Sulfur–Chromium Complex

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Cyclopentadienylchromium Complexes of 1,2,3,5-Dithiadiazolyls: η^2 π Complexes of Cyclic Sulfur–Nitrogen Compounds**

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The analogy of the Hückel 4*n*+2-electron rule has proven to be a useful guide to the diverse chemistry of unsaturated sulfur–nitrogen compounds since it was first suggested in 1972.[1] While these electron-rich unsaturated compounds provide numerous examples of "forbidden" 4*n*-electron species,[2] the most-stable and dominant ring compounds obey the rule.[3] At the same time there has been an intensive, and thus far unsuccessful, search for organometallic derivatives that show polyene-like π bonding to low-valent metal fragments. An early suggestion that cyclo-S_2N_2 might form η^4 complexes for example, with a {CpMn} fragment ($Cp = \eta^5$-C_5H_5)[4] may be contrasted with the fact that known metal complexes of binary S–N compounds are either σ bonded through an N lone pair (rare) or ring-opened by oxidative addition to the metal center (common).[5]

Many examples of the cyclo-1,2,3,5-dithiadiazolyl, XCN_2S_2 (X is a halogen or H atom, or an organic group),[6] which are thermally much more robust than S_2N_2, have been isolated as the 6π-electron cation or as the 7π-electron radical, which forms weak dimers, **1**, in the solid state (Scheme 1).[7] Reactions of these heterocycles with low-valent transition metals also lead exclusively to ring-opened adducts in which the S–S bond ($d_{S\text{-}S} \approx 2.1$ Å) is oxidatively added to iron ($d_{S\text{-}S} = 2.929$),[8,9] nickel ($d_{S\text{-}S} = 2.905$),[10] palladium ($d_{S\text{-}S} = 3.035$),[11] and platinum ($d_{S\text{-}S} = 3.066$ Å) atoms.[12] Recently, paramagnetic complexes of intact dithiadiazolyls, which coordinate to metal centers through nitrogen atoms

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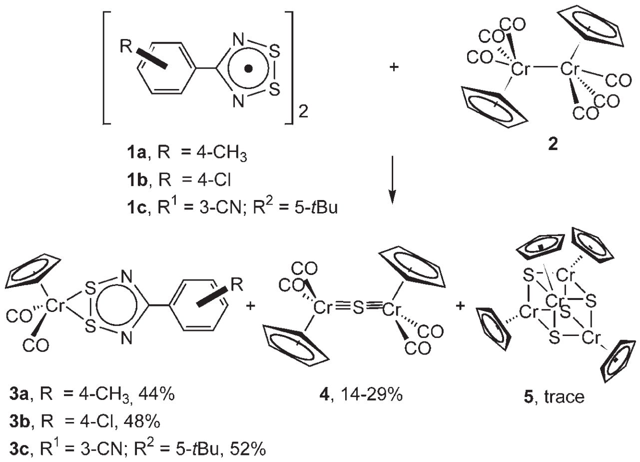


Scheme 1. Reaction of aryl-substituted dithiadiazolyl dimers **1a–c** with **2**.

with the assistance of 2-pyridyl groups, have been reported.[13] Such complexes are being exploited as potential molecular magnets from the interaction of the ligand and unpaired electrons of the metal atom.

To date, reactions with organometallic radicals have not been reported. Our studies on the reactivity of $[\{CpCr(CO)_3\}_2]$ (**2**) towards P–P- and S–S-bonded substrates—for example, polyatomic main-group elements,[14] or various classes of organic substrates—[15] have shown that the reactions are initiated by the 17-electron radical $[CpCr(CO)_3]^{\bullet}$ (**2A**), into which **2** readily dissociates in solution.[16] Thus, the resulting primary products from diphenyl dichalcogenide Ph_2E_2 (E = S, Se, Te),[17] $[Ph_2P(S)S]_2$,[18] the analogous $[(iPrO)_2P(S)S]_2$,[19] tetraalkyldiphosphine disulfide,[20] $[R_2NC(S)S]_2$,[21] $[(C_6H_4)NSCS]_2$,[22] $(C_5H_4NS)_2$,[23] and $(C_6H_5N_4CS)_2$[24] are inevitably generated in the coupling of **2A** with organic sulfur- or phosphorus-centered radicals. We therefore reasoned that **2A** represents a very mild reagent for radical-coupling reactions with **1**, although S–S bond-cleavage reactions are still expected to dominate.

Three aryl-substituted dithiadiazolyl dimers, **1a–c**, have been investigated in reactions with **2** (Scheme 1). In each case, exhaustive chromatography on silica gel led to isolation of intense red crystals of new adducts **3a–c** in yields of about 50% together with previously observed compounds **4**[25] and **5**[26] as well as green residues that could not be eluted or extracted from the support.[27] Structures of the adducts **3a–c** obtained from single-crystal X-ray diffraction are depicted in Figure 1.[28] Noteworthy, and unprecedented among metal complexes of **1**, is the virtually unchanged value of the S–S separation in the metal complexes ($d_{S-S} = 2.114(1)$ in **3a**, 2.132(2) in **3b**, 2.146(3) Å in **3c**) compared to that found in the dithiadiazolyl dimers[29] ($d_{S-S} = 2.096(7)$ in **1b**,[30] 2.101(2) Å in **1c**, unknown in **1a**). Hence ring-opening from oxidative addition has not occurred, and the S–S bond is retained in the metal complexes.

