

Reactions of [Cp*RuCl]₄ and [(p-cymene)RuCl₂]₂ with the Tridentate Ligand $[Ph(pz)B(\mu-O)(\mu-pz)B(pz)Ph]^{-1}$

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The reaction of the tridentate [N,O,N] (pyrazol-1-yl)borate ligand [Ph(pz)B(µ-O)(µ-pz)B(pz)Ph]⁻ $([L^1]^-)$ with $[Cp^*RuCl]_4$ and $[(p-cym)RuCl_2]_2$ gives the Ru^{II} complexes $[Cp^*Ru(L^1)]$ and [(p-cym)- $\operatorname{Ru}(L^{1})$]Cl, respectively (pz = pyrazolyl, Cp* = pentamethylcyclopentadienyl, p-cym = p-cymene). In order to avoid degradation of the $[(p-cym)Ru(L^{f})]^{+}$ complex in solution, its Cl⁻ counterion has been exchanged for PF_6^- , $[B(C_6F_5)_4]^-$, tosylate, and triflate. When the reaction between $[L^1]^-$ and [(p-cym)Ru-Cl₂]₂ is carried out in the presence of 4 equiv of TIPF₆, the dinuclear pyrazolyl-bridged complex [(p-cym)- $Ru(\mu-Cl)(\mu-pz)_2Ru(p-cym)]PF_6$ and the mononuclear species $[(p-cym)Ru(L^2)]$ are obtained $([L^2]^{2-} =$ $[Ph(pz)B(\mu-O)(\mu-OB(Ph)O)B(pz)Ph]^{2-})$. In a targeted synthesis, the lithium salt of the novel ligand $[L^2]^{2-}$ was prepared from 2 equiv of Lipz and 2,4,6-Ph₃B₃O₃ and successfully transformed into $[(p-cym)Ru(L^2)]$. $[Cp^*Ru(L^1)], [(p-cym)Ru(L^1)]PF_6, and [(p-cym)Ru(L^2)]$ have been characterized by NMR spectroscopy, X-ray crystallography, and (spectro)electrochemistry. One-electron oxidation of $[Cp*Ru(L^1)]$ by electro-chemical or chemical ($[Cp_2Fe]PF_6$) means leads to the Ru^{III} species $[Cp*Ru(L^1)]PF_6$, which has been isolated and fully characterized $(E_{1/2}(Ru^{II}/Ru^{III}) = -0.39 \text{ V}; CH_2Cl_2, \text{ vs FcH/FcH}^+)$. A comparison of the solid-state structures of $[Cp^*Ru(L^1)]$ and $[Cp^*Ru(L^1)]PF_6$ reveals that oxidation of the ruthenium center results in a lengthening of the average $Ru-Cp^*$ distances and a shortening of all $Ru-L^1$ bond lengths. According to the X-ray data, the angle strain within $[(p-cym)Ru(L^1)]PF_6$ is higher than in $[(p-cym)Ru(L^2)]$, which could account for the fact that $[L^1]^-$ is apparently less stable than $[L^2]^{2-}$.

Introduction

Tris(pyrazol-1-yl)borates ("scorpionates") are among the most prominent ligands in coordination chemistry, which is due to the fact that they are not only readily accessible but also very versatile.^{1,2} For example, introduction of appropriate substituents into the 3-positions of the pyrazolyl rings allows extensive control over the steric demand of the ligands and thus over their ability to kinetically stabilize reactive complex fragments. In contrast, an adjustment of the ligand field strengths of tris(pyrazol-1-yl)borates is much harder to achieve, because electronic substituent effects on the donor properties of the pyrazolyl rings turned out to be rather modest.³ Thus, a more efficient way to alter the donor/

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acceptor properties of scorpionate ligands is to replace one or more pyrazolyl rings by phosphorus-,⁴⁻⁸ oxygen-,⁹⁻²³

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Figure 1. Mixed-donor (pyrazol-1-yl)borates: classic scorpionate A and modified ligand architecture \mathbf{B} . Do = N-, P-, O-, or S-containing donor group.

or sulfur-containing²⁴⁻⁴¹ groups. For a systematic tuning of metal complex properties, it is particularly desirable to have complete homogeneous series of closely related homo- and heteroleptic scorpionates of the form $[RB(Do^{1})_{x}(Do^{2})_{3-x}]^{-1}$ (x = 0-3). Unfortunately, this is where scorpionate chemistry exhibits its weaknesses, because (i) the selective preparation of a specific mixed-donor borate is often difficult to achieve and (ii) borate ions have a tendency for substituent scrambling.

