

CpCr(CO)₃-initiated N–N bond cleavage in a thiotetrazole ligand in a cyclopentadienylchromium complex

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Abstract

The tetrazolythiolato complex CpCr(CO)₃(STz) (**4a**) was obtained from the facile reaction between [CpCr(CO)₃]₂ (Cp = C₅H₅) (**1**) and 5,5'-dithiobis(1-phenyl-1H-tetrazole), (abbrev. (PhN₄CS)₂ or (STz)₂). Further reaction of **4a** with **1** under thermolytic conditions led to isolation of low yields of the cubane-like complexes Cp₄Cr₄S₃(μ₃-N₃Ph) (**5**), Cp₄Cr₄S₂(μ₃-CO)(μ₃-NC≡CrCp(CO)₂) (**6**), Cp₄Cr₄S₂(μ₃-N₃Ph)(μ₃-NC≡CrCp(CO)₂) (**7**) and Cp₄Cr₄SO₂(μ₃-NPh) (**8**), containing μ₃-phenyltriazenido, imidocarbyne and phenylimido groups at the corners of cuboids, in addition to μ₃-sulfide, oxo or carbonyl groups. The predominant products were the decarbonylation derivative of **1**, i.e. [CpCr(CO)₂]₂(Cr≡Cr) (**9**), together with [CpCr(CO)₂]₂S (**10**) and its thermolytic cuboidal derivatives, mainly Cp₄Cr₄S₂O₂ (**11**) and Cp₄Cr₄S₄ (**13**). **1**-initiated homolytic fragmentation of the tetrazole ring was proposed to rationalize the formation of the derived cubanes. The structures of the complexes **4a**, **6–8** and **11** have been determined by single X-ray diffraction analysis.

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Keywords: Cyclopentadienylchromium; Thiotetrazole; Phenyltriazenido; Imidocarbyne; Phenylimido; Cubanes

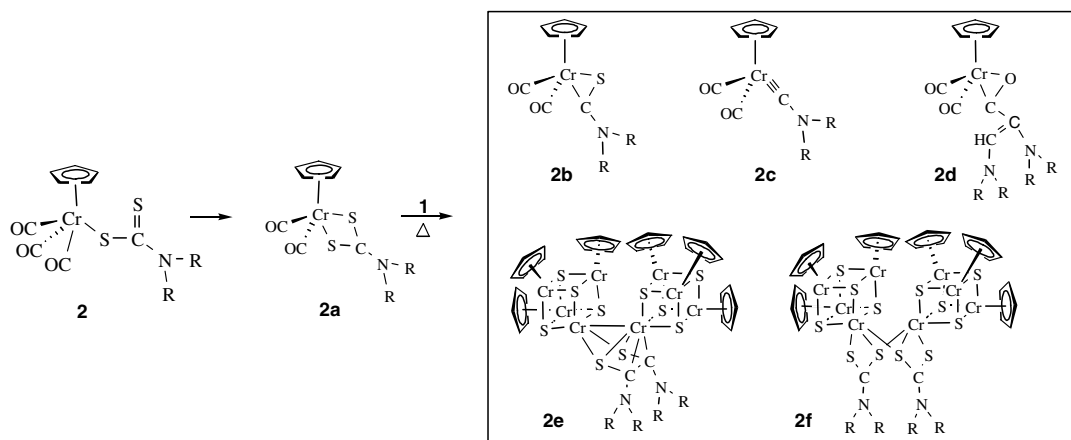
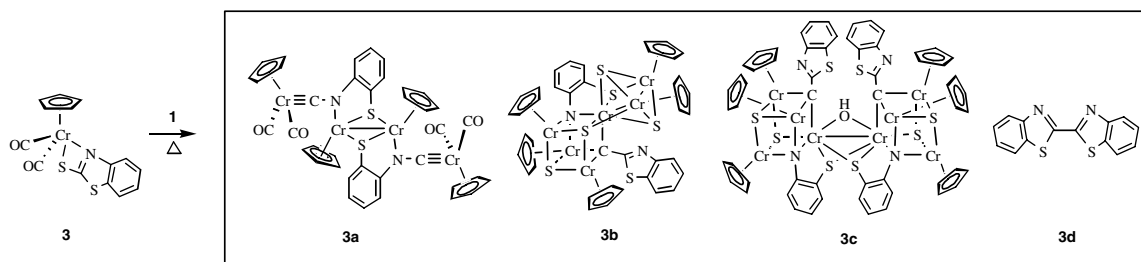
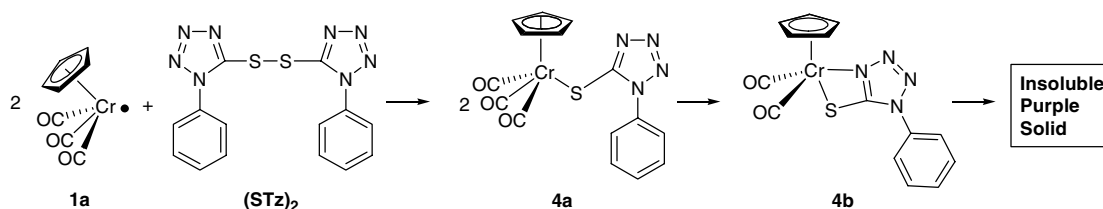
1. Introduction