In the crystal structures, **3a** is found as the *exo* isomer, while **3b** and **3c** exist as the *endo* isomers (Scheme 2). It has been previously demonstrated that the influence of the R groups on RCN_2S_2 reactivity is minimal as a consequence of the nodal properties of the frontier orbitals of the rings, which suggests that the R groups are not responsible electronically for the observed isomerism.[7] To probe the energetic preference for the two isomers, we have performed hybrid DFT calculations on the model system $[CpCrS_2N_2CH]$.

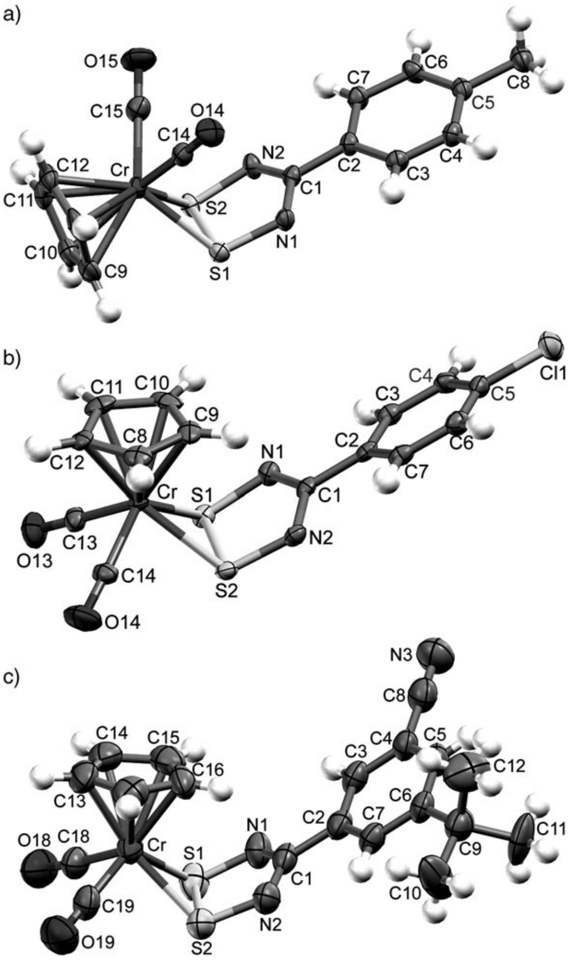
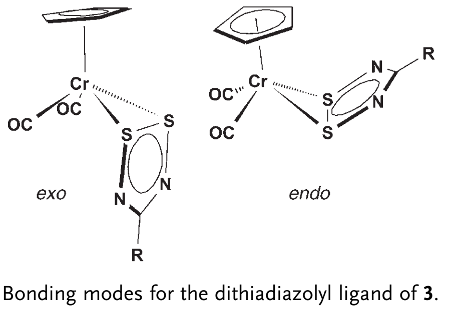


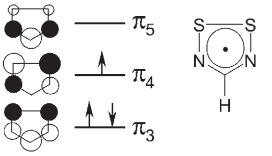
Figure 1. Thermal ellipsoid plots of the molecular structures in crystals of: a) **3a**, selected bond lengths [Å] and bond angles [°]: Cr–S1 2.3463(9), Cr–S2 2.3454(9), S1–N1 1.640(3), S2–N2 1.644(2), S1–S2 2.114(1); S1-Cr-S2 53.57(3), N1-S1-S2 94.77(9), N1-S1-Cr 114.76(10), S2-S1-Cr 63.19(3), N2-S2-S1 93.62(9), N2-S2-Cr 113.17(9), S1-S2-Cr 63.24(3); b) **3b**: Cr–S1 2.3602(13), Cr–S2 2.3537(12), S1–N1 1.642(4), S2–N2 1.635(4), S1–S2 2.1315(15); S1-Cr-S2 53.77(4), N1-S1-S2 93.79(13), N1-S1-Cr 112.62(14), S2-S1-Cr 62.96(4), N2-S2-S1 93.79(14), N2-S2-Cr 114.00(14), S1-S2-Cr 63.27(4); c) **3c**: Cr–S1 2.3540(19), Cr–S2 2.361(2), S1–N1 1.636(5), S2–N2 1.632(5), S1–S2 2.146(3); S1-Cr-S2 54.14(7), N1-S1-S2 93.3(2), N1-S1-Cr 110.99(19), S2-S1-Cr 63.10(7), N2-S2-S1 93.5(2), N2-S2-Cr 112.6(2), S1-S2-Cr 62.76(7).



