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Synthetic, X-ray structural and protonation studies of $CpCr(CO)_2SPy$ and $CpCr(CO)_2SPym$ (SPy = C_5H_4NS, SPym = $C_4H_3N_2S$)

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Abstract

The facile reaction of $[CpCr(CO)_3]_2$ (Cp = η^5-C_5H_5) (**1**) with one mole equivalent of 2,2′-dithiodipyridine ($(C_5H_4NS)_2$≡$(SPy)_2$) at ambient temperature led to the isolation of dark brown crystalline solids of $CpCr(CO)_2(\eta^2$-SPy) (**2**) in ca. 72% yield. **2** undergoes quantitative conversion to $CpCrCl_2(\eta^1$-SPyH) (**3**) with HCl. The reaction **1** with one mole equivalent of 2-mercaptopyrimidine ($C_4H_3N_2SH$≡HSPym) at ambient temperature led to the isolation of reddish-brown crystalline solids of $CpCr(CO)_2(\eta^2$-SPym) (**4**) and green solids of $CpCr(CO)_3H$ (**5**) in yields of ca. 42% and 46%, respectively. Reaction of **4** with HCl and subsequent workup in acetonitrile resulted in the cleavage of the thiolate ligand, giving the 15-electron chromium(III) species $CpCrCl_2(CH_3CN)$ (**6**) and free 2-mercaptopyrimidine. The complexes **2**–**4** have been determined by single X-ray diffraction analysis.

Keywords: Cyclopentadienylchromium; 15-electron chromium(III) complexes; 2-mercaptopyridine; 2-mercaptopyrimidine; X-ray crystal structures

1. Introduction

We have been interested in the cleavage of S–S bonds in both inorganic [1] and organic [2] substrates by $[CpCr(CO)_3]_2$ (Cp = η^5-C_5H_5) (**1**). The facile reactions with diphenyl dichalcogenide Ph_2E_2 (X = S, Se, Te) [3], thiophosphorus compounds bis(diphenylthiophosphinyl)disulfane $(Ph_2P(S)S)_2$ [4] and bis(thiophosphoryl)disulfane $[(RO)_2P(S)S]_2$ (R = ^{i}Pr) [5], dibenzothiazolyl disulfide $[(C_6H_4)NSCS]_2$ [6] and tetraalkylthiuram disulfanes $(R_2NC(S)S)_2$ [7] have been investigated and reviewed [2]. This present work is involved with a study of **1** with 2,2′-dithiodipyridine $(SPy)_2$ and 2-mercaptopyrimidine (HSPym), which is anticipated to lead to chromium thiopyridine ($CpCr(CO)_nSPy$) and thiopyrimidine ($CpCr(CO)_nSPym$) complexes (n = 2 or 3). These complexes belong to the class of heterocyclic thionates, which includes benzothiazole ($CpCr(CO)_2(SCSN(C_6H_4))$) that we have previously studied [2,6]. Such ligands possess at least one soft donor site (thionato sulfur) and one hard site (thioamido nitrogen) and hence are capable of coordination to a great variety of main-group and transition metals and in diverse bonding modes [8]. These compounds have received intense research interest because of their biological activity and numerous practical applications [9]. Indeed, the coordination and structural diversity of metal complexes with 2-mercaptopyridine and 2-mercaptopyrimidine, for instance, is an established field of study [8]. However, reactivity studies of these complexes still remain scarce [10]. Considering that there is much interest in such complexes, we have carried out an investigation on the chromium complexes of these ligands.

In reactivity studies in this area of work, we have so far concentrated on the facile interaction of **1** with the derived CpCr complexes, which have led to numerous unexpected interesting compounds [2]. In this present

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study, we report an investigation on their reactivity with hydrochloric acid. We expect that "halogenated" CpCr complexes will be formed; the special attention given to this class of compounds of Cr(II) and Cr(III) derives from their relevance to (i) catalysis, as in the use of $[\eta^5\text{-Cp*CrX}(\mu\text{-Cl})]_2$ (X = R, Cl), and related mononuclear compounds $[\text{CpCrX}_{3-m}\text{L}_m]^n$ (m = 0–3, corresponding to n = −1 to +2), Cp*Cr(L)(Cl)R as catalysts for the Phillips ethylene polymerization [11], and CpCrCl_2(THF) as precatalyst in coupling reactions [12], and (ii) syntheses involving reactivity of the Cr–halide bond, e.g., reactions of $[\text{Cp/Cp*CrX}_2]_2$ (X = Cl, Br) [11f,13], CpCrCl(benzamidinate) [14], $\text{CpCr(NO)}_2\text{Cl}$ [15] and $[\text{Cp*Cr}(\mu\text{-Cl})\text{R}]_2$ in which the Cr–C bond is also activated to allow an insertion of nitriles and other polar organic groups [11a,16].

