

Synthetic Applications of Arenetricarbonylchromium(0) Complexes: the Synthesis of Polyfunctionalised Thiophenes

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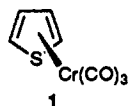
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Lithiation of thiophenetricarbonylchromium(0) complexes with butyllithium occurs preferentially at C-2/5 but when these are blocked, 3/4 lithiation is facile. Combinations of a bulky silyl (Pr_3Si or $\text{Bu}^t\text{Me}_2\text{Si}$) blocking group at C-2/5 and remote lithiation/electrophilic quench of C-3/4 followed by desilylation/lithiation/electrophilic quench allowed the synthesis of 2,3-, 2,3,5- and 2,3,4,5-polysubstituted thiophene complexes and their derived free thiophenes.

The attachment of a tricarbonylchromium(0) unit to carbocyclic arenes has allowed a rich array of regiocontrolled functionalisations of the aromatic ring to be developed.¹⁻³ In particular, directed lithiations⁴ and nucleophilic additions⁵ have been used to achieve unique functionalisations of substituted simple and heteroannulated benzenes and these methods have been applied successfully in the synthesis of highly functionalised compounds and natural products.⁶⁻¹⁵

The analogous heteroarene complexes have been much less studied, largely because of their instability or difficulty of access. Exceptions are thiophenetricarbonylchromium(0) complexes (as **1**) which have been made by a number of standard methods^{16,17} and we now report a study of the chemistry of these complexes which reveals markedly different behaviour to that observed with their carbocyclic analogues.



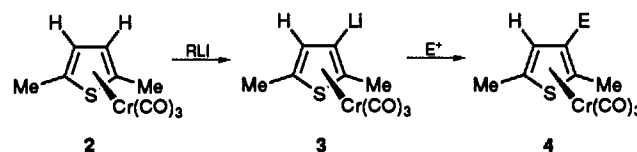
Among the synthetic methods which can be applied to the formation of the complexes, we have found the metal transfer process¹⁸ from naphthalenetricarbonylchromium(0)¹⁹ to be the most effective. In order to optimise this approach, a study of the different methods, developed by Kündig¹⁸ for arene complexations, was carried out. Methods A and B involved refluxing the thiophene with naphthalene complex in the absence of solvent (A), or in ethyl acetate-THF (10:1) (B). Method C used a sealed tube, containing the thiophene, naphthalene complex, diethyl ether or ethyl acetate and a few drops of THF, heated to 75 °C (see Experimental section for full details). The results for 2- and 3-substituted thiophenes are presented in Table 1.

For Method A, the yields were consistently good to excellent but the limiting factor is that a large excess of the thiophene (20 equiv.) was required and hence Method A is only appropriate for readily available thiophenes. Method B, using a moderate excess of substrate (≈ 5 equiv.) gave fair to good yields and offers an alternative to Method A especially for less available (or more expensive) thiophenes. Method C again gave good yields with ≈ 5 equiv. of the thiophene but the process was technically less convenient. The choice of method depended on the availability and nature of the thiophene.

Previous studies of metallation of thiophene complexes had been confined to α -deprotonation at C-2/5²⁰ and we were particularly concerned to establish the feasibility of direct β -deprotonation (Scheme 1), a process which is not attainable in uncomplexed thiophenes without directing groups,²¹⁻²⁴ and to

Table 1 Synthesis of monosubstituted thiophenetricarbonylchromium(0) complexes

Entry	R ¹	R ²	Method	Yield (%)
1	H	H	A	59
2	H	H	B	39
3	H	H	C	50
4	Me	H	A	85
5	H	Me	A	66
6	Me ₃ Si	H	A	64
7	Me ₃ Si	H	B	80
8	Me ₃ Si	H	C	92
9	Pr ^t ₃ Si	H	C	58
10	Pr ^t ₃ Si	H	B	34
11	Bu ^t Me ₂ Si	H	B	77
12	MeOCH ₂	H	A	16
13	Me ₃ SiCH ₂ CH ₂ OCH ₂	H	A	26



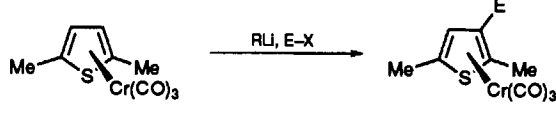
Scheme 1 β -Functionalisation of thiophenes

establish the stability of the 3-lithio-complex **3** with respect to the ring-opening process observed in the uncomplexed thiophenes.²⁵

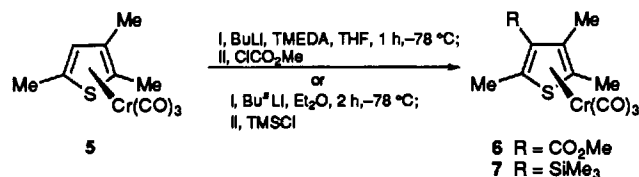
β -Deprotonation/electrophilic quench was investigated initially with 2,5-dimethylthiophene complex **2**. Deprotonation with butyllithium-TMEDA at -78 °C in THF solution proved to be optimal with yields of 4 up to 80% after electrophilic quench. The results are given in Table 2.

Not unexpectedly, no indication of ring opening²⁵ was observed at this temperature.

With the trisubstituted thiophene complex to hand, it was pertinent to determine whether the remaining β -hydrogen could be abstracted/substituted to give a tetrasubstituted complex. Treatment of the trimethylthiophene complex **5** with butyllithium-TMEDA-THF, followed by methyl chloroformate, gave the complex **6** as an air sensitive orange oil, in 35% yield (Scheme 2). Alternatively, *sec*-butyllithium-ether followed by a chlorotrimethylsilane quench gave complex **7** as a moderately air-stable orange solid, also in a 35% yield.

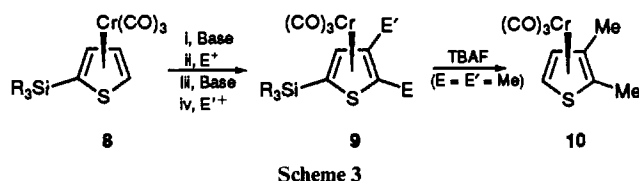
Table 2 Lithiations of 2,5-dimethylthiophenetricarbonylchromium(0)


Entry	RLi	Time (min)	TMEDA (equiv.)	E-X	Yield (%)
1	BuLi	60	0	MeI	19
2	BuLi	120	0	MeOTf	9
3	BuLi	120	0	Me ₃ SnCl	39
4	Bu ^t Li	40	0	Me ₃ SiCl	23
5	BuLi	60	3.0	Me ₃ SiCl	51
6	BuLi	90	3.0	MeI	80

**Scheme 2**

In contrast, the 3-trimethylsilyl analogue **4** (E = SiMe₃) could not be lithiated, presumably as a result of steric hindrance by the SiMe₃ group.

The establishment of conditions for β-lithiation in the simple complex **5** allowed the development of strategies for the synthesis of a variety of functionalised thiophenes. 2,3-Dimethylthiophene complex **10** was the initially chosen target, potentially available by the sequence outlined in Scheme 3. The

**Scheme 3**

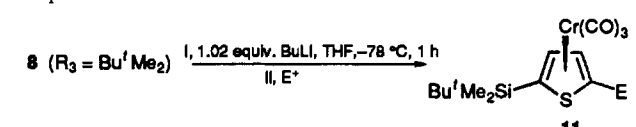
free thiophene would be readily obtainable from **10** by oxidative demetallation.²⁶

The viability of this plan rested on the key α-blocking group which, ideally, would need to be sterically demanding, removable and unreactive towards alkyllithium bases. An obvious choice was a trialkylsilyl group, which had been used to good effect in indole²⁷ and pyridinetricarbonylchromium^{28,29} chemistry.

Attempted α-lithiation of **8** (R = Me) with 1 equiv. of BuLi and protic work-up produced only thiophenetricarbonylchromium(0) **1**, the product of desilylation. This desilylation, which was found to be complete after ≈3 h at -78 °C, is presumably facilitated by the enhanced stabilisation of the α-anion. A detailed study of this desilylation process established that only the bulkiest silanes, triisopropyl-**8** (R = Prⁱ) and *tert*-butyldimethylsilyl-**8** (R₃ = Bu^tMe₂) were resistant to the alkyllithium bases.³⁰

The silylthiophene complex **8** (R₃ = Bu^tMe₂) (Table 1, entry 12) was lithiated (at C-5) with butyllithium and the lithio species quenched with a range of electrophiles. The results are given in Table 3.