Scheme 2. Bonding modes for the dithiadiazolyl ligand of **3**.

Geometry-optimized models within C_s symmetry at the B3PW91/6-311+G(2d,2p)//B3PW91/6-31G+(d) level of theory[31] have metric parameters in close agreement with the values determined from the crystal structures and indicate that the *endo* form is more stable than the *exo* by only 2.5 kJ mol^{-1}, a difference that is not significant at this level of theory. In solution at room temperature, ^{1}H NMR spectra of **3a** and **3b** in C_6D_6 display a single, sharp Cp resonance signal, and the expected AB doublets for the *ortho*- (lower frequency) and *meta*-aryl H atoms (higher frequency). In all three complexes, the *ortho* resonances are substantially line-broadened (see the Supporting Information), which is suggestive of dynamic effects in solution. Indeed, when $C_6D_5CD_3$ solutions of the metal complexes are cooled below −20 °C, the AB doublets split into two sets and the Cp resonances also separate. The resulting signals sharpen upon further cooling and the low-temperature spectra integrate to approximately equal intensities, which is consistent with the predictions from the calculations that the two isomers are quite similar in energy. We therefore attribute the low-temperature spectra to the presence of *exo* and *endo* isomers in approximately equal proportions, and the distribution of isomers in the obtained crystal structures to either crystal packing effects or fortuitous crystal selection.

The calculations also provide insight into the bonding in both isomers.[31] The three highest occupied molecular orbitals (HOMOs) of the complexes correspond approximately to the well-known Cr d-centered "t_{2g}-like" orbitals, and the HOMO itself consists of the interaction of the π_4 singly occupied molecular orbital (SOMO) of the 7π-electron dithiadiazolyl ring with one of these metal orbitals (Scheme 3). A second molecular orbital with considerable overlap between the metal and ring fragments lies seventh in sequence of filled orbitals and results from the interaction of the doubly occupied π_3 orbital of the ring with metal orbitals. This interpretation is consistent with the notion that the S_2N_2CR moiety acts as a three-electron π donor towards the 15-electron [CpCr(CO)$_2$] moiety, which results in 18-electron compounds that bear a formal resemblance to the very recently reported [CpCr(CO)$_2${R$_2$CC(R)CR$_2$}] π-allyl complexes.[32] The lower π orbitals of the heterocycle are of no consequence in metal binding owing to the high effective electronegativity of both the nitrogen and sulfur atoms.[2] It is therefore not surprising, in retrospect, that the stable products from the interaction of [CpCr(CO)$_x$] (x = 0–3) with S_2N_2CR are the observed [(η^5-Cp)Cr(CO)$_2$(η^2-S_2N_2CR)] structures in which the heterocycle acts as a three-electron donor, rather than the hypothetical [(η^5-Cp)Cr(η^5-S_2N_2CR)] in which the heterocycle would need to supply seven π electrons. It is likely that one of the hindrances to the preparation of π complexes from unsaturated sulfur–nitrogen and C,N,S-ring compounds has been a too-strict adherence to the metallocene paradigm.



Scheme 3. Frontier orbitals of dithiadiazolyl radicals.

Further investigations into the electronic,[33] structural, and dynamic behavior of these unprecedented metal complexes are in progress in our laboratories. In conclusion, we have prepared three RCN_2S_2 dithiadiazolyl complexes with [CpCr(CO)$_2$] in which the rings are coordinated as three-electron π donors with approximately equal-energy *exo* and *endo* isomers in dynamic exchange. These examples are the first π complexes of unsaturated C,N,S rings.

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[27] The complexes **3a–c** were found to be air-stable as solids for up to two weeks, as monitored by the carbonyl stretches in the IR spectra. ^{1}H NMR spectra of solutions of the complexes indicated significant decomposition to $[Cp_4Cr_4S_4]$ (**5**; identified by its spectral characteristics: ^{1}H NMR: $\delta(\mathrm{Cp}) = 4.90$ ppm in [D$_6$]benzene)[26] after two days at ambient temperature. Full details of the synthesis and characterization of the new complexes are provided in the Supporting Information.

[28] Crystal data: **3a** and **3c** crystallize in $P\bar{1}$ with $Z = 2$ while **3b** and **1c** are found in *Pbca* with $Z = 8$. CCDC-297903, 297904, 297905, and 299596 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[29] The value of $d_{\mathrm{S\text{-}S}}$ in monomeric dithiadiazolyl radicals and in the diamagnetic dimers is expected to be different, but quantum calculations show the difference to be small.[30] In a cobalt bis(hexafluoroacetonato) complex of a monomeric dithiadiazolyl with only σ coordination through a nitrogen atom and a substituent group, leaving the sulfur atoms uncoordinated, $d_{\mathrm{S\text{-}S}} = 2.091$ Å.[13b]

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[33] Preliminary voltammetric results for **3a** are provided in the Supporting Information.