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Mixed-sandwich Cp*Cr Complexes Containing Poly(methimazoly)borates (Cp* = C₅Me₅) – Syntheses, Structural and Electrochemical Studies

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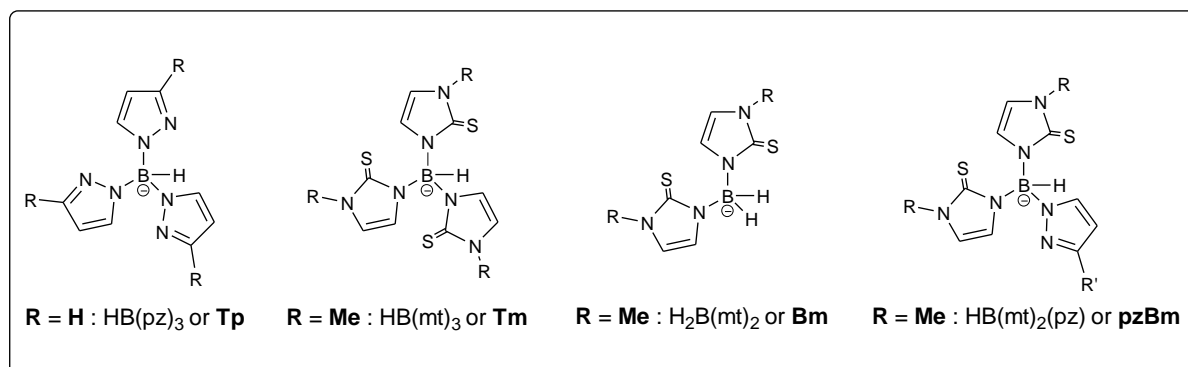
ABSTRACT

Reaction of the scorpionate salts, K[HB(mt)₃], Na[H₂B(mt)₂] and Li[HB(mt)₂(pz)] with [Cp*CrBr₂]₂ (**1**), gave the 15-electron Cr(III) complexes, [Cp*Cr(κ³-S,S',S'') {HB(mt)₃}]Br (**2**), [Cp*Cr(κ²-S,S') {H₂B(mt)₂}Br] (**3**) and [Cp*Cr(κ²-S,S') {HB(mt)₂(pz)}Br] (**4**) in moderate to high yields. These are the first examples of mixed sandwich chromium(III) complexes containing the poly(methimazoly)borate ligands. The tridentate coordination of the monoanionic ligands [H₂B(mt)₂] in **3** and [HB(mt)₂(pz)] in **4** can be effected by using a silver salt to remove the Br coligand, thus yielding the complexes [Cp*Cr(κ³-H,S,S') {H₂B(mt)₂}]PF₆ (**6**) and [Cp*Cr(κ³-N,S,S') {HB(mt)₂(pz)}]PF₆ (**7**). It was also found that in the presence of acetonitrile, the reaction of **3** with AgPF₆ afforded [Cp*Cr(κ²-S,S') {H₂B(mt)₂}(NCMe)]PF₆ (**5**). The coordination geometries of all the complexes have been determined by X-ray diffraction analyses. Cyclic voltammetric studies of complexes **2**, **4** and **7** showed that the oxidation and reduction processes are chemically reversible, and that the reduced and oxidized states of complexes **3**, **5** and **6** are very short-lived.

Introduction

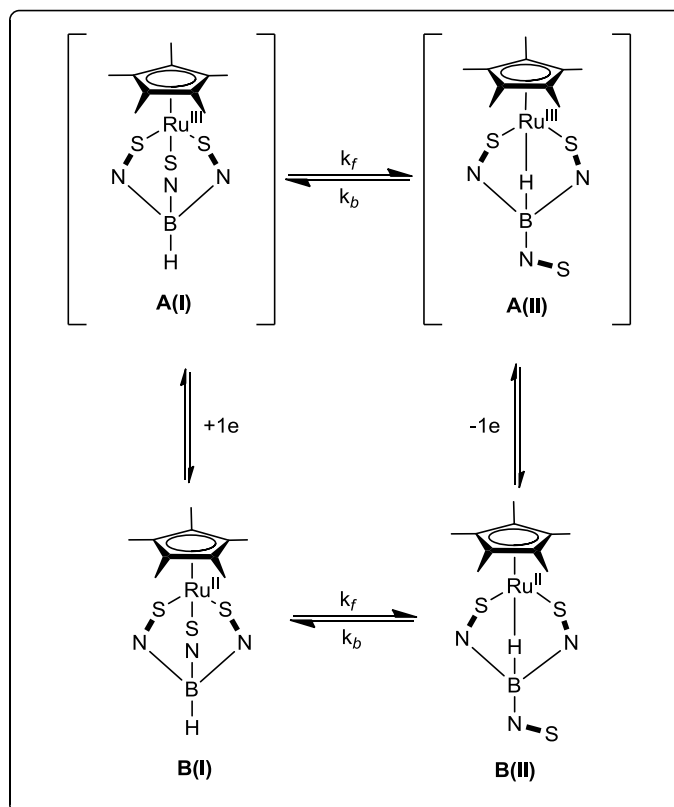
During the last decade, the coordination chemistry of the tris(methimazolyl)borate anion, $(\text{HB}(\text{mt}^{\text{R}})_3)^-$ (also abbreviated as Tm^{R}) ($\text{mt} = \text{N-methyl-2-mercaptoimidazol-1-yl}$),¹ the S_3 -donor soft analogue of Trofimenko's versatile N_3 -donor poly(pyrazolyl)borates, $\text{HB}(\text{pz})_3^-$ (also abbreviated as Tp^{R}),² and the allied ligand $\text{H}_2\text{B}(\text{mt}^{\text{R}})_2$ (also abbreviated as Bm^{R}),³ including the hybrid mt_2pz (pzBm^{R}) hydroborate ligand (Chart 1) has been intensely investigated in several laboratories. We now find in the literature, examples of binary compounds of types $\text{M}(\text{Tm})_n$ ($n = 1, 2$) and $\text{M}(\text{Bm})_n$ ($n = 2, 3$) and ternary compounds $[\text{M}(\text{Tm})\text{X}]$ [$\text{X} = \text{Cl}, \text{Br}, \text{I}$] of first row transition metals of Groups 4, 8-10, of Groups 11 and 12 metals and of the main group elements Tl, Sn, Pb, As and Bi.⁴ Interest in compounds of Group 12 metals containing the hybrid mt_2pz ligand has been stimulated by the search for biomimetic models of the zinc enzyme liver alcohol dehydrogenase (LADH),⁵ which contains Zn in an NS_2 coordination to one histidine and two cysteine residues. The compound $[\text{Mo}(\text{TmMe})(\text{O})_2\text{Cl}]$ has found application as an alternative functional model of the metalloenzyme sulfite oxidase.^{5g} The relevance of such compounds to enzyme modeling and biomedical applications has been thrice reviewed in 2009.⁶ Further interest stems from the emergence of potential applications in catalysis and surface science,⁷ the latter being recently encountered for complexes of the Group 1B metals (Cu, Ag and Au).⁸

Chart 1. Sulfur-containing analogues of Trofimenko's polypyrazolylborate ligand, $\text{HB}(\text{pz})_3$.