Our previous studies have shown that the ease with which [CpCr(CO)₃]₂ (Cp = η⁵-C₅H₅) (**1**) cleaves non-metal–nonmetal bonds decreases in the order: X–X (X = S, Se, Te) > P–X (X = S, Se) > P–P, to form a variety of complexes of CpCr(CO)_n (n = 2, 3) [1–4]. In recent investigations with C-, N- and S-containing organic disulfides, in particular with tetraalkylthiuram disulfanes [5] and dibenzothiazolyl disulfane [6], we have obtained complexes of different structural geometries belonging to various class types, which indicate that under thermolytic conditions **1** has efficiently

cleaved C–X (X = C, N, S) and Cr–X (X = N, S) bonds, giving radical species which are the precursors of the products. (Schemes 1 and 2) Having observed **1**-initiated extensive fragmentation of the metal chelate rings in **2a** and the N-coordinated heterocyclic thiazole ring of **3**, we have extended this investigation to an N-rich heterocyclic ligand, in order to test the capability of **1** to also cleave N–N bonds in a coordinated moiety, which has not been demonstrated before. We have selected for this purpose 5,5'-dithiobis(1-phenyl-1H-tetrazole) ((STz)₂) (see Scheme 3) for various reasons, which include the special interest in heterocycles on account of their presence as a component in many bioactive molecules [7], and in particular, the coordination versatility in mercapto-tetrazole arising from the presence of at least three potential nitrogen donor sites and an

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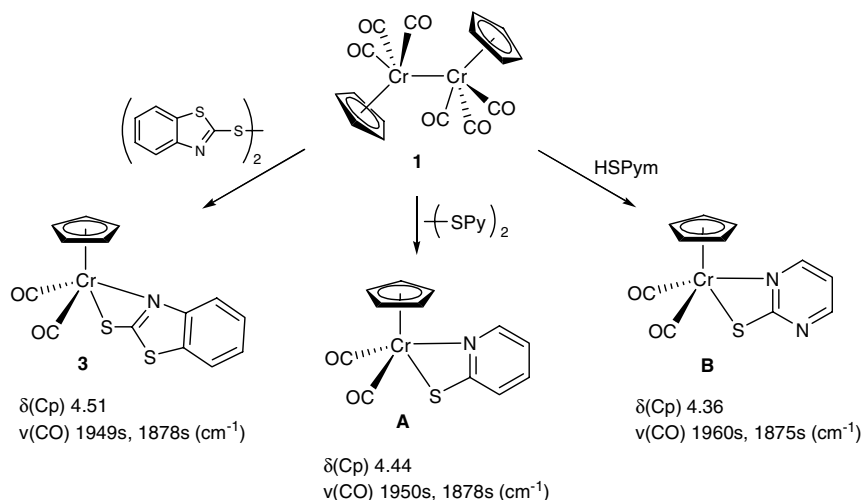
Scheme 1. Cr–Cr bonds in cubanes **2e** and **2f** are omitted for clarity.Scheme 2. Cr–Cr bonds in cubanes **3b** and **3c** are omitted for clarity.

Scheme 3.

exocyclic thiolate sulfur atom [8,9], the growing interest in compounds of tetrazoles for biological, medicinal and agricultural applications [8,10] and their potential usage as building blocks in the formation of polymers and supramolecules for conductivity and optical-related applications [11]. More importantly in the context of this aspect of our research is the presence of a potentially aromatic 6π CN₄ tetrazole ring in the anticipated product, chromium 5-mercapto(1-phenyl-1H-tetrazole) (CpCr(CO)_nSTz) complexes (**4a**: $n = 3$ or **4b**: $n = 2$); furthermore any forthcoming mechanistic information on ring-opening of such heterocycles relates to the current wider interest of such phenomena in biomolecules [7e]. This paper describes the reaction of **1** with (STz)₂ and the subsequent interaction of the primary product with **1**, resulting in fragmentation of the heterocyclic ring.

2. Results and discussion

A facile reaction between [CpCr(CO)₃]₂ (**1**) with 1 mol equiv. of 5,5'-dithiobis(1-phenyl-1H-tetrazole) (abbrev. (SCN₄Ph)₂ or (STz)₂) in toluene at ambient temperature produced a magenta solution, from which a workup at room temperature gave bright red crystals of CpCr(CO)₃(STz) (**4a**) in 33% yield, which could be maximized to 79% by rapidly cooling and maintaining the product solution at -30 °C for 4 days (Scheme 3). Low temperature slowed down considerably the facile decomposition of **4a** to an insoluble purple amorphous non-characterizable solid, via an unstable intermediate derivative **4b**, identified on the basis of its ¹H NMR and IR spectral characteristics (Scheme 3). Precedents of such four-membered CrSCN rings are complexes **3** [6, A and B [12], which we have recently synthesized



(Scheme 4) and the Cp* analogue of **A** from the work of Hoff and co-workers [13].

As proposed previously for the reactions of **1** with disulfanes [1,2], it is proposed that this reaction is also initiated by the homolytic attack of $\{\text{CpCr}(\text{CO})_3\}^{\cdot}$ (**1a**), the incumbent 17-electron organometallic radical from the facile dissociation of **1** [14], on the S–S bond of $(\text{STz})_2$, generating complex **4a** (Scheme 3).

