Lithiation of η^6-Fluorobenzenetricarbonylchromium(0) and Reaction with Dialkyl Disulfides: Synthesis of η^6-1,2-*bis*- and 1,2,3-*tris*-Alkylsulfanylbenzenetricarbonylchromium(0) Complexes

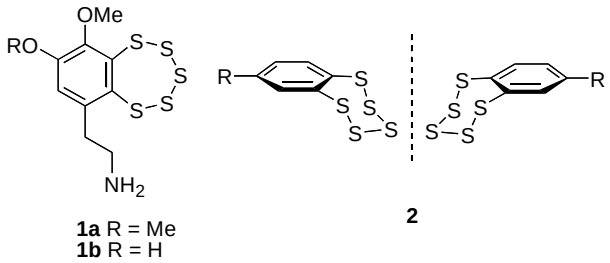
Helen Woolford, Mark R.J. Elsegood[‡] and George W. Weaver*
Department of Chemistry, Loughborough University, Loughborough, LE11 3TU UK
[*]Tel: 44 (0)1509 222584; E-mail: g.w.weaver@lboro.ac.uk
[‡] Author to whom correspondence about X-ray crystallography should be addressed; Tel: 44 (0)1509 228751; E-mail: m.r.j.elsegood@lboro.ac.uk.

Abstract
Directed lithiation of η^6-fluorobenzenetricarbonylchromium(0) and reaction with dialkyl disulfides affords η^6-1,2-*bis*-alkylsulfanylbenzenetricarbonylchromium(0) complexes by electrophilic addition of an alkylthio group at C-2 of the benzene ring, and subsequent S_NAr reaction with displacement of fluoride by the alkanethiolate generated in the first step. 1,2,3-*tris*-Alkylsulfanylbenzene complexes are formed as by-products. The structures of four of the new complexes have been confirmed by X-ray crystallography, one using synchrotron radiation.

Keywords
η^6-1,2-*bis*-alkylsulfanylbenzenetricarbonylchromium(0) complex, η^6-1,2,3-*tris*-alkylsulfanylbenzenetricarbonylchromium(0) complex, dialkyl disulfide, lithiation

1. Introduction
Naturally occurring benzopentathiepins such as varacin **1a** and lissoclinotoxin **1b** (Figure 1) exhibit potent anti-fungal and anti-tumour activity.[1] Substituted benzopentathiepins such as **2**, exhibit planar chirality due to the slow inversion of the puckered ring of sulfur atoms,[2] making such compounds interesting targets for synthetic and mechanistic study. Varacin has been synthesised by three different approaches to date,[3] and a number of methods have been developed for the preparation of substituted benzopentathiepins.[4] We have been interested in developing convenient methods to synthesise arenes substituted with adjacent sulfur substituents

which could be employed as precursors to benzopentathiepins, and as part of this investigation we have examined the use of η^6-arenetricarbonylchromium(0) complexes as substrates to allow the controlled introduction of two adjacent sulfur containing substituents onto the arene ring.



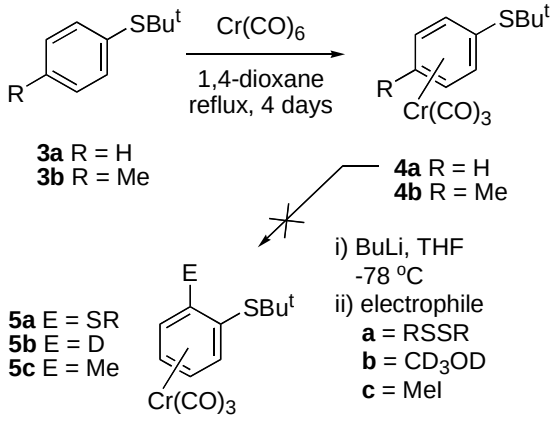
1a R = Me
1b R = H

2

Figure 1: Structures of planar chiral benzopentathiepins; **1a** = varacin, **1b** lissoclinotoxin A

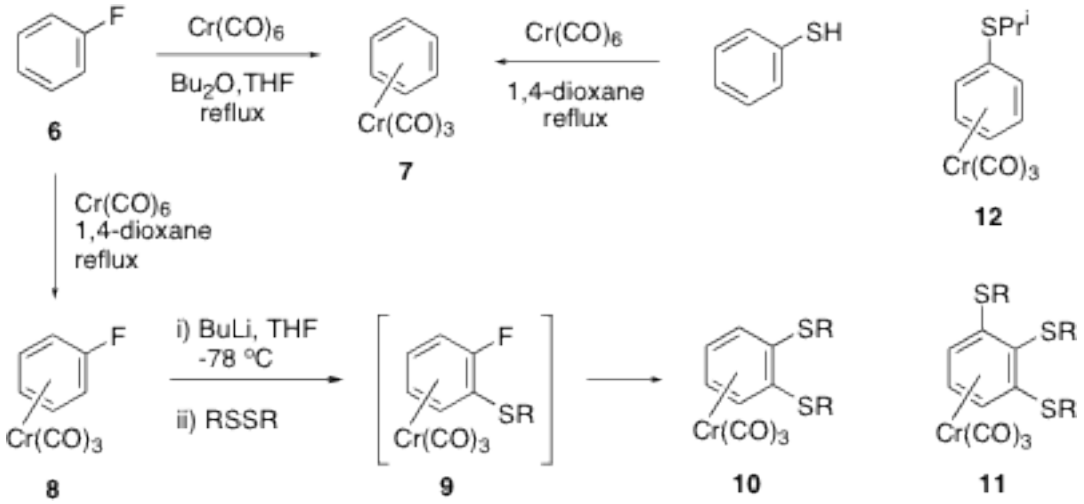
2. Results and Discussion

In this paper we report our initial results on functionalising arenetricarbonylchromium(0) complexes with sulfur-based electrophiles. Our first experiments involved the use of the *t*-butylsulfanylbenzene complexes **4** (Scheme 1). It was hoped that deprotonation *ortho* to the *t*-butylthio group could be effected with a strong base at low temperature as is well known[5] for a range of donor substituted benzenechromium complexes. Treatment with a sulfur electrophile such as a dialkyl disulfide was then expected to introduce a second alkylsulfanyl substituent forming complexes such as **5a**. It was envisaged that the *t*-butyl group could be removed at a later stage, enabling construction of a pentathiepin ring. Complexes **4a** and **4b** were formed in good yields (76% and 68% respectively) by heating the *t*-butylthioethers **3a** or **3b** with hexacarbonylchromium(0) in 1,4-dioxane for 4 days in the dark. Attempts to effect deprotonation with butyllithium and electrophilic addition at the *ortho* position in **4a** were, however, unsuccessful, and it was not possible to introduce deuterium or a methyl group (to form **5b** or **5c**) under conditions that were successful with the simple η^6-benzenetricarbonylchromium complex **7** (Scheme 2). This may be due to the steric bulk of the *t*-butylthio group preventing the base from reaching the *ortho*-hydrogen atoms.