The tridentate Tm or Bm acts as a capping ligand, normally in $\kappa^3\text{-S,S',S''}$ coordination, together with ancillary CO ligands, in the coordination sphere of the Group 6 metals, Mo and W,⁹ and the Group 7 metals, Mn, Tc and Re;¹⁰ those of Tc are of pharmaceutical interest. Non-carbonyl complexes of the mixed sandwich-type were first reported by Bailey for Ru(II), viz., $[(p\text{-cymene})\text{Ru}^{\text{II}}(\text{Tm})]\text{Cl}$ and $[\text{CpRu}^{\text{II}}(\text{Tm})]$.¹¹ We subsequently isolated the

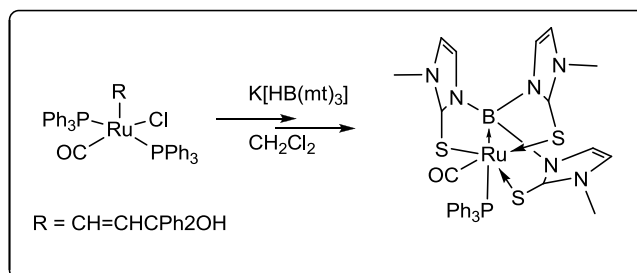
Cp*/(HMB)Ru-complexes with poly(methimazolyl)borates and have reported this series of compounds together with their electrochemical properties.¹² Notably, we were able to establish a facile $\kappa^3\text{-S,S',S''}$ and $\kappa^3\text{-H,S,S'}$ coordination exchange, detectable by cyclic voltammetry for the Cp* analogues, $[\text{Cp}^*\text{Ru}^{\text{II}}(\text{Tm})]$ and $[\text{Cp}^*\text{Ru}^{\text{III}}(\text{Tm})]\text{Cl}$ (Scheme 1).^{12a}



Scheme 1

These $\kappa^3\text{-S,S',S''}$ and $\kappa^3\text{-H,S,S'}$ forms had been indicated in the proton NMR spectrum of Bailey's complex $[\text{CpRu}^{\text{II}}(\text{Tm})]$.¹¹ Hill had obtained solid state structural evidence for $\kappa^3\text{-H,S,S'}$ coordination in $(\text{Tm})\text{RuH}(\text{CO})(\text{PPh}_3)$,^{13a} and Rabinovich had reported the predominance of $\kappa^3\text{-H,S,S'}$ over $\kappa^3\text{-S,S',S''}$ (for Tm) or $\kappa^2\text{-S,S'}$ (for Bm) in $(\text{dppe})\text{Ni}$ complexes.^{13b} We note also the current frequent occurrence of $\kappa^3\text{-H,S,S'}$ coordination mode of these soft scorpionate ligands, e.g., in two other ruthenium compounds, viz., $[\text{RuCl}(\text{DMSO})_2\{\kappa^3\text{-H,S,S',S''-HB}(\text{mt})_3\}]$ and $[\text{RuH}(\text{PPh}_3)_2\{\kappa^3\text{-H,S,S',S''-H}_2\text{B}(\text{mt})_2\}]$,^{13c} in the complexes of Mo and W,^{9f} and in the essentially linear Ta-H-B complex $(\text{Cp}^*)\text{Ta}(\text{IV})\text{Cl}_2\{\text{H}_2\text{B}(\text{mt})_2\}$.^{13d}

Interestingly, the chemistry of the poly(methimazolyl)borate complexes differs from that of the poly(pyrazolyl)borate analogues in the ready occurrence of B-H bond activation. Hill and coworkers isolated the first structurally characterized metallaboratrane, $[\text{Ru}\{\text{B}(\text{mt})_3\}(\text{CO})(\text{PPh}_3)]$, which exhibited a $\kappa^4\text{-B,S,S',S''}$ coordination, from the reaction of the complex $[\text{Ru}(\text{CH}=\text{CHCPh}_2\text{OH})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ with $\text{Na}[\text{HB}(\text{mt})_3]$ (Scheme 2).¹⁴

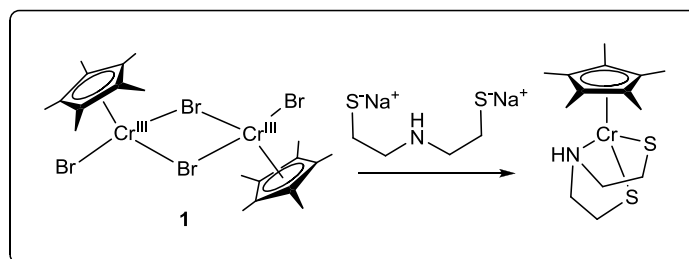


Scheme 2

Since then, Hill's group has characterised many such compounds of the Groups 8-10 metals, including those of Ru and Os,¹⁵ Pt,¹⁶ Ir(I),¹⁷ Rh(I),^{17b,18} and Ta,¹⁹ while Parkin's group has reported metallaboratranes of Ir and Rh,^{20a} Fe,^{20b} and Pd,^{20c} and Rabinovitch's the cobaltaboratrane.²¹ There is also a very recent report of static boratrane derivatives of fluxional rhodium scorpionate complexes.²² The B-H activation phenomenon has also been reported recently in a series of iridium boratranes, in which the metal centre is selectively bound to the two sulfur atoms of an *S2N* heteroscorpionate, $\text{H}[\text{B}(\text{mt})_2(\text{pz}^{\text{R}})]$, while the *N*-donor ring is pendant.²³

The above examples show the poly(methimazolyl)borate ligands coordinated to the "softer" metals (Mo and W) in Group 6, and metals in Groups 7-12. For "harder" metals, Hill and coworkers have synthesized for the Group 5 metals, the Ta(III) complex $[\text{Ta}(\eta^2\text{-RC}\equiv\text{CR})\text{Cl}_2(\text{HB}(\text{mt})_3)]$,^{19a} and were successful in the isolation of niobium(V) and tantalum(V) tris(methimazolyl)borate complexes by using appropriate co-ligands to tune the electrophilic nature of the Nb^{V} and Ta^{V} centers.^{19b} Notwithstanding, examples of complexes of poly(methimazolyl)borate with *hard* metal centers are scarce. Though there are a few cases of such compounds of Mo and W,⁹ there is only one report of methimidazolyl coordination complexes of Cr(III) in the literature.²⁴ On the other hand, Tp complexes of Cr(II) and Cr(III) are quite numerous.²⁵

Our successful ligation of a dithiolato ligand to Cp*Cr(III) as illustrated in Scheme 3,²⁶ with [Cp*CrBr₂]₂(**1**) as the metal substrate, prompted us to investigate similar reactions with the poly(methimazolyl)borate salts, viz., [HB(mt)₃]⁻, [H₂B(mt)₂]⁻ and [HB(mt)₂(pz)]⁻. The resultant mixed sandwich complexes of Cp*Cr are described in this paper.



Scheme 3

Experimental

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 ACF 300 or AMX 500 spectrometer, and the chemical shifts were referenced to residual solvent resonances in the respective deuterio solvents. The spectral window used for all ¹H NMR spectra of the Cr(III) complexes was from δ 30 to -60 ppm. 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 acquired on a Finnigan Mat 95XL-T or a Finnigan Mat LCQ spectrometer. Elemental analyses were carried out by the in-house microanalytical laboratory. The compounds [Cp*CrBr₂]₂ (**1**),²⁷ K[HB(mt)₃],²⁸ and Na[H₂B(mt)₂],²⁹ were synthesized as reported in the literature. Methimazole and pyrazole were purchased from Sigma Aldrich and used without further purification. Solvents were dried over sodium benzophenone ketyl or calcium hydride and distilled under argon before use. Celite (Fluka AG) and silica gel (Merck Kieselgel 60, 230-400 mesh) were dried at 140 °C overnight before use.