As observed with the carbocyclic complexes^{27,31} non-acidic electrophiles (entries 2–4) quench in moderate to good yields, but the yield of the iodo complex (entry 5) was unexpectedly low, given the high yields reported³² for the benzene complexes. The more reactive halides (entries 6, 7) gave no substitution product, only proton-quenched material, but these types of

Table 3 Lithiation/electrophilic substitution of 2-silylthiophene complexes **8**


Entry	E ⁺	E	Yield (%)
1	D ₂ O	D	≥97
2	MeI	Me	80
3	(MeS) ₂	SMe	70
4	PhNCO	CONHPh	44
5	I ₂	I	28
6	PhCH ₂ Cl	CH ₂ Ph	0
7	MeCOCl	COMe	0
8	B(OPr ⁱ) ₃	B(OH) ₂	0
9	CH ₂ =CHCH ₂ Br ^a	CH ₂ CH=CH ₂	72
10	ClCOMe ^a	COMe	54
11	MeCOCH=CH ₂ ^a	CH ₂ CH ₂ COMe	0

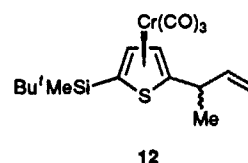
^a Via the cuprate complex formed with CuBr-SMe₂ at -20 °C.

substrate were successfully coupled *via* the copper complexes formed between copper bromide dimethyl sulfide complex and the lithio species³³ (entries 9, 10). The borate ester quench (entry 8) gave an adduct which proved to be too labile for practical isolation.

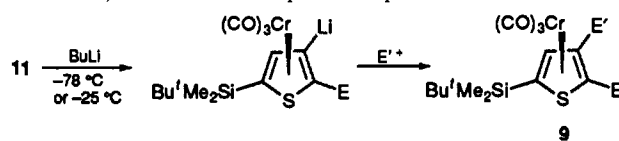
Using the conditions established above for β-substitution, the complexes **11** were lithiated and the lithio species quenched with a series of electrophiles; the results are given in Table 4.

The complexes **11** lithiated, as expected, at the 3-position remote from the bulky silyl group and the trisubstituted products were generated in moderate to good yields. As before, the allyl group was more efficiently introduced *via* the cuprate complexes (entries 6, 8).

Although the earlier results had demonstrated that a β-hydrogen was more acidic than methyl group hydrogens in the methylthiophene complex **2**, the site of lithiation of the 2-methylthiophene complex **11** (E = SMe) was uncertain. In the event, lithiation was only observed at the β-position and no *S*-methyl attack was detectable (entries 7, 8). In contrast, lithiation of the 2-allylthiophene complex **11** (E = CH₂CH=CH₂) at -78 °C followed by a deuterium quench gave a 1:1 mixture of 3'- and 1'-allyl deuteration. Lithiation at -25 °C followed by a D₂O quench produced a 1:3 mixture of these deuterated species. However, reaction of **11** (E = CH₂CH=CH₂) with BuLi-TMEDA at -60 °C followed by a methyl iodide quench gave only 1'-methylated material (70%) as a 3:2 mixture of epimers **12**. It would appear, therefore, that the proton quenching involved some equilibration of the products.

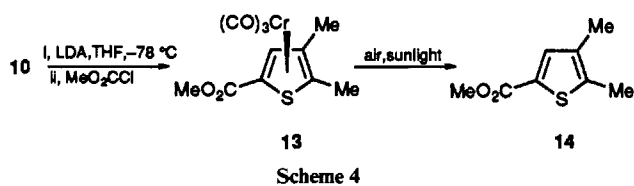


Having established general conditions for both α- and β-substitution of the silylated complex **8** (R₃ = Bu^tMe₂), to complete the synthesis of 2,3-disubstituted thiophenes would require the simple steps of fluoride desilylation and oxidative chromium removal. Optimum proto-desilylation of **9** (R₃ = Bu^tMe₂, E = E' = Me) was found to occur at -30 °C in THF with TBAF hydrate over 45 min. Despite some decomplexation, the isolated yield of 2,3-dimethylthiophene complex **10** was 62%. Decomplexation by the action of air/sunlight²⁶ on an

Table 4 Lithiation/electrophilic substitution of 2,5-disubstituted thiophene complexes 11

Entry	E	E'+	E'	Yield (%)
1	Me	MeOD	D	74 (91%D)
2	Me	MeI	Me	61
3	Me	MeOCOCl	CO ₂ Me	60
4	Me	Me ₃ SnCl	SnMe ₃	45
5	Me	I ₂	I	34
6	Me	CH ₂ =CHCH ₂ Br ^a	CH ₂ CH=CH ₂	35
7	SMe	MeOD	D	37 (60%D)
8	SMe	CH ₂ =CHCH ₂ Br ^a	CH ₂ CH=CH ₂	39
9	CH ₂ CH=CH ₂	MeOD	D	48 ^b

^a Via the cuprate complex formed with CuBr·SMe₂ at -20 °C. ^b 48% α-Deuteration of the allyl group was also observed.



etheral solution gave the target 2,3-dimethylthiophene in 96% yield.

This now provided a route for the synthesis of more generally functionalised 2,3,5-trisubstituted thiophenes²³ and this is exemplified in Scheme 4. In principle, this could have been a 'one-pot' reaction (8 → 13), but it proved impossible to capture the intermediate anion of the desilylation step and the reaction was carried out as a two-step process. Thus, deprotonation of the product 10 of the desilylation of 8 and treatment of the anion with methyl chloroformate gave 13. Decomplexation of 13 gave methyl 2,3-dimethylthiophene-5-carboxylate 14 in 45% overall yield.

Attempts to further develop this chemistry to the synthesis of tetrasubstituted thiophenes were thwarted by the very nature of the silyl blocking group at C-2. With the bulky TBDMS or TIPS groups, necessary for stability, no lithiation of an adjacent β-position was achieved.

Overall, these reactions constitute novel routes to specifically functionalised thiophenes. The methods rely on activation by the electron-withdrawing chromiumtricarboxyl group analogous to that observed in carbocyclic arenetricarbonylchromium(0) complexes.

It is interesting to note that all attempts to demonstrate the other characteristic aspects of arenetricarbonylchromium(0) chemistry; nucleophilic addition to and enhanced stabilisation of anions and cations adjacent to the aromatic ring completely failed. The reasons are not obvious, but this lack of reactivity imposes limitations on the use of the complexes in synthesis.

Experimental

Melting points were carried out on a Kofler hot-stage and are uncorrected; IR spectra were recorded on a Perkin-Elmer 1700 FT spectrometer; ¹H NMR spectra on a Bruker WH-250 FT (250 MHz), GE-300 FT (300 MHz), JEOL GSX FT (270 MHz—with a GSX data system) or Varian 60 MHz spectrometer. Chemical shifts are reported in ppm relative to residual undeuterated solvent *i.e.* δ 7.26 for chloroform and δ 7.37 for benzene. ¹³C NMR spectra were recorded on the Bruker

and JEOL instruments, with chemical shifts reported against CDCl₃ reference. All complexes are racemic unless otherwise stated. *J* Values are recorded in Hz.

All reactions involving complexes or butyllithiums were carried out under an atmosphere of dry, oxygen-free nitrogen and those involving the former had solvents degassed prior to reaction. Unless otherwise stated, petroleum refers to light petroleum, b.p. 40–60 °C, which was distilled before use. Butyllithiums were purchased from Aldrich Chemicals as ~1.6 or 2.5 mol dm⁻³ solutions in hexanes and were standardised by published methods.³⁴ Column chromatography was carried out using silica gel H. THF and diethyl ether were pre-dried with sodium metal and then distilled from sodium benzophenone ketyl immediately before use. Dibutyl ether was purchased from Aldrich Chemicals as anhydrous 99+ % grade and used without further purification. Other reagents were purified according to literature methods.³⁵ Aqueous work-up refers to a sequential water and brine wash, followed by drying of the organic solution over anhydrous magnesium sulfate, filtering and then removal of the solvents under reduced pressure.

2-(tert-Butyldimethylsilyl)thiophene.—Thienyllithium (1.0 mol dm⁻³ solution in THF; 50 cm³, 0.05 mol) was added *via* a cannula to a stirred solution of *tert*-butyldimethylchlorosilane (7.54 g, 0.05 mol) in THF (25 cm³) at -78 °C, the temperature being maintained < -50 °C. After 1 h, the brown solution was allowed to warm to room temperature. Aqueous work-up afforded a brown liquid which was purified by dry flash column chromatography (eluent: petroleum). The *title compound* was obtained as a colourless liquid (9.58 g, 97%); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 2955, 2929, 2885, 2858, 1471, 1464, 1407, 1251, 1052, 836, 706 and 675; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.34 [6 H, s, Si(CH₃)₂], 0.96 [9 H, s, Si(CH₃)₃], 7.23 (1 H, dd, *J* 4.6, 3.4, 4-H), 7.31 (1 H, d, *J* 3.18, 3-H) and 7.63 (1 H, dd, *J* 4.6, 0.7, 5-H); *m/z* (EI) 198 (M⁺), 141 and 28.

