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New polypyrazolylborate chemistry of ruthenium(II) complexes with weakly coordinating organonitrile ligands

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Abstract

A series of new (polypyrazolylborato)ruthenium(II) complexes, [RuCl(η^3-BPz$_4$)(L^1)(L^2)] (Pz = 1-pyrazolyl) (L^1 = L^2 = 4-picoline, PEt$_3$, P[OCH(CH$_3$)$_2$]$_3$, NCCH$_3$; L^1 = NCPh, L^2 = 2,4-lutidine, PPh$_3$), [Ru(η^3-BPz$_4$)(L)$_3$]PF$_6$ (L = NCCH$_3$, CO), [Ru(η^3-BR^{1}Pz$_3$)(η^3-BR^{2}Pz$_3$)] (R^1, R^2 = Pz, H) and [Ru(η^3-BRPz$_3$)(η^2-BHPz$_3$)(NCPh)] (R = Pz,H) were prepared from [RuCl(η^3-BRPz$_3$)(NCPh)$_2$], and were characterized by spectroscopic techniques.

Key words: Ruthenium complexes; Polypyrazolylborate complexes; Nitrile complexes

The coordination chemistry of polypyrazolylborate chelates [BH$_n$Pz$_{(4-n)}$]$^-$ (Pz = 1-pyrazolyl) with transition metals has developed extensively since their introduction by Trofimenko [1]. An initial attraction of tridentate polypyrazolylborate ligands was their apparent similarities in coordination and electronic structures to η^5-cyclopentadienyl ligands, and much of the polypyrazolylborate chemistry has involved compounds whose η^5-cyclopentadienyl counterparts were well established [1]. However for ruthenium, systematic development of the polypyrazolylborate chemistry seems to have been precluded so far, and only a limited number of studies have been described on the syntheses and characterization [2] and especially on the catalytic reactivities [3] of its polypyrazolylborate complexes, in spite of the vast chemistry on the corresponding η^5-cyclopentadienyl analogues [4] and of the well-known potentiality of ruthenium for affording highly efficient catalytic species in a variety of homogeneous catalytic reactions [5]. To our knowledge, this limitation was due to the lack of some conveniently available (polypyrazolylborato)ruthenium(II) complexes of synthetic potential for their subsequent systematic derivative formations. In a previous communication [3], we reported on the preparations of chloro(polypyrazolylborato)bis(benzonitrile)ruthenium(II) complexes, [RuCl(η^3-BRPz$_3$)(NCPh)$_2$] with R = Pz (**1a**) or H (**1b**), and on their catalytic olefin hydrogenations. Described herein is the synthetic utilization of these organonitrile complexes as convenient precursors to the new (polypyrazolylborato)ruthenium chemistry, as exemplified in Schemes 1 and 2**.

The ruthenium(II) complex **1a**, prepared from the reaction of *trans*-[RuCl$_2$(NCPh)$_4$] with K[BPz$_4$] under dichloromethane reflux [3]†, was treated with 4-picoline (4-pic) and 2,4-lutidine (2,4-lut) in benzene under reflux to give a disubstituted complex of [RuCl(η^3-BPz$_4$)(4-pic)$_2$] (**2**) and a monosubstituted one of [RuCl(η^3-BPz$_4$)(NCPh)(2,4-lut)] (**3**), respectively. As for 2,6-lutidine, its substitution for the benzonitrile did not occur under similar reaction conditions, and complex **1a** was recovered unchanged. Analogous substitution reactions were performed also by use of monodentate tertiary phosphorus compounds, i.e. PEt$_3$, P[OCH(CH$_3$)$_2$]$_3$ and PPh$_3$. The former two phosphorus compounds afforded disubstituted complexes of [RuCl(η^3-BPz$_4$)(PR$_3$)$_2$] with

