A reactivity study of [η^6-(*tert*-butylsulfonyl)benzene]-tricarbonylchromium(0)

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Addition of nucleophiles [$LiC(Me)_2CN$, $LiCHS(CH_2)_3S$, $BrMgCH_2CH{=}CH_2$, $LiCH_2CO_2Bu^t$] to tricarbonyl[η^6-(*tert*-butylsulfonyl)benzene]chromium(0) 4 followed by iodine oxidation gives moderate to excellent yields (43–97%) of the novel *para*-disubstituted arenes 5a–d. Treatment of complex 4 with 1.0 or 2.1 equiv. of butyllithium followed by an electrophilic quench ($ClSiMe_3$, $ClCO_2Me$, $ClPPh_2$, MeSSMe) gives the *ortho*- and di-*ortho*-substituted products 6a–b and 7a–d, respectively in moderate to excellent yield (40–90%). Addition of complex 4 to 1.0, 2.0 and 3.5 equiv. of LiTMP (LiTMP = lithium 2,2,6,6-tetramethylpiperidide) followed by a $ClSiMe_3$ quench gives the *ortho* silylated product 6a, the *ortho, meta* disilylated product 9 and, surprisingly, the *ortho, ortho, para* trisilylated product 10 respectively. The structure of [η^6-1-(*tert*-butylsulfonyl)-2,5-bis(trimethylsilyl)benzene]tricarbonyl-chromium(0) 9 has been established by an X-ray crystallographic analysis.

The fundamental chemistry of (η^6-arene)tricarbonylchromium(0) complexes and its application to various areas of organic chemistry continues to attract considerable attention. For example, seminal studies on chiral base mediated asymmetric functionalisation of (η^6-arene)tricarbonylchromium(0) complexes are currently being conducted by several groups,[1,2] whilst recent applications to topical areas of organic synthesis include an innovative synthesis of (−)-steganone, in which the key step is a stereoselective cross-coupling between an enantiopure chromium complex and an arylboronic acid,[3] and the application of an enantioselective (η^6-arene)tricarbonyl-chromium(0) based catalyst to the synthesis of the 10-membered macrolide phorcantholide.[4]

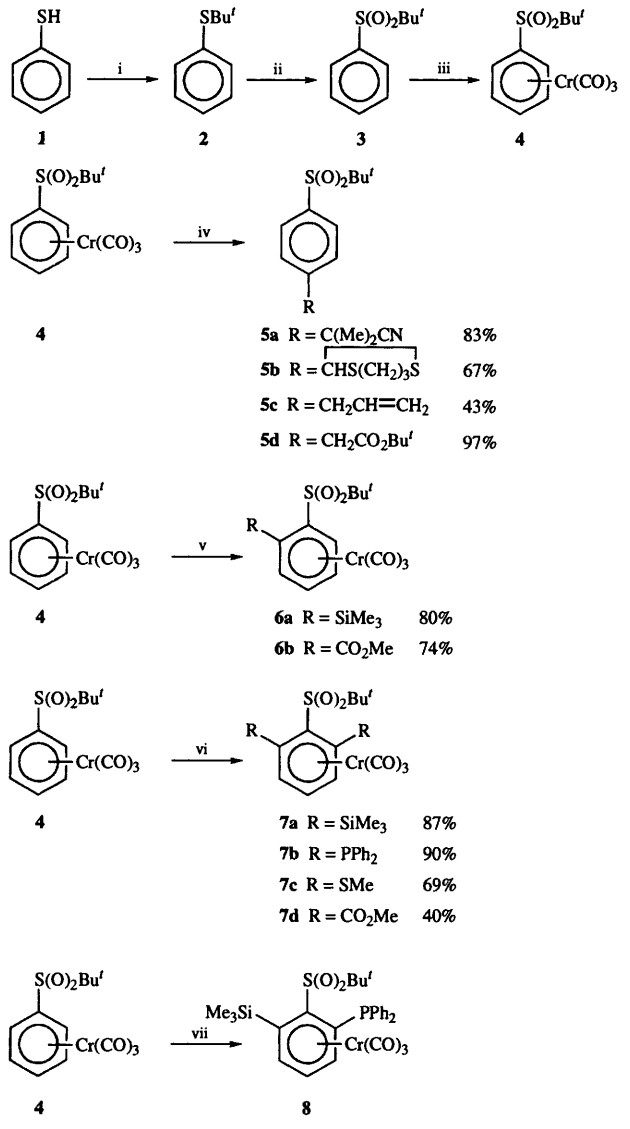
Earlier studies of the chemistry of (η^6-arene)tricarbonylchromium(0) complexes defined their reactivity towards nucleophiles[5] and achiral bases.[6] In general, these studies focused on complexes bearing donor substituents (*e.g.* OR, NR_2, alkyl). Recently we reported the synthesis of the first sulfonyl-substituted (η^6-arene)tricarbonylchromium(0) complexes.[7] In view of the strong electron withdrawing properties of the sulfonyl functional group, which we anticipated would lead to reactivity that was complementary to that of the majority of complexes examined to date, we initiated a study of the reactions of this type of complex. The results of our study, which not only defined the reactivity of sulfonyl-substituted (η^6-arene)tricarbonylchromium(0) complexes with respect to nucleophiles and bases, but also led to the unprecedented production of a trisubstituted product from a deprotonation–electrophilic quench sequence, are described herein.

Results and discussion

[η^6-(*tert*-Butylsulfonyl)benzene]tricarbonylchromium(0) **4** was selected as the substrate for our investigations, as it was envisaged that the relatively acidic methyl hydrogens of the previously synthesised tricarbonyl[η^6-(methylsulfonyl)benzene]chromium(0)[7] would be incompatible with the proposed nucleophilic addition and deprotonation studies. Thus thiophenol **1** was reacted with *tert*-butyl alcohol in the presence of perchloric acid and acetic anhydride in acetic acid (Scheme 1), using a modified literature procedure,[8] to give (*tert*-butylsulfanyl)benzene **2**[9] (93%). Oxidation of **2** with potassium hydrogen persulfate, using a modified literature procedure,[10] provided (*tert*-butylsulfonyl)benzene **3**[9] (90%) which was subsequently converted into its tricarbonylchromium(0) complex **4** by heating with hexacarbonylchromium(0) in 1,4-dioxane under reflux for 4 days. Column chromatography and crystallisation gave the novel complex **4** as yellow crystals in acceptable yield (68%).

Nucleophilic addition studies

It is firmly established that nucleophilic addition to (η^6-arene)tricarbonylchromium(0) complexes generates anionic cyclohexadienyl complexes that are readily oxidised to uncomplexed arenes, thus effecting nucleophilic aromatic substitution of the arene ring. The regioselectivity of this process has been the subject of numerous studies,[5] the results of which may be summarised as follows. Nucleophilic addition to arene complexes bearing NMe_2, OMe and F substituents is strongly directed to the *meta* position; only small amounts of *ortho*-substituted products (0–10%) are ever formed and *para*-substitution is not observed at all. The selectivity is less pronounced for attack on arene complexes bearing Me or Cl substituents. *meta*-Substitution is always significant but *ortho*-substitution may account for 50–70% of the product mixture; again *para*-substitution is insignificant. Significant *para*-substitution has only been observed to date in the following cases: (i) nucleophilic addition of a cyano stabilised anion to tricarbonyl(η^6-$C_6H_5CF_3$)chromium(0) which gave a 33% combined yield of *para*- and *meta*-substituted products in a ratio of 7:3, (ii) nucleophilic addition to complexes substituted with very sterically demanding alkyl groups as exemplified by the addition of $LiC(Me)_2CN$ to tricarbonyl[η^6-$C_6H_5CH(Bu^t)_2$]chromium(0) which gave a 63% yield of the *para*-substituted product (less bulky alkyl groups give predominantly *meta* attack), and (iii) nucleophilic addition of $LiC(Me)_2CN$ to tricarbonyl(η^6-$C_6H_5SiMe_3$)chromium(0) which gave a 65% combined yield of *para*- and *meta*-substituted products in a ratio of 98:2.



