

Chemistry of cyclopentadienyl tricarbonylchromium dimer. Cleavage of bis(thiophosphinyl)disulfanes and bis(thiophosphoryl)disulfanes. Syntheses of $\text{CpCr}(\text{CO})_2(\text{S}_2\text{PPh}_2)$ and $\text{CpCr}(\text{S}_2\text{PPh}_2)_2$. X-ray crystal structure of $\text{CpCr}(\text{S}_2\text{PPh}_2)_2$

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Dedicated to Professor Martin A. Bennett on the occasion of his retirement.

Abstract

The facile reaction of $[\text{CpCr}(\text{CO})_3]_2$ with one mole equivalent of bis(diphenylthiophosphinyl)disulfane, $\text{Ph}_2\text{P}(\text{S})\text{SSP}(\text{S})\text{PPh}_2$, led to the isolation of dark purplish brown solids of $\text{CpCr}(\text{CO})_2(\text{S}_2\text{PPh}_2)$ (**2**) and blue solids of $\text{CpCr}(\text{S}_2\text{PPh}_2)_2$ (**3**) in 50 and 10% yields, respectively. Proton NMR spectral studies demonstrated that **3** is derived from **2**, the primary product. IR spectral data indicated that **2** possesses *cis* CO ligands and a bidentate $\text{SP}(\text{S})\text{Ph}_2$ ligand, whilst **3** contains both a unidentate and a bidentate ligand, as confirmed by its X-ray diffraction analysis. 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 -80 – 60°C . © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Chromium; Cyclopentadienylchromium; Diphenyldithiophosphinate; Phosphinodithioato; Crystal structure

1. Introduction

Previous work from one of our laboratories has demonstrated the extreme ease with which the monomeric $\text{CpCr}(\text{CO})_3$ species cleaves the inter-element S–S, P–P and S–P bonds in polyatomic chalcogen molecules [1], pnictogen molecules [2], mixed phosphorus–chalcogen cages [3] and diaryl dichalcogenides [4], and lately, also the bonds between main group metals and sulfur in Sb_2S_3 [5]. The rich chemistry arising therefrom, as described in our recent review [6], indicated to us that similar investigations involving the bis(thiophosphinyl)disulfanes, $\text{R}_2\text{P}(\text{S})\text{SSP}(\text{S})\text{PR}_2$, and bis(thiophosphoryl)disulfanes, $(\text{RO})_2\text{P}(\text{S})\text{SSP}(\text{S})\text{P}(\text{OR})_2$, would be a potentially fruitful exercise. Indeed, as we

had also observed for the reactions of $[\text{CpCr}(\text{CO})_3]_2$ with diaryl dichalcogenides [4], these disulfanes are known to undergo facile S–S homolytic bond cleavage in reactions with low oxidation state compounds, giving rise to metal phosphinodithioato, $\text{M}-\text{S}(\text{S})\text{PR}_2$ and phosphorodithioato, $\text{M}-\text{S}(\text{S})\text{P}(\text{OR})_2$ derivatives.

A large number of main group metal organometallic dithiophosphates and dithiophosphinates have been characterized structurally [7], but to date, there are only a few reported cases of organometallic transition metal dialkyl or diaryl dithiophosphates; these include some metal carbonyl derivatives [8] and some specific compounds, e.g. (i) $\text{Cp}_2\text{Nb}(\text{S}_2\text{P}(\text{OR})_2)_2$ from the reaction of $\text{Cp}_2\text{Nb}(\text{CH}_3)_2$ with $[\text{S}_2\text{P}(\text{OR})_2]_2$ ($\text{R} = \text{Pr}, \text{Et}$) [9]; (ii) $[\text{Cp}_2\text{V}(\text{S}_2\text{P}(\text{OR})_2)_2]^+[\text{S}_2\text{P}(\text{OR})_2]^-$ from the reaction of Cp_2V with $[\text{S}_2\text{P}(\text{OR})_2]_2$ ($\text{R} = \text{Et}$) [10]; (iii) $\text{CpFe}(\text{CO})_2(\text{S}_2\text{P}(\text{OR})_2)_2$, derived from the reaction of $[\text{CpFe}(\text{CO})_2]_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5, \eta^5\text{-C}_5\text{Me}_5$) with

