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Syntheses and characterization of new (pyrazolato)(pyrazole) rutheniums with κ^3-polypyrazolylborates: Halogeno-anion binding through the tris(pyrazole) moiety

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Abstract

(Polypyrazolylborato)(benzonitrile) ruthenium(II) complexes $[RuCl\{BR(pz)_3\}(PhCN)_2]$ (R = pz, H; pz = pyrazol-1-yl), prepared from *trans*-$[RuCl_2(PhCN)_4]$ and $K[BR(pz)_3]$, were allowed to react with potassium 3,5-dimethyl-substituted polypyrazolylborate salt $K[BH(3,5\text{-}Me_2pz)_3]$, and gave (pyrazolato)(pyrazole) species of $[Ru\{BR(pz)_3\}(3,5\text{-}Me_2pz)(3,5\text{-}Me_2pzH)_2]$ {R = pz (**1**), H (**2**)}, respectively. Upon protonation with $HBF_4(Et_2O)$, the species **1** was converted to a fairly stable tris(pyrazole) derivative $[Ru\{B(pz)_4\}(3,5\text{-}Me_2pzH)_3]BF_4$ (**3**), which worked as a novel halogeno-anion receptor. Moreover, the complex $[RuCl_2(PhCN)_4]$ was treated with $K[BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3]$ in the presence of 3,5-dimethyl-4-bromopyrazole, 3,5-Me_2-4-BrpzH, to afford $[Ru\{BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3\}(3,5\text{-}Me_2\text{-}4\text{-}Brpz)(3,5\text{-}Me_2\text{-}4\text{-}BrpzH)_2]$ and $[Ru\{BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3\}(3,5\text{-}Me_2\text{-}4\text{-}Brpz)(3,5\text{-}Me_2\text{-}4\text{-}BrpzH)(PhCN)]$. Single-crystal X-ray structural analyses were carried out for **1**, **3** · $CHCl_3$, $[Ru\{B(pz)_4\}(3,5\text{-}Me_2pzH)_2(OH_2)]O_3SC_6H_4CH_3 \cdot CH_3OH$, and $[RuCl\{B(pz)_4\}(3,5\text{-}Me_2pzH)_2] \cdot CHCl_3$.

Keywords: Ruthenium; Polypyrazolylborate; Halogeno anion receptor; Pyrazole; Supramolecule

1. Introduction

Polypyrazolylborate anions $[BR(pz)_3]^-$ (pz = pyrazol-1-yl) have been used as versatile supporting ligands for a wide range of transition- and rare earth-metal complexes [1]. Wide-spread considerable attention paid to the anionic tridentate κ^3-$BR(pz)_3$ coordination stems probably from their comparison with the well-known η^5-cyclopentadienyl family [1a–3]. As part of our objectives in developing new (κ^3-polypyrazolylborato)ruthenium chemistry [4], we have prepared some half-sandwich-type complexes, involving $[RuCl\{BR(pz)_3\}(PhCN)_2]$ and $[RuCl_2\{BR(pz)_3\}(NO)]$ (R = pz, H). Stable half-sandwich rutheniums with mono (κ^3-polypyrazolylborate) contain mostly some auxiliary ligands with competent capabilities in stabilization of the complexes, such as organo nitrile and nitrosyl ligands in

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Abbreviations used in this paper: The group 3,5-Y_2pz represents a pyrazol-1-yl group with Y substituents at its 3- and 5-positions; The 3,5-Y_2-4-Xpz indicates additional substitution of X at the 4-position of the 3,5-disubstituted group. Their neutral pyrazole molecules are expressed as 3,5-Y_2pzH and 3,5-Y_2-4-XpzH, respectively. General expression of tridentate polypyrazolylborate ligands and their substituted ones, ligating triply via 2-N nitrogen atoms of the groups, are abbreviated simply as $BR(pz)_3$ and $BR(pz^*)_3$, respectively, and those in other coordination modes are shown in appropriately specified forms, such as κ^2-*N*,*N*′-$BR(pz)_3$ for the bidentately coordinated $BR(pz)_3$ via two pyrazolyl nitrogen atoms.

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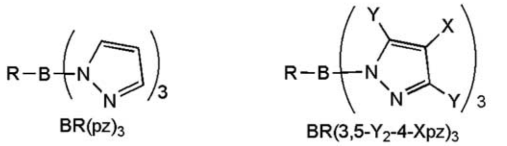

$[Ru\{BR(pz)_3\}(3,5\text{-}Me_2pz)(3,5\text{-}Me_2pzH)_2]$ (**1**, R = pz; **2**, R = H)
$[Ru\{B(pz)_4\}(3,5\text{-}Me_2pzH)_3]BF_4$ (**3**)
$[Ru\{B(pz)_4\}(3,5\text{-}Me_2pzH)_2(OH_2)]OTs$ (**4**)
$[RuCl\{B(pz)_4\}(3,5\text{-}Me_2pzH)_2]$ (**5**)
$[Ru\{BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3\}(3,5\text{-}Me_2\text{-}4\text{-}Brpz)(3,5\text{-}Me_2\text{-}4\text{-}BrpzH)_2]$ (**6**)
$[Ru\{BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3\}(3,5\text{-}Me_2\text{-}4\text{-}Brpz)(3,5\text{-}Me_2\text{-}4\text{-}BrpzH)(PhCN)]$ (**7**)

Chart 1.

our cases [4] and tertiary phosphines, carbonyl, π-arene aromatics, and many types of polydentate chelate ligands described in the literatures [1]. As examples without these competent auxiliary ligands, in contrast to the well-known halo(η^5-pentamethylcyclopentadienyl)rutheniums $[Ru(Cp^*)X_n]_m$ (X = Cl, Br, I) [3], the corresponding halo(κ^3-polypyrazolylborato)ruthenium analogs have not been afforded so far. Moreover, it also seems to be noteworthy that only a few ruthenium complexes have been described, with polypyrazolylborates substituted at 3-positions of their metal-linking pyrazolyl groups [4c–6], in spite of many researches [1,7] of modified electro- and stereochemical properties of analogous polypyrazolylborato complexes with other metal ions. In this paper, we report the syntheses and characterization of a few (pyrazolato)(pyrazole) ruthenium(II) complexes with κ^3-polypyrazolylborate systems, $BR(pz)_3$ (R = pz, H) and $BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3$ [8], and also halogeno-anion trapping function [9] of a tris(pyrazole) derivative with the $B(pz)_4$ system (See Chart 1).

