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Chemistry of cyclopentadienyl tricarbonylchromium dimer. Cleavage of bis(thiophosphoryl)disulfanes. Syntheses and X-ray crystal structures of $CpCr(CO)_2(S_2P(OR)_2)$, $CpCr(S_2P(OR)_2)_2$ and $Cr(S_2P(OR)_2)_3$ ($R = {}^{i}Pr$)

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Abstract

The facile reaction of $[CpCr(CO)_3]_2$ ($Cp = \eta^5\text{-}C_5H_5$) with one mole equivalent of bis(thiophosphoryl)disulfanes, $(RO)_2P(S)SSP(S)(OR)_2$ ($R = {}^{i}Pr$), at ambient temperature, led to the isolation of dark-purple solids of $CpCr(CO)_2(S_2P(OR)_2)$ (**2**, yield: 32%) and blue solids of $CpCr(S_2P(OR)_2)_2$ (**3**, yield: 30%). At 70–80 °C, the reaction gave **3** (yield: 35%) and $Cr(S_2P(OR)_2)_3$ (**4**, yield: 11%). ^1H-NMR spectral studies demonstrated that **3** and **4** were derived from **2**, the primary product. X-ray diffraction analyses showed that **2** possesses *cis* CO ligands and a bidentate $SP(S)(OR)_2$ ligand, while **3** contains both an unidentate and a bidentate ligand, and in **4** the Cr atom is octahedrally symmetrically coordinated to the three bidentate phosphorylthioato ligand. Variable temperature ^1H and ^{31}P spectral studies showed the occurrence of very rapid unidentate–bidentate exchange between the ligands in **3** in the temperature range −65 to 80 °C. It is also shown that the Cr≡Cr complex $[CpCr(CO)_2]_2$ reacted with $[({}^{i}PrO)_2P(S)S]_2$, albeit much less readily, generating **3** as the eventual product. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 15-Electron chromium(III); Cyclopentadienylchromium; Di-isopropyldithiophosphate; Phosphorodithioato; Crystal structures

1. Introduction

In an ongoing investigation on the reactivity of $[CpCr(CO)_3]_2$ ($Cp = \eta^5\text{-}C_5H_5$) towards the inter-element S–S, P–P and S–P bonds in both inorganic [1–5] and organic substrates [6], we have recently found a facile reaction with bis(diphenylthiophosphinyl)disulfane, $Ph_2P(S)SSP(S)Ph_2$ [7]. We have extended this work to the analogous bis(thiophosphoryl)disulfane, $(RO)_2P(S)$-$SSP(S)(OR)_2$ ($R = {}^{i}Pr$). This was also aimed at contributing to the chemistry of phosphorodithioato complexes of organotransition metals, particularly that of cyclopentadienylchromium, examples of which have not yet been reported. Indeed, in contrast to the rich and well-studied coordination chemistry of phosphorodithioato ligands with the main group elements [8], as well as with some transition elements, e.g. Ti and Zr [9], the organometallic chemistry of phosphorodithioates is much less developed. Examples reported in the last two decades are limited in number, describing mainly the cyclopentadienyl or permethylcyclopentadienyl complexes of Nb [10,11], Fe [12], V [13], Mo [11,14–16], W [14], Rh [17], Ti, Zr and Hf [18], a few carbonyl derivatives of Mo [19,20] and W [21,22], and other complexes containing (η^3-allyl)Mo [23,24], (η^5-indenyl)Mo [25], (η^6-arene)Ru [26], cyclometallated Pd [27] and MePt [28] moieties.

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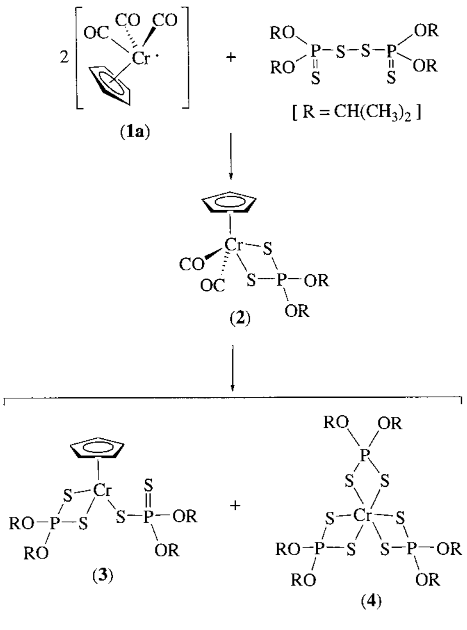
2. Results and discussion

2.1. Products isolation, characterisation and reaction pathways

The reaction of $[CpCr(CO)_3]_2$ (**1**) with one mole equivalent of bis(di-isopropyl)thiophosphoryl)disulfane, $(Pr^iO)_2P(S)SSP(S)(O^iPr)_2$, in toluene at ambient temperature produced a greenish-blue solution, from which the dark-purple solids of $CpCr(CO)_2(S_2P(O^iPr)_2)$ (**2**, Yield: 32%) and blue solids of $CpCr(S_2P(O^iPr)_2)_2$ (**3**, Yield: 30%) were isolated. The same reaction at 70–80 °C, gave a greenish-brown solution, from which were isolated **3** (Yield: 35%) and purple solids of $Cr(S_2P(O^iPr)_2)_3$ (**4**, yield: 11%). At both temperatures, a small amount of $Cp_2Cr_2(CO)_4S$ (ca. 5%) was also isolated.

