η^1 and η^2 complexes of λ^3-1,2,4,6-thiatriazinyls with CpCr(CO)$_x$†

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The title heterocyclic radicals coordinate to either 17e CpCr(CO)$_3$ or 15e CpCr(CO)$_2$ moieties as one-electron or as three-electron donors, respectively; in the former the bonding is *via* the perpendicular p orbital of the sulfur atom, while in the latter bonding is *via* p$_\pi$ orbitals on both sulfur and nitrogen.

Unsaturated N,S and C,N,S ring compounds are of interest as electron-rich analogues to unsaturated hydrocarbons.[1] There is an intensive search for metal derivatives containing these intact rings in polyene-like π-bonding mode, driven in part by their potential for the formation of molecular magnets from the interaction of the ligand and metal unpaired electrons.[2] However, to date, the quest has been futile, as these heterocycles are either σ-bonded through a N lone pair (rare) or are ring-opened by oxidative addition to the metal centre (common).[3] Recently we reported **1** and **2** (Chart 1), the first π-complexes of unsaturated C,N,S rings, in which the heterocycle contributes three electrons to complete the 18-electron count.[4] Noteworthy in these complexes are the unopened S–S bonds which lengthen by only ~2%,[5] indicating that oxidative addition has not occurred. These complexes were prepared by reaction of the dimeric organometallic radical precursor [CpCr(CO)$_3$]$_2$[6] with the dimeric dithiadiazolyl precursor [RCN$_2$S$_2$]$_2$,[7] species which are redox compatible in their neutral radical forms.‡ In order to establish the generality of these results, we are exploring the reactivity of other unsaturated heterocyclic main group radicals with "CpCr(CO)$_3^{\bullet}$". Herein we report on two distinct coordination modes of one such class of compounds, λ^3-1,2,4,6-thiatriazinyls (TTA), with CpCr(CO)$_x$ moieties. Dithiadiazolyls and thiatriazinyls as neutral monomers are both 7π-electron ring systems, but they differ in the important aspect that the latter contain only S–N and no S–S partial multiple bonds.

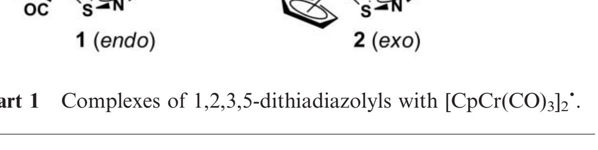


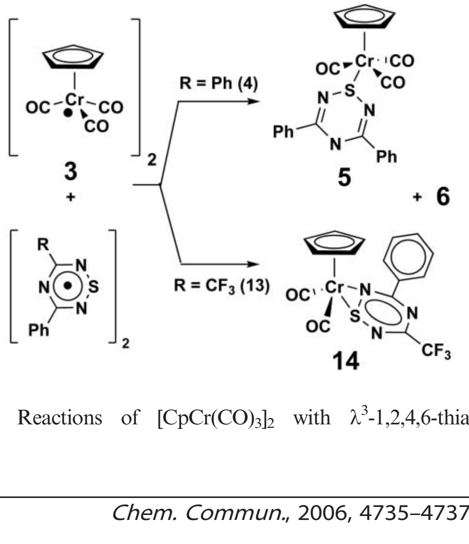
Chart 1 Complexes of 1,2,3,5-dithiadiazolyls with [CpCr(CO)$_3$]$_2^{\bullet}$.

The two solid dimers [CpCr(CO)$_3$]$_2$, **3**, and [TTA]$_2$ were stirred together in dry toluene at room temperature under argon. The progression of the reaction was monitored at intervals *via* the observation of the broadened but easily observable Cp resonance of **3** in the ^{1}H NMR spectrum.[10] When 3,5-diphenyl-λ^3-1,2,4,6-thiatriazinyl, **4**, was employed, a red crystalline solid of **5** could be obtained from the reaction mixture by fractional crystallization, along with a smaller amount of the well-known sulfur-abstraction product [CpCr(O)$_2$]$_2$S, **6**§ (see Scheme 1).

Crystallographic analysis¶ establishes the molecular structure of a new metal complex, **5** (Fig. 1) in which a CpCr(CO)$_3$ moiety is coordinated side-on to the ring in an *exo* orientation, and bonding only through sulfur. The Cr–S distance at 2.4908(11) Å is longer than that found in CpCr(CO)$_3${SC(S)N(CH$_3$)$_2$}, **7**, (2.4406(5))[11] or CpCr(CO)$_3${SC(NPh)N$_3$}, **8**, (2.4482(7) Å),[12] both of which have unambiguously σ-bonded monodentate sulfur coordinated structures.

