Enhanced Lability of α-Silyl Groups in Thiophenetricarbonylchromium(o) Complexes

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Deprotonation of 2-(trialkylsilyl)-5-methylthiophenetricarbonylchromium(o) complexes **8a–e** with Bu^{t}Li resulted in intermolecular silyl transfer reactions which generated, *inter alia*, 2-methyl-3-(trialkylsilyl)thiophenetricarbonylchromium(o) **9** and 3,5-bis(trialkylsilyl)-2-methylthiophenetricarbonylchromium(o). The bulky silanes **8d, e** were stable under these conditions.
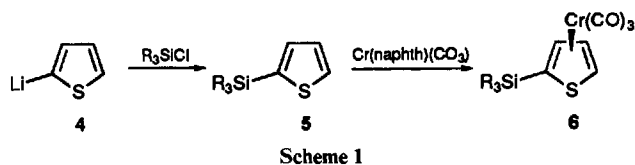
Benezenetricarbonylchromium(o) complexes **1** are well defined, generally stable compounds, with a rich chemistry[1–4] and many applications in organic synthesis have been demonstrated.[5–14] A distinctive feature of these applications has been the use of the trimethylsilyl group as a readily removable (tetrabutylammonium fluoride–THF–room temperature) protecting and blocking group for particular sites on the benzene ring.[15–17]

In contrast, the heteroaromatic complexes tend to be more labile and difficult to prepare and handle[18,19] and, in consequence, their chemistry has been little explored. The usefulness of silane protection has only been demonstrated for one group, the η^6-pyridine complexes **2** where, most notably, silane groups at C-2 and C-6 were used to block the otherwise dominant σ-coordination of the chromium atom by the pyridine nitrogen atom.[16,20]

So far, only for one heterocyclic system, thiophene, has the corresponding η-tricarbonylchromium complex **3** proved to be of comparable stability to the benzene complexes.[21] It was during a study of the possible synthetic applications of thiophene complexes that we noted the unusually high lability of silyl groups attached to the thiophene α-positons.[22] We report here a full account of those observations.
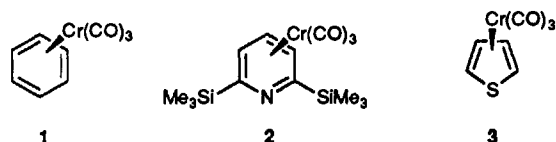
Complexes **6** were readily prepared from commercially available 2-thienyllithium **4** (Scheme 1). Silylation of **4** with the
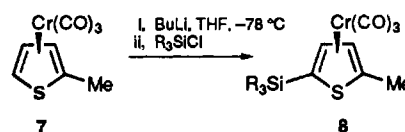

Scheme 1

appropriate chlorosilane and complexation of the resultant 2-(trialkylsilyl)thiophenes **5** by ligand transfer from naphthalenetricarbonylchromium(o),[23] in an 8:1 mixture of ethyl acetate and THF under an inert atmosphere, at reflux, for 2–3 h gave **6**.

The 5-lithiation of **6** (R = Me) was expected to be relatively trivial but treatment with 1 equiv. of butyllithium alone at −78 °C in THF produced a new material of lower R_F than **6** (R = Me) on TLC analysis. The material proved to be thio-

phene complex **3**, the product of desilation and the process was found to be complete after ~3 h at −78 °C, conditions under which such trimethylsilyl groups are normally stable.[15–17] Surprisingly, treatment of **6** with *tert*-butyllithium under the same conditions also produced complete desilylation and the amide bases, lithium diisopropylamide and lithium 2,2,6,6-tetramethylpiperidide also caused partial desilylation.

It is not clear, therefore, whether these desilylations occurred by a direct attack of the bases on the silicon centre to form an 'ate' complex intermediate or whether electron transfer reactions are involved, but the practical consequence is that trimethylsilyl groups are not suitable as blocking groups on thiophene complexes. We therefore undertook to study a range of silyl groups in order to determine the minimum requirement for stability. In doing so, further complications were uncovered.