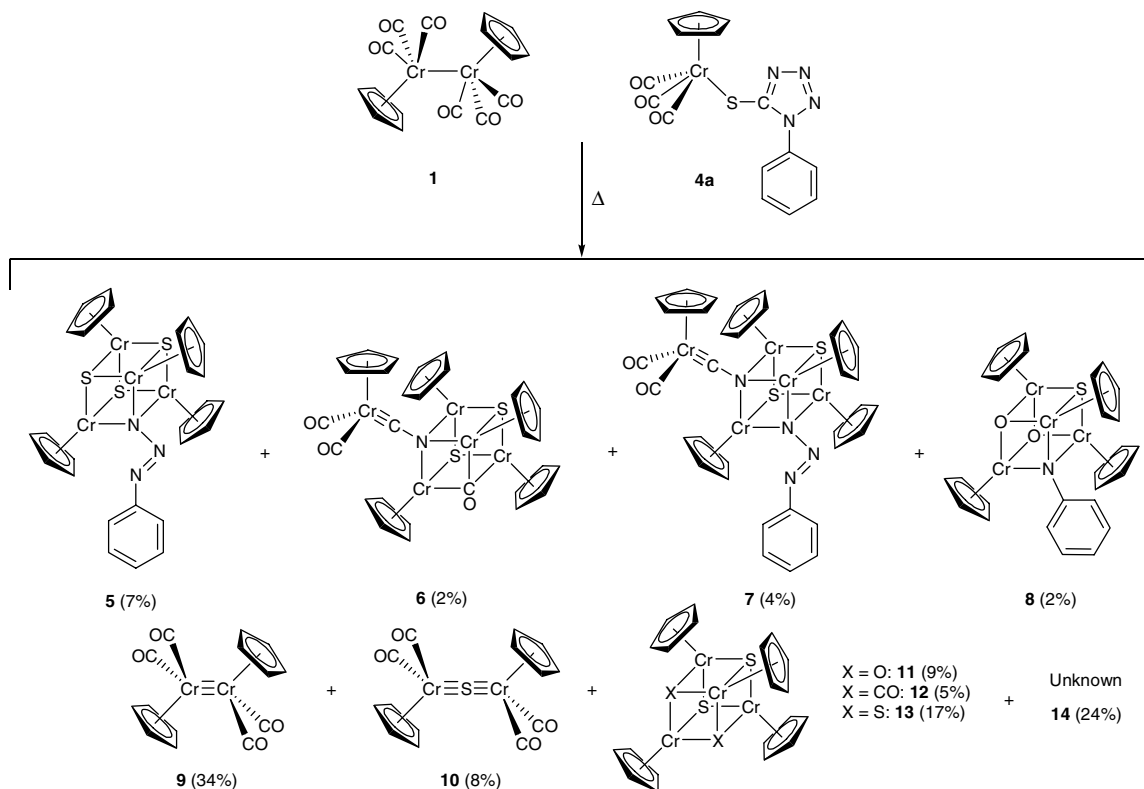
The thermal interaction of **4a** and **1** in refluxing toluene for 2 h produced a brown-black mixture, which upon concentration gave a fine dark green solid (**14**), accounting for ca. 24% of total weight of the reactants (the proton NMR spectrum of this species indicated the presence of four CpCr groups with three of them in equivalent environments, while the mass spectrum also supported a multinuclear species, but unfortunately an X-ray crystal structure could not be obtained). Chromatographic workup of the supernatant gave an isolated mixture of deep green crystals of $[\text{CpCr}(\text{CO})_2]_2$ (**9**) and $[\text{CpCr}(\text{CO})_2]_2\text{S}$ (**10**) in estimated yields of 34% and 8%, respectively, the triazenido cubane $\text{Cp}_4\text{Cr}_4\text{S}_3(\mu_3\text{-N}_3\text{Ph})$ (**5**) as brown microcrystals (7%), the imidocarbyne cubane $\text{Cp}_4\text{Cr}_4\text{S}_2(\mu_3\text{-CO})(\mu_3\text{-NCCrCp}(\text{CO})_2)$ (**6**) as an olive-green crystalline solid (2%), the phenyltriazenido-disulfido-imidocarbyne cubane $\text{Cp}_4\text{Cr}_4\text{S}_2(\mu_3\text{-N}_3\text{Ph})(\mu_3\text{-NCCrCp}(\text{CO})_2)$ (**7**) as a brown crystalline solid (4%), the phenylimidodioxosulfido cubane complex $\text{Cp}_4\text{Cr}_4\text{SO}_2(\mu_3\text{-NPh})$ (**8**) as a dirty-green crystalline solid (2%), the dioxodisulfido cubane $\text{Cp}_4\text{Cr}_4\text{S}_2\text{O}_2$ (**11**) (9%) as dark greenish crystals, the dicarbonyldisulfido cubane $\text{Cp}_4\text{Cr}_4\text{S}_2(\text{CO})_2$ (**12**) (5%) as dark greenish crystals and the tetrasulfido cubane $\text{Cp}_4\text{Cr}_4\text{S}_4$ (**13**) (17%), as presented in Scheme 5.

The complexes **4a**, **6–8** and **11**, were structurally characterized by X-ray diffraction analysis. Their formulation was also supported by NMR, IR and mass spectral data; however, microanalytical data were only

available for **4a**; for the others the low yields rendered this non-feasible even after repeat reactions. The structure of **5** was not available, but its elemental composition was supported by its microanalytical data and mass spectrum which shows the mother ion, while its proposed structural formulation is consistent with the ^1H and ^{13}C NMR spectra which show the presence of two pairs of equivalent Cp rings, and with the presence of $\nu(\text{N}=\text{N}=\text{N})$ in the IR spectrum at a frequency very close to that in complex **7**.

