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Organometallic Radical-Initiated Cleavage of the Metal Chelate and Thiazole Rings in a Cyclopentadienylchromium Complex

Lai Yoong Goh,* Zhiqiang Weng, Weng Kee Leong, and Jagadese J. Vittal
Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260

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Our previous studies have established the efficacy of $[CpCr(CO)_3]_2$ (**1**) in the cleavage of element−element bonds in homo- and heteropolyatomic molecules of elements of Groups 15 and 16,[1] and expectedly, also of chalcogen−chalcogen bonds in the diaryl compounds Ph_2X_2 (X = S, Se, Te),[2a,b] the bis(thiophosphinyl)-disulfanes, $(Ph_2P(S)S-)_2$[2c] and tetraalkyl thiuram disulfanes $(R_2NC(S)S-)_2$.[2d] It was therefore of interest to us to explore this aspect of the chemistry of **1** toward bonds in metal chelates and heterocyclic ligands, especially C−C, C−S, and C−N bonds, since the reactivity of these bonds bears relevance to many significant biological and industrial processes.[3] We have chosen for this investigation the complex **2** containing a benzothiazole ring, since heterocycles such as thiazoles often form a component in many bioactive molecules[4a−d] and compounds of thionates and the related thiazoles are of much interest, due to their numerous commercial applications, including usage as biocides and environmental control of toxic metals.[5] Indeed, mechanistic studies of ring-opening and -closure of heterocycles in biomolecules are emerging as an area of current active research.[4e] We report here extensive bond cleavage in **2**, effected by an organometallic radical.

The instantaneous reaction of $[CpCr(CO)_3]_2$ (**1**) with 1 mol equiv of 2,2′-dibenzothiazolyl disulfide at ambient temperature led to the isolation of dark-red crystals of $CpCr(CO)_2(SCSN(C_6H_4))$ (**2**) in 78% yield. The cothermolysis of **2** with **1** at 110 °C for 2 h gave a product mixture from which were isolated $[Cp_2Cr_2(CO)_2(\equiv CNS(C_6H_4))]_2$ (**3**) (23%), $Cp_5Cr_6S_4(SN(C_6H_4))(SNC_2(C_6H_4))$ (**4**) (24%), $Cp_6Cr_8S_4(OH)(SN(C_6H_4))_2(SNC_2(C_6H_4))_2$ (**5**) (9%), 2,2′-bibenzothiazole $(C_6H_4NSC)_2$ (**6**) (14%), and $Cp_4Cr_4S_4$ (**7**) (22%). The overall reaction is summarized in Scheme 1. Control experiments demonstrated that none of these complexes were formed from the thermolytic degradation of **2**, **3**, or **4**, or the cothermolysis of **6** with **1**.

The complexes **2**−**5** were fully characterized by elemental, spectroscopic, and X-ray diffraction analyses.[6] The molecular structures of **3**−**5** are illustrated in Figures 1−3; the structural composition of **3**−**6** supports their formation from moieties, either discrete or quasi-associated, arising from the sequential cleavage of C−S, Cr−S, Cr−N, and C−N bonds in **2**, as proposed in Scheme 2; thus, **3** is a Cr−Cr bonded dimer of the product arising from the interaction of $CpCr(CO)_2$ with a SCrN chelate of moiety **IVA**, while **4** and **5** both originate from the interaction of $CpCr(CO)_2$ with the moieties, **IIIB**, **IIIC**, and **IVB** with loss of Cp and CO ligands. Investigations are under way to delineate some of the reactions involved. However, at this stage, it is clear that **1** plays a vital role in these transformations, via its incumbent monomer, $CpCr(CO)_3$ (**1A**), derived from its facile dissociation in solution.[7] The isolation of the cubane **7**, the ultimate thermolysis product of $[CpCr(CO)_2]_2S$,[1a] indicated that **1A** had abstracted a sulfur atom from **2**, probably in an initial step in the process, and the isolation of 2,2′-bibenzothiazole **6** provides evidence for a subsequent Cr−N bond cleavage to yield the precursor benzothiazole radical, **IIIC**, which subsequently underwent C−C coupling. In context, it is noted that an instance of C−C coupling of benzazoles, as found in the formation of **6**, had been effected via the mediation of dichlorocarbene.[8]

