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Cooperative B-H bond activation: dual site borane activation by redox active κ^2 -N,S-chelated complexes†

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Cooperative dual site activation of boranes by redox-active 1,3-N,S-chelated ruthenium species, mer- $[PR_3\{\kappa^2-N,S-(L)\}_2Ru\{\kappa^1-S-(L)\}]$, (mer-2a: R=Cy, mer-2b: R=Ph; $L=NC_7H_4S_2$), generated from the aerial oxidation of borate complexes, $[PR_3(\kappa^2-N,S-(L))Ru(\kappa^3-H,S,S'-BH_2(L)_2)]$ (trans-mer-1a: R = Cy, transmer-1b: R = Ph; $L = NC_7H_4S_2$), has been investigated. Utilizing the rich electronic behaviour of these 1,3-N,S-chelated ruthenium species, we have established that a combination of redox-active ligands and metal-ligand cooperativity has a big influence on the multisite borane activation. For example, treatment of mer-2a-b with BH_x·THF led to the isolation of $fac-[PR_3Ru\{\kappa^3-H,S,S'-(NH_2BSBH_2N)(S_2C_7H_4)_2\}]$ (fac-3a: R = Cy and fac-3b: R = Ph) that captured boranes at both sites of the κ^2 -N,S-chelated ruthenacycles. The core structure of fac-3a and fac-3b consists of two five-membered ruthenacycles [RuBNCS] which are fused by one butterfly moiety [RuB₂S]. Analogous fac-3c, [PPh₃Ru{ κ^3 -H,S,S'-(NH₂BSBH₂N)(SC₅H₄)₂)], can also be synthesized from the reaction of BH₃·THF with [PPh₃{ κ^2 -N,S-(SNC₅H₄)}{ κ^3 -H,S,S'- $BH_2(SNH_4C_5)_2$ Ru], cis-fac-1c. In stark contrast, when mer-2b was treated with BH_2Mes (Mes = 2,4,6trimethyl phenyl) it led to the formation of trans- and cis-bis(dihydroborate) complexes [κ^3 -S,H,H- $(NH_2BMes)Ru(S_2C_7H_4)\}_2$, (trans-4 and cis-4). Both the complexes have two five-membered $[Ru-(H)_2-B-(H)_2-B-(H)_2]$ NCS] ruthenacycles with κ^2 -H-H coordination modes. Density functional theory (DFT) calculations suggest that the activation of boranes across the dual Ru-N site is more facile than the Ru-S one.

Introduction

Metal-ligand cooperation (MLC) is an important model in catalytic reactions that generates new reactivity patterns in many inorganic/organic transformations.^{1,2} Unlike the sole participation of the metal center in classical catalysis, MLC involves a reactive ligand bound to metal that can activate small molecules across the metal-ligand bond, such as, H₂, CO₂, boranes, silanes, alcohols, *etc.*³⁻⁶ Among them, the activation of the B–H bond of boranes along with their catalytic applications in hydroboration became of interest.⁷ Metal complexes with polarized M–L bonds (L = O, N, S or C) proved to be very effective for B–H bond activation to yield M–H–B–L species. For example, the M–O bond cooperation (M = Ru or Rh and Ir) can capture H₂BMes or HBCy₂ across the metal–oxygen bond.^{4c,7b,8}

Transition metal complexes with M–S (M = Ru and Fe) or redox non-innocent ligands in combination with MLC can activate BH_3 and 9-BBN molecules. 9,10 For example, ruthenium complexes containing o-(N-arylamino) thiophenol derivatives show oxidative aromatic ring cleavage in the presence of the superoxide ion (I, Chart 1). 11 Reactions such as hydrogen atom transfer and proton-coupled electron transfer (PCET) reactions that determine the reactivity of H_2 noticeably occurred at the

Chart 1 Non-innocent redox-active ligand complexes of various transition metals (I-V).

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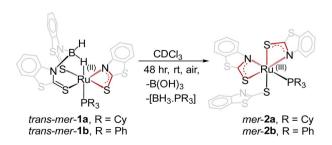
redox-active sites of complexes (II–IV, Chart 1).^{12,13} On the other hand, for the B–H activation the engagement of MLC with multifunctional reactive sites with redox-active ligands is more useful for accessing key organic transformations.¹⁴

As part of our current interest in activation of boranes utilizing cooperative reactivity, ¹⁵ we have synthesized a number of molybdenum(II) hydroborate species, in which BH₃ is stabilized through Mo–H–B(H₂)–E molybdacycles (E = S, Se or Te). ¹⁶ Further, very recently, we have established cooperative Si–H and B–H bond activations by a κ^2 -N,S-chelated borate complex, trans–mer-1b that led to the formation of six-membered ruthenahetero-cycles through hemilabile ring-opening of Ru–N bonds. ¹⁷ While working on κ^2 -N,S-chelated species trans–mer-1a–b, we have observed that aerial oxidation of these Ru(II) complexes unusually generates redox-active Ru(III) species, mer-2a–b that contain dual reactive sites. As a result, we have explored the reactivity of these redox-active Ru(III) species with different types of boranes that demonstrate the synergetic effect of metal and redox active ligands for the activation of boranes.