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$[\text{S}_2\text{P}(\text{OR})_2]_2$ ($\text{R} = \textit{i}\text{Pr}, \text{Et}$) [11]; and (iv) $\text{CpNbCl}_3\text{-(S}_2\text{P}(\text{OR})_2)_2$, $\text{CpNbCl}(\mu\text{-Cl})_2\text{Nb(S}_2\text{P}(\text{OR})_2)_2\text{Cp}$ and $\text{MeCpMo(CO)}_2(\text{S}_2\text{P}(\text{OR})_2)_2$ ($\text{R} = \textit{i}\text{Pr}$) from the reaction of $\text{HS}_2\text{P}(\text{OR})_2$ with CpNbCl_4 and $[(\text{MeCp})\text{Mo(CO)}_3]_2$, respectively [12]. More recent reports have described the reactions of specific transition metal complexes with $\text{NH}_4(\text{S}_2\text{P}(\text{OEt})_2)_2$ to yield phosphorodithioato compounds like $(\eta^6\text{-arene})\text{RuCl(S}_2\text{P}(\text{OR})_2)_2$ (arene = benzene, *p*-cymene; $\text{R} = \text{Et}, \textit{rPr}, \textit{iPr}, \textit{nBu}$ or \textit{sBu}) [13a], $\text{Cp}^*\text{RhCl(S}_2\text{P}(\text{OR})_2)_2$ ($\text{R} = \text{Et}, \textit{rPr}, \textit{iPr}$) and $\text{Cp}^*\text{Rh(S}_2\text{P}(\text{OEt})_2)_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) [13b], and allyl complexes of Mo, viz. $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo(CO)}_2\text{-(S}_2\text{P}(\text{OEt})_2)_2(\mu\text{-NH}_2\text{NH}_2)]$ [8e] and $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo(MeCN)(CO)}_2(\text{S}_2\text{P}(\text{OEt})_2)]$ [14].

Similar complexes of the corresponding dithiophosphinates are rarer; they include $[\text{Cp}_2\text{V(S}_2\text{P}(\text{Et})_2)]^+[\text{S}_2\text{P}(\text{Et})_2]^-$ [10]; $\text{W(CO)}_3(\text{S}_2\text{PR}_2)_2$ from the reaction of $\text{W(CO)}_3(\text{NCMe})_3$ with $[\text{SP}(\text{S})\text{R}_2]_2$ ($\text{R} = \text{Et}, \text{Pr}$) [8c]; (arene) $\text{Ru(S}_2\text{PR}_2)_2$ ($\text{R} = \text{Me}, \text{Ph}$) and $(\text{C}_5\text{Me}_5)\text{M(S}_2\text{PR}_2)_2$ ($\text{M} = \text{Ru}, \text{Rh}, \text{Ir}; \text{R} = \text{Me}, \text{Ph}$) from the reaction of $[(\text{arene})\text{RuCl}_2]_2$ and $[(\text{C}_5\text{Me}_5)\text{MCl}_2]_2$ ($\text{M} = \text{Ru}, \text{Rh}, \text{Ir}$), respectively, with $[\text{S}_2\text{PR}_2]^-$ ($\text{R} = \text{Me}, \text{Ph}$) [15]; $(\eta^3\text{-C}_3\text{H}_5)\text{Mo(MeCN)(CO)}_2(\text{S}_2\text{PPh}_2)$ and $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo(CO)}_2(\text{S}_2\text{PPh}_2)]_2(\mu\text{-NH}_2\text{NH}_2)]$ from the reaction of $(\eta^3\text{-C}_3\text{H}_5)\text{Mo(MeCN)}_2(\text{CO})_2\text{Br}$ with $\text{NH}_4(\text{S}_2\text{PPh}_2)$, followed by NH_2NH_2 [8e]; and the coordination compound, $[(\text{dcpe})\text{Pd(S}_2\text{PR}_2)]^+[\text{S}_2\text{PR}_2]^-$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) from the reaction of $\text{Pd}_2(\mu\text{-dcpe})_2$ with $[\text{SP}(\text{S})\text{R}_2]_2$ ($\text{R} = \text{Et}, \text{Ph}$) [16]. In this paper, we report results from a study with bis(diphenylthiophosphinyl)disulfane, $\text{Ph}_2\text{P(S)SSP(S)-PPh}_2$.