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New (polypyrazolylborato)ruthenium(II) complexes were isolated and satisfactorily characterized by elemental analyses, mass spectrometry, NMR and IR spectroscopies in accord with the assigned structures. Color, melting points and selected spectroscopic data of the new complexes; IR data (cm^{-1}) in KBr disc except **10c, **11a** and **11b** in CH$_2$Cl$_2$; ^{1}H NMR data (400 MHz, CDCl$_3$, standard SiMe$_4$) (those for [BH$_n$Pz$_{(4-n)}$] moieties are omitted). **2**: yellow, >300 °C, ^{1}H δ 2.33 [6H, s, CH$_3$], 6.95 [4H, d, 6.1, 3,5-H(pic)], 8.50 [4H, d, 6.1, 2,6-H(pic)]. **3**: golden yellow, 235 °C, ν(CN) 2220, ^{1}H (major isomer at −40 °C) δ 1.13 [3H, s, CH$_3$], 2.34 [3H, s, CH$_3$]. **4**: yellow, 250 °C, ^{1}H δ 0.80 [18H, dt, 12.8, 7.3, CH$_3$], 1.91 [12H, c, CH$_2$]. **5**: white, 130–135 °C, ^{1}H δ 1.17 [18H, d, 5.9, CH$_3$], 1.19 [18H, d, 6.2, CH$_3$], 4.54 [6H, c, CH]. **6**: off white, 224 °C, ν(CN) 2240. **7**: yellow, 120 °C, ν(CN) 2260, ^{1}H δ 2.45 [6H, s, CH$_3$]. **8**: white, 250 °C, ν(CN) 2290, ν(PF) 840, ^{1}H δ 2.54 [9H, s, CH$_3$]. **9**: white, > 300 °C, ν(CO) 2075w and 1980, ν(PF) 840. **10c**: white, 268–272 °C, ν(BH) 2470. **11a**: golden yellow, 195 °C, ν(BH) 2405, ν(CN) 2220, ^{1}H δ 7.43 [2H, dd, 7.3, 7.7, 3,5-H(Ph)], 7.52 [1H, t, 7.3, 4-H(Ph)], 7.62 [2H, d, 7.7, 2,6-H(Ph)]. **11b**: yellow, 105–110 °C, ν(BH) 2470 and 2400, ν(CN) 2220, ^{1}H δ 7.42 [2H, dd, 7.3, 7.7, 3,5-H(Ph)], 7.51 [1H, t, 7.3, 4-H(Ph)], 7.59 [2H, d, 7.7, 2,6-H(Ph)].

†In spite of our still-continuing attempts to characterize the reaction products from *trans*-[RuCl$_2$(NCPh)$_4$] and sodium cyclopentadienide, the complex [RuCl(η^5-C$_5$H$_5$)(NCPh)$_2$], an η^5-cyclopentadienyl analogue for **1a** and **1b**, has not been obtained.

