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

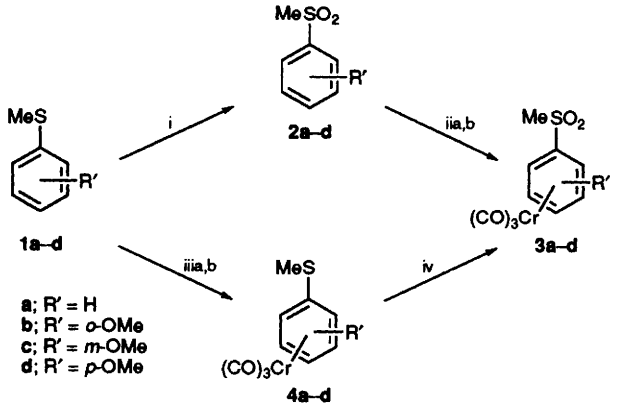
Carlos F. Marcos,[a] Stéphane Perrio,[a] Alexandra M. Z. Slawin,[b] Susan E. Thomas*[a] and David J. Williams[b]

[a] Department of Chemistry, [b] Chemical Crystallography Laboratory, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY

Sulfonyl substituted tricarbonyl(η⁶-arene)chromium(0) complexes may be prepared by thermolysis of sulfonyl substituted arenes with $Cr(CO)_6$/BuOAc and/or selective oxidation of sulfenyl substituted tricarbonyl(η⁶-arene)chromium(0) complexes with cumene hydroperoxide in the presence of a $Ti(OPr^i)_4$/diethyl tartrate/H_2O catalyst.

There has been considerable interest in the synthesis and applications of tricarbonyl(η⁶-arene)chromium(0) complexes for more than three decades now.[1] Focusing on complexes of sulfur substituted arenes, the literature reveals that sulfenyl substituted tricarbonyl(η⁶-arene)chromium(0) complexes have been known for many years.[2] In contrast the first synthesis of sulfinyl substituted tricarbonyl(η⁶-arene)chromium(0) complexes was reported only very recently.[3] This was achieved by dimethyldioxirane oxidation of tricarbonylchromium(0) complexes of sulfenyl substituted arenes as direct complexation methods led to the reduction of the sulfoxide functional group. The next highest oxidation state analogues in this series *i.e.* tricarbonylchromium(0) complexes of sulfonyl substituted arenes, are to the best of our knowledge unknown.† Here, we report the first examples of these complexes. In addition, the results of a study designed to determine the most efficient routes to sulfonyl complexes bearing *ortho*, *meta* and *para* substituents are presented.

Although complexation of electron poor arenes is frequently unsuccessful or low yielding, direct complexation was examined initially as the simplest approach to sulfonyl substituted tricarbonyl(η⁶-arene)chromium(0) complexes.



Scheme 1 *Reagents*: i, *m*CPBA; iia, $Cr(CO)_6$; iib, $Cr(CO)_6$/BuOAc; iiia, $Cr(CO)_6$; iiib, $Cr(CO)_6$/BuOAc; iv, $Ti(OPr^i)_4$/diethyl L-(+)-tartrate/H_2O–cumene hydroperoxide

Thus, *m*CPBA oxidation of (methylsulfenyl)benzene **1a** gave (methylsulfonyl)benzene **2a** in quantitative yield (Scheme 1). Subsequent thermolysis of sulfone **2a** with 2.5 equiv. of $Cr(CO)_6$ in 1,4-dioxane at reflux for 48 h followed by filtration and crystallisation from chloroform led to the isolation of yellow air-stable crystals which were tentatively identified as the novel sulfone complex **3a** on the basis of their analytical and spectroscopic data.†§ This identification was confirmed by an X-ray crystal structure analysis¶ (see Fig. 1), and the yield of complex **3a** was calculated to be 47% based on arene **2a** (see Table 1). When the complexation was performed in the presence of 2 equiv. of BuOAc,[5] **3a** was obtained in 56% yield.