In complex **5**, **4** acts as a 1e ligand to the 17e organometallic fragment. Consistent with this, the M–S bond is much longer than that found in **1** and **2** (av. 2.353 Å over three exemplars) where the ligands are 3e donors.[4] In Table 1 the geometrical parameters of a series of derivatives of **4** in different formal oxidation states are compared with those of the ligand in **5** (structures defined in Chart 2). It is seen that the coordinated TTA in this complex is intermediate between a neutral and a monoreduced form. Furthermore, the ring adopts a distinct boat conformation in **5**, which is also present in a more pronounced form in the TTA anion (in its protonated imine form **12**).[13c] DFT calculations provide support for this interpretation.†

In contrast, when 3-trifluoromethyl-5-phenyl-λ^3-1,2,4,6-thiatriazinyl, **13**, is employed (Scheme 1), a red crystalline solid **14** could be obtained along with some **6** and other as yet unidentified



Scheme 1 Reactions of [CpCr(CO)$_3$]$_2$ with λ^3-1,2,4,6-thiatriazinyls (TTA).

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† Electronic supplementary information (ESI) available: description of calculated structures. See DOI: 10.1039/b610089a

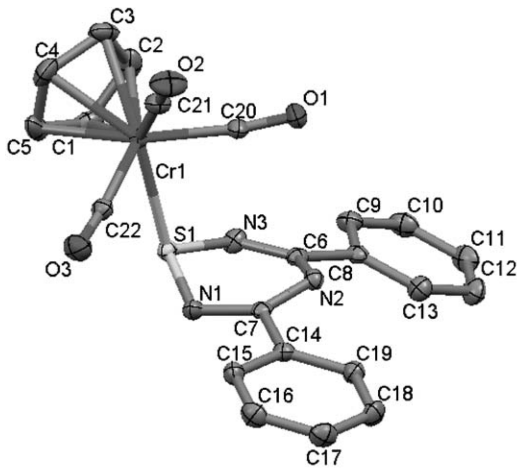

Fig. 1 Thermal ellipsoid plot (30%) of **5** with atom numbering scheme (H atoms omitted). Selected bond lengths [Å] and bond angles [°]. Cr1–S1 2.4908(11), S1–N1 1.659(3), S1–N3 1.675(3), N1–C7 1.325(4), N3–C6 1.317(4), C6–N2 1.363(4), C7–N2 1.345(4), N1–S1–N3 106.13(15), S1–N1–C7 115.2(2), S1–N3–C6 114.9(2), N1–C7–N2 127.4(3), C6–N2–C7 117.2(3), N2–C6–N3 128.2(3).

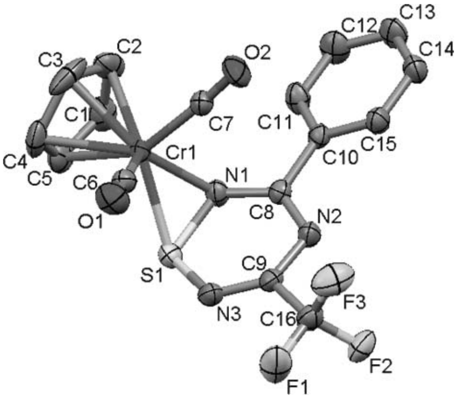

Fig. 2 Thermal ellipsoid plot (30%) of **14** with atom numbering scheme (H atoms omitted). Selected bond lengths [Å] and bond angles [°]. Cr1–S1 2.2965(11), Cr1–N1 2.098(3), S1–N1 1.679(3), S1–N3 1.689(3), N1–C8 1.361(4), N3–C9 1.277(5), C9–N2 1.372(5), C8–N2 1.311(5), N1–S1–N3 107.95(16), S1–N1–C8 116.7(3), S1–N3–C9 114.9(3), N1–C8–N2 128.0(3), C8–N2–C9 117.6(3), N2–C9–N3 132.3(4).