Scheme 1: Inert behaviour of the *t*-butylsulfanyl benzenechromium complex

We then turned to the use of the fluorobenzene complex[6] **8** (Scheme 2), in which substitution adjacent to fluorine is well documented.[7] Preparation of **8** was found to be best carried out in 1,4-dioxane as solvent. Reaction of fluorobenzene with chromium hexacarbonyl in the di-*n*-butyl ether/THF mixtures commonly employed, caused loss of fluorine and production of the unsubstituted benzene complex **7** (32%) (identified by NMR spectroscopy and from the unit cell dimensions of crystals produced[8]). Interestingly η^6-benzene complex **7** was also formed in 72% yield in an attempt to form a thiophenol chromium complex by heating thiophenol with chromium hexacarbonyl in 1,4-dioxane. Attempts to displace the fluorine atom in complex **8** by treatment with NaSH in aqueous THF or in DMF were unsuccessful, while reaction in ethanol gave a 19% yield of the corresponding ethoxybenzene complex and 25% starting material. No evidence of formation of a η^6-thiophenoltricarbonyl-chromium complex was obtained.



Scheme 2: Formation of di- and tri-alkylsulfanylbenzene-chromium complexes **10**-**12** from the fluorobenzene complex **8**. Conditions: Step i) ^{n}BuLi (1.6 M) 1.2 eq, THF, –78 °C, 90 min; Step ii) Disulfide (1.5 eq.), –78 °C to room temp, 16 h.

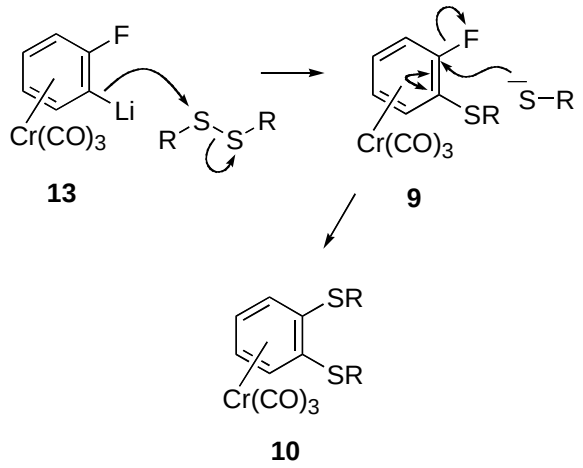
The reaction of the η^6-fluorobenzene complex **8** with dialkyl disulfides was then investigated. Treatment of the complex **8** with *n*-butyllithium in THF at low temperature followed by addition of a dialkyl disulfide and warming to room temperature afforded, not the expected η^6-1-alkylsulfanyl-2-fluorobenzenetricarbonyl-chromium(0) complexes **9**, but the η^6-1,2-*bis*-alkylsulfanylbenzene complexes **10**, in which the fluorine atom has been replaced by an alkylthio group. The reaction was successful for dimethyl, diethyl, diisopropyl and dibenzyl disulfides (Table 1).

Entry	**R**	**Conversion of 8**[a] (%)	**Ratio of Products**[a] **mono : di : tri and isolated yield (%)**
a	Me	70	0 : 100 (**10a**, 46%) : 0
b	Et	82	0 : 71 (**10b**, 42%): 11 (**11b**)
c[b]	^{i}Pr	70	40 (**12**) : 21 (**10c**) : 9 (**11c**)
d	^{t}Bu	0	n/a
e	CH_2Ph	67	0 : 50 (**10e**) : 17 (**11e**)

Table 1
[a] Conversion of starting material **8**, and product ratio obtained by integration of the ^{1}H NMR spectrum of the crude product mixture.
[b] All three products were characterised as a mixture as they could not be separated by flash chromatography or recrystallisation.

The reaction with di-*t*-butyl disulfide was unsuccessful with only a mixture of starting material and uncomplexed decomposition products obtained. In the reactions involving diethyl-, diisopropyl- and dibenzyl-disulfides the corresponding tri-substituted benzenechromium(0) complexes **11b**, **11c** and **11d** were formed as by-products. The reaction with diisopropyl disulfide also afforded the mono-substituted complex **12** as the major product in 40% yield.

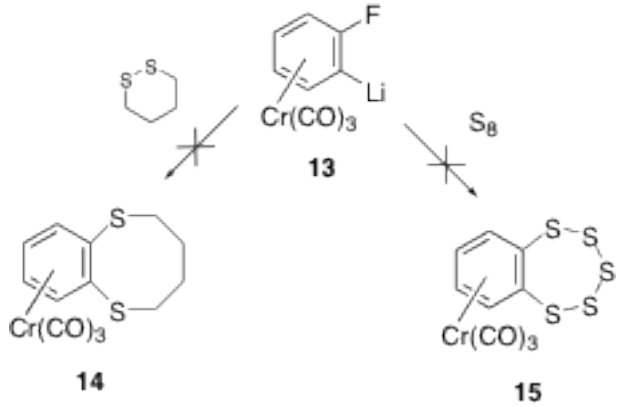
We propose the mechanism shown in Scheme 3 to account for the formation of the di-substituted compounds **10a-e**.



Scheme 3: Proposed mechanism of formation of disubstituted complexes **10a-e**.

Attack by the lithiated fluorobenzene complex **13** on the disulfide will release the corresponding alkylthiolate anion which can then effect nucleophilic aromatic substitution (S_NAr) of the fluorine atom in the first formed product **9**. A similar mechanism has been proposed by Widdowson in reactions with lactones and isocyanates which lead to bicyclic complexes by intramolecular S_NAr reaction.[9] It is less obvious how the tri-substituted complexes **11** are formed, but excess base may deprotonate the di-substituted product **10** *ortho* to one of the alkylthio groups, which are not bulky enough to restrict attack by the base, unlike the *t*-butylthio group which appeared to block proton abstraction in the unsuccessful attempts to lithiate **4a**. Alternatively, the thiolate released in the first step may diffuse away from the intermediate product **14** before it can effect S_NAr reaction, leaving the fluorine in place to activate deprotonation of the remaining *ortho*-hydrogen. The thiolate generated in a second reaction with further disulfide would then effect the necessary S_NAr substitution of the fluorine atom forming **11**. The formation of the mono-substituted complex **12**, generated in the reaction with diisopropyl disulfide, can be accounted for if the *ortho*-lithio complex **13**, which is known to be highly basic,[10] abstracted the H-2 proton from the diisopropyl disulfide, eliminating isopropylthiolate, which could then effect S_NAr reaction on the regenerated complex **8**, displacing the fluorine atom.

In an attempt to extend the scope of the reaction, the lithiated fluorobenzene complex **13** (Scheme 4) was treated with 1,2-dithiane in the hope of forming the benzo[*b*]-1,4-dithiocane complex **14**. This reaction, and an attempt to react **13** with elemental sulfur to form the benzopentathiepin complex **15**, were both unsuccessful, and no evidence for the formation of either complexes **14** or **15** was obtained.



Scheme 4: No reaction occurred with a cyclic disulfide or S_8

3. X-Ray Crystal Structures.

X-ray crystal structures were determined for disubstituted complexes **10a** (two polymorphs) **10aα** (Figs. 2, 3, 4) & **10aβ** (Figs. 5, 6, 7), **10b** (Figs. 8, 9), and **10e** (Figs. 10, 11), as well as for trisubstituted compound **11e**[11] (Figs. 12, 13). Selected geometrical parameters are presented in Table 2.