Results and discussion

As shown in Scheme 1, the room temperature aerial oxidation of Ru(II) borate complexes, trans-mer-1a-b in CDCl₃ yielded green Ru(III) complexes, mer-2a-b. In order to get insight into these reactions, we have monitored the aerial oxidation of one of the molecules 1a in CDCl₃ by ¹¹B{¹H} NMR that converted to transmer-2a after 48 h. The ¹¹B{¹H} NMR spectrum shows two peaks at $\delta = 19.4$ and -43 ppm that correspond to boric acid [B(OH)₃] and the borane adduct [BH₃·PCy₃]. We believe that boric acid (H₃BO₃) has been generated from the aerial oxidation of BH₃ and the [BH3·PCy3] adduct has been generated from the reaction of released BH3 and PCy3, believed to be produced during the course of the reaction. The ¹H and ³¹P{¹H} NMR spectra show broad resonances that suggest the presence of paramagnetic species. The ESI-MS spectra show peaks at m/z881.0789 (mer-2a) and 862.9324 (mer-2b) with isotopic distribution patterns.

Single crystals for one of these species (mer-2a) appropriate for XRD analyses were grown from the slow diffusion of a CH₂Cl₂-hexane solution. The geometry of mer-2a around the Ru center is octahedral (Ma₃b₂c type) comprising two κ^2 -1,3-N,S-chelated rings along with one dangling mercaptobenzo-thiazole



Scheme 1 Conversion of ruthenium(\shortparallel) borate complexes, trans-mer-1a-b to ruthenium(\shortparallel) N,S-chelating mercapto-benzothiazole complexes, mer-2a-b.

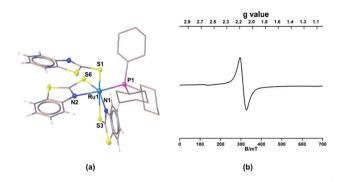


Fig. 1 Molecular structures of *mer*-2a. (a) Selected bond lengths (Å) and angles (°): Ru1–P1 2.347(2), Ru1–S1 2.278(2), Ru1–S3 2.491(2), Ru1–S6 2.342(2), Ru1–N1 2.138(6), Ru1–N2 2.164(6); N1–Ru1–S3 66.88(18), N2–Ru1–S6 68.49(18); (b) EPR spectrum of *mer*-2a.

and phosphine ligand (Fig. 1a). In the meridional form, the PPh₃ ligand is *trans* to the N atom of one of the κ^2 -N,S-mercaptobenzothiazole donor ligands. The asymmetric unit of *mer*-2a possesses a $\pi \cdots \pi$ interaction arising from the overlap of one of the κ^2 -N,S-heterodentate ligands and the dangling one (Fig. S29†). The torsion angles of the four-membered [SCNRu] rings $(1.6(6)^\circ$ and $-0.4(6)^\circ$) match well with that of *trans-mer-1a* $(0.9(4)^\circ)$. The Ru–S distances of 2.491(2) and 2.342(2) Å in the four-membered chelate rings are longer as compared to the pendant one (2.278(2) Å).

Further, to understand the nature of these species, the gas phase geometry of *mer*-2a was optimized with a doublet spin state by the DFT method with the X-ray coordinates. The computed Ru–P and Ru–S bond lengths were found to be slightly longer than the experimental values (Table S1†). The molecular orbital analysis shows that the unpaired electron typically lies on the orbital with a significant ruthenium d_{yz} -character and a smaller p_y -character of the sulfur atom of the dangling as well as κ^2 -N,S-benzothiazole ligand (SOMO, Fig. 2a). Indeed, the Mulliken spin density for the unpaired electron in *mer*-2a is located mostly on the Ru atom (+0.64) with a smaller contribution from the ligated sulfur (+0.20) atom, which is consistent with the spin density plot (Fig. 2b). The Wiberg bond indices (WBI) for Ru–S and Ru–N of 0.771 and 0.340 respectively, suggest two different types of interactions (Table S1†).