A time-dependent ^{1}H-NMR spectral study of the reaction at ambient temperature showed that **2** was the only product formed after the total consumption of the ligand in ca. 1 h, with no sign of any other compound up to 2 h. However, after 14 h, ca. 20% of **2** had degraded to **3**. A separate study showed that this degradation in a 31 mM solution of C_6D_6 had a half-life of ca. 40 h. At 70–80 °C, a 40 mM solution of **2** in C_6D_6 solution was converted totally within 30 min into a 1:1 molar mixture of **3** and **4**, together with trace amounts of other unknown Cp-containing compounds. An 80 mM solution of **3** in C_6D_6 at ambient temperature was transformed totally in ca. 20 days to **4**, alongside trace quantities of unidentified Cp-containing compounds, and a small amount of the free disulfane ligand. The ease of degradation of **2** to **3** is also reflected in the failure to observe any sign of the molecular ion of **2** (m/z 386) in the mass spectrum, which possessed only the main mass fragments of **3**.



Scheme 1.

An NMR study of the reaction of a 20 mM solution of $[CpCr(CO)_2]_2$ ($Cr \equiv Cr$) with one molar equivalent of $[(^iPrO)_2P(S)S]_2$ in C_6D_6 was about 90% complete after 5 days at ambient temperature, producing **3** and a trace amount of **2**, which was observed throughout the reaction, suggesting that **2** might also be the primary product as in the reaction of **1**.

As postulated earlier in the reaction with bis(thiophosphinyl)disulfane [7], it is also envisaged that the initial step here involves the attack of the $CpCr(CO)_3$ radical (**1a**) [29] on the S–S bond of the bis(thiophosphoryl)disulfanes, generating complex **2** as the primary product. The results of NMR studies on its formation and degradation, as described above, demonstrated that it transformed to **3**, together with **4** as well at elevated temperatures; this sequence of reactions is presented in Scheme 1. Obviously, the conversion of **2** to **3** has involved the loss of CO ligands with concomitant or subsequent intermolecular association, followed by bond dissociations. The slower conversion rate in a capped NMR tube ($t_{1/2}$ ca. 40 h) is indicative of an essential prior loss of CO. Likewise the formation of a molecule of **4** from **3**, must have involved the interaction between at least two molecules of the latter, with the apparent loss of a $CpCr(S_2P(O^iPr)_2)$ moiety and the cleavage of a Cp ring from the Cr atom which then becomes the central atom in complex **4**, synthesised first from the reaction of chromic chloride with *O,O′*-diisopropyldithiophosphoric acid [30]. The dissociation of the Cp and disulfane ligands in the degradation of **3** is evident in the proton NMR spectrum of the degraded solutions, but unfortunately the Cp-containing species remained elusive to isolation and characterisation. Such a facile cleavage of a η^5-Cp–M bond is uncommon in organometallic compounds, although some examples have been reported, mainly for dicyclopentadienyl metal complexes, e.g. the early transition metals, Ti, V, Y and Zr [31a–f], the early lanthanide metals, La and Nd [31g], and of Ni [31h] and Ru [31i], and a few cases of monocyclopentadienyl metal complexes, e.g. Mo, Mn and Fe [31f], Rh [32a,b], Cr, Mo, W [31f,32c,d]. In addition, it is noted that the complex **3**, like its analogue $CpCr(S_2PPh_2)_2$ [7], is a stable 15-electron complex of Cr(III), numerous examples of which have now been documented [33]; these belong to the expanding family of ‘18e-non-compliant’ complexes in the grey area between the classical Werner-coordination and the 18-electron organometallic types of the open-shell compounds.

Complex **2** possesses a Cp resonance at δ 4.54 (^{1}H) and δ 94.3 (^{13}C) in C_6D_6, within the range observed for the CpCr moiety [1–5]. The *i*-propyl protons are observed at δ 4.47 (m, CH) and δ 1.11 (d, $J = 6$ Hz, CH_3);

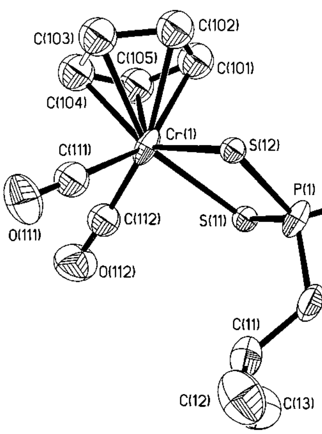


Fig. 1. Molecular structure of $CpCr(CO)_2(S_2P(O^iPr)_2)$ (**2**).

