Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 2697–2704
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

A *tert*-butyl/cyano substituted (1,2,3,5-dithiadiazolyl)benzene and η^2 π complexes with $CpCr(CO)_2$ ☆

René T. Boeré [a,*], Lai-Yoong Goh [b,*], Chwee Ying Ang [b], Seah Ling Kuan [b], Hiu Fung Lau [b], Victor Wee Lin Ng [b], Tracey L. Roemmele [a], Sonja D. Seagrave [a]

[a] *Department of Chemistry and Biochemistry, The University of Lethbridge, Lethbridge, Alberta, Canada T1K 3M4*
[b] *Department of Chemistry, National University of Singapore, Kent Ridge 119260, Singapore*

Received 13 October 2006; received in revised form 24 November 2006; accepted 24 November 2006
Available online 9 December 2006

Abstract

A rational synthesis for 5-*tert*-butyl-3-cyano-1-(1,2,3,5-dithiadiazolyl)benzene, which was first observed from thermal cleavage of the bis-dithiadiazolyl, has been developed. Voltammetry and electron paramagnetic resonance (EPR) spectra for this radical are reported and its X-ray structure is described. Despite the bulky ^{t}Bu substituent, the cyano supramolecular synthon is still able to maintain links to a single neighbouring sulfur atom of the S_2 unit, as previously observed in cyano-substituted dithiadiazolyls. In the η^2 complex with $CpCr(CO)_2$, no such interactions are observed; the nitrile group forms a centrosymmetric dimer through weak contacts with the *para* H atom on the aryl ring of the partner molecule. This behaviour is contrasted to similar complexes of less bulky dithiadiazolyls, where intermolecular interactions are retained in the crystalline lattice.

Keywords: Chromium–sulfur complexes; Main-group heterocycles; Free-radicals; EPR spectroscopy; Electrochemistry

1. Introduction

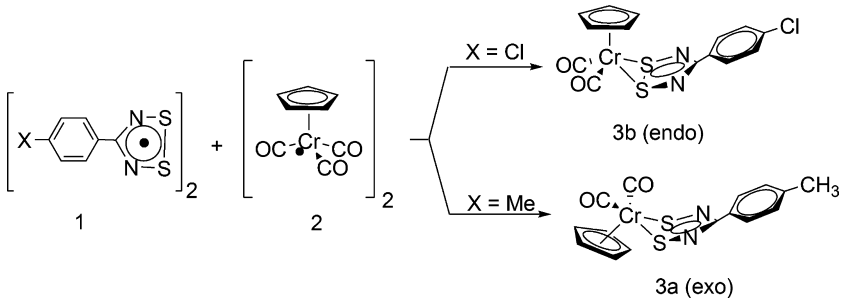
We have recently communicated the first *bona fide* π-complexes of unsaturated electron-rich C,N,S heterocycles [1,2]. The reaction of two different 1,2,3,5-dithiadiazolyls, **1**, with the radical released from $[CpCr(CO)_3]_2$, **2** ($Cp = \eta^5$-C_5H_5) led to synthesis in ca. 50% yield of new complexes with η^2 coordination across S–S bonds, which crystallize in either *exo* (**3a**) or *endo* (**3b**) isomeric forms (Scheme 1) [1]. Reaction of two different 1,2,4,6-thiatriazinyls (**4a**,**b**) with the same organometallic radical likewise yielded new complexes with either η^1, **5**, or η^2, **6**, coordination across S=N bonds (Scheme 2) [2]. The novelty in all of these reactions is the suppression of oxidative addition which normally results from the reaction of unsaturated S–N bonds with low-valent transition metal complexes [3]. We attribute the success of our method to the employment of radical coupling reactions under mild conditions. Our strategy is an alternative to the recently reported use of β-pyridyl groups in the building of multi-spin magnetic complexes incorporating C,N,S radicals [4].

Previous studies on the reactivity of $[CpCr(CO)_3]_2$, **2**, towards polyatomic main group elements [5] or various classes of organic substrates [6] containing P–P and S–S bonds, have shown that the reactions were initiated by the 17-electron radical $[CpCr(CO)_3\cdot]$ **2a**, into which **2** readily dissociates in solution (Chart 1) [7]. Thus, the resulting primary products, **A**, from dibenzothiazolyl disulfide $[(C_6H_4)$-$NSCS]_2$ [8], **B**, tetraalkylthiuram disulfanes $(R_2NC(S)S)_2$ [9], **C**, tetraalkyldiphosphine disulfide [10], **D** and **E**, diphenyl dichalcogenide Ph_2E_2 (X = S, Se, Te) [11], **F**, thiophosphorus compounds bis(diphenylthiophosphinyl)disulfane

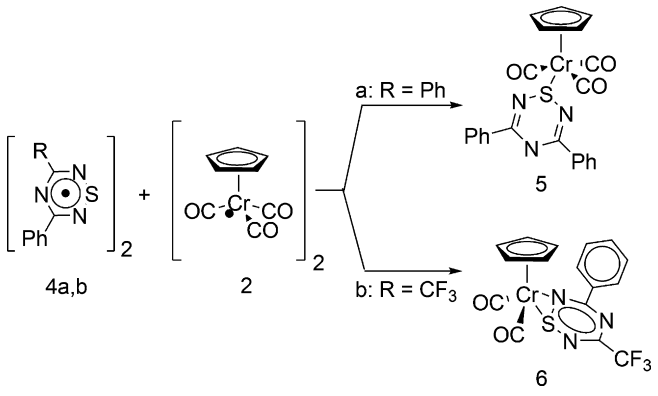
☆ This article is based on the oral presentation by René T. Boeré (Abstract 61) at the 11th International Symposium on Inorganic Ring Systems, Oulu, Finland, July 30–August 4, 2006.