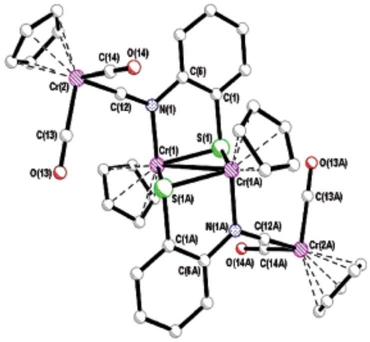

Figure 1. Molecular structure of **3**.

The molecular structure of **3** (Figure 1) possesses a crystallographic center of symmetry at the midpoint of the Cr(1)−Cr(1A) bond. A salient feature is the chair configuration in the central portion of the molecule with the planar four-membered Cr_2S_2 ring forming the “seat”; the Cr−Cr distance of 3.070(1) Å is indicative of the presence of a single bond for which a range of 2.676−3.343 Å[2a,9] has been observed. The $CrSC_2N$ rings annelated to benzene rings are planar. The N atom of this five-membered ring is part of a Cr carbyne moiety, viz. Cr(2)C(12)N(1). The Cr(2)−C(12) distance of 1.733(7) Å compares favorably with the values of 1.735(4)-1.745(3) Å in the half-sandwich aminocarbyne complexes $CpCr(CNR_2)(tBuNC)_2X$ (X = Br, *t*BuNC).[10] Likewise, the C(12)−N(1) bond length of 1.290(9) Å matches the corresponding distances in the aminocarbyne complexes (range 1.278(5)−1.300(4) Å),[10] suggestive of substantial double bond character.[11] The molecule possesses 18 electrons at Cr(2) and 17 electrons at Cr(1), consistent with broad Cp signals in the ^1H and ^{13}C NMR spectra.

The significant feature in the structure of **4** (Figure 2) is the Cr_4S_2CN cube, wherein three of the Cr corners are still attached to η^5-Cp rings, while at the fourth corner (Cr(6)) the Cp ring is replaced by a capping dichromium−trisulfur moiety, Cr(2)Cr(3)S(1)S(2)S(3), where S(1) is a component of the benzothiolatonitrido unit, which thus edge-bridges Cr(6) and the N(1) corner of the cube. The μ_4-bonding S(4) is linked to Cr(3)−Cr(6). The carbido C(1) corner of the cube is singly bonded (bond length 1.465(4) Å) to C(2), a component atom of a benzothiazole unit, indicative of the occurrence of C−C coupling. The total valence electron counting (VEC) of 69 is in agreement with the nonobservation of NMR signals in **4**.

The structure of **5** (Figure 3) consists of double cubanes (Cr_4S_2-CN), quadruply bridged by a weak Cr−Cr bond, a hydroxo ligand, and the thiolato sulfur atoms of two benzothiolatonitrido units, the N atom of each of which constitutes one of the corners of each

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* To whom correspondence should be addressed. E-mail: chmgohly@nus.edu.sg.

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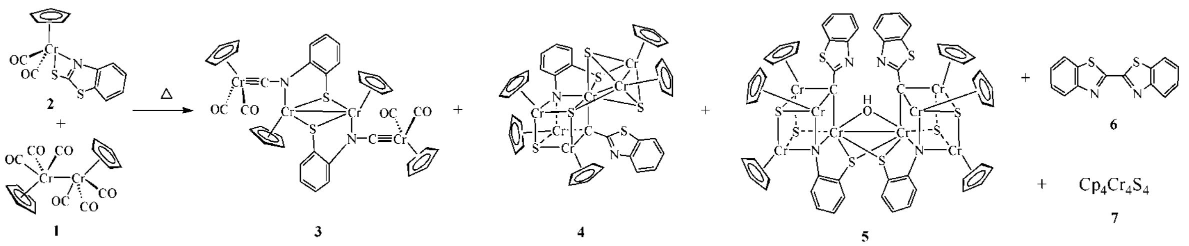
Scheme 1