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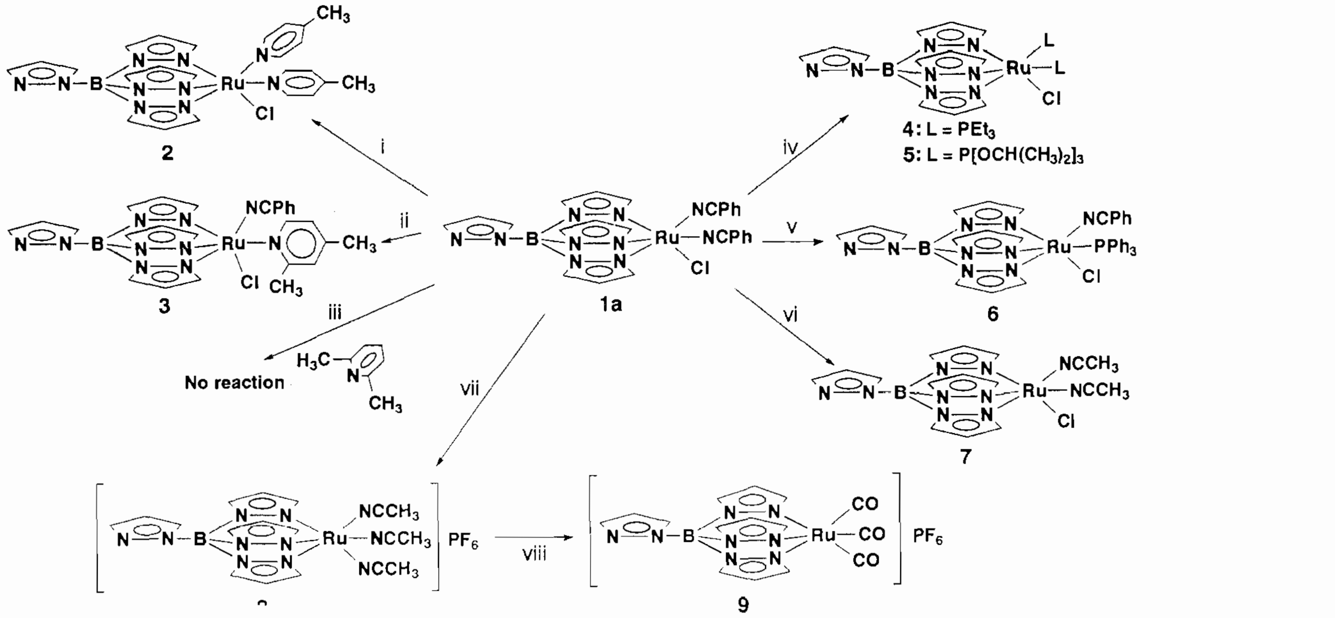
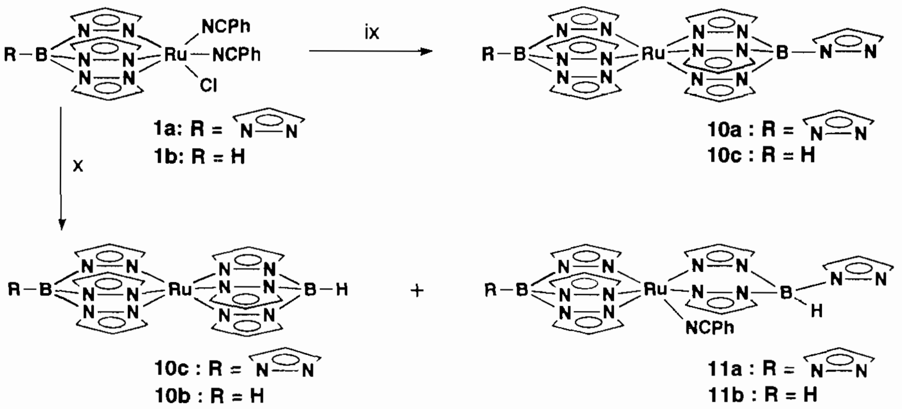


Scheme 1. (i) 4-picoline, benzene reflux, 34%; (ii) 2,4-lutidine, benzene reflux, 50%; (iii) 2,6-lutidine, benzene reflux; (iv) PEt_3 or $P[OCH(CH_3)_2]_3$, benzene reflux, 26% for **4** and 51% for **5**; (v) PPh_3, benzene reflux, 42%; (vi) acetonitrile reflux, 80%; (vii) $K[PF_6]$, acetonitrile reflux, 78%; (viii) CO, ethanol reflux, 76%.



Scheme 2. (ix) $K[BPz_4]$, ethanol reflux for 2 h, 85% for **10a** and 94% for **10c** from **1a** and **1b**, respectively; (x) $K[BHPz_3]$, ethanol reflux for 2 h, 16 and 28% for **10c** and **11a** from **1a**, respectively, and 22 and 37% for **10b** and **11b** from **1b**, respectively.