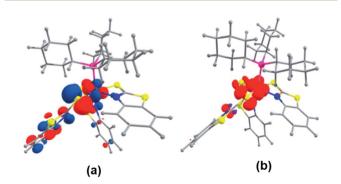


Fig. 2 (a) Calculated SOMO of mer-2a (isovalue ± 0.04 [e bohr⁻³]^{1/2}). (b) A spin density plot for mer-2a (isovalue 0.004 [e bohr⁻³]^{1/2}).

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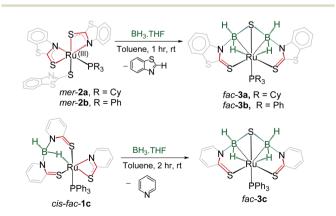
The solid-state EPR spectra of *mer*-2a and *mer*-2b at 195 K display signals with the g values of 2.116 and 2.118, respectively that confirm the presence of spin delocalization over Ru and the ligand (Fig. 1b and S7†). Although the EPR study confirms the contribution of both $[(L^-)Ru^{III}]$ and $[(L^+)Ru^{II}]$ components to the ground state, the g values of 2.116 (*mer*-2a) and 2.118 (*mer*-2b) differ from that of the organic radical. Note that the typical range of g values for Ru^{III} complexes is 2.033–2.205. Thus, this may be due to the distinctive contribution of $[(L_{NCS}^-)Ru^{III}]$ species. ^{14,18} Although the EPR spectra of any open-shell metal based paramagnetic species typically exhibit rhombohedral signals at low temperature, no observable hyperfine splitting was observed for these species due to the ¹⁴N (I = 1) nucleus. ^{19,20 α}

The UV-Vis spectra of mer-2a-b show a strong absorption band at 240 nm due to the $\pi \to \pi^*$ transitions and a weak absorption at 430 nm (Fig. S30†). By comparing the UV-Vis spectra of trans-mer-1a and mer-2a-b, shown in Fig. S9,† we presume that the broad absorption at 720 nm for mer-2a and 740 nm for mer-2b is due to the contribution of the $(L_{NCS})Ru^{II}$ organic radical in which the ligand has been reduced to the 2mercaptobenzothiazolate form $[(L_{NCS}^{-})Ru^{III} \leftrightarrow (L_{NCS}^{-})Ru^{II}].$ Note that similar systems describing amido and aminyl radical complexes of Ru(II) have recently been reported by Ghosh and co-workers.20a The TD-DFT calculations further suggest that the low energy absorption band for mer-2a corresponds to the SOMO-LUMO(β) transition (Table S5†). The redox behaviour of both trans-mer-1a and mer-2a-b species has further been supported by cyclic voltammetry (CV) studies. The cyclic voltammograms of mer-2a and mer-2b in acetonitrile show reversible waves at $E_{1/2} = -0.57$ V, $(I_{pc}/I_{pa} = 0.97)$ for mer-2a and -0.25 V $(I_{\rm pc}/I_{\rm pa}=0.98)$ for mer-2b (Fig. S8†), which are assigned to the [Ru^{II}(L')/Ru^{II}(L⁻)] redox couple.^{20a} In addition, the quasireversible waves at 0.79 V (mer-2a) and 0.87 V (mer-2b) arised due to the RuIII/RuII redox centered couple.20

The redox behaviours of mer-2a and mer-2b species were compared with those of other ruthenium complexes containing N₂P₂ or N₂S₂ ligands derived from o-phenylenediamine. For example, Mascharak and co-workers reported the cyclic voltammogram of [cis-(dppQ)RuCl₂] (dppQ = 1,2-bis-N-[2'(diphenylphosphanyl) benzoyl]benzoquinonediimine) that shows two reversible redox events at -0.28 and 0.90 V versus Fc⁺/Fc and an irreversible event at -1.35 V.^{20c} The irreversible feature at -1.35V was assigned to the ligand-centered reduction of the o-diiminosemi-quinone radical to a fully reduced o-phenylenediamine unit. The reversible wave at -0.28 V was assigned to the second ligand-centered redox event, and the reversible wave at 0.90 V was assigned to the Ru^{III/}Ru^{II} redox couple. Similarly, Daly and co-workers reported two reversible redox events at -0.78 V and −0.28 V versus Fc⁺/Fc (Ru^{II}/Ru^I and Ru^{III}/Ru^{II} redox couples) and irreversible features at -2.46 V as the ligand centered redox event.12 Therefore, based on the above results, the additional irreversible half-wave potentials, appearing at 0.46 V (mer-2a) and 0.54 V (mer-2b), have been assigned to the oxidation of the second N,S-donor mercapto-benzothiazolyl ligand.20e Nonetheless, to gain further insight into the nature of the half-wave potentials of these complexes, we performed the molecular orbital analysis of the oxidised form of *mer*-2a and *mer*-2b that shows mixing of orbitals between Ru-metal and the heterocyclic ligand (Fig. S39†). Thus, based on the DFT calculations, the assignments of the redox couples as ligand or metalcentered oxidation are unclear. We have also recorded the current vs. square root of scan rate for one of the molecules *mer*-2a and the corresponding plot (current vs. square root of scan rate) is provided in the revised ESI (Fig. S31–S33†). Note that the redox couple observed at -0.57 V shows reversible wave linearity with increasing scan rate (Fig. S32†). However, the peak current at 0.79 V is not proportional to the square root of scan rate and thus, it may be considered as a quasi-reversible wave. The peak current at 0.46 V shows an irreversible half wave.

