Mixed-Sandwich ($\text{Cp}^*/(\text{HMB})$)Ru complexes containing Bis(methimazolyl)(pyrazolyl)borate ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{HMB} = \eta^6\text{-C}_6\text{Me}_6$)

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Mixed-sandwich (Cp^{*}/(HMB))Ru Complexes Containing

bis(methimazolyl)(pyrazolyl)borate (Cp^{*} = η^5 -C₅Me₅, HMB = η^6 -C₆Me₆)

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ABSTRACT

Reaction of the scorpionate salt Li[HB(mt)₂(pz)] (mt = *N*-methyl-2-mercaptoimidazol-1-yl, pz = pyrazolyl) with the organometallic complexes [Cp^{*}RuOMe]₂ (Cp^{*} = η^5 -C₅Me₅) (**1**) and [(HMB)RuCl₂]₂ (HMB = η^6 -C₆Me₆) (**2**) gave the 18-electron Ru(II) complexes [Cp^{*}Ru(κ^3 -*H,S,S'*)-{HB(mt)₂(pz)}] (**3**) and [(HMB)Ru(κ^3 -*H,S,S'*)-{HB(mt)₂(pz)}](**4B**)PF₆ in moderate yields. In the absence of the PF₆⁻ anion, [(HMB)Ru(κ^2 -*S,S'*)-{HB(mt)₂(pz)}](Cl)] [**4C**] was isolated as a co-product with (**4B**)Cl. These complexes are the first examples of organoruthenium(II) complexes containing bis(methimazolyl)(pyrazolyl)borate ligands. Isomers of **4B** were observed in solution and the isomerisation process was studied using variable temperature ¹H NMR spectroscopy. The reactivity of **3** towards O₂ and CO was investigated, and in the process we isolated the first Ru(IV) peroxo complex containing a poly(methimazolyl)borate ligand, [Cp^{*}Ru(κ^2 -*S,S'*)-{HB(mt)₂(pz)}](η^2 -O₂)] (**5**), and a CO adduct, [Cp^{*}Ru(κ^2 -*S,S'*)-{HB(mt)₂(pz)}](CO)] (**6**), respectively. The oxidation process was reversible,

but treatment of **5** with CO converted it irreversibly to **6**. All the new compounds were fully characterized, including by x-ray diffraction analyses. Cyclic voltammetric studies were also conducted for complexes **3**, **5** and **6**.

INTRODUCTION

We have been interested in the organo-ruthenium¹ and chromium² chemistry of the sulfur scorpionate ligands such as tris(methimazolyl)borate, $[\text{HB}(\text{mt})_3]^-$ and the allied compounds, bis(methimazolyl)borate, $[\text{H}_2\text{B}(\text{mt})_2]^-$ and the hybrid bis(methimazolyl)(pyrazolyl)borate, $[\text{HB}(\text{mt})_2(\text{pz})]^-$. These poly(methimazolyl)borates (Chart 1) are the soft analogues of Trofimenko's versatile nitrogen donor poly(pyrazolyl)borates $(\text{HB}(\text{pz})_3)$,³ and they have been studied extensively in the laboratories of Reglinski, Santos, Parkin, Hill and others,⁴ since their first reported synthesis.⁵ To date, numerous coordination compounds are known, in which the S-scorpionates serve as sole or coligands to main group elements like Sn and Pb, As and Bi and Tl,⁶ the group 12 metals,⁷ the first row transition metals of groups 6-10,⁸ and the coinage metals.⁹

Chart 1. Poly(methimazolyl)borate ligands.

An interesting aspect of their coordination chemistry is the wide range of coordination modes, varying from the expected $\kappa^3\text{-S,S',S''}$ for $[\text{HB}(\text{mt})_3]^-$, $\kappa^3\text{-H,S,S'}$ for $[\text{H}_2\text{B}(\text{mt})_2]^-$, and $\kappa^3\text{-N,S,S'}$ for $[\text{HB}(\text{mt})_2(\text{pz})]^-$, to more unusual $\kappa^4\text{-B,S,S',S''}$ for the metallaboranes,^{4d, 10} and $\mu\text{-}\kappa^J\text{-S}$: $\kappa^J\text{-S}$ in $[\text{Au}\{\text{HB}(\text{mt})_3\}]_2$.^{9b} Hill has attributed the formation of the metallaboranes to the increased flexibility brought about by an 8-membered ring, inducing isomerism between $\kappa^3\text{-S,S',S''}$ and $\kappa^3\text{-H,S,S'}$ coordination of the ligand, which subsequently led to B–H bond activation.^{10a,c,12} Despite numerous reports of the formation and isolation of metallaboranes, however, this isomerisation of the $[\text{HB}(\text{mt})_3]$ ligand has not been observed directly. This is not

surprising since isomerisation from $\kappa^3\text{-S,S',S''}$ to $\kappa^3\text{-H,S,S'}$ is most probably followed by rapid transformation to the metallaborane. Using a combination of VT- ^1H NMR spectroscopic and cyclic voltammetric techniques, we were able to examine in detail the isomerisation process in $\text{Cp}^*\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ complexes containing the $[\text{HB}(\text{mt})_3]^-$ ligand, in solution.^{1a} We believe that the isomerisation is observable in these Cp^* complexes because the firmly bound Cp^* ligand blocks the B-H activation route to the metallaboranes. Our investigations revealed that the tripodal scorpionate ligand underwent a facile $\kappa^3\text{-S,S',S''}$ and $\kappa^3\text{-H,S,S'}$ redox-dependent coordination exchange, resulting in an electrochemical square scheme mechanism illustrated in Scheme 1

Scheme 1. Electrochemical square scheme.^{1a}

We note that Bailey observed the $\kappa^2\text{-S,S'}$ isomer in solution for $[\text{CpRu}\{\text{HB}(\text{mt})_3\}]$ and isolated the $\kappa^3\text{-S,S',S''}$ isomer in the solid state for $[(p\text{-cymene})\text{Ru}\{\text{HB}(\text{mt})_3\}]^+$.¹¹ Hill had obtained solid state structural evidence for the $\kappa^3\text{-H,S,S'}$ coordination in $\text{RuH}(\text{CO})(\text{PPh}_3)\{\text{HB}(\text{mt})_3\}$,¹² and Rabinovich had reported the predominance of the $\kappa^3\text{-H,S,S'}$ over the $\kappa^3\text{-S,S',S''}$ isomer for $\text{Ni}(\text{dppe})\{\text{HB}(\text{mt})_3\}$.¹³ There are a number of reports on the occurrence of the $\kappa^3\text{-H,S,S'}$ coordination mode for these soft scorpionate ligands, for instance, in two other ruthenium

compounds, viz., $[\text{RuCl}(\text{DMSO})_2\{\text{HB}(\text{mt})_3\}]$ and $[\text{RuH}(\text{PPh}_3)_2\{\text{H}_2\text{B}(\text{mt})_2\}]$,^{8c} in complexes of Mo and W,¹⁴ and in the essentially linear Ta-H-B complex $[\text{Cp}^*\text{TaCl}_2\{\text{H}_2\text{B}(\text{mt})_2\}]$.¹⁵