2. Results and discussion

2.1. Formation of (pyrazolato)(pyrazole)rutheniums and halogeno-anion incorporation with the tris(pyrazole) moiety

Reactions of the benzonitrile complex *trans*-$[RuCl_2(PhCN)_4]$ with an equimolar quantity of unsubstituted polypyrazolylborate salts, $K[BR(pz)_3]$ (R = pz, H), in refluxing dichloromethane afforded half-sandwich species of $[RuCl\{BR(pz)_3\}(PhCN)_2]$ [4]. As preliminarily communicated [10], these half-sandwich species have been converted to hetero sandwich derivatives $[Ru\{BR(pz)_3\}\{BR'(pz')_3\}]$ by further treatment with other polypyrazolylborate anions $BR'(pz')_3$ free from substitution at the 3-position of the pz′ group, and the sandwich complexes have demonstrated their utility in the evaluation of electrochemical properties of the respective polypyrazolylborato ligands.

As one extension, the half-sandwich complexes $[RuCl\{BR(pz)_3\}(PhCN)_2]$ were treated with an equimolar amount of $K[BH(3,5\text{-}Me_2pz)_3]$ for the preparation of the sandwiches $[Ru\{BR(pz)_3\}\{BH(3,5\text{-}Me_2pz)_3\}]$ retaining 3-Me substituents, but separated yellowish green powdery products were found to be (pyrazolato)(pyrazole) species $[Ru\{BR(pz)_3\}(3,5\text{-}Me_2pz)(3,5\text{-}Me_2pzH)_2]$ (**1**) and (**2**) with pz and H as R, respectively. Coordination structure of **1** was crystallographically disclosed (Fig. 1). Bond cleavages between boron and 1-N nitrogen atoms in polypyrazolylborate anions have been observed in the course of their reactions with some transition- and rare earth-metal compounds [4c,11,12]. In solution state, each NMR spectrum of these products showed spectroscopic equivalence of three metal-linking pz groups in the $BR(pz)_3$ moiety and also of one $3,5\text{-}Me_2pz$ and two $3,5\text{-}Me_2pzH$ ligands, indicating that two NH protons in the $(3,5\text{-}Me_2pz)(3,5\text{-}Me_2pzH)_2$ part are moving fast on the three non-ligating nitrogen atoms (Fig. 2(a)).

(Pyrazolato)bis(pyrazole)ruthenium moieties in solution state were presumed to retain a trigonal prism-like conformation compelled by intra-molecular hydrogen bonding between pyrazolato and pyrazole ligands (Fig. 2(a)). This motivated us to the study of protonation and deprotonation properties of the moieties as a proton pool. Treatment of the complex **1** in $CDCl_3$ with an equimolar quantity of HBF_4 (Et_2O) changed two ^1H NMR signals of the pyrazolyl methyl groups at δ 2.46 and 0.77 to those at δ 2.54 and 1.16, respectively. Significant lower-field shift of the latter signal is especially noteworthy, and was probably associated with the NH-neighboring 5-Me protons in the

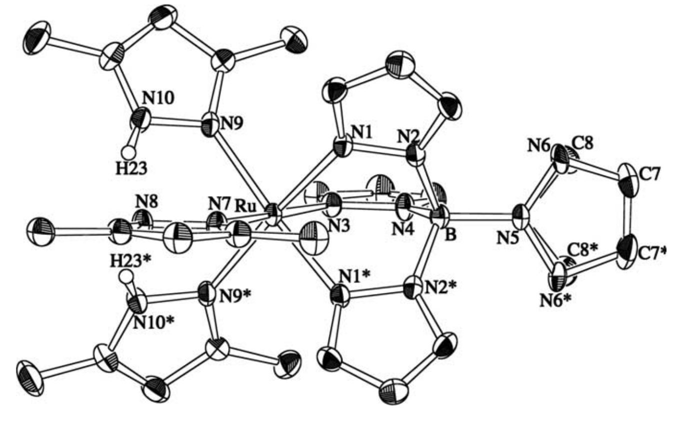

Fig. 1. ORTEP drawing of **1** with 30% probability thermal ellipsoids and atom labels only for important atoms. Hydrogen atoms are omitted for clarity, except NH protons. Selected bond lengths and inter-atomic distances (Å): Ru–N(1) 2.041(3), Ru–N(3) 2.048(4), Ru–N(7) 2.125(4), Ru–N(9) 2.120(3), Ru–B 3.126(5), N(8)–N(10) 2.707(4), N(10)–N(10*) 3.411(6).

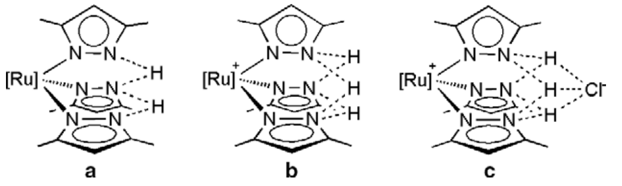

Fig. 2. (Pyrazolato)(pyrazole) and its related derivative species of ruthenium. (a) (pyrazolato)bis(pyrazole) species; (b) tris(pyrazole) species; (c) chloride anion incorporated species.