Given this background, we became interested in the question how the molecular framework of "classic" mixed-donor scorpionates A (Figure 1) has to be modified if we want to avoid the problems mentioned above but still take advantage of (pyrazol-1-yl)borate chemistry. For the following reasons, we came to the conclusion that **B**-type molecules (Figure 1) would be promising lead structures for future investigations: (i) many of the established design principles of scorpionate chemistry are still valid for \mathbf{B} ; (ii) the bonding situation of the central donor moiety (Do) is distinctly different from the way the pyrazolyl rings are attached to the molecule, which should help to deal with selectivity and substituent scrambling issues; (iii) molecular modeling studies indicate that ligands **B** are able to adopt both facial and (distorted) meridional coordination modes.

In a previous publication, we reported on the ligand behavior of $[L^1]^-$ (Scheme 1; **B**-type ligand with Do = O,

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Scheme 1. Synthesis of $[Li(thf)L^1]^a$



^a Legend: (i) toluene, reflux, 2 h; (ii) toluene/THF, reflux, 8 h.

R = Ph) toward Fe^{II} , Fe^{III} , and Cu^{II} .⁴² The three corresponding complexes [(pyridine)(Cl)Fe(L^1)], [Cl₂Fe(L^1)], and [ClCu(L¹)] have been structurally characterized by X-ray crystallography. Both iron complexes possess a distortedtrigonal-bipyramidal configuration with the pyrazolyl rings occupying equatorial positions and the oxygen donor being located at an apical position. The copper complex crystallizes as the chloro-bridged dimer $[ClCu(L^1)]_2$, in which the ligand environments are intermediate between a square-planar and a trigonal-bipyramidal geometry. This leads to the conclusion that $[L^1]^-$ has a higher tendency to act as a trans chelator than scorpionates A, which are always facially coordinating.

The purpose of this paper is to explore possible applications of $[L^1]^-$ in organometallic chemistry. We have chosen Ru^{II} as the central metal ion, because ruthenium scorpionate complexes have already been shown to be useful in such diverse areas as C–H activation reactions,⁴³ the catalytic hydroarylation of olefins,^{44,45} C–C coupling reactions,^{46,47}

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$[Cp*Ru(L^1)]PF_6$

 a Legend: (i) THF, room temperature, 12 h; (ii) CH₂Cl₂, room temperature, 12 h.

the radical polymerization of electron-deficient olefins,⁴⁸ the transfer hydrogenation of ketones,⁴⁹ and the catalytic cis– trans isomerization of functionalized epoxides.⁵⁰ Pentamethylcyclopentadienide (Cp*) and *p*-cymene (*p*-cym) will be employed as organic ligands, because they will force $[L^1]^$ into as much of a facial coordination mode as possible, which, together with our earlier investigations, will allow important insights into the conformational flexibility of $[L^1]^-$.

Results and Discussion

For the synthesis of $[\text{Li}(thf)L^1]$ (Scheme 1), the literature protocol⁴² has been slightly modified. Instead of preparing the 1,3-diboroxane intermediate (Me₂N(Ph)B)₂O via the controlled hydrolysis of Me₂N(Ph)BBr,⁴² we now allowed bis(dimethylamino)phenylborane, (Me₂N)₂(Ph)B,⁵¹ to react with 2,4,6-triphenylboroxine, Ph₃B₃O₃,⁵² in refluxing to-luene⁵³ and obtained (Me₂N(Ph)B)₂O in 65% yield.

Further treatment of $(Me_2N(Ph)B)_2O$ with Lipz and Hpz (1:2) in a toluene/THF mixture at reflux temperature (approximately 80 °C) led to [Li(thf)L¹] in 80% yield.

Synthesis, Characterization, and Reactivity of $[Cp^*Ru(L^1)]$. The room-temperature reaction of $[Li(thf)L^1]$ with $[Cp^*Ru-Cl]_4^{54}$ in THF resulted in the formation of complex $[Cp^*Ru-(L^1)]$ in good yield (60–70%; $Cp^* = [C_5Me_5]^-$; Scheme 2). Recrystallization of the crude product from hexane led to yellow-orange crystals suitable for X-ray analysis. $[Cp^*Ru-(L^1)]$ is only moderately air-stable, even in the solid state, and should be stored under nitrogen. It is readily soluble in hexane, CH_2Cl_2 , and THF but rapidly decomposes in strongly coordinating solvents such as CH_3CN and acetone. In contrast, the related complexes $[Cp*Ru(pz_3BH)]^{55}$ and $[Cp*Ru(pz_3CH)]PF_6^{56}$ are relatively stable in CH_3CN .