2. Results and discussion

2.1. Reaction of $[\text{CpCr(CO)}_3]_2$ (1) with $(\text{C}_5\text{H}_4\text{NS})_2$ at ambient temperature

A facile reaction between $[\text{CpCr(CO)}_3]_2$ (**1**) and one mole equivalent of 2,2′-dithiodipyridine at ambient temperature produced a reddish-brown solution, from which dark brown crystals of $\text{CpCr(CO)}_2(\eta^2\text{-SPy})$ (**2**) were obtained in 72% yield. Consonant with the established mode of reaction of **1**, via its monomer $\{\text{CpCr(CO)}_3^{\bullet}\}$ (**1A**), it is proposed that the reaction is initiated by the homolytic attack of the 17-electron organometallic radical species **1A** on the S–S bond of 2,2′-dithiodipyridine, generating complex **2** (Scheme 1). In the syntheses of the Mo and W analogues of **2**, Abrahamson and coworkers generated the respective organometallic radicals $\{\text{CpM(CO)}_3^{\bullet}\}$ via UV photolytic cleavage of the M–M bonds of $[\text{CpM(CO)}_3]_2$ [10a].

While this work was in progress, the Cp* analogue of **2** and its monodentate precursor, $\text{Cp*Cr(CO)}_3(\eta^1\text{-SPy})$, was synthesized by Hoff and coworkers from the reaction of $[\text{Cp*Cr(CO)}_3]_2$ with pyridine thione [17] (Scheme 2). It was proposed that the reaction was initiated by attack of the 17-e Cr monomer on the C=S bond, which is known to be readily susceptible to radical attack [18]. The resulting complex $\text{Cp*Cr(CO)}_3(\eta^1\text{-SPy})$ (**2A***) readily underwent CO loss to give $\text{Cp*Cr(CO)}_2(\eta^2\text{-SPy})$ (**2***).

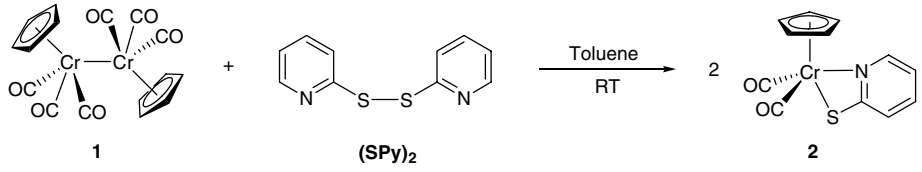
2.2. Reaction of $\text{CpCr(CO)}_2(\eta^2\text{-SPy})$ (2) with HCl

A slow reaction of **2** with excess HCl at ambient temperature gave $\text{CpCrCl}_2(\eta^1\text{-SPyH})$ (**3**) in 90% isolated yield. The crystal structural analysis shows the **2** had undergone Cr–N bond cleavage, resulting in protonation of the heterocyclic N in the strongly acidic medium. It is apparent that HCl had oxidized the Cr(II) centre to Cr(III) (Scheme 3).

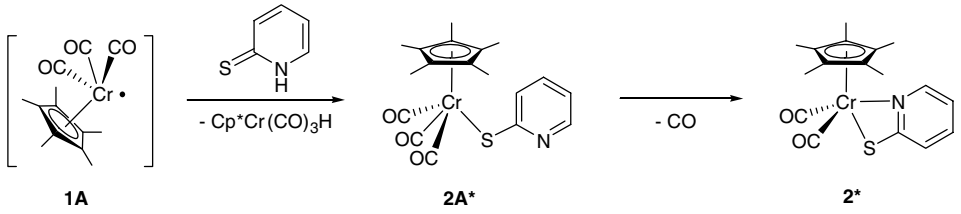
The product illustrates the "chlorophilicity" of the CpCr center, a reactivity feature commonly found for most complexes of CpCr [19]. In the absence of a coordinating solvent in this synthesis, 'SPy' remains coordinated, but the underlying reason for the preference of a relatively hard metal center for the softer donor atom in 'SPy' is not immediately clear.