Ru(3,5-Me_2pzH)$_3$ moiety of the mono-protonated species [Ru{B(pz)$_4$}(3,5-Me_2pzH)$_3$]BF_4 (**3**). A broad signal at δ 10.4 was observed with 3H integral, assignable to NH protons of the moiety. In addition, orange crystals of **3** · $CHCl_3$ were precipitated and confirmed to be the mono-protonated species **3** as formulated above, by a single-crystal X-ray structural analysis (Fig. 3). When further treatment of **3** was performed with another equimolar amount of HBF_4 (Et_2O), we could not isolate any generated species in a pure state, but ^{1}H NMR signals ($CDCl_3$) of the uncoordinated pz ring protons in the B(pz)$_4$ ligand changed from a set of δ 6.76, 8.11, and 8.32 to a new one of δ 7.14, 8.48, and 8.97. Remarkable lower-field shifts of these signals probably indicated additional protonation of the 2-N nitrogen in the uncoordinated pz group. Addition of more quantities of HBF_4 (Et_2O) gave rise to decomposition of the B(pz)$_4$ fragment, probably generating some (pyrazole)ruthenium species on the basis of ^{1}H NMR spectra.

As for similar mono-protonation of the BH(pz)$_3$ analogue **2**, the corresponding methyl signals in its ^{1}H NMR spectra ($CDCl_3$) showed only slight shifts from δ 2.53 and 0.74 to δ 2.49 and 0.88, respectively, and the ^{11}B NMR doublet ($J_{BH} = 79$ Hz) at δ −22.3 for the BH part disappeared apparently. In this case, the corresponding tris(pyrazole) species was not generated, and these findings were probably associated with other reaction proceedings of HBF_4 (Et_2O) with the BH part, rather than protonation of the pyrazolato ligand 3,5-Me_2pz to form the expected tris(pyrazole) moiety.

On the other hand, the complex **1** was also treated with an equimolar amount of *p*-toluenesulfonic acid monohydrate (TsOH · H_2O) in place of HBF_4 (Et_2O), and crystallization of the reaction mixture gave orange-colored crystals of [Ru{B(pz)$_4$}(3,5-Me_2pzH)$_2$(OH_2)]OTs (**4**). Structure of **4** was crystallographically characterized as shown in Fig. 4, and confirmed dissociation of one 3,5-Me_2pzH molecule. Moreover, it is noted that deprotonation experiments of **1** and **2** were attempted by use of [NEt_4]OH (CH_3OH) in a molar ratio of 1/1, but obvious results were not attained satisfactorily.

Concerning the fairly stable complex **3** (Fig. 2(b)), tris(pyrazole)ruthenium moiety with three NH protons led us to the study of its halogeno anion binding functionality [9,13]. Phosphonium salts [PPh_4]X (X = Cl, Br, I) were added to dichloromethane and deuterated chloroform solutions of **3**, and some precipitates of moderately insoluble [PPh_4]BF_4 were removed for liquid-state spectroscopic observation. Fig. 5 exhibits IR spectral change by the increase in the quantity of the added [PPh_4]Cl, in the region of ca. 2550–4000 cm^{-1}. Upon the successive increase in the [PPh_4]Cl quantity by the increment of 1/4 mole relative to **3**, IR absorption band at 3226 cm^{-1} grew strong, and the band at 3424 cm^{-1} was decreased to disappear finally. The former band was the ν(NH) for the tris(pyrazole)ruthenium moiety with three NH parts holding up the chloride anion through NH···Cl$^-$ hydrogen-bonding (Fig. 2(c)), and the latter band was attributed to the one for the moiety without the anion binding. Addition of only equimolar quantity of [PPh_4]Cl was enough for apparently complete conversion from **3** to "{(pz)B(pz)$_3$}Ru(3,5-Me_2pzH)$_3$Cl", demonstrating a high affinity for the chloride incorporation.

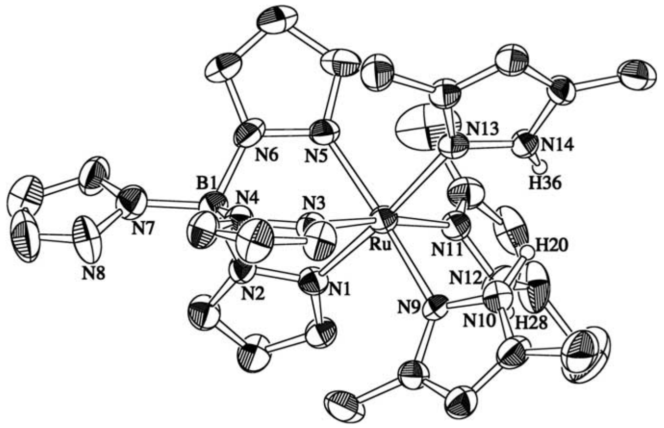

Fig. 3. ORTEP drawing of molecular cationic part of **3** · $CHCl_3$ with 30% probability thermal ellipsoids and atom labels only for important atoms. Hydrogen atoms are omitted for clarity, except NH protons. Selected bond lengths and inter-atomic distances (Å): Ru–N(1) 2.045(6), Ru–N(3) 2.052(6), Ru–N(5) 2.047(7), Ru–N(9) 2.126(6), Ru–N(11) 2.150(7), Ru–N(13) 2.131(6), Ru–B(1) 3.153(9), N(10)–N(12) 3.48(1), N(10)–N(14) 3.07(1), N(12)–N(14) 3.57(1).

