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Preparation of bis(η^6-2-R-benzo[*b*]thiophene)-chromium and -molybdenum (R = H, Me, $SiMe_3$) sandwich complexes via metal vapour synthesis. Crystal structure of $[Cr(\eta^6\text{-2-Me } C_8H_5S)_2]$

Nicolas C. Burton, F. Geoffrey N. Cloke *, Peter B. Hitchcock, Gary O. Mepsted,
Claire Newton, Hasmita Patel

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

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Abstract

Co-condensation of chromium atoms with benzo[*b*]thiophene, 2-methylbenzo[*b*]thiophene or 2-trimethylsilylbenzo[*b*]thiophene at 77 K yields the sandwich complexes $[Cr(\eta^6\text{-}C_8H_6S)_2]$ (**1**), $[Cr(\eta^6\text{-2-Me}C_8H_5S)_2]$ (**2**) and $[Cr(\eta^6\text{-2-SiMe}_3C_8H_5S)_2]$ (**3**). The molybdenum complex $[Mo(\eta^6\text{-2-Me}C_8H_5S)_2]$ (**4**) was prepared analogously. Complexes **1**, **2** and **4** exist as a mixture of diastereoisomers as indicated by ^1H and ^{13}C NMR spectroscopy, with mesomeric and racemic forms present in the ratios 1:1 for **1** and 1:2 for **2** and **4**. The mesomeric form of complex **2** was also studied by single-crystal X-ray diffraction which confirmed η^6-ligation of the arene function of both 2-methylbenzo[*b*]thiophene rings.

Keywords: Chromium; Molybdenum; Metal vapour synthesis; Benzathiophene; Crystal structure; Sandwich

1. Introduction

The metal vapour synthesis (MVS) reactions of heteroatom-containing arenes are unpredictable, because they may lead to desulphurisation (thiophenes) or different bonding preferences, e.g. η^1 or η^6 bonding of pyridines. In particular, the MVS reaction of chromium atoms with thiophene has been examined by Timms and Chivers [1], and co-condensation of chromium atoms with a mixture of pyridine and trifluorophosphine affords both $[Cr(\eta^6\text{-}C_5H_5N)(PF_3)_3]$ and $[Cr(\eta^1\text{-}C_5H_5N)(PF_3)_5]$ [2]. However, the bonding mode of pyridines can be directed by application of 2,6-substitution to restrict access to the heteroatom lone pair, and subsequently the MVS method was used to synthesise the sandwich complexes $[M(\eta\text{-NC}_5H_3\text{-2,6-Me}_2)_2]$ (M = Ti, V, Cr, Mo) [3,4], $[M(\eta\text{-NC}_5H_3\text{-2,6-SiMe}_3)_2]$ [5] and $[M(\eta\text{-NC}_5H_2\text{-2,4,6-}^tBu_3)_2]$ (M = Sc, Ti, Zr, Hf) [6].

We were interested in investigating benzo[*b*]thiophene and some 2-substituted derivatives as potential ligands, since this area of hetero-organic MVS chemistry had been previously unexplored. Herein we report the synthesis and characterisation of the first bis(η^6-benzothiophene) sandwich complexes of chromium and molybdenum.

2. Results and discussion

Co-condensation of chromium atoms with benzo[*b*]thiophene (BT), 2-methylbenzo[*b*]thiophene (2-MeBT) or 2-trimethylsilylbenzo[*b*]thiophene (2-TMSBT) at 77 K gave a brick red matrix on the inner walls of the reaction vessel which turned to a cream colour upon warming (ca. 243 K).

After attaining room temperature, the contents of the bell jar were extracted by washing the matrix off the inner walls with toluene. The suspension of the excess of metal and the metal sulphide was removed by filtration, and removal of solvent in vacuo yielded a dark red residue. Unchanged ligand was removed by sublimation in the case of BT and 2-MeBT, and the final red residue was dissolved in toluene, and the solution filtered and concentrated. Cooling (−30°C) of the filtrate overnight afforded well-formed crystals of deep red $[Cr(\eta^6\text{-}C_8H_6S)_2]$ (**1**) or brick red $[Cr(\eta^6\text{-2-Me}C_8H_5S)_2]$ (**2**).