Cyclic voltammetry studies. Voltammetric experiments were conducted with a computer controlled Eco Chemie Autolab III potentiostat using planar 1 mm diameter Pt and glassy carbon (GC) working electrodes in conjunction with a Pt auxiliary electrode and an Ag wire reference electrode connected to the test solution *via* a salt bridge containing 0.5 M Bu₄NPF₆ in CH₃CN. Accurate potentials were obtained using ferrocene as an internal standard. The electrochemical cell was thermostated at 233 and 293 K using an Eyela PSL-1000 variable temperature cooling bath. EPR spectra were recorded on a Bruker ESP 300e spectrometer

with liquid He cooling. Cyclic voltammograms were recorded at a scan rate of 100 mV s⁻¹ at a 1 mm planar Pt electrode with 0.25 M Bu₄NPF₆ of solutions containing 2-7. The $E^{\text{r}}_{1/2}$ -value [that approximates the formal potential (E^0)] was calculated from CV data under conditions where the ratio of the oxidative (i_{p}^{ox}) to reductive ($i_{\text{p}}^{\text{red}}$) peak currents were equal to unity and using the relationship

$$E^{\text{r}}_{1/2} = (E_{\text{p}}^{\text{ox}} + E_{\text{p}}^{\text{red}})/2 \quad (\text{i})$$

where E_{p}^{ox} and $E_{\text{p}}^{\text{red}}$ are the anodic and cathodic peak potentials respectively.³⁰

X-Ray structure determination. The crystals were mounted on glass fibers. X-ray data were collected on a Bruker APEX AXS diffractometer, equipped with a CCD detector, using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The program SMART was used for collecting frames of data, indexing reflection and determination of lattice parameter,³¹ SAINT for integration of the intensity of reflections, scaling, and for correction of Lorentz and polarization effects,³¹ SADABS for absorption correction,³² and SHELXTL for space group and structure determination, and least-squares refinements on F².³³ The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

There were two crystallographically distinct molecules of **3** in the unit cell. One of them was located on a mirror plane, with disorder of one of the methyl groups of the Cp* about the mirror. The other was modeled as disordered about a mirror which included the Cr, Br and one of the S atoms. There was also a disordered ether solvate present, with occupancy of 0.25; the disorder was about a mirror plane passing through the O atom, and was modeled with two alternative sites for the ethyl groups. The [PF₆]⁻ counterions in both **5** and **6** were disordered. In **5**, this was modeled with two sites for each F atom, with occupancies fixed at 0.8 and 0.2. In **6**, there were two sites of equal occupancies for the [PF₆]⁻ ion; one was on a 2-fold axis, while the other was on a mirror. Both sites were disordered, which were each modeled with two orientations of equal occupancies. Appropriate restraints were placed on all disordered parts.

The crystal data collection and processing parameters are given in Table 1.

Synthesis of lithium hydrobis(methimazolyl)(pyrazolyl)borate. A modified literature method was adopted³⁴: A mixture of 2-mercapto-1-methylimidazole (505 mg, 4.43 mmol) and LiBH₄ (39 mg, 1.77 mmol) in toluene:THF (4:1, 20 mL) was heated at 60 °C overnight. The solvents were then removed *in vacuo*, giving a white solid which was washed with Et₂O (5 x 3 mL), followed by DCM:hex (1:2, 3 x 6 mL) to remove excess 2-mercapto-1-

methylimidazole. The resultant white solid, Li[H₂B(mt)₂] (310 mg, 1.26 mmol) and pyrazole (100 mg, 1.47 mmol) in toluene (20 mL) were heated at 105 °C for 48 h. After cooling to RT, the white precipitate was isolated by filtration and washed with toluene (5 x 4 mL), followed by Et₂O (3 x 2 mL), THF:Et₂O (1:5, 3 x 2 mL) and DCM (5 x 2 mL). The residue was washed with THF:Et₂O (4:1, 2 x 10 mL) and the colourless extract was evacuated to dryness to give a white solid, Li[HB(mt)₂(pz)] (330 mg, 1.06 mmol, 60% yield).

Data for Li[HB(mt)₂(pz)]: ¹H NMR (*d*₆-DMSO): δ 7.46 (d, 1H, J=2.1Hz), 7.33 (d, 1H, J=0.9Hz), 6.78 (d, 1H, J=2.1Hz), 6.20 (d, 1H, J=2.2Hz), 6.00 (t, 1H, J=1.7Hz), 3.74 (s, 6H). [Lit. values³³: δ 7.44 (d, 1H, J=2Hz), 7.34 (d, 1H, J=2 Hz), 6.78 (d, 2H, J=2 Hz), 6.18 (d, 2H, J=2 Hz), 6.00 (t, 1H, J=2 Hz), 3.74 (s, 6H)]

Reactions of [Cp*CrBr₂]₂ (1)

(a) *with K[HB(mt)₃]*. To a blue-green solution of **1** (70 mg, 0.10 mmol) in THF:MeOH (4:1, 10 mL) was added K[HB(mt)₃] (80 mg, 0.20 mmol). The mixture was stirred for 18 h, resulting in a suspension of a white precipitate of KCl in a deep blue supernatant. The suspension was filtered through celite and washed with Et₂O (5 x 2 mL). The blue filtrate was evacuated to dryness and recrystallised from MeOH/ether at -30 °C. Multiple recrystallisations gave a blue solid of [Cp*Cr{HB(mt)₃}]Br (**2**) (70 mg, 0.11 mmol, 57% yield). Diffraction-quality single crystals were obtained as blue plates by slow diffusion of ether into a acetonitrile solution after 1 week at -30 °C. Anal. Found: C, 42.3; H, 4.9; N, 13.4; S, 15.4%. Calc. for C₂₂H₃₁BBrCrN₆S₃: C, 42.7; H, 5.1; N, 13.6; S, 15.6%. IR (KBr, cm⁻¹): ν(B-H) 2443wbr, ν(others) 3111w, 3067w, 2974w, 2911w, 2859w, 1557w, 1466m, 1375m, 1209s, 1155w, 1088w, 1018w, 748mbr, 687w, 523w. FAB⁺-MS: *m/z* 538 [M⁺]; 300 [M⁺-(C₄H₅N₂S)₂H]; FAB⁻-MS: *m/z* 81 [Br⁻]. ¹H NMR (δ, CD₃CN): -16.4 (s, vbr, *ν*_{1/2} ca. 1000 Hz)

(b) *with Na[H₂B(mt)₂]*. To a blue-green solution of **1** (69 mg, 0.10 mmol) in THF (10 mL) was added Na[H₂B(mt)₂] (54 mg, 0.20 mmol). The mixture was stirred for 18 h, resulting in a suspension of a white precipitate of NaBr in a bright blue supernatant. The suspension was evacuated to dryness and the resultant mixture was extracted with toluene (5 x 3 mL). The blue extract was filtered through a thin disc of celite, and the blue filtrate was evaporated to dryness to give a blue microcrystalline solid of Cp*Cr[H₂B(mt)₂]Br (**3**) (95 mg, 0.19 mmol, 94% yield). Diffraction-quality single crystals were obtained as blue blocks by slow diffusion of ether into a acetonitrile solution after a week at -30 °C. Anal. Found: C, 42.8; H, 5.5; N, 11.1; S, 12.2%. Calc. for C₁₈H₂₇B₁Br₁Cr₁N₄S₂: C, 42.7; H, 5.4; N, 11.1; S,