The ¹H NMR spectrum (CDCl₃) of [Cp*Ru(L¹)] is consistent with the presence of one Cp* and one tridentate [L¹]⁻ ligand in the molecule. A sharp singlet at 1.26 ppm clearly arises from the Cp* ring. A virtual triplet at 6.24 ppm and a triplet at 6.44 ppm (integral ratio 2:1) can be assigned to magnetically inequivalent pzH-4 protons and thus confirm the presence of two types of pyrazolyl rings in the molecule. The pzH-3,5 resonance of the bridging pyrazolyl ring appears as a doublet at 7.51 ppm. The pzH-3,5 protons of the pyrazolyl rings coordinated to the Ru^{II} center give two signals at 7.24–7.28 and 7.61 ppm. The first multiplet partially overlaps with resonances of the phenyl protons.

The cyclic voltammogram of the complex $[Cp^*Ru(L^1)]$ in CH_2Cl_2 shows a reversible one-electron wave at $E_{1/2} = -0.39$ V arising from the Ru(II)/Ru(III) transition ($\Delta E_p = 126 \text{ mV}$; vs FcH/FcH⁺; cf. the Supporting Information for more details). This redox potential is comparable to the potential of the related complex $[Cp^*Ru(pz_3BH)]$, which undergoes one quasi-reversible oxidation.^{55,57,58} Moreover, the fact that the oxidation of $[Cp^*Ru(L^1)]$ is a one-electron process resembles the electrochemical behavior of ferrocene but is different from the behavior of ruthenocene, which undergoes a one-step, two-electron transition upon oxidation at a Pt electrode.^{59,60}

In line with our electrochemical studies, chemical oxidation of $[Cp*Ru(L^1)]$ with $[Cp_2Fe]PF_6$ (0.8 equiv) in CH_2Cl_2 gave the Ru^{III} complex $[Cp*Ru(L^1)]PF_6$ in good yield (88%; Scheme 2). $[Cp*Ru(L^1)]PF_6$ was isolated as a dark red crystalline compound by slow diffusion of pentane into its CH_2Cl_2 solution.

The molecular structures of $[Cp*Ru(L^1)]$ and $[Cp*Ru(L^1)]PF_6$ are shown in Figures 2 and 3S (cf. the Supporting Information; the numbering scheme is the same in both structure plots); selected crystallographic data are summarized in Table 3S (cf. the Supporting Information).

The crystal lattice of $[Cp^*Ru(L^1)]$ contains two independent molecules in the asymmetric unit $([Cp^*Ru(L^1)]_A$ and $[Cp^*Ru(L^1)]_B)$; since the key structural parameters of both molecules are the same within the experimental error margins, only the structure of $[Cp^*Ru(L^1)]_A$ will be discussed further.

The Ru atom binds to ligand $[L^1]^-$ via Ru–O and Ru–N bonds with bond lengths of Ru(1)–O(1) = 2.227(3) Å, Ru(1)–N(12) = 2.139(4) Å, and Ru(1)–N(22) = 2.140(5) Å. The Ru–N bond lengths are similar to the Ru–N distances in related complexes (e.g., (Ru–N)_{av} = 2.128(3) Å in [CpRu(pz₃BH)]⁵⁵ and 2.145(3) Å in [Cp*Ru(pz₃CH)]PF₆).⁵⁶ The distance between the Ru^{II} ion and the centroid (COG) of the Cp* ring in [Cp*Ru(L¹)]_A equals 1.772 Å, which is in good agreement with the case for other Cp*Ru complexes (e.g., 1.782 Å for [Cp*Ru(pz₃CH)]PF₆).⁵⁶

In $[Cp*Ru(L^1)]PF_6$, we observe a Ru(1)-O(1) bond length of 2.173(2) Å and Ru-N bond lengths of 2.078(2)

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Figure 2. Molecular structure of $[Cp^*Ru(L^1)]_A$. H atoms are omitted for clarity; displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (A) and bond angles (deg): Ru(1)-O(1) = 2.227(3), Ru(1)-N(12) = 2.139(4), Ru(1)-N(22) =2.140(5), $Ru(1) \cdots COG(Cp^*) = 1.772$; O(1) - Ru(1) - N(12) = 76.8-(1), O(1)-Ru(1)-N(22)=76.7(2), N(12)-Ru(1)-N(22)=85.1(2),O(1)-B(1)-N(11) = 108.7(4), O(1)-B(1)-N(31) = 101.2(4),O(1)-B(2)-N(21) = 108.9(4), O(1)-B(2)-N(32) = 100.8(4),B(1)-O(1)-B(2) = 115.6(4). Corresponding structure parameters of $[Cp^*Ru(L^1)]PF_6$: Ru(1)-O(1) = 2.173(2), Ru(1)-N(12) =2.078(2), Ru(1)-N(22) = 2.086(2), $Ru(1)\cdots COG(Cp^*) = 1.830$; O(1)-Ru(1)-N(12) = 78.2(1), O(1)-Ru(1)-N(22) = 76.9(1),N(12)-Ru(1)-N(22) = 95.8(1), O(1)-B(1)-N(11) = 106.5(2),O(1)-B(1)-N(31) = 101.1(2), O(1)-B(2)-N(21) = 105.8(2),O(1)-B(2)-N(32) = 100.9(2), B(1)-O(1)-B(2) = 115.6(2). COG-(Cp*) denotes the centroid of the Cp* ring.