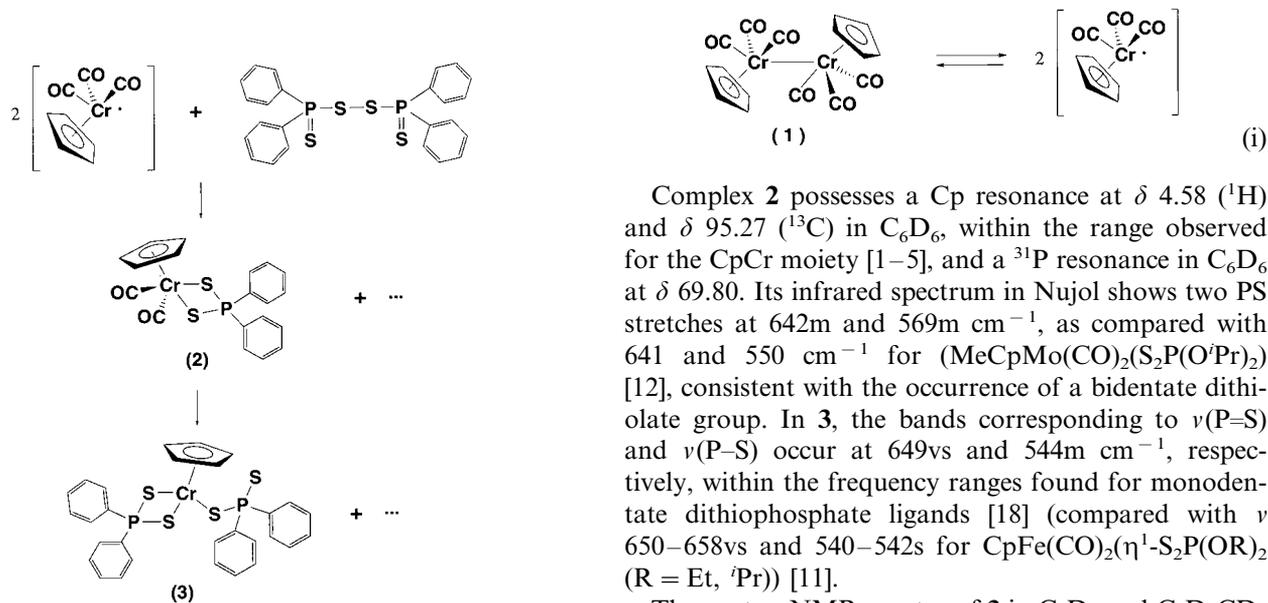
2. Results and discussion

2.1. Products isolation, characterization and reaction pathways

A facile reaction between $[\text{CpCr(CO)}_3]_2$ (**1**) and one mole equivalent of bis(diphenylthiophosphinyl)disulfane in toluene produced a brown solution, from which was isolated dark purplish brown solids of $\text{CpCr(CO)}_2(\text{S}_2\text{PPh}_2)$ (**2**) and blue solids of $\text{CpCr(S}_2\text{PPh}_2)_2$ (**3**) in 50 and 10% yields, respectively.

A time-dependent proton NMR spectral study of the reaction mixture showed that **2** was the primary product. The reaction was observed to be complete within 10 min. The progression of the reaction was followed by obtaining the time-dependent relative ratio of the integrals of the Cp resonances of **2** and **3**, which decreased from 1:0.14 (10 min) through 1:0.55 (1 h) followed by 1:1.48 (7 h) to 1:35 (72 h), reaching complete decomposition after 4 days. Indeed, the facile degradation of **2** to **3**, as monitored for a 24 mM solution of **2** in C_6D_6 at ambient temperature, indicated a half-life of conversion of ca. 3 h. This ease of degradation is also reflected in the failure to observe any sign of the molecular ion of **2** (m/z 422) in the mass spectrum, which only possessed the main mass fragments of **3**.

In view of the facile dissociation of the chromium dimer (**1**) (Eq. (i)) [17], it is conceivable that the reaction is initiated by the homolytic attack of the 17-electron CpCr(CO)_3 species on the S–S bond of the bis(thiophosphinyl)disulfane, generating complex **2**, which must have undergone intermolecular association, followed by bond dissociations to finally yield **3** (Scheme 1).



Scheme 1.

Complex **2** possesses a Cp resonance at δ 4.58 (^1H) and δ 95.27 (^{13}C) in C_6D_6 , within the range observed for the CpCr moiety [1–5], and a ^{31}P resonance in C_6D_6 at δ 69.80. Its infrared spectrum in Nujol shows two PS stretches at 642m and 569m cm^{-1} , as compared with 641 and 550 cm^{-1} for $(\text{MeCpMo(CO)}_2(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2))$ [12], consistent with the occurrence of a bidentate dithiolate group. In **3**, the bands corresponding to $\nu(\text{P-S})$ and $\nu(\text{P-S})$ occur at 649vs and 544m cm^{-1} , respectively, within the frequency ranges found for monodentate dithiophosphate ligands [18] (compared with ν 650–658vs and 540–542s for $\text{CpFe(CO)}_2(\eta^1\text{-S}_2\text{P}(\text{OR})_2)$ ($\text{R} = \text{Et}, \textit{iPr}$) [11]).

The proton NMR spectra of **3** in C_6D_6 and $\text{C}_6\text{D}_5\text{CD}_3$ at 27°C show only one broad *unsymmetrical* signal,

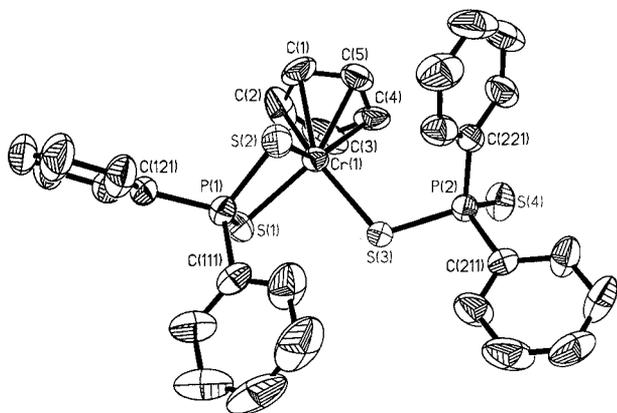


Fig. 1. Molecular structure of $\text{CpCr}(\text{S}_2\text{PPh}_2)_2$ (**3**).