2.3. Reaction of $[\text{CpCr(CO)}_3]_2$ (1) with $\text{C}_4\text{H}_3\text{N}_2\text{SH}$ at ambient temperature

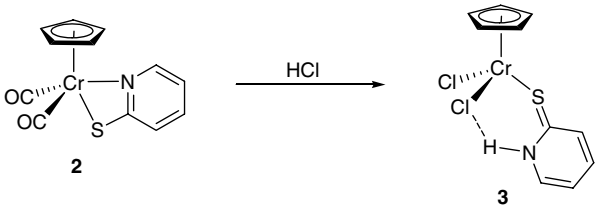
A sluggish reaction between **1** and one mole equivalent of 2-mercaptopyrimidine at ambient temperature produced a reddish-brown solution, from which reddish-brown crystals of $\text{CpCr(CO)}_2(\eta^2\text{-SPym})$ (**4**) were obtained in 42% yield together with $\text{CpCr(CO)}_3\text{H}$ in 46% yield (Scheme 4).



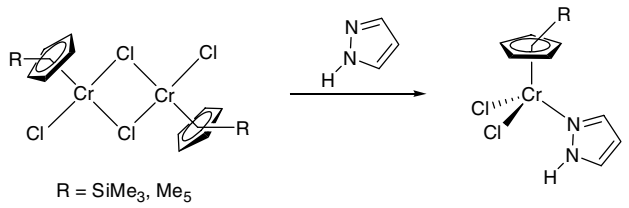
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 6.

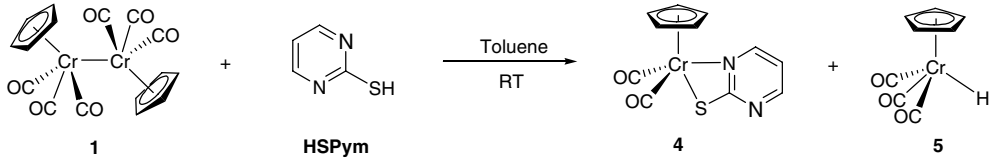
It is proposed that the reaction is initiated by the homolytic attack of $\{CpCr(CO)_3^{\bullet}\}$ (**1A**) on the S–H bond of the 2-mercaptopyrimidine, generating complex **4** and the hydride **5** in 1:1 mole equivalents. In this context, we noted that Hoff and coworkers have obtained kinetic and thermodynamic parameters for the reaction of $\{Cp^*Cr(CO)_3^{\bullet}\}$ with hydrogen sulfides [20] and thiols [21]. Their studies showed that the oxidative addition of the $\{Cp^*Cr(CO)_3^{\bullet}\}$ radical to butanethiol and thiophenol followed third-order kinetics.

2.4. Reaction of $CpCr(CO)_2(\eta^2$-SPym) (4) with HCl

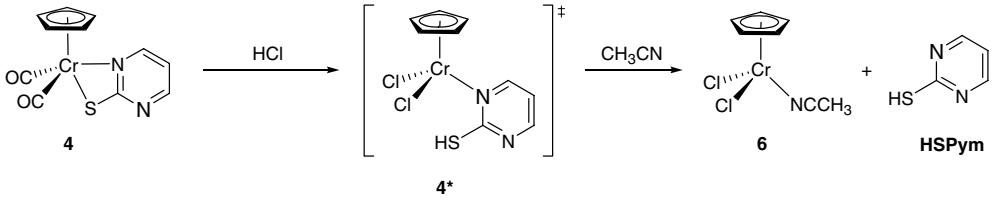
An instantaneous reaction between **4** and HCl occurred at ambient temperature. Recrystallisation of the product in CH_3CN led to precipitation of free HSPym and isolation of $CpCrCl_2(NCCH_3)$ (**6**), which was previously obtained by Goh and coworkers from the insertion–displacement of selenium in $Cp_2Cr_2(CO)_4Se$ with $SnCl_2$ [22]. The formation of **6** was proposed to go via an intermediate **4***, resulting from Cr–S(thiolate) cleavage, consequential to protonation at sulfur in a strongly acidic medium. Subsequent substitution of N-coordinated HSPym by acetonitrile, a good coordinating solvent, would then lead to release of HSPym (Scheme 5). Based on this proposed pathway there exists a marked difference in the lability of the M–S bonds in **2** and **4** in the presence of a strong acid. It appears that the extra nitrogen in the pyrimidine ring has facilitated protonation at the coordinated thiolate atom. Unfortunately, complex **4*** could not be characterized owing to its insolublility in non-polar non-coordinating solvents, e.g., hexane or toluene, and its high ligand lability in polar solvents, e.g., THF or acetonitrile. As in complex **3**, HCl had oxidized Cr(II) to Cr(III) in this reaction. We note that complexes of the **4***-type are prevalent in CpCr(III) chemistry. A fairly recent example came from the work of Valderrama and coworkers, where the Cp^RCrCl_2(pyrazole) ($R = SiMe_3$, Me_5) complex was synthesized from $[Cp^RCrCl_2]_2$ [11d] (Scheme 6).