Thus, the 2-trialkylsilyl-5-methylthiophene complexes **8a–e** were synthesised (Scheme 2) in moderate **8e** (R = Pr^i) (37%) to

Scheme 2

good **8a** (R = Me) (96%) yield by lithiation (BuLi–THF at −78 °C) of the complex **7** followed by a chlorosilane quench. The regiochemistry of the substitution was confirmed unambiguously by an NOE experiment (see Experimental section). In the case of the triethylsilyl complex, the product was accompanied by 5% of the 3,5-bistriethylsilyl analogue which was readily separated by flash chromatography.

The complexes **8**, upon treatment with alkyllithium, offer competition between desilylation and deprotonation at a β-position. In the event, treatment of complexes **8a–e** (see Table 1) with 1 equiv. of Bu^{t}Li in THF for 3 h at −78 °C gave, after protic work-up and in varying proportions, one or more of four products (Table 1).

The trimethylsilyl complex **8a**, as before with butyllithium, gave the desilylation product **7** in an isolated yield of 80%. With its slightly more sterically demanding triethylsilyl group, **8b** gave the expected desilylation product **7** and, in addition, the interesting 2,3-disubstituted thiophene complex **9b**. With increasing steric demand, the proportion of the rearranged silane **9** increased and indeed a third product, the desilylated compound **10c**, appeared in the reaction of **8c**. The hindered complexes **8d, e** each gave unchanged starting material under these conditions. That lithiation had, nevertheless, occurred
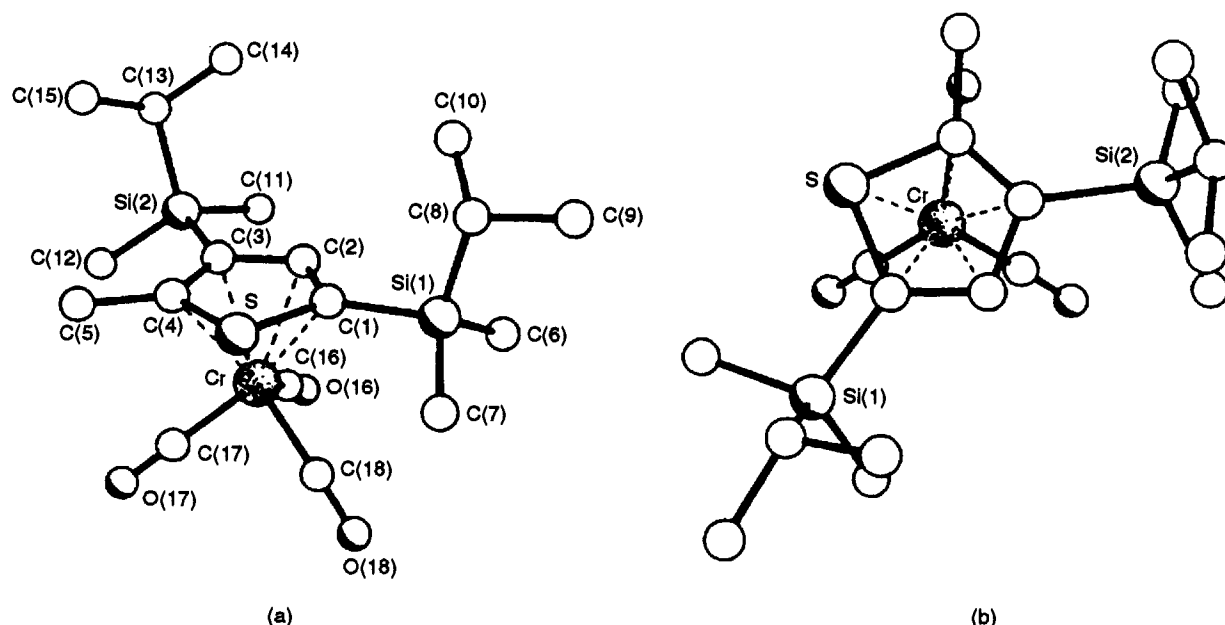
(a)   (b)

Fig. 1   (a) Molecular structure of complex 10c; (b) plan view showing the orientation of the carbonyl groups relative to the thiophene substituents

Table 1   Silyl group migrations

8	R₃	Cr(CO)₃ 7 %	(OC)₃Cr SiR₃ 9 %	(OC)₃Cr X 8, X = H %	10, X = SiR₃ %
a	Me₃	80	–	–	–
b	Et₃	51	27	–	–
c	Pr^{i}Me₂	30	59	–	11
d	Bu^{t}Me₂	–	–	90	–
e	Pr$^i_3$	–	–	95	–

Scheme 3

was demonstrated by a ^{2}H₂O work-up on complex **8d** which produced the 3-deuteriated (93% ^{2}H) complex **8d** (3-^{2}H) in 82% yield.