Each of the five structures adopts the piano-stool arrangement. A staggered arrangement of carbonyl groups relative to the carbon atoms of the η^6-arene is observed for **10aα**, **10aβ**, while the others are eclipsed. Analysis of the geometrical data in Table 2 reveals considerable consistency among the five structures. There is some variation in Cr(1)–C_{arene} distances, with a difference of *ca*. 0.05–0.09 Å between longest and shortest in any one structure. The bonds from the metal to the substituted carbons tend to be longest, but this is not universally true, with Cr(1)–C(1) in **10b** being among the shorter lengths. The ranges observed are consistent with the mean value of 2.22(3) Å observed among 1191 examples of ArCrCO fragments in the CSD[11]. The Cr(1)–C_{CO} distances also show some small variation, but with a difference no greater than 0.02 Å in any one structure. This observation is consistent with the narrow range observed among the 1191 examples reported in the CSD[12] which have a mean distance of 1.83(3) Å. The C_{arene}–S distances also fall into a

narrow range. There is no compelling evidence for η^6-aromatic bond length alternation, with the average of the three longest C–C bonds not statistically significantly different from the three shorter lengths. Finally, the Cr(1) to η^6-arene centroid distances also fall into a narrow range between 1.7131(9) and 1.7442(9) Å and are consistent with the CSD mean of 1.73(2) Å[11]. The two polymorphs of **10a** both exhibit very similar S···S interactions between pairs of molecules, but differ in the way these pairs arrange in space (Figs 3, 4, 6, 7). A search of the CSD revealed that these interactions, at ca. 3.32 Å, are towards the lower end of S···S interactions, which are generally no shorter than 3.2 Å, and are often 3.5–3.6 Å or longer[12].

Table 2. Selected lengths (Å) and angles (°) for **10aα**, **10aβ**, **10b**, **10e**, and **11e**.

	10aα	**10aβ**	**10b**	**10e**	**11e**
Cr(1)–C_{CO} range	1.831(2) – 1.846(2)	1.814(14) – 1.836(15)	1.8357(12) – 1.8486(13)	1.8436(19) – 1.855(2)	1.847(2) – 1.860(2)
Cr(1)–C_{arene} range	2.217(2) – 2.291(2)	2.211(15) – 2.278(13)	2.1816(11) – 2.2717(10)	2.2038(19) – 2.2517(17)	2.185(2) – 2.254(2)
av. of alternate η^6-arene C–C, long	1.420(3)	1.422(19)	1.4172(17)	1.421(3)	1.420(3)
av. of alternate η^6-arene C–C, short	1.402(3)	1.415(19)	1.4110(17)	1.404(3)	1.412(3)
C_{arene}–S	1.762(2), 1.764(2)	1.747(12), 1.759(13)	1.7560(11), 1.7677(11)	1.7701(18), 1.7792(18)	1.767(2), 1.769(2), 1.769(2)
Cr(1)···Cg {(C(1) > C(6)}	1.7442(9)	1.731(6)	1.7175(5)	1.7134(7)	1.7131(9)

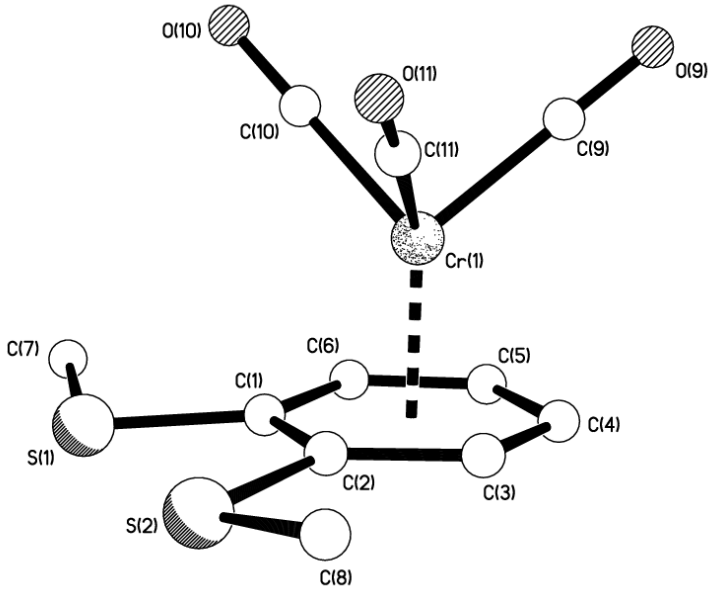


Fig. 2. The molecular structure of **10aα** showing the piano-stool, half-sandwich arrangement.

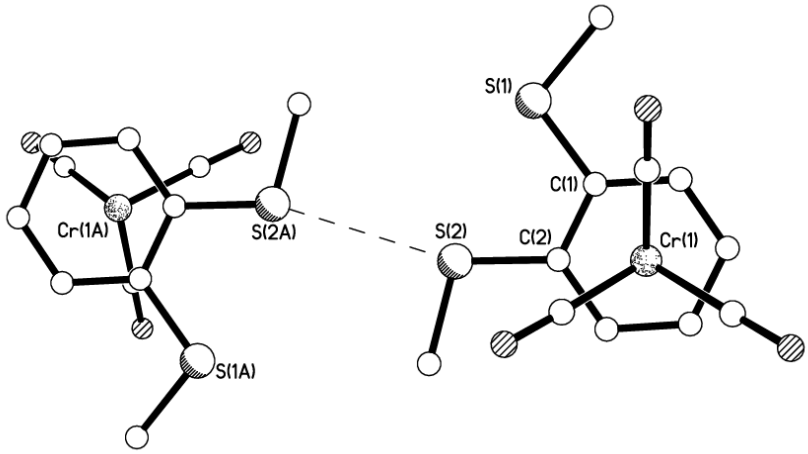


Fig. 3. View of a pair of neighbouring molecules of **10aα** showing an S···S intermolecular interaction and staggered arrangement of arene ring *vs* carbonyl groups. S···S = 3.330 Å.

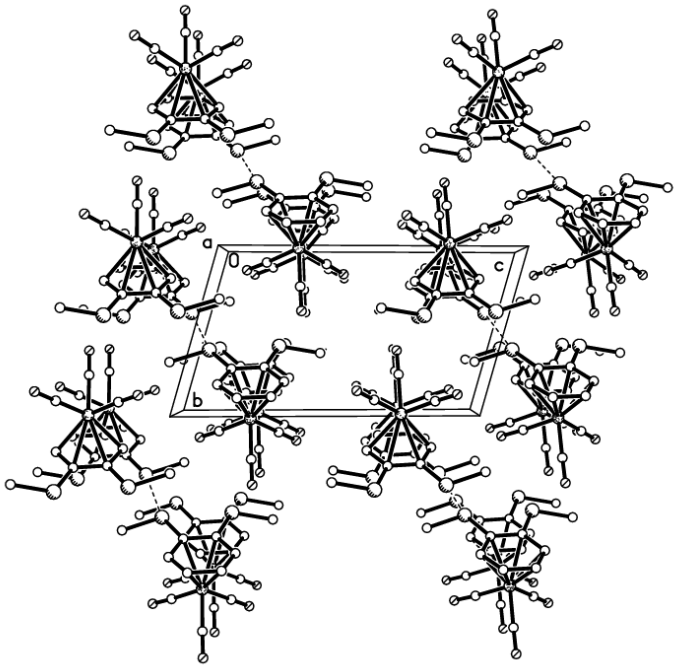


Fig. 4. Packing plot of **10aα** showing columns of S···S paired molecules in a parallel arrangement.