12.7 %. IR (KBr, cm^{-1}): $\nu(\text{B-H})$ 2486w; $\nu(\text{others})$ 3121w, 3073w, 2914w, 2860w, 1693mbr, 1516mbr, 1188w, 1125w, 1020mbr, 808m, 729m, 684m, 569w. ESI⁺-MS: m/z 426 [$\text{M}^+ - \text{Br}$, $\text{M}^+ = \text{C}_5\text{Me}_5\text{Cr}(\text{Br})\{(\text{C}_4\text{H}_5\text{N}_2\text{S})_2\text{BH}_2\}$]. FAB⁺-MS: m/z 505 [M^+], 426 [$\text{M}^+ - \text{Br}$], 300.1 [$\text{M}^+ - \text{Br} - \text{HB}(\text{mt})_2$]. ¹H NMR (δ , CD_3CN): -58.0 (s, vbr, $\nu_{1/2}$ ca. 830 Hz)

(c) *with Li[HB(mt)₂(pz)]*. To a blue-green solution of **1** (69 mg, 0.10 mmol) in THF (10 mL) was added Li[HB(mt)₂(pz)] (62 mg, 0.20 mmol). The mixture was stirred for 18 h, resulting in a suspension of a white precipitate of LiBr in a bright blue supernatant. The suspension was evacuated to dryness and extracted with DCM (5 x 2 mL). The blue extract was evacuated to dryness and recrystallised in THF/ether at -30 °C. Multiple recrystallisations gave a blue pure solid of Cp*Cr[HB(mt)₂(pz)]Br (**4**) (70 mg, 0.12 mmol, 61 % yield). Diffraction-quality single crystals were obtained as blue plates by slow diffusion of ether into a acetonitrile solution after 1 week at -30 °C. Anal. Found: C, 43.7; H, 5.1; N, 14.0; S, 11.1 %. Calc. for C₂₁H₂₉BBrcrN₆S₂: C, 44.1; H, 5.1; N, 13.4; S, 11.2 %. IR (KBr, cm^{-1}): $\nu(\text{B-H})$ 2542w and 2506w; $\nu(\text{others})$ 3122m, 3090w, 2974wsh, 2949w, 2910m, 2856w, 1693mbr, 1552m, 1466s, 1414m, 1377s, 1329m, 1296s, 1196vs, 1117s, 1090s, 1036m, 956w, 768s, 735m, 621w. ESI⁺-MS: m/z 574 [M^+ , C₅Me₅CrBr{(C₄H₅N₂S)₂(C₃H₃N₂)BH}]; 492 [$\text{M}^+ - \text{Br}$]. ¹H NMR (δ , CD_3CN): No signal observed in the spectral window.

Reactions of Cp*Cr[H₂B(mt)₂]Br (**3**) with AgPF₆.

(a) *In MeCN*: To a blue solution of **3** (52 mg, 0.10 mmol) in MeCN (10 mL) was added AgPF₆ (30 mg, 0.12 mmol). The mixture was stirred at RT for 6 h in the dark to give a dark blue suspension. The resultant suspension was filtered through a thin disc of celite on a glass frit to remove a white solid of AgBr and the dark blue filtrate was evacuated to dryness. Multiple recrystallisations in MeCN/Et₂O at -30 °C yielded more AgBr, which was removed by filtration. The purplish blue mother liquor was concentrated and dark blue needles of [Cp*Cr{H₂B(mt)₂}(NCMe)]PF₆ (**5**) (39 mg, 0.06 mmol, 64 % yield) was obtained after recrystallisation from MeCN/Et₂O at -30 °C. Diffraction-quality single crystals were obtained as dark blocks by slow diffusion of ether into a acetonitrile solution after 1 week at -30 °C. Anal. Found: C, 39.1; H, 5.0; N, 11.3; S, 10.9%. Calc. for C₂₀H₃₀BCrF₆N₅PS₂: C, 39.2; H, 4.9; N, 11.4; S, 10.5%. IR (KBr, cm^{-1}): $\nu(\text{B-H})$ 2491m, 2397m, 2360m, 2341m, 2294w; $\nu(\text{C}\equiv\text{N})$ 2249w; $\nu(\text{P-F})$ 845. ESI⁺-MS: m/z 467 [M^+ , C₅Me₅Cr(NCMe){(C₄H₅N₂S)₂BH₂}; 426 [$\text{M}^+ - \text{MeCN}$]; ESI⁻-MS: m/z 145 [PF₆⁻]. ¹H NMR (δ , CD_3CN): -58.8 (s, vbr, $\nu_{1/2}$ ca. 1060 Hz), -75.1 (s, vbr, $\nu_{1/2}$ ca. 1000 Hz)

(b) *In toluene:* To a blue solution of **3** (38 mg, 0.08 mmol) in toluene (15 mL) was added AgPF₆ (25 mg, 0.10 mmol). The mixture was stirred at RT for 4 h in the dark to give a greenish blue suspension. Filtration gave a blue filtrate of unreacted **3** and a dark green solid. This was extracted with DCM (3 x 2 mL) leaving behind the AgBr byproduct. A green solid of [Cp*Cr{H₂B(mt)₂}]PF₆ (**6**) (25 mg, 0.04 mmol, 55% yield) was obtained from the extract and was recrystallised in DCM/Et₂O at -30 °C. Diffraction-quality single crystals were obtained as green blocks by slow diffusion of ether into a dichloroethane solution after 1 week at -30 °C. Owing to the highly air-sensitive nature of **6**, we were unable to obtain satisfactory elemental analyses. IR (KBr, cm⁻¹): ν(B-H) 2491m, 2397m, 2360m, 2341m, 2294w, 2249w; ν(P-F) 845. ESI⁺-MS: *m/z* 426 [M⁺, C₅Me₅Cr{(C₄H₅N₂S)₂BH₂}]. ESI-MS: *m/z* 145 [PF₆⁻]. HR ESI⁺-MS: *m/z* 426.1182 (found); 426.1170 (calc.). ¹H NMR (δ, CD₂Cl₂): No signal was observed in the spectral window.