Table 1
Selected bond lengths (Å) and angles (°) for $\text{CpCr}(\text{S}_2\text{PPh}_2)_2$ (**3**)

Bond lengths

Cr(1)–Cp# ^a	1.847(2)
Cr(1)–S(3)	2.3756(8)
Cr(1)–S(2)	2.4233(9)
Cr(1)–S(1)	2.4104(8)
P(1)–C(111)	1.813(3)
P(1)–C(121)	1.818(3)
P(1)–S(2)	2.0209(11)
P(1)–S(1)	2.0229(10)
P(2)–C(221)	1.827(3)
P(2)–C(211)	1.834(3)
P(2)–S(4)	1.9688(10)
P(2)–S(3)	2.0537(10)
S(2)–Cr(1)–S(1)	84.92(3)
S(3)–Cr(1)–S(1)	90.10(3)

Bond angles

C(111)–P(1)–C(121)	105.38(13)
C(111)–P(1)–S(2)	112.22(11)
C(121)–P(1)–S(2)	110.12(10)
C(111)–P(1)–S(1)	110.48(10)
C(121)–P(1)–S(1)	111.09(11)
S(2)–P(1)–S(1)	107.60(4)
C(221)–P(2)–C(211)	103.81(12)
C(221)–P(2)–S(4)	111.58(10)
C(211)–P(2)–S(4)	111.70(10)
C(221)–P(2)–S(3)	108.27(9)
C(211)–P(2)–S(3)	104.50(9)
S(4)–P(2)–S(3)	116.06(5)
P(1)–S(1)–Cr(1)	83.50(3)
P(1)–S(2)–Cr(1)	83.21(3)
P(2)–S(3)–Cr(1)	113.81(4)

^a Cp#, centroid of Cp ring.

consisting of a peak at δ 9.75 ($\nu_{1/2}$ ca. 80 Hz) sitting on a very broad base hump, which became more prominent as the temperature is raised; at 60°C in $\text{C}_6\text{D}_5\text{CD}_3$, it is clear that there exists a sharper signal (δ 9.43 ($\nu_{1/2}$ 45 Hz)) sitting on a much broader signal ($\nu_{1/2}$ ca. 375 Hz) centered at ca. δ 9.9. The area relationship of the sharper peak to the latter suggests that it belong to the Cp ligand. The broad base signal can be assigned to the

phenyl rings of rapidly scrambling ligands as consistent with the ^{31}P -NMR observations described below. In contrast, the spectrum in CD_3CN shows two distinctly separate signals, occurring at 27°C at δ 7.80 ($\nu_{1/2}$ 30 Hz) and δ 10.08 ($\nu_{1/2}$ 75 Hz), assignable to the Cp and phenyl rings, respectively, on the basis of their relative integral ratio of ca. 1:4. In the temperature range of -30 – 70°C , the Cp peak varied from δ 7.74 ($\nu_{1/2}$ 23 Hz) at 70°C to ca. δ 7.90 ($\nu_{1/2}$ 189 Hz) at -30°C , whilst that of the phenyl rings varied from δ 9.68 ($\nu_{1/2}$ 54 Hz) at 70°C to ca. δ 10.35 ($\nu_{1/2}$ 270 Hz) at 0°C with extensive broadening below this temperature. These slight changes in a temperature range of 100°C pertain only to solvent changes with temperature. The observation of a single sharp singlet in the ^{31}P -NMR over the temperature range -80 – 60°C in $\text{C}_6\text{D}_5\text{CD}_3$ (δ 70.86, 69.58 and 69.32 at -80 , 27 and 60°C, respectively) for two P atoms in different molecular environments provides conclusive evidence for rapid unidentate–bidentate exchange in the temperature range studied. In this context, we note that in the VT ^{31}P -NMR spectral study of $\text{CpM}(\text{NO})(\text{S}_2\text{P}(\text{OR})_2)_2$ ($\text{M} = \text{Mo}, \text{W}$) in acetone- d_6 , the inter-ligand exchange began to freeze out at -14°C , until at -78°C , two distinct sharp ^{31}P signals were observed [18]. The ^{13}C spectrum in C_6D_6 shows only two signals, viz. at δ 150.86 and 138.05, presumably for the phenyl and Cp rings, respectively, in accordance with the relative field in which they occur in the proton spectrum. A single observed signal for the six carbons of the phenyl ring is consistent with rapid exchange of the ligands. Finally, we note that both the Cp and phenyl resonances of **3** are observed in unusually low fields; this together with the broad characteristics of the resonances is most probably associated with the paramagnetic nature expected of a formally Cr(III) center or a 15 electron count in the molecule. We have observed before extremely low-field occurrences of Cp and Me resonances, caused by the presence of 17-electron paramagnetic species from metal–metal bond dissociation in $[\text{CpCr}(\text{CO})_3]_2$ [17c], and its permethyl Cp analogue [17d].