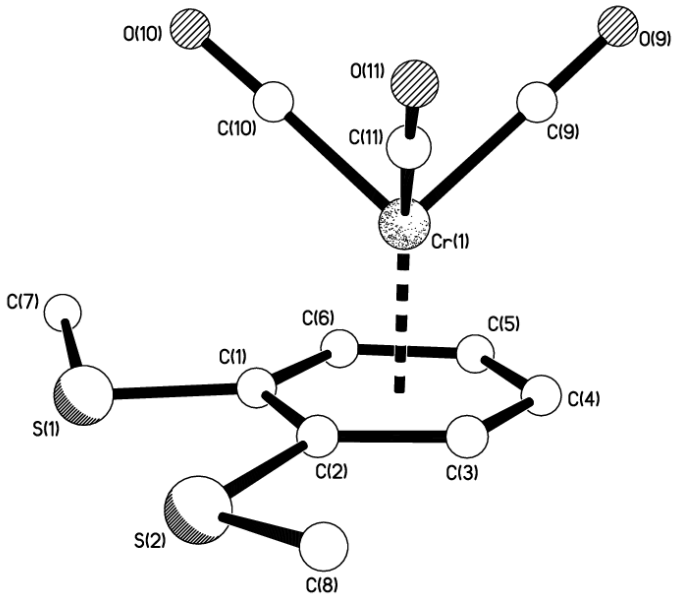


Fig. 5. The molecular structure of **10aβ** showing the piano-stool, half-sandwich arrangement.

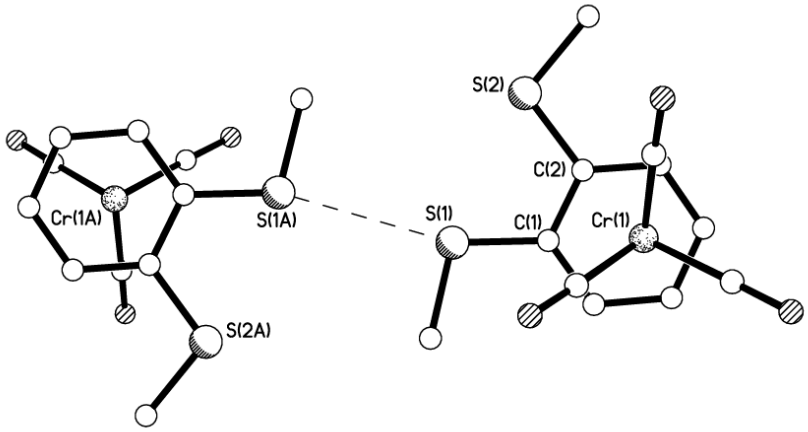


Fig. 6. View of a pair of neighbouring molecules of **10aβ** showing an S···S intermolecular interaction and staggered arrangement of arene ring *vs* carbonyl groups. S···S = 3.315 Å.

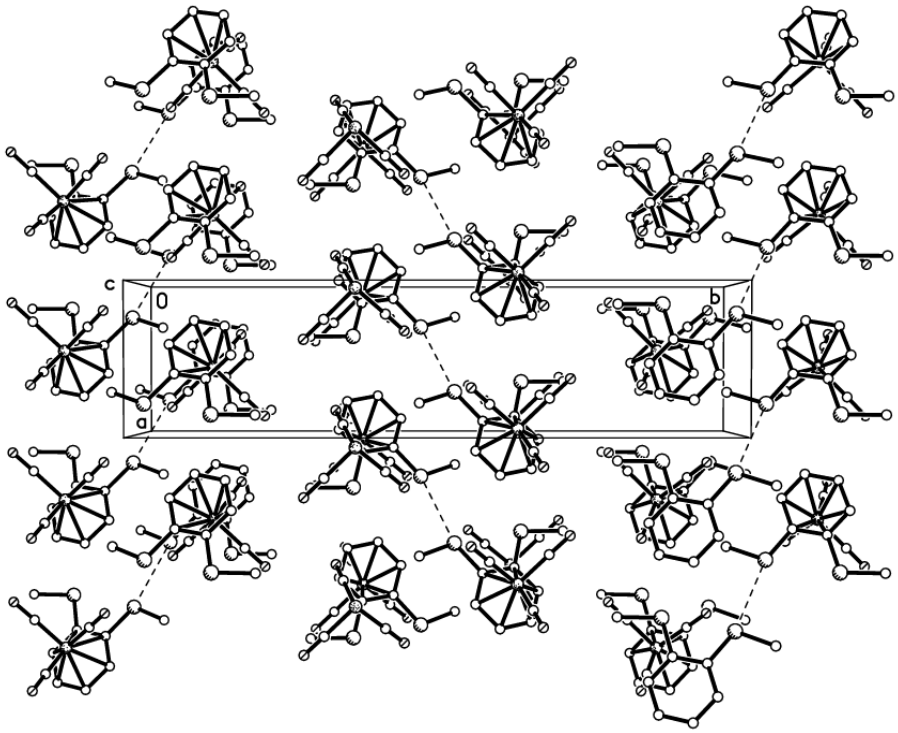


Fig. 7. Packing plot of **10aβ** showing columns of S···S paired molecules in a herring-bone arrangement. Although molecules of this polymorph still pair up, the packing is different to polymorph **10aα**; here the columns are stacked in an anti fashion.

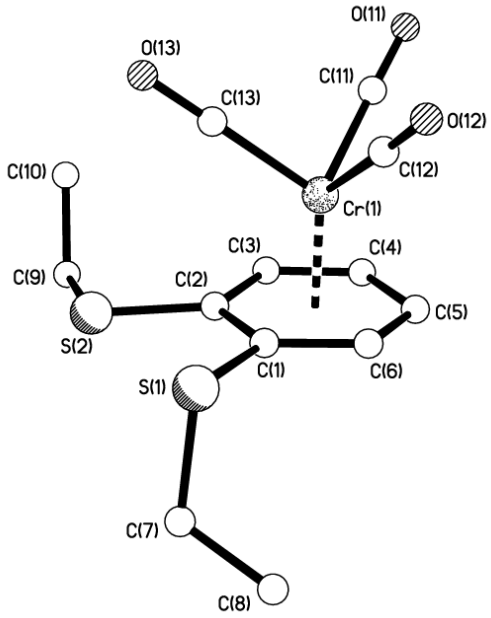


Fig. 8. The molecular structure of **10b** showing the piano-stool, half-sandwich arrangement.

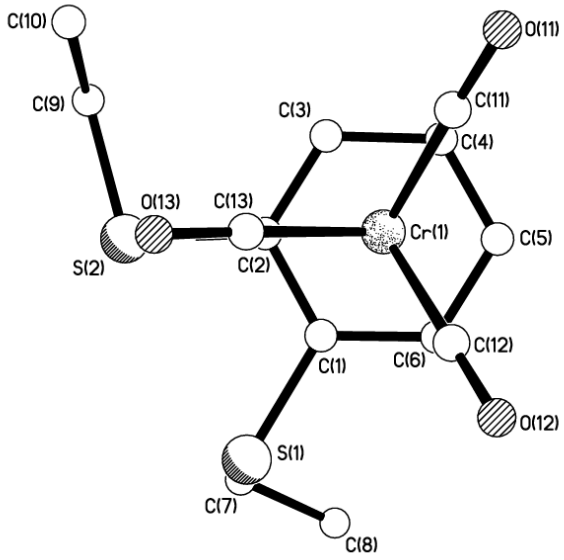


Fig. 9. View of **10b** showing the eclipsed arrangement of arene ring *vs* carbonyl groups.