* Corresponding authors. Tel.: +1 403 329 2045; fax: +1 403 329 2057 (René T. Boeré); fax: +65 6779 1691 (Lai-Yoong Goh).
E-mail addresses: boere@uleth.ca (R.T. Boeré), chmgohly@nus.edu.sg (L.-Y. Goh).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.11.049



Scheme 1.



Scheme 2.

$(Ph_2P(S)S)_2$ [12], or the analogous bis(thiophosphoryl)-disulfane $[(RO)_2P(S)S]_2$ ($R = {}^{i}Pr$) [13], are the inevitable consequence of the coupling of **2** and organic sulfur- or phosphorus-centered radicals, under conditions where thermally induced radical cleavage of E–E bonds occurs.

The dithiadiazolyl free radicals, and their diamagnetic dimers which are predominantly found in the solid-state, have been the subject of intense research because of their potential as spin-bearers for magnetic and electrically conductive molecular materials [14]. Substituent effects have been extensively investigated, especially regarding the effects of steric bulk and supra-molecular synthons on crystal engineering. Recently dithiadiazolyls bearing the super-bulky 2,4,6-*tris*(trifluoromethyl)phenyl substituent were shown to posses structure-dependent paramagnetism in the solid state [15]. We previously reported the formation of a "double column" structure when the bulky ^{t}Bu group on a bis-dithiadiazolyl **7** influences packing (Scheme 3), where the lipophilic organic group and the CN_2S_2 rings segregate in the crystal lattice [16]. Cyano-functionalised dithiadiazolyl rings have been favourite supramolecular synthons because of the highly polar nature of the S–N bond, leading to $CN^{\delta-} \cdots S^{\delta+}$ interactions that favour the formation of molecular sheets [17]. A number of other shape-directing substituents have been investigated as alternatives to CN for dithiadiazolyl lattice modification, including halogens [18]. In this paper, we report full synthetic, structural, and electrochemical details for a new dithiadiazolyl incorporating both *tert*-butyl and cyano substituents, and contrast the effects of these orienting groups on the structure of the parent radical dimer and its η^2-$CpCr(CO)_2$ complex, the structure of which was reported in a preliminary communication [1].

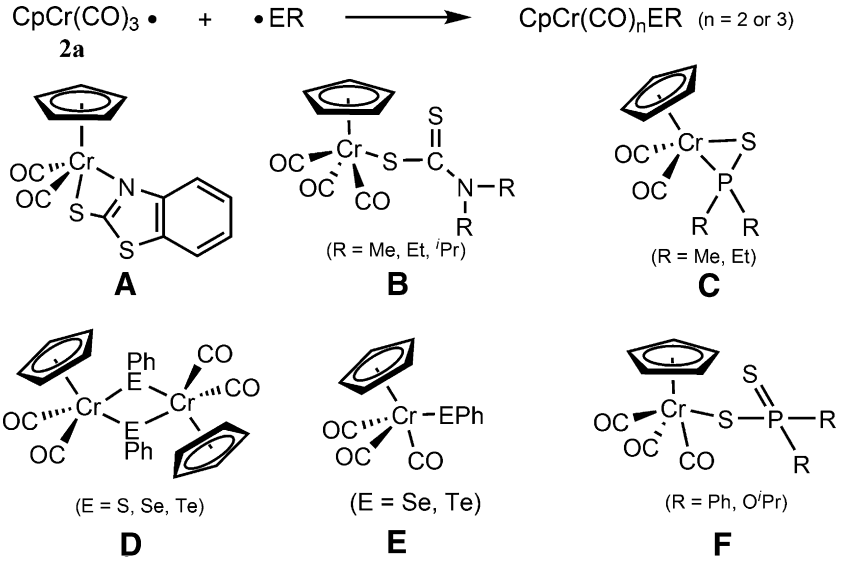
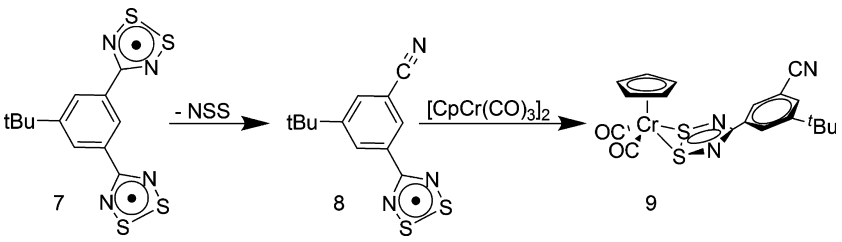


Chart 1.



Scheme 3.

2. Results and discussion

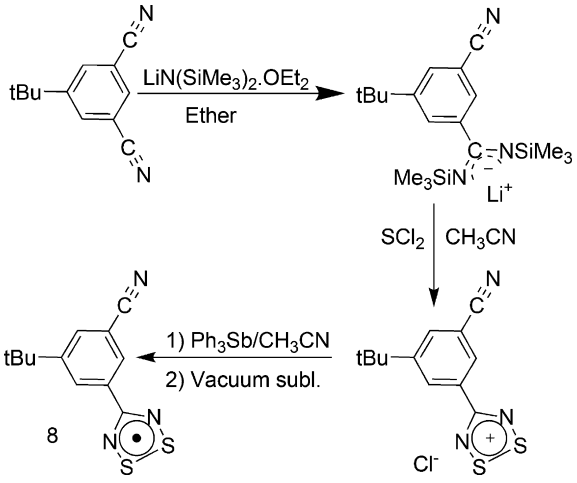
2.1. Discovery of 5-*tert*-butyl-3-cyano-1-(1,2,3,5-dithiadiazolyl)benzene, 8

The synthesis, solid-state structure, EPR spectra and electrochemistry of 5-*tert*-butyl-1,3-bis-(1,2,3,5-dithiadiazolyl)benzene **7** was reported some time ago [16]. During the sublimation of **7** in a thermal gradient tube furnace under dynamic vacuum, a secondary deposit of crystals was obtained which were more volatile than the major product. Mass spectroscopic evidence was consistent with the structure 5-*tert*-butyl-3-cyano-1-(1,2,3,5-dithiadiazolyl)benzene, **8**, which presumably is formed as a result of thermal cleavage of one of the two 1,2,3,5-dithiadiazolyl groups (Scheme 3), thereby converting diradical **7** into monoradical **8** with the elimination of [NSS]•.

