

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^tLi 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.

Benzenetricarbonylchromium(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}

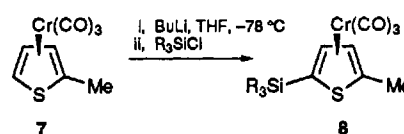
In contrast, the heteroaromatic complexes tend to be more labile and difficult to prepare and handle^{18,19} and, in consequence, their chemistry has been little explored. The usefulness of silane protection has only been demonstrated for one group, the η^6 -pyridine complexes **2** where, most notably, 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^5 -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 -positions.²² We report here a full account of those observations.

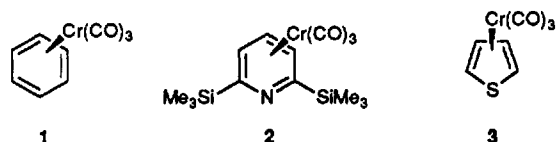
phenone complex **3**, the product of desilylation and the process was found to be complete after ~3 h at –78 °C, conditions under which such trimethylsilyl groups are normally stable.^{15–17} Surprisingly, treatment of **6** with *tert*-butyllithium under the same conditions also produced complete desilylation 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.

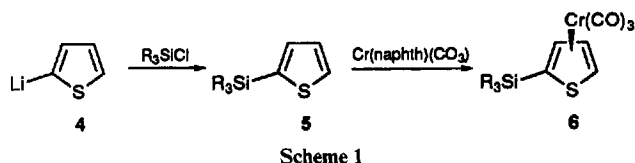
Thus, the 2-trialkylsilyl-5-methylthiophene complexes **8a–e** were synthesised (Scheme 2) in moderate **8e** (R = Prⁱ) (37%) to



Scheme 2



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-

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 alkylolithium, 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^tLi 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

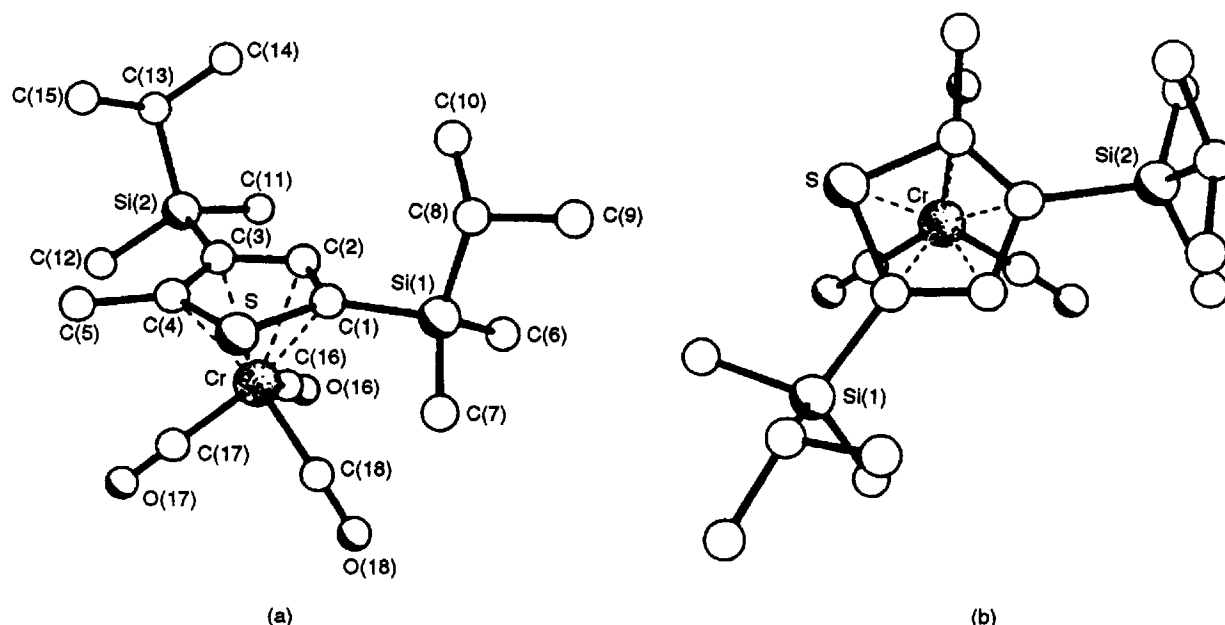


Fig. 1 (a) Molecular structure of complex **10c**; (b) plan view showing the orientation of the carbonyl groups relative to the thiophene substituents