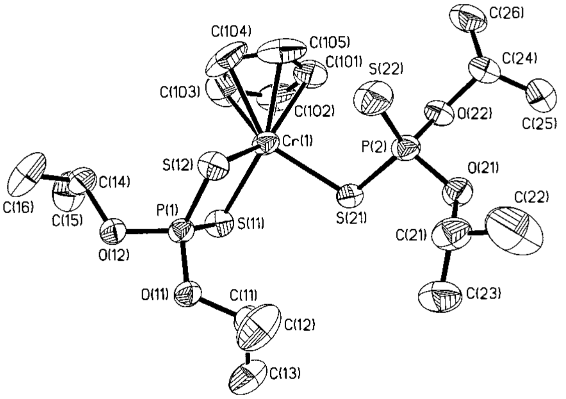


Fig. 2. Molecular structure of $CpCr(S_2P(O^iPr)_2)_2$ (**3**).

and the carbon atoms at δ 73.4 (br, CH), δ 24.4 (CH_3) and δ 266.6, 266.5 (CO's). A ^{31}P resonance is seen at δ 81.1. Its infrared spectrum in Nujol shows two PS stretches at 636 m and 564 m cm^{-1}, as compared with 642 and 569 cm^{-1} for $CpCr(CO)_2(S_2PPh_2)$ [7], 641 and 550 cm^{-1} for $MeCpMo(CO)_2(S_2P(O^iPr)_2)$ [11]. These PS stretching frequencies occur at 656m ($\nu_{(P=S)}$) and 550w ($\nu_{(P–S)}$) cm^{-1} in **3**, and 644vs and 540 s cm^{-1} in **4**, as compared with 649 and 544 cm^{-1} for $CpCr(S_2PPh_2)_2$ [7], ν 650–658vs and 540–542s for $CpFe(CO)_2(\eta^1$-$S_2P(OR)_2$ (R = Et, ^{i}Pr) [12].

The proton NMR spectrum of complex **3** in C_6D_6 at 27 °C shows two broad symmetrical signals, at δ 5.7 ($\nu_{1/2}$ ca. 470 Hz) and δ 2.51 ($\nu_{1/2}$ ca. 120 Hz), respectively, with relative intensity ca. 1:6, which is assignable to the CH and CH_3 protons, respectively, of the *iso*-propyl ligand. In an attempt to detect the Cp resonance, a variable-temperature NMR study in $C_6D_5CD_3$ was carried out, but to no avail. In this solvent, only one broad signal was observed, with its half-width decreasing with rise in temperature: δ 2.97 ($\nu_{1/2} > 1000$ Hz), δ 2.76 ($\nu_{1/2} > 900$ Hz), δ 2.51 ($\nu_{1/2}$ ca. 129 Hz), δ 2.28 ($\nu_{1/2}$ ca. 57 Hz) at −65, −40, 27, 80 °C, respectively. This is accompanied by a shift in the single ^{31}P resonance from δ 81.1 to 83.2. The observation of a single ^{31}P resonance for **3** containing two P atoms in different molecular environments, suggests that there exists a rapid unidentate–bidentate exchange over the wide temperature range studied, as observed earlier for $CpCr(S_2PPh_2)_2$ [7]. These observations in the VT ^{31}P-NMR spectral changes of phosphorodithioato and phosphinodithioato complexes of Cr are distinctively different from other such metal complexes, e.g. in $CpM(NO)(S_2P(OR)_2)_2$ (M = Mo, W), the inter-ligand exchange began to 'freeze out' at −14 °C to show two distinct sharp ^{31}P signals in acetone-d_6 [14]. The ambient temperature ^{13}C spectrum of **3** in C_6D_6 shows only two signals at δ 192.9 (very broad) and δ 45.7; in an attempt to assign these signals, a H-coupled ^{13}C spectrum was obtained, but unfortunately it showed only the first signal unchanged and the second (δ 44.8) very much broadened but without any fine structure. Nonetheless, it is reasonable to assume that the signal at δ 45.7 pertains to the CH_3 carbon of the *iso*-propyl ligand, and δ 193 to the Cp ring carbons in agreement with previous observations of such low-field Cp resonances in $CpCr(S_2PPh_2)_2$ [7] and $[CpCr(CO)_3]_2$ [29c] and its permethyl analogue [29d]. The other Cr(III) complex **4** in C_6D_6 possesses only one broad symmetrical signal at δ 1.83 ($\nu_{1/2}$ ca. 350 Hz) (in CD_3OD the signal shifts from δ 2.3 ($\nu_{1/2}$ ca. 800 Hz) at −20 °C, through δ 1.91 ($\nu_{1/2}$ ca. 230 Hz) at 27 °C to δ 1.85 ($\nu_{1/2}$ ca. 150 Hz) at 58 °C), a ^{31}P resonance at δ 81.1 and two broad ^{13}C signals at δ 45.9 and 37.8, assignable to the ligand CH and CH_3 carbon atoms, respectively.

2.2. Crystallographic studies

Although **4** had been prepared earlier from $CrCl_3$ [30] and $Cr(acac)_3$ [34], its structure had not been determined; hence its molecular structure together with those of **2** and **3**, were determined here by X-ray diffraction analysis. The ORTEP drawings are displayed in Figs. 1–3. Selected bond lengths and angles are listed in Table 1 and compared with those of the related complexes in Table 2.