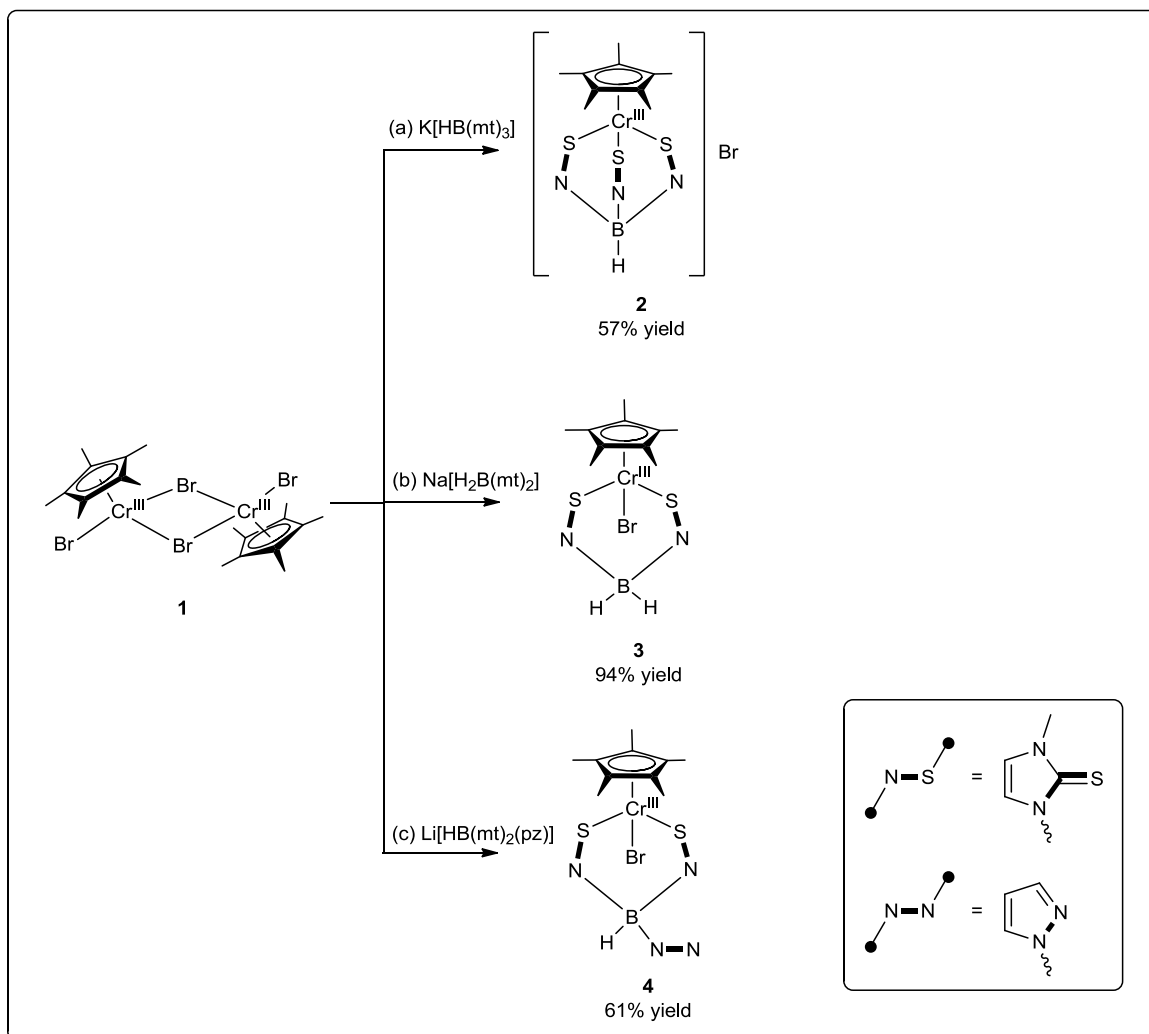
Reactions of Cp*Cr[HB(mt)₂(pz)]Br (**4**) with AgPF₆.

To a blue solution of **4** (58 mg, 0.04 mmol) in MeCN (*ca.* 10 mL) was added AgPF₆ (14 mg, 0.06 mmol). The mixture was stirred at RT for 6 h in the dark to give a purplish blue suspension. This suspension was evacuated to dryness and the resulting solid was extracted with DCM (4 x 2 mL). The purplish blue extract was evacuated to dryness and recrystallised in MeCN/Et₂O at -30 °C, removing a white solid of AgBr, followed by concentration of the purplish blue mother liquor, finally yielding dark blue needles of [Cp*Cr(HB(mt)₂(pz))]PF₆ (**7**) (18 mg, 0.03 mmol, 71 % yield). Diffraction-quality single crystals were obtained as blue blocks by slow diffusion of ether into an acetonitrile solution after 1 week at -30 °C. Anal. Found: C, 39.6; H, 4.8; N, 14.1; S, 9.7 %. Calc. for C₂₁H₂₉BCrF₆N₆PS₂·0.4 CH₃CN; C, 40.1; H, 4.7; N, 13.7; S, 9.8 %. IR (KBr, cm⁻¹): ν(B-H) 2486wm, 2374m, 2255w; ν(P-F) 845. ESI⁺-MS: *m/z* 492 [M⁺, C₅Me₅Cr{(C₄H₅N₂S)₂(C₃H₃N₂)BH}]]; ESI-MS: *m/z* 145 [PF₆⁻]. ¹H NMR (δ, CD₃CN): -30.7 (s, vbr, *ν*_{1/2} *ca.* 600 Hz), -64.5 (s, vbr, *ν*_{1/2} *ca.* 980 Hz).

Results and Discussion

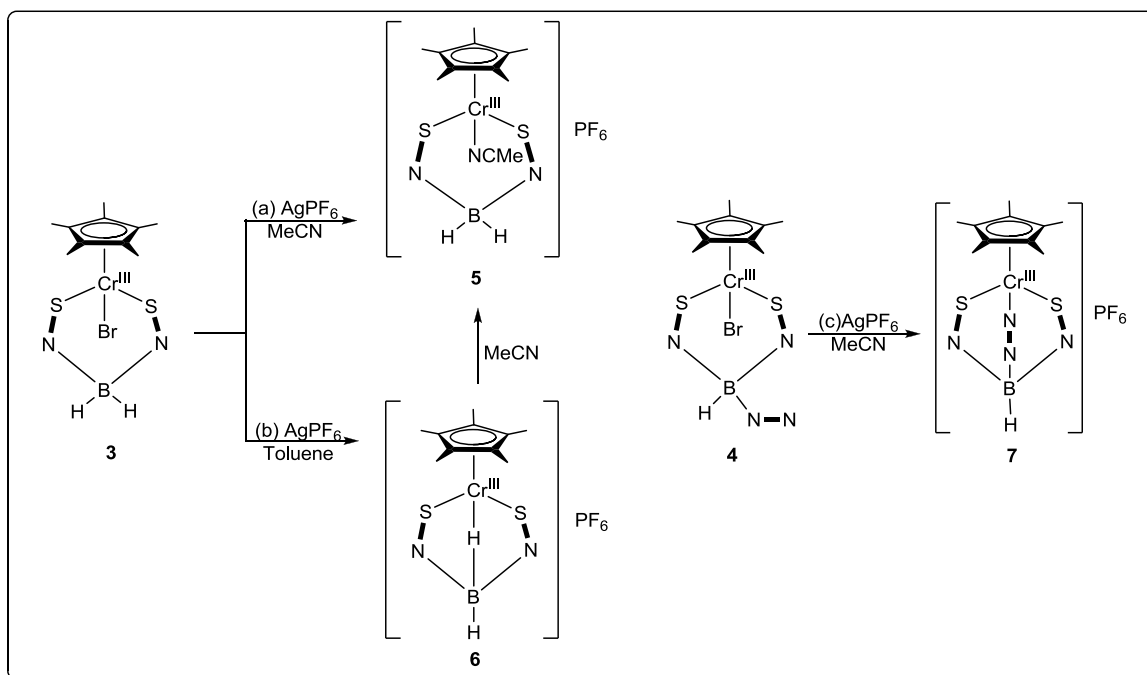
Reactivity

The reaction of [Cp*CrBr₂]₂ (**1**) with (i) K[HB(mt)₃], (ii) Na[H₂B(mt)₂] and (iii) Li[HB(mt)₂(pz)] gave the 15-electron Cr(III) complexes, [Cp*Cr{HB(mt)₃}]Br (**2**), [Cp*Cr{H₂B(mt)₂}]Br (**3**) and [Cp*Cr{HB(mt)₂(pz)}]Br (**4**) as blue solids in moderate to high yields (Scheme 4). As far as we are aware, these are the first examples of poly(methimazolyl)borate complexes of Cr(III).