The *organometallic* chemistry of the hybrid *mt/pz* ligand $[\text{HB}(\text{mt})_2(\text{pz})]^-$ is less developed compared to that of the $[\text{HB}(\text{mt})_3]^-$ and $[\text{H}_2\text{B}(\text{mt})_2]^-$ ligands. Very recently, we reported the synthesis of chromium complexes containing the hybrid ligand in both $\kappa^2\text{-S,S'}$ and $\kappa^3\text{-N,S,S'}$ coordination modes (Scheme 2).²

Scheme 2. Synthesis of half sandwich chromium complexes of $[\text{HB}(\text{mt})_2(\text{pz})]^-$.²

However, examples of organometallic complexes of the $[\text{HB}(\text{mt})_2(\text{pz})]^-$ ligand remain scarce. The known examples to date are the $[\{(\text{HB}(\text{mt})_2)(\text{pz})\}\text{Mn}(\text{CO})_3]$ complex in which the ligand adopts a $\kappa^3\text{-N,S,S'}$ coordination,¹⁶ and a series of iridium boratrane complexes reported recently.^{4e} Interestingly, the B-H activation phenomenon has also been observed for this series of iridium boratranes in which the metal center is selectively bound to the two sulfur atoms of an S_2N heteroscorpionate, $\text{H}[\text{B}(\text{mt})_2(\text{pz}^{\text{R}})]$, and the *N*-donor ring is pendant (Chart 2).

Chart 2. Iridium boratranes with [HB(mt)₂(pz^R)] ligands.^{4e}

This paper describes the synthetic and reactivity aspects of the [HB(mt)₂(pz)] analogues of the (Cp^{*}/arene)Ru^{II}[HB(mt)₃] complexes which were described in our earlier work.

EXPERIMENTAL

General Procedures. [Cp^{*}RuOMe]₂ (**1**),¹⁷ [(HMB)RuCl₂]₂ (**2**),¹⁸ and Li[HB(mt)₂(pz)],² were synthesized as reported in the literature. RuCl₃·xH₂O was purchased from Ockem Limited, and methimazole and pyrazole from Sigma Aldrich, and were used without further purification.

Cyclic voltammetry studies. Voltammetric experiments were conducted with a computer-controlled Eco Chemie μ Autolab III Potentiostat with a 1 mm diameter GC working electrode. Potentials were referenced to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple, which was used as an internal standard. The electrochemical cell was thermostated at 253 and 293 K using a Thermo Electron Neslab RTE 740 variable temperature, circulating cooling bath.

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 Mo K α radiation (λ 0.71073 Å). The program SMART was used for collecting frames of data, indexing reflection and determination of lattice parameter,¹⁹ SAINT for integration of the intensity of reflections, scaling, and for correction of Lorentz and polarization effects,¹⁹ SADABS for absorption correction,²⁰ and SHELXTL for space group and structure determination, and least-squares refinements on F².²¹ The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

In **4B**(PF₆), there were two half molecules for both the cation and anion. One of the C₆Me₆ group was disordered about a mirror plane, as well as the pyrazole in both half molecules; these were modelled with two alternative sites each of equal occupancies. In **5**, the THF solvate

was modelled as disordered over two main sites and an additional site for one of the O atoms. Appropriate restraints were placed on all disordered parts. The crystal data, collection and processing parameters are given in Table S1.

Reaction of Li[HB(mt)₂(pz)] with

(a) [Cp*RuOMe]₂ (1). To a dark pink solution of **1** (52 mg, 0.10 mmol) in hexane (*ca.* 8 mL) was added Li[HB(mt)₂(pz)] (62 mg, 0.20 mmol) in DCM (*ca.* 2 mL), and the suspension was stirred for 1 h at RT. The resultant orange suspension was evacuated to dryness. The brownish orange residue was dissolved in DCM (*ca.* 1 mL) and chromatographed on a silica gel column packed in hexane (1.5 cm x 8 cm). Elution with toluene:Et₂O (1:2, 30 mL) gave a red eluate, leaving behind an immovable brown band on the column. Upon concentration and addition of hexane to the red eluate, reddish-orange microcrystalline solids of [Cp*Ru^{II}{HB(mt)₂(pz)}] (**3**) (64 mg, 0.11 mmol, 59% yield) were obtained after a day at -30 °C. Diffraction-quality single crystals of **3** were obtained as red blocks from a THF-hexane solution after 3 days at -30 °C.

Data for **3**. Anal. Found: C, 46.8; H, 5.8; N, 15.3; S, 11.6%. Calc. for C₂₁H₂₉B₁N₆Ru₁S₂: C, 46.6; H, 5.4; N, 15.5; S, 11.8%. IR (KBr, cm⁻¹): ν(BH) 2114mbr. ν(other bands) 1565m, 1456s, 1420m, 1289m, 1191s, 1087m, 1039s and 728s. ESI⁺-MS (m/z): 541 [M-H⁺ = C₅Me₅Ru(C₄H₅N₂S)₂(C₃H₃N₂)BH. ¹H NMR (C₆D₆): δ 7.97 (d, 1H, ³J = 1.2 Hz, HC=CHNNCH), 7.91 (d, 1H, ³J = 2.3 Hz, HC=CHNNCH), 7.34 (d, 2 x 1H, ³J = 2.5 Hz, SCN₂HC=CH), 6.41 (t, 1H, ³J = *ca.* 1.9 Hz, HC=CHNNCH), 5.68 (d, 2 x 1H, ³J = 2.2 Hz, SCN₂HC=CH), 2.81 (s, 2 x 3H, NCH₃), 1.81 (s, 15H, CpCH₃), -7.20 (q of equal intensity, 1H, J = 79 Hz, μ-HB). ¹³C NMR (C₆D₆): δ 161.2 (s, SCN₂HC=CH), 141.9 (C_{pyrazole}), 135.7 (C_{pyrazole}), 120.2 (s, C imidazole), 119.2 (C_{imidazole}), 106.1 (s, C_{pyrazole}), 79.3 (s, C₅(CH₃)₅), 34.3 (s, NCH₃), 11.5 (s, C₅(CH₃)₅).