2.5. Crystallographic studies

The X-ray crystal structural analyses of **2–4** have been carried out. The crystal data collection and processing parameters are given in Table 1. Selected bond lengths and angles are listed in Tables 2–4. The molecular structure of **2** (Fig. 1) shows a four-legged piano-stool configuration at Cr(II), being coordinated to a bidentate thiopyridine and two CO ligands, similar to the coordination found in the analogous complexes $CpM(CO)_2(SPy)$ (M = Mo, W) [10a,10b]. The S(2)–C(2) bond length of 1.723(2) Å is within the range of the single C–S bonds of 1.55–1.81 Å [23]. The thiopyri-



Scheme 4.



Scheme 5.

Table 1
Data collection and processing parameters

complexes	**2**	**3**	**4**
Formula	$C_{12}H_9CrNO_2S$	$C_{10}H_{10}CrCl_2NS$	$C_{11}H_8CrN_2O_2S$
M_r	283.26	299.15	284.25
Temperature (K)	223(2)	223(2)	223(2)
Crystal color and habit	Dark Brown, rhombus	Bluish-green, needle	Dark Brown, rhombus
Crystal size, mm	$0.36 \times 0.24 \times 0.18$	$0.40 \times 0.12 \times 0.02$	$0.30 \times 0.20 \times 0.08$
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a (Å)	12.7123(4)	8.3745(6)	6.646(2)
b (Å)	7.4752(2)	6.6935(5)	12.530(5)
c (Å)	12.6061(4)	21.7625(17)	13.754(5)
α (°)	90	90	90
β (°)	100.4160(10)	99.440(2)	90
γ (°)	90	90	90
V (Å^3)	1178.01(6)	1203.37(16)	1145.3(7)
Z	4	4	4
Density (Mg m^{-3})	1.597	1.651	1.648
Absorption coefficient (mm^{-1})	1.134	1.532	1.169
F(0 0 0)	576	604	576
θ Range for data collection	2.18–28.28	1.90–27.49	2.20–24.99
Index ranges	$-16 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 9$, $0 \leqslant l \leqslant 16$	$-16 \leqslant h \leqslant 16$, $-8 \leqslant k \leqslant 8$, $-21 \leqslant l \leqslant 28$	$-7 \leqslant h \leqslant 7$, $-14 \leqslant k \leqslant 14$, $-13 \leqslant l \leqslant 16$
No. of reflns collected	19518	8101	6281
Indepenedent reflections	2868	2755	2010
Max. and min. transmission	0.8219 and 0.6856	0.9700 and 0.5793	0.9123 and 0.7205
No. of data/restraints/parameters	2868/0/190	2755/0/176	2010/0/154
Final R indices $[I > 2\sigma(I)]$[a,b]	$R_1 = 0.0443$, $wR_2 = 0.1091$	$R_1 = 0.0324$, $wR_2 = 0.0729$	$R_1 = 0.0566$, $wR_2 = 0.1318$
R indices (all data)	$R_1 = 0.0518$, $wR_2 = 0.1138$	$R_1 = 0.0400$, $wR_2 = 0.0760$	$R_1 = 0.0629$, $wR_2 = 0.1351$
Goodness-of-fit on F^2[c]	1.065	1.067	1.159
Large diff peak and hole, e Å^{-3}	0.775 and −0.224	0.420 and −0.232	1.138 and −0.402

[a] $R = (\sum|F_o|-|F_c|)\sum|F_o|$.
[b] $wR_2 = [(\sum\omega|F_o|-|F_c|)^2/\sum\omega|F_o|)^2]^{1/2}$.
[c] GoF $= [(\sum\omega|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

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

Bond lengths			
Cr(1)–N(1)	2.0668(18)	Cr(1)–S(2)	2.4584(7)
S(2)–C(2)	1.723(2)	N(1)–C(2)	1.339(3)
N(1)–C(6)	1.343(3)	C(2)–C(3)	1.408(3)
C(3)–C(4)	1.369(4)	C(4)–C(5)	1.388(4)
C(5)–C(6)	1.374(3)		
Bond angles			
N(1)–Cr(1)–S(2)	66.68(5)	S(2)–C(1)–N(1)	109.36(16)

dine ligand bite angle (N(1)–Cr(1)–S(2)) is 66.68(5)° while the S(2)–C(1)–N(1) angle is 109.36(16). These four atoms, namely Cr(1), C(1), N(1) and S(2) form a strained four-membered metallacycle [24]. It is not surprising therefore that the ring is easily cleaved, as observed in the reaction with HCl to give **3**.