The molecular structure of $\text{CpCr}(\text{CO})_3(\text{SCN}_4\text{Ph})$ (**4a**) is shown in Fig. 1. The Cr center achieves a four-legged piano-stool 18e configuration with coordination to $\eta^5\text{-Cp}$, the thiolate sulfur of STz and three terminal CO ligands. The S(1)–C(4) bond length of 1.730(2) Å is within the range (1.6822(19)–1.7568(18) Å) of the single C–S bonds, that we have found for complexes $\text{CpCr}(\text{CO})_3(\eta^1\text{-S}_2\text{CNMe}_2)$ (**2**) and $\text{CpCr}(\text{CO})_2(\eta^2\text{-S}_2\text{CNMe}_2)$ (**2a**) [5a]. The N–N distances (N(1)–N(2), 1.364(3) Å; N(2)–N(3), 1.287(3) Å; and N(3)–N(4), 1.370(3) Å) lie between Pauling's values for a single bond (1.48 Å) and a double bond (1.22 Å); likewise, the C(4)–N(1) and C(4)–N(4) bond lengths (1.3321(3) and 1.348(3) Å, respectively) are between values for a single bond (1.512 Å) and a double bond (1.287 Å) [15]. These findings are indicative of π -electron delocalization in the ring. The Cr(5)–S(1) distance of 2.4485(7) Å is very close to the value of 2.4406(5) Å found in **2** [5a].

The molecular structures illustrated in Figs. 2–4 show that the thermolytic products **6–8** all possess cubane cores, which may be considered to be S-substituted derivatives of the parent $\text{Cp}_4\text{Cr}_4\text{S}_4$ cubane (**13**), the thermodynamic sink from degradation of $[\text{CpCr}(\text{CO})_2]_2\text{S}$ (**10**) [1,16]; thus there exists cuboidal cores of $\text{Cr}_4\text{S}_2\text{NC}$ in **6**, $\text{Cr}_4\text{S}_2\text{N}_2$ in **7** and Cr_4SNO_2 in **8**, and by inference from elemental and spectroscopic data a core of $\text{Cr}_4\text{S}_3\text{N}$



Scheme 5. The four Cr–Cr bonds in the cubanes of **5–8** and **11–13** are omitted for clarity. Yields of all are given in mol% (based on **1**), except that of **14** which is given as wt.% of total reactants, since its structural composition is unknown. Values for **9** and **10** were estimated.

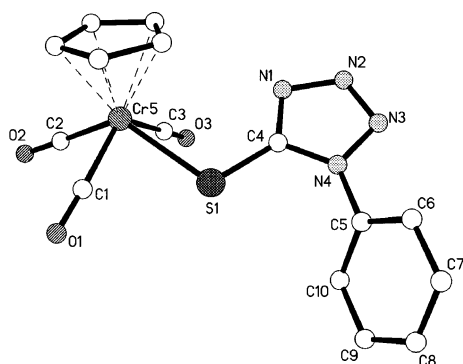


Fig. 1. Molecular structure of $\text{CpCr(CO)}_3(\text{SCN}_4\text{Ph})$ (**4a**). Selected metric data: Cr(5)–S(1) 2.4485(7) Å, S(1)–C(4) 1.730(2) Å, N(1)–N(2) 1.364(3) Å, N(2)–N(3) 1.287(3) Å, N(3)–N(4) 1.370(3) Å, C(4)–N(1) 1.332(3) Å, C(4)–N(4) 1.348(3) Å, N(4)–C(5) 1.425(3) Å, Cr(5)–S(1)–C(4) 109.37(8)°, N(3)–N(4)–C(5) 120.58(18)°.

in **5**. Selected metric data are given in the figure captions. A brief comparison is given here of notable features. Both **6** and **7** possess a CpCr carbyne moiety linked to a cuboidal imido vertex, with Cr≡C distances of 1.750(5) and 1.746(4) Å, respectively; these values compare favourably with the distances of 1.735(4)–1.745(3) Å in the half-sandwich aminocarbene complexes $\text{CpCr(CNR)}_2(\text{tBuNC})_2\text{X}$ (X = Br, tBuNC) [**17**], 1.740(2) Å in $\text{CpCr(CO)}_2(\text{CNMe}_2)$ (**2c**) [**5c**] and 1.733(7) Å in **3a** [**6**]. The C(4)–N(1) distances are

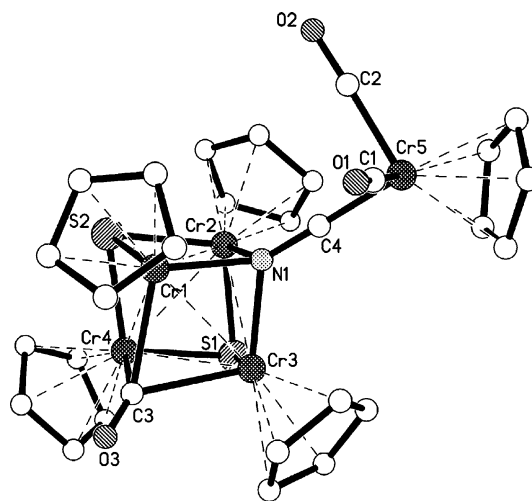


Fig. 2. Molecular structure of $\text{Cp}_4\text{Cr}_4\text{S}_3(\mu_3\text{-CO})(\mu_3\text{-NC}\equiv\text{CrCp(CO)}_2)$ (**6**). Selected metric data: in the cuboid, Cr–Cr 2.6320(11)–2.8092(12) Å, Cr–S 2.2340(15)–2.2526(15) Å, Cr–C(3) 2.041(6)–2.266(5) Å and Cr–N(1) 1.978(4)–1.997(4) Å. Cr(5)≡C(4) 1.750(5) Å, C(4)–N(1) 1.283(7) Å, Cr(5)–C(4)–N(1) 178.2(4)°.