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* Corresponding author.

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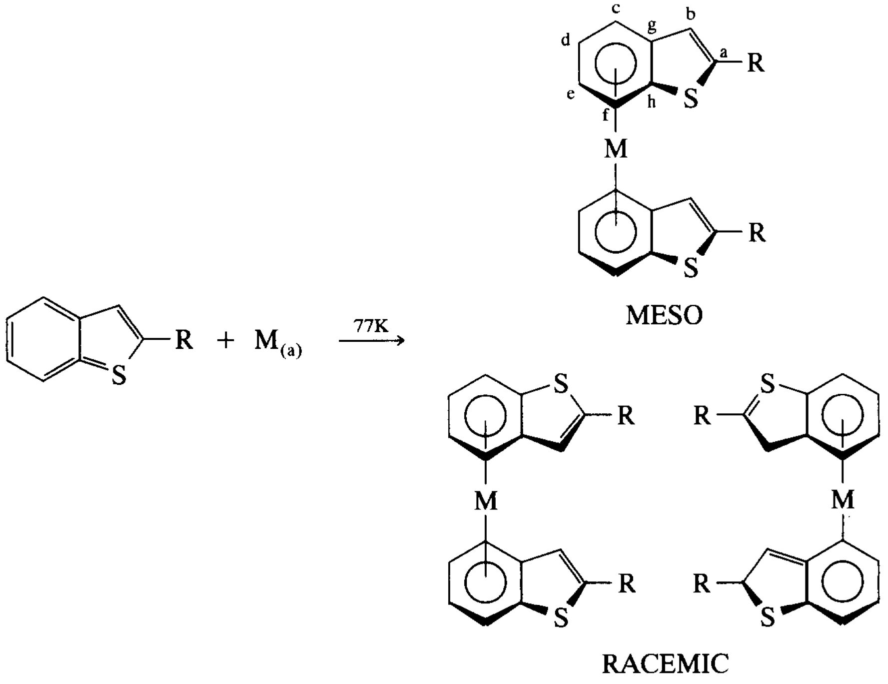
Brown, crystalline [Mo(η^6-2-MeC_8H_6S)$_2$] (**4**) was prepared analogously from molybdenum vapour and 2-MeBT. Attempts to purify the product of the reaction of chromium atoms with 2-TMSBT were complicated by the presence of an excess of ligand of relatively low volatility and the limited thermal stability of the product. Thus the existence of [Cr(η^6-2-SiMe$_3C_8H_5S$)$_2$] (**3**) could only be demonstrated by mass spectral analysis of a concentrated mixture of **3** and 2-TMSBT; however a simulation of the isotopic pattern of the molecular ion region was in excellent agreement with the experimental spectrum. Mass spectra showing molecular ions were also recorded for complexes **1**, **2** and **4**, and were completely consistent with the simulated spectra.

Compounds **1**, **2** and **4** are highly soluble in polar solvents, moderately soluble in toluene and benzene but practically insoluble in 40–60°C petroleum ether. Solutions were very air-sensitive, while crystalline material decomposed over a period of a few minutes (**4**) or hours (**1** and **2**) in air. Whilst the yields of **1** and **2** were low (5% and 10%, respectively), the relatively higher yield of **2** is noteworthy and is presumably a reflection of less efficient ligand desulphurisation to the steric effect of the methyl substituent adjacent to sulphur. The comparable yield of **4** is also interesting, given the high reactivity of molybdenum atoms; attempts to make the unsubstituted analogue [Mo(η^6-C_8H_6S)$_2$] were unsuccessful, and only intractable products (assumed to be molybdenum sulphides) were obtained from the co-condensation of molybdenum vapour with BT.