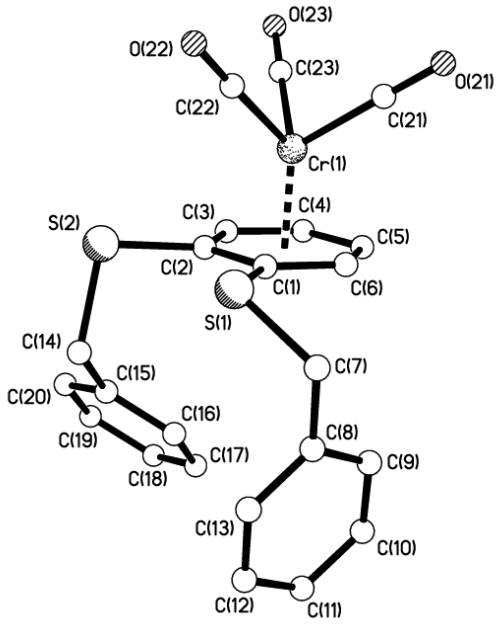


Fig. 10. The molecular structure of **10e** showing the piano-stool, half-sandwich arrangement.

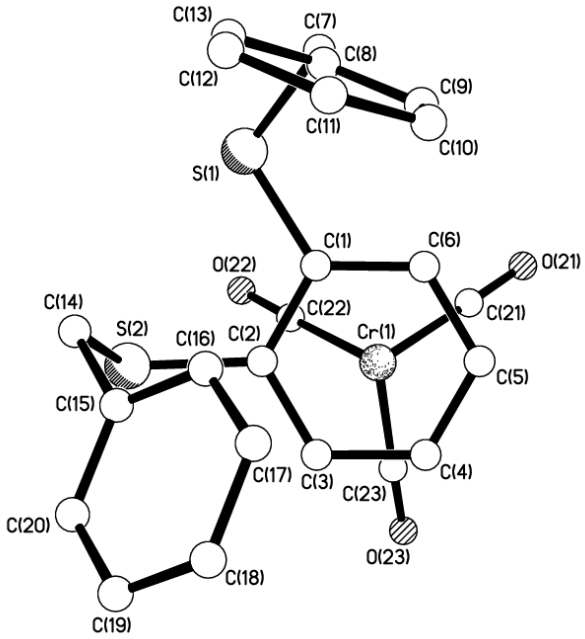


Fig. 11. View of **10e** showing the staggered arrangement of arene ring *vs* carbonyl groups.

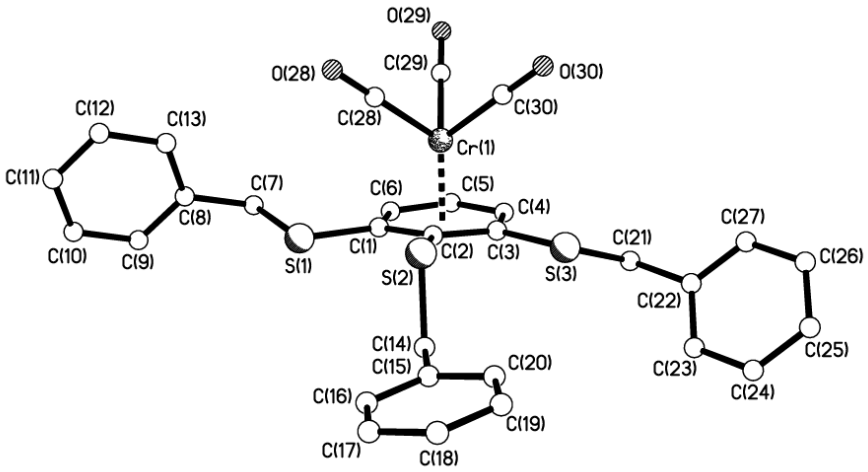


Fig. 12. The molecular structure of **11e** showing the piano-stool, half-sandwich arrangement.

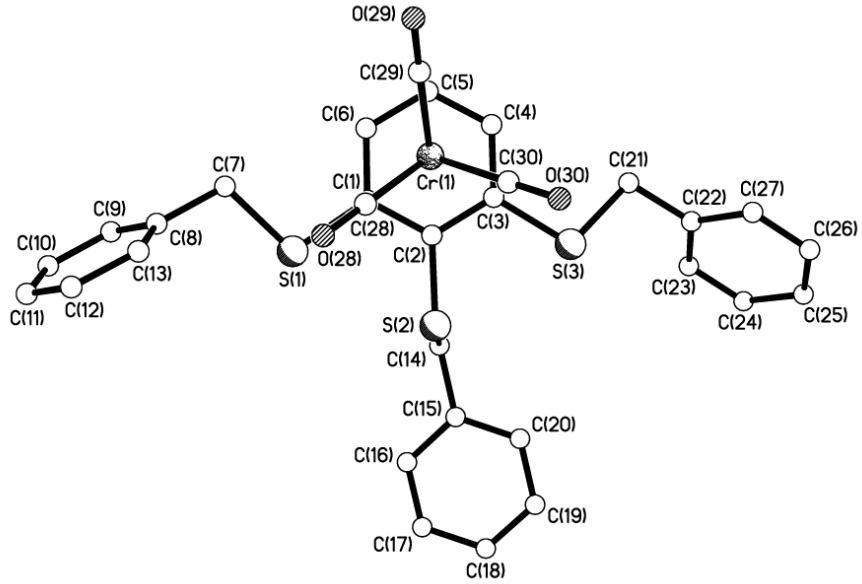


Fig. 13. View of **11e** showing the almost eclipsed arrangement of arene ring *vs* carbonyl groups.

Future work is aimed at developing an asymmetric version of this reaction by desymmetrisation of a 4-substituted η^6-fluorobenzenechromium complex with a chiral base[13] as this would allow construction of enantiomerically enriched, planar, chiral benzopentathiepins after decomplexation of the arene from chromium.

4. Conclusions

In conclusion we have shown that lithiation of η^6-fluorobenzene-chromium(0) tricarbonyl and reaction with disulfides is an effective method to introduce two adjacent sulfur substituents onto an arene ring, and that η^6-arenechromium complexes are stable towards normally strongly metal binding sulfur reagents.

5. Experimental

5.1 Material and Methods

All reactions, unless otherwise stated, were run under nitrogen, using glassware that had been dried in an oven at 150 °C for 2 hours prior to use. Room temperature refers to ambient temperature (18–22 °C). A temperature of 0 °C implies use of an ice-slush bath, and −78 °C refers to use of a dry ice-acetone bath. Heated experiments were conducted using thermostatically controlled oil baths. Reactions were monitored by TLC using aluminium backed silica gel F_{254} plates (Merck) and visualised using UV_{254} nm or $KMnO_4$ dip. R_f values are given under these conditions. Flash column chromatography was carried out using 60 Å silica gel (Fluorochem).

"Petrol" refers to petroleum ether of the 40–60 °C boiling range and was distilled prior to use. Anhydrous THF and anhydrous Bu_2O were dried by refluxing over Na-benzophenone prior to distillation. Anhydrous 1,4-dioxane was purchased from Aldrich and not further purified. Other reagents were from commercial sources and were used without purification unless otherwise stated. All chromium-based compounds were stored in the dark. All chromium-based reactions were carried out in foil-wrapped glassware. Deoxygenated solvents were prepared by bubbling a stream of nitrogen through the solvent for at least 20 minutes prior to use.

NMR spectra were recorded on a Bruker DPX-400 MHz spectrometer operating at 100.61 MHz for carbon and 400.13 MHz for proton spectra, employing a high-resolution broad-band HX probe. The ^{13}C and ^{1}H chemical shifts are reported in δ units, parts per million downfield from TMS. All NMR samples of chromium-based materials were filtered through a plug of silica and charcoal prior to running the sample. Coupling constants (J) are measured in hertz (Hz). IR spectra were recorded using a Perkin Elmer, Paragon 1000 Spectrometer using NaCl plates. The sample was

loaded onto the plates as a solution in dichloromethane and the solvent was allowed to evaporate prior to data acquisition.