2-(Triisopropylsilyl)thiophene.—Prepared using the same procedure and scale as for the preceding compound. The crude product was purified by column chromatography (eluent: 2–10% diethyl ether–petroleum gradient) affording two products. The first isolated fraction (*R_F* 0.8) was identified as 2,5-bis(triisopropylsilyl)thiophene which required further purification by a recrystallisation from hexane to give pure product, a colourless crystalline solid (1.19 g, 6%), m.p. 46 °C (Found: MH⁺, 397.2780. C₂₂H₄₅SSi₂ requires 397.2780); $\nu_{\text{max}}(\text{hexane})/\text{cm}^{-1}$ 1463, 1262, 1203, 1016, 1004, 884, 805, 695, 652, 574, 528 and 415; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.01 {36 H, d, *J* 7.5, 2 × Si[CH(CH₃)₂]₃}, 1.25 {6 H, sept., *J* 7.5, 2 × Si[CH(CH₃)₂]₃}

and 7.26 (2 H, s, 3,4-H); m/z (EI) 396 (M^+), 353, 325, 311, 297, 283, 269, 157, 59 and 43. The second isolated fraction (R_F 0.6) was identified as the title compound, a colourless liquid (9.16 g, 76%); δ_H (CDCl₃) 1.06 {18 H, d, J 7.5, Si[CH(CH₃)₂]₃}, 1.31 {3 H, sept., J 7.5, Si[CH(CH₃)₂]₃}, 7.18 (1 H, dd, J 5.0, 4.5, 4-H), 7.23 (1 H, dd, J 4.5, 1.0, 3-H) and 7.62 (1 H, dd, J 5.0, 1.0, 5-H). This material was carried through for complexation without further analysis.

2-Methoxymethylthiophene.—2-Thienylmethanol (4.09 cm³, 33.0 mmol) was added *via* a syringe to a mixture of sodium hydride (0.82 g, 1.05 equiv.) and DMF (20 cm³) at 0 °C over ~10 min (in order to control the effervescence) and was then stirred for 30 min. Iodomethane (3.0 cm³, 1.5 equiv.) was added dropwise to the rapidly stirred sodium salt solution. After 30 min at 0 °C, an aqueous work-up afforded an orange oil, which was purified by column chromatography (0–2% diethyl ether–petroleum; gradient elution). The starting thienylmethanol was eluted first from the column and collected as a colourless liquid (1.95 g, 52%); δ_H (CDCl₃) 3.07 (1 H, br s, OH), 4.73 (2 H, s, CH₂OH), 6.97 (2 H, m, 3,5-H) and 7.26 (1 H, m, 5-H); m/z (EI) 114 (M^+), 97, 85 and 81.³⁶ The title compound was then collected as a colourless oil (2.00 g, 47%); δ_H (CDCl₃) 3.39 (3 H, s, OCH₃), 4.63 (2 H, br s, CH₂OCH₃), 7.00 (2 H, m, 3,4-H) and 7.30 (1 H, dd, J 4.9, 1.5, 5-H). This material was carried straight through for complexation (see below).

2-(Trimethylsilylethoxymethyl)thiophene.—Butyllithium (1.0 equiv.) was slowly added dropwise to a solution of thiophene (2.0 cm³, 25.0 mmol) in diethyl ether (60 cm³) precooled to –50 °C, the temperature being maintained < –30 °C. The solution was stirred in the temperature range –30 °C to –40 °C for 1 h, and was then cooled to –78 °C. Trimethylsilylethoxymethyl chloride (4.2 cm³, 0.95 equiv.) was added dropwise, and the solution then warmed to room temperature when lithium chloride precipitated. After 4 h, the ethereal solution was subjected to an aqueous work-up, to give a yellow oil. This crude product was purified by reduced pressure distillation to afford the *title compound* as a colourless oil (4.02 g, 75%), b.p. 93 °C/20 mmHg [Found: ($M + NH_4^+$), 232.1191. C₁₀H₁₈OSSi requires 232.1191]; ν_{max} (film)/cm⁻¹ 2953, 2894, 2854, 1365, 1343, 1249, 1176, 1083, 915, 834, 753 and 698; δ_H (CDCl₃) 0.03 [9 H, s, Si(CH₃)₃], 0.99 (2 H, t, J 8.2, CH₂OCH₂CH₂TMS), 3.60 (2 H, t, J 8.2, CH₂OCH₂CH₂TMS), 4.65 (2 H, s, CH₂OCH₂CH₂TMS), 6.98 (2 H, m, 3,4-H) and 7.27 (1 H, dd, J 4.8, 1.7, 5-H); m/z (CI) 232 ($M + NH_4^+$), 114, 97, 90 and 73.

General Complexation Procedures

Complexation with Naphthalenetetracarboxylchromium(0).—**Method A.** A mixture of naphthalenetetracarboxylchromium(0) (0.6 g, 2.27 mmol; prepared by the modified method below), thiophene (20 equiv.) and THF (0.6 cm³) were degassed and refluxed for 75 min. The solution was filtered through silica, concentrated under reduced pressure and the product purified by flash column chromatography.

Method B. A mixture of naphthalene complex (0.9 g, 3.4 mmol), thiophene (5.0 equiv.), AnalaR® ethyl acetate (15 cm³) and THF (1.5 cm³) were degassed and refluxed for 4 h. Work-up as method A afforded the product complex.

Method C. A mixture of naphthalene complex (0.6 g, 2.27 mmol), thiophene (5.0 equiv.), diethyl ether or AnalaR® ethyl acetate (15 cm³) and a small quantity of THF (~0.2 cm³) were heated at 75 °C in a 'screw top' sealed tube for 8–12 h. Work-up as for method A afforded the product complex.

So prepared were the following compounds.

η^5 -(Thiophene)tricarboxylchromium(0).—Complexation of thiophene with naphthalenetetracarboxylchromium(0) by method A as described, gave the complex **1** as an orange crystalline solid (0.30 g, 59%); m.p. 154 °C (decomp.) [lit.,¹⁶ m.p. 160 °C (decomp.)]; δ_H (CDCl₃) 5.37 (2 H, dd, J 3.4, 1.5, 2,5-H) and 5.59 (2 H, dd, J 3.5, 3.0, 3,4-H).

Complex **1** was also prepared by the alternative methods B and C, giving yields of 39 and 50%, respectively.

η^5 -(2-Methylthiophene)tricarboxylchromium(0).—Complexation of 2-methylthiophene with naphthalenetetracarboxylchromium(0) (1.10 g, 4.18 mmol) by method A as described, gave the title compound as an orange crystalline solid (0.83 g, 85%); m.p. 123 °C (lit.,³⁷ m.p. 125 °C) (Found: C, 41.3; H, 2.5. Calc. for C₈H₆CrO₃S: C, 41.03; H, 2.58%); ν_{max} (CHCl₃)/cm⁻¹ 1966, 1888, 1870, 909 and 651; δ_H (CDCl₃)³⁷ 2.28 (3 H, s, 2-CH₃), 5.20 (1 H, d, J 3.7, 5-H), 5.33 (1 H, d, J 3.2, 3-H) and 5.52 (1 H, t, J 3.4, 4-H); m/z (EI) 234 (M^+), 206, 178, 150, 97, 52 and 28.

η^5 -(3-Methylthiophene)tricarboxylchromium(0).—Complexation of 3-methylthiophene with naphthalenetetracarboxylchromium(0) (0.50 g, 1.89 mmol) by method A as described, afforded the title complex as an orange-red crystalline solid (0.29 g, 66%); m.p. 122–123 °C (lit.,³⁷ m.p. 122 °C) (Found: M^+ , 233.9443. Calc. for C₈H₆CrO₃S, 233.9443); ν_{max} (CHCl₃)/cm⁻¹ 1966, 1887, 1865 and 908; δ_H (CDCl₃)³⁷ 2.28 (3 H, s, 3-CH₃), 5.12 (1 H, d, J 0.75, 2-H), 5.36 (1 H, d, J 3.17, 5-H) and 5.48 (1 H, dd, J 3.17, 0.75, 4-H); m/z (EI) 234 (M^+), 206, 178, 150, 97, 52 and 28.