The molecular structure of **3** possesses a three-legged piano-stool configuration at Cr(III), which is coordinated to monodentate thiopyridine and two chloro ligands. It is noteworthy that there exists a hydrogen bond between Cl(2)–H–N(1) forming a pseudo-chelate six-membered ring, containing N(1), H, Cl(2), Cr(1), S(1) and C(1A) as illustrated in Fig. 2. The H atom on the nitrogen was located in the electron density

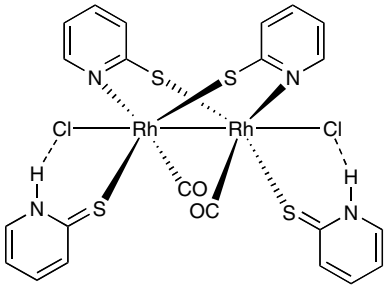
Table 3
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Cr(1)–Cl(1)	2.2972(6)	Cr(1)–Cl(2)	2.3157(6)
Cr(1)–S(1)	2.3830(6)	S(1)–C(1A)	1.726(2)
N(1)–C(5A)	1.340(3)	N(1)–C(1A)	1.346(3)
C(1A)–C(2A)	1.390(3)	C(2A)–C(3A)	1.364(4)
C(3A)–C(4A)	1.383(4)	C(4A)–C(5A)	1.355(4)
N(1)–H(1A)	0.81(3)	H(1A)...Cl(2)	2.39(3)
N(1)–Cl(2)	3.181(2)		
Bond angles			
Cl(1)–Cr(1)–Cl(2)	95.66(2)	Cl(1)–Cr(1)–S(1)	96.31(2)
Cl(2)–Cr(1)–S(1)	98.74(2)	C(1A)–S(1)–Cr(1)	108.47(7)
N(1)–C(1A)–C(2A)	116.4(2)	N(1)–C(1A)–S(1)	121.14(16)
C(2A)–C(1A)–S(1)	122.47(17)	C(3A)–C(2A)–C(1A)	120.4(2)
C(2A)–C(3A)–C(4A)	120.8(2)	C(5A)–C(4A)–C(3A)	118.3(2)
N(1)–C(5A)–C(4A)	119.9(2)	N(1)–H(1A)–Cl(2)	169(2)

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

Bond lengths			
Cr(1)–N(1)	2.067(4)	Cr(1)–S(1)	2.4487(17)
S(1)–C(4)	1.714(6)	N(1)–C(1)	1.344(7)
C(1)–C(2)	1.402(9)	C(2)–C(3)	1.347(10)
C(3)–N(2)	1.337(8)	N(2)–C(4)	1.329(8)
C(4)–N(1)	1.350(7)		
Bond angles			
N(1)–Cr(1)–S(1)	66.57(13)	S(1)–C(4)–N(1)	108.7(4)

difference map and refined. The distances of the N(1)–H(1A) and H(1A)...Cl(2) vectors were found to be 0.81(3) and 2.39(3) Å, respectively. The N(1)–H(1A)–Cl(2) bond angle was determined to be 169(2)°. The bond length of Cr(1)–Cl(2) (2.3157(6) Å) is slightly longer than that of Cr(1)–Cl(1) (2.2972(6) Å), a probable effect of the involvement of Cl(2) in hydrogen bonding. A reported example of such a pseudo ring was found in $Rh_2Cl_2(\mu\text{-}SPy)_2(\eta^1\text{-}SPyH)_2(CO)_2$ (**A**), prepared by Deeming and Meah [25]. The S(1)–C(1A) bond length of 1.726(2) Å in **3** is also comparable to 1.719(6) Å in the rhodium complex and is within the range (1.55–1.81 Å) for C═S bond length [23].