1.283(7) and 1.296(4) Å, respectively, very close to observed values of 1.278(5)–1.300(4) Å [**17**] and 1.290(9) Å in **3a** [**6**]. The Cr–C–N linkages are almost linear (Cr(5)–C(4)–N(1) 178.2(4) and 178.9(3)°, respectively). In the $\mu_3\text{-N–N=NPh}$ triazenido ligand of **7**, the

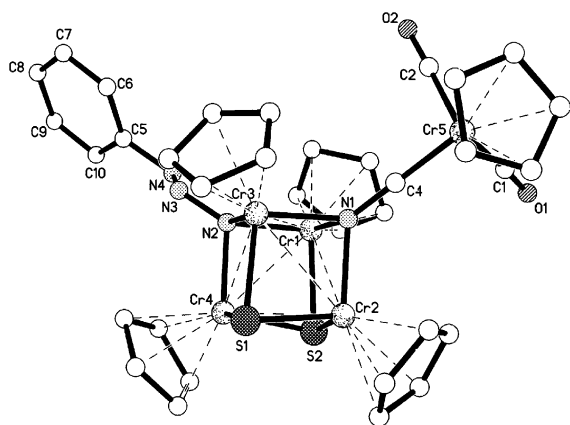


Fig. 3. Molecular structure of $\text{Cp}_4\text{Cr}_4\text{S}_3(\mu_3\text{-N}_3\text{Ph})(\mu_3\text{-NC}\equiv\text{CrCp}(\text{CO})_2)$ (**7**). Selected metric data: in the cuboid, Cr–Cr 2.7031(9)–2.8123(10) Å, Cr–S 2.2388(13)–2.2532(13) Å, and Cr–N 1.953(3)–2.012(3) Å, Cr(5)≡C(4) 1.746(4) Å, C(4)–N(1) 1.296(4) Å, N(2)–N(3) 1.372(5) Å, N(3)–N(4) 1.237(5) Å, N(4)–C(5) 1.438(6) Å, Cr(5)–C(4)–N(1) 178.9(3)°, N(2)–N(3)–N(4) 128.1(5)°, N(3)–N(4)–C(5) 119.9(5)°.

distance between Cr-bound N(2) and N(3) (1.372(5) Å) is longer than N(3)–N(4) (1.237(5) Å); these are similar to values reported for a series of group 10 metal triazenido complexes [18], though the NNN angle in **7** (128.1(5)°) is much larger than those in the Group 10 metal complexes (111(2)°–116(2)°). Complex **8** possesses a $\mu^3\text{-NPh}$ imido vertex, with N(4)–C(5) distance of 1.421(4) Å, which is similar to the distances (1.406(9), 1.407(9) and 1.411(4) Å) of similar bonds of benzothiolatnitrido units in **3b** and **3c** [6]. Imido- or nitrene-capped clusters such as **8** are of considerable interest, because of the perceived role of adsorbed nitrogen atoms as intermediates in the Haber process and other

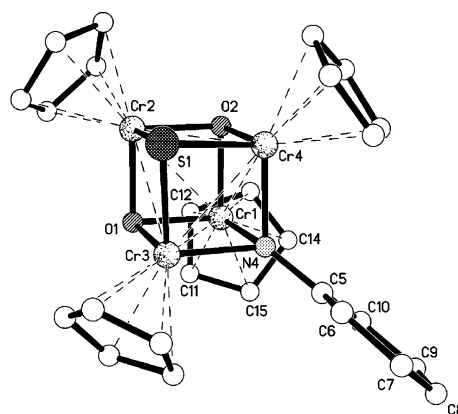


Fig. 4. Molecular structure of $\text{Cp}_4\text{Cr}_4\text{SO}_2(\mu_3\text{-NPh})$ (**8**). Selected metric data: in the cuboid, Cr–Cr 2.6862(7)–2.7829(7) Å, Cr–S 2.2802(9)–2.2880(10) Å, Cr–O 1.898(2)–1.914(2) Å and Cr–N 1.989(3)–1.992(3) Å, N(4)–C(5) 1.421(4) Å.

industrial chemical processes, and in the oxidation of ammonia [19].