(b) [(HMB)RuCl₂]₂ (2). (i) in the presence of NaPF₆. To an orange-red suspension of **2** (37 mg, 0.10 mmol) in CH₂Cl₂ was added Li[HB(mt)₂(pz)] (62 mg, 0.20 mmol) and NaPF₆ (84 mg, 0.50 mmol). The mixture was stirred for 18 h, resulting in a suspension of a white precipitate in a bright red supernatant. The suspension was filtered and the red filtrate was evacuated to dryness and recrystallised from MeCN/Et₂O at -30 °C. Multiple recrystallisations from MeCN/Et₂O yielded a red fine powder of [(HMB)Ru{HB(mt)₂(pz)}](**4**)PF₆ (105 mg, 0.15

mmol, 74 % yield). Diffraction-quality single crystals of **4B**(PF₆) were obtained as red needles by slow diffusion of ether into an acetonitrile solution over 2 weeks at -30 °C.

Data for **4**(PF₆). Anal. Found: C, 39.0; H, 4.6; N, 11.4; S, 9.0 %. Calc. for C₂₃H₃₂B₁F₆N₆P₁Ru₁S₂: C, 38.7; H, 4.5; N, 11.8; S, 9.0 %. IR (KBr, cm⁻¹): ν(B-H) 2459w; ν(μ-B-H) 2272w, 2185w. ESI⁺-MS (m/z): 569 [M⁺ = [C₆Me₆Ru(C₄H₅N₂S)₂(C₃H₃N₂)BH]⁺]; ESI⁻-MS (m/z): 145 [M⁻ = PF₆⁻]. ¹H NMR (CD₃CN): (the spectrum shows a 5:2 molar mixture of two isomers, **4A** and **4B**) - *isomer 4A*: δ 7.77 (d, 1H, ³J = 1.4 Hz, HC=CHNNCH), 7.45 (d, 1H, ³J = 2.3 Hz, HC=CHNNCH), 7.02 (d, 2 x 1H, ³J = 2.2 Hz, SCN₂HC=CH), 6.83 (d, 2 x 1H, ³J = 2.0 Hz, SCN₂HC=CH), 6.44 (t, 1H, ³J = ca. 1.8 Hz, HC=CHNNCH), 3.58 (s, 2 x 3H, NCH₃), 1.97 (s, 18H, C₆(CH₃)₆); *isomer 4B*: δ 7.95 (d, 1H, ³J = 2.2 Hz, HC=CHNNCH), 7.75 (d, 1H, ³J = 0.6 Hz, HC=CHNNCH), 6.95 (d, 2 x 1H, ³J = 2.1 Hz, SCN₂HC=CH), 6.74 (d, 2 x 1H, ³J = 2.1 Hz, SCN₂HC=CH), 6.32 (t, 1H, ³J = ca. 2.3 Hz, HC=CHNNCH), 3.65 (s, 2 x 3H, NCH₃), 2.09 (s, 18H, C₆(CH₃)₆), -10.6 (q of equal intensity, 1H, J = 60 Hz, μ-HB).

(ii) **in the absence of NaPF₆**. A mixture of **2** (4 mg, 0.01 mmol) and Li[HB(mt)₂(pz)] (6 mg, 0.02 mmol) in ca. 5 mL DCM was stirred at ambient temperature overnight. The NMe resonance in the ¹H NMR spectrum of an aliquot of the product solution showed the presence of **4A**, **4B** and **4C** in a ratio of approximately 1:3:2. Slow diffusion of ether into a CH₂Cl₂ solution gave, after 4 days at -30 °C, red blocks of presumably a mixture of crystals of **4B**(Cl) and **4C**. Fortuitously, we were able to select a diffraction-quality crystal of **4C** for X-ray crystallographic analysis.

Reactivity studies of Cp*Ru[HB(mt)₂(pz)](**3**)

(a) **Reaction with O₂**. Air was bubbled into a bright red solution of **3** (20 mg, 0.04 mmol) in THF (ca. 10 mL) for 10 min, resulting in a green solution. The solution was concentrated to ca. 2 mL. Repeated recrystallisation gave a mixture of Cp*Ru[HB(mt)₂(pz)](O₂) (**5**) (0.03 mmol, 86% yield) and **3** (14% recovery) (based on integration of the NMe resonances in the ¹H NMR spectrum). Attempts to separate **3** and **5** by column chromatography were also unsuccessful, as the reaction was found to be reversible. Thus, monitoring the ¹H NMR spectrum of **5** (5 mg) in C₆D₆ (0.5 mL) under Ar showed that **5** completely reverted to **3** after

heating overnight at 40 °C. Diffraction-quality single crystals of **5** were obtained as brown plates from a solution in THF-ether after 3 days at -30 °C.

Data for 5. Anal. Found: C, 44.8; H, 5.2; N, 13.0; S, 10.1%. Calc. for $C_{21}H_{29}B_1N_6O_2Ru_1S_2$: C, 44.0; H, 5.1; N, 14.7; S, 11.2%. IR (DCM, cm^{-1}): $\nu(O-O)$ 896 m; $\nu(BH)$ 2412 w, 2306 m. ESI⁺-MS (m/z): 572 [$M^+ = C_5Me_5Ru\{(C_4H_5N_2S)_2(C_3H_3N_2)BH\}(O_2)-2H\}$], 556 [M^+-O]. An exact mass of the mother ion could not be obtained, on account of the lability of the O_2 ligand. ¹H NMR (C_6D_6): δ 8.45 (d, 2 x 1H, ³J = 2.0 Hz, $SCN_2HC=CH$), 7.98 (d, 1H, ³J = 1.4 Hz, $HC=CHNNCH$), 7.91 (d, 1H, ³J = 2.2 Hz, $HC=CHNNCH$), 6.19 (t, 1H, ³J = 2.0 Hz, $HC=CHNNCH$), 5.91 (d, 2 x 1H, ³J = 2.1 Hz, $SCN_2HC=CH$), 3.28 (s, 2 x 3H, NCH_3), 1.30 (s, 15H, $CpCH_3$). ¹H NMR (CD_2Cl_2): δ 8.04 (d, 2 x 1H, ³J = 1.4 Hz, $SCN_2HC=CH$), 7.71 (s, 1H, $HC=CHNNCH$), 7.65 (s, 1H, $HC=CHNNCH$), 6.85 (d, 2 x 1H, ³J = 1.3 Hz, $SCN_2HC=CH$), 6.16 (d, 1H, ³J = 1.6 Hz, $HC=CHNNCH$), 3.73 (s, 2 x 3H, NCH_3), 1.44 (s, 15H, $CpCH_3$). ¹³C NMR (CD_2Cl_2): δ 156.5 (s, $SCN_2HC=CH$), 140.9 (s, $C_{pyrazole}$), 137.6 (s, $C_{pyrazole}$), 122.7 (s, $C_{imidazole}$), 120.8 (s, $C_{imidazole}$), 104.0 (s, $C_{pyrazole}$), 100.9 (s, $C_5(CH_3)_5$), 36.1 (s, NCH_3), 8.2 (s, $C_5(CH_3)_5$).