η^5 -(3-Methylthiophene)tricarboxylchromium(0) can also be prepared from the trispyridine complex Cr(CO)₃py₃³⁸ (60% yield), or from trisacetonitrile complex Cr(CO)₃(MeCN)₃³⁹ (21% yield).

η^5 -[2-(Trimethylsilyl)thiophene]tricarboxylchromium(0) **8 (R = Me).**—Complexation of 2-(trimethylsilyl)thiophene with naphthalenetetracarboxylchromium(0) (0.50 g, 1.89 mmol) by method C as described, gave the complex **8** (R = Me) as an orange crystalline solid (0.51 g, 92%); m.p. 105–106 °C (lit.,²⁰ m.p. 107–108 °C) (Found: C, 41.2; H, 4.1. Calc. for C₁₀H₁₂CrO₃SSi C, 41.08; H, 4.14%); ν_{max} (CHCl₃)/cm⁻¹ 1964, 1887, 1869, 1391, 1257, 1186, 926 and 846; δ_H (CDCl₃) 0.30 [9 H, s, Si(CH₃)₃], 5.53 (1 H, dd, J 4.0, 3.5, 4-H), 5.59 (2 H, dd, J 4.0, 3.5, 3,5-H); m/z (EI) 292 (M^+), 236, 208, 141, 73 and 52.

Complex **8** (R = Me) was also prepared using method A in yield of 64% and using method B in 80% yield.

η^5 -[2-(Triisopropylsilyl)thiophene]tricarboxylchromium(0) **8 (R = Prⁱ).**—Complexation of 2-(triisopropylsilyl)thiophene with the naphthalene complex (0.20 g, 0.76 mmol) by method C as described, gave the title compound **8** (R = Prⁱ) as an orange crystalline solid (0.15 g, 58%); m.p. 120–122 °C; ν_{max} (CHCl₃)/cm⁻¹ 1962, 1891 and 1869; δ_H (CDCl₃) 0.14 {18 H, d, J 7.0, Si[CH(CH₃)₂]₃}, 1.34 {3 H, sept., J 7.0, Si[CH(CH₃)₂]₃}, 5.59 (1 H, dd, J 3.5, 3.4, 4-H) and 5.69 (2 H, dd, J 3.5, 3.4, 3,5-H); m/z (CI) 341 (MH^+), 285, 257, 205, 162 and 28.

Complex **8** (R = Prⁱ) was also prepared using method B with the naphthalene complex (0.25 g, 0.94 mmol) to give a 34% yield of product.

Complexation of 2-(tert-Butyldimethylsilyl)thiophene.—Complexation of 2-(tert-butyldimethylsilyl)thiophene (14.0 g, 70.6 mmol) with the naphthalene complex (3.78 g, 14.3 mmol) by method B gave a crude product which was purified by column chromatography (2–10% diethyl ether–petroleum; gradient elution). The first fraction (0.58 g, 9%), isolated as a red crystalline solid, was found to be: η^5 -[2,5-bis(tert-butyl-

dimethylsilylthiophene]tricarbonylchromium(0) (R_F 0.8; 20% diethyl ether–petroleum). An analytically pure sample was obtained by recrystallisation from hexane under anaerobic conditions; m.p. 146–149 °C (Found: C, 50.9; H, 7.3. $C_{19}H_{32}CrO_3SSi_2$ requires C, 50.86; H, 7.19%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1958, 1893, 1883, 1258, 838 and 807; $\delta_H(CDCl_3)$ 0.25 (3 H, s, SiCH₃), 0.27 (3 H, s, SiCH₃), 0.91 [9 H, s, SiC(CH₃)₃] and 5.55 (2 H, s, 3,4-H); $\delta_C(CDCl_3)$ –6.02 (SiCH₃), –5.66 (SiCH₃), 17.35 (SiCMe₃), 26.17 [SiC(CH₃)₃], 99.14 (3,4-C), 100.38 (2,5-C) and 233.54 (CO); m/z (EI) 448 (M^+), 392, 364, 309, 255, 73 and 28.

The second fraction (3.68 g, 77%), isolated as an orange crystalline solid was found to be η^5 -[2-(*tert*-butyldimethylsilylthiophene)]tricarbonylchromium(0) **8** ($R_3 = Bu^tMe_2$) (R_F 0.6; 20% diethyl ether–petroleum), m.p. 125–129 °C (decomp.) (Found: C, 46.4; H, 5.4; M, 334.0151. $C_{13}H_{18}CrO_3SSi$ requires C, 46.69; H, 5.42%; M , 334.0151); $\nu_{max}(CHCl_3)/cm^{-1}$ 1965, 1888 and 1869; $\delta_H(CDCl_3)$ 0.24 [6 H, s, Si(CH₃)₂], 0.92 [9 H, s, SiC(CH₃)₃], 5.53 (1 H, d, J 2.6, 5-H) and 5.63 (2 H, dd, J 2.6, 1.2, 3,4-H); $\delta_C(CDCl_3)$ –6.08 (SiCH₃), –5.74 (SiCH₃), 17.28 (SiCMe₃), 26.03 [SiC(CH₃)₃], 90.58 (4-C), 93.06 (5-C), 93.12 (2-C), 98.27 (3-C) and 233.02 (CO); m/z (EI) 334 (M^+), 278, 250, 194, 158 and 52.

η^5 -[2-(*Methoxymethylthiophene*)]tricarbonylchromium(0).—Complexation of 2-methoxymethylthiophene (4.0 equiv.) with the naphthalene complex (1.15 g, 4.30 mmol) according to method B as described, gave the *title compound* as an air-sensitive orange crystalline solid (0.66 g, 58%); m.p. 101–102 °C (decomp.) (Found: C, 41.35; H, 3.0. $C_9H_8CrO_4S$ requires C, 40.91; H, 3.05%); $\delta_H(CDCl_3)$ 3.41 (3 H, s, OCH₃), 4.16 (1 H, d, J 12.2, CHHOCH₃), 4.27 (1 H, d, J 12.2, CHHOCH₃), 5.31 (1 H, d, J 3.4, 5-H), 5.45 (1 H, d, J 2.9, 3-H) and 5.54 (1 H, dd, J 3.4, 2.9, 4-H); m/z (EI) 264 (M^+), 236, 208, 180, 128, 97 and 52.

η^5 -[2-(*Trimethylsilylethoxymethylthiophene*)]tricarbonylchromium(0).—Complexation of 2-(trimethylsilylethoxymethylthiophene) (3.0 equiv.) with the naphthalene complex (0.50 g, 1.89 mmol) according to complexation method A as described, gave the *title compound* as an orange crystalline solid (0.17 g, 26%), m.p. 113–114 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1943, 1891 and 1870; $\delta_H(CDCl_3)$ 0.02 [9 H, s, Si(CH₃)₃], 0.96 (2 H, t, J 8.3, CH₂OCH₂CH₂TMS), 3.61 (2 H, t, J 8.3, CH₂OCH₂CH₂TMS), 4.17 (1 H, d, J 12.0, CHHOCH₂CH₂TMS), 4.31 (1 H, d, J 12.0, CHHOCH₂CH₂TMS), 5.30 (1 H, d, J 4.0, 5-H), 5.46 (1 H, br s, 3-H) and 5.34 (1 H, br s, 4-H); m/z (EI) 322 ($M^+ - CO$), 266, 213, 183, 155, 89 and 52.

η^5 -[2,5-(*Dimethylthiophene*)]tricarbonylchromium(0). **2**—(i) Complexation of 2,5-dimethylthiophene with naphthalene complex (2.31 g, 8.75 mmol) by method A as described, gave the *title compound 2* as an orange crystalline solid (1.80 g, 83%), m.p. 130 °C (lit.,³⁷ m.p. 132 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 1962, 1882 and 1866; $\delta_H(CDCl_3)$ ³⁷ 2.22 (6 H, s, 2,5-CH₃), 5.26 (2 H, s, 3,4-H); m/z (EI) 248 (M^+), 220, 192, 164, 111, 52 and 28. Complexation by method B gave **2** in a 64% yield.

(ii) Butyllithium (1.0 equiv.) was added to a solution of 2-methylthiophenetricarbonylchromium(0) (0.19 g, 0.80 mmol) in THF (10 cm³) at –78 °C. After 1 h, iodomethane (2.0 equiv.) was added and the solution was then allowed to warm to room temperature. Aqueous work-up and subsequent purification by column chromatography (3% diethyl ether–petroleum as eluent) gave the complex **2** (0.15 g, 75%) spectroscopically identical with that obtained above. Complex **2** was additionally prepared by methylation, in a similar manner to (ii) using KH-18-crown-6–MeI, in 46% yield and *via* the use of LiHMDS in 61% yield.