and 2.086(2) Å. The Ru···COG(Cp*) distance amounts to 1.830 Å. Oxidation of [Cp*Ru(L¹)] thus leads to a shortening of all Ru–L¹ contacts (Δ (Ru–O) = -0.054 Å; Δ (Ru–N)_{av} = -0.058 Å with respect to [Cp*Ru(L¹)]_A) and to a lengthening of the Ru–Cp* bonds (Δ (Ru··· COG(Cp*)) = +0.058 Å with respect to [Cp*Ru(L¹)]_A). The contraction of the Ru–L¹ contacts in [Cp*Ru(L¹)]PF₆ results in a widening of the N(12)–Ru(1)–N(22) angle by a value of 10.7° ([Cp*Ru(L¹)]PF₆, 95.8(1)°; [Cp*Ru(L¹)]_A, 85.1(2)°). In related tris(pyrazol-1-yl)borate complexes, the average N–Ru–N' angles are 83.8(1)° ([CpRu(pz₃BH)])⁵⁵ and 81.7(1)° ([Cp*Ru(pz₃CH)]PF₆).⁵⁶

Synthesis, Characterization, and Reactivity of $[(p-cym)Ru-(L^1)]X$ Complexes (X = Cl, PF₆, B(C₆F₅)₄, Tos, Tfl). The reaction of $[(p-cym)RuCl_2]_2$ with $[Li(thf)L^1]$ (1:2; THF) gave the cationic complex $[(p-cym)Ru(L^1)]Cl$ in 70% yield (Scheme 3). Within a time span of 2 h, $[(p-cym)Ru(L^1)]Cl$ precipitated from the reaction mixture as a yellow solid which should be isolated without further delay, since prolonged stirring of the reactants leads to significantly lower yields (ca. 20% after 24 h, close to 0% after 72 h).

An exchange of the counteranion can be achieved quantitatively using NH₄PF₆ or K[B(C₆F₅)₄] in CH₂Cl₂; the corresponding tosylate (Tos) or triflate (Tfl) salts have been prepared using Ag[Tos] or Ag[Tfl] in THF. In the solid state, the complexes [(*p*-cym)Ru(L¹)]X (X = PF₆, B(C₆F₅)₄, Tos, Tfl) are inert toward air and moisture over a period of several months. They are readily soluble in CHCl₃, CH₂Cl₂, CH₃CN, and acetone, and the solutions were found to be stable at least for several hours under inert conditions (¹H and ¹¹B NMR spectroscopic control). Scheme 3. Synthesis of $[(p-cym)Ru(L^1)]X (X = Cl, PF_6)$ and Formation of $[(p-cym)Ru(L^2)]$ and $[(p-cym)Ru(\mu-Cl)(\mu-pz)_2Ru-(p-cym)]PF_6^a$



^{*a*}Legend: (i) THF, room temperature, 2 h; (ii) CH_2Cl_2 , room temperature, 2 h; (iii) THF, room temperature, 12 h.

The ¹¹B NMR spectra of $[(p\text{-cym})\text{Ru}(\mathbf{L}^1)]X$ (X = PF₆, B(C₆F₅)₄, Tos, Tfl) are characterized by signals in the range between 5.9 and 8.1 ppm, testifying to the presence of fourcoordinate boron atoms.^{61,62} The ¹H and ¹³C NMR features of the $[\mathbf{L}^1]^-$ part of $[(p\text{-cym})\text{Ru}(\mathbf{L}^1)]\text{PF}_6$ are similar to those of $[\text{Li}(thf)\mathbf{L}^1]$, and the chemical shifts of the *p*-cymene resonances also do not show any peculiarities. We note, however, that one pyrazolyl resonance and the signals arising from the aromatic *p*-cymene protons are quite sensitive to changes in the counterion X⁻ (cf. the Supporting Information for synthesis protocols and NMR data of $[(p\text{-cym})\text{Ru}(\mathbf{L}^1)]X$ (X = B(C₆F₅)₄, Tos, Tfl)).