The structure of **2** possesses a four-legged piano-stool configuration at Cr, coordinated to a bidentate dithioato and two CO ligands, similar to that found for $CpCr(CO)_2(S_2PPh_2)$ [7] and the analogous Mo complex $MeCpMo(CO)_2(S_2P(O^iPr)_2)$ [11]. On the other hand, the structure of **3** reveals a three-legged piano-stool geometry about chromium similar to that in $CpCr(S_2PPh_2)_2$, with η^5-coordination to the Cp ring and with a monodentate and a bidentate dithiophosphato ligand forming the three legs [7]. The Cr atom is situated at a distance of 1.884 Å from one side of the near-planar Cp ring, which has a mean deviation of 0.0036 Å from their least-squares plane. As seen in Table 1, the Cr–S bond length in the monodentate

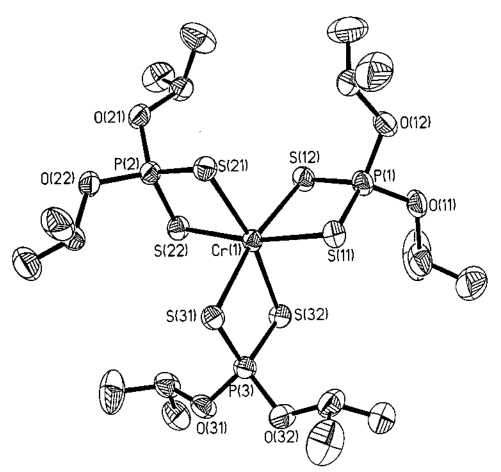


Fig. 3. Molecular structure of Cr(S$_2$P(O^{i}Pr)$_2$)$_3$ (**4**).

ligand is significantly shorter (2.3711(8) Å) than the corresponding bond lengths in the bidentate ligand (2.4021(9), 2.4015(8) Å), which are closer to those in **4** (2.4197(11)–2.4312(11) Å), than to those in **2** (2.457(8)–2.517(8) Å). The P=S bond in the unidentate ligand (1.9378(11) Å) in **3** is, as expected, significantly shorter than the other P–S bonds (2.0258(11), 2.0006(10), 1.9872(10) Å), as well as those in **2** (1.992(5)–2.002(5) Å) and in **4** (1.9919(15)–2.0009(15) Å). Indeed, the double bond character of the P=S bond in **3** is stronger than in the related unidentate dithio ligands in other complexes, e.g. CpCr(S$_2$PPh$_2$)$_2$ (P=S bond length 1.9688(10) Å) [7], and analogous Fe complexes (bond length 1.944(2), 1.940(1) Å) [12]. Additionally, as expected the S–P=S angle (118.30(5)°) involving the non-bonded S atom of the unidentate ligand in **3** is much larger than the S–P=S angles of the bidentate ligands in **2** (104.1(2), 105.1(2)°) and in **4** (105.22(6)°), although close to those in CpCr(S$_2$PPh$_2$)$_2$ (116.06(5)°), and in the Fe complexes (112.5(1), 119.9(1)°) [12]. The Cr(1)–S(22) distance is 3.875(1) Å, in agreement with the absence of any bonding interaction. Complex **4** displays a formally octahedral geometry, with a CrS$_6$

Table 1
Selected bond lengths (Å) and angles (°) for **2**–**4**

Complexes	CpCr(CO)$_2$(S$_2$P(O^{i}Pr)$_2$) (**2**)	CpCr(S$_2$P(O^{i}Pr)$_2$)$_2$ (**3**)	Cr(S$_2$P(O^{i}Pr)$_2$)$_3$ (**4**)
Bond lengths			
Cr(1)–S(11)	2.517(8), 2.505(7)	2.4021(9)	2.4221(11)
Cr(1)–S(12)	2.481(8), 2.457(8)	2.4015(8)	2.4227(11)
Cr(1)–S(21)	-	2.3711(8)	2.4201(11)
Cr(1)–S(22)	-	3.875(1)	2.4197(11)
Cr(1)–S(31)	–	–	2.4244(10)
Cr(1)–S(32)	–	–	2.4312(11)
P(1)–S(11)	2.001(6), 1.984(6)	2.0006(10)	1.9930(14)
P(1)–S(12)	2.002(5), 1.992(5)	1.9872(10)	2.0009(15)
P(2)–S(21)	–	2.0258(11)	1.9973(14)
P(2)–S(22)	–	1.9378(11)	1.9919(15)
P(3)–S(31)	–	–	1.9949(14)
P(3)–S(32)	–	–	1.9958(14)
Bond angles			
S(11)–Cr(1)–S(12)	78.9(2), 78.4(2)	83.65(3)	81.83(4)
S(21)–Cr(1)–S(22)	–	–	81.97(4)
S(31)–Cr(1)–S(32)	–	–	81.99(4)
S(11)–P(1)–S(12)	105.1(2), 104.1(2)	106.88(4)	105.22(6)
O(11)–P(1)–O(12)	95.1(3)	96.75(10)	96.68(15)
O(11)–P(1)–S(11)	118.9(3)	112.82(8)	113.26(12)
O(12)–P(1)–S(12)	120.8(3)	113.71(8)	113.81(12)
S(21)–P(2)–S(22)	–	118.30(5)	105.44(6)
O(21)–P(2)–O(22)	–	100.14(11)	96.18(14)
O(21)–P(2)–S(21)	–	105.97(9)	113.64(12)
O(22)–P(2)–S(22)	–	114.60(9)	114.56(13)
S(31)–P(3)–S(32)	–	–	105.91(6)
O(31)–P(3)–O(32)	–	–	96.47(15)
O(31)–P(3)–S(31)	–	–	114.25(12)
O(32)–P(3)–S(32)	–	–	114.54(12)
Cr(1)–S(11)–P(1)	87.4(3), 88.0(2)	84.57(3)	86.56(5)
Cr(1)–S(12)–P(1)	88.4(3), 89.2(3)	84.87(3)	86.38(5)
Cr(1)–S(21)–P(2)	–	106.85(4)	86.23(5)
Cr(1)–S(22)–P(2)	–	–	86.36(5)
Cr(1)–S(31)–P(3)	–	–	86.15(5)
Cr(1)–S(32)–P(3)	–	–	85.95(5)