The structures of these products were again defined by NOE correlation of the proximal ring/side chain protons and by an X-ray diffraction analysis of the desilylated product **10c** (Fig. 1). In addition to the identification of the substitution pattern, the crystal structure shows that, as with thiophene complex itself, the tricarbonylchromium unit adopts a solid-state comformation with one CO group *anti* to the sulfur atom and the other two exlipsing the C-2/-5 positions. This is indicative of enhanced electron deficiency, and thus enhanced anion stabilisation, at these centres.[24]

The formation of the observed products can be rationalised in terms of two competing reactions, α-desilylation and β-deprotonation, of **8** (Scheme 3). It is pertinent to note that the trimethylsilyl group in β-trimethylsilylthiophene complexes is inert to alkyllithium bases under the conditions used in these experiments and any migration of silyl group to a β-site can, therefore, be assumed to be irreversible. Thermodynamically, α-desilylation, driven by the high stability of the α-lithio-anions, **11, 12**, would be favoured over the β-deprotonation, but steric hindrance to attack at silicon would kinetically favour the latter.

In the compounds **8**, when R = Me₃, 2-desilylation by Bu^{t}Li in THF is rapid and is the only process observed, affording the anionic complex **11** of the isolated product 2-methylthiophenetricarbonylchromium(o) **7**. When R₃ = Et₃, regioselective
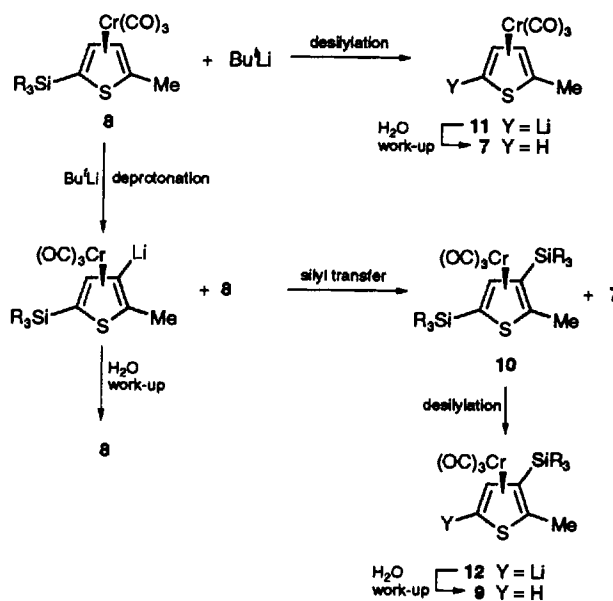
β-deprotonation competes with 2-desilylation. The former, by silyl group transfer,[25] gives the trisubstituted complex **10b** which is then completely desilylated to the disubstituted complex anion **12b** of the protonated product **9b**. When R₃ = Pr^{i}Me₂, increased steric hindrance of the alkylsilane results in preferential deprotonation and the 2,4-disilylated product **10c** remains in the product mixture. When R₃ = Bu^{t}Me₂ or Pr$^i_3$, β-deprotonation is the only reaction observed and therefore the proton quench regenerates the starting complexes **8d, e**.

Such facile desilylation by alkyllithium is unprecedented in arenetricarbonylchromium chemistry for which fluoride ion is the normal reagent. These observations impose limitations on the use of silane protecting/directing groups in these complexes as the size of the base stable silyl groups (**8–12d** and **e** series) dictates that only remote functionalisation is possible by established procedures.