Table 1 Bond lengths [Å] in various 3,5-diphenylthiatriazines and complex **5**

Species	Formal oxidation states	C–N2	C–N1,3	S–N1,3	Ref
PF_6^- salt of **9**	+1	1.332	1.369	1.535	13*c*
Covalent Cl (**10**)	+1	1.340	1.340	1.587	13*a*
Covalent I (**11**)	+1	1.338	1.339	1.603	13*d*
π-Dimer (**[4]₂**)	0	1.342	1.335	1.624	13*b*
5	–	1.355	1.321	1.667	This work
Covalent imine (**12**)	−1	1.386	1.280	1.696	13*c*

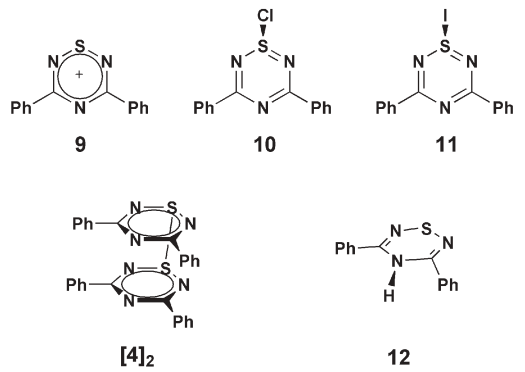

Chart 2 Structures of 3,5-diphenylthiatriazine derivatives.

products.|| Unlike **5**, **14** retains only two CO ligands, as shown by X-ray crystallography (Fig. 2).** The metal atom is attached side-on *via* the S1 and adjacent N1 atoms, the nitrogen atom that is furthest away from the electron withdrawing CF_3 group attached to C9, with overall *exo* configuration. EPR spectroscopy on solutions of **13** indicates a higher spin density on this side of the heterocycle, as indicated by somewhat larger ^{14}N hyperfine coupling constants to N1 than to the other ring nitrogen atoms.[14] The Cr–S1 distance in **14** is 8% shorter than in **5**, and indeed shorter than in either **1** or **2** by ∼2%. These geometric considerations are thus consistent with a stronger bond as a consequence of the ligand acting as a 3e donor. The coordinated TTA ring remains much flatter than in **5**, with less distortion of the bond angles, in accord with a higher degree of charge transfer to the metal and hence a more oxidized state. There is precedence for η^2 bonding of S=N bonds to transition metals. Hursthouse has prepared and structurally characterized a number of complexes of isolated "Ph–S=N–^{t}Bu" to Ti, Zr, Mo, Ni and Ru, often with multiple sulfenamido ligands to a single metal centre.[15] In all these examples, the coordination is highly skewed in favour of the (anionic) nitrogen centre, accompanied by very short M–N and very long M–S bond distances. A similar effect is seen in a chelated sulfenamido V complex,[16] and in a Zr complex of an alkylated 8-membered S,N,P ring in which only one S=N bond is coordinated to the metal.[17] However, in a closely related, non-alkylated analogue coordinated to Rh, the 8-membered ring chelates through an η^1 S and η^2 S=N linkage.[18] The Rh–N bond at 2.136 and Rh–S at 2.273 Å in this species resemble the bonds to the S=N linkage in **14**, and given the larger radius in Rh represent proportionately stronger bonding than in our complex, albeit in a chelating environment.

Considerable alteration in bond lengths upon coordination also occurs in **14**. Two of the bonds are shortened by an average 2% in the parent radical **13**, while four are correspondingly lengthened by an average 4%. This pattern is consistent with bond localization as a consequence of metal coordination of a single S=N bond from the heterocycle. A search of the CCDC database does not reveal any η^2-bonded benzene derivative to any kind of Cr centre. However, a fascinating Pt complex 3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl with its two *meta* CF_3 groups, is a hydrocarbon complex in which one of the arene rings contributes 2e to produce a 16e complex.[19] In this complex, direct comparison is possible between analogous bonds in the coordinated and the uncoordinated aryl rings, which reveals bond localization with two that shorten by an average ∼3%, while four are found to increase in length by an average ∼4% in the coordinated ring. This analysis supports the notion that the bond-length changes in **14** are quite normal for an η^2-coordinated aromatic ring system.