η^5 -[2,3,5-(*Trimethylthiophene*)]tricarbonylchromium(0) **4** (E = Me).—Butyllithium (1.05 equiv.) was added dropwise to a solution of 2,5-dimethylthiophene complex **2** (0.25 g, 3.02 mmol), TMEDA (0.46 cm³, 3.0 equiv.) in THF (10 cm³) at –78 °C, producing a significant darkening of the orange solution. After 1.5 h, iodomethane (0.32 cm³, 5.0 equiv.) was added dropwise and the solution then warmed to ambient temperature, during which time some precipitation occurred. TLC (multiple development in CCl₄) revealed a product spot, together with unchanged starting material. The reaction was quenched with deoxygenated water (1.0 cm³) and then filtered through a pad of silica. Aqueous work-up and subsequent purification by column chromatography (0–5% diethyl ether–hexane; gradient elution) afforded the η^5 -[2,3,5-trimethylthiophene]tricarbonylchromium(0) **4** (E = Me) as an orange crystalline solid (0.21 g, 80%), m.p. 145 °C (decomp.) (lit.,³⁷ m.p. 127 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 1957, 1878 and 1865; $\delta_H(CDCl_3)$ 2.16 (3 H, s, 3-CH₃), 2.18 (3 H, s, 5-CH₃), 2.20 (3 H, s, 2-CH₃) and 5.29 (1 H, s, 4-H); m/z (EI) 262 (M^+), 206, 178, 126, 111, 52 and 28. Less efficient results are given in Table 2.

η^5 -[2,5-(*Dimethyl-3-(trimethylsilylthiophene)*)]tricarbonylchromium(0) **4** (E = SiMe₃).—Butyllithium (1.05 equiv.) was added dropwise to a solution of the 2,5-dimethylthiophene complex **2** (1.0 g, 4.03 mmol), TMEDA (1.84 cm³, 3.0 equiv.) in THF (20 cm³) at –78 °C. After 1 h, TMSCl (1.28 cm³, 2.5 equiv.) was allowed to react with the β -lithio adduct and the complex **4** (E = SiMe₃) was collected as an orange crystalline solid (0.65 g, 51%), m.p. > 140 °C (decomp.) (Found: M^+ , 319.9994. $C_{12}H_{16}CrO_3SSi$ requires M , 319.9994); $\nu_{max}(\text{hexane})/cm^{-1}$ 1967, 1899, 1881 and 1216; $\delta_H(CDCl_3)$ 0.36 [9 H, s, Si(CH₃)₃], 2.17 (3 H, s, 5-CH₃), 2.21 (3 H, s, 2-CH₃) and 5.17 (1 H, s, 4-H); m/z (EI) 320 (M^+), 264, 250, 236, 221, 184, 73, 52 and 28. Less efficient results are given in Table 2.

η^5 -[2,5-(*Dimethyl-3-(trimethylstannylthiophene)*)]tricarbonylchromium(0) **4** (E = SnMe₃).—Butyllithium (0.89 cm³, 1.02 equiv.) was added dropwise to a solution of 2,5-dimethylthiophene complex **2** (0.54 g, 2.18 mmol) in THF (10 cm³) at –78 °C. After 2 h, trimethyltin chloride (0.47 g, 1.1 equiv.) was added and the solution then stirred for 1 h before being allowed to warm to ambient temperature. The reaction was quenched with water (5.0 cm³) and the mixture then filtered through a pad of silica and finally concentrated under reduced pressure. Purification by column chromatography (2–10% diethyl ether–hexane; gradient elution) gave, as the major product, the complex **4** (E = SnMe₃), isolated as an orange crystalline solid (0.35 g, 39%), m.p. 140 °C (Found: M^+ , 411.9247. $C_{12}H_{16}CrO_3SSn$ requires M , 411.9247); $\nu_{max}(CHCl_3)/cm^{-1}$ 1964, 1896 and 1875; $\delta_H(CDCl_3)$ 0.43 [9 H, s, Sn(CH₃)₃], 2.17 (3 H, s, 5-CH₃), 2.19 (3 H, s, 2-CH₃) and 5.12 (1 H, s, 4-H); m/z (EI) 412 (M^+), 356, 328, 297, 204 and 52; m/z (CI) 413 (MH⁺), 278, 249, 182 and 86.

η^5 -[4-(*Methoxycarbonyl-2,3,5-trimethylthiophene*)]tricarbonylchromium(0) **6**.—Butyllithium (2.0 equiv.) was added dropwise to a mixture of 2,3,5-trimethylthiophene complex **5** (50.0 mg, 0.19 mmol), TMEDA (0.08 cm³, 3.0 equiv.) and THF (2 cm³) at –78 °C. After 1 h, methyl chloroformate (0.03 cm³, 2.0 equiv.) was added and the solution stirred for a further 1 h, before quenching of the reaction with deoxygenated water (0.5 cm³). Aqueous work-up of the mixture and subsequent column chromatography (eluent: 15% diethyl ether–hexane) afforded the complex **6** as an air-sensitive orange oil (69.7 mg, 35%) (Found: M^+ , 319.9810. $C_{12}H_{12}CrO_5S$ requires M , 319.9810); $\delta_H(CDCl_3)$ 2.14 (3 H, s, 2-CH₃), 2.35 (3 H, s, 3-CH₃), 2.44 (3 H, s, 5-CH₃) and 3.90 (3 H, s, CO₂CH₃); m/z (EI) 320 (M^+), 264, 236, 184, 153, 125 and 28.

η^5 -[2,3,5-Trimethyl-4-(trimethylsilyl)thiophene]tricarbonylchromium(0) **7**.—*sec*-Butyllithium (1.0 equiv.) was added dropwise to a solution of 2,3,5-trimethylthiophene complex **5** (158 mg, 0.60 mmol) in dry diethyl ether (10 cm³) at -78°C . After 2 h, TMSCl (0.20 cm³, 2.5 equiv.) was added and the solution stirred for a further 1 h, before quenching of the reaction with water (0.5 cm³). Aqueous work-up and flash vacuum chromatography (eluent: 1% diethyl ether–hexane) afforded the *tetra*-substituted complex **7** as an orange solid (69.7 mg, 35%). Recrystallisation of this from hexane yielded a crop of fine thread-like crystals, m.p. 165–166 °C (Found: C, 46.6; H, 5.5; S, 9.4. C₁₃H₁₈CrO₃SSi requires C, 46.69; H, 5.43; S, 9.59%); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1953, 1875 and 1854; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.43 [9 H, s, Si(CH₃)₃], 2.10 (3 H, s, 2 or 5-CH₃), 2.17 (3 H, s, 5 or 2-CH₃) and 2.21 (3 H, s, 3-CH₃); $\delta_{\text{C}}(\text{CDCl}_3)$ 1.60 (SiCH₃), 13.63 (3-CH₃), 15.35 (2-CH₃), 17.00 (5-CH₃), 100.32 (ring C), 100.86 (ring C), 108.68 (ring C), 114.32 (ring C) and 234.47 (CO); m/z (EI) 334 (M⁺), 278, 250, 198 and 183.

η^5 -[2-(*tert*-Butyldimethylsilyl)-5-methylthiophene]tricarbonylchromium(0) **11** (E = Me).—Butyllithium (1.0 equiv.) was added to a solution of 2-(*tert*-butyldimethylsilyl)thiophene complex **8** (R₃ = Bu^tMe₂) (0.50 g, 1.49 mmol) in THF (10 cm³) at -78°C . After 1 h, iodomethane (0.24 cm³, 3.74 mmol) was added and the solution allowed to warm to ambient temperature. Purification of the product by column chromatography (1–4% diethyl ether–petroleum; gradient elution) afforded the complex **11** (E = Me) as an orange crystalline solid (0.42 g, 80%), m.p. 103 °C (decomp.) (Found: C, 48.5; H, 5.8. C₁₄H₂₀CrO₃SSi requires C, 48.25; H, 5.79%); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1957, 1873, 676, 652 and 628; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.19 (3 H, s, SiCH₃), 0.21 (3 H, s, SiCH₃), 0.92 [9 H, s, SiC(CH₃)₃], 2.32 (3 H, s, 5-CH₃), 5.38 (1 H, d, *J* 3.8, 4-H) and 5.47 (1 H, d, *J* 3.8, 3-H); $\delta_{\text{C}}(\text{CDCl}_3)$ –6.11 (SiCH₃), –5.76 (SiCH₃), 15.35 (5-CH₃), 17.30 [SiC(CH₃)₃], 26.05 [SiC(CH₃)₃], 93.42 (2-C), 93.90 (4-C), 99.17 (3-C), 111.41 (5-C) and 233.52 (CO); m/z (EI) 348 (M⁺), 292, 264, 208, 155 and 52.