2.1. NMR spectroscopy of 1, 2 and 4

The η^6-binding of BT or its derivatives to a metal centre in a sandwich structure is expected to result in the formation of two diastereoisomers in which the sulphurs are eclipsed (*meso*) or staggered (*rac*), as illustrated in Scheme 1. The ^{1}H and ^{13}C{^{1}H} NMR data (see Table 1) confirm this to be the case, and although some of the signals for the *meso*- and *rac*-isomers were coincident in both ^{1}H and ^{13}C{^{1}H} spectra, chemical shift differences allowed spectral resolution of the isomers. The ^{1}H and ^{13}C assignments were made by use of standard decoupling, 2D and DEPT techniques. Extraction of coupling constant data for **1** was straightforward, but simulation of the second-order spectra for the arene hydrogens in **2** and **4** was not attempted. The ratio of isomers, as determined by integration, was approximately 1 : 1 for **1** and 1 : 2 for **2** and **4**.

Evidence for the formation of the η^6 sandwich compounds **1**, **2** and **4** was also supported by the large shifts (relative to those of the free ligand) to low frequency of the resonances due to both the carbons and the hydrogens of the six-membered ring, characteristic of arene



M = Cr, R = H, **1**
M = Cr, R = Me, **2**
M = Cr, R = SiMe$_3$, **3**
M = Mo, R = Me, **4**

Scheme 1. NMR assignments.

ligands π-bound to transition metal centres [7]. The ^{13}C chemical shifts for the BT ligand in **1** are comparable with those found in $[Ru(\eta\text{-}Cp)(\eta^6\text{-}BT)]^+[BF_4]^-$ [8], although the low-frequency shift of the η^6-ring carbons in the latter is less marked, presumably due to lower charge density on the metal.

2.2. Single-crystal X-ray structure of 2

A single crystal selected from a batch of **2** was examined. As discussed previously, crystalline material showed evidence of decomposition after some hours, and so a crystal was quickly wrapped in epoxy glue in air and data collected as soon as possible. Two perspectives are shown in Fig. 1, with bond distances and angles listed in Table 2 and fractional atomic coordinates in Table 3. The X-ray structure shows that the crystal isolated was the *meso*-diastereoisomer and that both 2-MeBT ligands are η^6-bound via the arene rings.

The C—C bond distances of the six-membered rings range from 1.38(2) Å to 1.45(2) Å and are consistent with those found in the related complexes $[Ru(\eta\text{-}Cp)(\eta^6\text{-}BT)]^+[BF_4]^-$ [8] and [2-LiBT] [9]. The metal-to-ring centroid distances for both ligands in **2** are almost equivalent at 1.61 Å and 1.62 Å. The dihedral angle between the least-squares planes of the two BT ligands is 6(2)°. However, since the methyl groups of both rings are coplanar with the BT framework, this deviation is probably not due to steric repulsion between them, but is best explained in terms of the degree of bonding of the chromium centre to each arene carbon. Examination of the metal–carbon distances in **2** shows that the chromium–arene ring carbon distances decrease in the order Cr—C(4), Cr—C(3) < Cr—C(5) and Cr—C(2) < Cr—C(1), Cr—C(6); a similar progression is evident in the second ring. These variations lead to the ring tilt; this feature is observed in other transition metal complexes of fused rings, e.g. $[Cr(CO)_3(\eta^6\text{-triphenylene})]$ [10] and $[Cr(CO)_3(\eta^6\text{-}C_{10}(Me)_8]$ [11], and also for the BT complex $[Ru(\eta\text{-}Cp)(\eta^6\text{-}BT)]^+[BF_4]^-$ [8]. To calculate the slipped distance of the ring defined by carbons C(1) to C(6), the mean of the separations Cr—C(4) and Cr—C(3) was subtracted from the mean of the separations Cr—C(1) and Cr—C(6). The resultant slippage value of 0.093 Å for **2** falls within the range found for other complexes of

Table 1
NMR data for compounds **1**, **2** and **4** [a]