The presence of dual reactive sites and the redox active hemilabile κ^2 -1,3-N,S-bidentate chelate ligands in mer-2a**b** encouraged us to study their reactivity with various boranes. As a result, we treated these species with an excess of BH₃·THF that resulted in the formation of yellow 3a and 3b with 38% and 42% yields, respectively (Scheme 2). Both the complexes were characterized by ¹H and ¹³C{¹H} NMR, IR spectroscopy, and single crystal X-ray diffraction studies. The 11B{1H} NMR spectra of both the complexes feature a single resonance at δ –11.5 and δ -10.1 ppm, respectively for 3a and 3b. The ¹H NMR spectra show the presence of the mercaptobenzothiazole ligand in the region of δ 7.87–7.26 ppm. In addition, two broad resonances, appearing at δ 2.97 and -14.43 ppm for 3a and 3.01 and -13.24ppm for 3b, have been assigned to B-H and Ru-H-B hydrides. The broad ¹H chemical shifts were resolved into a doublet and an apparent triplet upon ¹¹B decoupling (${}^{2}J_{HP} = 14.1 \text{ Hz}, {}^{2}J_{HH} =$ 14.1 Hz (3a); and ${}^{2}J_{HP} = 12.0$ Hz, ${}^{2}J_{HH} = 12.0$ Hz (3b). These NMR signatures indirectly ensure that the hydride is cis oriented to the phosphine ligand. The ³¹P{¹H} NMR revealed a singlet at δ 71.0 for 3a and 60.9 ppm for 3b. The mass spectra showed a molecular ion peak at m/z 772.1165 for 3a and 776.9636 for 3b. Based on all the spectroscopic data along with mass spectrometric data, it was clear that both the species are diamagnetic. However, a clear explanation eluded us until the single-crystal X-ray diffraction analysis of one of these species 3a was performed.

The solid-state X-ray structure of 3a, shown in Fig. 3a, displays a symmetrical structure with C_s symmetry, wherein the



Scheme 2 Reactivity of mer-2a-b and cis-fac-1c with BH₃·THF.

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P1

S1

Ru1

S3

H1B

H2B

H2B

H3B

N2

B2

S1

Ru1

H3B

S2

S1

Ru1

N1

S2

(a)

(b)

Fig. 3 Molecular structures of *fac*-3a (a) and *fac*-3c (b). Selected bond lengths (Å) and angles (°): *fac*-3a (a) Ru1-B2 2.276(2), Ru1-B1 2.293(3), Ru1-P1 2.307(6), Ru1-S1 2.384(6), Ru1-S3 2.383(6), Ru1-S5 2.4184(6), Ru1-H1B 1.69(3), Ru1-H2B 1.69(3), B2-Ru1-B1 75.66(9), B2-Ru1-S5 48.08(7); *fac*-3c (b) Ru1-B2 2.285(4), Ru1-B1 2.281(4), Ru1-P1 2.2830(9), Ru1-S1 2.3611(8), Ru1-S3 2.3535(9), Ru1-S2 2.4090(9), Ru1-H2B 1.63(3), Ru1-H3B 1.66(3), B2-Ru1-B1 77.74(14), B2-Ru1-S5 48.17(10).