Table 2
A comparison of selected significant bond lengths (Å) and bond angles (°) in related cyclopentadienyl metal complexes [a]

	$CpCr(CO)_2$-$(S_2P(O^iPr)_2)$ (**2**) [b]	$CpCr(S_2P(O^iPr)_2)_2$ (**3**) [b,c]	$CpCr(S_2PPh_2)_2$ [b,c] [7]	$CpM(CO)_2(S_2P(OR)_2)$				$Cp^*RhCl(S_2P(OEt)_2)$ [17]
				$CpMo(CO)_2$-$(S_2P(O^iPr)_2)$ [b,d] [11]	$CpFe(CO)_2(S_2P(O^iPr)_2)$ [c]		$CpFe(CO)_2(S_2P(OEt)_2)$ [c] [12c]	
					$Cp = C_5H_5$ [12b]	$Cp = C_5Me_5$ [12d]		
Bond lengths								
M–S(11)	2.517(8), 2.505(7)	2.4021(9)	2.4104(8)	2.550(1)	–	–	–	2.440(2)
M–S(12)	2.481(8), 2.457(8)	2.4015(8)	2.4233(9)	2.559(1)	–	–	–	2.4270(13)
M–S(21)	–	2.3711(8)	2.3756(8)	–	2.322(2)	2.311(1)	2.304(1)	–
P(1)–S(11)	2.001(6), 1.984(6)	2.0006(10)	2.0229(10)	1.992(1)	–	–	–	1.985(2)
P(1)–S(12)	2.002(5), 1.992(5)	1.9872(10)	2.0209(11)	1.994(1)	–	–	–	1.985(2)
P(2)–S(21)	–	2.0258(11)	2.0537(10)	–	2.026(2)	2.021(1)	2.018(1)	–
P(2)–S(22)	–	1.9378(11)	1.9688(10)	–	1.944(2)	1.940(1)	1.933(1)	–
Bond angles								
S(11)–M–S(12)	78.9(2), 78.4(2)	83.65(3)	84.92(3)	76.5(1)	–	–	–	80.99(5)
S(11)–P(1)–S(12)	105.1(2), 104.1(2)	106.88(4)	107.60(4)	105.0(1)	–	–	–	105.51(8)
S(21)–P(2)–S(22)	–	118.30(5)	116.06(5)	–	112.5(1)	111.9(1)	112.1(1)	–
P(1)–S(11)–M	87.4(3), 88.0(2)	84.57(3)	83.50(3)	89.1(1)	–	–	–	86.46(6)
P(1)–S(12)–M	88.4(3), 89.2(3)	84.87(3)	83.21(3)	88.8(1)	–	–	–	86.82(6)
P(2)–S(21)–M	–	106.85(4)	113.81(4)	–	109.1(1)	112.0(1)	111.2(1)	–

[a] $Cp = C_5H_5$, unless otherwise specified.

[b] Contains bidentate ligand.

[c] Contains unidentate ligand.

[d] $Cp = C_5H_4Me$.

chromophore involving three bidentate dithio ligands, as observed before for other dithiophosphinate and dithiophosphate complexes of Cr(III) [35]. Like its (OEt) [35a] and ($OCH_2CH(Me)CH_2O$) [35d] analogues, **4** crystallises in the centrosymmetric space group *C*2/*c*; the Cr–S bond distances fall in the range of 2.4197(11)–2.4312(11) Å, the angles subtended by the ligands at Cr are all similar (81.83(4)–81.99(4)°), as are the Cr–S–P angles at S (85.95(5)–86.56(5)°), the P atoms are tetrahedral, the S–P–S angles being close to ideal.

3. Experimental

All reactions were carried out using the conventional Schlenk techniques under an inert atmosphere of nitrogen or under argon in an M. Braun Labmaster 130 Inert Gas System.