Scheme 4

The complexes **3** and **4** were reacted with AgPF_6 in an attempt to remove the bromide ligand. The reaction of **3** in MeCN afforded the acetonitrile derivative, **5**, as a royal blue solid (Scheme 5, route (a)), whereas the reaction in toluene led to the grayish green complex **6**, wherein the $[\text{H}_2\text{B}(\text{mt})_2]$ is bound to a Cr^{III} center via a $\kappa^3\text{-H,S,S'}$ coordination (Scheme 5, route (b)). The weak $\text{Cr}\dots\text{HB}$ bond was instantaneously cleaved on dissolution in MeCN to generate **5**. In the reaction of **4** with AgPF_6 in acetonitrile, however, only the $\kappa^3\text{-N,S,S'}$ coordinated complex, **7**, was isolated (Scheme 5, route (c)). This is not surprising, considering that MeCN is not expected to cleave a $\text{Cr}(\text{III})\text{-N}(\text{pz})$ bond, since both are *hard* centers. In a similar context, we believe that the isolation of the stable bromo complex **4** was a consequence of the fact that the pz nitrogen-donor ligand could not displace Br from the coordination sphere of $\text{Cr}(\text{III})$.



Scheme 5

Crystallographic studies

The molecular structures of the monocations of the Cr(III) complexes **2-7** are depicted in Figure 1, and their bond parameters are given in Table 1. In view of the crystallographic disorder in **3**, the discussion on it will be on one of the two crystallographically distinct molecules which showed less disorder. Each of the complexes contains Cr(III) sandwiched between a Cp* ring and a poly(methimazolyl)borate ligand. With the exception of **2**, the molecular structures possess crystallographic mirror planes that cut through the Cp* ring and Cr center. The [HB(mt)₃] ligand in **2** binds to the Cp*Cr^{III} moiety in κ^3 -S,S',S'' tridentate mode, similar to that found in the Ru^{II} complexes of Bailey, [(*p*-cymene)Ru{HB(mt)₃}]Cl,¹¹ and ours, viz. Cp*Ru^{II}{HB(mt)₃} and the [(HMB)Ru{HB(mt)₃}]Cl.¹² The coordination structures of **3-5** are very similar, each containing a [H₂B(mt)₂] ligand in bidentate κ^2 -S,S' mode, together with a Br co-ligand in **3** and **4**, and a solvent (MeCN) co-ligand in **5**. In **6**, the [H₂B(mt)₂] ligand binds to the Cr metal center with κ^3 -H,S,S' coordination, for which there are now several precedents.^{9f, 11-13} The Cr – HB bond distance of 1.885(10) Å is much shorter than the Cr ... HB non-bonding distances found in **3-5** (3.842-3.971 Å). The [HB(mt)₂(pz)] ligand in **7** coordinates to the Cp*Cr^{III} in a κ^3 -N,S,S' manner and the Cr-N bond distance in **7** (2.0566(16) Å) was found to be shorter compared to that for Cp*Cr^{II}[HB(pz)₃] (2.092(2)-2.439(2) Å), and marginally longer than in **5**, where Cr – N (of MeCN) = 2.041(2) Å. It is noted that the observed C-S distances (range 1.675(14) - 1.731(7)

Å) fall intermediate between values of a single bond (*ca.* 1.81 Å) and a double bond (*ca.* 1.56 Å).³⁵ The C-N bond in **5** is 1.139(3) Å, which is intermediate between values of a double bond (1.262 Å) and a triple bond (1.150 Å),³⁵ consistent with the observation of the C≡N coordination in the IR spectrum of **5**.

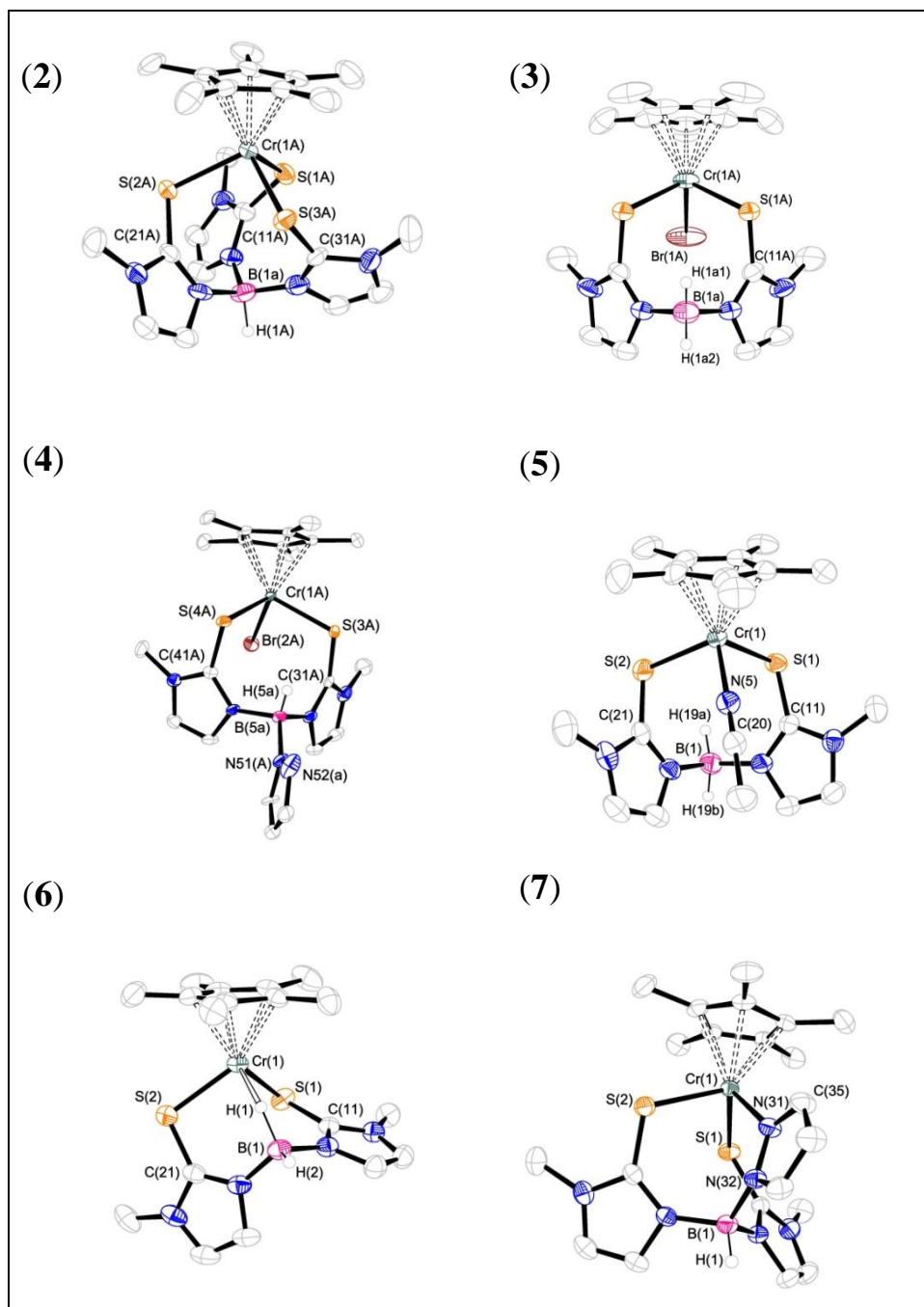
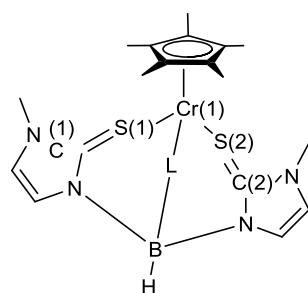
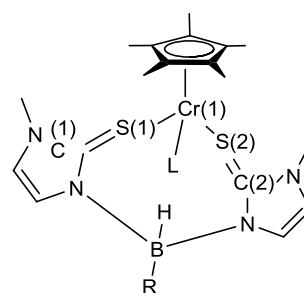


Figure 1. ORTEP plots for the molecular structures of the monocations of compounds **2-7**. Thermal ellipsoids are drawn at the 50% probability level and all hydrogen atoms except those on the boron are omitted for clarity.