Compound	^1H NMR data [b,c]			$^{13}C\{^1H\}$ NMR data [d]		
	Isomer A	Isomer B	Assignment	Isomer A	Isomer B	Assignment
1	6.66 (2H, d)	6.68 (2H, d)	H_a, $^3J_{Ha-Hb} = 5.2$	126.5	126.4	C_a
	6.32 (2H, d)	6.50 (2H, d)	H_b, $^3J_{Hb-Ha} = 5.2$	124.4	124.3	C_b
	4.79 (2H, m)	4.88 (2H, m)	H_c, $^3J_{Hc-Hd} \sim 5$	72.6	72.6	C_c
	3.99 (2H, m)	4.06 (2H, m)	H_d, $^3J_{Hd-He} \sim 5$	75.8	75.7	C_d
	3.96 (2H, m)	3.91 (2H, m)	H_e, $^3J_{He-Hf} \sim 5$	75.7	75.6	C_e
	4.89 (2H, m)	4.73 (2H, m)	H_f, $^5J_{Hf-Hb} < 0.5$, cf. **2**	72.4	71.8	C_f
				94.2	94.2	C_g
				103.0	103.0	C_h
				126.6	126.8	C_a
2	5.85 (2H, qd)	6.09 (2H, qd)	H_b, $^4J_{Hb-HMe} = 1.34$, $^5J_{Hb-Hf} = 0.7$	122.4	122.2	C_b
	4.81 (2H, m)	4.84 (2H, m)	H_c	73.0	73.0	C_c
	3.99 (2H, m)	4.04 (2H, m)	H_d	76.2	76.2	C_d
	3.97 (2H, m)	3.92 (2H, m)	H_e	76.0	76.0	C_e
	4.86 (2H, m)	4.80 (2H, m)	H_f, $^5J_{Hf-Hb} = 0.7$	72.9	72.9	C_f
	2.02 (6H, d)	2.11 (6H, d)	H_{Me}, $^4J_{HMe-Hb} = 1.34$	30.3	30.3	CH_3
				94.4	94.2	C_g
				103.2	103.2	C_h
				122.2	122.1	C_a
4	5.63 (2H, qd)	5.90 (2H, qd)	H_b, $^4J_{Hb-HMe} = 1.3$, $^5J_{Hb-Hf} = 0.9$	121.8	121.6	C_b
	5.04 (2H, m)	5.05 (2H, m)	H_c	70.9	70.6	C_c
	4.43 (2H, m)	4.50 (2H, m)	H_d	77.1	76.4	C_d
	4.40 (2H, m)	4.38 (2H, m)	H_e	76.2	75.7	C_e
	5.09 (2H, m)	5.02 (2H, m)	H_f, $^5J_{Hf-Hb} = 0.9$	70.2	69.6	C_f
	2.08 (6H, d)	2.07 (6H, d)	H_{Me} $^4J_{HMe-Hb} = 1.3$	16.74	16.74	CH_3
				98.0	98.0	C_g
				104.8	104.8	C_h

[a] The NMR spectra were recorded in C_7D_8 at 293 K. For labelling, see Scheme 1. Data: chemical shift (δ), relative intensity, multiplicity, *J* in Hz.

[b] Free BT: δ: $H_a = 7.61$; $H_b = 7.41$; $H_c = 7.87$; $H_d = 7.37$; $H_e = 7.35$; $H_f = 7.95$ [19].

[c] Assignments confirmed by ^1H 2D spectra.

[d] $[Ru(\eta\text{-}Cp)(\eta\text{-}BT)^+BF_4^-]$: δ: C_a, 137.7; C_b, 123.7; C_c, 81.6; C_d, 84.4; C_e, 83.9; C_f, 81.3; C_g, 106.2; C_h, 110.2 [8].
Free BT: δ: C_a, 126.2; C_b, 123.8; C_c, 123.6; C_d, 124.1; C_e, 124.2; C_f, 122.4; C_g, 139.6; C_h, 139.7 [19].

0.03 Å [10] to 0.12 Å [11]. Two explanations for the cause of this slippage have been proposed. The first is that the fused ring carbons, i.e. C(1) and C(6), cannot interact with the metal as efficently as the other four carbons of the arene ring because the former are involved in bonding to three other carbons [12,13]; CNDO molecular orbital calculations for the atoms of BT suggest that there is less electron density at C(1) and C(6) available for bonding to a metal fragment [14]. The second explanation places emphasis on the need for the uncomplexed part of the ligand to retain a degree of aromatic character which would otherwise be lost [8].