(b) Reaction with CO. 1 atm of CO was charged into a Carius tube containing **3** (55 mg, 0.11 mmol) in THF (*ca.* 10 mL). The solution turned from bright red to deep red within 5 mins and was allowed to stir overnight at R.T. The resultant red solution was evacuated to dryness. Repeated washing with Et_2O :hex (1:2, v/v) removed **3**, leaving behind $Cp^*Ru[HB(mt)_2(pz)](CO)$ (**6**) as a dark red solid (30 mg, 53% yield). The reaction is irreversible and **6** did not revert to **3** even with prolonged heating at 80 °C in solution. Diffraction-quality single crystals of **6** were obtained as red plates from a THF-hexane solution after 3 days at -30 °C.

Data for 6. Anal. Found: C, 46.9; H, 5.2; N, 14.5; S, 11.2%. Calc. for $C_{22}H_{29}B_1N_6ORu_1S_2$: C, 46.4; H, 5.1; N, 14.8; S, 11.3%. IR (KBr, cm^{-1}): $\nu(C-O)$ 1913 s; $\nu(BH)$ 2369 m, 2338 m. ESI⁺-MS (m/z): 570 [$MH^+ = C_5Me_5Ru\{(C_4H_5N_2S)_2(C_3H_3N_2)BH\}(CO)H\}$], 542 [MH^+-CO]. ¹H NMR (C_6D_6): δ 8.02 (d, 1H, ³J = 0.6 Hz, $HC=CHNNCH$), 8.01 (d, 1H, ³J = 1.3 Hz, $HC=CHNNCH$), 7.47 (d, 2 x 1H, ³J = 1.4 Hz, $SCN_2HC=CH$), 6.34 (t, 1H, ³J = 1.1 Hz, $HC=CHNNCH$), 5.74 (d, 2 x 1H, ³J = 1.2 Hz, $SCN_2HC=CH$), 3.00 (s, 2 x 3H, NCH_3), 1.59 (s, 15H, $CpCH_3$). ¹³C NMR (C_6D_6): δ 206.2 (s, CO), 158.9 (s, $SCN_2HC=CH$), 141.1 ($C_{pyrazole}$),

136.5 (C_{pyrazole}), 121.7 (s, C imidazole), 118.1, (C_{imidazole}), 104.0 (s, C_{pyrazole}), 92.5 (s, C₅(CH₃)₅), 33.9 (s, NCH₃), 9.3 (s, C₅(CH₃)₅).

Conversion of Cp*Ru[HB(mt)₂(pz)](O₂) (5**) to Cp*Ru[HB(mt)₂(pz)](CO) (**6**).**

A green solution of Cp*Ru[HB(mt)₂(pz)](O₂) (**5**) (5 mg, 0.001 mmol) in THF (*ca.* 8 mL) placed in a Carius tube was subjected to three cycles of freeze-pump-thaw and then charged with CO. The dark green solution turned bright red, then deep red, after 20 min of stirring. The reaction mixture was left to stir overnight to ensure complete conversion to Cp*Ru[HB(mt)₂(pz)](CO) (**6**), as indicated by the total disappearance of the Cp* peak of **5** in the ¹H NMR spectrum. The reverse reaction did not occur in THF solution in a Schlenk flask under O₂ even under prolonged reflux.

RESULTS AND DISCUSSION

SYNTHETIC STUDIES

The reaction of [Cp*RuOMe]₂ (**1**) with Li[HB(mt)₂(pz)] gave a moderate yield of Cp*Ru[HB(mt)₂(pz)] (**3**), in which the scorpionate ligand is in the κ^3 -H,S,S' bonding mode (Scheme 3a). The analogous reactions of **1** with Na[H₂B(mt)₂]^{1b} and K[HB(mt)₃]^{1a} had yielded products possessing an identical κ^3 -H,S,S' and an alternative κ^3 -S,S',S'' bonding mode for the scorpionate ligand (Scheme 3b).

Scheme 3. Reaction of [Cp*Ru*(OMe)] (**1**) with (a) Li[HB(mt)₂(pz)] and (b) K[HB(mt)₃]^{1a} and Na[H₂B(mt)₂]^{1b}.

The reaction of [(HMB)RuCl₂]₂ (**2**) with Li[HB(mt)₂(pz)] in the presence of NaPF₆ led to isolation of [(HMB)Ru{HB(mt)₂(pz)}](**4B**)PF₆ as an orange red solid in high yield; its structural analysis (discussed below) shows that the scorpionate ligand has an identical binding mode to that in **3**. However, the precursor **4A**(PF₆), in which the ligand was in a κ^3 -N,S,S' coordination mode, was detected (Scheme 4a). An NMR study of the **4A**⁺ $\leftrightarrow$ **4B**⁺ equilibrium was carried out (see below). In the absence of NaPF₆, [**4A**(Cl)] and [**4B**(Cl)] were obtained together with the complex [(HMB)Ru(κ^2 -S,S'-{HB(mt)₂(pz)})(Cl)] [**4C**] (Scheme 4b) as a side product. Structural analysis of the latter showed that a chlorido ligand remained. Tocher and coworkers have previously reported that the reaction of a series of [(η^6 -arene)RuCl₂]₂ complexes with [HB(pz)₃]⁻ gave a similar chlorido complex [(η^6 -arene)Ru(κ^2 -N,N'-{HB(pz)₃})(Cl)] in admixture with [(η^6 -

arene)Ru(κ^3 -N,N',N''-{HB(pz)₃})]Cl. They had also observed that the hapticity change of the scorpionato ligand from κ^2 to κ^3 could be effected by treatment with [NH₄][PF₆].²²

Scheme 4. Reaction of $[(\text{HMB})\text{RuCl}_2]_2$ (**2**) with $\text{Li}[\text{HB}(\text{mt})_2(\text{pz})]$: (a) in the presence of NaPF_6 , (b) in the absence of NaPF_6 .