The nature of the groups at the corners of the cuboids, viz. $\mu_3\text{-N-N}\equiv\text{N-Ph}$ found in **5** and **7**, $\mu_3\text{-N-C}\equiv\text{CrCp}(\text{CO})_2$ found in **6** and **7**, $\mu_3\text{-N-Ph}$ in **8** and additionally $\mu_3\text{-CO}$ and $\mu_3\text{-O}$ in **6** and **8**, respectively, are suggestive of extensive cleavage of the tetrazole ring, as well as the C–S and the metal–ligand Cr–S bonds in **4a**, leading to the formation of radical fragments, either discrete or quasi-associated, illustrated in Chart 1. Subsequent or concomitant aggregation of these will form the isolated products; for instance the structure of **7** shows the presence of fragments **M**, **1A**, **IIIA** and **IIIB**. We have previously postulated such pathways for the formation of complex molecular structures from similar reactions of compounds of CpCr(dithiocarbamate) [5]

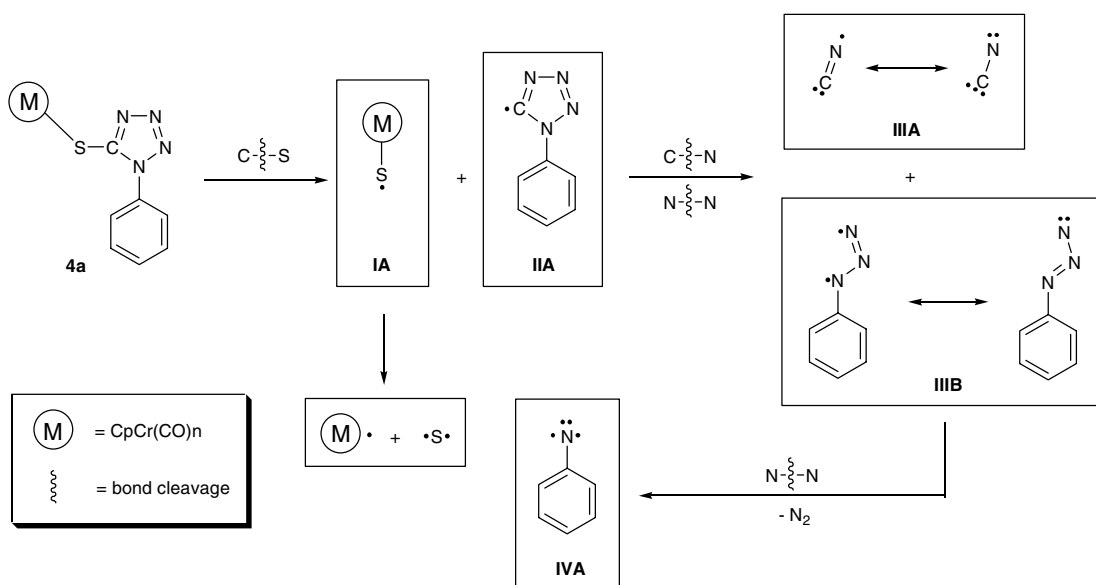


Chart 1. Proposed fragmentation pathways of the thiotetrazole ligand in **4a**.

and CpCr(benzothiazole) [6] and of CpCr systems containing P,S-ligands [20]. Complexes **9**–**13** have all been previously characterized [1,16,21–23]. The high yield of [CpCr(CO)₂]₂ (**9**), the decarbonylation derivative of **1** [21] is indicative of the relative difficulty of N–N bond scission in this complex. Cubane complexes **12** and **13** are isolated thermolytic derivatives of [CpCr(CO)₂]₂S (**10**) [16]; Cp₄Cr₄S₂O₂ (**11**) [23] is also in all likelihood one of the thermolysis products of **10**, by inference from the formation of its Se analogue from thermal degradation of the Se analogue of **10** [24]. The combined substantial yield (ca. 39%) of **10**–**13** is consistent with the frequently manifested thiophilicity of **1a** in all its reactions with S-containing CpCr compounds [2].

3. Conclusion

The homolytic S–S bond cleavage in 5,5'-dithiobis(1-phenyl-1H-tetrazole) (C₆H₅N₄CS)₂ by {CpCr(CO)₃} (**1a**) has provided a facile route to the cyclopentadienyl 5-mercapto(1-phenyl-1H-tetrazole) chromium complex CpCr(CO)₃(SCN₄Ph) (**4a**). Further reaction of **4a** with [CpCr(CO)₃]₂ (**1**) resulted in extensive fragmentation of the tetrazole ring leading to a variety of cuboidal complexes, viz. Cp₄Cr₄S₃(μ₃-N₃Ph) (**5**), Cp₄Cr₄S₂(μ₃-CO)(μ₃-NC≡CrCp(CO)₂) (**6**), Cp₄Cr₄S₂(μ₃-N₃Ph)(μ₃-NC≡CrCp(CO)₂) (**7**) and Cp₄Cr₄SO₂(μ₃-NPh) (**8**). Notably this study led to the first instance of N–N bond cleavage by **1**; though the low yields of products from aggregation of radical fragments, relative to the Cr≡Cr bonded complex **9** and the Cr≡S≡Cr complex **10** and its thermolytic derivatives **11**–**13**, indicates that scission of N–N bonds in the tetrazole ring is a high energy process and is not competitive with decarbonylation of **1** to give **9**, nor cleavage of Cr–S and C–S bonds in **4a**, which are the precursor steps to **10** and its incumbent thermolytic derivatives.

4. Experimental

4.1. 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 ¹³C chemical shifts were referenced to residual C₆H₆ in C₆D₆. 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 = η⁵-C₅H₅) (**1**) was synthesized as described by

Manning [25] from chromium hexacarbonyl (98% purity from Fluka). 5,5'-Dithiobis(1-phenyl-1H-tetrazole) was obtained from Sigma–Aldrich. All solvents were dried over sodium-benzophenone and distilled before use. Celite (Fluka AG) and silica gel (Merck Kieselgel 60, 230–400 mesh) were dried at 140 °C overnight before chromatographic use.