This compound was also prepared by lithiation of 2-methylthiophenetricarbonylchromium(0) (0.20 g, 0.85 mmol) with butyllithium (1.0 equiv.), as described above, followed by a quench with TBSCl (1.05 equiv.). Purification as above afforded **11** (E = Me) (0.12 g, 41%).

η^5 -[2-(*tert*-Butyldimethylsilyl)-5-(methylsulfanyl)thiophene]tricarbonylchromium(0) **11** (E = SMe).—The complex **8** (R₃ = Bu^tMe₂) (0.25 g, 0.75 mmol) was treated with butyllithium as described above. To this solution was added dimethyl disulfide (0.13 cm³, 1.50 mmol) and the solution allowed to warm to ambient temperature. After aqueous work-up, the product was purified by column chromatography (eluent: 10% EtOAc–petroleum) to afford the complex **11** (E = SMe) as a red crystalline solid (0.20 g, 70%), m.p. > 50 °C (decomp.) (Found: MH⁺, 381.0106. C₁₄H₂₀CrO₃S₂Si requires 381.0107); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1967, 1895, 1880, 1258 and 1047; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.20 (3 H, s, SiCH₃), 0.22 (3 H, s, SiCH₃), 0.93 [9 H, s, SiC(CH₃)₃], 2.27 (3 H, s, SCH₃), 5.44 (1 H, d, *J* 3.17, 3-H) and 5.55 (1 H, d, *J* 3.17, 4-H); m/z (CI) 381 (MH⁺), 245, 199, 158, 132, 86 and 52.

η^5 -[5-(*tert*-Butyldimethylsilyl)-2-(*N*-phenylcarboxamido)thiophene]tricarbonylchromium(0) **11** (E = CONHPh).—The complex **8** (R₃ = Bu^tMe₂) (0.25 g, 0.75 mmol) was treated with butyllithium as described above. To this solution was added freshly distilled phenyl isocyanate (0.08 cm³, 1.02 equiv.) and the solution allowed to warm to ambient temperature. After aqueous work-up, despite its air sensitivity, the product was purified by column chromatography (10–30% diethyl ether–petroleum; gradient elution) to give the complex **11** (E = CONHPh), which was collected as a 'tacky' red solid (151 mg,

44%); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.20 (3 H, s, SiCH₃), 0.23 (3 H, s, SiCH₃), 0.93 [9 H, s, SiC(CH₃)₃], 5.40 (1 H, d, *J* 3.2, 3-H), 6.08 (1 H, d, *J* 3.2, 4-H) and 7.50 (5 H, m, Ph). Further characterisation was carried out on the uncomplexed thiophene (decomplexed by air/sunlight),²⁶ a white crystalline solid (123 mg, 36%), m.p. 132–133 °C (Found: M⁺, 317.1270. C₁₁H₂₃CrNOSSi requires M, 317.1270); $\nu_{\text{max}}(\text{hexane})/\text{cm}^{-1}$ 2940, 2963, 2858, 1664, 1523, 1441, 1320, 987, 840, 822 and 805; m/z (EI) 317 (M⁺), 260, 149, 32 and 28.

η^5 -[2-(*tert*-Butyldimethylsilyl)-5-iodothiophene]tricarbonylchromium(0) **11** (E = I).—The complex **8** (R₃ = Bu^tMe₂) (0.15 g, 0.45 mmol) was treated with butyllithium as described. To this solution was added a solution of iodine (0.11 g, 0.45 mmol) in dry THF (7 cm³) over 35 min, affording a purple–black solution. The reaction was quenched at -78°C with 2 mol dm⁻³ aqueous sodium thiosulfate (10 cm³) followed by an aqueous work-up to give the crude product as a brown viscous oil. Purification of this by column chromatography (eluent: 5% diethyl ether–hexane) afforded the complex **11** (E = I) as an air-sensitive orange crystalline solid (57.5 mg, 28%), m.p. 106–108 °C (Found: M⁺, 459.9119. C₁₃H₁₇CrIO₃SSi requires M⁺, 459.9120); $\nu_{\text{max}}(\text{CHCl}_3)$ 1970, 1899, 1467, 1382, 1098 and 917; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.22 (3 H, s, SiCH₃), 0.24 (3 H, s, SiCH₃), 0.91 [9 H, s, SiC(CH₃)₃], 5.32 (1 H, d, *J* 3.17, 4-H) and 5.70 (1 H, *J* 3.17, 3-H); $\delta_{\text{C}}(\text{CDCl}_3)$ –6.10 (SiCH₃), –5.83 (SiCH₃), 17.41 [SiC(CH₃)₃], 26.02 [SiC(CH₃)₃], 100.61, 136.56 (2,3,4,5-C) and 232.82 (CO); m/z (EI) 460 (M⁺), 404, 376, 324, 267, 141, 83, 73, 52 and 28.

η^5 -[2-(*tert*-Butyldimethylsilyl)-5-(*prop*-2-enyl)thiophene]tricarbonylchromium(0) **11** (E = CH₂CH=CH₂).—Butyllithium (1.02 equiv.) was added dropwise to a solution of the thiophene complex **8** (R₃ = Bu^tMe₂) (0.25 g, 0.75 mmol) in THF (12 cm³) at -78°C . After 1 h, CuBr·SMe₂ (0.30 g, 2.0 equiv.) was added *via* a solid addition tube. The mixture was allowed to warm to -15°C and then stirred for 40 min. After the reaction mixture had been recooled to -78°C , allyl bromide (0.19 cm³, 2.24 mmol) was added to it and the whole left for 1 h before being allowed to warm to room temperature. The dark brown solution was filtered through a pad of silica, treated to an aqueous work-up and purified by column chromatography (eluent: 2% diethyl ether–petroleum) to afford the complex **11** (E = CH₂CH=CH₂) as an orange crystalline solid (0.20 g, 72%), m.p. 63–64 °C (Found: C, 51.3; H, 5.9%. M⁺, 374.0464. C₁₆H₂₂CrO₃SSi requires C, 51.6; H, 5.9%; M, 374.0464); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1960, 1883, 1863 and 1258; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.21 (3 H, s, SiCH₃), 0.22 (3 H, s, SiCH₃), 0.92 [9 H, s, SiC(CH₃)₃], 3.27 (1 H, dd, *J* 16.90, 7.33, CHHCH=CH₂), 3.36 (1 H, dd, *J* 16.80, 6.59, CHHCH=CH₂), 5.18 (1 H, m, CH₂CH=CHH), 5.23 (1 H, m, CH₂CH=CHH), 5.37 (1 H, d, *J* 3.0, 4-H), 5.49 (1 H, d, *J* 3.0, 3-H) and 5.88 (1 H, ddt, *J* 17.20, 10.0, 6.80, CH₂CH=CH₂); $\delta_{\text{C}}(\text{CDCl}_3)$ –6.03 (SiCH₃), –5.68 (SiCH₃), 17.40 [SiC(CH₃)₃], 26.17 [SiC(CH₃)₃], 33.74 (CH₂CH=CH₂), 92.67 (3-C), 93.57 (2-C), 99.30 (4-C), 115.45 (5-C), 118.99 (CH₂CH=CH₂), 133.98 (CH₂CH=CH₂) and 233.50 (CO); m/z (EI) 374 (M⁺), 318, 290, 234, 181 and 52.