Table 1 Silyl group migrations

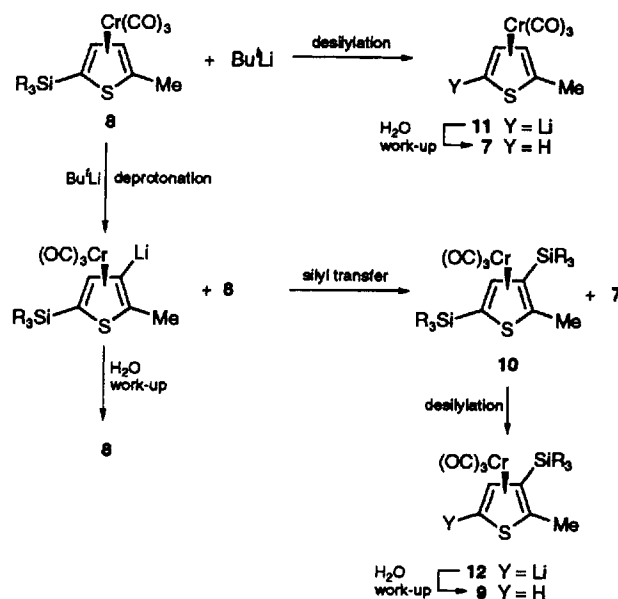
$\text{8} \xrightarrow[1 \text{ equiv. Bu}^t\text{Li}]{\text{H}^+} \text{Cr(CO)}_3 + (\text{OC})_3\text{Cr} \begin{array}{c} \text{SiR}_3 \\ \text{S} \end{array} + (\text{OC})_3\text{Cr} \begin{array}{c} \text{X} \\ \text{S} \end{array}$					
8	R ₃	7	9	8, X = H	10, X = SiR ₃
		%	%	%	%
a	Me ₃	80	—	—	—
b	Et ₃	51	27	—	—
c	Pr ⁱ Me ₂	30	59	—	11
d	Bu ⁱ Me ₂	—	—	90	—
e	Pr ⁱ ₃	—	—	95	—

was demonstrated by a ²H₂O work-up on complex **8d** which produced the 3-deuteriated (93% ²H) complex **8d** (3-²H) 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 conformation with one CO group *anti* to the sulfur atom and the other two exlipping 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 alkylolithium 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^tLi in THF is rapid and is the only process observed, affording the anionic complex **11** of the isolated product 2-methylthiophenetricarbonylchromium(0) **7**. When R₃ = Et₃, regioselective



Scheme 3

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 = PrⁱMe₂, increased steric hindrance of the alkylsilane results in preferential deprotonation and the 2,4-disilylated product **10c** remains in the product mixture. When R₃ = BuⁱMe₂ or Prⁱ₃, β -deprotonation is the only reaction observed and therefore the proton quench regenerates the starting complexes **8d**, **e**.

Such facile desilylation by alkylolithium 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

General reagents and procedures were as previously described.²⁶

η^5 -[2-Methyl-5-(trimethylsilyl)thiophene]tricarbonylchromium(0) **8a**.—Addition of butyllithium (1.02 equiv.) over ~10 min to a solution of 2-methylthiophenetricarbonylchromium(0) **7**²⁶ (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. $C_{11}H_{14}CrO_3SSi$ requires M , 305.9838); $\nu_{\max}(\text{hexane})/\text{cm}^{-1}$ 1970, 1900, 1889, 1481, 1389 and 739; $\delta_H(\text{CDCl}_3)$ 0.27 [9H, s, $\text{Si}(\text{CH}_3)_3$], 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.