4.2. Reaction of [CpCr(CO)₃]₂ (**1**) with (SCN₄Ph)₂ ((STz)₂)

(a) A deep green solution of **1** (40 mg, 0.10 mmol) in 2 mL THF was mixed with a solution of (STz)₂ (35 mg, 0.10 mmol) in 2 mL THF in a test tube; the magenta mixture was immediately kept at –30 °C. After 4 days, bright red rhombic-shaped crystals of CpCr(CO)₃(η¹-SCN₄Ph) (**4a**) (60 mg, 0.16 mmol, 79%) were obtained.

(b) In a repeat reaction in toluene (5 mL) for 30 min at RT, the resultant dark brown product solution was concentrated to 2 mL and layered with *n*-hexane (2 mL). Standing 1 day at –30 °C gave a mixture of microcrystalline solids (total 57 mg), the ¹H NMR spectrum of which indicated a 1:15 molar mixture of CpCr(CO)₃(η¹-SCN₄Ph) (**4a**) and CpCr(CO)₂(η²-SCN₄Ph) (**4b**). However, it was not possible to obtain **4b** in a pure form unmixed with a fine purple solid, the ultimate degradation product (69 mg, 92% by weight of total reactants from a 2 h reaction at RT). The purple solid was insoluble in all common organic solvents, including DMSO and DMF, and in water. Its IR spectrum does not possess any CO stretches.

An attempt was made to obtain some spectroscopic data of **4b** as follows:

(i) *NMR tube reaction.* A mixture of **1** (4 mg, 0.01 mmol) and (STz)₂ (3.5 mg, 0.01 mmol) was dissolved in benzene-d₆ (0.5 mL) in a 5-mm NMR tube, and the ¹H NMR spectrum of the magenta product solution immediately scanned and subsequently monitored at intervals (5, 10, 30, 60, 120 min). Initially, the Cp signal (δ 4.32) of **4a** was observed and was increasingly replaced over a period of 30 min by δ 4.58, which was assigned to the Cp signal of **4b**; this subsequently disappeared as purple solids totally precipitated out of solution after ca. 2 h.

(ii) *IR spectrum.* To obtain a sample for an IR spectrum, a product solution was concentrated to dryness at the point of total disappearance of the signal of **4a**.

4.3. Data for **4a**

Anal. Found: C, 47.9; H, 2.9; N, 14.6; S, 8.5. Calcd. for C₁₅H₁₀CrN₄O₃S: C, 47.6; H, 2.7; N, 14.8; S, 8.5. IR (KBr, cm⁻¹): ν(CO) 2044s, 1937s and 1894s; ν(N–N=N) 1275m; ν(C–S) 696s, 685s and 627s. FAB⁺-MS: *m/z* 379 [M⁺ + H, CpCr(CO)₃(SCN₄Ph)], 351 [M⁺ – CO, CpCr(CO)₂(SCN₄Ph)], 294 [M⁺ – 3CO CpCr-

(SCN₄Ph)], 219 [CpCr(SCN₄)], 136 [(CN₄)₂], 69 [CN₄]. ¹H NMR (300 MHz, 300 K, C₆D₆): δ 4.32 (s, 5H, C₅H₅); δ 7.63, 7.66 (m, 5H, C₆H₅). The ¹³C NMR spectrum could not be obtained, owing to the instability of the complex in solution.

4.4. Data for **4b**

IR (KBr, cm⁻¹): ν(CO) 1964s and 1891s. ¹H NMR (300 MHz, 300 K, C₆D₆): δ 4.58 (s, 5H, C₅H₅); δ 7.84, 7.82 (d, *J* = 6 Hz, 2H, C₆H₅), 6.81–6.97 (m, 3H, C₆H₅).

4.5. Cothermolysis of CpCr(CO)₃(SCN₄Ph) with [CpCr(CO)₃]₂ at 90 °C

A typical reaction was performed as follows: A dark brown mixture of [CpCr(CO)₃]₂ (**1**) (80 mg, 0.20 mmol) and CpCr(CO)₃(SCN₄Ph) (**4a**) (76 mg, 0.20 mmol) in toluene (7 mL) was stirred at 90 °C for 2 h. The resultant blackish-brown reaction mixture was concentrated to ca. 3 mL and filtered to remove some blackish-green precipitate (**14**) (38 mg). The filtrate was then loaded onto a silica gel column (2.5 × 15 cm) prepared in *n*-hexane. Elution gave eight fractions: (i) a bright green eluate in *n*-hexane (15 mL), the ¹H NMR spectrum of which showed a 4:1 molar mixture (total ca. 30 mg) of [CpCr(CO)₂]₂ (**9**) and [CpCr(CO)₂]₂S (**10**) which were not separated, but identified by their well-documented Cp resonances (δ 4.23 [**4b**] and δ 4.36 [**1,22**]) and mass spectral characteristics [**4b,22b**], and estimated to be present in 0.07 mmol (34%) and 0.02 mmol (8%) yields, respectively; (ii) a greyish-green eluate in *n*-hexane/toluene (2:1, 5 mL), which on concentration gave Cp₄Cr₄S₄ (**13**) (10 mg, 0.02 mmol, 17%); (iii) a dark brown eluate in *n*-hexane/toluene (1:1, 5 mL), which yielded brown crystals of Cp₄Cr₄S₃(μ₃-N₃Ph) (**5**) (5 mg, 7.3 μmol, 7%); (iv) a dirty-green eluate in *n*-hexane/toluene (1:2, 5 mL), which yielded greyish-green crystals of Cp₄Cr₄S₂(μ₃-CO)(μ₃-NC≡CrCp(CO)₂) (**6**) (~1 mg, 1.3 μmol, 2%). (v) a brown eluate in *n*-hexane/toluene (1:2, 5 mL), which yielded brown crystals of Cp₄Cr₄S₂(μ₃-N₃Ph)(μ₃-NC≡CrCp(CO)₂) (**7**) (3 mg, 3.5 μmol, 4%) (vi) a greyish-green eluate in toluene/THF (1:1, 5 mL), which on concentration gave greyish-green crystals of Cp₄Cr₄SO₂(μ₃-NPh) (**8**) (~1 mg, 1.6 μmol, 2%); (vii) a dirty green eluate in THF (5 mL), which on concentration gave black-green crystals of Cp₄Cr₄S₂O₂ (**11**) (5 mg, 8.8 μmol, 9%); (viii) a pale green eluate in THF (10 mL), which yielded greyish microcrystalline solids of Cp₄Cr₄S₂(CO)₂ (**12**) (3 mg, 1.6 μmol, 5%). A pale purplish-blue band remained unmoved on top of the column.