The reduction part of the cyclic voltammogram of the complex $[(p-cym)Ru(L^1)]PF_6$ in CH_2Cl_2/NBu_4PF_6 exhibits a

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Figure 3. Molecular structure of the complex $[(p\text{-cym})\text{Ru}(\mathbf{L}^1)]\text{PF}_6$. The anion is not shown, and all H atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (deg): Ru(1)-O(1) = 2.135(3), Ru(1)-N(2) = 2.070(4), Ru-(1)-N(12) = 2.079(4), Ru(1)\cdotsCOG(p\text{-cym}) = 1.689; O-(1)-Ru(1)-N(2) = 78.1(2), O(1)-Ru(1)-N(12) = 78.1(2), N(2)-Ru(1)-N(12) = 86.5(2), O(1)-B(1)-N(1) = 108.9(5), O(1)-B(1)-N(21) = 101.2(4), O(1)-B(2)-N(11) = 106.9(4), O(1)-B(2)-N(22) = 100.9(4), B(1)-O(1)-B(2) = 115.5(4). COG(p-cym) denotes the centroid of the p-cymene ring.

partially reversible wave at $E_{1/2} = -1.78$ V (vs FcH/FcH⁺; cf. the Supporting Information for more details).

The molecular structure of $[(p-cym)Ru(L^1)]PF_6$ is presented in Figure 3; selected crystallographic data are summarized in Table 3S (cf. the Supporting Information). The Ru^{II} ion, which possesses a distorted-octahedral ligand sphere, is η^6 -coordinated to the *p*-cymene ring and establishes Ru–N and Ru–O bonds to the $[L^1]^-$ ligand. The distance between the Ru^{II} ion and the centroid of the *p*-cymene ring amounts to $Ru(1)\cdots COG(p$ -cym) = 1.689 Å, in accordance with other (arene)Ru^{II} complexes (e.g., $[(p-cym)Ru(C_5H_4R)]PF_6$, Ru \cdots COG(p-cym) = 1.70 Å, $[(p-\text{cym})\text{Ru}(\text{pz}_3\text{BH})]\text{PF}_6$, $\text{Ru}\cdots\text{COG}(p-\text{cym}) = 1.70 \text{ Å}).^{64}$ The Ru–O and Ru–N bond lengths are equal to 2.135(3) and 2.070(4)/2.079(4) Å, respectively. These values are significantly smaller than in the corresponding Cp* complex $[Cp^*Ru(L^1)]_A$ (Ru-O = 2.227(3) Å; Ru-N = 2.139(4)/ 2.140(5) Å) but comparable to those of the cationic Ru^{III} congener $[Cp^*Ru(L^1)]PF_6 (Ru-O = 2.173(2) \text{ Å}; Ru-N =$ 2.078(2)/2.086(2) Å).

Hoping to circumvent problems arising from the deleterious effects of chloride ions on $[(p\text{-cym})\text{Ru}(\text{L}^1)]^+$ (see above), we decided to test the possibility of improving our synthesis protocol by adding appropriate Tl⁺ or Ag⁺ salts already at the beginning of the reaction. Because of the good solubility of LiCl in THF, 4 equiv of Tl⁺/Ag⁺ ions has to be employed per equiv of $[(p\text{-cym})\text{RuCl}_{2}]_2$ in order to achieve complete removal of chloride. However, the presence of larger quantities of Tl⁺/Ag⁺ salts at an early stage of the reaction sequence may influence the outcome also by changing the chemical composition of the starting material. For example, it has been established that treatment of $[(p-cym)-RuCl_2]_2$ with AgPF₆ (1:1) in acetone leads to the formation of the cationic dinuclear complex $[(p-cym)Ru(\mu-Cl)_3Ru-(p-cym)]PF_6$.⁶⁵ When the ratio Ag⁺: $[(p-cym)RuCl_2]_2$ is increased to 4:1, even the dicationic species $[(p-cym)Ru-(solv)_3]^{2+}$ can be obtained (solv = acetone, H₃CCN).^{66,67}

In the course of our own studies, we confirmed that $[(p-cym)Ru(\mu-Cl)_3Ru(p-cym)]PF_6$ also forms upon stirring of $[(p-cym)RuCl_2]_2$ with TIPF₆ in THF. In contrast to the reaction with Ag⁺ ions, however, the reaction with TIPF₆ stops at the stage of the dinuclear complex, even when a 4-fold excess of the Tl⁺ salt is added (¹H NMR spectroscopic control; note that the use of THF as solvent is essential).