We have, naturally, considered whether the tricarbonyl complex **5** can be converted to the corresponding dicarbonyl complex. Thus far we have been unable to confirm such a transformation either thermally or by photolysis with the aid of a tungsten/UV lamp. The different courses of the two reactions may be due to either the increased polarity in **13** *vs.* the symmetrical **4** or the somewhat more potent oxidizing strength of **13** *vs.* **4**.††

The significant observation is that $[CpCr(CO)_3]^{\bullet}$, an extremely strong thiophile as well as a potent radical for the cleavage of both homo- and hetero- nonmetal–nonmetal bonds and Cr–nonmetal bonds,[6] has not ruptured an S,N bond, except insofar as by-products such as **6** are produced. Here ring-opening "oxidative addition" reactions, the dominant pathway for the reaction of unsaturated S=N bonds with low-valent transition metal ions or organometallics,[3,15*c*] has been suppressed. The mild radical-coupling reactions that we employ have allowed us to trap the π complexes that have been assumed as intermediates in incipient oxidative addition reactions.[2*c*] Finally, we note that these are in fact the first metal complexes of any kind reported for thiatriazinyls. These results set the stage for further investigations with other examples of symmetric and asymmetric thiatriazinyl species, with an added intent to probe the little-understood underlying cause for the competitive pathways leading to preferred η^1 *vs.* η^2 coordination modes in the metal derivatives, and to determine if, in fact, other coordination modes can be induced under suitable conditions.

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Notes and references

‡ For example, in CH_3CN solution, the $[CpCr(CO)_3]^{-1/0}$ couple occurs at −0.28 V,[8] while typical dithiadiazolyl couples in this solvent system are −1/0 at −0.8 V and 0/+1 at +0.6 V,[9] all potentials *vs.* SCE.

§ $[CpCr(CO)_2]_3$ (**3**) (8 mg, 0.02 mmol) and $[Ph_2C_2N_3S]_2$ (**4**) (10 mg, 0.02 mmol) in toluene (12 ml) was stirred at ambient temperature for 4 h to give a 4 : 1 molar mixture of $CpCr(CO)_2SN_3C_2Ph_2$ (**5**) and $[CpCr(CO)_2]_2S$ (**6**) (^1H NMR). Filtering and concentration (3 mL), layering of n-hexane (6 mL) and storage at −29 °C for 1 d afforded dark red microcrystalline solids of $CpCr(CO)_3SN_3C_2Ph_2$ (**7**) (*ca.* 10 mg, 0.02 mmol, 55% yield). Satisfactory combustion analysis and fitting mass and NMR spectra were obtained for the product. The mother liquor retained only **6**.

¶ Crystal data for **5**: $C_{22}H_{15}CrN_3O_3S$, M_r = 453.43, monoclinic, $P2_1/n$, a = 8.4611(17), b = 20.509(4), c = 11.757(2) Å, β = 104.453(7)° V = 1975.6(7) Å^3, Z = 4, T = 223(2) K, μ(Mo-Kα) = 0.715 mm^{-1}, 13844 reflections collected, 4526 unique (R_{int} = 0.048), R_1 = 0.0677 [$I > 2\sigma(I)$], wR_2 = 0.1439 (all data). CCDC 614495. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610089a

‖ $[CpCr(CO)_3]_2$ (**2**) (5 mg, 0.01 mmol) and $[PhC_2N_3SCF_3]_2$ (**13**) (6 mg, 0.01 mmol) were reacted in 3 mL toluene for 3 d at −29 °C. Concentration to *ca.* 2 mL, followed by addition of n-hexane (4 mL) at −29 °C for 1 d afforded 2 crops of dark red microcrystalline solids analyzing for $CpCr(CO)_2SN_3C_2PhCF_3$ (**14**) (*ca.* 4 mg, 0.007 mmol, 30% yield). Satisfactory combustion analysis and fitting mass and NMR spectra were obtained for the product. Diffraction quality crystals of **14** were grown from toluene layered with n-hexane at −29 °C for three days. The presence of **6** was determined by NMR; other products have not been identified to date.

** Crystal data for **14**: $C_{16}H_{10}CrF_3N_3O_2S$, M_r = 417.33, triclinic, $P\bar{1}$, a = 8.0929(8), b = 10.3160(10), c = 11.2405(11) Å, α = 70.032(2), β = 72.076(2), γ =82.375(2)° V = 838.81(14) Å^3, Z = 2, T = 223(2) K, μ(Mo-Kα) = 0.854 mm^{-1}, 11159 reflections collected, 3845 unique (R_{int} = 0.039), R_1 = 0.0663 [$I > 2\sigma(I)$], wR_2 = 0.1560 (all data). CCDC 614496. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610089a.

†† For example, in CH_3CN solution, the $[TTA]^{-1/0}$ couple occurs at −0.46 V in **4**,[10] while in **13** this couple occurs at −0.16 V,[14] all potentials *vs.* SCE.

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