Whilst the formation of the sulfone complex **3a** in 56% yield is acceptable with respect to future reactivity studies, it was of interest to determine whether or not **3a** could be made more efficiently by oxidation of the sulfenyl substituted complex **4a**. Thus, (methylsulfenyl)benzene **1a** was converted into its tricarbonylchromium(0) derivative **4a** [in 77% yield (93% with addition of BuOAc)] and the oxidation of this complex was examined. Addition of 2 equiv. $KMnO_4$, 2 equiv. $NaIO_4$, 2 equiv. *N*-methylmorpholine *N*-oxide/cat. OsO_4,[6] or 2 equiv. PhIO/cat. $RuCl_2(PPh_3)_3$[7] led only to the reisolation of complex **4a**. In contrast, decomposition ensued using 2 equiv. dimethyldioxirane,[3] 2 equiv. methyl(trifluoromethyl)dioxirane,[8] 2 equiv. trifluoroacetone diperoxide,[9] 2 equiv. magnesium monoperoxyphthalate,[10] 2 equiv. cumene hydroperoxide/cat. $VO(acac)_2$[11] or 2 equiv. $KHSO_5$.[12] Finally, it was discovered that the $Ti(OPr^i)_4$/diethyl L-(+)-tartrate/H_2O–cumene hydroperoxide system[13] oxidised the sulfide complex **4a** to the sulfone complex **3a** in 56% yield.‖ Thus, this complexation–oxidation route to sulfone complex **3a** is essentially identical in efficiency to the oxidation–complexation route described above (52 *vs.* 56% over two steps).

The oxidation–complexation route (reactions i and ii) was subsequently compared with the complexation–oxidation route (reactions iii and iv) for *o*-OMe, *m*-OMe and *p*-OMe substituted systems in order to determine the most efficient route to sulfone complexes bearing electron-donating substituents. In addition, each $Cr(CO)_6$ complexation was performed with and without 2 equiv. of BuOAc in order to determine whether or not this additive would significantly increase the yield of complex formed. The most efficient route

Table 1 Yields of reactions i–iv (%)[a]

Reaction	Yields for series **a** (R' = H)	Yields for series **b** (R' = *o*-OMe)	Yields for series **c** (R' = *m*-OMe)	Yields for series **d** (R' = *p*-OMe)
i *m*CPBA oxidation of sulfide **1** to sulfone **2**	100	100	100	100
iia Complexation[b] of sulfone **2** using $Cr(CO)_6$	47	51	18[c]	15% conversion
iib Complexation[b] of sulfone **2** using $Cr(CO)_6$/BuOAc	56	70	22	25
iiia Complexation[b] of sulfide **1** using $Cr(CO)_6$	77	72	50% conversion	61
iiib Complexation[b] of sulfide **1** using $Cr(CO)_6$/BuOAc	93	83	94	89
iv Ti Mediated oxidation of complex **4** to complex **3**	56	0[d]	16% conversion[d]	59

[a] All yields are isolated yields unless stated otherwise. Where % conversion is given, the low concentration of product in the product mixture led to purification problems. [b] All complexations times were 46–51 h unless stated otherwise (see footnote *c*). [c] Complexation time = 18 h; after this time the rate of decomplexation > rate of complexation. [d] Major product = sulfoxide complex.

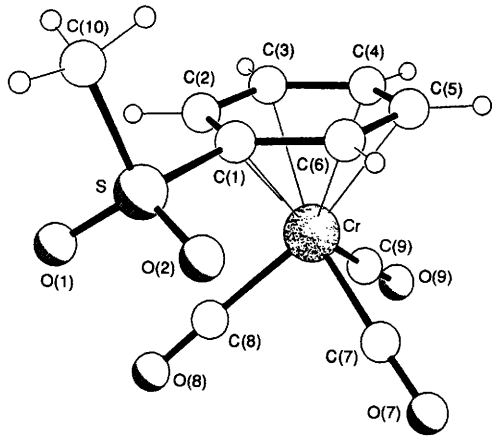


Fig. 1 Molecular structure of complex **3a** ($C_{10}H_8CrO_5S$). Selected bond lengths (Å) and bond angles (°): C(1)–C(2) 1.413(3), C(2)–C(3) 1.393(3), C(3)–C(4) 1.406(4), C(4)–C(5) 1.385(4), C(5)–C(6) 1.404(3), C(6)–C(1) 1.403(3), C(1)–S 1.765(2), S–C(10) 1.750(3), S–O(1) 1.435(2), S–O(2) 1.428(2), Cr–C(1) 2.172(2), Cr–C(2) 2.197(3), Cr–C(3) 2.213(3), Cr–C(4) 2.178(3), Cr–C(5) 2.199(3), Cr–C(6) 2.177(2) Cr–C(7) 1.851(3), Cr–C(8) 1.864(3), Cr–C(9) 1.844(2); O(1)–S–O(2) 120.0(1), O(1)–S–C(10) 107.9(1), O(2)–S–C(10) 108.4(1), O(1)–S–C(1) 107.8(1), O(2)–S–C(1) 107.6(1), C(10)–S–C(1) 104.0(1), Cr–C(7)–O(7) 178.8(2), Cr–C(8)–O(8) 179.2(2), Cr–C(9)–O(9) 177.5(2).

to the *ortho*-substituted sulfone complex **3b** proved to be the oxidation–complexation route (70 *vs.* 0% over two steps), whilst the best route to the *para*-substituted sulfone complex **3d** proved to be the complexation–oxidation route (53 *vs.* 25% over two steps). Neither route was really satisfactory for the generation of the *meta*-substituted sulfone complex **3c** (22 *vs.* 15% over two steps). Finally, it is of note that in every $Cr(CO)_6$ complexation performed, addition of BuOAc led to a significant improvement in the yield of complex obtained.