Given this background, we have treated a THF solution of $[(p-cym)RuCl_2]_2$ with $[Li(thf)L^1]$ in the presence of TlPF₆ (1:2:4 equiv, respectively; Scheme 3). A ¹H NMR spectrum of the crude reaction mixture revealed the formation of new complexes; however, the target compound [(p-cym)Ru- (L^{1})]PF₆ could not be detected. Removal of TlCl, followed by layering of the concentrated filtrate with hexane, gave two kinds of crystals, yellow plates and light orange plates, which were identified by X-ray analysis as $[(p-cym)Ru(L^2)]$ and $[(p-cym)Ru(\mu-Cl)(\mu-pz)_2Ru(p-cym)]PF_6$, respectively (cf. the Supporting Information for details of the X-ray crystal structure analysis of $[(p-cym)Ru(\mu-Cl)(\mu-pz)_2Ru(p-cym)]PF_6$ (Figure 5S) and for a compilation of related complexes). We were able to isolate the complex $[(p-cym)Ru(L^2)]$ in pure form (yield 20%) by column chromatography of the product mixture on silica gel with CH2Cl2 as eluent (for a targeted synthesis and full characterization of $[(p-cym)Ru(L^2)]$, see below).

There are two likely scenarios of how the boroxine backbone of the complex $[(p\text{-cym})\text{Ru}(\text{L}^2)]$ might have formed: (i) hydrolysis of the ligand $[\text{L}^1]^-$ by water possibly originating from the hygroscopic TIPF₆; (ii) degradation of 3 equiv of $[\text{L}^1]^-$ and reassembly of the new ligand molecule. Both scenarios can also explain the source of the bridging pyrazolide ligands in the byproduct $[(p\text{-cym})\text{Ru}(\mu\text{-Cl})(\mu\text{-pz})_2\text{-}\text{Ru}(p\text{-cym})]\text{PF}_6$.

In order to exclude adventitious traces of water in our setup, we repeated the reaction with preformed [(*p*-cym)Ru- $(\mu$ -Cl)₃(*p*-cym)]PF₆⁶⁸ and [Li(thf)L¹] (1:2) in THF under strictly anhydrous conditions. This modified protocol again afforded a complicated product mixture; however, the complex [(*p*-cym)Ru(L²)] was absent in this mixture according to ¹H and ¹¹B NMR spectroscopy.

In view of these results, we abandoned TlPF₆ and switched to AgBF₄. In contrast to *a priori* expectations, treatment of $[(p-cym)RuCl_2]_2$ with AgBF₄ (1:4, THF) followed by addition of [Li(thf)L¹] gave neither $[(p-cym)Ru(L^1)]BF_4$ nor $[(p-cym)Ru(L^2)]$ but an inseparable mixture of other products (¹H and ¹¹B NMR spectroscopic control). The situation changed when Ag[Tos] (4 equiv, THF) was used instead of AgBF₄, because now $[(p-cym)Ru(L^1)]$ [Tos] could be isolated in 67% yield (cf. the Supporting Information). The analogous reaction with Ag[Tf1] led to $[(p-cym)Ru(L^1)]$ [Tf1] in 28% yield (cf. the Supporting Information).

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Our findings are most likely attributable to the different natures of the intermediate species formed in the mixture after the reaction between $[(p-cym)RuCl_2]_2$ and Ag^+ has occurred. We assume that addition of AgBF₄ generates [(p $cym)Ru(thf)_{x}^{2+}$ (with noncoordinated $[BF_4]^{-}$ counterions), which in turn induces degradation of the ligand $[L^1]^-$. Since the [Tos]⁻ ion is more prone to metal coordination than $[BF_4]^-$, the use of Ag[Tos] leads to more stable complexes, among them the dimer $[(p-cym)Ru(Tos)(\mu-Cl)_2Ru(Tos)-$ (*p*-cym)], which we have identified in the reaction mixture by comparison of its NMR data with those of an authentic sample (cf. the Supporting Information for the synthesis, elemental analysis, and X-ray crystal structure analysis of $[(p-cym)Ru(Tos)(\mu-Cl)_2Ru(Tos)(p-cym)]$ (Figure 6S)). To find out whether $[(p-cym)Ru(Tos)(\mu-Cl)_2Ru(Tos)-$ (p-cym)] is indeed a viable precursor of $[(p-cym)Ru(L^1)]$ -[Tos], we treated a THF solution of the dinuclear complex with 2 equiv of $[Li(thf)L^1]$ and isolated $[(p-cym)Ru(L^1)][Tos]$ in 70% yield. In contrast to [(p-cym)Ru(L¹)]Cl, [(p-cym)Ru- (L^{1}) [Tos] does not show signs of degradation upon prolonged stirring of the reaction mixture.

