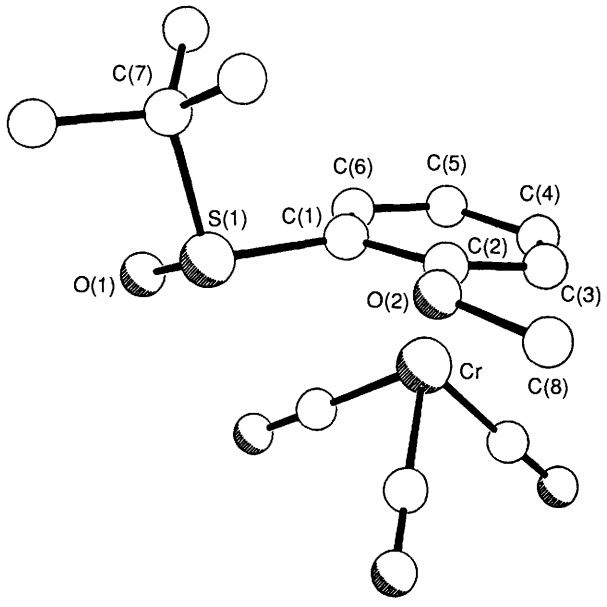


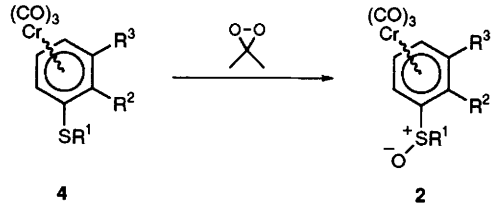
Fig. 2 Molecular structure of one of the pair of crystallographically independent molecules of complex $\mathbf{2b_X}$ ($C_{14}H_{16}CrO_5S$). Selected bond lengths (Å) and bond angles (°) (values in square brackets refer to the second independent molecule): Cr–C(1) 2.210(5) [2.218(5)], Cr–C(2) 2.255(5) [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)].

† A complex observed during a study of the use of dimethyldioxirane for decomplexing tricarbonyl(η^6-arene)chromium(0) complexes was assigned as tricarbonyl(η^6-methylsulfinylbenzene)chromium(0) on the basis of its ^1H NMR spectrum alone.[7]

‡ The novel sulfinyl substituted complexes $\mathbf{2a_X}$, $\mathbf{2a_Y}$, $\mathbf{2b_X}$, $\mathbf{2c_Y}$, $\mathbf{2d_X}$, $\mathbf{2e_{X/Y}}$ and **2f**, and the novel sulfenyl substituted complexes **4a–e** all gave satisfactory microanalytical, IR, ^1H NMR, ^{13}C NMR and mass spectral data.

§ The sulfenyl substituted complexes **4a–f** were synthesised in 71–96% yield by heating with $[Cr(CO)_6]$ in either dioxane at 100 °C for 40–67 h or 10 : 1 Bu_2O–tetrahydrofuran at 135 °C for 14.5 h.

¶ ^1H and ^{13}C NMR data of sulfinyl substituted complexes $\mathbf{2a_X}$ and $\mathbf{2a_Y}$: δ_H ($\mathbf{2a_X}$) 2.79 [3H, s, S(O)CH_3], 3.82 (3H, s, OCH_3), 5.01 (1H, t, *J* 6 Hz, H-5), 5.02 (1H, d, *J* 6 Hz, H-3), 5.57 (1H, t, *J* 6 Hz, H-4), and 6.19 (1H, d, *J* 6 Hz, H-6); δ_H ($\mathbf{2a_Y}$) 2.93 [3H, s, S(O)CH_3], 3.83 (3H, s, OCH_3), 4.90 (1H, t, *J* 6 Hz, H-5), 5.01 (1H, d, *J* 5 Hz, H-3), 5.75 (1H, t, *J* 6 Hz, H-4) and 6.34 (1H, d, *J* 6 Hz, H-6); δ_C ($\mathbf{2a_X}$) 42.7 [S(O)CH_3], 56.3 (OCH_3), 71.6, 83.8, 88.1, 93.8 (C-3–C-6), 101.5 (C-1), 140.2 (C-2) and 230.8 (C≡O); δ_C ($\mathbf{2a_Y}$) 46.9 [S(O)CH_3], 56.3 (OCH_3), 70.9, 81.4, 94.3, 95.6 (C-3–C-6), 106.6 (C-1), 139.8 (C-2) and 231.4 (C≡O).



4 2

Table 1 Oxidation of sulfenyl substituted complexes **4** to sulfinyl substituted complexes **2**[a]

Entry	Sulfide complex **4**	R^1	R^2	R^3	Sulfoxide complex **2**	Ratio of diastereoisomers formed (**X** : **Y**)	Yield of diastereoisomer(s) indicated (%)
1	**a**	Me	OMe	H	**a**	7:93	80 (**2a**$_Y$)
2	**b**	Bu^t	OMe	H	**b**	≥98:≤2	77 (**2b**$_X$)
3	**c**	Me	Me	H	**c**	10:90	78 (**2c**$_Y$)
4	**d**	Bu^t	Me	H	**d**	≥98:≤2	92 (**2d**$_X$)
5	**e**	Me	H	OMe	**e**	50:50	65 (**2e**$_{X/Y}$)
6	**f**	Me	H	H	**f**	n/a	93