2.2. Crystallographic studies

The molecular structure of **3** is illustrated in Fig. 1. Selected bond parameters are given in Table 1. The structure is unique in possessing both a monodentate and a bidentate dithiophosphinato ligand; to date only NMR spectral evidence had been presented for the occurrence of intramolecular unidentate–bidentate scrambling of such dithio ligands in solution, e.g. in the organometallic compounds $\text{CpM}(\text{NO})(\text{S}_2\text{P}(\text{OR})_2)_2$ ($\text{M} = \text{Mo}, \text{W}$) [18], $(\text{arene})\text{Ru}(\text{S}_2\text{PR}_2)_2$ ($\text{R} = \text{Me}, \text{Ph}$) and $(\text{C}_5\text{Me}_5)\text{M}(\text{S}_2\text{PR}_2)_2$ ($\text{M} = \text{Ru}, \text{Rh}, \text{Ir}; \text{R} = \text{Me}, \text{Ph}$) [15], in the coordination compounds $[\text{Pt}(\text{S}_2\text{PR}_2)_2(\text{PPh}_3)]$ ($\text{R} = \text{Me}, \text{Et}$) and $[\text{Pd}(\text{S}_2\text{PR}_2)_2(\text{PMe}_2\text{R}')]_2$ ($\text{R} = \text{Me}, \text{Ph}$;

R' = Me, Ph) [19] and in $(C_5Me_5)Rh(S_2P(OEt)_2)_2$ [13b]. These dithiophosphinato and dithiophosphato ligands are normally bidentate in bonding mode, as found in the majority of examples listed in Table 2, with the exception of the complex $CpFe(CO)_2(\eta^1-S_2P(OR)_2)$ and its (C_5Me_5) analogue, which contains a monodentate thiophosphato ligand, coordinated via one of its two S atoms to the Fe center [11]. In Table 2, some of the significant bond parameters of **3** are compared with their equivalents in the bidentate complexes known to date, and the monodentate complexes $CpFe(CO)_2(\eta^1-S_2P(OR)_2)$ [11]. In general, there exists a close similarity in the magnitudes of the equivalent bond distances and angles between the complexes, with only a small spread of values. The P=S distance (1.9688(10) Å) in the unidentate ligand of **3** was found to be slightly longer than the equivalent distances (1.944(2), 1.940(1) and 1.933(1) Å) in the Fe complexes. Likewise, the S–P–S angle (116.06(5)°) in **3** is larger than those in the Fe complexes [11].

Attempts to obtain a good diffraction-quality crystal of **2** was frustrated by its tendency to degrade in solution to **3** even at $-29^\circ C$. A modification of the synthetic method, as described in Section 3.1.2, gave a crystal which diffracted sufficiently to show the existence of a molecular structure (with two independent molecules in the asymmetric unit), closely resembling that of the dithiophosphato Mo complex, $(MeCpMo(CO)_2(S_2P(O^iPr)_2))_2$ [12]. It is seen that the Cr atom assumes a four-legged piano-stool configuration, being bonded to a bidentate (S,S) ligand, with its PPh_2 appendage suspended from the two S atoms. As in the case of $(MeCpMo(CO)_2(S_2P(O^iPr)_2))_2$ [12], the *cis*-juxtaposition of the CO ligands is supported by the IR data (ν 1967vs, 1886vs cm^{-1}) [20], while the low-frequency stretches at 569m and 475m cm^{-1} indicates the presence of a bidentate ligand. Unfortunately the poor quality of the X-ray data did not allow for meaningful comparisons of bond parameters.

3. Experimental

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

NMR spectra were measured on a Bruker 300 MHz FT-NMR spectrometer; for 1H and ^{13}C spectra, chemical shifts were referenced to residual C_6H_6 in C_6D_6 , $C_6D_5CH_2D$ in $C_6D_5CD_3$, or CH_2DCN in CD_3CN ; for ^{31}P spectra, chemical shifts were referenced to external H_3PO_4 . IR spectra in Nujol mulls were measured in the range 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 performed by the microanalytical laboratory in-house.

$[CpCr(CO)_3]_2$ (**1**) was synthesized as described by Manning [21] from chromium hexacarbonyl (98% purity from Fluka). The bis(thiophosphinyl)disulfane, $Ph_2P(S)SSP(S)PPh_2$ was prepared according to published procedures [22]. 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 $140^\circ C$ overnight before chromatographic use.

3.1. Reaction of $[CpCr(CO)_3]_2$ (**1**) with $[Ph_2P(S)S]_2$

3.1.1. Isolation of products

A deep green mixture of $[CpCr(CO)_3]_2$ (**1**) (201 mg, 0.50 mmol) and $[Ph_2P(S)S]_2$ (249 mg, 0.50 mmol) in toluene (10 ml) was stirred at ambient temperature for 20 min. The resultant brown product mixture was filtered through a disc (2×1.5 cm) of silica gel, removing some blue solids, to give a reddish–brown filtrate. Concentration of the filtrate under vacuo to ca. 3 ml, followed by addition of *n*-hexane (2 ml) and subsequent cooling at $-29^\circ C$ for 30 min, gave dark microcrystalline solids of $CpCr(CO)_2(S_2PPh_2)$ (**2**) (212 mg, 0.50 mmol, 50.0% yield). Anal. Found: C, 53.21; H, 3.67; Cr, 11.73; P, 6.56; S, 15.41. $C_{19}H_{15}O_2S_2PCr$ Calc.: C, 54.02; H, 3.58; Cr, 12.31; P, 7.33; S, 15.18%. NMR (C_6D_6): 1H δ (Cp) 4.58; ^{13}C δ (Cp) 95.27; δ (C_6H_5) 132.29, 130.30, 130.14 and 129.46; ^{31}P δ 69.80. NMR (CD_3CN): 1H δ (Cp) 5.17, δ (C_6H_5) 7.73 (s, br), 7.56 (m) and 7.17 (m); ^{13}C δ (Cp) 96.09; δ (C_6H_5) 132.92, 129.69; δ (CO) 203.84; ^{31}P δ 74.44. IR (Nujol, cm^{-1}): ν (CO) 1967vs, 1886vs, 1862wsh; ν (other bands) 1309w, 1146w, 1101m, 1060w, 999w, 825m, 742m, 707s, 696m, 642m, 580s, 569m, 515m, 490m, 475m. MS (FAB⁺): shows the higher intensity mass fragments of $CpCr(S_2PPh_2)_2$ (**3**) given below, viz. *m/z* 615, 550, 365, 301, 256, 217, 181 and 148.