The NMR spectra were measured on a Bruker 300 MHz FT NMR spectrometer; for ^{1}H and ^{13}C spectra, chemical shifts were referenced to residual C_6H_6 in C_6D_6, or $C_6D_5CH_2D$ in $C_6D_5CD_3$; for ^{31}P spectra, chemical shifts were referenced to external H_3PO_4. IR spectra in Nujol mulls were measured in the range of 4000–200 cm^{-1} by means of a BioRad FTS-165 FTIR instrument. Mass spectra were run on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were carried out by the microanalytical laboratory in-house.

$[CpCr(CO)_3]_2$ (**1**) was synthesised as described by Manning [36] from chromium hexacarbonyl (98% purity from Fluka). The bis(thiophosphoryl)disulfane, $({}^{i}PrO)_2P(S)SSP(S)(O^{i}Pr)_2$, was prepared according to the procedures published earlier [37]. All solvents were dried over sodium–benzophenone and distilled before use. Celite (Fluka AG), silica gel (Merck Kieselgel 60, 230–400 mesh) were dried at 140 °C overnight before the chromatographic use.

3.1. Reaction of $[CpCr(CO)_3]_2$ (1) with $[({}^{i}PrO)_2P(S)S]_2$

3.1.1. At ambient temperature

A deep-green mixture of $[CpCr(CO)_3]_2$ (**1**) (201 mg, 0.50 mmol) and $[({}^{i}PrO)_2P(S)S]_2$ (213 mg, 0.50 mmol) in toluene (8 ml) was stirred at ambient temperature for 5 h. The resultant homogeneous greenish-blue reaction mixture was concentrated to ca. 3 ml and loaded on to a silica gel column (2×15 cm^2) prepared in *n*-hexane. Elution gave four fractions as follows: (i) A greenish-brown eluate in *n*-hexane–toluene (2:1, 10 ml), which on concentration gave deep-green crystals of $Cp_2Cr_2(CO)_4S$ (9 mg, 0.024 mmol, yield: 4.8%), identified by its colour characteristics and ^{1}H Cp resonance in benzene-*d*$_6$ at δ 4.36 [1a,c]; (ii) A purple eluate in toluene (15 ml), from which were obtained dark-purple crystalline solids of $CpCr(CO)_2(S_2P(O^{i}Pr)_2)$ (**2**) (125 mg, 0.32 mmol, yield: 32.4%). Anal. Found: C, 40.4; H, 4.8; Cr, 12.8; P, 7.3; S, 16.6. Calc. for $C_{13}H_{19}O_4S_2PCr$: C, 40.4; H, 5.0; Cr, 13.5; P, 8.0; S, 16.6%. ^{1}H-NMR (C_6D_6): δ 4.54 (s, Cp), 4.47 (m, CH), 1.11 (d, CH_3, $J = 6$ Hz). ^{13}C-NMR (C_6D_6): δ 94.3 (Cp), 73.4 (br, CH), 24.4 (CH_3), 266.6, 266.5 (CO). ^{31}P-NMR (C_6D_6): δ 81.1. IR (Nujol, cm^{-1}): ν(CO) 2001sh, 1965vs, 1899vs, 1872sh; ν(other bands) 2725w, 1179w, 1140w, 1104w, 993m, 971s, 889w, 847w, 818m, 792w, 764w, 769w, 723w, 677vw, 653vw, 636m, 564m, 549w, 526m, 462w. FAB-MS (+ve): *m*/*z*: identical with that of **3** given below: (iii) A greenish-blue eluate in toluene–ether (1:1, 15 ml), which gave deep-blue crystalline solids of $CpCr(S_2P(O^{i}Pr)_2)_2$ (**3**) (103 mg, 0.189 mmol, yield: 18.9%). Anal. Found: C, 38.0; H, 6.1; Cr, 8.5; P,10.7; S, 23.1. Calc. For $C_{17}H_{33}O_4S_4P_2Cr$: C, 37.6; H, 6.1; Cr, 9.6; P, 11.4; S, 23.6%. IR (Nujol, cm^{-1}): ν 2724vw, 1176w, 1141w, 1108m, 1012m, 986s, 968s, 946s, 880m, 823w, 787m, 761m, 678m, 656m, 633w, 581vw, 559w, 550w, 537w. FAB-MS (+ve): *m*/*z*: 543 $[CpCr(S_2P(O^{i}Pr)_2)]$, 478 $[Cr(S_2P(O^{i}Pr)_2]$, 436, 394, 352 (for three consecutive losses of CMe_2 fragments), 330 $[CpCr(S_2P(O^{i}Pr)_2)]$, 310 $[Cr(S_2P(OH)_2)_2]$, 246 $[CpCr(S_2P(OH)_2)]$, 212 $[S_2P(O^{i}Pr)_2)]$, 181 $[SP(O^{i}Pr)_2]$, 52 [Cr]. ^{1}H-NMR (C_6D_6): δ 5.7 ($\nu_{1/2}$ 470 Hz) and 2.51 ($\nu_{1/2}$ 120 Hz) with relative intensity ca. 1:6. ^{13}C-NMR (C_6D_6): δ 45.7 and 192.9 (very br). ^{31}P-NMR (C_6D_6): δ 85.4; in $C_6D_5CD_3$ this shifts from δ 81.1 (−65 °C) through 82.6 (27 °C), δ 82.9 (60 °C) to 83.2 (80 °C); (iv) A blue eluate in THF (10 ml), which on concentration yielded a second crop of **3** (62 mg, 0.11 mmol, yield: 11.4%).