Scheme 1 *Reagents:* i, Bu^{t}OH, AcOH, $HClO_4$, Ac_2O, 93%; ii, $KHSO_5$, 90%; iii, $Cr(CO)_6$, 68%; iv, RLi or RMgBr, then I_2; v, BuLi (1 equiv.), then RCl; vi, BuLi (2.1 equiv.), then RCl or RSMe; vii, BuLi (1 equiv.), then Me_3SiCl, then BuLi (1 equiv.), then PPh_2Cl, 48%

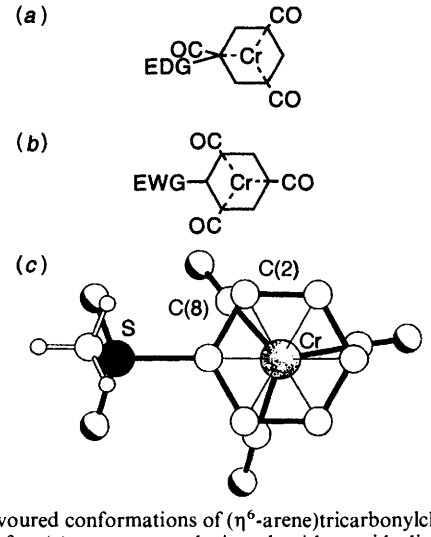


Fig. 1 Favoured conformations of (η^6-arene)tricarbonylchromium(0) complexes for (*a*) an arene substituted with an idealised electron donating group (EDG), (*b*) an arene substituted with an idealised electron withdrawing group (EWG), and (*c*) an arene substituted with the methylsulfonyl group [dihedral angle C(2)–X–Cr–C(8) = 11.2°, where X = the calculated centroid of the six ring carbons]. An accurate determination of the structure of this complex has already been reported (R = 2.8%) (ref. 7).

Addition of LiC(Me)$_2$CN to the *tert*-butylsulfonyl-substituted complex **4** was examined by reacting 1.2 equiv. of LiC(Me)$_2$CN with complex **4** in THF in the presence of 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU) at 0 °C for 1.5 h and then quenching with iodine at −78 °C and stirring for a day at room temperature. Work-up, column chromatography and crystallisation gave white crystals which were identified as the novel *para*-disubstituted arene, 1-(*tert*-butylsulfonyl)-4-(1-cyano-1-methylethyl)benzene **5a** (83%), on the basis of their microanalytical data and their IR, ^{1}H NMR, ^{13}C NMR and mass spectra. Similarly, addition of LiCHS(CH$_2$)$_3$S, BrMgCH$_2$CH=CH$_2$ and LiCH$_2$CO$_2$Bu^t to complex **4** led to the novel *para*-disubstituted arenes **5b**, **5c** and **5d** in 67, 43 and 97% yield respectively. [It is of note that the reaction between BrMgCH$_2$CH=CH$_2$ and the unsubstituted complex, (η^6-benzene)tricarbonylchromium(0), gave <5% of product[11] thus suggesting that the electron-withdrawing *tert*-butylsulfonyl group activates the arene towards less reactive nucleophiles].

The strong preference for *para*-substitution, and thus presumably *para* nucleophilic attack, may be rationalised either by simple substituent-derived charge density arguments and/or by invoking the directing effect of the tricarbonylchromium(0) unit. The latter theory, which accounts for the majority of the results recorded in this area to date, proposes that nucleophilic attack occurs preferentially at arene carbons that are eclipsed by the carbonyl groups.[12] Structural studies on a reasonably extensive series of (η^6-arene)tricarbonylchromium(0) complexes have led to the generalisation that electron donating groups favour the *syn*-eclipsed structure [Fig. 1(*a*)] whilst electron withdrawing substituents favour the *anti*-eclipsed structure [Fig. 1(*b*)], and this has been rationalised theoretically.[13] Examination of the X-ray crystallographic analysis of [η^6-(methylsulfonyl)benzene]tricarbonylchromium(0)[7] revealed that in the solid state this complex adopts an *anti*-eclipsed conformation in which the metal carbonyls essentially eclipse the *ortho* and *para* carbons of the arene ring [Fig. 1(*c*)]. Thus, assuming that attack at the *ortho* position is disfavoured on steric grounds {and that the structure of [η^6-(methylsulfonyl)benzene]tricarbonylchromium(0) and complex **4** are analogous}, our observation that nucleophilic attack on [η^6-(*tert*-butylsulfonyl)benzene]tricarbonylchromium(0) **4** occurs predominantly at the *para* position is consistent with the theory that the conformational preference of the tricarbonylchromium(0) unit exerts significant control over the site of nucleophilic attack.

Deprotonation–electrophilic quench studies

Studies and applications of ring deprotonation of (η^6-arene)tricarbonylchromium(0) complexes have mainly employed strong bases such as butyllithium to date.[6] The regioselectivity of deprotonation by butyllithium followed by an electrophilic quench has been investigated for several substituents and may be summarised as follows. For alkyl substituents, the regioselectivity is generally poor and little development of this reaction has occurred. In contrast, fluoro substituents give good *ortho* selectivity and a range of electrophiles have been introduced in good yield; experiments with chloro and heavier halide substituents, however, led either to metal–halogen exchange or benzyne formation. Ether substituents give very high *ortho* selectivity (except if the substituent is very bulky, in which case *meta*-substitution is observed), and a good range of electrophiles may be introduced; as a result this system has found many applications. Amine substituents give predominantly *meta*-substitution and this has been rationalised by considering the favoured *syn*-eclipsed conformation of the tricarbonylchromium(0) unit [Fig. 1(*a*)] which is believed to lead to electron deficiency at the ring carbons eclipsed by the metal carbonyls. Some disubstitution

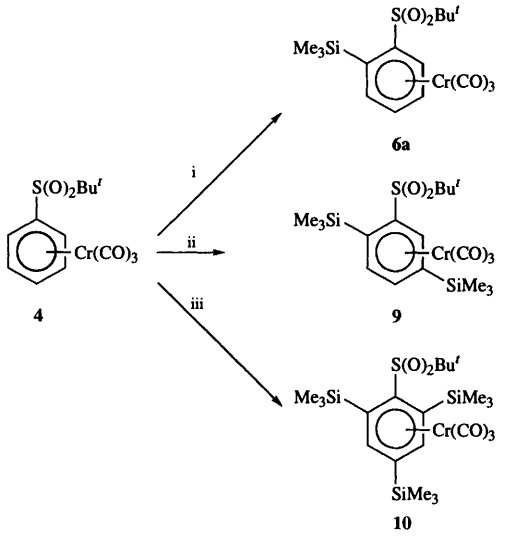
products were observed during the course of the investigations summarised above, but, on the whole, attention was focused on monosubstitution and such products were disregarded.