Both [SNS]• [19] and [NSS]• isomers have been produced along with other nitrogen sulfides when a mixture of N and S vapor was subjected to a microwave discharge and have been unambiguously characterized by matrix infrared spectroscopy [20]. Interestingly, upon irradiation with near-ultraviolet light, the [NSS]• species underwent isomerization to the more symmetrical [SNS]• isomer. This observation is in line with results of *ab initio* molecular orbital calculations [21] which showed that the C_{2v} species [SNS]• ($^2A_1$) is about 80.3 kJ/mol lower in energy than the C_s species [NSS]• ($^2A'$). More recently, [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole has been used to generate [SNS]•, despite the rather complex re-organization of the starting material that is required to form the product [22].

2.2. Synthesis of 5-tert-butyl-3-cyano-1-(1,2,3,5-dithiadiazolyl)benzene, 8

In contrast to the original, accidental production of **8**, we set out do design a rational synthesis of this heterocyclic radical (Scheme 4). In our hands the fully silylated amidine, which is normally the most versatile reagent for the preparation of the 1,2,3,5-dithiadiazolium chlorides [23], could not be prepared from 5-*tert*-butyl-1,3-dicyanobenzene [24]. However, the intermediate *N*-lithio carboximidamide was found to be a suitable starting material for its preparation. The free-radical **8** turned out to be remarkably soluble in acetonitrile, quite unlike the disubstituted analogue **7** which is extremely insoluble in this solvent. We found that



Scheme 4.

the majority of the co-produced Ph_3SbCl_2 could be fractionally crystallized at −35 °C, leaving **8** to slowly precipitate at RT over several days from the remaining mother liquor. Crude **8** is pyrophoric when dry, but the crystalline material produced by vacuum sublimation can be handled briefly in air.

2.3. EPR spectroscopy of 8

The EPR spectrum of a solution of **8** in CH_2Cl_2, prepared in a sealed "T" cell under vacuum with rigorous exclusion of air, was investigated over a range of subambient temperatures because it was observed that the lines at RT were substantially broadened. At 253 K a sharp spectrum (Fig. 1) was obtained of the expected five-line pattern for coupling to two equivalent ^{14}N nuclei, with $a_N = 0.509$ mT and a g value of 2.011. The a_N value is typical for dithiadiazolyl radicals; e.g. **7** at 250 K has $a_N = 0.510$ mT.

We were able to obtain an excellent fit to the theoretically expected Lorentzian lineshape by fitting additional hyperfine coupling to two *ortho* H atoms with equivalent hfc constants of 0.024 mT using the program WinSim [25]. Without this contribution, the spectrum requires Gaussian admixture into the lineshape to achieve a good fit. It is possible that modulation of the coupling to the ring H atoms with rotation about the Aryl-CN_2S_2 bond on the EPR timescale is responsible for the observed small temperature dependence of the linewidth, an effect that is

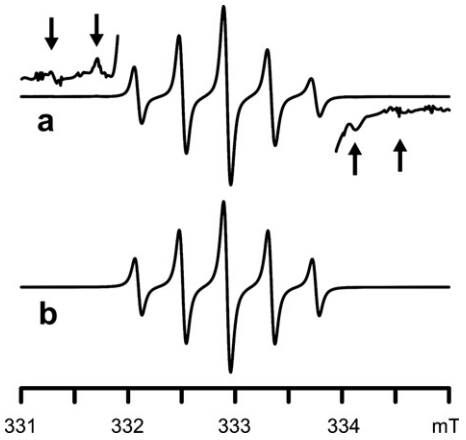


Fig. 1. EPR spectrum of **8**. (a) Experimental spectrum at 253 K in CH_2Cl_2 at high dilution, $g = 2.011$; expansion at low- and high-field with very high gain; arrows indicate ^{33}S satellite peaks. (b) Computer simulation: 80% Gaussian line-shape admixture; $a_N = 0.509$ mT; $a_S = 0.63$ mT.

approximately linear over the range 253–293 K (variation of 0.7 nT/K).

The spectrum obtained at 253 K displayed a very high signal-to-noise ratio which allowed for enlargement of the intensity axis of this spectrum until the satellite peaks from the ^{33}S isotope at natural abundance (0.75%, $I = 3/2$) become clearly visible (Fig. 1, inset). A good match was obtained at $a_S = 0.630$ mT. Preston and Sutcliffe measured such a constant to be 0.62 mT in a single-crystal EPR study of $PhCN_2S_2$ [26], in good agreement with the value obtained here for **8**. There is no reason to expect a large substituent effect on the ^{33}S hfc because none has been observed for ^{14}N hfc.

2.4. Voltammetry of *8*

The voltammetry of **8** has been investigated using both cyclic- and Osteryoung square wave voltammetry (Table 1 and Fig. 2). Both the 0/+1 and the −1/0 redox processes are essentially reversible, with $E_a - E_c$ values of 97 and 66 mV, respectively, under conditions where the internal reference ferrocene/ferrocenium couple displays 105 mV. Platinum wire electrodes were employed as the working and auxiliary and a platinum button as the pseudo reference electrodes in an all-glass electrochemical cell operated under vacuum [27]. The observed potentials of +0.658 V for the 0/+1 and −0.787 V for the −1/0 couples on the SCE scale are almost identical to that measured by us previously for