Experimental

η⁵-[2-*Methyl*-5-(*trimethylsilyl*)*thiophene*]*tricarbonyl-chromium*(o) **8a**.—Addition of butyllithium (1.02 equiv.) over ~ 10 min to a solution of 2-methylthiophenetricarbonyl-chromium(o) 7²⁶ (1.00 g, 4.27 mmol) in THF (17 cm³) at −78 °C slowly converted the orange solution to a 'mustard' coloured suspension. After 1 h, chlorotrimethylsilane (1.2 equiv.) was added dropwise to the suspension to produce a red solution. This, after warming to room temperature followed by an aqueous work-up afforded the product which was purified by column chromatography (eluent: 5% diethyl ether–petroleum) to give the *complex* **8a** as an orange crystalline solid (1.26 g, 96%), m.p. 115–116 °C (decomp.) (Found: M⁺, 305.9838. C₁₁H₁₄CrO₃SSi requires *M*, 305.9838); *v*ₘₐₓ(hexane)/cm⁻¹ 1970, 1900, 1889, 1481, 1389 and 739; δ_H(CDCl₃) 0.27 [9H, s, Si(CH₃)₃], 2.31 (3 H, s, 2-CH₃), 5.34 (1 H, d, *J* 3.17, 3-H) and 5.46 (1 H, d, *J* 2.93, 4-H); *m/z* (EI) 306 (M⁺), 250, 222, 170, 155, 141, 127, 73, 52 and 28.

η⁵-[2-*Methyl*-5-(*triethylsilyl*)*thiophene*]*tricarbonyl-chromium*(o) **8b** *and* η⁵-[2-*methyl*-3,5-*bis*(*triethylsilyl*)*thio-phene*]*tricarbonylchromium*(o) **10b**.—Butyllithium (1.0 equiv.) was added to a solution of the 2-methylthiophene complex 7 (0.40 g, 1.70 mmol) in THF (10 cm³). After 1 h, chlorotri-ethylsilane (0.57 cm³, 2.0 equiv.) was added to the mixture which was then warmed to room temperature. After aqueous work-up, column chromatography (eluent: 5% diethyl ether–petroleum) separated two products. The first component was identified as η⁵-[2-*methyl*-3,5-*bis*(*triethylsilyl*)*thiophene*]*tricarb-onylchromium* **10b** as a red crystalline solid (39.2 mg, 5%), m.p. 65 °C (Found: M⁺, 462.1172. C₂₀H₃₄CrO₃SSi₂ requires *M*, 462.1172); *v*ₘₐₓ(CHCl₃)/cm⁻¹ 1963, 1894 and 1880; δ_H-(CDCl₃) 0.75 [6 H, m, 3-Si(CH₂CH₃)₃], 0.90 [6 H, m, 5-Si(CH₂CH₃)₃], 1.00 [18 H, m, 3,5-Si(CH₂CH₃)₃], 2.31 (3 H, s, 2-CH₃) and 5.38 (1 H, s, 4-H); *m/z* (EI) 462 (M⁺), 433, 406, 378, 350, 322, 297, 269, 241, 87, 59, 52 and 28.

The second component was the desired title product **8b**, isolated as an orange oil (0.51 g, 87%) (Found: M⁺, 348.0309. C₁₄H₂₀CrO₃SSi *M*, requires 348.0307); *v*ₘₐₓ(CHCl₃)/cm⁻¹ 1957, 1897, 1881, 674, 650 and 632; δ_H(CDCl₃) 0.76 [6 H, m, Si(CH₂CH₃)₃], 1.01 [9 H, t, *J* 8.0, Si(CH₂CH₃)₃], 2.32 (3 H, s, 2-CH₃), 5.34 (1 H, d, *J* 2.93, 3-H) and 5.51 (1 H, d, *J* 2.93, 4-H); *m/z* (EI) 348 (M⁺), 292, 264, 236, 208, 183, 155, 127, 52 and 28.