Monosubstitution of [η^6-(*tert*-butylsulfonyl)benzene]tricarbonylchromium(0) **4** initially proved problematic. Using several sets of conditions and bases, only mixtures of monosubstituted product, disubstituted product and starting material were obtained. Eventually, monosubstitution was achieved in acceptable yield by exploiting the difference in solubility between complex **4** and its lithiated species. Thus the reaction was carried out in a 1:2 mixture of THF and diethyl ether, which was found to be the solvent system required to just solubilise complex **4** at −78 °C. Addition of 1.0 equiv. of butyllithium to **4** at −78 °C, stirring for 1 h at −78 °C followed by quenching with chlorotrimethylsilane or methyl chloroformate and stirring at −78 °C for 1 h gave, after work-up, the novel monosubstituted products **6a** and **6b** in good yield (80 and 74% respectively). Disubstitution of complex **4** proved much less troublesome. After adding 2.1 equiv. of butyllithium to complex **4** in THF at −78 °C, the reaction mixture was stirred for 15 min at −78 °C. The reaction mixture was then treated with chlorotrimethylsilane, chlorodiphenylphosphine, dimethyl disulfide or methyl chloroformate at −78 °C and stirred at this temperature for 1 h. After work-up, the novel disubstituted products **7a–d** were isolated in 87, 90, 69 and 40% yield respectively. Introduction of two different *ortho* substituents onto **4** also proved possible once the conditions for clean monolithiation had been established. Thus execution of a one-pot double deprotonation–quench sequence on **4** led to the synthesis of [η^6-1-(*tert*-butylsulfonyl)-2-(trimethylsilyl)-6-(diphenylphosphino)benzene]tricarbonylchromium(0) **8** in moderate yield (48%).

The results described above indicate that deprotonation of complex **4** occurs preferentially at its *ortho* positions when butyllithium is used, an observation which is probably best explained by invoking a combination of the strong inductive effect of the *tert*-butylsulfonyl substituent and coordination of the lithium counterion of the base to the sulfonyl substituent (lithiation of the uncomplexed analogue of **4** also occurs at the *ortho* position [14]), but is also consistent with the *anti*-eclipsed conformation of the tricarbonylchromium(0) rotor.

Although butyllithium has been used for the majority of deprotonation studies to date, a small number of investigations have used hindered bases such as lithium diisopropylamide (LDA) [15] and lithium 2,2,6,6-tetramethylpiperidide (LiTMP) [16] to deprotonate (η^6-arene)tricarbonylchromium(0) complexes. Recent interest in using chiral hindered bases to desymmetrise (η^6-arene)tricarbonylchromium(0) complexes [1,17] means increasing attention is now being given to how relatively hindered amide bases interact with these complexes. In view of this, we decided to investigate deprotonation of complex **4** using LiTMP as the base and chlorotrimethylsilane as the electrophilic quench.

Addition of complex **4** to 1.0 equiv. of LiTMP at −78 °C, stirring at −78 °C for 10 min, addition of chlorotrimethylsilane, further stirring at −78 °C for 1 h and subsequent work-up gave the same product as was obtained when butyllithium was used as the base (**6a**) (Scheme 2). In contrast, addition of complex **4** to 2.0 equiv. of LiTMP at −78 °C followed by a chlorotrimethylsilane quench gave a disilylated product which from its spectroscopic data was clearly not **7a**, the product obtained when butyllithium was used as the base. The new product was tentatively identified as [η^6-1-(*tert*-butylsulfonyl)-2,5-bis(trimethylsilyl)benzene]tricarbonylchromium(0) **9** from its spectroscopic and microanalytical data and was confirmed as such by an X-ray crystallographic analysis (Fig. 2). Finally, to our surprise, addition of complex **4** to 3.5 equiv. of LiTMP at −78 °C followed by a chlorotrimethylsilane quench gave the 2,4,6-trisilylated product **10** in acceptable yield (50%).



Scheme 2 *Reagents:* i, LiTMP (1 equiv.), then Me_3SiCl, 51%; ii, LiTMP (2 equiv.), then Me_3SiCl, 59%; LiTMP (3.5 equiv.), then Me_3SiCl, 50%

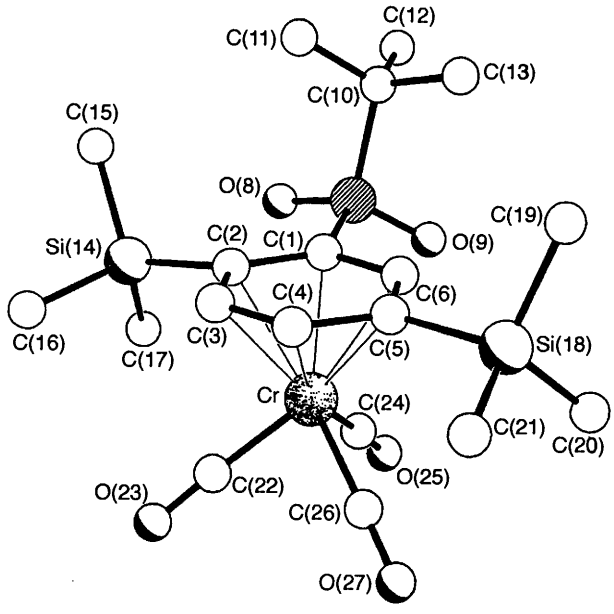


Fig. 2 Molecular structure of complex **9** ($C_{19}H_{30}CrO_5SSi_2$). Selected bond lengths (Å) and bond angles (°): C(1)–C(2) 1.420(5), C(2)–C(3) 1.438(6), C(3)–C(4) 1.399(6), C(4)–C(5) 1.415(6), C(5)–C(6) 1.399(5), C(6)–C(1) 1.425(5), C(1)–S(7) 1.784(4), C(2)–Si(14) 1.932(4) and C(5)–Si(18) 1.894(4); C(22)–Cr–C(24) 88.2(2), C(24)–Cr–C(26) 87.9(2), C(26)–Cr–C(22) 85.1(2), Cr–C(22)–O(23) 177.5(4), Cr–C(24)–O(25) 176.9(4) and Cr–C(26)–O(27) 178.8(4).

The production of the 2,5-disubstituted product **9** from the LiTMP reaction contrasts not only with the isolation of the 2,6-disubstituted product **7a** from the BuLi-promoted reaction reported in this paper, but also with the isolation of a 2,6-disubstituted dideuteriated product from the reaction of the phenylsulfinyl analogue of complex **4** with 2 equiv. of LDA followed by a CD_3OD quench. [18] It is consistent, however, with the observation of some 2,5-disubstituted material in the product mixture obtained on reacting (η^6-anisole)tricarbonylchromium(0) with one equivalent of LDA followed by a chlorotrimethylsilane quench. [1d] It thus appears that the combination of a hindered amide base and a relatively bulky electrophile provides access to 2,5-disubstituted systems presumably by facilitating anion equilibration and promoting electrophilic attack at a relatively unhindered site. Finally, the introduction of three substitutents onto an (η^6-arene)tricarbonylchromium(0) complex by a deprotonation–quench sequence is, to the best of our knowledge, unprecedented. We tentatively

propose that this occurs *via* dilithiation of *in situ* generated **6a**, although the formation of a trianion cannot be entirely discounted.

Experimental

All reactions were performed under nitrogen using standard vacuum line and Schlenk tube techniques.[19] Reactions and operations involving (arene)tricarbonylchromium(0) complexes were protected from light. Tetrahydrofuran (THF), diethyl ether and 1,4-dioxane were distilled from sodium benzophenone ketyl. Chlorotrimethylsilane, dimethyl disulfide, 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU), isobutyronitrile, *tert*-butyl acetate and 2,2,6,6-tetramethylpiperidine (TMP) were distilled from CaH_2. Methyl chloroformate and acetyl chloride were distilled from K_2CO_3. 1,3-Dithiane was sublimed at 40 °C under vacuum (0.1 mmHg). All other reagents were used as obtained from commercial sources. The concentrations of butyllithium and methyllithium were determined by titration against diphenylacetic acid.[20] Column chromatography was performed on silica gel (40–63 μm, BDH Laboratory Supplies). Light petroleum (bp 40–60 °C) was redistilled for all column chromatography.