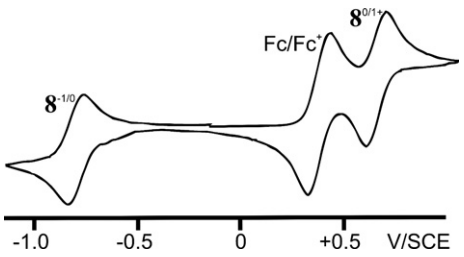


Fig. 2. Cyclic voltammogram of **8** plus internal ferrocene reference in $CH_2Cl_2/[^nBu_4N][PF_6]$; scan rate 0.1 V s^{-1}.

a phenyldithiadiazole with a *para* CF_3 group [27]. This is consistent with Hammet parameters for *meta* cyano almost identical to those for *para* CF_3; evidently the much smaller inductive effect of the *meta tert*-butyl group is swamped by the larger influence of the cyano substituent. As is common for 4-substituted 1,2,3,5-dithiadiazolyls, all remote substituent effects are small, consistent with a node at the carbon atom of the five-membered ring in the SOMO of the free radical [27]. The voltammetric behaviour, as the EPR also suggests, reflects the dominance of the free radical rather than its diamagnetic dimer in dilute solution in both CH_3CN and CH_2Cl_2 [27].

2.5. Crystal structure of *8*

The crystal structure of **8** was reported in our preliminary communication, but the geometrical parameters were not provided. A thermal ellipsoid plot is provided of the molecular structure of **8** in Fig. 3. The *tert*-butyl group displays typical rotational disorder and was adequately modelled using two full sets of methyl carbon atoms fixed at half-occupancy, constrained to have similar bond lengths to C9 and to have approximate isotropic temperature coefficients.

The crystal structure of the new dithiadiazolyl radical **8** bears a resemblance to that of the bis radical **7** insofar as in each case, the large out-of-plane *tert*-butyl group seems to control the observed crystal architecture. In **8**, as usual for dithiadiazolyls, the thiazyl rings form discrete dimers, leading to a diamagnetic ground state, but they display a rare example of the *trans*-cofacial arrangement (Fig. 4) [14a]. This motif has been reported previously in the structure of 4-I–C_6H_4–CN_2S_2 [28] and in a 2,2′-dimethylbiphenylene (DMBP) bridged bisdithiadiazolyl [29].

Cyano groups have been extensively utilized as crystal engineering building blocks in dithiadiazolyl chemistry

Table 1
Voltammetric data for the dithiadiazolyls[a]

Compound	$E_{1/2}$/V	$E_{1/2}$/V	$E_{1/2}$/V	$E_{1/2}$/V	Reference
	CH_3CN "Oxidation"	"Reduction"	CH_2Cl_2 "Oxidation"	"Reduction"	
8	+0.658	−0.787			This work
7	+0.61	−0.80	+0.78	−0.72	[16]

[a] Measured at Pt wire or button electrodes in an all-glass cell operating under vacuum [27], employing a *pseudo* reference electrode and calibrated against added Fc/Fc^+ at +0.38 V vs. SCE in CH_3CN and +0.48 V vs. SCE in CH_2Cl_2 [27b].

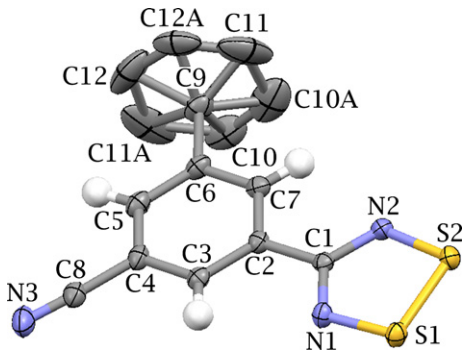


Fig. 3. Thermal elipsoid plot (Mercury) of the molecular structure of **8** as found in the crystal. Selected bond lengths (Å) and angles (°): S1–S2 2.101(2), S1–N1 1.624(4), S2–N1 1.626(4), C1–N1 1.334(6), C1–N2 1.334(6), N3–C8 1.125(7), C1–C2 1.476(6), C2–C3 1.391(7), C3–C4 1.389(7), C4–C8 1.456(7), C4–C5 1.375(7), C5–C6 1.389(8), C6–C7 1.393(7), C7–C2 1.396(7), N1–S1–S2 93.8(2), S1–S2–N2 94.4(2), C1–N1–S1 115.2(3), C1–N2–S2 114.6(3), C4–C8–N3 177.2(6).

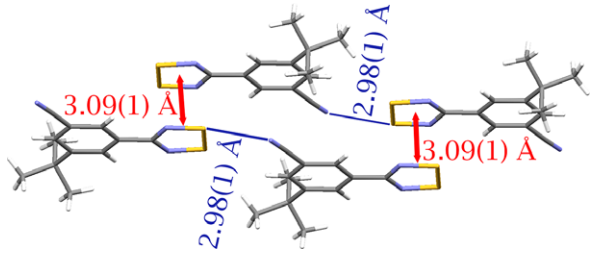


Fig. 4. Intermolecular interactions in the crystal found for **8** include a relatively-rare *trans*-cofacial dithiadiazolyl dimer (average S ··· N distances are 3.09(1) Å) as well as nitrile orienting links with CN ··· S1 contacts of 2.98(1) Å. The CN ··· S2 distance is 3.37(1) Å. The view is down the *c* axis with the *b* axis horizontal.