5.2 General Procedure for the preparation of [η^6-(1,2-bis-alkylthio)benzene]-tricarbonylchromium(0) complexes 10

A stirred solution of freshly recrystallised *(η^6*-fluorobenzene)tricarbonylchromium(0)[6] **8** (100 mg, 0.43 mmol) in anhydrous THF (5.0 ml) was cooled to −78 °C with vigorous stirring in the dark. ^{n}BuLi (0.33 ml of a 1.6 M solution in hexanes, 0.43 mmol) was added dropwise at a moderate rate and the mixture was stirred at −78 °C for 90 minutes. After this time the appropriate disulfide (0.65 mmol) was added to the flask in one portion. The mixture was then allowed to warm to room temperature overnight with stirring. The mixture was quenched by the addition of saturated aqueous NH_4Cl solution (25 ml) and extracted with Et_2O (2 × 50 ml). The combined organic extracts were dried ($MgSO_4$) and evaporated to give an orange oil, which was purified as described below.

5.2.1 [η^6-1,2-*bis*(Methylthio)benzene]tricarbonylchromium(0) 10a

Dimethyl disulfide (0.058 ml, 0.65 mmol) was used. ^{1}H NMR analysis of the crude reaction mixture showed a 70% conversion of starting material **8**. This mixture was purified by flash chromatography over silica, eluting with 0%→5% EtOAc-petrol. The product **10a** and starting material **8** co-eluted. This fraction was then recrystallised from CH_2Cl_2-petrol, giving pure *[η^6-1,2-*bis*(methylthio)benzene] tricarbonylchromium(0)* **10a** (61 mg, 46%) as a yellow-orange solid, mp 124-125 °C (CH_2Cl_2-petrol); δ_H($CDCl_3$; 400MHz) 5.47 (2H, m, AA'BB' system, 2 × *ortho*-ArH), 5.27 (2H, m, AA'BB' system, 2 × *meta*-ArH), 2.47 (6H, s, 2 × CH_3) ppm; δ_C($CDCl_3$; 100MHz) 232.3 (3 × CO), 112.3 (2 × *ipso*-ArC), 91.3 (2 × *ortho*- or *meta*-ArC), 89.9 (2 × *ortho*- or *meta*-ArC), 17.8 (2 × CH_3) ppm; ν_{max} (NaCl plate, neat) 1937 and 1844 (CO), 1417 cm^{-1}; *m/z* (EI) 306 (31%, $^{32}M^+$), 307 [8, M^+(^{32}S+^{33}S)], 308 (5, $^{33}M^+$), 309 [1, M^+(^{33}S+^{34}S)], 250 (40, M–2CO), 222 (59, M–3CO), 207 [100, M–(3CO+CH_3)], 192 [68, M–(3CO+2CH_3)](Found: 305.9475, $C_{11}H_{10}CrO_3S_2$ requires 305.9471).

5.2.2 [η^6-1,2-*bis*(Ethylthio)benzene]tricarbonylchromium(0) 10b and [η^6-1,2,3-*tris*(ethylthio)benzene]tricarbonyl chromium(0) 11b

Diethyl disulfide (0.08 ml, 0.65 mmol) was employed. After the usual work-up, a 71:18:11 mixture of [η^6-1,2-*bis*(ethylthio)benzene]tricarbonylchromium(0) **10b**, (η^6-fluorobenzene)tricarbonyl chromium(0) **8** and a second product, [η^6-1,2,3-*tris*(ethylthio)benzene]tricarbonyl chromium(0) **11b** was evident in the ^{1}H NMR spectrum of the crude mixture, giving an overall 82% conversion of starting material. The crude mixture was purified by flash column chromatography to remove baseline material, eluting with 0%→1%→2% EtOAc-petrol. The three compounds co-eluted in this solvent system, but recrystallisation of the mixture obtained using CH_2Cl_2-petrol gave the major product *[η^6-1,2-*bis*(ethylthio)benzene]tricarbonylchromium(0)* **10b** (61 mg isolated pure, 42%, with some remaining in the mother liquor) as an orange-yellow solid, mp 59–60 °C (CH_2Cl_2-petrol); δ_H($CDCl_3$; 400MHz) 5.49 (2H, AA'BB' system, 2 × *ortho*-ArH), 5.25 (2H, m, AA'BB' system, 2 × *meta*-ArH), 2.91 (4H, m, 2 × CH_2), 1.38 (6H, t, *J* 7.6, 2 × CH_3) ppm; δ_C($CDCl_3$; 100MHz) 220.1 (3 × CO), 128.1 (2 × *ipso*-ArC), 92.8 (2 × *ortho* or *meta*-ArC), 90.1 (2 × *meta*-or *ortho*-ArC), 28.9 (2 × CH_2), 13.8 (2 × CH_3) ppm; ν_{max} (NaCl plate, neat) 1962 and 1886 (CO) cm^{-1}. Evidence for the presence of the minor product [η^6-1,2,3-*tris*(ethylthio)benzene]tricarbonylchromium(0) **11b** was given by the following data: δ_H($CDCl_3$; 400MHz) 5.64 (1H, t, *J* 6.4, ArH), 4.95 (2H, d, *J* 6.4, 2 × *ortho*-ArH), 2.96–2.84 (6H, m, AB system obscured by peaks from disubstituted compound **10b**, 3 × CH_2), 0.91–0.80 (9H, m, obscured by peaks from di-substituted compound **10b**, 3 × CH_3) ppm; *m/z*(CI) 395 [5%, $^{32}MH^+$], 335 (30, MH^+–SCH_2CH_3), 259 [88, $^{32}MH^+$–$Cr(CO)_3$], 260 [14, MH^+–$Cr(CO)_3$, ^{32}S+^{33}S], 199[100, MH_2^+–$Cr(CO)_2SCH_2CH_3$], 61 (52, SCH_2CH_3) (Found: 394.9900, $C_{15}H_{19}Cr^{32}S_3O_3$ requires 394.9896).

5.2.3 [η^6-(*Iso*-Propylthio)benzene]tricarbonylchromium(0), 12^i [η^6-1,2-bis-(*iso*-propyl thio)benzene]tricarbonylchromium(0) 10c and [η^6-1,2,3-tris-(*iso*-propylthio)-benzene]tricarbonyl chromium(0) 11c

