Electrochemical Influence of Tridentate Polypyrazolylborate Ligands: Syntheses and Electrochemistry of Bis(η^3-polypyrazolylborato)ruthenium(II) Complexes

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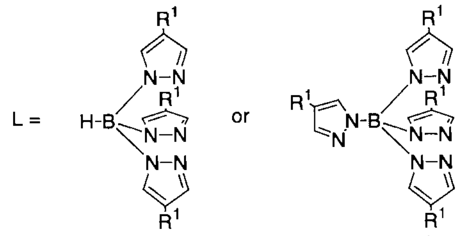
Concerning electrochemically reversible [Ru(III)]/[Ru(II)] redox couples of the substituted bis(η^3-polypyrazolylborato)-ruthenium(II) complexes [Ru(L^1)(L^2)], two polypyrazolylborate ligands, L^1 and L^2, were independently exerted on the oxidation half-wave potentials ($E_{1/2}$) of the couples. Relative contributions ΔE(L) of the respective polypyrazolylborates to the $E_{1/2}$ values were evaluated.

Polypyrazolylborate anions $[BR(pz)_3]^-$ (pz = 1-pyrazolyl group), abbreviated as L, have been used as versatile supporting ligands for a wide range of transition-metal and lanthanide complexes.[1] Widespread considerable attention paid to the polypyrazolylborates stems probably from the similarity of the tridentate $[BR(pz)_3]^-$ ligands in the 6e-donative coordination form[1] to the well-known η^5-cyclopentadienyls in transition-metal organometallic chemistry, and also from the capability for supporting some chemically reactive organometallics, such as dihydrogen, hydride, carbene, and vinylidene ruthenium species reported in these years.[2] Moreover, in view of easy access to substituted pyrazoles Hpz*, various substituents have been introduced on the pyrazolyl rings in this tripodal ligand system,[1] with the hope of fine tuning of the electronic and steric properties of reaction sites on the central metal ions in the complexes. Concerning their stereochemical properties, steric bulkiness effects of the substituted polypyrazolylborates, which were extended over the reaction environment around the central metal ions, were studied abundantly in terms of cone and wedge angles.[1] However, in contrast, only scattered studies have been reported on their electronic properties,[3,4] which involve pK_a determinations of hydrogen polypyrazolylborates[5] and substituent effects on the ^{119}Sn NMR and Mössbauer spectroscopies of their organotin(IV) compounds.[6]



BH(pz)$_3$: R^1 = H
BH(4-Brpz)$_3$: R^1 = Br
BH(4-Mepz)$_3$: R^1 = Me
B(pz)$_4$: R^1 = H
B(4-Mepz)$_4$: R^1 = Me

In the present study, the ruthenocene-like bis(η^3-polypyrazolylborato)ruthenium(II) complexes, $[Ru\{B(pz)_4\}_2]$ (**1**),[7] $[Ru\{BH(pz)_3\}_2]$ (**2**),[7] $[Ru\{BH(4\text{-}Brpz)_3\}_2]$ (**3**), $[Ru\{B(4\text{-}Mepz)_4\}_2]$ (**4**), and $[Ru\{BH(4\text{-}Mepz)_3\}_2]$ (**5**), and the mixed ruthenocene-type analogs, $[Ru\{B(pz)_4\}\{BH(pz)_3\}]$ (**6**), $[Ru\{B(pz)_4\}\{BH(4\text{-}Brpz)_3\}]$ (**7**), $[Ru\{B(pz)_4\}\{B(4\text{-}Mepz)_4\}]$ (**8**), and $[Ru\{B(pz)_4\}\{BH(4\text{-}Mepz)_3\}]$ (**9**) were prepared from the reactions of $[RuCl_2(nitrile)_4]$ and half-sandwich-type $[RuCl\{B(pz)_4\}(nitrile)_2]$[7] with potassium polypyrazolylborate salts K[L], respectively. These complexes obtained as colorless or pale brown microcrystals, were characterized by means of ^{1}H, ^{13}C, and ^{11}B NMR, IR and mass spectroscopies, besides their elemental analyses. Moreover, single crystal X-ray structural analyses were performed for the complexes, **1**, **2**, and **6**.[8]