Synthesis and Characterization of Li[Li(thf)L²] and $[(p-cym)Ru(L^2)]$. The serendipitous discovery of the complex $[(p-cym)Ru(L^2)]$ illustrates only one facet of a more serious problem: on several occasions we already had to recognize that the stability of [Li(thf)L¹] toward water and/or strongly Lewis acidic transition-metal ions is less than desirable for a universally applicable new ligand system. Looking at the structural parameters of ligand $[L^1]^-$, it is reasonable to assume that the μ -pz linker is a little too small to span the distance between the two boron atoms without forcing the molecule to adopt nonideal bond angles (cf. O–B–N-(μ -pz) = 101.6(2), 101.7(2)° as opposed to 109.5°).⁴²

The ligand backbone in $[(p-cym)Ru(L^2)]$ consists of a three-atom O–B–O bridge instead of the two-atom N–N bridge, which should alleviate the angle strain. We therefore decided to work out a targeted synthesis of the free ligand $[L^2]^{2-}$ (Scheme 4) in order to arrive at a chelator that is potentially more stable but still features the main coordination characteristics of $[L^1]^{-}$.

Niedenzu⁵³ and Köster⁶⁹ already reported on the roomtemperature reaction of 2,4,6-triphenylboroxine, Ph₃B₃O₃, with pyrazole (1:1), which gives the monoadduct $Ph_3B_3O_3$. Hpz. Both authors, however, had conflicting opinions about the molecular architecture of Ph₃B₃O₃·Hpz: Niedenzu proposed the unusual tricyclic structure (PhB(μ -OB(Ph)O)- $(\mu$ -OH) $(\mu$ -pz)BPh) in which both pyrazolyl nitrogen atoms are involved in boron coordination, while Köster suggested that only one B-N adduct bond was present in the molecule. Niedenzu et al. further claimed the formation of the triadduct Ph₃B₃O₃·3Hpz after they had increased the stoichiometric ratio Ph₃B₃O₃:Hpz to 1:3. They described Ph₃B₃O₃. 3Hpz as being unstable in time and reverting slowly to the OBO-bridged pyrazabole $PhB(\mu-OB(Ph)O)(\mu-pz)_2BPh.^{53}$ This view was again questioned by Köster, who provided NMR evidence that even a 3-fold excess of pyrazole leads to coordination of only one nitrogen atom per boroxine molecule. Both authors further conclude that $Ph_3B_3O_3$ · Hpz is in a multistep equilibrium with the OBO-bridged pyrazabole. The dehydration sequence to $PhB(\mu-OB(Ph)O)(\mu-pz)_2BPh$ can be driven to completion by heating (145 °C, mesitylene) or, more efficiently, by azeotropic distillation.53,69 Refluxing

Scheme 4. Targeted Synthesis of $\text{Li}[\text{Li}(\text{thf})\text{L}^2]$ and $[(p\text{-cym})-\text{Ru}(\text{L}^2)]^{\alpha}$



^{*a*}Legend: (i) THF, room temperature, 30 min; (ii) THF, room temperature, 12 h.

a neat mixture of $Ph_3B_3O_3$ and Hpz affords the pyrazabole $Ph_2B(\mu$ -pz)₂BPh₂.⁵³

Since a pyrazolide ion should have an even stronger tendency to bridge adjacent boron atoms of $Ph_3B_3O_3$ than the parent pyrazole, we reasoned that the entire project of a targeted synthesis of ligand $[L^2]^{2-}$ would be put into jeopardy if Niedenzu's suggestion of the molecular structure of $Ph_3B_3O_3$. Hpz was indeed correct. We therefore investigated $Ph_3B_3O_3$. Hpz by X-ray crystallography (Figure 4; cf. also Table 4S in the Supporting Information), and thereby confirmed that the compound possesses an ordinary adduct structure with only one boron–nitrogen bond, as proposed by Köster and as required for further transition-metal complexation.

The N(1)–B(1) bond length amounts to 1.613(4) Å and is thus slightly shorter than the N–B bond in the pyridine monoadduct Ph₃B₃O₃·Py (1.635(4) Å⁷⁰/1.640(3) Å⁷¹). Ph₃B₃O₃·Hpz is further stabilized by an O(2)–H–N(2) hydrogen bond (O(2)···N(2) = 2.835(3) Å, O(2)–H(2) = 2.52(3) Å). Such an intramolecular hydrogen-bonding motif has previously been reported by Wang et al. for the 7-azaindole adduct of Ph₃B₃O₃·(7-azaind) = 2.792 Å; these researchers already suggested that Ph₃B₃O₃·Hpz should also have a hydrogen bond structure in the solid state).⁷¹ Similar to Ph₃B₃O₃·Py, the B₃O₃ core in Ph₃B₃O₃·Hpz adopts an almost planar conformation; all bond lengths and angles within the boroxine ring possess comparable values in both compounds and therefore do not merit further discussion.