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Footnotes

† It should be noted in this context that tricarbonyl(η^6-arene)-chromium(0) complexes with benzylic sulfonyl substituents have been synthesised.[4]

‡ Analytical and spectroscopic data for complex **3a**: mp 152–153 °C; satisfactory C and H analyses were obtained; $\nu_{max}(CH_2Cl_2)$ cm^{-1} 1991vs, 1921vs (C≡O) and 1266vs (SO_2); δ_H (270 MHz; $CDCl_3$) 3.18 (3H, s, SO_2Me), 5.18 (2H, t, *J* 6 Hz, H_{meta}), 5.60 (1H, t, *J* 6 Hz, H_{para}) and 5.97 (2H, t, *J* 6 Hz, H_{ortho}); δ_C {^1H} (125.8 MHz; $CDCl_3$) 44.6 (SO_2Me), 86.3 (C_{meta}), 92.6 (C_{ortho}), 94.6 (C_{para}), 104.7 (C_{ipso}) and 228.9 (C≡O); *m/z* (EI) 292 (M^+, 9.8%), 236 (M − 2CO, 20.6) 208 (M − 3CO, 100) and 193 (M − 3CO-Me, 15.2).

§ The novel sulfonyl substituted complexes **3a–d** and the novel sulfenyl complex **4d** all gave satisfactory microanalytical, IR, ^1H NMR, ^{13}C NMR and mass spectral data.

¶ *Crystal data* for **3a**: $C_{10}H_8CrO_5S$, *M* = 292.2, monoclinic, *a* = 6.990(5), *b* = 11.496(4), *c* = 14.178(2) Å, β = 100.60(2)°, *U* = 1119.8(7) Å^3, space group $P2_1/c$, *Z* = 4, D_c = 1.73 g cm^{-3}, μ(Mo-Kα) = 12.1 cm^{-1}, *F*(000) = 592. Data were measured on a Siemens P4/PC diffractometer (2θ < 50°) with Mo-Kα radiation (graphite monochromator) using ω–scans. 1974 Independent reflections were measured and of these 1828 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 analysis to give *R* = 0.028, R_w = 0.033 [$w^{-1} = \sigma^2(F) + 0.0006F^2$]. The maximum residual electron density in the final Δ*F* map was 0.37 e Å^3. Computations were carried out on a 486 PC using the SHELXTL-PC program system. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‖ *Oxidation of* **4a** to **3a**: $Ti(OPr^i)_4$ (0.3 cm^3, 1 mmol) was added to a stirred solution of diethyl L-(+)-tartrate (0.34 cm^3, 2.0 mmol) in dry distilled dichloromethane (4 cm^3) at 0 °C under nitrogen. After stirring the resulting colourless solution at 0 °C for 20 min., distilled water (0.018 cm^3, 1.0 mmol) was added dropwise. Stirring at 0 °C for a further 30 min gave a colourless solution of the active catalyst which was added to a solution of tricarbonyl[η^6-(methylsulfenyl)benzene]-chromium(0) **4a** (0.260 g, 1.00 mmol) in dry distilled dichloromethane (52 cm^3). Cumene hydroperoxide (0.370 cm^3 of 80% solution in cumene alcohol, 2.00 mmol) was added dropwise and the reaction mixture was then stirred for 24 h at room temp. in the dark. Degassed 20% aqueous $Na_2S_2O_5$ solution (175 cm^3) was added and the mixture stirred vigorously for 15 min. The organic layer was then loaded *via* a cannula onto a short pad of Kieselguhr in a fritted funnel and eluted with degassed dichloromethane. Dichloromethane extracts of the aqueous layer (3 × 50 cm^3) were transferred and filtered in a similar manner. The combined filtrates were washed with degassed water (2 × 30 cm^3), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow powder. Purification by column chromatography (SiO_2; dichloromethane) and crystallisation from chloroform gave **3a** (0.164 g, 0.56 mmol, 56%) as yellow air-stable crystals. [*NB*. Preparation of the $Ti(OPr^i)_4$/diethyl L-(+)-tartrate/H_2O catalyst at temperatures > 0 °C led to much lower yields of **3a**].

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