Melting points were obtained on a Gallenkamp capillary melting point apparatus and are uncorrected. Elemental analyses were performed by the Imperial College Microanalytical Service. IR Spectra were obtained on Mattson 5000 FTIR and Perkin-Elmer 1710 FTIR instruments. NMR Spectra were recorded in $CDCl_3$ at room temperature on Bruker AM 300 and Bruker AM 500 spectrometers. *J* Values are given in Hz. Mass spectra were recorded on VG Micromass 7070E and AutoSpec-Q instruments using EI, CI and FAB (*m*-nitrobenzyl alcohol matrix) techniques. For clarity, the carbon atom attached to the *tert*-butylsulfonyl substituent in the [η⁶-(*tert*-butylsulfonyl)benzene]tricarbonylchromium(0) complexes is always denoted as C-1.

(*tert*-Butylsulfanyl)benzene 2[8,9]

To a 150 cm^3 round-bottomed flask cooled in an ice bath were successively added acetic acid (10 cm^3), perchloric acid (70% solution, 4 cm^3) and acetic anhydride (6 cm^3) and the solution was stirred for 20 min. Thiophenol **1** (6.2 g, 56 mmol) and *tert*-butyl alcohol (5.0 g, 67 mmol) were added to the mixture, the volume of which was adjusted to 50 cm^3 with acetic acid. The mixture was stirred for 2 h at room temperature, then diluted with saturated brine (25 cm^3) and extracted with diethyl ether (4 × 25 cm^3). The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate (3 × 50 cm^3) and water (50 cm^3) and then dried ($MgSO_4$). Column chromatography (SiO_2; light petroleum) gave the title sulfide as a colourless oil (8.6 g, 51.8 mmol, 93%); $\nu_{max}(neat)/cm^{-1}$ 3073m, 3059m, 3033m and 3020m (C–H arom.) and 2961s, 2941s, 2922s, 2898s and 2861s (C–H alkyl); δ_H(300 MHz) 1.31 [9 H, s, $C(CH_3)_3$], 7.33–7.40 (3 H, m, ArH) and 7.54–7.57 (2 H, m, ArH); $\delta_C\{^1H\}$ (75 MHz) 30.9 [$C(CH_3)_3$], 45.8 [$C(CH_3)_3$], 128.4 (C-2,6 or -3,5), 128.6 (C-4), 132.7 (C-1) and 137.4 (C-2,6 or -3,5); *m*/*z* (EI, 70 eV, 200 °C) 166 (M^+, 8%), 77 (M − SC_4H_9, 89) and 57 (C_4H_9, 100).

(*tert*-Butylsulfonyl)benzene 3[9,10]

A solution of (*tert*-butylsulfanyl)benzene **2** (8.5 g, 51.2 mmol) in methanol (200 cm^3) was cooled in an ice bath. To this was added a solution of Oxone® (47.2 g, 76 mmol) in water (200 cm^3). The resulting slurry was stirred for 2 h at room temperature. Methanol was removed by evaporation under reduced pressure and the mixture was diluted with water (100 cm^3) and extracted with diethyl ether (3 × 200 cm^3). The combined organic layers were washed with water (2 × 300 cm^3) and brine (2 × 300 cm^3), and then dried ($MgSO_4$). Solvent removal under reduced pressure gave a white solid, recrystallisation of which from hexane yielded the title sulfone as white needles (9.1 g, 46.0 mmol, 90%); mp 98 °C (lit.,[9] 98–99 °C); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3061m (C–H arom.), 2988m and 2936m (C–H alkyl) and 1297s and 1135s (S=O); δ_H(300 MHz) 1.34 [9 H, s, $C(CH_3)_3$], 7.54–7.59 (2 H, m, ArH), 7.64–7.67 (1 H, m, ArH) and 7.88–7.91 (2 H, m, ArH); $\delta_C\{^1H\}$ (75 MHz) 23.6 [$C(CH_3)_3$], 59.8 [$C(CH_3)_3$], 128.6 (C-2,6 or -3,5), 130.4 (C-2,6 or -3,5), 133.5 (C-4) and 135.3 (C-1); *m*/*z* (EI, 70 eV, 200 °C) 198 (M^+, 1%), 125 (M − O − C_4H_9, 4), 77 (M − $SO_2C_4H_9$, 12) and 57 (C_4H_9, 100).

[η⁶-(*tert*-Butylsulfonyl)benzene]tricarbonylchromium(0) 4

(*tert*-Butylsulfonyl)benzene **3** (2.0 g, 10.1 mmol) and hexacarbonylchromium(0) (4.5 g, 20.5 mmol) in nitrogen-saturated 1,4-dioxane (250 cm^3) were placed in a 500 cm^3 round-bottomed flask fitted with a Liebig air condenser with a water condenser on top, and heated under reflux, with stirring, for 4 days. The resulting mixture was cooled in an ice bath and filtered through Kieselguhr, eluting with diethyl ether. The filtrate was concentrated under reduced pressure leaving a yellow solid which was purified by column chromatography (SiO_2; light petroleum–dichloromethane, 3:1 to 1:3 gradient). Crystallisation from dichloromethane gave the *title complex* as yellow crystals (2.3 g, 6.9 mmol, 68%); mp 179 °C (Found: C, 46.7; H, 4.3. $C_{13}H_{14}CrO_5S$ requires C, 46.71; H, 4.22%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1996vs and 1935vs (C≡O); δ_H(300 MHz) 1.42 [9 H, s, $C(CH_3)_3$], 5.14 (2 H, t, *J* 6.2, ArH *meta*), 5.59 (1 H, t, *J* 6.2, ArH *para*) and 5.88 (2 H, d, *J* 6.2, ArH *ortho*); $\delta_C\{^1H\}$ (75 MHz) 23.7 [$C(CH_3)_3$], 60.3 [$C(CH_3)_3$], 85.8 (C-2,6 or -3,5), 94.4 (C-4), 94.9 (C-2,6 or -3,5), 99.2 (C-1) and 228.9 [$Cr(CO)_3$]; *m*/*z* (EI, 70 eV, 200 °C) 334 (M^+, 2%), 278 (M − 2CO, 4), 250 (M − 3CO, 18), 57 (C_4H_9, 40) and 52 (Cr, 100).

