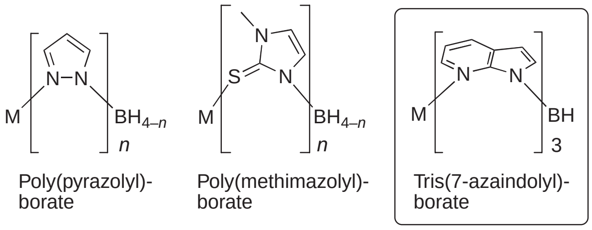
Synthesis and Reactivity of Tris(7-azaindolyl)boratoruthenium Complex. Comparison with Poly(methimazolyl)borate Analogue

Tomoyuki Saito, Shigeki Kuwata,* and Takao Ikariya*
Department of Applied Chemistry, Graduate School of Science and Engineering,
Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552

(Received August 29, 2006; CL-060981; E-mail: skuwata@apc.titech.ac.jp, tikariya@apc.titech.ac.jp)

A reaction of $[\mathrm{Cp^*RuCl}]_4$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5(CH_3)_5}$) with $\mathrm{K[HB(aza)_3]}$ (aza = 7-azaindolyl) afforded the first organometallic $\mathrm{HB(aza)_3}^-$ complex $[\mathrm{Cp^*Ru\{HB(aza)_3}\text{-}\kappa^3 H,N,N'\}]$, which lost one of the aza-units coordination upon treatment with carbon monoxide to give the mono(carbonyl) complex $[\mathrm{Cp^*Ru\{HB(aza)_3}\text{-}\kappa^2 H,N\}\mathrm{(CO)}]$. The crystal structures of these complexes have been determined by X-ray crystallography.

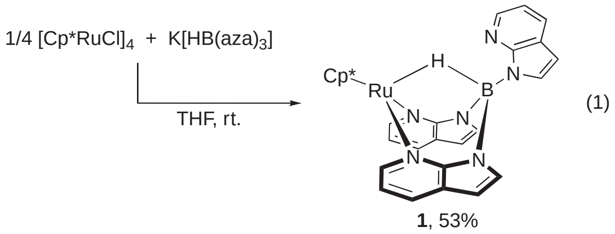
In the last decade, rapidly increasing research activities have been focused on the complexes bearing poly(methimazolyl)borate ligands, typified by $\mathrm{HB(mt)_3}^-$ (mt = 2-mercapto-1-methylimidazolyl), as "soft analogues" of conventional poly(pyrazolyl)borate ligands in organometallic and bioinorganic chemistry.[1] An additional feature of this class of ligands is the increased ring size of the chelate, which leads to the ligand fluxionality induced by facile mt-dissociation,[2] for example. In this context, coordination chemistry of the tris(7-azaindolyl)borate ligand ($\mathrm{HB(aza)_3}^-$; aza = 7-azaindolyl), developed quite recently by Wang et al.,[3] is intriguing because this ligand is furnished with both hard nitrogen donor atoms and larger chelating framework (Chart 1). Indeed, dynamic exchange of the coordinated and non-coordinated aza groups in $[\mathrm{Cu\{HB(aza)_3}\text{-}\kappa^3 H,N,N'\}\{\mathrm{P(C_6H_5)_3}\}]$ has been documented.[3] We report here the first organometallic $\mathrm{HB(aza)_3}^-$ complex $[\mathrm{Cp^*Ru\{HB(aza)_3}\text{-}\kappa^3 H,N,N'\}]$ (**1**; $\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5(CH_3)_5}$) and their distinctive coordination behavior.



Poly(pyrazolyl)-borate Poly(methimazolyl)-borate Tris(7-azaindolyl)-borate

Chart 1.

Treatment of $[\mathrm{Cp^*RuCl}]_4$[4] with $\mathrm{K[HB(aza)_3]}$[3] afforded the tris(7-azaindolyl)boratoruthenium complex **1**, a hitherto unknown $\mathrm{HB(aza)_3}^-$ complex of the second and third transition series metals, in moderate yield (eq 1). The $^1\mathrm{H}$ NMR spectrum of **1** demonstrates the presence of two sets of signals ascribed to the aza groups in a 1:2 ratio. A B–H stretching band at $2102\,\mathrm{cm^{-1}}$ in the IR spectrum suggests the agostic coordination of the B–H group, which has been confirmed by an X-ray crystallographic analysis of **1** (Figure 1).[5] It is noteworthy that the tris(azolyl)borate analogues $[\mathrm{Cp^*Ru\{HB(pz)_3}\text{-}\kappa^3 N,N',N''\}]$[6] (pz = 1-pyrazolyl) and even $[\mathrm{Cp^*Ru\{HB(mt)_3}\text{-}\kappa^3 S,S',S''\}]$,[2] in which the boron and donor atoms in each azolyl arm are separated by two atoms as in **1**, have C_3-symmetric solid-state structures without agostic Ru–H–B interactions. The Ru–B separation of 2.786(6) Å in **1** lies in the middle of those in the related poly(azolyl)borate complexes $[\mathrm{Cp^*Ru\{H_2B(mt)_2}\text{-}\kappa^3 H,S,S'\}]$[7] (**2**; 2.82(1) Å) and $[\mathrm{(cod)Ru(CH_3)\{HB(pz^*)_3}\text{-}\kappa^3 H,N,N'\}]$[8] (2.632(4) Å; cod = 1,5-cyclooctadiene, pz* = 3,5-dimethyl-1-pyrazolyl).[9] These structural differences are ascribed to the geometric characteristics of $\mathrm{HB(aza)_3}^-$, that is, both the increased ring size of the chelete and the directional $\mathrm{sp^2}$-nitrogen donor atoms.