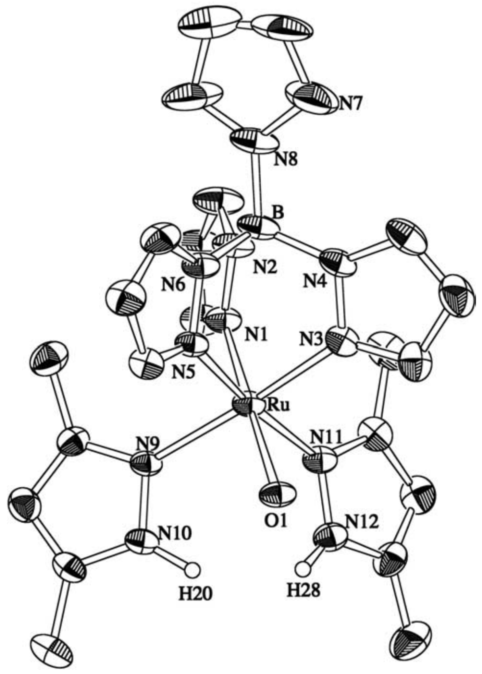

Fig. 4. ORTEP drawing of molecular cationic part of **4** · CH_3OH with 30% probability thermal ellipsoids and atom labels only for important atoms. Hydrogen atoms are omitted for clarity, except NH protons. Selected bond lengths and inter-atomic distances (Å): Ru–N(1) 2.007(4), Ru–N(3) 2.044(4), Ru–N(5) 2.038(4), Ru–N(9) 2.108(4), Ru–N(11) 2.111(4), Ru–O(1) 2.159(3), Ru–B 3.121(6), N(10)–O(1) 3.026(5), N(12)–O(1) 3.002(5).

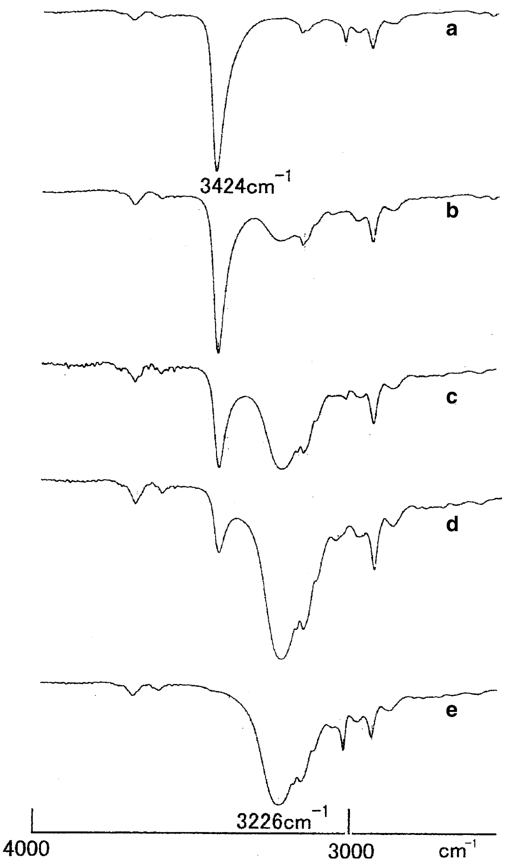

Fig. 5. IR spectral change of **3** in $CDCl_3$ by the increase in the $[PPh_4]Cl$ quantities added (a) complex **3**; (b) **3** with 1/4 mole of $[PPh_4]Cl$; (c) **3** with 2/4 mole of $[PPh_4]Cl$; (d) **3** with 3/4 mole of $[PPh_4]Cl$; (e) **3** with 4/4 mole of $[PPh_4]Cl$.

Although IR spectral change has not been regarded as a reliable signal for halogeno anion sensing [14], Fig. 5 displays the extent of captured chloride anion distinctly. Moreover, addition of $[PPh_4]X$ (X = Br, I) in $CDCl_3$ brought about new IR band growth at 3258 and 3261 cm^{-1}, respectively, certifying analogous binding toward these X^- anions. Incorporation of halogeno anions would also be supported by ^1H NMR signal shifts of the methyl groups in the $(3,5\text{-}Me_2pzH)_3$ moiety; the signals were observed at δ 2.57 and 0.62 for Cl^-, δ 2.54 and 0.81 for Br^-, and δ 2.52 and 0.97 for I^-, respectively. It is noted that a mixture of **1** with the equimolar HCl (Et_2O) demonstrated the same IR and NMR signal patterns as those obtained by treatment of **3** with $[PPh_4]Cl$. Thus, the present system is a new example for the halogeno anion incorporation with the tris(pyrazole) moieties, additionally to the preceding examples; "$\{HB(3,5\text{-}Me_2pz)_3\}Pb(3,5\text{-}Me_2pzH)_3Cl$" [13a], "$[\{HB(3\text{-}^tBupzH)_3\}Cl]AlCl_4$" [13b], and "fac-$[Re(CO)_3(pzH)_3]Cl$" [14].

In order to reveal the structural characteristics of the tris(pyrazole) frame with captured halogeno anions through its three NH parts, we attempted to grow their single crystals for X-ray structural analyses. For example, the complex **3** was mixed with $[PPh_4]Cl$ in chloroform, followed by slow introduction of *n*-hexane vapor. After prolonged standing of the solution to precipitate the species "$\{(pz)B(pz)_3\}Ru(3,5\text{-}Me_2pzH)_3Cl$", some crystals were deposited, but were found to be only its decomposed product $[RuCl\{B(pz)_4\}(3,5\text{-}Me_2pzH)_2]$ (**5**) with a chloroform molecule. Fig. 6 shows the crystal structure of **5**, which was probably supported by the intra-molecular hydrogen bonding [15] between the chloride ligand and two acidic NH protons of the ligating $3,5\text{-}Me_2pzH$ molecules retained. Their inter atomic distances were 2.49(8) and 2.69(8) Å.