Following the general procedure, *iso*-propyldisulfide (0.10 ml, 0.65 mmol) was used as the disulfide. After the usual work-up, ^{1}H NMR analysis of the crude reaction mixture showed 70% conversion of starting material η^6-(fluorobenzene)-tricarbonylchromium(0) **8** to a mixture of [η^6-(*iso*-propylthio)benzene]tricarbonyl

chromium(0) **12**, [η^6-1,2-*bis*-(*iso*-propylthio)benzene]tricarbonyl- chromium(0) **10c** and [η^6-1,2,3-*tris*-(*iso*-propylthio)benzene]tricarbonylchromium(0) **11c** in a 40:21:9 ratio. The mixture of products was purified by flash column chromatography, eluting with 0%→1%→2%→5% EtOAc-petrol, to remove baseline material. This also gave a small portion of major product **12** as a yellow solid, with the majority remaining as part of a mixture with the other two products **10c** and **11c**. Data for [η^6-(*iso*-propylthio)benzene]tricarbonylchromium(0) **12**i: δ_H($CDCl_3$; 400MHz) 5.43 (2H, br dd, *J* 6.8 and 1.2, 2 × *ortho*-ArH), 5.34 (2H, t, *J* 6.8, 2 × *meta*-ArH), 5.20 (1H, br tt, *J* 6.4 and 1.0, *para*-ArH), 3.25 [1H, septet, *J* 6.6, C*H*(CH_3)$_2$], 1.34 [6H, d, *J* 6.6, CH(C*H*$_3$)$_2$] ppm; δ_C($CDCl_3$; 100MHz) 109.5 (*ipso*-ArC), 95.13 (2 × *ortho*-ArC), 91.43 (2 × *meta*-ArC), 89.29 (*para*-ArC), 38.75 (CH), 22.2 (2 × CH_3) ppm; ν_{max} (NaCl plate, neat) 2923 (CH), 1964 and 1887 (CO), 1454 (S–C). The two minor products **10c** and **11c** could not be further separated by flash chromatography or recrystallisation and were characterised as far as possible as a mixture. Data for *[η^6-1,2-bis-(iso-propylthio)benzene]tricarbonylchromium(0)* **10c**: δ_H($CDCl_3$; 400MHz) 5.43 (2H, AA'BB' system, 2 × *ortho*-ArH), 5.19 (2H, AA'BB' system, 2 × *meta*-ArH), 3.25 [2H, sept, *J* 6.8, 2 × C*H*(CH_3)$_2$], 1.32 [6H, d, *J* 6.4, 2 × CH(C*H*$_3$)$_2$] ppm; δ_C($CDCl_3$; 100MHz) 106.2 (2 × *ipso*-ArC), 93.0 (2 × *ortho*-ArC0, 89.3 (2 × *meta*-ArC), 37.3 (2 × CH), 21.7 (4 × CH_3) ppm; ν_{max} (NaCl plate, neat, mixture of products **10c** and **11c**) 2952 (CH) 1964, 1887 (CO), 1455 (C–S), 1448 (C–S) cm^{-1}; *m/z*(CI) 363 [12%, $(M+H)^+$], 227 [100, $^{32}MH^+$–$Cr(CO)_3$], 228 [13, MH^+–$Cr(CO)_3$, ^{32}S+^{33}S], 229 [11, $^{33}MH^+$–$Cr(CO)_3$][ES (M+H) Found: 363.0178, $C_{15}H_{19}CrS_2O_3$ requires 363.0175]. Data for [η^6-1,2,3-tris-(*iso*-propylthio)benzene]tricarbonylchromium(0) **11c**: δ_H($CDCl_3$; 400MHz) 5.67 (1H, t, *J* 6.4, ArH), 5.04 (2H, d, *J* 6.4, 2 × *ortho*-ArH), 3.60–3.46 [3H, m, 3 × CH(CH_3)$_2$], 1.46–1.41 [18H, m, 3 × CH(CH_3)$_2$] ppm; *m/z*(CI) 437[6%, $(M+H)^+$], 301 [64, $^{32}MH^+$–$Cr(CO)_3$], 302 [12, MH^+–$Cr(CO)_3$, ^{32}S+^{33}S], 303 [11, $^{33}MH^+$–$Cr(CO)_3$][ES, (M+H) Found: 437.0363, $C_{18}H_{24}CrS_3O_3$ requires 437.0365]. Further analysis of this compound was not possible due to contamination with products **10c** and **12** and starting material **8**.

5.3 Synthesis of Chromium Complexes 4a[16] and 4b

Anhydrous dioxane (20 ml) was transferred *via* syringe to a dry single neck flask under N_2. The solvent was then degassed by bubbling with N_2 for 20 min. The arene

3a[14] or **3b**[15] (typically 4.0 mmol) and hexacarbonylchromium(0) (10 mmol) were then added to the flask and the flask was equipped with an air condenser leading to a water condenser (to prevent blockage of the water condenser with $Cr(CO)_6$ sublimate. The mixture was then heated under reflux under nitrogen in the dark for 3-5 days. After this time a brown-yellow solution was present and the reaction was allowed to cool to ambient temperature. The mixture was filtered through celite, eluting with Et_2O and the filtrate evaporated to dryness. The crude product was purified by flash chromatography to give the following compounds.

(η^6-*tert*-Butylthiobenzene)tricarbonylchromium(0) 4a[16]

(η^6-*tert*-Butylthiobenzene)tricarbonylchromium(0) **4a** was obtained as a yellow solid after refluxing the reaction mixture in the dark for 5 days. Chromatography, eluting with 0%→5% EtOAc-petrol (increasing in 1% increments) to give (η^6-*tert*-butylthiobenzene)tricarbonyl chromium(0) **10**[16] (920 mg, 76%) as yellow needles; δ_H($CDCl_3$; 400MHz) 5.47 (2H, br d, *J* 6, 2 × *o*-ArH), 5.23 (3H, br m, 3 × ArH), 1.27 [9H, s, $C(CH_3)$] ppm; *m/z* (EI) 304 (3%, $^{34}M^+$), 303 (7, $^{33}M^+$), 302 (26, $^{32}M^+$), 248 (3, $^{34}MH–{}^t Bu$), 247 (6, $^{33}MH–{}^t Bu$), 246 (22, $^{32}MH–{}^t Bu$), 218 (38, $^{32}M–3CO$), 162 (100, PhCrSH); ν_{max}(NaCl plate, neat) 3083 and 2959 (CH), 1962, 1889 and 1860 (CO), 1394 and 1366 [$C(CH_3)_3$] cm^{-1}.

[η^6-(4-Methyl-*tert*-butylthio)benzene]tricarbonylchromium(0) 14

Using the general method described above, and heating for 3 days, the crude mixture obtained was purified by flash chromatography, eluting with 0%→5% EtOAc-petrol (increasing in 1% increments. This gave *[η^6-(4-methyl-tert-butylthio)benzene]tricarbonylchromium(0)* **14** (860 mg, 68%) as a yellow solid, mp 92-93°C (DCM-petrol); δ_H($CDCl_3$; 400MHz) 5.55 (2H, d, *J* 6.5, 2 × ArH, *ortho*-S^tBu), 5.02 (2H, d, *J* 6.4, 2 × ArH, *ortho*-Me), 2.13 (3H, s, CH_3-Ar), 1.25 [9H, s, $C(CH_3)_3$] ppm; δ_C($CDCl_3$; 100MHz) 109.2 (1 × ArC, *ipso*-to S^tBu), 103.4 (2 × ArC, *ortho*- to S^tBu), 96.9 (1 × ArC, *ipso*- to Me), 91.9 (2 × ArC, *ortho*- to Me), 47.2 [$SC(CH_3)_3$], 30.7 [3C, $SC(CH_3)_3$], 20.5 (1C, CH_3Ar) ppm; ν_{max}(NaCl plate, neat) 2958(CH), 1964, 1910 and 1884 (CO) cm^{-1}.