η⁵-[2-(*Dimethylisopropylsilyl*)-5-*methylthiophene*]*tricarb-onylchromium*(o) **8c**.—Butyllithium (1.0 equiv.) was added over ~ 10 min to a solution of the 2-methylthiophene complex 7 (1.50 g, 6.4 mmol) in THF (25 cm³) at −78 °C. After 1 h, chlorodimethylisopropylsilane (2.0 cm³, 2.0 equiv.) was added dropwise to the mixture, so as to produce a colour change to red. Aqueous work-up and flash chromatography (eluent: 5% diethyl ether–petroleum), gave the *complex* **8c** as an orange crystalline solid (2.00 g, 92%); m.p. 96–97 °C (Found: M⁺, 334.0151. C₁₃H₁₈CrO₃SSi requires *M*, 334.0151); *v*ₘₐₓ(CHCl₃)/cm⁻¹ 1970, 1899, 1889, 1470, 1458 and 764; δ_H(CDCl₃) 0.32 (3 H, s, SiCH₃), 0.37 (3 H, s, SiCH₃), 0.89 [1 H, m, SiCH(CH₃)₂], 1.02 [6 H, d, *J* 7.3, SiCH(CH₃)₂], 5.35 (1 H, dd, *J* 3.17, 0.49, 4-H) and 5.46 (1 H, d, *J* 3.17, 3-H); *m/z* (EI) 334 (M⁺), 278, 250, 208, 198, 167, 155 and 52.

η⁵-[2-*Methyl*-5-(*triisopropylsilyl*)*thiophene*]*tricarbonyl-chromium*(o) **8e**.—Butyllithium (1.0 equiv.) was added to a solution of the 2-methylthiophene complex 7 (1.80 g, 7.69 mmol) in THF (25 cm³) at −78 °C to form an orange–brown suspension over 1.5 h. Chlorotriisopropylsilane (1.0 equiv.) was added dropwise to the suspension which changed to a red solution. After the solution had warmed to room temperature, it was stirred for 12 h and then subjected to aqueous work-up. The product was purified by anaerobic recrystallisation from

hexane to afford the *complex* **8e** as a red crystalline solid (1.10 g, 37%), m.p. 111 °C (Found: M⁺, 390.0777. C₁₇H₂₆CrO₃SSi requires *M*, 390.0777); *v*ₘₐₓ(CHCl₃)/cm⁻¹ 1981, 1885 and 1865; δ_H(CDCl₃) 1.11 {18 H, d, *J* 7.0, Si[CH(CH₃)₂]₃}, 1.26 {3 H, sept., *J* 7.0, Si[CH(CH₃)₂]₃}, 2.34 (3 H, s, 2-CH₃), 5.36 (1 H, d, *J* 2.5, 3-H) and 5.59 (1 H, d, *J* 2.5, 4-H); *m/z* (CI) 391 (MH⁺), 324, 255, 228, 174 and 86.

η⁵-[2-(tert-*Butyldimethylsilyl*)-5-*methylthiophene*]*tricarb-onylchromium*(o) **8d**.—Butyllithium (1.0 equiv.) was added dropwise to a solution of 2-(*tert*-butyldimethylsilyl)thio-phenetricarbonylchromium(o) 6 (R₃ = BuᵗMe₂)²⁶ (0.50 g, 1.49 mmol) in THF (10 cm³) at −78 °C. After 1.5 h, iodomethane (0.24 cm³, 3.74 mmol) was added dropwise to the resulting solution which was then allowed to attain room temperature. After aqueous work-up, the product was purified by column chromatography (1–4% diethyl ether–petroleum; gradient elution) to give the *complex* **8d** 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%); *v*ₘₐₓ(CHCl₃)/cm⁻¹ 1957, 1873, 676, 652 and 628; δ_H(CDCl₃) 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); δ_C(CDCl₃) −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.

δ 5.37   δ 5.47

NOE of 8d
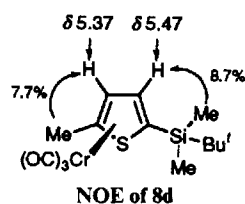
The complex **8d** was also prepared by lithiation of the 2-methylthiophene complex 18 (0.20 g, 0.85 mmol) with butyllithium (1.0 equiv.) in an analogous manner with a chloro-*tert*-butyldimethylsilane (1.05 equiv.) quench. Purification as above gave **8d** (0.12 g, 42%).