[17]. In most of these structures, the nitrile nitrogen donor atom coordinates to both sulfur acceptor atoms of (another) dithiadiazolyl ring. In **8**, this donating ability is apparently incompatible with the steric demands of the *tert*-butyl groups. Instead an asymmetric arrangement is found, with a short contact of 2.98(1) Å between the nitrile nitrogen N3 and sulfur S1 on a neighbouring thiazyl ring, and a longer distance of 3.37(1) Å to S2. The latter corresponds more or less to the sum of the v.d. Waals radii of these elements. This link results in an infinite flat ribbon of molecules coordinated *via* the nitrile. As can be seen in Fig. 4, the *trans*-cofacial dimerization, along with the CN coordination, results in two ribbons running in opposite directions along the *b* direction of the crystal lattice. Between the dimeric $[CN_2S_2]_2$ units are double layers of the aryl ring. The resulting architecture provides a lamellar structure with alternating layers of the *tert*-butyl groups and aromatic nitrile/thiazyl ring layers parallel to the crystallographic {0 0 1} planes (Fig. 5). The crystal packing seems to be as much determined by the steric and lipophilic preferences of the *tert*-butyl groups as by the Lewis base interactions of the cyano groups. A similar effect was observed in the crystal structure of the bisdithiadiazolyl **7**, where the *tert*-butyl groups aggregate around fourfold rotation axes to form long lipophilic columns [16].

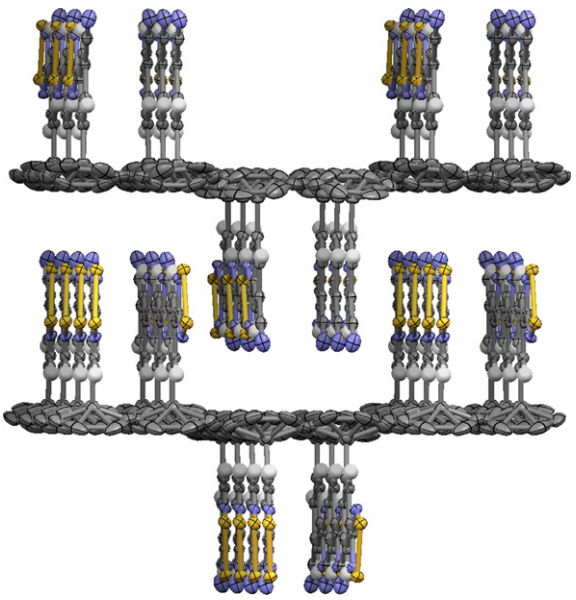


Fig. 5. Lipophilic and stacked-ring regions in the crystal structure of **8**. The view is down horizontally oriented *ab* planes of the orthorhombic lattice.

The specific structural motif of *layers* of lipophilic and heterocyclic regions in a thiazyl crystal structure is, to our knowledge, known elsewhere only in the case of adamantyl-CN_2S_2 [30]. In the reported crystal structure of this molecule, there are double layers of hydrocarbon groups separated by interleaved layers of thiazyl rings. The lipophilic preference of the adamantyl groups seems to drive the lattice geometry, and leads to rather unconventional intermolecular interactions between the polar thiazyl groups. This motif is thus highly reminiscent of that found in **8** (see Fig. 5), with the difference that in the latter structure, the heterocyclic and the substituted phenyl rings are interleaved.

A slightly different, but related, packing behaviour is observed in a DMBP bridged bisdithiadiazolyl (*vide supra*), in which the methyl-substituted biphenylenes form lipophilic zones parallel to the crystallographic $\{\bar{1}\,0\,0\}$ planes, and the CN_2S_2 rings form bilayers between these zones [29].

2.6. Crystal structure of 9

Radical **8** reacts with $[CpCr(CO)_3]_2$ to produce complex **9** (Scheme 3) [1]. The $CpCr(CO)_2$ group is coordinated *endo* to the thiazyl ring as in **3b**, unlike the *exo* orientation obtained in the solid-state structure of **3a** [1]. In the crystal structure, in contrast to the parent radical structure **8**, the dithiadiazolyl ring does not participate in any secondary contacts. Instead two molecules of **9** form centrosymmetric dimers *via* duplicate C≡N3 ··· H5–C contacts of 2.69(1) Å, consistent with $P\bar{1}$ space symmetry (Fig. 6). Given the dominance of nitrile-to-sulfur contacts in dithiadiazolyl structures mentioned above, it seems almost certain that the combined steric shielding of the *meta tert*-butyl and the $CpCr(CO)_2$ groups serves to isolate the thiazyl rings from each other.

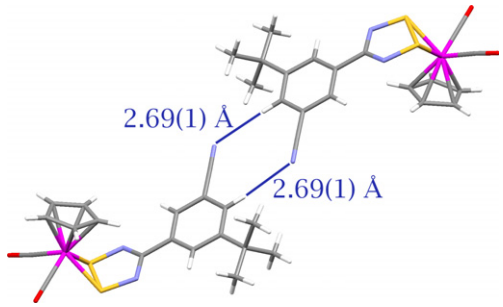


Fig. 6. Nitrile to aromatic C–H dimer motif in the crystal structure of **9**.

In other respects, the structure of **9** closely resembles that of **3a**,**b** [1].

The behaviour in this sterically congested complex may be compared with those observed in the crystal lattices of **3a** and **3b** [1]. The short intermolecular contacts in **3a** are displayed in Fig. 7. This complex is quite remarkable in that despite the large $CpCr(CO)_2$ groups, the dithiadiazolyl rings still manage to pack as side-by-side pairs. Such sideways interactions have been observed in numerous crystal structures of dithiadiazolyl radical dimers. For example, in **1** (X = Cl), S ··· N contacts of 3.130 and 3.207 Å were reported [27b], while in several of the cyano-substituted complexes mentioned above this motif also occurs, with S ··· N contacts ranging from 3.211 to 3.284 Å [17a,17b].

As mentioned previously, other substituents have been investigated as supramolecular synthons in dithiadiazolyls, in particular halogens. In the crystal structure of **1** (X = Cl) [27b], short, somewhat asymmetric (3.385 and 3.521 Å), contacts are observed between the Cl atom and both sulfur atoms of the heterocycle, although the interactions are not strong enough to induce sheet-structures as commonly observed for cyano complexes [17]. In the metal complex **3b** similar intermolecular contacts are found (Fig. 8). The interactions are to sulfur atoms on *two different* molecules, perhaps because the Cr coordination partly blocks access to the sulfur atoms, and their strength as indicated by distances is slightly weaker (3.473 and 3.549 Å). The interactions in **3b** lead to an infinite network connecting the complexes *via* $Cl^{\delta-} \cdots S^{\delta+}$ interactions.