2.2. (Pyrazolato)(pyrazole) ruthenium complexes with the substituted κ^3-polypyrazolylborato system $BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3$

Syntheses of (κ^3-polypyrazolylborato) complexes, substituted at the 3-position in their metal-linking pyrazolyl groups, have been performed for tuning electro- and stereo-chemical properties of the reaction fields built up on the central metal ions [1a,7], but to our knowledge, for ruthenium there are only a few examples, involving $[RuH\{BH(3\text{-}i\text{Pr-}4\text{-}Brpz)_3\}(cod)]$, $[Ru\{BH(3,5\text{-}i\text{Pr}_2pz)_3\}(py)(OH_2)_2]OTf$, and $[Ru(Cp)\{BH(3,5\text{-}Me_2pz)_3\}]$ [5]. In our reactions of $[RuCl_2(PhCN)_4]$ with potassium 3,5-dimethyl-substituted polypyrazolylborate $K[BH(3,5\text{-}Me_2pz)_3]$, we have not isolated any assignable products except the free pyrazole (i.e., $3,5\text{-}Me_2pzH$). On the other hand, similar reactions with its 4-bromo-substituted salt $K[BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3]$ [8c], in the presence of the pyrazole ($3,5\text{-}Me_2\text{-}4\text{-}BrpzH$), gave two (pyrazolato)(pyrazole)

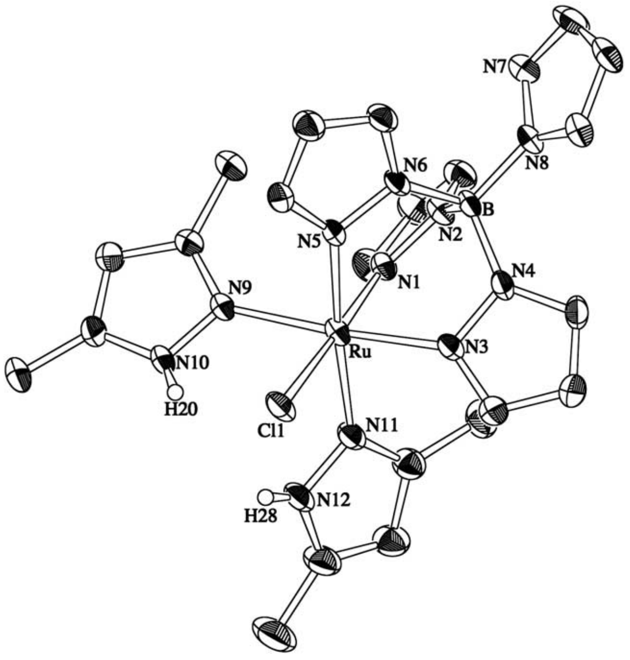

Fig. 6. ORTEP drawing of molecular cationic part of $\mathbf{5} \cdot CHCl_3$ with 30% probability thermal ellipsoids and atom labels only for important atoms. Hydrogen atoms are omitted for clarity, except NH protons. Selected bond lengths and inter-atomic distances (Å): Ru–N(1) 2.069(4), Ru–N(3) 2.045(4), Ru–N(5) 2.023(4), Ru–N(9) 2.103(4), Ru–N(11) 2.107(4), Ru–Cl(1) 2.451(1), Ru–B 3.120(5), N(10)–Cl(1) 3.243(5), N(12)–Cl(1) 3.282(5).

products, which were spectroscopically characterized as [Ru{BH(3,5-Me_2-4-Brpz)$_3$}(3,5-Me_2-4-Brpz)(3,5-Me_2-4-BrpzH)$_2$] (**6**) and [Ru{BH(3,5-Me_2-4-Brpz)$_3$}(3,5-Me_2-4-Brpz)(3,5-Me_2-4-BrpzH)(PhCN)] (**7**). These new products retain 3-Me-substituents on the metal-linking pyrazolyl groups in the (κ^3-polypyrazolylborato) ruthenium moiety "Ru{BH(3,5-Me_2-4-Brpz)$_3$}", similarly to our previously reported complex [$RuCl_2${BH(3,5-Me_2pz)$_3$(NO)}] [4c]. In case of the reactions without addition of 3,5-Me_2-4-BrpzH, quantities of the (pyrazolato)bis(pyrazole) complex **6** were small (less than 4% yields), and the (pyrazolato)(pyrazole)(benzonitrile) **7** was the sole major product, infrequently accompanied by generation of a bis(benzonitrile) species of [RuCl{BH(3,5-Me_2-4-Brpz)$_3$}$(PhCN)_2$] (**8**) in significantly lower yields. These κ^3-BH(3,5-Me_2-4-Brpz)$_3$ half-sandwich rutheniums with the 3-Me-substituents in their metal-linking pyrazolyl groups have readily replaceable coexistent ligands, i.e., pyrazole, pyrazolato, and benzonitrile, and in comparison with the BR(pz)$_3$ complexes **1** and **2**, their chemical reactivity studies are further in progress.

2.3. Conclusion

(Pyrazolato)(pyrazole) ruthenium(II) complexes with κ^3-polypyrazolylborates were separated, which involve [Ru{BR(pz)$_3$}(3,5-Me_2pz)(3,5-Me_2pzH)$_2$] {R = pz (**1**), H (**2**)}, [Ru{BH(3,5-Me_2-4-Brpz)$_3$}(3,5-Me_2-4-Brpz)(3,5-Me_2-4-BrpzH)$_2$] (**6**), and [Ru{BH(3,5-Me_2-4-Brpz)$_3$}(3,5-Me_2-4-Brpz)(3,5-Me_2-4-BrpzH)(PhCN)] (**7**). Moreover, the derived tris(pyrazole) complex of [Ru{B(pz)$_4$}(3,5-Me_2pzH)$_3$]BF_4 (**3**) was found to work as a novel halogeno-anion receptor. Single-crystal X-ray structural analyses were carried out for **1**, **3** · $CHCl_3$, [Ru{B(pz)$_4$}(3,5-Me_2pzH)$_2(OH_2)$]$O_3SC_6H_4CH_3$ · CH_3OH (**4** · CH_3OH), and [RuCl{B(pz)$_4$}(3,5-Me_2pzH)$_2$] · $CHCl_3$ (**5** · $CHCl_3$).