η^5 -[2-Methyl-5-(triethylsilyl)thiophene]tricarbonylchromium(0) **8b** and η^5 -[2-methyl-3,5-bis(triethylsilyl)thiophene]tricarbonylchromium(0) **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, chlorotriethylsilane (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 η^5 -[2-methyl-3,5-bis(triethylsilyl)thiophene]tricarbonylchromium **10b** as a red crystalline solid (39.2 mg, 5%), m.p. 65 °C (Found: M^+ , 462.1172. $C_{20}H_{34}CrO_3SSi_2$ requires M , 462.1172); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1963, 1894 and 1880; $\delta_H(\text{CDCl}_3)$ 0.75 [6 H, m, 3- $\text{Si}(\text{CH}_2\text{CH}_3)_3$], 0.90 [6 H, m, 5- $\text{Si}(\text{CH}_2\text{CH}_3)_3$], 1.00 [18 H, m, 3,5- $\text{Si}(\text{CH}_2\text{CH}_3)_3$], 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.

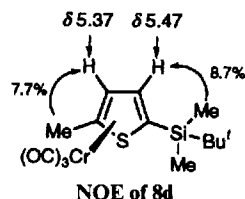
The second component was the desired title product **8b**, isolated as an orange oil (0.51 g, 87%) (Found: M^+ , 348.0309. $C_{14}H_{20}CrO_3SSi$ requires M , 348.0307); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1957, 1897, 1881, 674, 650 and 632; $\delta_H(\text{CDCl}_3)$ 0.76 [6 H, m, $\text{Si}(\text{CH}_2\text{CH}_3)_3$], 1.01 [9 H, t, J 8.0, $\text{Si}(\text{CH}_2\text{CH}_3)_3$], 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.

η^5 -[2-(Dimethylisopropylsilyl)-5-methylthiophene]tricarbonylchromium(0) **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. $C_{13}H_{18}CrO_3SSi$ requires M , 334.0151); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1970, 1899, 1889, 1470, 1458 and 764; $\delta_H(\text{CDCl}_3)$ 0.32 (3 H, s, SiCH_3), 0.37 (3 H, s, SiCH_3), 0.89 [1 H, m, $\text{SiCH}(\text{CH}_3)_2$], 1.02 [6 H, d, J 7.3, $\text{SiCH}(\text{CH}_3)_2$], 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.

η^5 -[2-Methyl-5-(triisopropylsilyl)thiophene]tricarbonylchromium(0) **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

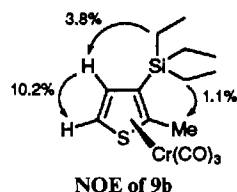
hexane to afford the complex **8e** as a red crystalline solid (1.10 g, 37%), m.p. 111 °C (Found: M^+ , 390.0777. $C_{17}H_{26}CrO_3SSi$ requires M , 390.0777); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1981, 1885 and 1865; $\delta_H(\text{CDCl}_3)$ 1.11 [18 H, d, J 7.0, $\text{Si}[\text{CH}(\text{CH}_3)_2]_3$], 1.26 [3 H, sept., J 7.0, $\text{Si}[\text{CH}(\text{CH}_3)_2]_3$], 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.

η^5 -[2-(*tert*-Butyldimethylsilyl)-5-methylthiophene]tricarbonylchromium(0) **8d**.—Butyllithium (1.0 equiv.) was added dropwise to a solution of 2-(*tert*-butyldimethylsilyl)thiophenetricarbonylchromium(0) **6** ($R_3 = \text{Bu}^t\text{Me}_2$)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. $C_{14}H_{20}CrO_3SSi$ requires C, 48.25; H, 5.79%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1957, 1873, 676, 652 and 628; $\delta_H(\text{CDCl}_3)$ 0.19 (3 H, s, SiCH_3), 0.21 (3 H, s, SiCH_3), 0.92 [9 H, s, $\text{SiC}(\text{CH}_3)_3$], 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); $\delta_C(\text{CDCl}_3)$ -6.11 (SiCH_3), -5.76 (SiCH_3), 15.35 (5-CH₃), 17.30 [$\text{SiC}(\text{CH}_3)_3$], 26.05 [$\text{SiC}(\text{CH}_3)_3$], 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.



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%).