4.6. Data

Elemental analyses for **6–8** are incomplete or unavailable, owing to extremely low yields of compounds. Likewise also for the NMR spectra of **6** and **7**. In all cases,

the observed and calculated isotropic distribution pattern of the mother ions in the mass spectra were found to match.

5. Anal. Found: C, 46.1; H, 4.0; N, 6.5; S, 13.5. Calc. for C₂₆H₂₅Cr₄N₃S₃: C, 45.7; H, 3.7; N, 6.1; S, 14.1. IR [KBr, cm⁻¹] ν(N–N=N) 1431m, 1278w and 1175s; ν(C–N) 1009mbr. FAB⁺-MS: *m/z* 683 [M⁺, Cp₄Cr₄S₃(N₃Ph)], 617 [M⁺ – Cp], 513 [M⁺ – Cp – N₂Ph]. HR-FAB⁺-MS: for [M⁺] 682.8845 (found), 682.8831 (calcd). ¹H NMR (300 MHz, 300 K, C₆D₆): δ 5.08 (s, 15H, C₅H₅), 4.87 (s, 5H, C₅H₅); 7.42–7.72 (m, 5H, C₆H₅). ¹³C NMR (75 MHz, 300 K, C₆D₆): δ 91.0, 94.0 (C₅H₅); 127.9, 130.0, 130.9, 132.7 (C₆H₅).

6. IR [KBr, cm⁻¹] ν(CO) 1924s and 1853s, ν(μ₃-CO) 1655s; ν(C–N) 1066sbr. FAB⁺-MS: *m/z* 759 [M⁺, Cp₄Cr₄S₂(CO)(NCCrCp(CO)₂)].

7. IR [KBr, cm⁻¹] ν(CO) 1923s and 1854s; ν(N–N=N) 1401m, 1203m and 1167m; ν(C–N) 1030sb. ¹H NMR (300 MHz, 300 K, C₆D₆): δ 4.64 (s, 5H, C₅H₅), 4.93 (s, 5H, C₅H₅), 5.13 (s, 10H, C₅H₅), 5.48 (s, 5H, C₅H₅); 7.42–7.72 (m, 5H, C₆H₅). FAB⁺-MS: *m/z* 850 [M⁺, Cp₄Cr₄S₂(N₃Ph)(NCCrCp(CO)₂)].

8. ¹H NMR: no peaks in the normal region, possibly due to paramagnetism. FAB⁺-MS: *m/z* 623 [M⁺, Cp₄Cr₄SO₂(NPh)].

14. ¹H NMR (300 MHz, 300 K, C₆D₆): δ 5.10 (s, 15H, 3 × C₅H₅), 4.84 (s, 5H, C₅H₅); 7.42–7.72 (m, 5H, C₆H₅). Elemental analyses: C, 44.8; H, 3.6; N, 13.1; S, 9.9, could not be rationalized. FAB⁺-MS shows the highest mass fragment at 914, followed by 698, indicative of a multinuclear species.

9–13. These complexes were identified by comparison of their ¹H NMR and mass spectral data with published values [16,21–23].

4.7. Structure determinations

Diffraction-quality single crystals were obtained from solutions in *n*-hexane–toluene after 2–3 days at –30 °C as follows: **4a** as bright red rhombus, **6** as olive-green crystals, **7** as reddish-brown rhombus and **8** as dark-green crystals; **11** was similarly obtained as dirty dark green crystals from hexane–THF.

The crystals were mounted on quartz fibres. The intensity data were collected on a Bruker AXS APEX CCD diffractometer, equipped with a CCD detector, using Mo Kα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarization effects with the SMART suite of programs [26] and for absorption effects with SADABS [27]. Structure solution and refinement were carried out with the SHELXTL suite of programs. [28] 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. The crystallographic data together with data collection details are given in

Table S1. In the diagrams for the molecular structures, H atoms have been omitted for clarity.

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Appendix A. Supplementary data

Table S1, giving crystal data collection and processing parameters for compounds **4a**, **6–8** and **11**. **Table S2**, giving IR spectral data of the new compounds. Structure of **11**. **Figure S1** for the molecular structure of **11**. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 250685–250689 for compounds **4a**, **6–8** and **11**, 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>). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.11.045.

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