Reactivity of $\text{Cp}^*\text{Ru}[\text{HB}(\text{mt})_2(\text{pz})]$ (**3**) towards O_2 and CO

While attempting to obtain single crystals of **3**, we found that some of the crystals readily underwent aerial oxidation to give an apparently stable green complex. The reaction of **3** with O_2 gave an 86% conversion to a Ru(IV)-peroxo complex, $[\text{Cp}^*\text{Ru}\{\text{HB}(\text{mt})_2(\text{pz})\}(\eta^2\text{-O}_2)]$ (**5**), which was isolated as a green solid, as a mixture with **3**. The IR spectrum of **5** shows a stretch of medium intensity at 896 cm^{-1} , which falls in the range typical for O–O stretch in metal peroxo complexes ($800\text{--}900\text{ cm}^{-1}$).²³ Complete removal of **3** was not possible, either by column chromatography or multiple recrystallisations, owing to the reversibility of the reaction. However, the microanalytical data indicated a very high degree of purity. Indeed, it was found

(via ^1H NMR spectroscopy) that **5** completely reverted to **3** after heating overnight at 40 °C under Ar (Scheme 5). As far as we are aware, there is only one other case of such a reversible oxygen coordination: a remarkably facile and reversible O_2 coordination to the tetrakiscarbene Ru cation $[\text{Ru}(\text{I}^i\text{Pr}_2\text{Me}_2)_4\text{H}]^+$ ($\text{I}^i\text{Pr}_2\text{Me}_2 = 1,3\text{-diisopropyl-4,5-dimethylimidazol-2-ylidene}$) occurred in solution at temperatures as low as 193 K, or in the solid state at 1 atm O_2 at 298 K, while the reverse reaction can be effected by application of vacuum.²⁴

Complex **5** is the first example of a $\text{Ru}^{\text{IV}}(\text{peroxo})$ complex containing a poly(methimazolyl)borate ligand, and its synthetic pathway via the displacement of an ‘agostic-like’ $\text{Ru}\cdots\text{H}-\text{B}$ bond is also unique. There are two pathways that have been reported for the formation of transition metal peroxo complexes, *viz.*, (i) oxidative addition of an O_2 molecule to a low-valent metal precursor, mainly of the d^6 Cp^*ML_2 , d^6 Cp^*ML_5 , and d^8 Cp^*ML_4 types, and (ii) displacement of a weakly coordinating ligand by O_2 . Peroxo complexes arising from route (i) include $[\text{Cp}^*\text{Ru}(\eta^2\text{-O}_2)(\text{dppe})]^+$ from the oxidation of $[(\text{Cp}^*\text{Ru}(\text{dppe}))]^+$,²⁵ and $[\text{RuH}(\eta^2\text{-O}_2)(\text{dcpe})_2]^+$ from the 16-electron hydride species $[\text{RuH}(\text{dcpe})_2]^+$ ($\text{dcpe} = 1,2\text{-bis(dicyclohexylphosphino)ethane}$).²⁶ Under the route (ii) category, common precursors are those containing labile ligands like hydride/dihydrogen, chloride or solvents (mainly MeCN), e.g. $[\text{Cp}^*\text{Ru}(\text{H}_2)(\text{dppm})]^+$, $[\text{Cp}^*\text{RuCl}(\text{dppm})]$,²⁷ $\text{Ru}(\text{Ph}_2\text{PNMeNMePPh}_2)_2\text{H}_2$,²⁸ $[\text{Cp}^*\text{RuCl}(\text{dippe})](\text{dippe} = 1,2\text{-bis(diisopropylphosphino)ethane})$,²⁹ and $[\text{Tp}^*\text{RhCl}(\mu\text{-EPh})_2\text{RuCp}^*(\text{MeCN})]$ ($\text{Tp}^* = \text{hydrotris(3,5-dimethylpyrazol-1-yl)}$); in the latter, O_2 displaces MeCN at the Ru, but not Cl^- at the Tp^* -supported Rh moiety.³⁰ In fact, scorpionato (Tp/Tp^*)-supported ruthenium(IV) peroxo($\eta^2\text{-O}_2$) complexes are unknown. We note that O_2 has been reported to react with $[\text{TpRu}(\text{L}_2)(\text{H}_2)]^+$ ($\text{L}_2 = \text{dppm}$, dppp , or $(\text{PPh}_3)_2$) to give a Ru^{III} -superoxo complex $[\text{TpRu}(\text{L}_2)(\eta^1\text{-O}_2)]^+$. This correlated well with B3LYP calculations by the authors (Lin, Lau and co-workers) on the model complex $[\text{TpRu}(\text{PH}_3)_2(\text{O}_2)]^+$ which showed the order of stability: $\eta^1\text{-superoxo complex } [\text{TpRu}^{\text{III}}(\text{L}_2)(\eta^1\text{-O}_2)]^+ > \text{peroxo complex } [\text{TpRu}^{\text{IV}}(\text{L}_2)(\eta^2\text{-O}_2)]$, and a reverse order for the CpRu analogue. This was rationalised on the basis of the *harder* character of the Tp-Ru fragment $[\text{TpRu}(\text{L}_2)]^+$ as compared with the analogous $[\text{CpRu}(\text{L}_2)]^+$ fragment.³¹ Indeed, a softness order of $[(\text{HB}(\text{mt})_3)] > \text{Cp} > \text{Tp}$ had been deduced for these 6e⁻ donor ligands from the successful isolation of the unusual Bi(III) cation $[\text{Bi}\{\text{HB}(\text{mt})_3\}]^+$.³²

Recent DFT studies by Lin and coworkers showed that the ligation of η^2 -O₂ to metal fragments occurred via a η^1 -O₂ intermediate,³³ in agreement with observations that the reaction is facilitated by the availability of a labile ligand in the substrate complex. This is related to the ease of formation of the peroxo complex **5** in this study, as there exists a weak Ru $\cdots$ H–B ‘agostic-like’ bond in the precursor complex **3**. An additional case in point was the finding that the apparent direct oxidation of [Cp*Ru(NiS₂N₂)]₂²⁺ to [Cp*Ru(NiS₂N₂)(η^2 -O₂)]⁺ actually occurred via the solvento intermediate [Cp*Ru(NiS₂N₂)(MeCN)]⁺ formed in solution.³⁴

Scheme 5. Reaction of **3** with O₂.