Table 1. Selected bond distances (Å) and bond angles (°) of **2-7**.



L = SCNMeC₂H₂N (**2**)
 = MeCN (**5**)
 = H (**6**)
 = N₂C₃H₃ (**7**)



L = Br and R = H (**3**)
 L = Br and R = N₂C₃H₃ (**4**)

Complex	2	3	4	5	6	7
Cr(1)-S(1)	2.366(2) 2.399(2)	2.385(2) 2.365(6)	2.4000(19)	2.3900(7)	2.3616(10)	2.3694(5)
Cr(1)-S(2)	2.363(2) 2.355(2)	-	2.4018(19)	2.3716(6)	2.3805(9)	2.3687(6)
Cr(1)-L(1)	2.378(2) 2.375(2)	2.4544(17)	2.4591(12)	2.041(2)	1.872(10)	2.0566(16)
C(1)-S(1)	1.721(8) 1.725(8)	1.722(7) 1.69(2)	1.718(7)	1.722(7) 1.721(7)	1.722(3)	1.717(2)
C(2)-S(2)	1.731 (7) 1.727(7)	1.675(14)	1.721(7)	1.728(2)	1.717(3)	1.720(2)
C(3)-S(3)	1.714(7) 1.717(8)	-	-	-	-	-
C(20)-N(5)	-	-	-	1.139(3)	-	-
Cr(1)-H(1)	-	3.971	-	3.842	1.872(10)	-
S(1)-Cr(1)- S(2)	95.97(7) 97.70(8)	98.62(10) 98.86(10)	97.21(7)	100.33(20)	99.45(4)	100.79(5)
S(2)-Cr(1)-S(3)	92.98(3) 96.16(7)	-	-	-	-	-

The presence of a paramagnetic d^3 -Cr(III) center is substantiated for **3** by both a broad linewidth axial shaped EPR spectrum at low temperature (Figure 2) and a very broad signal for Cp* at δ -58 in its ^1H NMR spectrum in CD_3CN . Complexes **2**, **5** and **7** similarly exhibit such characteristically low-field and exceedingly broad signals in their proton NMR spectra, while **4** and **6** show no signals at all.

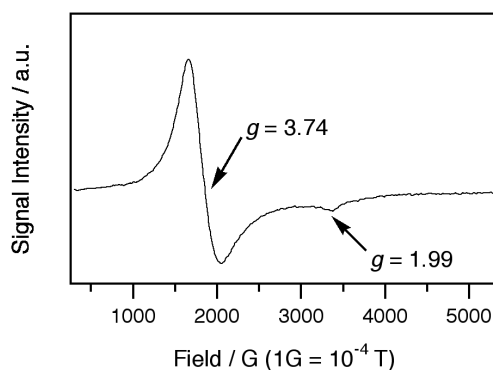


Figure 2. X-band EPR spectrum of **3** in CH_3CN recorded at 10 K.

Electrochemistry

The cyclic voltammetric responses observed at a scan rate (ν) of 100 mV s^{-1} for CH_3CN solutions containing **2**, **4** and **7** at two temperatures are shown in Figure 3. Each compound underwent an oxidation process at positive potentials and a reduction process at negative potentials, with the potential separation between the two processes between 2 – 3 V. The chemical reversibility of the oxidation and reduction processes can be estimated from the ratio of the anodic (i_p^{ox}) to cathodic (i_p^{red}) peak currents ($i_p^{\text{ox}}/i_p^{\text{red}}$) for each process. For a fully chemically reversible process, the $i_p^{\text{ox}}/i_p^{\text{red}}$ -ratio approach unity. Interestingly, in several instances the chemical reversibility of the oxidation and reduction processes appeared to decrease as the temperature was lowered, seen by how the $i_p^{\text{ox}}/i_p^{\text{red}}$ -ratio shifted away from unity at low temperature (Figure 3). A decrease in apparent chemical reversibility at low temperature is unusual, since lowering the temperature normally increases the stability of the oxidized or reduced states. Therefore, it is more likely that when this effect is observed, it involves a follow-up homogeneous chemical reaction such as an equilibrium processes, so that varying the temperature changes the equilibrium constants and thereby makes the processes *appear* less chemically reversible.

A coordination exchange following reduction or oxidation of the Cr containing complex is possible. However, the electrochemical data is not clear to confirm this hypothesis

for **2**. In CH_2Cl_2 , the oxidation and reduction processes for **2** appear less chemically reversible at high and low temperatures compared to the voltammetric data in CH_3CN . The chemical irreversibility of the voltammetric data in CH_2Cl_2 is likely to be caused by less chemical stability of the Cr complex in the chlorinated solvent.

In contrast to the reduction process, the oxidation process of **4** appeared to become more chemically reversible as the temperature was lowered (Figure 3b), suggesting that lowering the temperature helped to stabilise the oxidized state. Also, at lower temperatures, the peak shape for the oxidation of **4** appeared similar to what is expected for a one-electron process. At higher temperatures the oxidative peak shape was broadened, possibly due to multiple electron transfer steps. At low temperatures ($< 243 \text{ K}$), **3** can be oxidized in a one-electron chemically reversible process at $E_{1/2}^{\text{r}} = +0.245 \text{ V vs. Fc/Fc}^+$ ($E_{1/2}^{\text{r}} = (E_{\text{p}}^{\text{ox}} + E_{\text{p}}^{\text{red}})/2$). As the temperature was increased progressively up to 293 K , the chemical reversibility of the oxidation process diminished due to instability of 3^+ at higher temperatures (Figure 4a).

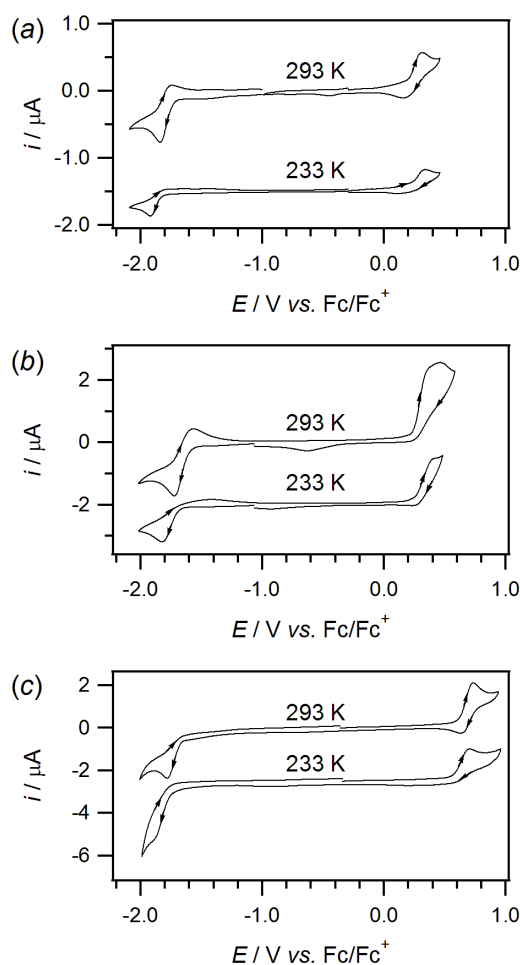


Figure 3. Cyclic voltammograms recorded in CH_3CN of 1.0 mM solutions of (a) **2**, (b) **4**, and (c) **7**. CVs at 233 K are offset by (a) $-1.5 \mu\text{A}$, (b) $-2 \mu\text{A}$, and (c) $-2.5 \mu\text{A}$.