The mother liquor had to be subjected to a chromatographic separation on silica gel, on which compound **2** was found to rapidly degrade; since the mother liquor still contained some of **2**, as indicated in its proton NMR spectrum, it was stirred for a further 2 h at ambient temperature to allow all of **2** to convert to the complex **3** which then colored the resultant solution blue–green. Concentration of the solution to ca. 4 ml followed by filtration then removed a fine purple insoluble precipitate (15 mg) of a compound (the elemental analysis of which possessed an empirical formula $C_{14.7}H_{15.0}S_{1.8}P_{0.90}Cr$, i.e. in the proximity of $[CpCrS_2P(C_6H_5)_2]_n$, indicative of a polymeric form of **3**. The filtrate was next loaded on to a silica gel column (1.5×20 cm) prepared in hexane. Elution gave four fractions: (i) a greenish brown eluate in *n*-hexane (15 ml), which on concentration gave deep green crystals of $Cp_2Cr_2(CO)_4S$ (9 mg, 0.024 mmol, 4.6% yield), identified by its color characteristics and Cp resonance in

Table 2
A comparison of selected significant bond parameters ^a

	CpCr(S ₂ PPh ₂) ₂ (3) ^{b,c}	CpM(CO) ₂ (S ₂ P(OR) ₂)			[(η ³ -C ₃ H ₅)Mo(CO) ₂ (S ₂ P(OEt) ₂) _n X ^b		Other complexes ^b			
		CpMo(CO) ₂ - (S ₂ P(O ⁱ Pr) ₂) ^{b,d} [12]	CpFe(CO) ₂ (S ₂ P(O ⁱ Pr) ₂) ^c Cp = C ₅ H ₅ [11b]	Cp = C ₅ Me ₅ [11c]	CpFe(CO) ₂ - (S ₂ P(OEt) ₂) ^c [11b]	<i>n</i> = 2, X = (μ-NH ₂ -NH ₂) [8e]	<i>n</i> = 1, X = CH ₃ CN [14]	[(η ⁶ - <i>p</i> -cymene) Ru(PPh ₃) (S ₂ P(OEt) ₂) BPh ₄ [13a]	Cp*RhCl(S ₂ P- (OEt) ₂) [13b]	[cy ₂ P(CH ₂ CH ₂) Pcy ₂ Pd- (S ₂ P(Et) ₂)] ⁺ ^e [16]
<i>Bond lengths (Å)</i>										
M–S(1)	2.4104(8)	2.550(1)	–	–	–	2.551(1)	2.5648(18)	2.4312(14)	2.440(2)	2.404(2)
M–S(2)	2.4233(9)	2.559(1)	–	–	–	2.642(1)	2.6377(21)	2.431(2)	2.4270(13)	2.398(2)
M–S(3)	2.3756(8)	–	2.322(2)	2.311(1)	2.304(1)	–	–	–	–	–
P(1)–S(1)	2.0229(10)	1.992(1)	–	–	–	1.991(1)	1.976(3)	1.989(2)	1.985(2)	2.015(3)
P(1)–S(2)	2.0209(11)	1.994(1)	–	–	–	1.988(1)	1.973(3)	1.971(2)	1.985(2)	2.016(3)
P(2)–S(3)	2.0537(10)	–	2.026(2)	2.021(1)	2.018(1)	–	–	–	–	–
P(2)–S(4)	1.9688(10)	–	1.944(2)	1.940(1)	1.933(1)	–	–	–	–	–
<i>Bond angles (°)</i>										
S(1)–M–S(2)	84.92(3)	76.5(1)	–	–	–	77.32(5)	75.97(7)	80.43(5)	80.99(5)	83.99(7)
S(1)–P(1)–S(2)	107.60(4)	105.0(1)	–	–	–	109.3(1)	108.36(12)	104.88(8)	105.51(8)	105.7(1)
S(3)–P(2)–S(4)	116.06(5)	–	112.5(1)	111.9(1)	112.1(1)	–	–	–	–	–
P(1)–S(1)–M	83.50(3)	89.1(1)	–	–	–	87.61(6)	88.82(8)	83.54(7)	86.46(6)	84.21(9)
P(1)–S(2)–M	83.21(3)	88.8(1)	–	–	–	85.18(7)	86.84(10)	83.92(7)	86.82(6)	84.35(9)
P(2)–S(3)–M	113.81(4)	–	109.1(1)	112.0(1)	111.2(1)	–	–	–	–	–

^a Cp = C₅H₅, unless otherwise specified.