3. Experimental

3.1. General procedures

Starting materials, such as potassium polypyrazolyl borate salts [8] and *trans*-[$RuCl_2(PhCN)_4$] [16], were prepared according to the literature methods. Solvents were dried and distilled over appropriate drying agents. All other reagents were purchased and used without further purification. Under dry oxygen-free nitrogen atmosphere, reactions were performed with using Schlenk flasks, whereas column-chromatographic separations and handling the starting materials and the products in solid state were performed in air. Infrared (IR) spectra were recorded on a JASCO FT-IR 420 spectrometer. NMR spectra were obtained on a JEOL model JNM GX-400 spectrometer, operating at 400 MHz (^1H) and 128 MHz (^{11}B) by the use of tetramethylsilane as an internal standard and trimethyl borate as an external one, respectively. Elemental analyses were performed on a Yanaco MT-3 CHN Cordre by the Centre for Instrumental Analyses of Nagasaki University.

3.2. Reactions of [RuCl{BR(pz)$_3$}$(PhCN)_2$] and K[BH(3,5-Me_2pz)$_3$] to give [Ru{BR(pz)$_3$}(3,5-Me_2pz)(3,5-Me_2pzH)$_2$] (1)

In refluxing benzene, the complex [RuCl{B(pz)$_4$}$(PhCN)_2$] (110 mg, 0.18 mmol) was treated with K[BH(3,5-Me_2pz)$_3$] (90 mg, 0.27 mmol) for 2 days. On silica-gel column chromatography, the fraction eluted by dichloromethane/diethyl ether (10/1) was collected to give yellowish green powder of [Ru{B(pz)$_4$}(3,5-Me_2pz)(3,5-Me_2pzH)$_2$] (**1**) (30 mg, 0.045 mmol) in 25% yield.

Mp.; 210–225 °C. ^1H NMR ($CDCl_3$); δ 0.77 (s, 9H, CH_3), 2.46 (s, 9H, CH_3), 5.70 (s, 3H, 4-H of 3,5-Me_2pz), 6.08 (dd, $J = 1.8$ and 2.2, 3H, pz), 6.64 (dd, $J = 1.5$ and 2.2, 1H, pz), 6.96 (bs, 3H, pz), 7.90 (d, $J = 2.5$, 3H, pz), 8.01 (bs, 1H, pz), 8.19 (d, $J = 2.2$, 1H, pz). ^{11}B NMR ($CDCl_3$); δ −18.3 (s). MS (FAB); 669 for $[M + 1]^+$. *Anal.* Calc. for $C_{27}H_{35}BN_{14}Ru$: C, 48.58; H, 5.28; N, 29.38, Found: C, 48.30; H, 5.44; N, 29.20%.

Similar reaction of [RuCl{BH(pz)$_3$}$(PhCN)_2$] was performed to afford yellowish green [Ru{BH(pz)$_3$}(3,5-Me_2pz)(3,5-Me_2pzH)$_2$] (**2**) in 49% yield. Mp.; 176–194 °C. IR (KBr); 2476 cm^{-1} for ν(BH). ^1H NMR ($CDCl_3$); δ 0.74 (s, 9H, CH_3), 2.53 (s, 9H, CH_3), 5.63 (s, 3H, 4-H of 3,5-Me_2pz), 6.03 (dd, $J = 2.0$ and 2.4, 3H, pz), 6.83 (bs, 3H, pz), 7.76 (d, $J = 2.4$, 3H, pz), 13.5 (bs, 2H, NH). ^{11}B NMR ($CDCl_3$); δ −22.3 (d, $J = 79$). MS (FAB); 602 for M^+. *Anal.* Calc. for $C_{24}H_{33}BN_{12}Ru$: C, 47.93; H, 5.53; N, 27.94. Found: C, 47.78; H, 5.76; N, 27.85%.

3.3. Preparation of [Ru{B(pz)$_4$}(3,5-Me_2pzH)$_3$]BF_4 (3) from 1 and its further protonation

To the dichloromethane solution of [Ru{B(pz)$_4$}(3,5-Me_2pz)(3,5-Me_2pzH)$_2$] (16 mg, 0.023 mmol), diethyl ether solution (50%) of HBF_4 (3.4 ml, 0.023 mmol) was injected. After 10 min stirring and solvent evaporation under vacuum, recrystallization of the residue from dichloromethane and diethyl ether gave orange powder of [Ru{B(pz)$_4$}(3,5-Me_2pzH)$_3$]BF_4 (**3**) (14 mg, 0.018 mmol) in ca. 75% yield.

^1H NMR($CDCl_3$); δ 1.16 (s, 9H, CH_3), 2.54 (s, 9H, CH_3), 5.88 (s, 3H, 4-H of 3,5-Me_2pz), 6.15 (bs, 3H, pz), 6.62 (bs, 3H, pz), 6.76 (bs, 1H, pz), 7.77 (bs, 3H, pz), 8.11 (bs, 1H, pz), 8.32 (bs, 1H, pz), 10.4 (bs, 3H, NH). ^{11}B NMR ($CDCl_3$); δ −18.4 (s, B(pz)$_4$), −19.2 (s, BF_4). MS (FAB); 669 for $[M(\text{cationic part})]^+$. *Anal.* Calc. for $C_{27}H_{36}B_2F_4N_{14}Ru \cdot 0.5CH_2Cl_2$: C, 41.40; H, 4.67; N, 24.58. Found: C, 41.08; H, 4.95; N, 24.32%.