Lithiation of η⁵-[2-*Methyl*-5-(*triethylsilyl*)*thiophene*]*tri-carbonylchromium*(o) **8b**.—*tert*-Butyllithium (1.02 equiv.) was added dropwise to a solution of the complex **8b** (0.14 g, 0.41 mmol) in THF (7 cm³) at −78 °C. After being stirred for 3 h, the solution was quenched with deoxygenated water (0.5 cm³) followed by an aqueous work-up. TLC analysis of the crude product (20% EtOAc–petroleum) revealed a two-component mixture with *R*_F s of 0.6 and 0.2. Separation of these by flash chromatography (2–20% diethyl ether–hexane; gradient elution) gave firstly (*R*_F 0.6) η⁵-[2-*methyl*-3-(*triethylsilyl*)*thiophene*]-*tricarbonylchromium*(o) **9b**, as an orange gummy solid (38.1 mg, 27%) (Found: M⁺, 348.0308. C₁₄H₂₀CrO₃SSi requires *M*, 348.0307); *v*ₘₐₓ(CHCl₃)/cm⁻¹ 1960, 1884 and 1863; δ_H(CDCl₃) 0.91 [6 H, q, *J* 7.8, Si(CH₂CH₃)₃], 1.06 [9 H, t, *J* 7.8, Si(CH₂CH₃)₃], 2.28 (3 H, s, 2-CH₃), 5.12 (1 H, d, *J* 3.42, 5-H) and 5.43 (1 H, d, *J* 3.41, 4-H); *m/z* (EI) 348 (M⁺), 292, 264, 236, 208, 183, 155, 127 and 52.

NOE of 9b
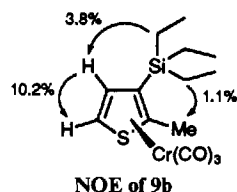
The second component (*R*_F 0.2) was identified as η⁵-(2-

methylthiophene)tricarbonylchromium(o) 7 (48.5 mg, 51%) by comparison with authentic material.

Lithiation of η⁵-[2-(*Dimethylisopropylsilyl*)-5-*methylthio-phene*]*tricarbonylchromium*(o) **8c**.—*tert*-Butyllithium (1.02 equiv.) was added dropwise to a solution of the complex **8c** (0.20 g, 0.60 mmol) in THF (10 cm³) at −78 °C. After being stirred for 3 h, the solution was quenched with deoxygenated water (0.5 cm³). Aqueous work-up and TLC analysis of the crude product (20% EtOAc–petroleum) revealed a three-component mixture with R_Fs of 0.8, 0.6 and 0.2. Separation of these by flash chromatography (2–100% diethyl ether–hexane; gradient elution) gave firstly (R_F 0.8) η⁵-[3,5-*bis*(*dimethylisopropylsilyl*)-2-*methylthiophene*]*tricarbonyl-chromium*(o) **10c** (R_F 0.8) as an orange crystalline solid (52.6 mg, 11%), m.p. 72–73 °C (Found: M⁺, 434.0859. $C_{18}H_{30}CrO_3SSi_2$ requires M, 434.0859); $δ_H$(CDCl₃) 0.18 (3 H, s, 3-SiCH₃), 0.21 (3 H, s, 3-SiCH₃), 0.32 (3 H, s, 5-SiCH₃), 0.35 (3 H, s, 5-SiCH₃), 0.98 [14 H, m, 2 × SiCH(CH₃)₂], 2.31 (3 H, s, 2-CH₃) and 5.33 (1 H, s, 4-H); $δ_C$(CDCl₃) −5.07 (3-SiCH₃), −4.55 (3-SiCH₃), −4.36 (5-SiCH₃), −3.36 (5-SiCH₃), 14.24 [3-CH(CH₃)₂], 14.67 [5-CH(CH₃)₂], 17.32 [3-CH(CH₃CH₃)], 17.45 [3-CH(CH₃CH₃)], 17.61 [5-CH(CH₃CH₃)], 17.75 [5-CH(CH₃CH₃)], 29.68 (2-CH₃), 92.86 (3-C), 100.09 (5-C), 106.84 (4-C), 116.96 (2-C) and 234.02 (CO); m/z (CI) 435 (MH⁺), 351, 299, 200, 118 and 86.