1-(*tert*-Butylsulfonyl)-4-(1-cyano-1-methylethyl)benzene 5a

Lithium diisopropylamide (0.27 cm^3 of a 1.35 M solution in cyclohexane, 0.36 mmol) was added to a solution of isobutyronitrile (0.033 cm^3, 0.36 mmol) in dry nitrogen-saturated THF (2 cm^3) in a Schlenk tube kept at −78 °C. The reaction mixture was stirred for 15 min at 0 °C and cooled again to −78 °C. To this were successively added DMPU (0.11 cm^3, 0.9 mmol) and a solution of [η⁶-(*tert*-butylsulfonyl)benzene]tricarbonylchromium(0) **4** (100 mg, 0.30 mmol) in dry nitrogen-saturated THF (2 cm^3). After stirring at 0 °C for 1.5 h, the reaction mixture was quenched with iodine (381 mg, 1.50 mmol) at −78 °C and stirred for 1 day at room temperature. It was then partitioned between diethyl ether (2 × 20 cm^3) and 20% aqueous sodium hydrogen sulfite (20 cm^3). The organic layers were washed with water (20 cm^3) and saturated brine (20 cm^3), dried ($MgSO_4$) and concentrated to leave a white solid. Column chromatography (SiO_2; light petroleum–dichloromethane, 1:1 to 0:1 gradient) gave the *title product* (67 mg, 0.25 mmol, 83%) which crystallised from hexane–dichloromethane as white crystals; mp 150 °C (Found: C, 63.1; H, 7.0; N, 5.2. $C_{14}H_{19}NO_2S$ requires C, 63.37; H, 7.22; N, 5.28%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3058m, 3056m and 3019m (C–H arom.), 2981m, 2940m, 2913m and 2875m (C–H alkyl), 2243w (C≡N), 1214vs and 1101s (S=O); δ_H(300 MHz) 1.36 [9 H, s, $C(CH_3)_3$], 1.76 [6 H, s, $C(CH_3)_2(CN)$], 7.67 (2 H, d, *J* 8.5, H-3,5) and 7.92 (2 H, d, *J* 8.5, H-2,6); $\delta_C\{^1H\}$ (75 MHz) 23.6 [$C(CH_3)_3$], 28.9 [$C(CH_3)_2(CN)$], 37.4 [$C(CH_3)_2(CN)$], 60.0 [$C(CH_3)_3$], 123.5 (CN), 125.6 (C-3,5), 131.2 (C-2,6), 135.3 (C-4) and 147.2 (C-1); *m*/*z* (CI, NH_3) 283 (MNH_4^+, 100%).

1-(*tert*-Butylsulfonyl)-4-[2-(1,3-dithianyl)]benzene 5b

The general procedure was the same as described for the preparation of compound **5a**. Butyllithium (0.22 cm^3 of a 1.67 M solution in hexanes, 0.36 mmol) was added to a solution of 1,3-dithiane (43 mg, 0.36 mmol) in THF (2 cm^3) at −78 °C and the mixture was stirred for 20 min at −20 °C and recooled to −78 °C. To this were successively added DMPU (0.11 cm^3, 0.9

mmol) and a solution of **4** (100 mg, 0.30 mmol) in THF (2 cm^3) at −78 °C. After stirring at 0 °C for 1.5 h, the reaction was quenched with iodine (381 mg, 1.50 mmol) at −78 °C and stirred for 1 day at room temperature. A white solid was obtained after the usual work-up. Column chromatography (SiO_2; light petroleum–dichloromethane, 1:1 to 0:1 gradient) gave the *title product* (63 mg, 0.20 mmol, 67%) which crystallised from hexane–dichloromethane as white needles; mp 189 °C (Found: C, 52.9; H, 6.1. $C_{14}H_{20}O_2S_3$ requires C, 53.13; H, 6.37%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3076m, 3070m and 3020m (C–H arom.), 2989m, 2976m, 2956m, 2937m and 2906m (C–H alkyl) and 1214vs and 1134vs (S=O); δ_H(300 MHz) 1.34 [9 H, s, $C(CH_3)_3$], 1.90–2.07 (1 H, m, SCH_2CHHCH_2S), 2.19–2.27 (1 H, m, SCH_2CHHCH_2S), 2.90–3.15 (4 H, m, $SCH_2CH_2CH_2S$), 5.23 (1 H, s, ArCH), 7.66 (2 H, d, *J* 8.3, H-3,5) and 7.87 (2 H, d, *J* 8.3, H-2,6); $\delta_C\{^1H\}$ (75 MHz) 23.6 [$C(CH_3)_3$], 24.9 ($SCH_2CH_2CH_2S$), 31.9 ($SCH_2CH_2CH_2S$), 50.6 (ArCH), 59.9 [$C(CH_3)_3$], 128.3 (C-3,5) 130.9 (C-2,6), 135.4 (C-4) and 144.9 (C-1); *m/z* (EI, 70 eV, 200 °C) 316 (M^+, 9%), 260 (MH − C_4H_9, 17), 196 (MH − $SO_2C_4H_9$, 13), 121 ($SO_2C_4H_9$, 10) and 57 (C_4H_9, 100).

4-Allyl-1-(*tert*-butylsulfonyl)benzene 5c

The general procedure was the same as described for the preparation of compound **5a**. A solution of **4** (100 mg, 0.30 mmol) in THF (2 cm^3) at −78 °C was transferred *via* a cannula to a mixture of allylmagnesium bromide (0.45 cm^3 of a 1.0 M solution in diethyl ether, 0.45 mmol) and DMPU (0.16 cm^3, 1.3 mmol) in THF (2 cm^3) kept at −78 °C. The reaction mixture was stirred for 1.5 h at 0 °C, quenched with iodine (381 mg, 1.50 mmol) and stirred for 1 day at room temperature. After the usual work-up, purification by column chromatography (SiO_2; light petroleum–diethyl ether, 4:1) gave the *title product* (31 mg, 0.13 mmol, 43%) which crystallised from hexane as white crystals; mp 62 °C (Found: C, 65.2; H, 7.4. $C_{13}H_{18}O_2S$ requires C, 65.51; H, 7.61%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3055m (C–H arom.), 2987m, 2954m, 2931m, 2871m and 2854m (C–H alkyl and alkenyl); δ_H(300 MHz) 1.34 [9 H, d, $C(CH_3)_3$], 3.49 (2 H, s, $ArCH_2$), 5.10–5.18 (2 H, m, $CHCH_2$), 5.90–6.05 (1 H, ddt, *J* 6.7, 10.2, 16.9, $CHCH_2$), 7.38 (2 H, d, *J* 8.2, H-3,5) and 7.81 (2 H, d, *J* 8.2, H-2,6); $\delta_C\{^1H\}$ (125.8 MHz) 23.6 [$C(CH_3)_3$], 40.0 ($ArCH_2$), 59.7 [$C(CH_3)_3$], 117.2 ($CHCH_2$), 128.9 (C-3,5), 130.6 (C-2,6), 133.1 (C-4), 135.8 ($CHCH_2$) and 146.4 (C-1); *m/z* (CI, NH_3) 256 (MNH_4^+, 100%), 239 (MH, 2), 182 (MH − C_4H_9, 3), 118 (MH − $SO_2C_4H_9$, 4) and 57 (C_4H_9, 3).

4-(*tert*-Butoxycarbonylmethyl)-1-(*tert*-butylsulfonyl)benzene 5d

The general procedure was the same as described for the preparation of compound **5a**. Lithium diisopropylamide (0.27 cm^3 of a 1.35 M solution in cyclohexane, 0.36 mmol) was added to a solution of *tert*-butyl acetate (0.048 cm^3, 0.36 mmol) in THF at −78 °C. After this mixture had been stirred for 30 min, DMPU (0.11 cm^3, 0.9 mmol) and a solution of **4** (100 mg, 0.30 mmol) in THF were successively added. After 1.5 h at 0 °C, the reaction mixture was quenched with iodine (381 mg, 1.50 mmol) at −78 °C and stirred for 1 day at room temperature. After the usual work-up, column chromatography (SiO_2; diethyl ether) gave the *title product* (90 mg, 0.29 mmol, 97%) which crystallised from hexane as white needles; mp 97 °C (Found: C, 61.4; H, 7.6. $C_{16}H_{24}O_4S$ requires C, 61.51; H, 7.74%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3058w (C–H arom.), 2981m, 2954m, 2935m, 2906m, 2873m (C–H alkyl), 1730s (C=O) and 1265vs and 1133vs (S=O); δ_H(300 MHz) 1.34 [9 H, s, $SO_2C(CH_3)_3$], 1.44 [9 H, s, $CO_2C(CH_3)_3$], 3.64 (2 H, s, $ArCH_2$), 7.45 (2 H, d, *J* 8.3, H-3,5) and 7.84 (2 H, d, *J* 8.3, H-2,6); $\delta_C\{^1H\}$ (75 MHz) 23.6 [$SO_2C(CH_3)_3$], 28.0 [$CO_2C(CH_3)_3$], 42.4 ($ArCH_2$), 59.8 [$SO_2C(CH_3)_3$], 81.6 [$CO_2C(CH_3)_3$], 129.6 (C-3,5), 130.6 (C-2,6), 134.0 (C-4), 140.8 (C-1) and 169.6 (CO_2); *m/z* (CI, NH_3) 330 (MNH_4^+, 100%) and 274 (MNH_4 − C_4H_9, 9).