η^5 -[2-Acetyl-5-(*tert*-butyldimethylsilyl)thiophene]tricarbonylchromium(0) **11** (E = COMe).—The 2-thienylcopper species was prepared as described above, from the complex **8** (R₃ = Bu^tMe₂) (0.20 g, 0.60 mmol), butyllithium, THF (10 cm³) and CuBr·SMe₂ (0.24 g; added *via* a solid addition tube). Acetyl chloride (0.21 cm³, 2.95 mmol) was added and the mixture was left for 1 h before being allowed to warm to room temperature. The solution was quenched with 2 mol dm⁻³ aqueous sodium hydrogencarbonate and then treated to an aqueous work-up. The crude red–black solid was purified by column chromatography

graphy (5–20% diethyl ether–hexane; gradient elution) to give the complex **11** (E = COMe) as an oily red crystalline solid (0.13 g, 54%) (Found: M^+ , 376.0259. $C_{15}H_{20}CrO_4SSi$ requires M , 376.0257); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1970, 1930, 1886, 1669, 1267, 1252, 836, 822, 806 and 776; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.20 (3 H, s, SiCH_3), 0.22 (3 H, s, SiCH_3), 0.94 [9 H, s, $\text{SiC}(\text{CH}_3)_3$], 2.32 (3 H, s, COCH_3), 5.47 (1 H, d, J 3.6, 3-H) and 5.99 (1 H, d, J 3.6, 4-H); $\delta_{\text{C}}(\text{CDCl}_3)$ –6.30 [$\text{Si}(\text{CH}_3)_2$], 17.26 [$\text{SiC}(\text{CH}_3)_3$], 26.02 [$\text{SiC}(\text{CH}_3)_3$ and COCH_3], 93.43 (3-C), 97.87 (4-C), 98.47 (5-C), 103.74 (2-C), 193.58 (COCH_3) and 231.93 [$\text{Cr}(\text{CO})_3$]; m/z (EI) 376 (M^+), 320, 292, 236, 183 and 52.

η^5 -[5-(*tert*-Butyldimethylsilyl)-2,3-dimethylthiophene]tricarbonylchromium(0) **9** (E = E' = Me).—Butyllithium (1.02 equiv.) was added dropwise to a 0.1 mol dm^{-3} solution of 2-(*tert*-butyldimethylsilyl)-5-methylthiophenetricarbonylchromium complex **11** (E = Me) (1.84 g, 5.29 mmol) in dry THF (25 cm^3) at -78°C . After 2 h, iodomethane (0.66 cm^3 , 2.0 equiv.) was added and the solution stirred for a further 1 h, followed by warming to ambient temperature. The resulting solution was filtered through a pad of silica and then treated to an aqueous work-up to afford the crude product. Purification by flash column chromatography (eluent: 2% diethyl ether–petroleum) afforded the complex **9** (E = E' = Me) as an orange crystalline solid (1.39 g, 73%), m.p. 152–155 $^\circ\text{C}$ (Found: C, 49.8; H, 6.0%; MH^+ , 363.0542. $C_{14}H_{20}CrO_3SSi$ requires C, 49.70; H, 6.02%; MH^+ , 363.0542); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1956, 1878, 1859, 1111 and 837; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.18 (3 H, s, SiCH_3), 0.21 (3 H, s, SiCH_3), 0.92 [9 H, s, $\text{SiC}(\text{CH}_3)_3$], 2.19 (3 H, s, 3- CH_3), 2.24 (3 H, s, 2- CH_3) and 5.45 (1 H, s, 4-H); $\delta_{\text{C}}(\text{CDCl}_3)$ –6.16 (SiCH_3), –5.76 (SiCH_3), 13.82 (3- CH_3), 13.90 (2- CH_3), 17.34 (SiCMe_3), 26.16 [$\text{SiC}(\text{CH}_3)_3$], 91.30 (5-C), 102.76 (4-C), 108.08 and 109.44 (2,3-H) and 234.12 (CO); m/z (EI) 362 (M^+), 306, 278, 222, 169, 58, 52 and 28.

η^5 -[5-(*tert*-Butyldimethylsilyl)-3-methoxycarbonyl-2-methylthiophene]tricarbonylchromium(0) **9** (E = Me, E' = CO_2Me).—The complex **11** (E = Me) (83.4 mg, 0.43 mmol) was treated with butyllithium as described above. To the resulting solution was added methyl chloroformate (0.04 cm^3 , 2.0 equiv.) and the mixture worked up as above. Purification by column chromatography (eluent: 2% diethyl ether–petroleum) afforded the complex **9** (E = Me, E' = CO_2Me) as an orange crystalline solid (57.8 mg, 60%), m.p. 110–115 $^\circ\text{C}$ (decomp.) (Found: MH^+ , 407.0441. $C_{16}H_{22}CrO_5SSi$ requires MH^+ 407.0441); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1971, 1899 and 1885; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.210 (3 H, s, SiCH_3), 0.213 (3 H, s, SiCH_3), 0.94 [9 H, s, $\text{SiC}(\text{CH}_3)_3$], 2.59 (3 H, s, 2- CH_3), 3.38 (3 H, s, CO_2CH_3) and 5.95 (1 H, s, 4-H); $\delta_{\text{C}}(\text{CDCl}_3)$ –6.05 (SiCH_3), –5.56 (SiCH_3), 15.82 (2- CH_3), 17.39 [$\text{SiC}(\text{CH}_3)_3$], 26.12 [$\text{SiC}(\text{CH}_3)_3$], 52.47 (CO_2CH_3), 90.33 (4-C), 92.37 (5-C), 101.70 (2-C), 112.32 (3-C), 165.55 (CO_2CH_3) and 228.91 [$\text{Cr}(\text{CO})_3$]; m/z (CI) 407 (MH^+), 271, 230, 213 and 125.

η^5 -[5-(*tert*-Butyldimethylsilyl)-2-methyl-3-(trimethylstannyl)thiophene]tricarbonylchromium(0) **9** (E = Me, E' = SnMe_3).—The complex **11** (E = Me) (0.15 g, 0.43 mmol) was allowed to react with butyllithium as described above. To this solution was added a solution of trimethyltin chloride (94.3 mg, 1.1 equiv.) in dry THF (1 cm^3), the temperature being maintained at $< -70^\circ\text{C}$ and the mixture worked up as above. Purification by column chromatography (eluent: 3% diethyl ether–petroleum) afforded the stannyl complex **9** (E = Me, E' = SnMe_3) as a red oil (0.10 g, 45%) (Found: M^+ , 511.9958. $C_{17}H_{28}CrO_3SSiSn$ requires M , 511.9955); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1953, 1880 and 1860; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.17 (3 H, s, SiCH_3), 0.21 (3 H, s, SiCH_3), 0.44 [9 H, s, $\text{Sn}(\text{CH}_3)_3$], 0.91 [9 H, s, $\text{SiC}(\text{CH}_3)_3$],

2.26 (3 H, s, 2- CH_3) and 5.27 (1 H, s, 4-H); m/z (EI) 512 (M^+), 456, 428, 376, 372, 319, 242, 155, 73, 52 and 28.

η^5 -[5-(*tert*-Butyldimethylsilyl)-3-iodo-2-methylthiophene]tricarbonylchromium(0) **9** (E = Me, E' = I).—The complex **11** (E = Me) (0.15 g, 0.43 mmol) was allowed to react with butyllithium as described above. To this solution, was added a solution of iodine (0.11 g, 1.0 equiv.) in dry THF (7 cm^3) slowly over 10 min, a very dark brown solution being generated. After being allowed to warm to room temperature, the solution was shaken with a 2 mol dm^{-3} aqueous sodium thiosulfate (10 cm^3), prior to aqueous work-up. Purification of the product by column chromatography (eluent: petroleum) afforded the iodo complex **9** (E = Me, E' = I) as an orange crystalline solid (69.6 mg, 34%), m.p. 118–118.5 $^\circ\text{C}$ (Found: C, 35.2; H, 4.0%; MH^+ , 474.9364. $C_{14}H_{19}CrIO_3SSi$ requires C, 35.45; H, 4.04%; MH^+ , 474.9354); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1964, 1893, 1861 and 1255; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.19 (3 H, s, SiCH_3), 0.21 (3 H, s, SiCH_3), 0.94 [9 H, s, $\text{SiC}(\text{CH}_3)_3$], 2.38 (3 H, s, 2- CH_3) and 5.59 (1 H, s, 4-H); $\delta_{\text{C}}(\text{CDCl}_3)$ –6.27 (SiCH_3), –5.77 (SiCH_3), 17.42 (2- CH_3), 17.49 [$\text{SiC}(\text{CH}_3)_3$], 26.07 [$\text{SiC}(\text{CH}_3)_3$], 105.81 (4-C) and 233.52 (CO); m/z (CI) 475 (MH^+), 418, 391, 348, 339, 323, 281, 241, 213, 197, 155 and 133.