3. Experimental details

All manipulations were carried out under dinitrogen or argon using standard Schlenk techniques, or in a Miller–Howe dry box (< 10 ppm H_2O, < 1 ppm O_2) under dinitrogen. The design of the metal vapour synthesis apparatus has been described previously [15].

Light petroleum (b.p. 40–60°C) and toluene were dried over sodium wire prior to refluxing over and subsequent distillation (under dinitrogen) from sodium–potassium alloy and molten sodium, respectively, then degassed and stored over potassium mirrors. NMR solvents were degassed and dried over potassium mirrors prior to use. Celite 545 filter aid was dried in an oven at 200°C.

Chlorotrimethylsilane was freed from acidic impurities by standing over magnesium turnings at 40°C, and then transferred by trap-to-trap distillation under vacuum. All other reagents were used as supplied. 2-Methylbenzo[*b*]thiophene [16] and 2-trimethylsilylbenzo[*b*]thiophene [17] were made by the standard procedures.

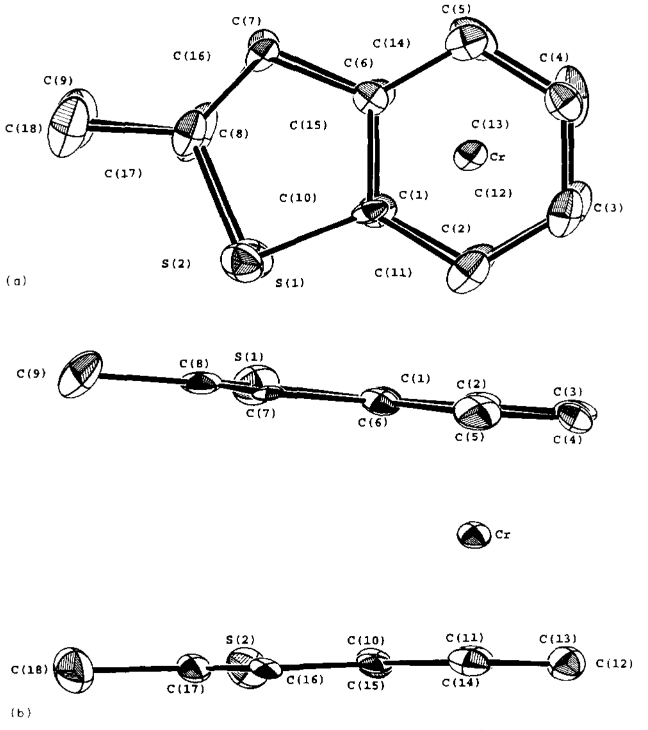


Fig. 1. Two views of the X-ray structure of $[Cr(\eta^6\text{-}2\text{-}Ne\text{-}C_8H_5S)_2]$, 2.