By increasing the voltammetric scan rate for the experiments performed on **3** at $T \geq 253$ K, it was possible to outrun the chemical step and obtain $i_p^{\text{ox}}/i_p^{\text{red}}$ -ratios approaching 1. At 293 K, a scan rate of approximately 10 V s^{-1} was needed in order to have $i_p^{\text{ox}}/i_p^{\text{red}} = 1$, indicating that $\mathbf{3}^+$ has a half-life ≈ 0.1 s at room temperature (assuming a first order decomposition/reaction of $\mathbf{3}^+$).

The electrochemical behavior of **3** is typical of compounds that undergo an EC mechanism (electron transfer followed by a chemical step), where the oxidized compound quickly reacts/decomposes. The oxidation product formed by reaction/decomposition of $\mathbf{3}^+$ is evident in the cyclic voltammograms of solutions of **3** at 293 K (Figure 4a, dashed line) at potentials approximately 0.4 V more positive than the first oxidation process. At lower temperatures (< 243 K) or faster scan rates ($> 10 \text{ V s}^{-1}$), the second oxidation process is not voltammetrically detectable, due to increased stability of $\mathbf{3}^+$ at low temperatures and because the chemical step is outrun at faster scan rates.

The reaction of **3** with AgPF_6 in CH_3CN leads to the formation of **5** in moderate yield. Cyclic voltammograms of **5** in CH_3CN at two different temperatures at a Pt electrode are displayed in Figure 4b. **5** undergoes chemically irreversible oxidation and reduction processes at high and low temperatures, indicating that the reduced and oxidized states are very unstable or reactive (Figure 4b). The anodic peak current (i_p^{ox}) for the oxidation process is greater than the cathodic peak current (i_p^{red}) for the reduction process, indicating more electrons are transferred during the oxidation process. The oxidation process detected in cyclic voltammograms of **5** occurs at a very similar potential to the second oxidation process detected in cyclic voltammograms of **3** at 293 K (compare Figures 4a and 4b). Therefore, it can be concluded that the most positive oxidation process in Figure 4a at 293 K (dashed line) is associated with the oxidation of **5** that is formed from the rapid reaction of $\mathbf{3}^+$ with CH_3CN . The CVs obtained for **6** were very complicated (Figure 4c), indicating that the reduced and oxidized states were likely be very reactive at high and low temperatures.

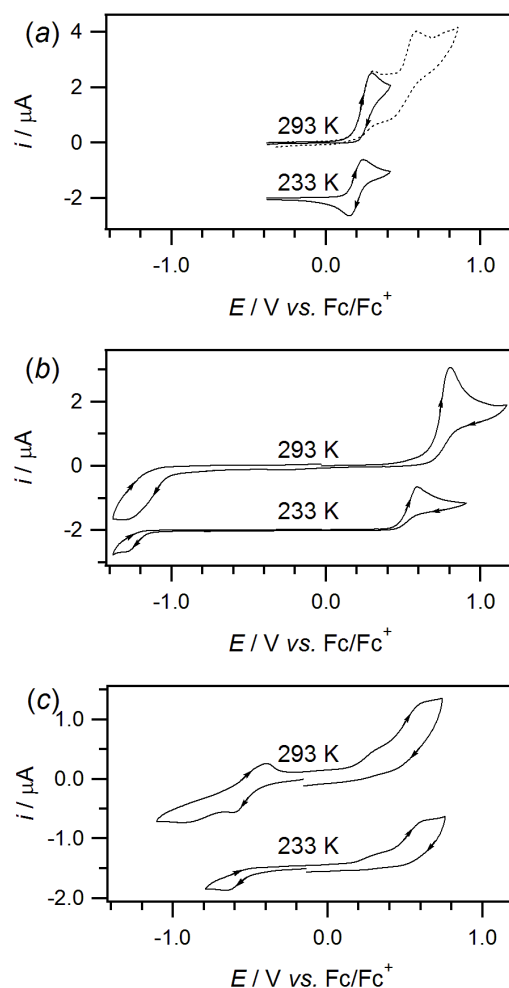


Figure 4. Cyclic voltammograms recorded in CH_3CN of 1.0 mM solutions of (a) **3**, (b) **5** and (c) **6**. CVs at 233 K are offset by (a) $-2 \mu\text{A}$, (b) $-2 \mu\text{A}$, and (c) $-1.5 \mu\text{A}$.

Conclusion

A new class of mixed sandwich Cr^{III} complexes containing the Cp^* and poly(methimazolyl)borate ligands have been synthesized from the reaction of $[\text{Cp}^*\text{Cr}^{\text{III}}\text{Br}_2]_2$ (**1**) with the corresponding poly(methimazolyl)borate salts. Our results represent a direct synthetic route to such mixed-sandwich complexes with Cp^* and poly(methimazolyl)borate ligands. In the case of $[\text{Cp}^*\text{Cr}\{\text{HB}(\text{mt})_3\}]\text{Br}$ (**2**), the $[\text{HB}(\text{mt})_3]^-$ ligand adopted $\kappa^3\text{-S,S',S''}$ coordination. In complexes **3** – **5**, the poly(methimazolyl)borates adopted $\kappa^2\text{-S,S'}$ coordination, with the 6th coordination site occupied by a Br^- coligand in **3** and **4** and a MeCN ligand in **5**. Cyclic voltammetry studies of complexes **2**, **4** and **7** have shown that the chemical reversibility of the oxidation and reduction processes appear to decrease as the temperature was lowered in several instances, which could possibly involve a follow-up

homogeneous chemical reaction such as an equilibrium processes. In contrast, the reduced and oxidized states of complexes **3**, **5** and **6** were found to very unstable or reactive.

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Supporting Information Available. X-ray crystallographic files in CIF format and crystallographic data and refinement details for the structural determinations of **2-7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Mixed-sandwich Cp*Cr Complexes Containing Poly(methimazolyl)borates (Cp* = C₅Me₅) – Syntheses, Structural and Electrochemical Studies

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Synthesis of the first examples of mixed sandwich, 15 electron, chromium(III) complexes containing the poly(methimazolylborate) ligands, *viz.*, **2-4**, are reported. In the presence of acetonitrile, **3** reacted with AgPF₆ to afford **5**, while tridentate coordination in **3** and **4** can be effected by removal of the Br coligand with a silver salt to yield **6** and **7**, respectively. Cyclic voltammetric studies show that oxidation and reduction of **2**, **4** and **7** are chemically reversible, while the reduced and oxidized states of **3**, **5** and **6** are very short-lived.