Cyclic voltammetry (CV) of the present ruthenium(II) complexes was measured in dichloromethane solutions, and displayed electrochemically reversible one-electron redox-couples of the [Ru(III)]/[Ru(II)].[9] Upon stepwise replacement of the two B(pz)$_4$ ligands in **1** with other polypyrazolylborates L, good linear relationship was obtained for the oxidation half-wave potentials ($E_{1/2}$) of the redox couples versus the number n (0, 1, and 2) in $[Ru\{B(pz)_4\}_{(2-n)}(L)_n]$ as shown in Figure 1, and contributions by the respective tridentate polypyrazolylborate ligands were found to be additive for the potentials $E_{1/2}$ of the com-

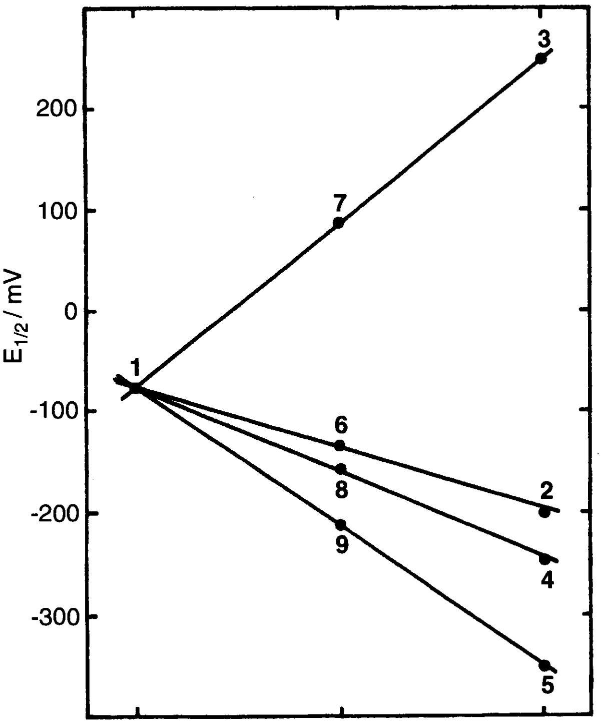
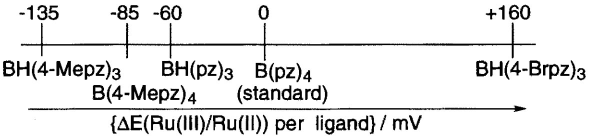


Figure 1. Oxidation half-wave potentials of [Ru(L^1)(L^2)].

plexes. On the [Ru(L^1)(L^2)] complexes, therefore, electrochemical properties of the two polypyrazolylborate ligands, L^1 and L^2, were independently exerted on the [Ru(III)]/[Ru(II)] redox potentials $E_{1/2}$, which are thus expressed by simply adding respective contributions of the two ligands. Relative contributions ΔE(L) by the respective polypyrazolylborate ligands L, compared with that of $B(pz)_4$, were evaluated from the best averaged slope-values (Figure 1) through the least-squares method, and are summarized in Scheme 1.

For (α-diimine)ruthenium(II) complexes, $[Ru(diimine)_3]^{2+}$ (diimine; bpy, phen, etc.), similar ligand additivity effects have been described previously on their oxidation potentials of [Ru(III)]/[Ru(II)].[10] The bis(polypyrazolylborato)ruthenium(II) complexes were another example showing the ligand additivity effect on the [Ru(III)]/[Ru(II)] redox potentials. It is noteworthy that the present electrochemical characterization of the respective polypyrazolylborate ligands, demonstrated in the Scheme 1, provides a valuable and useful measure for molecular design to build up new diversely reactive polypyrazolylborato transition-metal, especially ruthenium complexes with tailor-made electrochemical characters.



Scheme 1. The relative contributions ΔE(Ru(III)/Ru(II)) of the ligands.

Scheme 1 for the electrochemical characterization of the polypyrazolylborates revealed two remarkable features definitely. The first feature was that the electron-withdrawing substituent (Br) shifted the potential $E_{1/2}$ of the redox couples positive, indicating more reluctant oxidation of the complexes, and the reverse trend was also observed on the introduction of the electron-releasing substituent (Me). As the second feature, compared with tetrakis(1-pyrazolyl)borate counterparts $B(pz^*)_4$, the respective tris(1-pyrazolyl)borate ligands $BH(pz^*)_3$ shifted the $E_{1/2}$ potentials more negative.