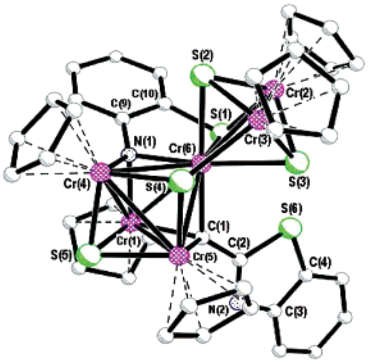


Figure 2. Molecular structure of **4**.

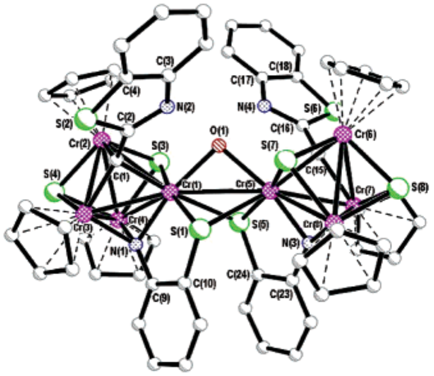
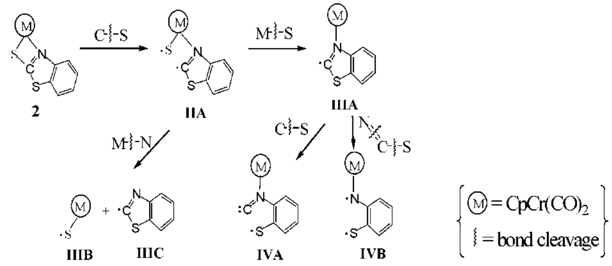


Figure 3. Molecular structure of **5**.

Scheme 2. Proposed cleavage initiated by **1A**



cube. The C atom in each cube is linked to a benzothiazole unit, indicative of the occurrence of coupling at C(2)−C(1) and C(16)−C(15). The nature of the components of the cubes and of the bridge of this double cubane has no precedent among the numerous cubanes and double cubanes, which have been extensively studied by Holm, Coucouvanis, and Sykes.[12] The lengths of the Cr−Cr bridges in the two independent molecules in the unit cell are 3.079(1) and 3.087(1) Å, respectively, which are much longer than such distances in the cubes (range 2.6611(17)−2.8211(18) Å). Allowing for the difference between the covalent radii of O and S, the Cr−O distances in the hydroxo bridge (2.085(5), 2.079(4) Å) are in close agreement with the Cr−S distances in the Cr−S−Cr bridges (2.413(2) and 2.562(2) Å). Except for the bridged Cr atom, the other three Cr corners of the cubanes are η^5-coordinated to Cp rings. While the X-ray crystal data cannot differentiate between an oxo or a hydroxo bridge, the presence of the latter is supported by the exact mass obtained from its mass spectrum, and a total odd VEC (119), giving rise to paramagnetism, as indicated by extremely broad signals in the proton NMR spectrum.

This study demonstrates an unexpected reactivity of cyclopentadienylchromium tricarbonyl in extensive cleavage of the metal chelate and thiazole rings of a mercaptobenzothiazole chromium complex generating polynuclear chromium compounds with novel structural features. The results may have implications for reactivity studies of other aromatic nitrogen- and sulfur-containing heterocyclic molecules coordinated to metal centers, and for the synthesis of substituted bibenzothiazoles.

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Supporting Information Available: Experimental details and spectroscopic and X-ray structural data for **2**, **3**, **4**, and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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