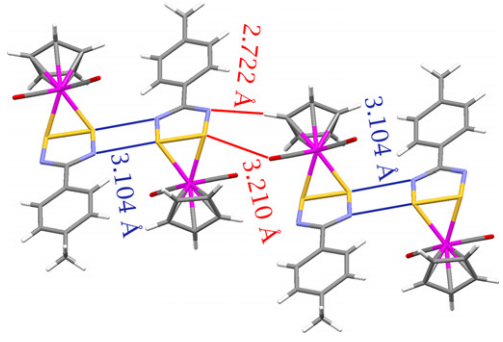


Fig. 7. Intermolecular contacts in the crystalline lattice of **3a**. Side-by-side dimerization of the complexed 1,2,3,5-dithiadiazole ring occurs through $N^{\delta-} \cdots S^{\delta+}$ interaction at 3.104 Å. Weaker van der Waals interactions link the dimeric pairs through CH ··· N (2.722 Å) and CO ··· S (3.210 Å) contacts.

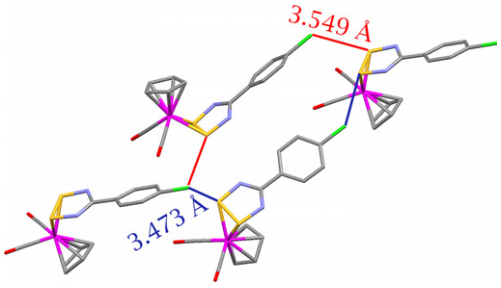


Fig. 8. Intermolecular contacts in the crystalline lattice of **3b**. The short contacts fall into two groups of 3.473 and 3.549 Å. These distances are similar to, but slightly longer than the 3.385 and 3.521 Å, observed in the crystal structure of the free dithiadiazolyl dimer [27b].

3. Conclusions

The bulky *tert*-butyl group does not hinder η^2-coordination to $CpCr(CO)_2$, and the structure of complex **9** is analogous to that of the less sterically-hindered analogues **3**. However, in the solid-state structure, in contrast to the free dithiadiazolyl **8**, complex **9** displays a crystal structure in which the orienting influence of the cyano group *towards the thiazyl ring* has been shut down. Only a C≡N ··· H–C interaction remains to form weakly associated centrosymmetric, isolated, pairs in the crystal lattice. By contrast, the less sterically congested ligands in **3a** and **3b** show supramolecular interactions in the crystalline lattices, which though weakened by electronic and steric changes as a result of complexation to $CpCr(CO)_2$, are not eliminated.

The most significant observation of this work, however, is that the potent thiophile $[CpCr(CO)_3]^{\bullet}$ reacts with 1,2,3,5-dithiadiazolyl radicals or their dimers without rupturing S–S bonds, even though the resulting "oxidative addition" products are known to dominate in the coordination compounds of thiazyl radicals. Investigations on the generality of this principle for the reactivity of organometallic radicals and unsaturated main-group ring compounds are ongoing in our laboratories.

4. Experimental

4.1. General methods

5-*tert*-Butylisophthalic acid, sulfur dichloride, lithium bis(trimethylsilyl)amide, *n*-butyllithium, thionyl chloride, chlorotrimethylsilane, and triphenylantimony were all obtained commercially (Aldrich). Sulfur dichloride was distilled before use. Lithium bis(trimethylsilyl)amide diethyl etherate [23a], 5-*tert*-butyl-1,3-dicyanobenzene [24] and 5-*tert*-butyl-1,3-bis-(1,2,3,5-dithiadiazolyl)benzene [16] were prepared as described previously. NMR spectra (250 or 300 MHz) were referenced to the solvent (^1H and ^{13}C) or to external H_3PO_4 (^{31}P). EPR spectra were recorded on a Bruker EMX 113 spectrometer operating in X band; temperature was adjusted and controlled by the Bruker VT accessory. All manipulations were conducted under exclusion of the atmosphere by either vacuum or a nitrogen blanket.

4.2. Synthesis of 5-tert-butyl-3-cyano-1-(1,2,3,5-dithiadiazolyl)benzene **8**

Solid 5-*tert*-butyl-1,3-dicyanobenzene (10.00 g, 54.3 mmol) and solid lithium bis(trimethylsilyl)amide diethyl etherate (13.06 g, 54.1 mmol) were slurried in 100 mL anhydrous diethyl ether for 2 h. ^{1}H NMR analysis of the supernatant displayed a single peak (δ −0.30 ppm referenced to the ether methyl peak at 1.12 ppm) characteristic of the lithiated amidine [23b]. Evaporation of volatiles left a white solid *N*-lithio-5-*tert*-butyl-3-cyano-1-(1,3-bistrimethylsilylcarboximidamide, which was taken up in 80 mL CH_3CN and reacted drop-wise with SCl_2 (11.4 mL, 179 mmol) with vigorous stirring, whereupon the solution was heated to reflux for 2 h. After cooling, orange dithiadiazolium chloride was filtered and dried *in vacuo*. The salt was suspended in 25 mL of CH_3CN and a solid-addition funnel containing Ph_3Sb (10.1 g, 28.7 mmol) was attached to the flask, the solvent deoxygenated 3× by freeze–thaw cycles, whereupon the Ph_3Sb was added. After stirring a while, the resulting slurry was heated to reflux for 2 h, and then cooled to −35 °C overnight. The precipitate was largely Ph_3SbCl_2 (11.5 g dry); the dark filtrate was left at RT for 2 d, and the black precipitate collected and dried. The powder is extremely oxygen sensitive until it is purified by sublimation in a three-zone tube furnace (24/45/120 °C) under dynamic vacuum, yielding black crystals of **8** (4.00 g, 28.2% yield based on nitrile). Analytical sample and crystals suitable for X-ray crystallography obtained on re-sublimation. IR, Raman: $\nu(C{\equiv}N) = 2229\ cm^{-1}$, EI-MS: *m/z* 262 ($[M]^+$, 100%), 247 ($[M-CH_3]^+$, 100%), 219 ($[M-4CO+1]^+$, 60%), 169 ($[C_{11}H_9N_2]^+$, 55%), 141 ($[C_{11}H_9]^+$, 95%), 78 ($[S_2N]^+$, 82%).