Polypyrazolylborate anions have a negative charge formally on boron atoms, but the charge is delocalized onto the 2-N atoms in the pyrazolyl groups to some extent.[11] The second feature observed was probably attributed to the different extents of electron delocalization of the anionic charge to the three ligating 2-N atoms, between the $BH(pz^*)_3$ and $B(pz^*)_4$ systems.[12] The uncoordinated pz*-B moiety withdrew more quantities of the electron from the three coordinated pz* groups than the HB moiety in the $BH(pz^*)_3$.[13] Accordingly, the $BH(pz^*)_3$ system with larger electron densities localized on the three ligating 2-N atoms was expected to bring about larger destabilization of the electron-filled dπ-orbitals (d^6) of ruthenium(II), and more negative shifts of the [Ru(III)]/[Ru(II)] redox couples than those of the $B(pz^*)_4$, as shown in Scheme 1. Further comparative studies of the two ligand systems are currently in progress on EHMO calculations for some ruthenocene-type bis(η^3-polypyrazolylborato)ruthenium(II) complexes.[14]

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8 Crystal data for **1**; $C_{24}H_{24}B_2N_{16}Ru$, MW = 659.25, triclinic, space group $P\bar{1}$ (No. 2), a = 9.6843(7), b = 12.007(2), c = 12.310(1) Å, α = 100.012(4)°, β = 95.847(1)°, γ = 102.0193(8)°, V = 1364.5(2) $Å^3$, Z = 2, D_{calc} = 1.604 g/cm^3, $R(R_w)$ = 0.051(0.156) for 5839 unique observations with 392 variables, R_1 = 0.034 for 4764 observations (I>2.0σ(I)), GOF = 1.27, Ru–B = 3.152(4) Å.
Crystal data for **2**; $C_{18}H_{20}B_2N_{12}Ru$, MW = 527.13, monoclinic, space group $P2_1/c$ (No. 14), a = 12.1347(9), b = 11.812(2), c = 16.3290(6) Å, β = 106.098(1)°, V = 2248.8(4) $Å^3$, Z = 4, D_{calc} = 1.557 g/cm^3, $R(R_w)$ = 0.049(0.126) for 4700 unique observations with 362 variables, R_1 = 0.036 for 3384 observations (I>2.0σ(I)), GOF = 1.24, Ru–B = 3.139(4) Å. The complex **2** has shown two polymorphic forms, one obtained in this study and the other described in the previous paper.[7]
Crystal data for **6**; $C_{21}H_{22}B_2N_{14}Ru\cdot1/2C_4H_{10}O$, MW = 630.25, triclinic, space group $P\bar{1}$ (No. 2), a = 11.9816(6), b = 12.4200(9), c = 19.969(1) Å, α = 94.856(1)°, β = 103.7031(6)°, γ = 101.5379(7)°, V = 2801.4(3) $Å^3$, Z = 4, D_{calc} = 1.494 g/cm^3, $R(R_w)$ = 0.073(0.135) for 12091 unique observations with 736 variables, R_1 = 0.048 for 8321 observations (I>2.0σ(I)), GOF = 1.37, Ru–B = 3.144(5) and 3.157(5) Å for $BHpz_3$ and Bpz_4, respectively.

9 Cyclic voltammetry (CV) of the ruthenium(II) complexes was observed in dichloromethane solutions of 0.1 M tetraethylammonium perchlorate, with a 1.6 mmϕ Pt-disk as the working electrode. $E_{1/2}$ vs $[FeCp_2]^+$ / $[FeCp_2]$; **1**, –77 mV; **2**, –202 mV; **3**, 247 mV; **4**, –248 mV; **5**, –350 mV; **6**, –135 mV; **7**, 87 mV; **8**, –156 mV; **9**, –212 mV.

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11 Electron donation from the boron atoms to the pyrazolyl groups has been mentioned briefly for accounting fairly high pK_a values of hydrogen polypyrazolylborates.[5]

12 For the two ligand systems of $BR(pz)_3$ (R = H, pz), difference in interatomic distances, B–Ru seemed to be negligible,[8] and was not responsible to the different electrochemical properties of their ruthenium(II) complexes.

13 The uncoordinated pyrazolyl groups were regarded as electron-withdrawing substituents introduced on the $B(\mu\text{-}pz^*)_3Ru$ moieties. Electron-withdrawing character of pyrazolyl groups is clearly exemplified by the well-known acidic property of their 1-N protons in pyrazoles.

14 Comparative elucidation of the π-back bonding effects also seems to be necessary between these two systems of $BH(pz^*)_3$ and $B(pz^*)_4$. The authors expect that the EHMO calculations and molecular orbital analyses will give useful clues to the π-bonding effects on the electrochemical properties of the ruthenium complexes.