The complex **1** in a NMR tube ($CDCl_3$) was treated with twofold moles of HBF_4 (Et_2O), and the NMR spectra showed additional protonation of the uncoordinated pyrazolyl group in the B(pz)$_4$ ligand. However, isolation of the generated species was not succeeded. ^1H NMR($CDCl_3$); δ

1.44 (s, 9H, CH_3), 2.43 (s, 9H, CH_3), 5.91 (s, 3H, 4-H of 3,5-Me_2pz), 6.26 (bs, 3H, pz), 6.71 (bs, 3H, pz), 7.14 (bs, 1H, pz), 7.55 (bs, 3H, pz), 8.48 (bs, 1H, pz), 8.97 (bs, 1H, pz), 10.0 (bs, 4H, NH). ^{11}B NMR ($CDCl_3$); δ −18.4 (s, $B(pz)_4$), −19.6 (s, BF_4).

3.4. Halogeno-anion incorporation with the tris(pyrazole) species [Ru{B(pz)₄}(3,5-Me₂pzH)₃]⁺

The complex **1** in dichloromethane was treated with HBF_4 (Et_2O) in an equimolar quantity to produce **3**. After 10 min stirring and evaporation in vacuo, the residue was dissolved in $CDCl_3$ and combined with the phosphonium halides $[Ph_4P]X$ (X = Cl, Br, I) in prescribed quantities. NMR and IR spectroscopic measurements were performed for these solutions.

3.5. Reactions of K[BH(3,5-Me₂-4-Brpz)₃] with trans-[RuCl₂(PhCN)₄]

The (benzonitrile) ruthenium(II) $[RuCl_2(PhCN)_4]$ (200 mg, 0.34 mmol) was treated with $K[BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3]$ (450 mg, 0.79 mmol) in benzene and the mixture was heated with 3,5-Me_2-4-BrpzH (300 mg, 1.71 mmol) under reflux overnight. Benzene-extracted material was chromatographed on a silica-gel column, and benzene elution gave off-white powder of $[Ru\{BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3\}(3,5\text{-}Me_2\text{-}4\text{-}Brpz)(3,5\text{-}Me_2\text{-}4\text{-}BrpzH)_2]$ (**6**) (95 mg, 0.082 mmol) in a 24% yield.

Mp.; 155–165 °C. IR (KBr); 2525 cm^{-1} for ν(BH). ^1H NMR ($CDCl_3$); δ 0.81 (s, 9H, CH_3), 0.95 (s, 9H, CH_3), 2.42 (s, 9H, CH_3), 2.52 (s, 9H, CH_3). MS (FAB); 1160 for M^+. *Anal.* Calc for $C_{30}H_{39}BBr_6N_{12}Ru$: C, 31.09; H, 3.39; N, 14.50. Found: C, 31.36; H, 3.34; N, 13.96%.

Moreover, the benzene elution also afforded the (pyrazolato)(pyrazole)(benzonitrile) complex $[Ru\{BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3\}(3,5\text{-}Me_2\text{-}4\text{-}Brpz)(3,5\text{-}Me_2\text{-}4\text{-}BrpzH)(PhCN)]$ (**7**) (134 mg, 0.12 mmol) as yellow microcrystals in 36% yield. Mp.; 150–160 °C. IR (KBr); 2523 cm^{-1} for ν(BH), 2217 for ν(CN). ^1H NMR ($CDCl_3$); δ 0.95 (s, 6H, CH_3), 1.02 (s, 3H, CH_3), 1.79 (s, 6H, CH_3), 2.39 (s, 6H, CH_3), 2.46 (s, 6H, CH_3), 2.52 (s, 3H, CH_3), 7.4–7.6 (c, 5H, Ph). MS (FAB); 1087 for M^+. *Anal.* Calc. for $C_{32}H_{37}BBr_5N_{11}Ru$: C, 35.35; H, 3.43; N, 14.17. Found: C, 35.63; H, 3.47; N, 13.88%.

Reactions in refluxing benzene without coexistence of free pyrazole were undergone to give **7** and **6** in 43% and 2% yields, respectively, whereas analogous reactions in dichloromethane and chromatographic separation with a dichloromethane and diethyl ether solvent mixture (5/1) infrequently afforded a brown bis(benzonitrile) species of $[RuCl\{BH(3,5\text{-}Me_2\text{-}4\text{-}Brpz)_3\}(PhCN)_2]$ (**8**) additionally in significantly low yields. IR (KBr); 2526 cm^{-1} for ν(BH), 2220 for ν(CN). ^1H NMR ($CDCl_3$); δ 2.41 (bs, 9H, CH_3), 2.55 (s, 3H, CH_3), 2.74 (s, 6H, CH_3), 7.48 (t, J = 7.5, 4H, m-Ph), 7.59 (t, J = 7.4, 2H, p-Ph), 7.68 (d, J = 7.4, 4H, o-Ph). MS (FAB); 878 for M^+. *Anal.* Calc. for $C_{29}H_{29}BBr_3ClN_8Ru \cdot CH_2Cl_2$: C, 37.47; H, 3.25; N, 11.65. Found: C, 37.15; H, 3.79; N, 11.64%.