mirror plane of symmetry passed through the S5-Ru1-P1. The ruthenium center adopts an octahedral geometry in the facial form in which the phosphine ligand is present in trans to the sulfur atom. Thus, we believe that complex 3a, now fac-3a, is generated from the insertion of two BH2 moieties across the initial Ru-N bonds of κ^2 -N,S-chelated heterocycles. The S atom in the butterfly core is presumably generated from the C-S bond cleavage of the pendant mercaptobenzothiazole ligand. To validate this concept, we have monitored the reaction of mer-2a with $BH_3 \cdot THF$ by $^{13}C\{^1H\}$ and 1H NMR spectroscopy in toluened₈. The ¹³C{¹H} NMR spectrum (after 2 h) shows chemical shifts in the range of $\delta = 149-134$ ppm that correspond to the benzothiazole ligand. On the other hand, the ¹H chemical shift at $\delta = 9.4$ ppm corresponds to the C–H proton of the benzothiazole ligand.21 Thus, we firmly believe that the source of sulphide for the formation of 3a or 3b is the mercapto-benzothiazole ligand. Note that recently Wang and co-workers reported a similar type of reaction that yielded the Mo(II)hydride complex, [Cp*MoH(1,2-Ph₂PC₆H₄SBH₂)] in which a BH₂ moiety is coordinated with the Mo-S bond.²² The BH₂ moieties in fac-3a and fac-3b are further stabilized by one sulfur atom (S5, fac-3a), generating two unique five-membered RuBNCS ruthenacycles, which are fused by one {RuB₂S} butterfly unit. The average Ru-B distance (2.284 Å) in fac-3a is comparable with the bond lengths of 2.266(8) Å and 2.216(6) Å observed in [RuH(PCy₃)₂{(μ-H)₂-BMeCH₂SMe $\}$]²³ and [Cp*Ru(μ -H)₂B(NC₇H₄S₂)],²⁴ respectively. Similarly, the average B-S bond distance of 1.917 Å is consistent with borane-thiolate species that typically fall in the range of 1.949-1.911 Å.25 The DFT analysis further established that the borane activation across the Ru-N bond is more favourable than the Ru-S bond with a lower energy of 50.2 kcal mol⁻¹. This has also been supported by NBO analysis, where the Wiberg bond index of Ru-S (0.771) is significantly stronger than that of Ru-N (0.340) (Table S1†).

The meridional and facial orientations of all the complexes have been assigned largely based on the coordination of hydride

and phosphine ligands to metal. The coordination modes were established in comparison with the $J_{\rm PH}$ coupling constants of similar molecules. ^{14,23,26a} For example, the ¹H NMR spectrum of trans–mer-1b shows a broad hydride peak at $\delta=-3.71$ ppm that converted to a doublet of doublet upon ¹¹B decoupling ($^2J_{\rm HP}=33.1$ Hz, $^2J_{\rm HH}=16.4$ Hz). This indirectly suggests that the hydride is trans to the phosphine ligand, and all mercaptobenzothiazole sulfurs are arranged in the meridional fashion (Fig. S10†). However, in facial-orientation, the broad hydride peak at $\delta=-13.24$ ppm transformed to an apparent triplet with coupling constants $^2J_{\rm HP}=12.0$ Hz and $^2J_{\rm HH}=12.0$ Hz. This is due to the presence of the adjacent cis-oriented phosphine group in which the mercaptobenzothiazolyl sulfur coordinated facially. ^{26b,c}

Note that analogous fac-3c, $[PPh_3Ru\{\kappa^3-H,S,S'-(NH_2BSBH_2)\}]$ N)(SC₅H₄)₂}] was synthesized as a yellow crystalline solid from the room temperature reaction of $[\{\kappa^3-H,S,S'-H_2B(SNC_5H_4)_2\}Ru$ $\{\kappa^2 - N, S - (SNC_5H_4)\}PPh_3\}^{27}$ cis-fac-1c and $BH_3 \cdot THF$ (Scheme 2). Complex fac-3c was characterized by comparing its spectroscopic data with the mass spectrometric data of fac-3a-b that show a molecular ion peak at 642.0321, and a solid-state X-ray diffraction analysis. The ¹¹B{¹H} NMR spectrum shows a sharp peak in the upfield region $\delta = -3.8$ ppm. The ¹H NMR spectrum of fac-3c displayed an upfield resonance at $\delta = -12.27$ ppm due to the Ru-H-B proton. This broad ¹H chemical shift was resolved into an apparent triplet upon 11B decoupling with coupling constants ${}^{2}J_{HP} = 13.1$ Hz and ${}^{2}J_{HH} = 13.1$ Hz. The solid-state X-ray structure of fac-3c, shown in Fig. 3b, shows a butterfly core containing the S atom similar to that of fac-3a. The S atom in the butterfly core has presumably been generated from the C-S bond cleavage of the pendant mercaptopyridyl ligand. Further, to get some insight into the reaction intermediates, we have monitored the reaction of cis-fac-1c with BH₃-·THF using ¹H and ¹³C NMR in toluene-d₈. The ¹³C{¹H} NMR spectrum (after 2 h) shows chemical shifts in the range of δ = 134-148.6 ppm that correspond to free pyridine. On the other