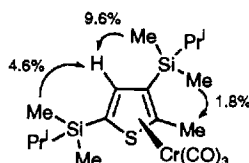
Lithiation of η^5 -[2-Methyl-5-(triethylsilyl)thiophene]tricarbonylchromium(0) **8b.**—*tert*-Butyllithium (1.02 equiv.) was added dropwise to a solution of the complex **8b** (0.14 g, 0.41 mmol) in THF (7 cm³) at -78 °C. After being stirred for 3 h, the solution was quenched with deoxygenated water (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) η^5 -[2-methyl-3-(triethylsilyl)thiophene]tricarbonylchromium(0) **9b**, as an orange gummy solid (38.1 mg, 27%) (Found: M^+ , 348.0308. $C_{14}H_{20}CrO_3SSi$ requires M , 348.0307); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1960, 1884 and 1863; $\delta_H(\text{CDCl}_3)$ 0.91 [6 H, q, J 7.8, $\text{Si}(\text{CH}_2\text{CH}_3)_3$], 1.06 [9 H, t, J 7.8, $\text{Si}(\text{CH}_2\text{CH}_3)_3$], 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.



The second component (R_F 0.2) was identified as η^5 -(2-

methylthiophene)tricarbonylchromium(0) **7** (48.5 mg, 51%) by comparison with authentic material.

Lithiation of η^5 -[2-(Dimethylisopropylsilyl)-5-methylthiophene]tricarbonylchromium(0) **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_F s 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) η^5 -[3,5-bis(dimethylisopropylsilyl)-2-methylthiophene]tricarbonylchromium(0) **10c** (R_F 0.8) as an orange crystalline solid (52.6 mg, 11%), m.p. 72 – 73°C (Found: M^+ , 434.0859. $\text{C}_{18}\text{H}_{30}\text{CrO}_3\text{SSi}_2$ requires M , 434.0859; $\delta_{\text{H}}(\text{CDCl}_3)$ 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 \times SiCH(CH₃)₂], 2.31 (3 H, s, 2-CH₃) and 5.33 (1 H, s, 4-H); $\delta_{\text{C}}(\text{CDCl}_3)$ -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 η^5 -[3,5-bis(dimethylisopropylsilyl)-2-methylthiophene]tricarbonylchromium(0) **10c** suitable for X-ray crystallography were grown from ether–hexane, $\text{C}_{18}\text{H}_{30}\text{CrO}_3\text{SSi}_2$, $M = 434.7$, monoclinic, $a = 21.428(11)$, $b = 7.245(3)$, $c = 15.228(7)$ Å, $\beta = 99.22(4)^\circ$, $U = 2334(3)$ Å³, space group $P2_1/c$, $Z = 4$, $D_c = 1.237$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 6.95$ cm⁻¹, $F(000) = 920$. Data were measured on a Siemens P4/PC diffractometer ($2\theta < 45^\circ$) with Mo-K α radiation (graphite monochromator) using ω -scans. 3055 Independent reflections were measured and of these, 2064 had $|F_o| > 4\sigma(|F_o|)$ 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, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares to give $R = 0.0552$, $R_w = 0.0560$ ($w^{-1} = \sigma^2(F) + 0.001F^2$). The maximum residual electron density in the final ΔF map was 0.64 eÅ⁻³, 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 η^5 -[3-(dimethylisopropylsilyl)-2-methylthiophene]tricarbonylchromium(0) **9c**, isolated as an orange crystalline solid (114 mg, 59%), m.p. 80 – 81°C (Found: M^+ , 334.0151. $\text{C}_{13}\text{H}_{18}\text{CrO}_3\text{SSi}$ requires M , 334.0151; $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1973, 1906 and 1885; $\delta_{\text{H}}(\text{CDCl}_3)$ 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 η^5 -(2-methylthiophene)tricarbonylchromium(0)⁷ (R_F 0.2; 37.8 mg, 27%) by comparison with authentic material.

η^5 -[5-(*tert*-Butyldimethylsilyl)-3-deuterio-2-methylthiophene]tricarbonylchromium(0) **8** (3-²H, R = Bu^tMe₂).—2-(*tert*-Butyldimethylsilyl)-5-methylthiophene complex **8** (R = Bu^tMe₂) (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 deuterated 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. $\text{C}_{14}\text{H}_{19}\text{CrDO}_3\text{SSi}$ requires C, 48.25; H, 5.79%). (Found: M^+ , 379.0370 requires M , 379.0370); $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 1957, 1889, 1873, 673, 651 and 628; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.21 (3 H, s, SiCH₃), 0.22 (3 H, s, SiCH₃), 0.92 [9 H, s, SiC(CH₃)₃], 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.

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