4.3. Electrochemistry

Voltammetry was performed in a previously described all-glass electrochemical cell under vacuum [27]. CH_3CN was used as solvent, containing 7.62×10^{-3} M **9** and 9.6×10^{-2} M [^{n}Bu$_4$N][PF$_6$] as electrolyte. Ferrocene was added at the end of the measurements as internal reference to 5.2×10^{-3} M concentration. After verifying the solvent/electrolyte background current, the analyte was added and CV (scan rates 0.1–1.0 V s^{-1}) and OSV were measured starting at the limit of detectability. No change was observed in the essential characteristics of the system up to the maximum concentration. Currents range from 1 to 600 μA from the lowest up to full concentration in OSV, and from ∼1 to 450 μA for the anodic peak of the 0/+1 redox couple in CV.

5. Supplementary material

CCDC 299596 contains the supplementary crystallographic data for **8**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council (Canada) and the National University of Singapore for financial support. T.L.R. acknowledges NSERC for a PGS-D scholarship and the Alberta Ingenuity Fund for a Doctoral Scholar award. The University of Lethbridge Travel Fund and the Faculty of Arts and Science helped to defray the costs of the delivery of the oral form of this paper. R.T.B. thanks Dr. J.-P. Majoral of LCC-Toulouse, France, for hospitality on a Sabbatical leave where this paper was written.

References

[1] H.F. Lau, V.W.L. Ng, L.L. Koh, G.K. Tan, L.Y. Goh, T.L. Roemmele, S.D. Seagrave, R.T. Boeré, Angew. Chem. 118 (2006) 4610;
Angew. Chem. Int. Ed. 45 (2006) 4498.
[2] C.Y. Ang, R.T. Boeré, L.Y. Goh, L.L. Koh, S.L. Juan, G.K. Tan, X. Yu, Chem. Commun. (2006) 4735, doi:10.1039/b610089a.
[3] (a) J. Van Droogenbroeck, C. Van Alsenoy, S.M. Aucott, J.D. Woollins, A.D. Hunter, F. Blockhuys, Organometallics 24 (2005) 1004;
(b) S.M. Aucott, P. Bhattacharyya, H.L. Milton, A.M.Z. Slawin, J.D. Woollins, New J. Chem. 27 (2003) 1466;
(c) S.M. Aucott, A.M.Z. Slawin, J.D. Woollins, Can. J. Chem. 80 (2002) 1481;
(d) W.-K. Wong, C. Sun, W.-Y. Wong, D.W.J. Kwong, W.-T. Wong, Eur. J. Inorg. Chem. (2000) 1045;
(e) A.J. Banister, I. May, J.M. Rawson, J.N.B. Smith, J. Organomet. Chem. 550 (1998) 241;
(f) T. Chivers, F. Edelmann, Polyhedron 5 (1986) 1661.
[4] (a) M. Jennings, K.E. Preuss, J. Wu, Chem. Commun. (2006) 341;
(b) N.R.G. Hearns, K.E. Preuss, J.F. Richardson, S. Bin-Salamon, J. Am. Chem. Soc. 126 (2004) 9942.
[5] (a) L.Y. Goh, Coord. Chem. Rev. 185–186 (1999) 257, and references therein;
(b) L.Y. Goh, W. Chen, R.C.S. Wong, Chem. Commun. (1999) 1481;
(c) L.Y. Goh, W. Chen, R.C.S. Wong, Organometallics 18 (1999) 306.
[6] Z. Weng, L.Y. Goh, Acc. Chem. Res. 37 (2004) 187, and references therein.
[7] (a) R.D. Adams, D.E. Collins, F.A. Cotton, J. Am. Chem. Soc. 96 (1974) 749;
(b) T. Madach, H. Vahrenkamp, Z. Naturforsch. B 33b (1978) 1301;
(c) L.Y. Goh, M.J. D'Aniello Jr., S. Slater, E.L. Muetterties, I. Tavanaiepour, M.I. Chang, M.F. Fredrich, V.W. Daz, Inorg. Chem. 18 (1979) 192–197;
(d) S.J. McLain, J. Am. Chem. Soc. 110 (1988) 643;
(e) M.C. Baird, Chem. Rev. 88 (1988) 1217;
(f) L.Y. Goh, Y.Y. Lim, J. Organomet. Chem. 402 (1991) 209;
(g) D.C. Woska, Y. Ni, B.B. Wayland, Inorg. Chem. 38 (1999) 4135.
[8] L.Y. Goh, Z. Weng, W.K. Leong, J.J. Vittal, J. Am. Chem. Soc. 124 (2002) 8804.
[9] (a) L.Y. Goh, Z. Weng, W.K. Leong, P.H. Leung, Angew. Chem. Int. Ed. 40 (2001) 3236;
(b) L.Y. Goh, Z. Weng, W.K. Leong, P.H. Leung, Organometallics 21 (2002) 4398;
(c) L.Y. Goh, Z. Weng, T.S.A. Hor, W.K. Leong, Organometallics 21 (2002) 4408.