3.1.2. At 70–80 °C

A deep-green mixture of **1** (201 mg, 0.50 mmol) and $[({}^{i}PrO)_2P(S)S]_2$ (213 mg, 0.50 mmol) in toluene (8 ml) was stirred at 70–80 °C for 1 h. The resultant greenish-brown reaction mixture was filtered to remove a dirty dark-green insoluble unidentifiable precipitate (15 mg). The filtrate was concentrated to ca. 4 ml and loaded on to a silica gel column (2×15 cm^2) prepared in *n*-hexane. Elution gave four fractions: (i) A greenish-brown eluate in *n*-hexane–toluene (2:1, 10 ml), which on concentration gave deep-green crystals of $Cp_2Cr_2(CO)_4S$ (10 mg, 0.026 mmol, yield: 5.2%); (ii) A purple eluate in *n*-hexane–toluene (1:2, 20 ml), from which was obtained purple crystalline solids of $Cr(S_2P(O^{i}Pr)_2)_3$ (**4**) (74 mg, 0.11 mmol, yield: 10.7%). Anal. Found: C, 31.2; H, 6.1; Cr, 6.8; P, 12.6; S, 28.1. Calc. for $C_{18}H_{42}O_6S_6P_3Cr$: C, 31.3; H, 6.1; Cr, 7.5; P, 13.4; S, 27.8%. IR (Nujol, cm^{-1}): ν 2729w, 1755w, 1569w, 1333m, 1179vs, 1142s, 1102m, 1081w, 1018vs, 973vs, 891s, 789vs, 742m, 723w, 644vs, 636sh, 540s, 449m, 411m. FAB-MS (+ve): *m*/*z* 691 $[Cr(S_2P(O^{i}Pr)_2)_3]$, 478 $[Cr(S_2P(O^{i}Pr)_2)_2]$, 436, 394, 352 (for three consecutive losses of CMe_2 fragments), 310 $[Cr(S_2P(OH)_2)_2]$, 277 $[Cr(S_2P(OH)_2)$ $(S_2PH)]$, 181 $[SP(O^{i}Pr)_2]$, 52 [Cr]. ^{1}H-

NMR (C_6D_6): δ 1.83 ($\nu_{1/2}$ 350 Hz); in CD_3OD this shifts from δ 2.3 ($\nu_{1/2}$ 800 Hz) at −20 °C through 1.91 ($\nu_{1/2}$ 230 Hz) at 27 °C to 1.85 ($\nu_{1/2}$ 150 Hz) at 58 °C. ^{13}C-NMR (C_6D_6): δ 37.8 and 45.9 (both br). ^{31}P-NMR (C_6D_6): δ 81.1. (iii) A blue eluate in toluene (15 ml), which gave **3** (105 mg, 0.19 mmol, yield: 19.3%). (iv) A blue eluate in THF (10 ml), from which was obtained a second crop of **3** (84 mg, 0.16 mmol, yield: 15.5%).

3.2. NMR tube reactions

*3.2.1. Reaction of $[CpCr(CO)_3]_2$ (**1**) with $[(^iPrO)_2P(S)S]_2$*

A deep-green mixture of $[CpCr(CO)_3]_2$ (**1**) (4 mg, 0.01 mmol) and $[(^iPrO)_2P(S)S]_2$ (4.3 mg, 0.01 mmol) in benzene-d_6 (0.5 ml) in a 5 mm NMR tube was manually shaken for 2 min, and then its proton NMR spectra scanned and subsequently monitored at regular intervals (5, 10, 20, 40, 60, 120 min and 14 h).

3.2.2. Reaction of $[CpCr(CO)_2]_2$ (Cr≡Cr) with $[(^iPrO)_2P(S)S]_2$

A dark-green mixture of $[CpCr(CO)_2]_2$ (Cr≡Cr) (3.5 mg, 0.01 mmol) and $[(^iPrO)_2P(S)S]_2$ (4.3 mg, 0.01 mmol) in benzene-d_6 (0.5 ml) in a 5 mm NMR tube was manually shaken for 2 min, and then its proton NMR spectra scanned and subsequently monitored at regular time intervals (5, 15, 40, 120 min and 20, 120 h).

*3.2.3. Thermolysis of **2***

At ambient temperature. The proton NMR of a 31 mM solution of **2** (6 mg, 0.15 mmol) in benzene-d_6 (0.5 ml) was monitored at hourly intervals up to 8 h; the change in the integrals of the resonance of **2**, gave an approximate conversion rate from 11% at 4 h, through 57% at 48 h to 69% at 76 h.

At 70–80 °C. A deep-purple solution of $CpCr(CO)_2(S_2P(O^iPr)_2)$ (**2**) (8 mg, 0.02 mmol) in benzene-d_6 (0.5 ml) in a 5 mm NMR tube was maintained at 70–80 °C for 30 min, followed by a measurement of its proton NMR spectrum.