The reactivity of **3** towards CO was also investigated, and it was found to lead to the formation of [Cp*Ru{HB(mt)₂(pz)}(CO)] (**6**) (Scheme 6, route a). The IR spectrum of **6** shows a strong C≡O stretch at 1913 cm⁻¹. A similar complex, [Cp*Ru{HB(aza)₃-κ²H,N}(CO)] (aza = 7-azaindoly) was also formed via displacement of one of the aza-unit coordination in [Cp*Ru{HB(aza)₃-κ³H,N,N'}] upon treatment with carbon monoxide.³⁵ Unlike the oxidation of **3** discussed above, the reaction of **3** with CO is irreversible, even with prolonged heating. We have also found that **5** could be completely converted to **6** after overnight treatment with CO at ambient temperature (Scheme 6, route c), but the reverse reaction did not take place (Scheme 6, route d), as may be expected from the stronger M-CO bond compared to the M-(η^2 -O₂) bond. In contrast, we note a report that the O₂ ligand in [Cp*Ru(NiS₂N₂)(η^2 -O₂)]⁺ cannot be displaced by CO.³⁴

Scheme 6. Reactivity of $[\text{Cp}^*\text{Ru}\{\text{HB}(\text{mt})_2(\text{pz})\}]$ towards (a) CO and (b) O_2 .

SPECTROSCOPIC STUDIES

The ^1H NMR spectrum of **3** (in C_6D_6) shows two doublets and a set of triplet for the pyrazole ring protons, two doublets for the methimazolyl ring protons, and a singlet for the NMe protons. Both the methimazolyl ring protons are in the same chemical environment, with a quartet of equal intensity at δ -7.20 for the ‘agostic-like’ $\text{Ru}\cdots\text{H}-\text{B}$ moiety, in agreement with a $\text{Cp}^*\text{Ru}[(\kappa^3\text{-H},\text{S},\text{S}')\text{-}\{\text{HB}(\text{mt})_2(\text{pz})\}]$ formulation. The ^1H NMR spectrum is consistent with the solid state structure determined by x-ray crystallography. A d_8 -toluene solution of **3** did not show any signs of a fluxional process down to 253K.

The ^1H NMR spectrum of **4**(PF_6) shows eight sets of doublets and two sets of triplets at δ 7.95-6.44, corresponding to the methimazolyl and pyrazolyl rings, and two singlets at δ 3.65 and 3.58, corresponding to the NMe group on the methimazole. In addition, the presence of a quartet of equal intensity at δ -10.6 ($J = 60$ Hz), which corresponds to the ‘agostic-like’ B-H interaction with the metal center, suggests that **4**(PF_6) may exhibit isomerisation between the $\kappa^3\text{-N},\text{S},\text{S}'$ and $\kappa^3\text{-H},\text{S},\text{S}'$ forms in solution (Scheme 7). This is reminiscent of the solvent-dependent exchange equilibrium we had investigated for $\text{Cp}^*\text{Ru}^{\text{II}}\{(\text{HB}(\text{mt})_3)\}$ (Scheme 8).^{1a} It is noteworthy that for the Cp^*Ru analogues, the ligand adopted a bidentate $\kappa^2\text{-S},\text{S}'$ coordination in acetonitrile, with a solvent molecule coordinated to the vacant coordination site. In this case, however, **4B**(PF_6) is

insoluble in less polar solvents such as dichloromethane, and no solvent coordination was observed, as indicated by the ^1H NMR spectrum. In comparison we note that a similar $\kappa^3\text{-}N,S,S'/\kappa^3\text{-}S,S',S''$ and $\kappa^3\text{-}H,S,S'$ isomerisation was not observed for the $\text{Cp}^*\text{Cr}^{\text{III}}$ analogue, $[\text{Cp}^*\text{Cr}\{\text{HB}(\text{mt})_2(\text{pz})\}]\text{PF}_6$.² Since the H,S,S' coordination mode is “enroute” to B-H activation, this is expected to be disfavoured with the electron-poor centre in $[\text{Cp}^*\text{Cr}^{\text{III}}]^+$ compared to $[(\text{HMB})\text{Ru}^{\text{II}}]^+$.

Scheme 7. Isomerisation of 4^+ in solution.

Scheme 8. Isomerisation in $\text{Cp}^*\text{Ru}^{\text{II}}\{(\text{HB}(\text{mt})_3)\}$ via a solvent intermediate.^{1a}

A VT NMR spectroscopic study of $4\text{A}^+/4\text{B}^+$ conducted in CD_3CN in the temperature range 245 – 345 K showed no signs of line-broadening (Figure 1). We have assigned the two sets of doublets at δ 7.77 and 7.45, and the triplet at δ 6.44, to 4A^+ ; the two sets of doublets at δ 7.95 and 7.75, and the triplet at δ 6.74, are assigned to 4B^+ , the latter corresponding to an uncoordinated pyrazolyl ring. Integration of the NMe resonances of 4A^+ and 4B^+ gave their relative concentrations in solution at each temperature. Hence the relative concentrations of species at these temperatures were obtained by extrapolation of the linear ($R_2 = \text{ca. } 0.8$) concentration vs. temperature plot in the range 245 – 345 K. K_{eq} values listed in Table 1 were calculated directly from the integration ratios of $[4\text{B}^+]:[4\text{A}^+]$.

Figure 1. VT ^1H NMR spectra of 4^+ for range 300-345 K.

The thermodynamic parameters ΔH° [$-5.42(84)$ kJ mol $^{-1}$] and ΔS° [$-26.6(29)$ J mol $^{-1}$ K $^{-1}$] were obtained from a plot of $\ln K_{\text{eq}}$ vs. $(1/T)$ [$\ln K_{\text{eq}} = -(\Delta H^\circ / RT) + (\Delta S^\circ / R)$] and the ΔG° value [$2.6(17)$ kJ mol $^{-1}$ at 300 K] was calculated from the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The positive ΔG° value calculated for this equilibrium indicates that the backward reaction, i.e., $4\text{B}^+ \rightarrow 4\text{A}^+$, is spontaneous.

Table 1. Equilibrium constants in d_3 -acetonitrile for $4\text{A}^+ \leftrightarrow 4\text{B}^+$ equilibrium (Scheme 7).

$4\text{A}^+ \rightleftharpoons 4\text{B}^+$											
T/K	345	335	325	315	305	295	285	275	265	255	245
K_{eq}^a	0.24(1)	0.28(1)	0.27(1)	0.34(1)	0.36(1)	0.45(1)	0.43(1)	0.49(1)	0.52(1)	0.48(1)	0.43(1)

^aObtained from integration ratios of the NMe resonances in the ^1H NMR spectrum.