η^5 -[5-(*tert*-Butyldimethylsilyl)-2-methyl-3-(*prop*-2-enyl)thiophene]tricarbonylchromium(0) **9** (E = Me, E' = $\text{CH}_2\text{CH}=\text{CH}_2$).—The 3-thienylcopper species was prepared, analogously to the 2-thienyl isomer described above, from the complex **11** (E = Me) (0.25 g, 0.71 mmol), butyllithium, THF (12.5 cm^3) and $\text{CuBr}\cdot\text{SMe}_2$ (0.29 g; added *via* a solid addition tube). Allyl bromide (0.18 cm^3 , 3.0 equiv.) was added to the brown suspension at -78°C which was then allowed to warm to room temperature. An aqueous work-up applied as before together with purification by column chromatography (eluent: 2% diethyl ether–hexane), followed by flash chromatography (1% diethyl ether–hexane) afforded the pure complex **9** (E = Me, E' = $\text{CH}_2\text{CH}=\text{CH}_2$) as an orange crystalline solid (96.8 mg, 35%), m.p. 142–143 $^\circ\text{C}$ (Found: M^+ , 388.062. $C_{17}H_{24}CrO_3SSi$ requires M , 388.0620); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.20 (3 H, s, SiCH_3), 0.21 (3 H, s, SiCH_3), 0.92 [9 H, s, $\text{SiC}(\text{CH}_3)_3$], 2.23 (3 H, s, 2- CH_3), 3.15 (1 H, dd, J 17.0, 6.5, $\text{CHHCH}=\text{CH}_2$), 3.28 (1 H, dd, J 17.0, 6.1, $\text{CHHCH}=\text{CH}_2$), 5.08 (1 H, m, $\text{CH}_2\text{CH}=\text{CHH}$), 5.19 (1 H, m, $\text{CH}_2\text{CH}=\text{CHH}$), 5.45 (1 H, s, 4-H) and 5.94 (1 H, m, $\text{CH}_2\text{CH}=\text{CH}_2$); m/z (EI) 388 (M^+), 332, 304, 248, 212, 195 and 52.

η^5 -[5-(*tert*-Butyldimethylsilyl)-3-(*prop*-2-enyl)-2-methylsulfanylthiophene]tricarbonylchromium(0) **9** (E = SMe , E' = $\text{CH}_2\text{CH}=\text{CH}_2$).—The 3-thienylcopper species was prepared as described above from complex **11** (E = Me) (118 mg, 0.31 mmol), butyllithium, THF (10 cm^3) and $\text{CuBr}\cdot\text{SMe}_2$ (0.13 g; added *via* a solid addition tube). Allyl bromide (0.07 cm^3 , 0.75 mmol) was added and the mixture was left for 1 h, before being allowed to warm to room temperature. The dark brown solution was filtered through a pad of silica, and then treated to an aqueous work-up. Purification by column chromatography (eluent: 2% diethyl ether–petroleum) afforded an orange crystalline solid (0.10 g, ~77%) which was further purified by recrystallisation from hexane, to give deep red crystals of the complex **9** (E = SMe , E' = $\text{CH}_2\text{CH}=\text{CH}_2$) (40.4 mg, 31%), m.p. 92–93 $^\circ\text{C}$ (Found: C, 48.6; H, 5.8%; M^+ , 420.0340. $C_{17}H_{24}CrO_3S_2Si$ requires C, 48.55; H, 5.75%; M , 420.0341); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1963, 1899 and 1879; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.196 (3 H, s, SiCH_3), 0.206 (3 H, s, SiCH_3), 0.94 [9 H, s, $\text{SiC}(\text{CH}_3)_3$], 2.38 (3 H, s, SCH_3), 3.34 (2 H, d, J 6.35, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.16 (1 H, dd, J 16.85, 1.47, $\text{CH}_2\text{CH}=\text{CHH}$), 5.20 (1 H, dd, J 10.25, 1.46, $\text{CH}_2\text{CH}=\text{CHH}$), 5.45 (1 H, s, 4-H) and 6.07 (1 H, ddt, J 16.72, 10.25, 6.35, $\text{CH}_2\text{CH}=\text{CH}_2$); $\delta_{\text{C}}(\text{CDCl}_3)$ –6.18 (SiCH_3), –5.95 (SiCH_3), 17.40 [$\text{SiC}(\text{CH}_3)_3$], 22.40 (SCH_3), 26.20

[SiC(CH₃)₃], 33.00 (CH₂CH=CH₂), 94.71 (4-C), 100.86 (5-C), 107.43 (2-C), 115.70 (3-C), 117.42 (CH₂CH=CH₂), 135.64 (CH₂CH=CH₂) and 233.04 (CO); *m/z* (CI) 421 (MH⁺), 285, 271, 239, 132, 58 and 45; (EI) 420 (M⁺), 336, 284, 227, 73 and 52.

η^5 -(2,3-Dimethylthiophene)tricarbonylchromium(0) **10**.—TBAF (3.0 equiv.) was dissolved in THF (13 cm³) and then added *via* a cannula to the complex **9** (E = E' = Me) (0.20 g, 0.55 mmol) in THF at -30 °C. The solution darkened over 45 min at -30 °C and was then warmed to room temperature. Aqueous work-up afforded an orange solid which was purified by flash chromatography (eluent: 6% diethyl ether-hexane), to yield the complex **10** as orange crystals (85.2 mg, 62%), m.p. 123–125 °C (lit.,³⁷ m.p. 100 °C) (Found: M⁺, 247.9600. C₉H₈CrO₃S requires *M*, 247.9599); ν_{\max} (CHCl₃)/cm⁻¹ 1962, 1893 and 1882; δ_{H} (CDCl₃)³⁷ 2.198 (3 H, s, 3-CH₃), 2.202 (3 H, s, 2-CH₃), 5.19 (1 H, d, *J* 3.56, 5-H) and 5.50 (1 H, d, *J* 3.56, 4-H); δ_{C} (CDCl₃) 13.59 (3-CH₃), 13.76 (2-CH₃), 83.19 (4-C), 95.54 (5-C), 103.00 (3-C), 106.93 (2-C) and 233.70 (CO); *m/z* (EI) 248 (M⁺), 220, 192, 164, 111, 97 and 52; *m/z* (CI) 249 (MH⁺), 221, 199, 182, 86 and 52.

2,3-Dimethylthiophene.—A solution of the 2,3-dimethylthiophene complex **10** (0.20 g, 0.81 mmol) in diethyl ether (25 cm³) was placed in direct sunlight for 6–12 h resulting in complete oxidation, as seen by a total loss of the orange colouration with concomitant green precipitation. The suspension was dried and then filtered through a pad of silica, followed by solvent removal to give 2,3-dimethylthiophene as a colourless liquid (87.5 mg, 96%); δ_{H} (CDCl₃) 2.06 (3 H, s, 2-CH₃), 2.31 (3 H, s, 3-CH₃), 6.78 (1 H, d, *J* 5.4, 4-H) and 6.87 (1 H, d, *J* 5.4, 5-H), identical with the reported data.⁴⁰

η^5 -[2,3-Dimethyl-5-methoxycarbonylthiophene]tricarbonylchromium(0) **13**.—LDA (0.37 cm³, 0.74 mmol; 1.2 equiv.) was added dropwise to a solution of 2,3-dimethylthiophene complex **10** (115 mg, 0.46 mmol) in THF (8 cm³) at -78 °C producing a significant colour change from yellow to red. After 1 h, methyl chloroformate (0.09 cm³, 2.5 equiv.) was added and the solution then warmed to room temperature. Filtration through a pad of silica, followed by an aqueous work-up, afforded an air-sensitive red oil. Purification by column chromatography (0–25% diethyl ether-petroleum; gradient elution) afforded the complex **13** as a red crystalline solid (74.7 mg, 53%); m.p. 87–89 °C (decomp.) (Found: M⁺, 306.9653. C₁₁H₁₀CrO₃S requires *M*, 306.9654); ν_{\max} (CHCl₃)/cm⁻¹ 1976, 1908, 1880 and 1718; δ_{H} (CDCl₃) 2.18 (3 H, s, 3-CH₃), 2.22 (3 H, s, 2-CH₃), 3.79 (3 H, s, CO₂CH₃) and 6.07 (1 H, s, 4-H); *m/z* (EI) 306 (M⁺), 250, 222, 170, 139, 111, 52 and 28.

5-Methoxycarbonyl-2,3-dimethylthiophene **14**.—Decomplexation of the complex **13** (35.0 mg, 0.11 mmol) as described above, afforded the title compound **14** as a yellow oil (17.0 mg, 91%) (Found: M⁺, 170.0402. C₈H₁₀O₂S requires *M*, 170.0402); ν_{\max} (film)/cm⁻¹ 2360, 1705, 1455, 1296, 1261, 1222, 1115 and 1072; δ_{H} (CDCl₃) 2.14 (3 H, s, 3-CH₃), 2.37 (3 H, s, 2-CH₃), 3.84 (3 H, s, CO₂CH₃) and 7.50 (1 H, s, 4-H); *m/z* (EI) 170 (M⁺), 139, 111, 67 and 57.

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