^b Containing bidentate ligand.

^c Containing unidentate ligand.

^d Cp = C₅H₄Me.

^e cy = cyclohexyl.

benzene- d_6 at δ 4.36 (^1H) and 89.20 (^{13}C) in its NMR spectra [1a,c]; (ii) a reddish–brown eluate in *n*-hexane–toluene (1:1, 10 ml), from which was obtained a minute quantity of an unidentified complex, possessing $\delta(\text{Cp})$ 4.29 and $\delta(\text{P})$ 75.54 in its proton and ^{31}P -NMR spectra, respectively, in benzene- d_6 ; (iii) a dirty brown eluate in toluene–ether (2:1, 10 ml), from which was isolated 2 mg of a black solid, presumably of $\text{Cp}_4\text{Cr}_4\text{S}_4$, based on its Cp resonance at δ 4.91 in the NMR spectrum [1d]; and (iv) a prussian blue eluate in THF (15 ml), which gave complex **3** as deep blue crystals (62 mg, 0.10 mmol, 10% yield). Anal. Found: C, 56.49; H, 4.19; Cr, 7.85; P, 9.33; S, 20.78. $\text{C}_{29}\text{H}_{25}\text{S}_4\text{P}_2\text{Cr}$ Calc.: C, 56.57; H, 4.09; Cr, 8.44; P, 10.06; S, 20.83%. IR (Nujol, cm^{-1}): ν 1572w, 1304m, 1181w, 1158w, 1097vs, 1068w, 1025w, 998w, 825s, 756m, 742s, 706vs, 690w, 683w 665w 649vs, 628m, 608m, 567vs, 544vs, 487s. MS (FAB $^+$): m/z 615 [$\text{CpCr}(\text{C}_6\text{H}_5)_4\text{P}_2\text{S}_4$], 550 [$\text{Cr}(\text{C}_6\text{H}_5)_4\text{P}_2\text{S}_4$], 365 [$\text{Cr}(\text{C}_6\text{H}_5)_2\text{PS}_4$], 301 [$\text{Cr}(\text{C}_6\text{H}_5)_2\text{PS}_2$], 256 [$\text{Cr}(\text{C}_6\text{H}_5)\text{PS}_3$], 217 [$(\text{C}_6\text{H}_5)_2\text{PS}$], 181 [CpCrS_2], 149 [CpCrS], 148 [CpCrP]. VT-NMR spectral characteristics are presented in Section 2.1.

Table 3
Crystal and structure refinement data for **3**

Empirical formula	$\text{C}_{29}\text{H}_{25}\text{CrP}_2\text{S}_4$
Formula weight	615.67
Temperature (K)	293(2)
Wavelength (\AA)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (\AA)	11.0329(2)
b (\AA)	11.4735(1)
c (\AA)	12.1129(2)
α ($^\circ$)	101.955(1)
β ($^\circ$)	98.373(1)
γ ($^\circ$)	90.645(1)
V (\AA^3)	1482.72(4)
Z	2
D_{calc} (Mg m^{-3})	1.379
Absorption coefficient (mm^{-1})	0.793
$F(000)$	634
Crystal size (mm^3)	$0.30 \times 0.18 \times 0.13$
θ range for data collection ($^\circ$)	2.23–29.19
Index ranges	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $0 \leq l \leq 16$
Reflections collected	11046
Independent reflections	6921 [$R_{\text{int}} = 0.0223$]
Completeness to θ (%)	86.2 (29.19 $^\circ$)
Absorption correction	SADABS
Max. and min. transmission	0.914549 and 0.751647
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6921/45/340
Goodness-of-fit on F^2	1.021
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0443$, $wR_2 = 0.0911$
R indices (all data)	$R_1 = 0.0764$, $wR_2 = 0.1062$
Largest difference peak and hole (e \AA^{-3})	0.299 and -0.291

3.1.2. Modified procedure for growth of diffraction-quality crystals of **2**

A deep green mixture of $[\text{CpCr}(\text{CO})_3]_2$ (**1**) (10 mg, 0.025 mmol) and $[\text{Ph}_2\text{P}(\text{S})\text{S}]_2$ (12.5 mg, 0.025 mmol) in THF (2 ml) was stirred vigorously at ambient temperature for 6 min, and then filtered through a sintered glass frit, removing some unreacted **1**. To the resultant deep greenish brown filtrate was added *n*-hexane (1.5 ml) and the solution stood at -29°C overnight. Some crystals of unreacted **1** was found to have fallen out of solution; after removal of these deep green crystals by filtration, the mother liquor yielded some purple diffraction-quality needle crystals of **2** (ca. 9 mg, 42% yield).