Unfortunately, we cannot make a fair comparison with the $\text{Cp}^*\text{Ru}^{\text{II}}\{(\text{HB}(\text{mt})_3)\}$ system,^{1a} because the mechanism there involves solvent coordination and hence the ΔG° values are solvent-dependent. Solvent-dependency of the isomerisation of 4^+ could not be studied owing to its insolubility in non-coordinating solvents.

CRYSTALLOGRAPHIC STUDIES

The molecular structures of complexes **3** - **6** are depicted in Figure 2, with selected bond parameters given in Table 2. The structures of **3** and **4B**(PF₆) are similar, each containing a ruthenium center sandwiched between a Cp*/HMB ring and a tripodal tridentate (κ^3 -H,S,S') poly(methimazoly)borate ligand. On the other hand, the structures of **5** and **6** show that the [HB(mt)₂(pz)] ligand coordinates in a bidentate (κ^2 -S,S') fashion with the third coordination site occupied by a peroxo and a carbonyl ligand, respectively. Similar to complexes **5** and **6**, the [HB(mt)₂(pz)] ligand in complex **4C** adopts a bidentate (κ^2 -S,S') fashion with the third coordination site occupied by a chlorido ligand.

Figure 2. ORTEP plots for the molecular structures of (a) Cp*Ru{ κ^3 -H,S,S'-HB(mt)₂(pz)} (**3**), (b) [(HMB)Ru{ κ^3 -H,S,S'-HB(mt)₂(pz)}]⁺ (**4B**⁺) cation, (c) (HMB)Ru{ κ^2 -S,S'-HB(mt)₂(pz)}(Cl) (**4C**), (d) Cp*Ru{ κ^2 -S,S'-HB(mt)₂(pz)}(η^2 -O₂) (**5**) and (e) Cp*Ru{ κ^2 -S,S'-HB(mt)₂(pz)}(CO) (**6**). Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms except those on the boron are omitted for clarity.

The C–S bonds of all five molecules fall in the range of 1.688(4) – 1.738(8) Å, intermediate between values for a single bond (*ca.* 1.81 Å) and a double bond (*ca.* 1.56 Å),³⁶ as commonly found in metal complexes of HB(mt^R)₃ and H₂B(mt^R)₂, e.g. Zn[H₂B(mt^{tBu})₂]₂ (1.735(8)–1.738(8) Å),^{7e} and [Mo₂Au{μ-H₂B(mt)₂}(CO)₇(PPh₃)] (1.730(5)–1.733(5) Å).³⁷ The κ³-H,S,S' coordination mode adopted by the [HB(mt)₂(pz)] ligand in complex **3** is similar to that we had previously reported for a 3c-2e Ru^{II}H–B bond in Cp*Ru[H₂B(mt)₂] complex (**A**). The H[⋯]Ru bond distance in **3** (1.899 (10) Å) is longer than that reported for **A** (1.813(10) Å). As in **3**, the [HB(mt)₂(pz)][−] ligand adopts κ³-H,S,S' coordination in complex **4B**(PF₆), but a κ²-S,S' ligation mode in **4C**. The Ru(1)[⋯]H(2) bond was found to be 1.82(1) Å in **4B**⁺, which is comparable to that for **A** (1.813(10) Å),^{1b} and longer than that found for [RuH(CO)(PPh₃)(κ³-H,S',S'-{HB(mt)₃})] (1.75(4) Å),^{12a} [Ru(PPh₃){κ³-H,S,S'-H₂B(mt)₂}{κ²-S,S'-H₂B(mt)₂}] (1.785(1) Å), [Ru(PPh₃){κ²-S,S'-H₂B(mt)₂}(Hmt)₂}]Cl (1.785(1) Å) and [Ru{κ³-H,S,S'-H₂B(mt)₂}]₂ (1.785(1) Å).^{12b} As expected, the B–H bond lengths in **3** and **4B**(PF₆) (1.163(1) Å and 1.33(1) Å, respectively), containing 3c-2e Ru^{II}H–B moieties, are longer than those in **4C**, **5** and **6** (1.059(10), 1.032(10) and 1.097(10) Å, respectively), where the [HB(mt)₂(pz)] ligand adopts a bidentate coordination mode. The Ru–S distances in all five molecules fall within the range found in [Cp*Ru^{III}{HB(mt)₃}]Cl (2.3213(8)– 2.4100(8) Å),^{1a} Cp*Ru^{II}{HB(mt)₂} (2.392(2)– 2.416(2) Å),^{1b} and [(*p*-cymene)Ru^{II}{HB(mt)₃}]Cl (2.3931(7) – 2.4274(14) Å).¹¹ The S–Ru–S angles in **3–6** (range 87.05(3) – 127.9(1)°) are close to similar bite angles in Cp*Ru^{II}{HB(mt)₃},^{1a} [(HMB)Ru^{II}{HB(mt)₃}]Cl,^{1b} [(*p*-cymene)Ru^{II}{HB(mt)₃}]Cl,¹¹ and ruthenaboratrane,¹² but generally larger than those found for the 9S3 complexes of (HMB)Ru(II) and Cp*Ru(III) (range 85.18(4) – 92.18(4)°).³⁸ This difference can be attributed to the steric bulk of the methimazolyl rings in [HB(mt)₂(pz)][−] and/or higher flexibility of the ligand, compared with that of the ethylene bridges in 9S3. The S–Ru–S angles in **5** (87.05(3)°) is smaller than that found for **3** (93.14(4)°) and **6** (97.66(4)°) while that for **4C** (88.48(5)°) is smaller than that for **4B**(PF₆) (92.1(2)°), presumably to accommodate the spatial demands of peroxo (O₂^{2−}) and chlorido ligand, respectively. The O–O distance in **5** falls within the range (1.35 – 1.6 Å) observed for metal peroxo complexes.³⁹ The span correlates with different degrees of O–O activation in peroxo complexes, with shorter O–O distances indicating a higher formal oxidation state of the metal, e.g. for Ru(IV) centers, these distances are in the range 1.36 – 1.37 Å, and for Ru(II) centers, the

distance can be as high as 1.432.³³ The distance in **5** is very close to those observed in other Cp*Ru(IV) peroxo complexes, e.g. [Cp*Ru(dppe)(O₂)]PF₆ (1.398(5) Å),^{25a} and [Cp*Ru(NiS₂N₂)(η^2 -O₂)]⁺ (1.371(8)).³⁴ However, the bond is much shorter than that in H₂O₂ (1.461(3) Å).⁴⁰

Table 2. Selected bond parameters for complexes **3** – **6**.