(A)

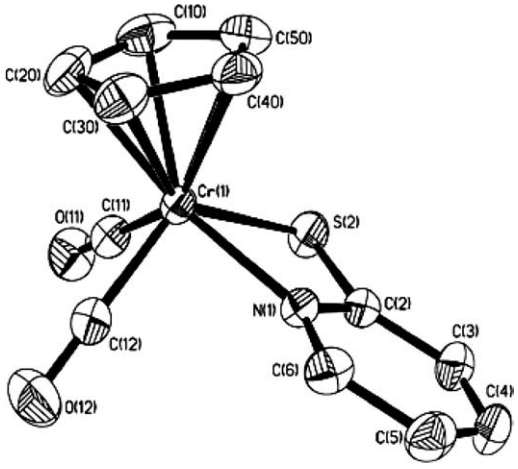


Fig. 1. Ortep plot of **2** (H atoms are omitted for clarity). Thermal ellipsoids are drawn at the 50% probability level.

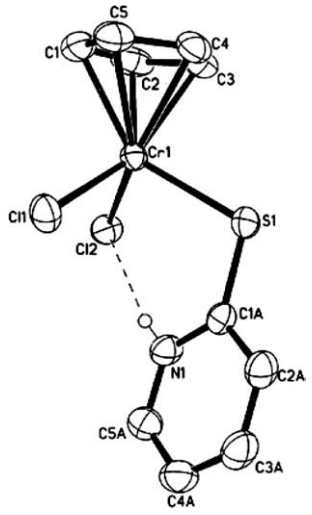


Fig. 2. Ortep plot of **3** (H atoms are omitted for clarity except for N–H). Thermal ellipsoids are drawn at the 50% probability level.

The molecular structure of **4** (Fig. 3) shows a four-legged piano-stool configuration at Cr(II), being coordinated to a bidentate 2-mercaptopyrimidine and two CO ligands, similar to the coordination found in complex **2**. The S(1)–C(4) bond length of 1.714(6) Å is within the range of the single C–S bonds of 1.55–1.81 Å [23]. The 2-mercaptopyrimidine ligand bite angle (N(1)–Cr(1)–S(1)) is 66.57(13)° while the S(1)–C(4)–N(1) angle is 108.7(4). As in complex **2**, these four atoms namely Cr(1), C(4), N(1) and S(1) also form a small four-membered metallacycle, the strain of which facilitates the cleavage of one of the chelating bonds.

It is noted that among the three structurally characterized compounds, complex **2** and **4** each contains an 18-electron Cr(II) possessing a four-legged piano-stool geometry, i.e., effectively 7-coordinate, while the 15-elec-

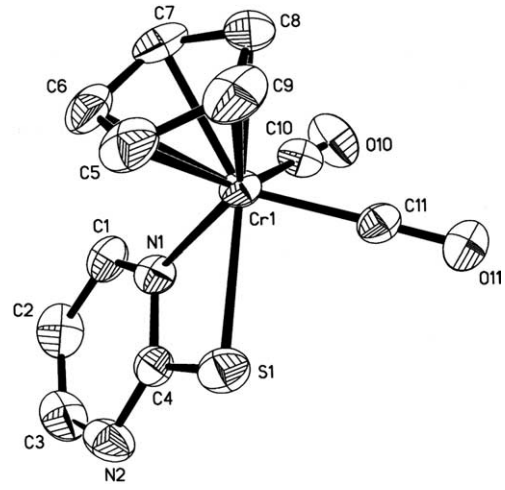


Fig. 3. Ortep plot of **4** (H atoms are omitted for clarity). Thermal ellipsoids are drawn at the 50% probability level.

tron Cr(III) complexes **3** possesses a three-legged pianostool environments. This conforms to observations to date that half-sandwich 15-e complexes of Cr(III) are generally of the three-legged type, which are found to be energetically favoured over those of the 17-e four-legged type, though a few of these are known [11c,13a,13e,26].

2.6. Conclusion

Facile cleavage of the S–S bond in 2,2′-dithiodipyridine by $[CpCr(CO)_3]_2$ (**1**) yielded the complex $CpCr(CO)_2(SPy)$ (**2**) while homolytic cleavage of the S–H bond in 2-mercaptopyrimidine by **1** gave $CpCr(CO)_2(SPym)$ (**4**) and CpCr(CO)3H (**5**). **2** reacted with hydrochloric acid resulting in Cr–N cleavage to give thione-S coordinated $CpCrCl_2(SPyH)$ (**3**). The similar reaction of **4** in CH_3CN led to both Cr–S and Cr–N cleavage, yielding $CpCrCl_2(NCCH_3)$ (**6**) and free HSPym, respectively.