1, 53%

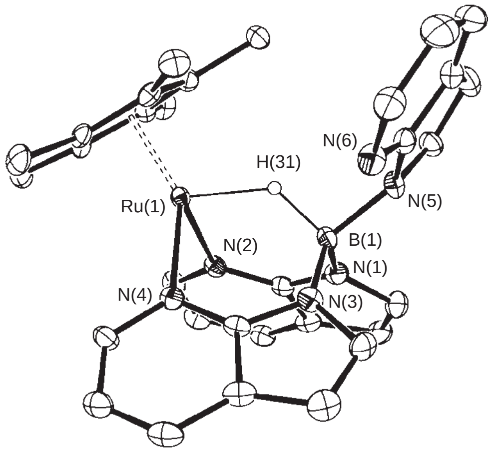
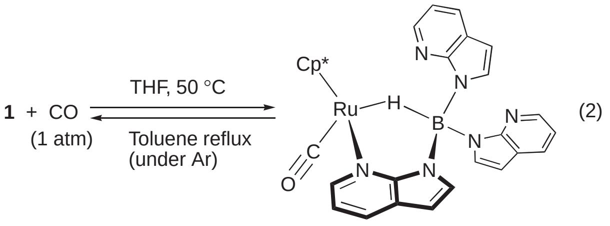


Figure 1. Molecular structure of **1**. Selected bond distances (Å) and angles (deg): Ru(1)–N(2), 2.155(4); Ru(1)–N(4), 2.159(5); Ru(1)–H(31), 1.77; B(1)–H(31), 1.30; Ru(1)–H(31)–B(1), 129.9.

Complex **1** reacted with CO at 50 °C to give the carbonyl complex $[\mathrm{Cp^*Ru\{HB(aza)_3}\text{-}\kappa^2 H,N\}\mathrm{(CO)}]$ (**3**) as shown in eq 2.



3, 24%

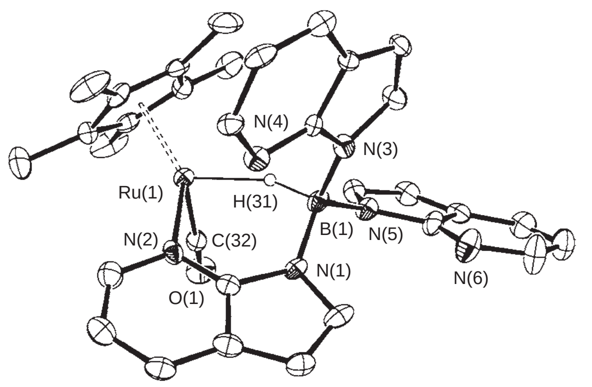
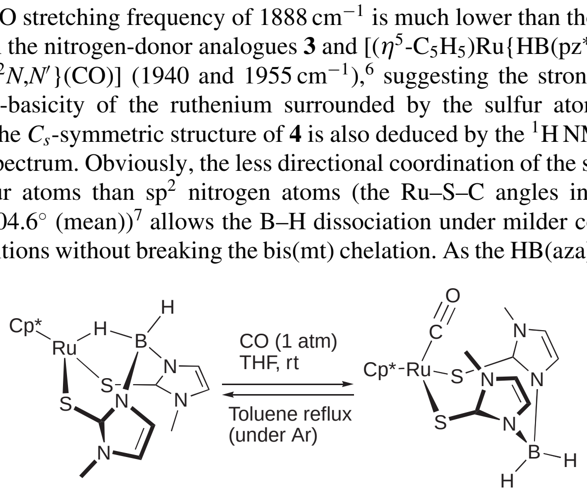


Figure 2. Molecular structure of **3**. Selected bond distances (Å) and angles (deg): Ru(1)–N(2), 2.116(7); Ru(1)–C(32), 1.870(9); C(32)–O(1), 1.15(1); Ru(1)–H(31), 1.84; B(1)–H(31), 1.13; Ru(1)–H(31)–B(1), 158.3.