[10] L.Y. Goh, Z. Weng, W.K. Leong, J.J. Vittal, I. Haiduc, Organometallics 21 (2002) 5287.
[11] (a) L.Y. Goh, M.S. Tay, T.C.W. Mak, R.-J. Wang, Organometallics 11 (1992) 1711;
(b) L.Y. Goh, M.S. Tay, Y.Y. Lim, T.C.W. Mak, Z.-Y. Zhou, J. Chem. Soc., Dalton Trans. (1992) 1239;
(c) L.Y. Goh, M.S. Tay, W. Chen, Organometallics 13 (1994) 1813.
[12] L.Y. Goh, W.K. Leong, P.-H. Leung, Z. Weng, I. Haiduc, J. Organomet. Chem. 607 (2000) 64.
[13] L.Y. Goh, Z. Weng, W.K. Leong, I. Haiduc, K.M. Lo, R.C.S. Wong, J. Organomet. Chem. 631 (2001) 67.
[14] (a) J.M. Rawson, A. Alberola, A. Whalley, J. Mater. Chem. 16 (2006) 2560;
(b) J.M. Rawson, J. Luzon, F. Palacio, Coord. Chem. Rev. 249 (2005) 2631.
[15] A. Alberola, C.S. Clarke, D.A. Haynes, S.I. Pascu, J.M. Rawson, Chem. Commun. (2005) 4726.
[16] R.A. Beekman, R.T. Boeré, K.H. Moock, M. Parvez, Can. J. Chem. 76 (1998) 85.
[17] (a) A.W. Cordes, C.M. Chamchoumis, R.G. Hicks, R.T. Oakley, K.M. Young, R.C. Haddon, Can. J. Chem. 70 (1992) 919;
(b) A.W. Cordes, R.C. Haddon, R.G. Hicks, R.T. Oakley, T.T.M. Palstra, Inorg. Chem. 31 (1992) 1802;
(c) G. Antorrena, S. Brownridge, T.S. Cameron, F. Palacio, S. Parsons, J. Passmore, L.K. Thompson, F. Zarlaida, Can. J. Chem. 80 (2002) 1568;
(d) A.W. Cordes, R.C. Haddon, R.G. Hicks, D.K. Kennepohl, R.T. Oakley, T.T.M. Palstra, L.F. Schneemeyer, S.R. Scott, J.V. Waszczak, Chem. Mater. 5 (1993) 820;
(e) A.J. Banister, N. Bricklebank, W. Clegg, M.R.J. Elsegood, C.I. Gregory, I. Lavender, J.M. Rawson, B.K. Tanner, Chem. Commun. (1995) 679;
(f) A.J. Banister, N. Bricklebank, I. Lavender, J.M. Rawson, C.I. Gregory, B.K. Tanner, W. Clegg, M.R.J. Elsegood, F. Palacio, Angew. Chem. Int. Ed. 35 (1996) 2533.
[18] (a) L. Beer, A.W. Cordes, D.J.T. Myles, R.T. Oakley, N.J. Taylor, Cryst. Eng. Commun. (2000) 20;
(b) A.M.T. Bell, J.N.B. Smith, J.P. Attfield, J.M. Rawson, K. Shankland, W.I.F. David, New J. Chem. (Nouv. J. Chim.) 23 (1999) 565;
(c) A.J. Banister, A.S. Batsanov, O.G. Dawe, P.L. Herbertson, J.A.K. Howard, S. Lynn, I. May, J.N.B. Smith, J.M. Rawson, T.E. Rogers, B.K. Tanner, G. Antorrena, F. Palacio, J. Chem. Soc., Dalton Trans. (1997) 2539;
(d) A.J. Banister, A.S. Batsanov, O.G. Dawe, P.L. Herbertson, J.A.K. Howard, S. Lynn, I. May, J.N.B. Smith, J.M. Rawson, T.E. Rogers, B.K. Tanner, G. Antorrena, F. Palacio, J. Chem. Soc., Dalton Trans. (1997) 2539.
[19] T. Amano, T. Amano, in: Proceedings of the 44th Symposium on Molecular Spectroscopy, June 12–16, 1989, Colombus, OH.
[20] P. Hassanzadeh, L. Andrews, J. Phys. Chem. 114 (1991) 83.
[21] Y. Yamaguchi, Y. Xie, R.S. Grev, H.F. Schaefer III, J. Chem. Phys. 92 (1990) 3683.
[22] M.T. Nguyen, R. Flamming, N. Goldberg, H. Schwarz, Chem. Phys. Lett. 236 (1995) 201.
[23] (a) R.T. Boeré, R.G. Hicks, R.T. Oakley, Inorg. Synth. 21 (1997) 94;
(b) R.T. Boeré, R.T. Oakley, R.W. Reed, J. Organomet. Chem. 331 (1987) 161.
[24] M.A. McCall, J.R. Caldwell, H.G. Moore, H.M. Beard, J. Macromol. Sci. Chem. A3 (1969) 911.
[25] WINSIM 2002: D.R. Duling, J. Magn. Res., Ser. B 104 (1994) 105.
[26] F.L. Lee, K.F. Preston, A.J. Williams, L.H. Sutcliffe, A.J. Banister, S.T. Wait, Magn. Reson. Chem. 27 (1989) 1161.
[27] (a) R.T. Boeré, T.L. Roemmele, Coord. Chem. Rev. 210 (2000) 369;
(b) R.T. Boeré, K.H. Moock, M. Parvez, Z. Anorg. Allg. Chem. 620 (1994) 1589;
(c) R.T. Boeré, K.H. Moock, J. Am. Chem. Soc. 117 (1995) 4755;
(d) K.H. Moock, M.H. Rock, J. Chem. Soc., Dalton Trans. (1993) 2459.
[28] N. Bricklebank, S. Hargreaves, S.E. Spey, Polyhedron 19 (2000) 1163.
[29] T.M. Barclay, A.W. Cordes, N.A. George, R.C. Haddon, M.E. Itkis, R.T. Oakley, Chem. Commun. (1999) 2269.
[30] J.N. Bridson, S.B. Copp, M.J. Schriver, S. Zhu, M.J. Zaworotko, Can. J. Chem. 72 (1994) 1143.