NOE of 10c
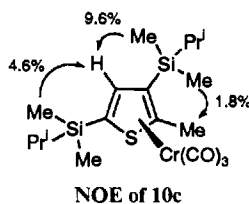
X-Ray Crystal Analysis.—*Crystal data:* Single crystals of η⁵-[3,5-bis(dimethylisopropylsilyl)-2-methylthiophene]-tricarbonylchromium(o) **10c** suitable for X-ray crystallography were grown from ether–hexane, $C_{18}H_{30}CrO_3SSi_2$, M = 434.7, monoclinic, a = 21.428(11), b = 7.245(3), c = 15.228(7) Å, β = 99.22(4)°, U = 2334(3) Å³, space group $P2_1/c$, Z = 4, D_C = 1.237 g cm⁻³, μ(Mo-Kα) = 6.95 cm⁻¹, F(000) = 920. Data were measured on a Siemens P4/PC diffractometer (2θ < 45°) with Mo-Kα radiation (graphite monochromator) using ω-scans. 3055 Independent reflections were measured and of these, 2064 had $|F_o| > 4σ(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; no absorption correlation was applied. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. The positions of all the hydrogen atoms were determined from a ΔF map; these positions were then idealised, C–H = 0.96 Å, and the atoms assigned isotropic thermal parameters, U(H) = 1.2U_{eq}(C), and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares to give R = 0.0552, R_w = 0.0560 (w^{-1} = σ²(F) + 0.001F²). The maximum residual electron density in the final ΔF map was 0.64 eÅ³, and the mean and maximum shift/error in the final refinement cycle was 0.003 and 0.027, respectively. Computations were carried out on a 486 PC using the SHELXTL-PC program system.²⁷ Atomic coordinates, bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

Selected bond lengths (Å): Cr–C(1) 2.240(6), Cr–C(2) 2.213(6), Cr–C(3) 2.234(6), Cr–C(4) 2.203(7), Cr–S 2.361(2),

C(1)–C(2) 1.404(8), C(2)–C(3) 1.437(7), C(1)–Si(1) 1.877(5), C(3)–Si(2) 1.894(6), C(4)–S 1.751(6) and S–C(1) 1.728(6).

The second component (R_F 0.6) was η⁵-[3-(*dimethyliso-propylsilyl*)-2-*methylthiophene*]*tricarbonylchromium*(o) **9c**, isolated as an orange crystalline solid (114 mg, 59%), m.p. 80–81 °C (Found: M⁺, 334.0151. $C_{13}H_{18}CrO_3SSi$ requires M, 334.0151); $ν_{max}$(CHCl₃)/cm⁻¹ 1973, 1906 and 1885; $δ_H$(CDCl₃) 0.32 (3 H, s, SiCH₃), 0.37 (3 H, s, SiCH₃), 0.87 [1 H, m, CH(CH₃)₂], 1.02 [6 H, d, J 4.9, CH(CH₃)₂], 2.27 (3 H, s, 2-CH₃), 5.12 (1 H, d, J 3.7, 5-H) and 5.43 (1 H, d, J 3.4, 4-H); m/z (EI) 334 (M⁺), 278, 250, 208, 198, 167, 155, 52 and 28.

The third component (R_F 0.2) was identified as η⁵-(2-methylthiophene)tricarbonylchromium(o)⁷ (R_F 0.2; 37.8 mg, 27%) by comparison with authentic material.

η⁵-[5-(tert-*Butyldimethylsilyl*)-3-*deuterio*-2-*methylthio-phene*]*tricarbonylchromium*(o) **8** (3-²H, R = Bu'Me₂).—2-(*tert*-Butyldimethylsilyl)-5-methylthiophene complex **8** (R = Bu'Me₂) (100 mg, 0.28 mmol), was lithiated with *tert*-butyllithium in THF at −78 °C for 3 h, followed by a ²H₂O quench (99.9 ²H; 3.0 equiv.). The deuteriated product was collected as a red crystalline solid which required no further purification (82.0 mg, 82% with 93% ²H); m.p. 86–87 °C (Found: C, 48.0; H, 5.8. $C_{14}H_{19}CrDO_3SSi$ requires C, 48.25; H, 5.79%) (Found: M⁺, 379.0370 requires M, 379.0370); $ν_{max}$(CHCl₃)/cm⁻¹ 1957, 1889, 1873, 673, 651 and 628; $δ_H$(CDCl₃) 0.21 (3 H, s, SiCH₃), 0.22 (3 H, s, SiCH₃), 0.92 [9 H, s, SiC(CH₃)₃], 2.32 (3 H, s, 2-CH₃) and 5.46 (1 H, s, 4-H); m/z (EI) 349 (M⁺), 293, 289, 265, 156, 73 and 52.

Acknowledgements

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