	3	4B[†]	4C	5[#]	6
Bond Distances (Å)					
Ru(1)-S(1)	2.3964(10)	2.393(4)	2.4274(14)	2.4332(6)	2.4344(11)
	2.3809(9)		2.4260(14)		2.4378(12)
C(1)-S(1)	1.688(4)	1.731(13)	1.722(5)	1.724(3)	1.723(4)
	1.694(4)		1.728(6)		1.715(5)
B(1)-H(1)	-	-	1.059(10)	1.032(10)	1.097(10)
B(1)-H(2)	1.163 (1)	1.33(1)	-	-	-
Ru(1)...H(2)	1.899 (10)	1.82(1)	4.13(1)	-	-
O(1)-O(1A)	-	-	-	1.405(5)	-
C(3)-(O3)	-	-	-	-	1.153(6)
Ru(1)-L(1)	-	-	-	2.0119(19)	1.842(5)
				(L(1) = O(1))	(L(1) = C(3))
Bond Angles (°)					
S(1)-Ru(1)-S(2)	93.14(4)	92.1(2)	88.48(5)	87.05(3)	97.66(4)
Ru(1)...H(2)-B(1)	141.86 (10)	127.9(1)	-		
O(1)-Ru(1)-O(1)	-	-	-	40.88(13)	-
O(1)-C(22)-Ru(1)	-	-	-	-	175.2(5)

[†] There are two disordered half molecules for the cation **4B**; the parameters here are for the one showing less disorder.

[#] Complex **5** possesses crystallographic mirror plane.

ELECTROCHEMISTRY

Cyclic voltammograms (CVs) performed at 253 K of solutions containing **3** show a chemical reversible oxidation process at $E_{1/2}^r = -0.65$ V vs. Fc/Fc⁺ [$E_{1/2}^r = (E_p^{ox} + E_p^{red})/2$], where

E_p^{ox} and E_p^{red} are the anodic and cathodic peak potentials respectively, measured when the anodic (i_p^{ox}) and cathodic (i_p^{red}) peak current ratios were equal to unity] (Figure 3a).⁴¹

Figure 3. Cyclic voltammograms recorded at a scan rate of 100 mV s^{-1} at a 1 mm planar GC electrode in CH_2Cl_2 solutions containing 0.2 M Bu_4NPF_6 and 1 mM (a) **3**, (b) **5**, and (c) **6**.

The anodic to cathodic peak-to-peak separation (ΔE_{pp}) was 70 mV, similar to that observed for ferrocene under identical conditions, indicating that it is likely a one-electron oxidation to 3^+ . When the temperature was increased to 293 K, the reverse reduction process was split into two processes, Red_A and Red_B (Figure 3a). Red_A is associated with the reduction of 3^+ back to **3**, while Red_B is associated with the reduction of an additional product that forms *via* decomposition/reaction of 3^+ (which appears to be semi-stable at 293 K on the voltametric time-scale). When the scan was extended in the positive direction, two chemically irreversible oxidation processes were detected at positive potentials, caused by chemical instability of more highly oxidised states of 3^+ . The very low oxidation potential for **3** provides an explanation for why it readily undergoes aerial oxidation with O₂ to form to form **5**. Complex **3** was not able to be electrochemically reduced within the solvent/electrolyte potential window accessible in CH₂Cl₂.

Complex **5** is more difficult to oxidise than **3** by approximately 0.8 V. The electrochemical oxidation of **5** occurs in a chemical irreversible process with $E_p^{ox} = +0.115$ V *vs.* Fc/Fc⁺ (Figure 3b). When the scan direction was reversed after the first oxidation process and applied in the negative direction, two reduction processes were detected (Red_A and Red_B) (Figure 3b) at identical potentials to those observed in the CVs of **3** at 293 K (Figure 3a). Therefore, it is likely that the chemically irreversible oxidation of **5** results in the formation of 3^+ (*via* loss of O₂), which then irreversibly reacts to form a new compound. The notion that **5** is oxidised (accompanied by the loss of O₂) to form 3^+ is supported by the observation that an additional oxidation peak (Ox_A) is evident in the CVs of **5** at an identical potential to that observed for **3** (compare Figures 3a and 3b).

Complex **6** can be oxidised in a chemically reversible process at -0.340 V *vs.* Fc/Fc⁺ (Figure 3c), with the CV data indicating that the oxidised compound (**6**⁺) is stable on the voltametric time-scale at high and low temperatures. Complex **6** also displayed oxidation processes at more positive potentials (> +0.4 V), but these do not correlate with the additional processes observed for **3** and **5**.

CONCLUSION

The reactions of Li[HB(mt)₂(pz)] with [Cp*RuOMe]₂ and [(HMB)RuCl₂]₂ yielded the first examples of organoruthenium(II) complexes containing bis(methimazolyl)(pyrazolyl)borate ligands, *viz.*, the mixed sandwich complexes [Cp*Ru(κ^3 -H,S,S')-{HB(mt)₂(pz)}] (**3**), [(HMB)Ru(κ^3 -H,S,S')-

$\{\text{HB}(\text{mt})_2(\text{pz})\}](\mathbf{4B})\text{PF}_6$ and $[(\text{HMB})\text{Ru}(\kappa^2\text{-S,S'})\text{-}\{\text{HB}(\text{mt})_2(\text{pz})\}](\text{Cl})$ [$\mathbf{4C}$]. Complex $\mathbf{3}$ underwent reversible oxidation with O_2 to give a Ru(IV) peroxo derivative $[\text{Cp}^*\text{Ru}\{\text{HB}(\text{mt})_2(\text{pz})\}\eta^2\text{-O}_2]$ ($\mathbf{5}$). It is proposed that the ease of formation of $\mathbf{5}$ derives from the lability of the $\text{Ru}\cdots\text{H}$ bond in an ‘agostic-like $\text{Ru}\cdots\text{H}\cdots\text{B}$ ’ interaction. The reversibility of this reaction may hold catalytic implications for oxidation processes in organic and biological transformations, as well as O_2 transport in biological systems.⁴² Both $\mathbf{3}$ and $\mathbf{5}$ reacted with CO to give $[\text{Cp}^*\text{Ru}\{\text{HB}(\text{mt})_2(\text{pz})\}(\text{CO})]$ ($\mathbf{6}$). An isomerisation process was observed for $\mathbf{4B}$ and it was found that the backward reaction, i.e., $\mathbf{4B}^+ \rightarrow \mathbf{4A}^+$, is spontaneous.

Supporting information

X-ray crystallographic files in CIF format and crystallographic data and refinement details (Table S1), for the structural determinations of $\mathbf{3-6}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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