3.6. Single-crystal X-ray structural determinations

Crystallographic data are summarized in Table 1. Single crystals for X-ray structural analyses were obtained as follows: $[Ru\{B(pz)_4\}(3,5\text{-}Me_2pz)(3,5\text{-}Me_2pzH)_2]$ (**1**) by serene built-up of two solvent layers, i.e., Et_2O and **1**-containing CH_2Cl_2 layers in test tubes; $[Ru\{B(pz)_4\}(3,5\text{-}Me_2pzH)_3]BF_4 \cdot CHCl_3$ (**3** · $CHCl_3$) by vapor diffusion of *n*-hexane into **3**-containing $CHCl_3$ solution; $[Ru\{B(pz)_4\}(3,5\text{-}Me_2pzH)_2(OH_2)]OTs \cdot CH_3OH$ (**4** · CH_3OH) by vapor diffusion of Et_2O and *n*-hexane into **1**-containing CH_2Cl_2 solution with equimolar *p*-toluenesulfonic acid monohydrate and small amount of CH_3OH; and $[RuCl\{B(pz)_4\}(3,5\text{-}Me_2pzH)_2] \cdot CHCl_3$ (**5** · $CHCl_3$) by slow vapor diffusion of *n*-hexane into **3**-containing $CHCl_3$ solution with equimolar amount of $[PPh_4]Cl$. These single-crystals were sealed in glass capillaries, and X-ray diffraction observations were carried out at 23 °C on an automated Rigaku AFC-7S diffractometer by using graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation.

For **1**, diffraction intensity data were collected with the four-circle goniometer and a NaI scintillation counter [11b]: scan type, ω–2θ; scan width in ω (deg, °), 0.68 + 0.30 tanθ; scan rate in ω (deg/min), 16.0.

For the remaining crystals, **3** · $CHCl_3$, **4** · CH_3OH, and **5** · $CHCl_3$, intensity data were obtained on a MSC/ADSC Quantum CCD area detector coupled with the AFC-7S diffractometer. Seven preliminary data frames were measured at 0.5° increments of ω, in order to assess the crystal quality and preliminary unit cell parameters. The intensity images were obtained with ω scans of 0.5° interval per frame for a duration of 35 s. The frame data were integrated using an MSC d*TREK program package, and the data sets were corrected for absorption using a REQAB program.

The crystal structures were solved by direct methods (SIR-92) [17] for **1**, **3** · $CHCl_3$, **4** · CH_3OH, and by heavy-atom Patterson method (DIR DIF 94 PATTY) [18] for **5** · $CHCl_3$, respectively, and further expanded using Fourier techniques. The structures were refined through full-matrix least squares method on F^2 by the Rigaku TEXSAN crystallographic package [19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions with C–H distance of 0.97 Å, except NH hydrogens in ligating pyrazoles of **1**, **4** · CH_3OH, and **5** · $CHCl_3$, which were located on the basis of the difference Fourier map and refined isotropically. Four protons were not placed, involving incorporated $CHCl_3$ proton in **3** · $CHCl_3$ and OH protons of ligating OH_2 and incorporated CH_3OH molecules in **4** · CH_3OH. In addition, 2-N nitrogen (N(6)) and 5-C carbon (C(8)) in the uncoordinated pyrazolyl group of **1** were disordered with occupancy factors of 0.5/0.5.

Table 1
Crystal and structure refinement data

	1[g]	$3 \cdot CHCl_3$	$4 \cdot CH_3OH$	$5 \cdot CHCl_3$
Empirical formula	$C_{27}H_{35}N_{14}BRu$	$C_{28}H_{37}N_{14}B_2Cl_3F_4Ru$	$C_{30}H_{41}N_{12}BO_5SRu$	$C_{23}H_{29}N_{12}BCl_4Ru$
F_w	667.55	874.74	793.67	727.25
Crystal system	orthorhombic	triclinic	triclinic	triclinic
Space group	*Pnma* (# 62)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
Color	green	orange	orange	orange
Crystal size (mm)	0.15 × 0.15 × 0.30	0.40 × 0.30 × 0.15	0.35 × 0.20 × 0.10	0.40 × 0.20 × 0.15
Lattice parameters				
a (Å)	26.196(4)	9.126 (3)	11.433(1)	10.102(3)
b (Å)	14.410(2)	12.924 (4)	12.0351(8)	10.851(2)
c (Å)	8.019(3)	17.066 (6)	14.876(2)	14.881(5)
α (°)		77.187 (6)	80.872(3)	78.156(5)
β (°)		79.092 (3)	71.365(2)	88.910(2)
γ (°)		83.527 (3)	72.341(1)	75.264(1)
V (Å^3)	3027(2)	1922.0 (10)	1843.8(3)	1543.0(8)
Z value	4	2	2	2
ρ_{calc} (g/cm^3)	1.465	1.511	1.429	1.565
μ (Mo Kα) (cm^{-1})	5.62	6.78	5.37	8.91
Structure solution	direct method (SIR-92)	direct method (SIR-92)	direct methods (SIR-92)	Patterson methods (DIR DIF 94 · PATTY)
Number of unique reflections	3620	8133	7854	6609
Number of observations[a]	3619	8095	7802	6586
Number of variables	230	409	459	378
R_1[b,c]	0.038	0.101	0.056	0.059
R[d]	0.068	0.197	0.102	0.109
Rw[e]	0.090	0.245	0.131	0.151
Goodness-of-fit S[f]	1.31	1.69	1.40	1.07

[a] All data.

[b] $I > 2.0\sigma(I)$.

[c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

[d] $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$.

[e] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

[f] $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o and N_v denote the number of observations and variables.

[g] Scan type, ω–2θ; scan width in ω (deg, °), 0.68 + 0.30 tanθ; scan rate in ω (deg/min), 16.0. See Section 3 in the text.

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Appendix A. Supplementary data

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre, CCDC reference numbers; 267921, 267922, 267924, and 267923 for compounds **1**, **3** · $CHCl_3$, **4** · CH_3OH, and **5** · $CHCl_3$, respectively. Copies of these information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.08.005.

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