3.2. NMR tube reactions

3.2.1. Reaction of $[\text{CpCr}(\text{CO})_3]_2$ with $[\text{Ph}_2\text{P}(\text{S})\text{S}]_2$

A deep green mixture of $[\text{CpCr}(\text{CO})_3]_2$ (**1**) (4 mg, 0.01 mmol) and $[\text{Ph}_2\text{P}(\text{S})\text{S}]_2$ (5 mg, 0.01 mmol) in benzene- d_6 (0.5 ml) in a 5-mm NMR tube was manually shaken up for 10 min, and then its proton NMR spectra scanned and subsequently monitored at intervals (1, 7, 24, 72, 96 h). The integral ratios of the Cp resonances of the products **2** to **3** were estimated.

3.2.2. Decomposition of **2**

The proton NMR of a 24 mM solution of **2** (5 mg in 0.5 ml benzene- d_6) was monitored at hourly intervals up to 6 h at ambient temperature; the change in the integrals of the resonance of **2** gave an approximate conversion rate from 33% at 1 h, through 62% at 4 h to 70% at 6 h; a final spectrum scanned after 24 h indicated that complete decomposition had already occurred.

3.3. Structure determinations

Owing to the unstable nature of **2** in solution, it was not possible to obtain good quality single crystals by conventional methods, e.g. diffusion or layering techniques, even at -29°C , which invariably gave mixtures with **3**. Fortunately, a modified procedure for the isolation of the primary crop of products from the reaction of **1** with the ligand, as detailed in Section 3.1.2 above, gave some diffraction-quality crystals.

Diffraction-quality single crystals of **3** were obtained as blue prisms from THF, layered with hexane, after 4 days at -29°C .

The crystallographic data together with data collection details are given in Table 3. The atomic coordinates and equivalent isotropic displacement parameters are given in Table 4.

The crystal of **3** were mounted on quartz fibers. X-ray data were collected on a Siemens SMART diffractometer, equipped with a CCD detector, using Mo- K_α

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cr(1)	9036(1)	15201(1)	12552(1)	40(1)
P(1)	7353(1)	13345(1)	10984(1)	42(1)
P(2)	7516(1)	17332(1)	14612(1)	39(1)
S(1)	8626(1)	13084(1)	12281(1)	48(1)
S(2)	7587(1)	15045(1)	10815(1)	53(1)
S(3)	7601(1)	15565(1)	13855(1)	43(1)
S(4)	8734(1)	17933(1)	15977(1)	62(1)
C(111)	5824(2)	13029(3)	11259(2)	50(1)
C(112)	5067(3)	13939(4)	11595(4)	86(1)
C(113)	3945(4)	13678(6)	11886(5)	121(2)
C(114)	3563(4)	12532(6)	11836(4)	109(2)
C(115)	4312(4)	11615(5)	11499(4)	97(2)
C(116)	5445(3)	11862(4)	11202(3)	75(1)
C(121)	7515(3)	12316(3)	9660(3)	49(1)
C(122)	8435(3)	11518(3)	9588(3)	64(1)
C(123)	8536(4)	10779(3)	8531(4)	84(1)
C(124)	7749(4)	10868(4)	7587(4)	94(2)
C(125)	6830(4)	11653(4)	7646(3)	93(1)
C(126)	6711(3)	12387(3)	8687(3)	70(1)
C(211)	5943(2)	17481(3)	14930(2)	43(1)
C(212)	5596(3)	18576(3)	15466(3)	69(1)
C(213)	4423(3)	18734(4)	15741(3)	81(1)
C(214)	3595(3)	17804(4)	15484(4)	81(1)
C(215)	3915(3)	16719(4)	14961(5)	102(2)
C(216)	5091(3)	16540(3)	14662(4)	81(1)
C(221)	7575(2)	18216(2)	13526(3)	44(1)
C(222)	8337(3)	19235(3)	13733(3)	64(1)
C(223)	8397(4)	19857(3)	12873(5)	87(1)
C(224)	7712(4)	19470(4)	11818(5)	96(2)
C(225)	6942(4)	18473(4)	11608(4)	84(1)
C(226)	6868(1)	17846(2)	12464(2)	57(1)
C(1)	10495(1)	15841(2)	11712(2)	73(3)
C(2)	10934(1)	14965(2)	12302(2)	93(5)
C(3)	10886(1)	15395(2)	13464(2)	90(5)
C(4)	10416(1)	16537(2)	13593(2)	65(3)
C(5)	10174(1)	16813(2)	12510(2)	59(3)
C(11)	10916(1)	15180(2)	12043(2)	69(3)
C(12)	11052(1)	14992(2)	13146(2)	58(3)
C(13)	10688(1)	16000(2)	13843(2)	59(3)
C(14)	10328(1)	16812(2)	13170(2)	59(3)
C(15)	10469(1)	16304(2)	12058(2)	74(3)

^a *U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

radiation at ambient temperature (298 K). An exposure time of 10 s was employed.

The data was corrected for Lorentz and polarization effects with the SMART suite of programs [23] and for absorption effects with SADABS [24]. The final cell parameters were obtained by least-squares on 5245 strong reflections. Structure solution and refinement were carried out with the SHELXTL suite of programs [25]. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The Cp and Ph hydrogens were placed in calculated positions. There was disorder of the Cp ring, which was modeled as two sites

with equal occupancies (0.5); all the C–C bond lengths were restrained to be equal. All non-hydrogen atoms were given anisotropic thermal parameters.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 140357. 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, or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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