3. Experimental

3.1. General procedures

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; ^1H and ^{13}C chemical shifts were referenced to residual C_6H_6 in C_6D_6, or CH_2DCN in CD_3CN. IR spectra in KBr discs were measured in the range of 4000–600 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. $[CpCr(CO)_3]_2$ ($Cp = \eta^5$-C_5H_5) (**1**) was synthesized as described by Manning [27] from chromium hexacarbonyl (98% purity from Fluka). The 2,2′-dithiodipyridine and 2-mercaptopyrimidine ligands were obtained from Fluka and Sigma–Aldrich, respectively. 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 chromatographic use.

3.2. Reaction of $[CpCr(CO)_3]_2$ (1) with $(C_5H_4NS)_2$ at ambient temperature

A deep green mixture of **1** (45 mg, 0.11 mmol) and 2,2′-dithiodipyridine (24.5 mg, 0.11 mmol) in toluene (5 mL) was stirred at ambient temperature for 1.5 h. The resultant reddish-brown mixture was filtered, but no residue was observed. Concentration of the filtrate to ca. 1 mL, followed by addition of *n*-hexane (ca. 1 mL) gave air-stable dark brown crystals of $CpCr(CO)_2(\eta^2$-SPy) (**2**) (45 mg, 0.016 mmol, 72% yield) after 2 h at −30 °C. Anal. Found: C, 51.0; H, 3.1; N, 4.8; S, 11.1. Calc. for $C_{12}H_9CrNO_2S$: C, 50.8; H, 3.2; N, 4.9; S, 11.3%. IR (KBr, cm^{-1}): ν(C≡O) 1950s, 1874s; ν(other bands) 1584 m, 1541 m, 1449 m, 1412 m, 1261 m, 1153 m, 1137 m, 1062 w, 1013 w, 852 m, 825s, 744s, 631 m, 567s, 524 m, 464 m. FAB^+-MS: *m/z* 283 [M^+, $CpCr(CO)_2(SPy)$], 227 [CpCr(SPy)], 195 [CpCr(Py)], 162 [Cr(SPy)]. ^1H NMR (300 MHz, 300 K, C_6D_6): δ 4.44 (s, 5 H, C_5H_5); δ 7.37 (d, $J = 6$ Hz, 1 H, Py); 6.48 (t, $J = 6$ Hz, 1 H, Py); 6.20 (d, $J = 6$ Hz, 1 H, Py); 5.97 (t, $J = 6$ Hz, 1 H, Py). $^{13}C\{^1H\}$ NMR (75 MHz, 300 K, C_6D_6): δ 94.2 (C_5H_5); δ 116.1, 126.9, 135.0, 154.8 and 179.0 (Py); δ 265.5 and 270.2 (CO).

3.3. Reaction of $CpCr(CO)_2(\eta^2$-SPy) (2) with HCl

To a stirred dark brown solution of **2** (57 mg, 0.20 mmol) in toluene (7 mL) was added HCl (1.0 M) in excess (1.0 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, followed by 18 h at ambient temperature. The bluish-green oil obtained was evacuated to dryness to remove the excess acid and solvent. The residue was redissolved in CH_3CN and filtered through a frit. The filtrate was concentrated to ca. 2 mL and diethylether (ca. 2 mL) was added. Subsequent cooling to −30 °C overnight gave air-sensitive bluish-green crystals of $CpCrCl_2(SPyH)$ (**3**) (54 mg, 0.17 mmol, 90% yield). Anal. Found: C, 39.6; H, 3.5; N, 5.1; S, 11.2. Calc. for $C_{10}H_{10}CrCl_2NS$: C, 40.1; H, 3.3; N, 4.7; S, 10.7%. IR (KBr, cm^{-1}): ν(N–H) 3429 sbr. ν(other bands) 2367 w, 2336 w, 1583 s, 1513 m, 1374 m, 1260 s, 1158 w, 1126 s, 1018 w, 1007 w, 819 s, 754 s, 485 w and 448 w. FAB^+-MS: *m/z* 298 [$M^+ - H$, $CpCrCl_2(SPy)$], 263 [CpCrCl(Spy)], 227 [CpCr(SPy)], 195 [CpCr(Py)], 112 [HSPy + H]. ^1H NMR shows no peaks, in agreement with a paramagnetic Cr(III) centre.