R = Et (**4**) or $OCH(CH_3)_2$ (**5**). On the other hand, the third compound PPh_3 gave only a monosubstituted $[RuCl(\eta^3\text{-}BPz_4)(NCPh)(PPh_3)]$ [**6**). A similar monosubstituted complex of $[RuCl(\eta^3\text{-}BHPz_3)(NCPh)(PPh_3)]$ was also obtained quantitatively from **1b**. Accordingly, in the course of the substitutions of the monodentate nitrogen and phosphorus compounds, their steric hindrance upon coordination was a dominant term in determination of the degree of substitutions for the benzonitrile on ruthenium [6].

The bis(benzonitrile) complex **1a** was heated in acetonitrile under reflux to form $[RuCl(\eta^3\text{-}BPz_4)(NCCH_3)_2]$ (**7**), an acetonitrile analogue, which was not obtainable from direct treatment of *trans*-$[RuCl_2(NCCH_3)_4]$ with $K[BPz_4]$ [3]. A similar reaction, but in the presence of $K[PF_6]$, gave a cationic tris(acetonitrile) complex of $[Ru(\eta^3\text{-}BPz_4)(NCCH_3)_3]PF_6$ (**8**) as white microcrystals. Complex **8** was also readily recognized as another convenient precursor for the syntheses of new heteroleptic (polypyrazolylborato)ruthenium(II) complexes, through displacement of its three labile acetonitrile ligands; for example, bubbling of carbon monoxide into a refluxing ethanol solution of **8** gave a cationic tris(carbonyl) complex of $[Ru(CO)_3(\eta^3\text{-}BPz_4)]PF_6$ (**9**) in a good yield.

In the course of a chemical reactivity survey of the bis(benzonitrile) complexes, **1a** and **1b**, the present authors performed their reactions with potassium polypyrazolylborates (Scheme 2). Substitution for the two benzonitrile ligands gave homo and mixed ruthenocene-type bis(η^3-polypyrazolylborato)rutheniums, i.e. complexes **10a** and **10b** as the former type [3] and complex **10c** as the latter. As for mixed bis(η^3-polypyrazolylborato) complexes, a few descriptions have appeared recently for first-row transition metals [7]. Along with these ruthenocene analogues, the reactions with K[BHPz$_3$] afforded intermediate complexes with one benzonitrile ligand retained, which were formulated as [Ru(η^3-BRPz$_3$)(η^2-BHPz$_3$)(NCPh)] with R = Pz (**11a**) or H (**11b**)*. Further heating of the intermediates in refluxing ethanol dissociated the benzonitrile from ruthenium to give the respective above-mentioned ruthenocene analogues. Displacement of the benzonitrile by carbon monoxide bubbling was found to occur also for **11a** in ethanol under reflux.

Thus, in the present study, the (organonitrile)(polypyrazolylborato)ruthenium(II) complexes proved convenient precursor reagents of synthetic utility for the fertile (polypyrazolylborato)ruthenium(II) chemistry. Organonitrile ligands in these complexes showed both proper lability as a leaving group and appropriate compatibility as a supporting ligand to the (polypyrazolylborato)ruthenium(II) moieties. Further studies are currently in progress on single-crystal X-ray structural analyses, catalytic reactivities and photochemical properties of the new (polypyrazolylborato)rutheniums**.

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*Spectroscopic characteristics of the η^2-BHPz$_3$ moieties in **11a** and **11b**; ν(BH) at *c.* 2400 cm^{-1} (CH$_2$Cl$_2$) and ^{11}B NMR signal at δ *c.* -20.2 from B(OCH$_3$)$_3$. Neutral η^3-BHPz$_3$ complexes in this study showed ν(BH) at *c.* 2470 cm^{-1} and ^{11}B NMR at δ *c.* -22.1.

**It is noted that NMR spectra of the new (polypyrazolylborato)ruthenium(II) complexes at room temperature did not show evidence of their stereochemically non-rigid, i.e. fluxional, motions [1], such as trigonal–twist rotation of the η^3-BRPz$_3$ ligands around the B–Ru axis and dynamic interexchange between coordinated and uncoordinated Pz groups.