[η⁶-1-(*tert*-Butylsulfonyl)-2-(trimethylsilyl)benzene]tricarbonylchromium(0) 6a

[η⁶-(*tert*-Butylsulfonyl)benzene]tricarbonylchromium(0) **4** (150 mg, 0.45 mmol) was dissolved in a mixture of dry nitrogen-saturated THF (4 cm^3) and diethyl ether (8 cm^3) in a Schlenk tube and cooled to −78 °C. Butyllithium (0.29 cm^3 of a 1.54 M solution in hexanes, 0.45 mmol) was added. The reaction mixture was stirred for 1 h at −78 °C and chlorotrimethylsilane (0.086 cm^3, 0.68 mmol) was then added. After stirring for 1 h at −78 °C, the mixture was allowed to warm to room temperature. The solvent was removed under reduced pressure. Column chromatography (SiO_2; light petroleum–diethyl ether, 4:1) gave the *title complex* (147 mg, 0.362 mmol, 80%) which crystallised from hexane–diethyl ether as orange crystals; mp 119–120 °C (Found: C, 47.0; H, 5.4. $C_{16}H_{22}CrO_5SSi$ requires C, 47.28; H, 5.46%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1982vs and 1920vs (C≡O) and 1248s and 1134s (S=O); δ_H(300 MHz) 0.48 [9 H, s, $Si(CH_3)_3$], 1.43 [9 H, s, $C(CH_3)_3$], 5.2 (1 H, t, *J* 6.2, ArH), 5.46 (1 H, d, *J* 6.5, ArH) and 5.61–5.70 (2 H, m, ArH); $\delta_C\{^1H\}$ (75 MHz) 2.8 [$Si(CH_3)_3$], 24.7 [$C(CH_3)_3$], 62.6 [$C(CH_3)_3$], 89.9, 90.1, 92.1 and 99.2 (C-3,4,5,6), 99.0 (C-2), 113.4 (C-1) and 230.4 [$Cr(CO)_3$]; *m/z* (EI, 70 eV, 200 °C) 406 (M^+, 2%), 350 (M − 2CO, 7), 322 (M − 3CO, 40), 271 (MH − 3CO − Cr, 3), 73 (SiC_3H_9, 29), 57 (C_4H_9, 87) and 52 (Cr, 100).

[η⁶-1-(*tert*-Butylsulfonyl)-2-(methoxycarbonyl)benzene]tricarbonylchromium(0) 6b

The general procedure was the same as described for the preparation of complex **6a**. Complex **4** (150 mg, 0.45 mmol) was treated with butyllithium (0.29 cm^3 of a 1.54 M solution in hexanes, 0.45 mmol) and methyl chloroformate (0.042 cm^3, 0.54 mmol). Column chromatography (SiO_2; light petroleum–diethyl ether, 1:1) gave the *title complex* (131 mg, 0.334 mmol, 74%) which crystallised from hexane–dichloromethane as yellow needles; mp 140 °C (Found: C, 45.7; H, 4.0. $C_{15}H_{16}CrO_7S$ requires C, 45.92; H, 4.11%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1940vs and 1932vs (C≡O) and 1739m (C=O); δ_H(500 MHz) 1.48 [9 H, s, $C(CH_3)_3$], 3.91 (3 H, s, CO_2CH_3), 5.14–5.18 (2 H, m, ArH), 5.76 (1 H, td, *J* 6 and 0.5, ArH) and 5.53 (1 H, dd, *J* 6 and 0.5, ArH *ortho*); $\delta_C\{^1H\}$ (125.8 MHz) 24.4 [$C(CH_3)_3$], 53.8 (CO_2CH_3), 62.6 [$C(CH_3)_3$], 85.8, 86.6, 91.6, 93.2 (C-3,4,5,6), 98.8, 106.8 (C-1,2), 165.5 (CO_2CH_3) and 228.1 [$Cr(CO)_3$]; *m/z* (CI, NH_3) 410 (MNH_4^+, 100%), 393 (MH, 20), 319 (MH − CO_2Me − CH_3, 43) and 52 (Cr, 2).

[η⁶-1-(*tert*-Butylsulfonyl)-2,6-bis(trimethylsilyl)benzene]tricarbonylchromium(0) 7a

[η⁶-(*tert*-Butylsulfonyl)benzene]tricarbonylchromium(0) **4** (100 mg, 0.30 mmol) was dissolved in dry nitrogen-saturated THF (6 cm^3) in a Schlenk tube and cooled to −78 °C with stirring. Butyllithium (0.39 cm^3 of a 1.60 M solution in hexanes, 0.62 mmol) was added to that solution. The mixture was stirred for 15 min. To this was added, *via* a cannula, a solution of chlorotrimethylsilane (0.114 cm^3, 0.90 mmol) in nitrogen-saturated THF (2 cm^3) at −78 °C. After stirring at −78 °C for 1 h, the reaction mixture was allowed to warm to room temperature. Removal of the solvent under reduced pressure produced a brown solid. Purification by column chromatography (SiO_2; light petroleum–diethyl ether, 1:1) afforded the *title complex* (125 mg, 0.262 mmol, 87%) which crystallised from hexane–diethyl ether as orange–red needles; mp 149 °C (Found: C, 47.7; H, 6.0. $C_{19}H_{30}CrO_5SSi_2$ requires C, 47.68; H, 6.32%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1977vs and 1915vs (C≡O); δ_H(300 MHz) 0.53 [18 H, s, $Si(CH_3)_3$], 1.32 [9 H, s, $C(CH_3)_3$], 5.00 (1 H, t, *J* 6.4, ArH) and 6.06 (2 H, d, *J* 6.4, ArH); $\delta_C\{^1H\}$ (125.8 MHz) 5.1 [$Si(CH_3)_3$], 25.8 [$C(CH_3)_3$], 64.2 [$C(CH_3)_3$], 90.3 (C-4), 96.9 (C-2,6), 103.2 (C-3,5), 122.0 (C-1) and 231.6 [$Cr(CO)_3$]; *m/z* (EI, 70 eV, 220 °C) 478 (M^+, 1.4%), 406 (MH − SiC_3H_9, 1), 422 (M − 2CO, 1), 394 (M − 3CO, 5), 343 (MH − 3CO −

Cr, 3), 271 (MH − 3CO − Cr − SiC_3H_9, 7), 73 (SiC_3H_9, 51), 57 (C_4H_9, 38) and 52 (Cr, 100).