5.4 X-ray Crystallography.

X-ray quality crystals were grown from CH_2Cl_2-petrol for **10aα**, **10b**, **10e**, and **11e**, and from THF-ether for **10aβ**. Crystal data were collected on a Bruker SMART 1000 CCD diffractometer using narrow slice 0.3° ω-scans for **10aα**, **10aβ**, **10e**, and **11e**.[17] Data for **10b** were collected at Daresbury Laboratory SRS Station 9.8 using silicon 111 monochromated X-radiation due to small, thin crystal habit. Diffractometer used at Daresbury was a Bruker Apex 2 CCD. Data were corrected for Lp effects and for absorption, based on repeated and symmetry equivalent reflections, and solved by direct methods (Patterson synthesis for **10b**).[18] Structures were refined by full matrix least squares on F^2.[18] All non-H atoms were refined anisotropically. H atoms were included in a riding model. Hydrogen atom U_{iso} values were constrained to be 120% of that of the carrier atom except for methyl H (150%). The structure refinements were routine with key parameters given in ref. 10. CCDC 830653 – 830657 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the EPSRC, STFC, and Loughborough University for support, and the EPSRC National Mass Spectrometry service at the University of Swansea. We also thank Drs J.E. Warren and T.J. Prior for scientific support at Daresbury Laboratory and acknowledge the use of the EPSRC's Chemical Database Service at Daresbury.

References

1. B. S. Davidson, T. F. Molinski, L. R. Barrows and C. M. Ireland, *J. Am. Chem. Soc.*, 1991, **113**, 4709.
2. B. S. Davidson, P. W. Ford and M. Wahlman, *Tetrahedron Lett.*, 1994, **35**, 7185.

3. V. Behar and S. J. Danishefsky, *J. Am. Chem. Soc*., 1993, **115**, 7017-7018; P. W. Ford, M. R. Narbut, J. Belli and B. S. Davidson, *J. Org. Chem*., 1994, **59**, 5955; F. D. Toste and I. W. Still, *J. Am. Chem. Soc.*, 1995, **117**, 7261.
4. B. L. Chenard, R. L. Harlow, A. L. Johnson and S. A. Vladuchick, *J. Am. Chem. Soc.*, 1985, **107**, 3871.
5. R. A. Ewin, A. M. MacLeod, D. A. Price, N. S. Simpkins and A. P. Watt, *J. Chem. Soc., Perkin Trans. 1*, 1997, 401; M.J. Dickens, J. P. Gilday, T. J. Mowlem and D. A. Widdowson, *Tetrahedron*, 1991, **47**, 8621-8634; S. E. Gibson, P. Ham, G. R. Jefferson and M. H. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1997, 2161; S. E. Gibson, P. O'Brien, E. Rahimian and M. H. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1999, 909.
6. C. A. L. Mahaffy and P. L. Pauson, *Inorg. Syntheses*, 1990, **28**, 136.
7. P. J. Dickens, J. P. Gilday, J. T. Negri and D. A. Widdowson, *Pure and Appl. Chem.*,1990, **62**, 575.
8. Y. Wang, K. Angermund, R.Goddard and C. Kruger, *J. Am. Chem. Soc*., 1987, **109**, 587.
9. M. Ghavshou and D. A. Widdowson, *J. Chem. Soc., Perkin Trans. 1*, 1983, 3065; J. P. Gilday and D. A. Widdowson, *Tetrahedron Lett.*, 1986, **27**, 5525; P. J. Beswick and D. A. Widdowson, *Synthesis*, 1985, 492; J. P. Gilday and D. A. Widdowson, *J. Chem. Soc., Chem. Commun.*, 1986, 1235.
10. J. Tsuji, *Transition Metal Reagents and Catayst*s, John Wiley & Sons, Chichester, 2000, p. 371.
11. Crystal data: For **10aα**: $C_{11}H_{10}CrO_3S_2$, M = 306.31, triclinic, a = 6.3675(9), b = 7.5155(11), c = 13.1748(19) Å, α = 105.757(2) β = 94.059(2), γ = 91.292(2) °, U = 604.69(15) Å^3, T = 150(2) K, space group $P\bar{1}$, Z = 2, μ(MoKα) = 1.281 mm^{-1}, 5042 reflections measured, 2727 unique (R_{int} = 0.0198), $R1$ for 2313 data with $I>2\sigma(I)$ = 0.0299, $wR2$ for all data = 0.0790. For **10aβ**: $C_{11}H_{10}CrO_3S_2$, M = 306.31, monoclinic, a = 6.349(3), b = 25.347(11), c = 7.531(3) Å, β = 91.629(6) °, U = 1211.5(9) Å^3, T = 150(2) K, space group $P2_1/n$, Z = 4, μ(MoKα) = 1.279 mm^{-1}, 8036 reflections measured, 1899 unique (R_{int} = 0.1360), $R1$ for 1205 data with $I>2\sigma(I)$ = 0.0971, $wR2$ for all data = 0.2693. For **10b**: $C_{13}H_{14}CrO_3S_2$, M = 334.36, monoclinic, a = 10.6871(12), b = 7.2672(8), c = 18.787(2) Å, β = 97.4396(13) °, U = 1446.8(3) Å^3, T = 150(2) K, space group $P2_1/n$, Z = 4,

synchrotron radiation, λ = 0.6719, μ = 1.078 mm^{-1}, 16190 reflections measured, 4899 unique (R_{int} = 0.0589), *R*1 for 4581 data with *I*>2σ(*I*) = 0.0372, *wR*2 for all data = 0.1058. For **10e**: $C_{23}H_{18}CrO_3S_2$, *M* = 458.49, triclinic, *a* = 9.0130(9), *b* = 10.2094(10), *c* = 12.8603(13) Å, α = 106.7566(15) β = 99.0147(16), γ = 109.5597(15) °, *U* = 1024.82(18) $Å^3$, *T* = 150(2) K, space group $P\ \bar{1}$, *Z* = 2, μ(MoKα) = 0.784 mm^{-1}, 9059 reflections measured, 4714 unique (R_{int} = 0.0151), *R*1 for 3947 data with *I*>2σ(*I*) = 0.0315, *wR*2 for all data = 0.0819. For **11e**: $C_{30}H_{24}CrO_3S_3$, *M* = 580.67, monoclinic, *a* = 11.7886(7), *b* = 24.6453(15), *c* = 10.2118(6) Å, β = 115.6251(9) °, *U* = 2675.1(3) $Å^3$, *T* = 150(2) K, space group $P2_1/c$, *Z* = 4, μ(MoKα) = 0.693 mm^{-1}, 23396 reflections measured, 6468 unique (R_{int} = 0.0223), *R*1 for 5276 data with *I*>2σ(*I*) = 0.0383, *wR*2 for all data = 0.1109.

12. The United Kingdom Chemical Database Service, Fletcher, D.A., McMeeking, R.F., Parkin, D., *J. Chem. Inf. Comput. Sci.* 1996, **36**, 746; F. H. Allen, *Acta Cryst.*, B**58**, 380-388, 2002. CSD version 5.21 + 4 updates, Aug 2011.
13. S. E. Gibson and E. G. Reddington, *Chem. Commun*¸2000, 989; A. Griffin, A. L. Blake, R. A. Ewin, W.-S. Li and N. S. Simpkins, *J. Chem. Soc., Perkin Trans. 1,* 1999, 3177.
14. S. E. Gibson (née Thomas), N. Guillo, A. J. P. White and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1,* 1996, 2575.
15. G. Mann, D. Boranao, J. F. Hartwig, A. L. Rheingold, I. A. Guzei, *J. Am. Chem. Soc.,* 1998, **120**, 9205.
16. A. Alemagna, P. Del Buttero, C. Gorini, D. Landini, E. Licandro and S. Maiorana, *J. Org. Chem.,* 1983, **48**, 605.
17. SMART (2001), SAINT (2001 & 2009), and APEX 2 (2009) software for CCD diffractometers. Bruker AXS Inc., Madison, USA.
18. G.M. Sheldrick, (2008), *Acta Crystallogr*. A64, 112.