Table 2
Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Bonds			
Cn–C(1)	2.176(13)	Cr–C(2)	2.137(13)
Cr–C(3)	2.100(14)	Cr–C(4)	2.084(13)
Cr–C(5)	2.130(12)	Cr–C(6)	2.193(12)
Cr–C(10)	2.170(10)	Cr–C(11)	2.160(11)
Cr–C(12)	2.137(13)	Cr–C(13)	2.108(15)
Cr–C(14)	2.143(13)	Cr–C(15)	2.174(12)
S(1)–C(1)	1.716(13)	S(1)–C(8)	1.735(15)
S(2)–C(10)	1.727(12)	S(2)–C(17)	1.764(14)
C(1)–C(2)	1.38(2)	C(1)–C(6)	1.45(2)
C(2)–C(3)	1.42(2)	C(3)–C(4)	1.38(2)
C(4)–C(5)	1.41(2)	C(5)–C(6)	1.41(2)
C(6)–C(7)	1.53(2)	C(7)–C(8)	1.38(2)
C(8)–C(9)	1.52(2)	C(10)–C(11)	1.45(2)
C(10)–C(15)	1.42(2)	C(11)–C(12)	1.41(2)
C(12)–C(13)	1.40(2)	C(13)–C(14)	1.42(2)
C(14)–C(15)	1.38(2)	C(15)–C(16)	1.46(2)
C(16)–C(17)	1.33(2)	C(17)–C(18)	1.51(2)
Cr–M1 [a]	1.609	Cr–M2 [a]	1.619
(b) Angles			
C(1)–S(1)–C(8)	91.6(6)	C(10)–S(2)–C(17)	90.0(6)
S(1)–C(1)–C(2)	130(1)	S(1)–C(1)–C(6)	110.5(9)
C(2)–C(1)–C(6)	120(1)	C(1)–C(2)–C(3)	120(1)
C(2)–C(3)–C(4)	121(1)	C(3)–C(4)–C(5)	120(1)
C(4)–C(5)–C(6)	120(1)	C(1)–C(6)–C(5)	119(1)
C(1)–C(6)–C(7)	114(1)	C(5)–C(6)–C(7)	127(1)
C(6)–C(7)–C(8)	105(1)	S(1)–C(8)–C(7)	119(1)
S(1)–C(8)–C(9)	119(1)	C(7)–C(8)–C(9)	122(1)
S(2)–C(10)–C(11)	126.3(8)	S(2)–C(10)–C(15)	112.3(9)
C(11)–C(10)–C(15)	121(1)	C(10)–C(11)–C(12)	117(1)
C(11)–C(12)–C(13)	121(1)	C(12)–C(13)–C(14)	122(1)
C(13)–C(14)–C(15)	118(1)	C(10)–C(15)–C(14)	120(1)
C(10)–C(15)–C(16)	111.4(9)	C(14)–C(15)–C(16)	128(1)
C(15)–C(16)–C(17)	111(1)	S(2)–C(17)–C(16)	115(1)
S(2)–C(17)–C(18)	115(1)	C(16)–C(17)–C(18)	130(1)
M1–Cr–M2 [a]	179		

[a] M1 and M2 are the centroids of the C(1) to C(6) and C(10) to C(15) rings.

NMR spectra were recorded on Bruker WM360 and ACP250 instruments at 25°C unless otherwise stated; ^1H and ^{13}C spectra were referenced to the residual proton and carbon shifts of the deuterated solvents.

Microanalysis was performed by the microanalytical laboratory of the School of Chemistry and Molecular Sciences.

Mass spectra were recorded on a MS80RF instrument equipped with a dedicated Kratos ion source.

3.1. General procedure for the synthesis of $[Cr(\eta^6\text{-}C_8H_6S)_2]$ (1), $[Cr(\eta^6\text{-}2\text{-}MeC_8H_5S)_2]$ (2), $[Cr(\eta^6\text{-}2\text{-}SiMe_3C_8H_5S)_2]$ (3) and $[Mo(\eta^6\text{-}2\text{-}MeC_8H_5S)_2]$ (4)

The electron-beam vaporised metal was co-condensed with an excess of the ligand (typically a 10-fold

Table 3
Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Cr	1573.6(11)	102.3(27)	4067.5(14)
S(1)	3238(2)	2531(6)	3629(4)
S(2)	3526(2)	−836(6)	5818(3)
C(1)	2246(7)	2096(16)	2433(10)
C(2)	1694(8)	2792(17)	3991(10)
C(3)	887(8)	2303(18)	3632(11)
C(4)	641(8)	1094(22)	2754(12)
C(5)	1191(8)	362(21)	2156(11)
C(6)	1993(7)	872(16)	2467(9)
C(7)	2664(6)	239(14)	1903(8)
C(8)	3324(8)	1120(19)	2495(11)
C(9)	4138(9)	842(29)	2231(13)
C(10)	2505(7)	−1046(15)	5442(9)
C(11)	1949(8)	−177(19)	6006(10)
C(12)	1142(7)	−638(20)	5610(10)
C(13)	902(7)	−1800(19)	4671(12)
C(14)	1448(7)	−2597(16)	4089(10)
C(15)	2245(7)	−2233(15)	4489(9)
C(16)	2915(6)	−2961(15)	4082(8)
C(17)	3603(7)	−2299(18)	4678(10)
C(18)	4440(9)	−2638(26)	4552(15)