The structure of **3** has been determined by an X-ray diffraction study (Figure 2).[5] Coordination of CO gives rise to the cleavage of one of the ruthenium–aza bonds in **1** whereas the agostic Ru–H–B interaction is preserved. The two dangling aza arms sit in positions to minimize the steric congestion. The $\kappa^2 H,N$ coordination of tris(azolyl)borate ligands is not so common even in the ubiquitous tris(pyazolyl)borate complexes.[10] In accordance with the solid-state structure, the ^{1}H NMR spectrum recorded at $-20\,^\circ$C indicates that all of the three aza groups are inequivalent. However, the signals are broadened at more elevated temperatures, suggesting the presence of an exchange process of the three aza groups. The IR spectrum of **3** (KBr disk) exhibits the ν_{CO} and ν_{BH} bands at 1938 and 2074 cm^{-1}, respectively. The carbonyl ligand in **3** could be removed upon heating in boiling toluene under Ar, resulting the regeneration of **1** along with a small amount of an uncharacterized by-product.

The robustness of the Ru–H–B linkage in **1** markedly contrasts with the facile cleavage of the agostic coordination of the $\kappa^3 H,S,S'$-$H_2B(mt)_2^-$ ligand in **2**.[11] Thus, the reaction of **2** with CO takes place even at room temperature to give the carbonyl complex [Cp*Ru{$H_2B(mt)_2$-$\kappa^2 S,S'$}(CO)] (**4**) as shown in eq 3. The lack of the Ru–H interaction is inferred by the IR spectrum, which displays only a non-coordinated B–H stretching band at 2441 cm^{-1} in contrast to **2** (2422 and 2073 cm^{-1}).[7] The CO stretching frequency of 1888 cm^{-1} is much lower than those in the nitrogen-donor analogues **3** and [(η^5-C_5H_5)Ru{HB(pz*)$_3$-$\kappa^2 N,N'$}(CO)] (1940 and 1955 cm^{-1}),[6] suggesting the stronger π-basicity of the ruthenium surrounded by the sulfur atoms. The C_s-symmetric structure of **4** is also deduced by the ^{1}H NMR spectrum. Obviously, the less directional coordination of the sulfur atoms than sp^2 nitrogen atoms (the Ru–S–C angles in **2**: 104.6° (mean))[7] allows the B–H dissociation under milder conditions without breaking the bis(mt) chelation. As the $HB(aza)_3^-$ complex **3**, the $H_2B(mt)_2^-$ complex **4** loses CO upon heating to give the parent complex **2**.



(3)

2 **4**, 43%

In summary, the tripodal scopionate ligand $HB(aza)_3^-$ on an organometallic platform exhibits unique coordination behavior because of the rigid aza groups in its skeleton. In contrast to the poly(pyrazolyl)- and poly(methimazolyl)borates, $HB(aza)_3^-$ does not favor the $\kappa^3 X,X',X''$ and $\kappa^2 X,X'$ ($X = $ N, S) coordination despite the superficial structural similarity of these borates. Further elucidation of the properties of the $HB(aza)_3^-$ complexes as well as the design of new poly(azolyl)borate ligands is in progress.

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5 Crystallographic data for **1**: $C_{31}H_{31}BN_6Ru$, M_r 599.51, monoclinic, *Cc*, $a = 18.69(2)$, $b = 11.868(10)$, $c = 14.23(1)$ Å, $\beta = 117.05(1)°$, $V = 2812(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.416$ g cm^{-3}, 6138 unique reflections, $R1 = 0.045$ [$I > 2\sigma(I)$], $wR2 = 0.118$ (all data). For **3**: $C_{32}H_{31}BN_6ORu$, M_r 627.52, orthorhombic, *Pbca*, $a = 13.960(6)$, $b = 18.284(8)$, $c = 22.604(10)$, $V = 5769.5(44)$ Å^3, $Z = 8$, $D_{calcd} = 1.445$ g cm^{-3}, 8918 unique reflections, $R1 = 0.059$ [$I > 2\sigma(I)$], $wR2 = 0.215$ (all data). Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-619777 (**1**) and -619778 (**3**). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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11 The lability of the B–H coordination in poly(methimazolyl)borate complexes is also supported by facile interconversion between [Cp*Ru{HB(mt)$_3$-$\kappa^3 S,S',S''$}] and [Cp*Ru{HB(mt)$_3$-$\kappa^3 H,S,S'$}].[2]

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