*3.2.4. Decomposition of **3** at ambient temperature*

The proton NMR of a deep-blue solution of $CpCr(S_2P(O^iPr)_2)_2$ (**3**) (16 mg, 0.04 mmol) in benzene-d_6 (0.5 ml) in a 5 mm NMR tube was monitored at regular intervals.

3.3. Structure determinations

Diffraction-quality single crystals were obtained from solutions at −29 °C as follows: **2** as dark-purple rhombus from *n*-hexane–toluene after 1 day; **3** as dark-blue prism from *n*-hexane–toluene after 4 days; and **4** as purple prism from *n*-hexane–toluene after 3 days.

The crystals were mounted on quartz fibres. X-ray data for **2** and **4** were collected on a Siemens SMART diffractometer, equipped with a CCD detector, using Mo–K_α radiation at 223 and 173 K, respectively, while that for **3** was collected on an Enraf–Nonius CAD-4 diffractometer, using Mo–K_α radiation at 298 K.

Data were corrected for Lorentz and polarisation effects with the SMART suite of programs [38] for **2** and **4**, and with the CAD-4 VAX/PC software [39] for **3**. The absorption effects for **2** and **4** were corrected with SADABS [40] and for **3** with the NRCVAX absorption correction routine using a set of psi-scan [41]. The final unit cell parameters were obtained by least squares on a number of strong reflections (3321 for **2**; 3759 for **3** and 8192 for **4**). Structural solution and refinement were carried out with the SHELXTL suite of programs [42].

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The hydrogen atoms (except the tertiary hydrogens of the ^{i}Pr groups in **2**) were placed in calculated positions (C–H = 0.95 Å) and allowed to ride on the attached carbon; they were assigned the isotropic thermal parameters 1.5 times that of the carbon atom that they rode on. All non-hydrogen atoms were given anisotropic displacement parameters in the final model.

In the case of **2**, disorder involving the Cp and CO's was quite apparent. The elongated shapes of the thermal ellipsoids for the Cr and S atoms also suggest disorder of these atoms. Thus each of these groups/atoms was modelled as disordered over two sites of equal occupancies. The Cp rings were restrained to be in a regular pentagon; the disordered atoms/groups were given equivalent thermal ellipsoids; and same bond types (Cr–C, Cr–S and S–P) were restrained to be similar in lengths.

Experimental details for the structure determinations are given in Table 3.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 154400, 154350, 154399 for compounds **2**, **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 3
Crystal and structure refinement data

Complexes	**2**	**3**	**4**
Empirical formula	$C_{13}H_{19}CrO_4PS_2$	$C_{17}H_{33}CrO_4P_2S_4$	$C_{18}H_{42}CrO_6P_3S_6$
Formula weight	386.37	543.61	691.79
Temperature (K)	223(2)	293(2)	223(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$
Unit cell dimensions			
a (Å)	6.2747(9)	8.6359(7)	$a = 23.3131(2)$
b (Å)	16.176(2)	12.8915(8)	$b = 14.8642(2)$
c (Å)	17.510(3)	13.2046(8)	$c = 21.24760(10)$
α (°)	90	67.933(5)	$\alpha = 90$
β (°)	90.260(5)	84.320(6)	$\beta = 111.75$
γ (°)	90	78.960(5)	$\gamma = 90$
V (Å^3)	1777.3(5)	1336.6(2)	6838.96(11)
Z	4	2	8
D_{calc} (g cm^{-3})	1.444	1.351	1.344
Absorption coefficient (mm^{-1})	0.978	0.879	0.869
F(000)	800	570	2904
Crystal size (mm^3)	$0.38 \times 0.24 \times 0.06$	$0.4 \times 0.5 \times 0.5$	$0.38 \times 0.38 \times 0.14$
θ range for data collection (°)	1.71–27.69	1.66–24.97	2.06–29.36
Index ranges	$-7 \le h \le 5$, $0 \le k \le 19$, $0 \le l \le 22$	$-10 \le h \le 10$, $0 \le k \le 15$, $-14 \le l \le 15$	$-30 \le h \le 29$, $0 \le k \le 20$, $0 \le l \le 28$
Reflections collected	14 826	4695	48 952
Independent reflections	2565 [$R_{int} = 0.0465$]	4695	8579 [$R_{int} = 0.0936$]
Absorption correction	SADABS	PSISCAN	SADABS
Max/min transmission	0.862081, 0.663114	0.876472, 0.757476	0.825233, 0.331657
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2565/63/184	4695/0/253	8579/0/307
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0937$, $wR_2 = 0.2062$	$R_1 = 0.0359$, $wR_2 = 0.1064$	$R_1 = 0.0593$, $wR_2 = 0.1277$
R indices (all data)	$R_1 = 0.1309$, $wR_2 = 0.2313$	$R_1 = 0.0464$, $wR_2 = 0.1165$	$R_1 = 0.1162$, $wR_2 = 0.1499$
Goodness-of-fit on F^2	1.161	0.740	0.958
Largest difference peak and hole (e Å^{-3})	0.543 and −0.531	0.308 and −0.248	0.655 and −0.656

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