[η⁶-1-(*tert*-Butylsulfonyl)-2,6-bis(diphenylphosphino)benzene]-tricarbonylchromium(0) 7b

The general procedure was the same as described for the preparation of complex **7a**. Complex **4** (100 mg, 0.30 mmol) was treated with butyllithium (0.38 cm^3 of a 1.67 M solution in hexanes, 0.63 mmol) and chlorodiphenylphosphine (0.176 cm^3, 0.90 mmol). Column chromatography (SiO_2; light petroleum–dichloromethane, 3:1 to 1:3 gradient) afforded the *title complex* (190 mg, 0.270 mmol, 90%) which crystallised as orange needles; mp 165–167 °C (decomp.) (Found: 703.0963. $C_{37}H_{32}CrO_5P_2S$ requires 703.0929); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1990vs and 1927vs (C≡O); δ_H(300 MHz) 1.60 [9 H, s, $C(CH_3)_3$], 4.95–5.05 (1 H, br s, H-4), 5.55–5.70 (2 H, br s, H-3), 7.22–7.27 (4 H, m, ArH), 7.32–7.42 (12 H, m, ArH) and 7.57–7.72 (4 H, m, ArH); *m/z* (FAB positive) 703 (MH^+, 24%), 618 (MH − 3CO, 38), 592 (MH − 3CO − C_4H_9, 36), 497 (M − 3CO − $SO_2C_4H_9$, 100), 77 (C_6H_5, 11) and 52 (Cr, 48).

[η⁶-1-(*tert*-Butylsulfonyl)-2,6-bis(methylsulfanyl)benzene]tricarbonylchromium(0) 7c

The general procedure was the same as described for the preparation of complex **7a**. Complex **4** (100 mg, 0.30 mmol) was treated with butyllithium (0.38 cm^3 of a 1.67 M solution in hexanes, 0.63 mmol) and dimethyl disulfide (0.081 cm^3, 0.90 mmol). Column chromatography (SiO_2; light petroleum–diethyl ether, 1:1) afforded the *title complex* (88 mg, 0.207 mmol, 69%) which crystallised from dichloromethane as orange crystals; mp 144 °C (Found: C, 42.0; H, 4.1. $C_{15}H_{18}CrO_5S_3$ requires C, 42.24; H, 4.25%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1984vs and 1921vs (C≡O); δ_H(300 MHz) 1.59 [9 H, s, $C(CH_3)_3$], 2.39 [6 H, s, $S(CH_3)$], 4.94 (2 H, d, *J* 6.5, ArH) and 5.84 (1 H, t, *J* 6.5, ArH); $\delta_C\{^1H\}$ (125 MHz, CD_2Cl_2) 18.4 (SCH_3), 26.0 [$C(CH_3)_3$], 66.3 [$C(CH_3)_3$], 83.5 (C-3,5), 95.0 (C-4), 99.3 (C-1), 121.8 (C-2,6) and 230.5 [$Cr(CO)_3$]; *m/z* (CI, NH_3) 444 (MNH_4^+, 100%), 398 (M − CO, 4), 308 (MNH_4 − 3CO − Cr, 60), 252 (MNH_4 − 3CO − Cr, 35), 234 (MH − 3CO − Cr − C_4H_9, 9), (MH − 3CO − Cr − C_4H_9 − CH_3, 58) and 52 (Cr, 10).

[η⁶-1-(*tert*-Butylsulfonyl)-2,6-bis(methoxycarbonyl)benzene]tricarbonylchromium(0) 7d

The general procedure was the same as described for the preparation of complex **7a**. Complex **4** (100 mg, 0.30 mmol) was treated with butyllithium (0.38 cm^3 of a 1.67 M solution in hexanes, 0.63 mmol) and methyl chloroformate (0.070 cm^3, 0.90 mmol). Column chromatography (SiO_2; light petroleum–dichloromethane, 1:1 to 0:1 gradient) afforded the *title complex* (54 mg, 0.120 mmol, 40%) which crystallised from hexane–dichloromethane as dark orange needles; mp 153 °C (Found: C, 45.1; H, 3.8. $C_{17}H_{18}CrO_9S$ requires C, 45.34; H, 4.03%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2008vs and 1946vs (C≡O), 1741s (C=O); δ_H(300 MHz) 1.60 [9 H, s, $C(CH_3)_3$], 3.96 (6 H, s, CO_2CH_3), 5.28 (2 H, d, *J* 6.2, ArH) and 5.52 (1 H, t, *J* 6.2, ArH); $\delta_C\{^1H\}$ (125.8 MHz, CD_2Cl_2) 26.8 [$C(CH_3)_3$], 53.9 (CO_2CH_3), 67.8 [$C(CH_3)_3$], 89.1 (C-3,5), 89.6 (C-4), 102.5 (C-1), 103.8 (C-2,6), 166.6 (CO_2CH_3) and 228.3 [$Cr(CO)_3$]; *m/z* (CI, NH_3) 468 (MNH_4^+, 67%), 410 (MH − $SO_2C_4H_9$, 5), 377 (MH − CH_3 − CO_2CH_3, 100), 332 [MNH_4 − $Cr(CO)_3$, 8], 136 [$Cr(CO)_3$, 3] and 52 (Cr, 4).

[η⁶-1-(*tert*-Butylsulfonyl)-2-(trimethylsilyl)-6-(diphenylphosphino)benzene]tricarbonylchromium(0) 8

[η⁶-(*tert*-Butylsulfonyl)benzene]tricarbonylchromium(0) **4** (150 mg, 0.45 mmol) was dissolved in a mixture of dry nitrogen-saturated THF (4 cm^3) and diethyl ether (8 cm^3) in a Schlenk tube and cooled to −78 °C. Butyllithium (0.29 cm^3 of a 1.54 M solution in hexanes, 0.45 mmol) was added. The reaction mixture was stirred for 45 min at −78 °C and then chlorotrimethylsilane (0.057 cm^3, 0.45 mmol) was added. After stirring for 30 min at −78 °C, butyllithium (0.29 cm^3 of a 1.54 M solution in hexanes, 0.45 mmol) was added and, after 30 min, chlorodiphenylphosphine (0.129 cm^3, 0.66 mmol) was added. The mixture was stirred for 30 min at −78 °C and then allowed to warm to room temperature. The solvent was removed under reduced pressure. Column chromatography (SiO_2; light petroleum–dichloromethane, 4:1) gave the *title complex* (127 mg, 0.215 mmol, 48%) which crystallised from hexane–diethyl ether as orange crystals; mp 160 °C (decomp.) (Found: C, 56.9; H, 5.4. $C_{28}H_{31}CrO_5PSSi$ requires C, 56.94; H, 5.29%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1982vs and 1921vs (C≡O); δ_H(300 MHz) 0.52 [9 H, s, $Si(CH_3)_3$], 1.48 [9 H, s, $C(CH_3)_3$], 4.99 (1 H, t, *J* 6, H-4), 5.89 (1 H, d, *J* 6, H-5), 5.95 (1 H, d, *J* 6, H-3), 7.29–7.40 (8 H, m, ArH) and 7.61–7.70 (2 H, m, ArH); $\delta_C\{^1H\}$ (125.8 MHz, CD_2Cl_2) 5.0 [$Si(CH_3)_3$], 27.7 [$C(CH_3)_3$], 65.9 [$C(CH_3)_3$], 88.7 (C-4), 99.3 (C-2), 102.4, 102.7 (C-3,5), 103.4 (C-1), 125.5 (d, *J* 28, C-6), 128.5, 128.9, 130.0, 130.2 (4 × ArH *meta* and 2 × ArH *para*), 134.2 (d, *J* 18, ArH *ortho*), 136.7 (d, *J* 23, ArH *ortho*), 140.2 (d, *J* 16, ArH *ipso*), 141.7 (d, *J* 22, ArH *ipso*) and 232.3 [$Cr(CO)_3$]; *m/z* (CI, NH_3) 591 (MH^+, 85%), 535 (MH − 2CO, 28), 469 (M − $SO_2C_4H_9$, 30), 455 (MH − 3CO − Cr, 13) and 335 (MH − 3CO − Cr − $SO_2C_4H_8$, 100).