[a] The experimental details for Entry 4 represent a typical oxidation procedure: the sulfenyl substituted complex **4d** (0.127 g, 0.4 mmol) was dissolved in nitrogen-saturated acetone (10 ml) and cooled to −78 °C under a nitrogen atmosphere. Dimethyldioxirane[15] (6.4 ml of a 0.075 mol l^{-1} solution in acetone, 1.2 equiv.) was diluted with nitrogen-saturated acetone (5 ml), cooled to −78 °C and added very slowly dropwise *via* a cannula to the yellow solution of **4d**. After the addition was complete, the reaction mixture was stirred for 15 min at −78 °C and then for 1 h at room temp. Removal of the solvent from the resulting slightly cloudy yellow product mixture gave a yellow–pale green solid, a small portion of which was analysed by ^{1}H NMR spectroscopy. Dichloromethane was added to the solid and the mixture was filtered through Kieselguhr. Recrystallisation from dichloromethane–light petroleum (b.p. 60–80 °C) gave yellow crystals of the sulfinyl substituted complex **2d** (0.123 g, 92%).

In order to determine whether or not the diastereoisomeric ratio of 93:7 observed in the oxidation of the sulfenyl substituted complex **4a** to the sulfinyl substituted complex **2a** could be improved significantly by increasing the size of the alkyl group R^1 of the sulfenyl substituent, the *tert*-butylsulfenyl complex **4b** was synthesised and then oxidised using dimethyldioxirane. Examination of the crude product obtained from the oxidation indicated that the diastereoisomeric ratio of sulfoxide products was ≥98 : ≤2. Subsequent crystallisation of the crude product gave pure sulfinyl substituted complex **2b** in 77% yield (Table 1, Entry 2). Interestingly, an X-ray crystal structure analysis‖ of one of the yellow crystals revealed that the relative stereochemistry of the major diastereoisomer obtained by oxidation of complex **4b** corresponded with stereochemistry **X** in Fig. 1 (R^1 = Bu^t, R^2 = OMe) (see Fig. 2). Therefore oxidation of the methylsulfenyl substituted complex **4a** and the *tert*-butylsulfenyl substituted complex **4b** had proceeded with complementary selectivity to give predominantly diastereoisomers **Y** and **X** respectively. Similar results were obtained when the methoxy substituent (R^2 = OMe) was replaced by a methyl group (R^2 = Me). Thus inspection of the spectroscopic data of the major diastereoisomers obtained from the products generated by oxidising the methylsulfenyl substituted complex **4c** and the *tert*-butylsulfenyl substituted complex **4d** indicated that they were diastereoisomers **Y** and **X** respectively (Table 1, Entries 3 and 4).

An explanation for the dramatic difference in diastereoselectivity between the methylsulfenyl substituted complexes and the *tert*-butylsulfenyl substituted complexes is illustrated in Fig. 3. When R^1 = Me, eclipsing interactions between R^1 and the hydrogen *ortho* to the sulfenyl group are inconsequential and so the methylsulfenyl 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 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*-butylsulfenyl 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 diastereoisomer **X**.

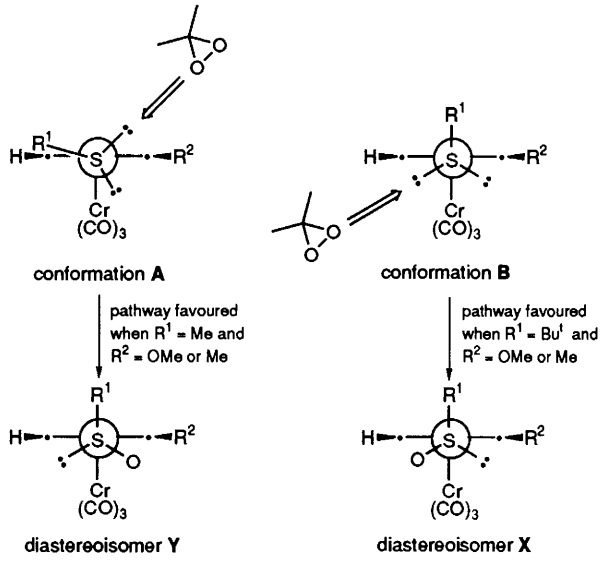


Fig. 3 Proposed origin of the complementary diastereoselectivity observed for oxidation of the methylsulfenyl and *tert*-butylsulfenyl substituted complexes

‖ *Crystal data* for (**2b**$_X$): $C_{14}H_{16}CrO_5S$, M = 348.3, monoclinic, a = 12.658(7), b = 15.544(11), c = 16.172(10) Å, β = 100.61(2)°, V = 3128(3) Å^3, space group $P2_1/n$, Z = 8, D_c = 1.480 Mg m^{-3}, μ = 0.881 mm^{-1}. Data were measured on a Siemens P4/PC diffractometer with Mo-Kα radiation (λ = 0.71073 Å) using ω scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give R = 0.053, R_w = 0.050 for 3710 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, 2θ ≤ 50°]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Finally, oxidation of the *meta* substituted sulfenyl complex **4e** was found to proceed unselectively (Table 1, Entry 5), and oxidation of tricarbonyl(η^6-thioanisole)chromium(0) **4f**[12] proceeded efficiently to give a 93% yield of **2f** (Table 1, Entry 6).

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