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hand, the 1H chemical shift at $\delta=8.68$ ppm corresponds to the C–H proton of the pyridine ligand. 28

To have a further understanding of the MLC binding effect in 1,3-N,S-chelated ruthenium complexes, the electrochemistry of fac-3a-b was studied (Fig. S8†). The single quasi-reversible redox observed at $E_{1/2}=0.59$ V (fac-3a) and 0.62 V (fac-3b) assigned to the Ru^{III}/Ru^{II} redox couple indicates that the MLC reduces the electrochemical activity of fac-3a-b when compared with trans-mer-1a-b and mer-2a-b species. As there exists no equilibrium between fac-3a-b and mer-2a-b under an applied potential (loss of BH₃), we believe that the cooperativity with two BH₃ units in fac-3a-b is stronger as compared to trans-mer-1a-b.

The NBO and QTAIM analyses show the coordination of BH₂ with S and Ru atoms. As shown in Fig. 4a-d, it is evident that one of the B-H bonds donates electron density to the Ru center and the S donates a lone pair of electrons to Ru. This was further supported by natural charge analysis that indicates positive natural charges both at S and B atoms ($q_B = 0.029$, $q_S = 0.026$). Thus, it is apparent that S and B act as donors and the Ru center $(q_{\rm Ru} = -0.429)$ can be considered as an acceptor. The Wiberg bond indices (WBI) of 0.984 and 0.979 with regard to B1-S5 and B2-S5 bonds support strong bonding interactions. The HOMO−2 of *fac-*3a, shown in Fig. 4c, suggests that the electron density is mostly localized on the B-S-B moiety and Ru center. Further, topology analysis of fac-3a reveals the presence of B-S, B-H, Ru-H and Ru-S bond critical points (BCPs) and ring critical points (RCPs). The topological features at BCPs of Ru-H, Ru-S and Ru-P bonds are characterized as dative interactions (Fig. 4d and Table S4†).

With the conditions for the formation of *fac*-3**a**-**c** in hand, reactivity of *mer*-2**a**-**b** with bulky borane such as mesityl borane

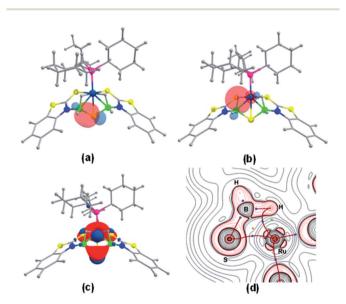
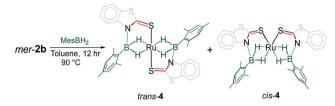


Fig. 4 Natural bond orbital interaction between the B–S bond (a) and the B–H–Ru bond (b) in fac-3a (isovalue ± 0.04 [e bohr⁻³]^{1/2}); (c) HOMO–2 of fac-3a; (d) contour-line map of the Laplacian of the electron density in the Ru–S–H plane of fac-3a. BCPs and RCPs correspond to blue and orange dots and red lines indicate bond paths.



Scheme 3 Reactivity of mer-2b with mesityl borane.

(H₂BMes) became of interest. Although the reaction of mer-2a with H₂BMes resulted in decomposition of the starting material over time, mild thermolysis of mer-2b with a stoichiometric amount of mesityl borane in toluene resulted in the formation of complex 4. Thin-layer chromatographic workup allowed us to isolate pure 4 as a yellow crystalline solid in 45% yield, which was characterized by multinuclear NMR and IR spectroscopic methods (Scheme 3). The ¹¹B{¹H} NMR spectrum of 4 shows two broad resonances at δ 39.4 and 31.2 ppm. In addition to ${}^{1}H$ chemical shifts for the mercaptobenzo-thiazolyl ligand, the ¹H NMR spectrum of 4 shows three up-field chemical shifts at δ -11.42, -10.41 and -10.01 ppm. The mass spectrum shows a molecular ion peak at m/z 698.0799. The $^{31}P\{^{1}H\}$ NMR shows the presence of no ³¹P chemical shift. All the spectroscopic data along with mass spectrometric data suggest 4 as a mixture of two Ru-borate species. However, the identity was unclear until an X-ray crystallographic analysis was carried out for one of them.