[η⁶-1-(*tert*-Butylsulfonyl)-2-(trimethylsilyl)benzene]tricarbonylchromium(0) 6a

Methyllithium (0.21 cm^3 of a 1.40 M solution in diethyl ether, 0.30 mmol) was added to a solution of 2,2,6,6-tetramethylpiperidine (0.061 cm^3, 0.36 mmol) in dry nitrogen-saturated THF (2 cm^3) maintained in a Schlenk tube at −78 °C. The mixture was stirred for 30 min at 0 °C then recooled to −78 °C. To this was added a solution of complex **4** (100 mg, 0.30 mmol) dissolved in dry nitrogen-saturated THF (3 cm^3) and cooled to −78 °C. The mixture was stirred for 10 min and chlorotrimethylsilane (0.076 cm^3, 0.60 mmol) was added. After stirring at −78 °C for 1 h, the cold bath was removed and the reaction mixture was allowed to warm to room temperature. The solvent was removed under reduced pressure. Purification by column chromatography (SiO_2; light petroleum–diethyl ether, 4:1) afforded the *title complex* (62 mg, 0.153 mmol, 51%) which crystallised from dichloromethane as yellow needles. Spectroscopic data were identical to those obtained from a fully characterised sample of complex **6a**.

[η⁶-1-(*tert*-Butylsulfonyl)-2,5-bis(trimethylsilyl)benzene]tricarbonylchromium(0) 9

Methyllithium (0.43 cm^3 of a 1.40 M solution in diethyl ether, 0.60 mmol) was added to a solution of 2,2,6,6-tetramethylpiperidine (0.111 cm^3, 0.66 mmol) in dry nitrogen-saturated THF (2 cm^3) maintained in a Schlenk tube at −78 °C. The mixture was stirred for 30 min at 0 °C and then recooled to −78 °C. To this was added a solution of complex **4** (100 mg, 0.30 mmol) dissolved in dry nitrogen-saturated THF (3 cm^3) and cooled to −78 °C. The mixture was stirred for 15 min and chlorotrimethylsilane (0.114 cm^3, 0.90 mmol) was added. After stirring at −78 °C for 30 min, the reaction mixture was allowed to warm to room temperature. Removal of the solvent under reduced pressure left a brown oil. Purification by column chromatography (SiO_2; dichloromethane–light petroleum, 4:1) afforded the *title complex* (85 mg, 0.178 mmol, 59%) which crystallised from hexane–diethyl ether as yellow needles; mp 144 °C (Found: C, 47.5; H, 6.1. $C_{19}H_{30}CrO_5SSi_2$ requires C, 47.68; H, 6.32%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1982vs and 1915vs (C≡O); δ_H(500 MHz) 0.34 [9 H, s, $Si(CH_3)_3$], 0.47 [9 H, s, $Si(CH_3)_3$], 1.41 [9 H, s, $C(CH_3)_3$], 5.34 (2 H, s, ArH) and 5.59 (1 H, s, ArH); $\delta_C\{^1H\}$ (125.8 MHz) 2.5 [$Si(CH_3)_3$], 24.7 [$C(CH_3)_3$], 64.4 [$C(CH_3)_3$], 95.9, 97.6, 96.9 (C-3,4,6), 97.9, 101.8 (C-2,5), 110.7 (C-1) and 230.2 [$Cr(CO)_3$]; *m/z* (EI, 70 eV, 180 °C) 478 (M^+, 1.4%), 422 (M − 2CO, 1), 394 (M − 3CO, 55), 343 (MH − 3CO − Cr,

2), 271 (MH − 3CO − Cr − SiC_3H_9, 21), 73 (SiC_3H_9, 53), 57 (C_4H_9, 46) and 52 (Cr, 100).

[η⁶-1-(*tert*-Butylsulfonyl)-2,4,6-tris(trimethylsilyl)benzene]tricarbonylchromium(0) 10

The general procedure was the same as described for the preparation of complex **9**. Methyllithium (0.78 cm^3 of a 1.35 M solution in diethyl ether, 1.05 mmol) was added to a solution of 2,2,6,6-tetramethylpiperidine (0.192 cm^3, 1.14 mmol) in THF (3 cm^3) at −78 °C. The mixture was stirred for 30 min at 0 °C and then cooled to −78 °C. To this was added, *via* a cannula, a solution of **4** (100 mg, 0.30 mmol) in THF (3 cm^3) cooled to −78 °C. The mixture was stirred for 2 h and chlorotrimethylsilane (0.152 cm^3, 1.20 mmol) was added. After stirring at −78 °C for 30 min, the cold bath was removed and the reaction mixture was allowed to warm to room temperature. Removal of the solvent under reduced pressure left a red oil. Purification by column chromatography (SiO_2; light petroleum–dichloromethane, 4 : 1 to 1 : 1 gradient) afforded the *title complex* (83 mg, 0.151 mmol, 50%) which crystallised from hexane–dichloromethane as orange needles; mp 192 °C (decomp.) (Found: C, 47.8; H, 6.8. $C_{22}H_{38}CrO_5SSi_3$ requires C, 47.97; H, 6.95%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1977vs and 1915vs (C≡O); δ_H(300 MHz) 0.30 [9 H, s, $Si(CH_3)_3$], 0.53 [18 H, s, 2 × $Si(CH_3)_3$], 1.33 [9 H, s, $C(CH_3)_3$] and 6.09 (2 H, s, ArH); $\delta_C\{^1H\}$ (75 MHz) 5.3 [$Si(CH_3)_3$], 27.0 [$C(CH_3)_3$], 64.3 [$C(CH_3)_3$], 96.2 (C-2,6), 99.3 (C-4), 107.7 (C-3,5), 124.2 (C-1) and 232 [$Cr(CO)_3$]; *m/z* (EI, 70 eV, 200 °C) 550 (M^+, 1%), 466 (M − 3CO, 4), 343 (MH − 3CO − Cr, 2), 73 (SiC_3H_9, 100) and 52 (Cr, 60).

X-Ray crystallographic analysis of 9

Crystal data. $C_{19}H_{30}CrO_5SSi_2$, M = 478.7, monoclinic, space group $P2_1/c$, a = 11.459(8), b = 16.939(9), c = 12.918(6) Å, β = 105.75(5)°, V = 2413(3) $Å^3$, Z = 4, D_c = 1.32 g cm^{-3}, Cu-Kα radiation, λ = 1.541 78 Å, μ(Cu-Kα) = 58.8 cm^{-1}, $F(000)$ = 1008. Orange prismatic needles, crystal dimensions 0.30 × 0.20 × 0.16 mm.

Data collection and processing. Data were measured on a Siemens P4/PC diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. Of the 3570 independent reflections measured ($2\theta \leqslant 120°$), 3066 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors and a Gaussian absorption correction (face-indexed numerical) was applied; the maximum and minimum transmission factors were 0.485 and 0.334 respectively.

Structure analysis and refinement. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}$(C–Me)] and allowed to ride on their parent atoms. Refinement was by full-matrix least-squares based on F^2 to give $R_1 = 0.050$, $wR_2 = 0.135$ for 254 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.43 and −0.58 e $Å^{-3}$ respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.000 and 0.001 respectively. Computations were carried out on a 50 MHz 486 PC computer using the SHELXTL PC program system.[21]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/52.

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