molar excess) at 77 K over a period of 2 h. The liquid nitrogen was drained off and the residue allowed to warm to room temperature under dinitrogen. The products were then extracted from the reactor by washing with toluene (750 cm^3), and the resultant suspension was filtered through a Celite bed supported on a frit. The solvent was removed from the filtrate under reduced pressure to leave a coloured residue. Excess was removed by sublimation ($50°C/10^{-4}$ mbar). The ligand residue was again dissolved in toluene (200 cm^3) and refiltered through Celite. Concentration of the filtrate in vacuo and subsequent cooling to −30°C afforded the crystalline sandwich complexes **1**, **2** and **4**, which were isolated, washed at low temperature (−50°C) with light petroleum ether of b.p. 40–60 °C, and dried in vacuo.

Bis(η-benzo[*b*]thiophene)chromium(0) (**1**): brick-red crystals. Yield, 0.25 g, ca. 5% based on chromium. M.p. 177°C, with decomposition. Mass spectrum (EI)m/z: 320 (M^+, 66%).

Bis(η-2-methylbenzo[*b*]thiophene)chromium(0) (**2**): brick-red crystals. Yield, 0.50 g, ca. 10% based on chromium. M.p. 173°C, with decomposition. Mass spectrum (EI) m/z: 348 (M^+, 80%). Microanalysis: Found: C, 62.76; H, 5.01%. $C_{18}H_{16}S_2Cr$ requires: C, 62.05; H, 4.63%.

Bis(η-2-trimethylsilylbenzo[*b*]thiophene)chromium(0) (**3**): Attempts to remove all the residual ligand by sublimation resulted in extensive decomposition and the product could only be characterised in a concentrated solution in an excess of the ligand. Mass spectrum (EI) m/z: 464 (M^+, 41%).

Bis(η-2-methylbenzo[*b*]thiophene)molybdenum(0) (**4**): brown crystals. Yield, 0.50 g, ca. 10% based on molybdenum. M.p. 155°C, with decomposition. Mass spectrum (EI) m/z: 394 (M^+, 60%). Microanalysis: Found: C, 53.34; H, 4.20%. $C_{18}H_{16}S_2Mo$ requires: C, 55.1; H, 4.11% (more accurate microanalysis results could not be obtained for this compound, despite repeated attempts, owing to combustion problems).

3.2. Crystal structure determination of 2

$C_{18}H_{16}CrS_2$, M.W. = 348.5, monoclinic, space group $P2_1/c$, $a = 17.307(5)$, $b = 7.896(3)$, $c = 11.361(5)$ Å, $\beta = 103.23(3)°$, U = 1511.4 Å^3, $Z = 4$, $D_{calc} = 1.53$ g cm^{-3}, $F(000) = 720$. Monochromated Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 9.9$ cm^{-1}.

Data were collected from a crystal ca. 0.8 × 0.6 × 0.01 mm, coated in epoxy glue, on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with $\Delta\theta = (0.8 + 0.35 \tan \theta)°$ and a maximum scan time of 1 min. A total of 2021 unique reflections were measured for $2 < \theta < 22°$ and $+h$ $+k$ $\pm l$, and 1091 reflections with $|F^2| > \sigma(F^2)$ were used in the refinement where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}Lp$. There was no crystal decay and no correction was made for absorption.

The structure was solved by direct methods using MULTAN [18] and non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Hydrogen atoms were held fixed at calculated positions with $B_{iso} = 1.3B_{eq}$ for the atom to which they are bonded. For C(9) and C(18) the hydrogen atoms were given two sites of occupancy 0.5, since a difference map indicated that they were disordered in this way. The weighting scheme was $w = 1/\sigma^2(F)$ and the final residuals were $R = 0.080$, $R' = 0.100$. A final difference map had extreme values of +0.60 and −1.05 e Å^{-3}. Programs from the Enraf-Nonius SDP-PLUS package were on a MicroVax computer.

Tables of anisotropic thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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