A slow evaporation of a $\rm CH_2Cl_2/hexane$ solution of 4 at -5 °C yielded two different types of crystals. The X-ray diffraction analysis was performed on a yellow crystal which was manually picked up from the Schlenk tube. The solid-state X-ray structure of this yellow crystal, shown in Fig. 5, shows a distorted-octahedral geometry in which four hydrogen atoms are placed in a square plane and two S atoms occupy the axial positions. This clearly shows that two units of $\rm H_2BMes$ have been inserted into two Ru–N bonds of κ^2 -N,S-chelated ligands of mer-2b resulting

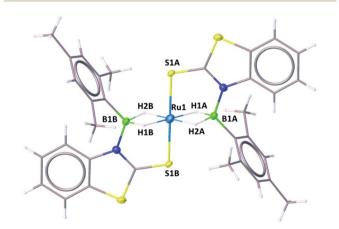


Fig. 5 Molecular structures of *trans*-4. Selected bond lengths (Å) and angles (°): Ru1–B1A 2.172(4), Ru1–S1A 2.3221(10), B1–N1 1.542(5), B1–C1 1.580(5), B1–Ru1–B1 180.0(2), B1–Ru1–S1 95.86(11), S1–Ru1–S1 180.0, C1–B1–Ru1 127.2(3).

in the formation of two five-membered Ru–B–NCS ruthenacycles. Interestingly, the geometry of this crystal has an inversion center on Ru. Thus, this molecule can be defined as *trans*- $[Ru\{\kappa^3-S,H,H-(NBH_2Mes)(S_2C_7H_4)\}_2]$ (*trans*-4).

Although we failed to get single crystals for the other species, all the spectroscopic data and mass spectrometric data clearly suggest the presence of both *trans-4* and *cis-4* species. For the *trans-4* isomer (C_{2h} symmetry) the 11 B chemical shift at $\delta=39.4$ ppm has been assigned to two equivalents of boron atoms and the 1 H chemical shift at $\delta=-11.42$ ppm has been assigned to four Ru–H–B protons which are in an equivalent environment. However, for the *cis-4* (C_{2V} symmetry), the 11 B chemical shift at

 $\delta=31.2$ ppm is due to the presence of two equivalents of boron. The two broad 1 H chemical shifts at $\delta=-10.41$ and $\delta=-10.01$ ppm for the Ru–H–B protons emanate from the presence of two different groups opposite to the hydrogen atom. Two Ru–H–B protons are *trans* to mercaptobenzothiazolyl sulphur and other two Ru–H–B protons are *trans* to each other (Fig. S26†).

As listed in Table 1, the Ru–B distance of 2.172(4) Å for *trans*-4 is consistent with that of the bis(dihydroborate) complex, Ru $[(\mu-H)_2 \text{ BC}_8H_{14}]_2(\text{PCy}_3)^{29}$ (2.160(2) Å) and other reported dihydroborate species.^{29–33} The Ru–B distances in *trans*-4 fall in the range of 2.103(2)–2.266(8) Å, ¹⁵ which are significantly longer as compared to those of σ -borane complexes, for example,

Table 1 Selected spectroscopic and structural parameters of transition metal bis-(dihydroborate) complexes and cis-4 and trans-4

	Spectroscopic parameters (ppm)		Structural parameters (Å)		
Bis-(dihydroborate)	¹ H(Ru–H)	$^{11}B\{^1H\}$	d[M-B]	d[M-H]	Ref.
IMes H + H B /Pr IMes	-15.50, -5.83	37.9	2.088(5)	1.85(12)	29a
PCy ₃ H B-Mes PCy ₃	-11.26, -6.10	58.0	1.938(4)	1.61(3), 1.59(3), 1.73(3), 1.77(3)	29b
Cy ₃ P H H H Ph ₂ P H B-N'Pr ₂	-13.22, -8.58, -6.71, -1.00	35.5	2.173(3)	1.59(3), 1.69(3), 1.49(3), 1.97(3)	33
Cy ₃ P H H Ph ₂ P CH ₃	-11.58, -6.29	46.0	-	_	33
Mes H Ru H B Mes	-11.42	39.4	2.172(4)	1.60(4), 1.62(4)	This work
Mes H H N	-10.41, -10.01	31.2	_	_	This work
NBB H BBN	-12.43	58.8	2.160(2), 2.085(2)	1.63(2), 1.66(2), 1.60(2), 1.63(2)	30
Bpin PCy ₃ H Ru H B PCy ₃	-11.4, -8.03, -7.13	37.3	2.157(5), 2.188(5)	1.48(3), 1.58(3), 1.49(3), 1.55(3)	31
H ₂ B H H H H H H H H H H H H H H H H H H H	-14.57, -5.78	11.9, 40.8	2.048(9), 2.333(9)	1.615, 1.629, 1.843, 1.860	32

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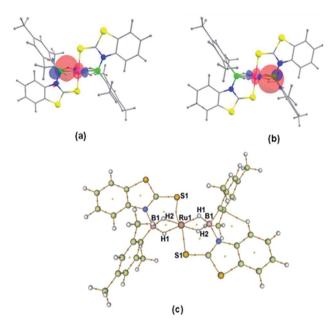


Fig. 6 (a and b) Donor–acceptor interaction between B–H and the Ru atom obtained by NBO analysis of *trans-4*. (c) QTAIM analysis of *trans-4*. Bond paths are indicated by yellow lines and BCPs and RCPs are represented by orange and yellow dots respectively.