3.4. Reaction of $[CpCr(CO)_3]_2$ (1) with $C_4H_3N_2SH$ at ambient temperature

A deep green mixture of **1** (80 mg, 0.20 mmol) and 2-mercaptopyrimidine (22.4 mg, 0.20 mmol) in toluene (5 mL) was stirred at ambient temperature for 4 h. The resultant reddish-brown product solution was concentrated to ca. 2 mL and loaded on to a silica gel column (2 × 10 cm) prepared in *n*-hexane. Elution gave 2 fractions: (i) a yellowish-green eluate in toluene (5 mL), which yielded green crystals of $CpCr(CO)_3H$ (**5**) (ca. 37 mg, 0.18 mmol, 46% yield), identified by its colour and spectral characteristics (^1H NMR (C_6D_6): $\delta(C_5H_5)$ 4.06 and δ(Cr–H) −5.61; FAB^+-MS: *m/z* 202) [28]; (ii) a reddish-brown eluate in ether (10 mL), which yielded reddish-brown crystals of $CpCr(CO)_2(\eta^2$-SPym) (**3**) (ca. 48 mg, 0.17 mmol, 42% yield). Concentration of

the filtrate to ca. 1 mL gave air-stable dark brown crystals of **4** after 1 day at −30 °C. Anal. Found: C, 46.8; H, 3.1; N, 9.8; S, 11.5. Calc. for $C_{11}H_8CrN_2O_2S$: C, 46.5; H, 2.8; N, 9.9; S, 11.3%. IR (KBr, cm^{-1}): ν(C≡O) 1960 s, 1875 s; ν(other bands) 1551 m, 1538 m, 1427 m, 1376 s, 1242 w, 1184 m, 1057 w, 1003 m, 830 m, 793 m, 758 m, 625 m, 567 m, 517 m, 468 w. FAB^+-MS: *m/z* 285 [$M^+ + H$, $CpCr(CO)_2(SPym)H$], 228 [CpCr(SPym)], 163 [Cr(SPym)]. ^1H NMR (300 MHz, 300 K, C_6D_6): δ 4.36 (s, 5 H, C_5H_5); δ 7.79 (d, $J = 2$ Hz, 1 H, Pym); 7.34 (d, $J = 4$ Hz, 1 H, Pym); 5.70 (t, $J = 1$ Hz, 1 H, Pym). $^{13}C\{^1H\}$ NMR (75 MHz, 300 K, C_6D_6): δ 93.8 (C_5H_5); δ 114.1, 158.1, 161.8 and 181.4 (Py); δ 263.1 and 268.8 (CO).

3.5. Reaction of $CpCr(CO)_2(\eta^2$-SPym) (4) with HCl

To a stirred reddish-brown solution of **4** (91 mg, 0.32 mmol) in toluene (7 mL) was added HCl (1.0 M) in excess (1.0 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, followed by 1 h at ambient temperature. There was a total decolourization of the reddish-brown solution accompanied by the formation of a bluish-green oil. The mixture was evacuated to dryness to remove the excess acid and solvent. When the oil was dissolved in CH_3CN, large amounts of yellow solids were precipitated. The yellow solids were confirmed to be 2-mercaptopyrimidine (30 mg, 0.27 mmol, 84% yield) via a complete match of the fragmentation pattern of its EI-mass spectrum with that of an authentic sample (*m/z* 112 (M^+), 85 ($M^+ - NCH$), 79 ($M^+ - SH$), 68 ($M^+ - CS$), 59 (NCSH), 53 (C_2N_2H), 26 (CN). From the bluish-green filtrate was obtained a deep blue solid, identified to be $CpCrCl_2(CH_3CN)$ (**6**) (60 mg, 0.26 mmol, 82% yield), based on its distinctive upfield ^1H NMR shift at δ 254 (C_5H_5) and δ 176 (CH_3CN) in $CDCl_3$ [19b].

3.6. Structure determinations

Diffraction-quality single crystals were obtained from solutions at −30 °C as follows: **2** as dark brown rhombus from toluene–*n*-hexane after 2 h; **3** as bluish-green needles from acetonitrile-diethylether after 3 days; **4** as reddish-brown rhombus from ether after 1 day.

The crystals were mounted on quartz fibres. X-ray data were collected on a Siemens SMART diffractometer, equipped with a CCD detector, using Mo Kα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effects with the SMART suite of programs [29] and for absorption effects with SADABS [30]. Structure solution and refinement were carried out with the SHELXTL suite of programs [31]. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The nitrogen H atom in complex **3** was located and refined. The Cp, SPy and SPym hydrogens were placed in calculated positions. The crystallographic data together with data collection details are given in Table 1.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 242594–242596 for compounds **2**, **4** and **3**, 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).

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