[Ru(PCy₃)₂(H)₂(BH₂Mes)]^{29b} (1.938(4) Å) and [Cp*Ru(PⁱPr₃)(-BH₂Mes)]B(C₆F₅)₄ (ref. 34) (1.921(2) Å). The B1–Ru1–B1 angle of 180.0(2)° shows a perfect symmetrical coordination of borane to the metal center, unlike tetrahydroborate species, [PBP](μ-H)₂Ru(η^2 -BH₄)]³² (177.4(4)°) and Ru[(μ-H)₂BC₈H₁₄]₂(PCy₃)³⁰ (147.68(8)°). The WBI of 0.369 for the Ru–B bonds of *trans*-4 also supports symmetrical interaction (Table S1†). The analysis further suggests that the *trans*-isomer is thermodynamically more stable in which the relative total energy for the *trans*-4 isomer is 0.46 kcal mol⁻¹ lower than that of the *cis*-4 isomer. The donor–acceptor interaction between the B–H bond and Ru is confirmed by second-order perturbation analysis with a stabilization energy of 11.34 kcal mol⁻¹ (Fig. 6a and b). Although the QTAIM analysis shows all the BCPs in *trans*-4, it can't identify the interaction between Ru and B (Fig. 6c).³⁵

Although mesityl borane, H₂BMes, has been accessible since 1994, 36 structurally characterized species, other than borylene complexes, are very limited.37 For example, the first ruthenium terminal borylene complex, [Ru(BMes)(PCy₃)₂], was synthesized by double B-H activation of H2BMes.37a Recently, Hayes and coworkers have isolated and structurally characterized the Rhborylene complex^{37b} from the rhodium pincer complex, $[(^{iPr}NNN)Rh(CO)]$ $(^{iPr}NNN) =$ $2,5-[^{i}Pr_{2}P=N(4-^{i}PrC_{6}H_{4})]_{2} N(C_4H_2)^{-1}$ and H_2B -Mes by reversible dehydrogenation of H₂BMes. Interestingly, not many examples are known where the addition of H₂BMes occurred in a κ²-coordination fashion into the polar M-L bonds.76,17,38 Some of the dihydroborate species, for example, $[Cp*Ru(\kappa^3-P,H,H-(^iPr)P(C_9H_6O-H_2BMes)]^{38}$ and $[M_6O-H_2BMes)^{-1}$ $\{\kappa^3-N,H,H-Xyl(N)P(OH_2 \text{ BMes})(OEt)_2\}(\eta^4-COD)\}$ (M = Rh and Ir), that have been isolated from the insertion of H₂BMes into the corresponding M-O bonds. The first bis(σ -borane) species,

[Ru(PCy₃)₂(H)₂ (η^2 : η^2 -BH₂Mes)], was reported by Sabo-Etienne and Alcaraz, isolated from the reaction of H₂BMes and [RuH₂ (PCy₃)₂(η^2 -H₂)₂].^{29b}

Conclusions

In summary, we have developed some redox-active complexes supported by hemilabile κ^2 -N,S-chelated ruthena-cycles that undergo unusual dual site B–H bond activation with free and bulky boranes. When the reaction was carried out with free borane, one of the B–H bonds of the BH $_3$ unit cleaved and the rest of the BH $_2$ moiety was captured by the Ru–N bond that led to two five-membered (RuBNCS) ruthenacycles. In contrast, bulky borane mesitylborane generated trans and cis species, in which two H $_2$ BMes units are coordinated to the Ru center. A combined experimental and theoretical study shows that a combination of redox-active ligands and metal–ligand cooperativity has a major role in multisite borane activation for smaller and bulky boranes.

Data availability

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC-1875697 (*mer*-2a), CCDC-1984218 (*fac*-3a), CCDC-2126931 (*fac*-3c), CCDC-2040802 (*trans*-4). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk/data_request/cif.

Author contributions

M. Zafar, A. Ahmad and S. Saha have executed the experimental synthesis, characterization, and analysis of the data. R. Ramalakshmi has conducted the theoretical calculations. All authors have contributed to the preparation of the manuscript. S. Ghosh has supervised the project.

Conflicts of interest

There are no conflicts to declare.

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