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Figure 4. Molecular structure of $Ph_3B_3O_3 \cdot Hpz$. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): O(1)-B(1) = 1.463(4), O(1)-B(3) = 1.352(3), O(2)-B(1) = 1.466(3), O(2)-B(2) = 1.360(3), O(3)-B(2) = 1.388(4), O(3)-B(3) = 1.400(4), N(1)-B(1) = 1.613(4); O(1)-B(1)-O(2) = 114.3(2), O(2)-B(2)-O(3) = 121.0(2), O(1)-B(3)-O(3) = 120.5(3), B(1)-O(1)-B(3) = 121.9(2), B(1)-O(2)-B(2) = 121.4(2), B(2)-O(3)-B(3) = 120.2(2); N(1)-B(1)-O(1)-B(3) = 104.3(2), N(1)-B(1)-O(2)-B(2) = -105.1(2), O(2)-B(1)-O(1)-B(3) = -10.0(3).

Literature has it that the formation of triorganoboroxine rings, R₃B₃O₃, via condensation of organylboronic acids, RB(OH)₂, is more facile in the presence of pyridine.^{72,73} In line with that, hydrolysis of Ph3B3O3 occurs readily in organic solvents at room temperature already with traces of water, whereas solutions of Ph₃B₃O₃·Py remain unchanged under the same conditions.⁷⁰ DFT calculations indicate the high stability of 1:1 boroxine-Lewis base complexes to be due to a relief of ring strain upon adduct formation.⁷⁰ A computational study by Kua and Iovine on the formation of para-substituted triphenylboroxines, however, revealed that not only ring-strain effects but also electronic effects are likely to play a role in stabilizing or destabilizing the amine adducts.^{74,75} Most importantly, all experimentally and theoretically obtained results are consistent with the view that the formation of 1:1 adducts, but not 1:2 adducts, between boroxine and amines is thermodynamically favorable.

In spite of these discouraging reports, we have now shown that stirring a mixture of 2 equiv of Lipz and 1 equiv of boroxine in THF affords the diadduct $\text{Li}[\text{Li}(\text{thf})\text{L}^2]$ (Scheme 4) in virtually quantitative yield.

The ¹¹B NMR spectrum (THF- d_8) of Li[Li(thf)L²] is characterized by resonances at ca. 30 and 5.5 ppm (integral ratio 1:2), corresponding to three- and four-coordinate boron atoms, respectively. In line with the proposed structure of Li[Li(thf)L²], two sets of ¹H and ¹³C NMR resonances can be assigned to magnetically inequivalent phenyl



Figure 5. Molecular structure of the $[\text{Li}(\text{thf})\text{L}^2]^-$ anion of Li-(thf)([12]-c-4)[Li(thf)\text{L}^2]. H atoms are omitted for clarity; displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): O(1)-Li(1) = 1.892(7), O-(61)-Li(1) = 1.939(7), N(12)-Li(1) = 2.035(8), N(22)-Li(1) = 2.055(8), O(1)-B(1) = 1.443(4), O(1)-B(2) = 1.447(4), O(2)-B-(2) = 1.464(4), O(2)-B(3) = 1.347(4), O(3)-B(1) = 1.469(4), O(3)-B(3) = 1.353(4), N(11)-B(1) = 1.605(4), N(21)-B(2) = 1.611(4); N(12)-Li(1)-N(22) = 125.3(4), O(1)-B(1)-O(3) = 114.5(3), O(1)-B(2)-O(2) = 115.1(2), O(2)-B(3)-O(3) = 123.2-(3), B(1)-O(1)-B(2) = 123.1(2), B(1)-O(3)-B(3) = 121.7(3), B(2)-O(2)-B(3) = 121.4(2), O(1)-B(1)-N(11) = 106.7(3), O(1)-B(2)-N(21) = 106.7(2).

substituents, whereas the two pyrazolyl rings give rise to only one signal set. Thus, in contrast to various complexes $Ph_3B_3O_3 \cdot L$, where L is a simple terminal ligand,⁷¹ Li[Li-(thf)L²] shows no signs of a dynamic B–N association/ dissociation equilibrium at room temperature on the NMR time scale.

Compound Li[Li(thf) L^2] was recrystallized from THF/ hexane in the presence of [12]-crown-4 as ether solvate Li(thf)([12]-c-4)[Li(thf) L^2]. Selected crystallographic data are summarized in Table 4S (cf. the Supporting Information). The molecular structure of the anionic subunit [Li(thf) L^2]⁻ is presented in Figure 5.

The Li⁺ ion of [Li(thf)L²]⁻ binds to the [Ph₃B₃O₃·2pz]²⁻ ligand via Li–N and Li–O bonds. The bond lengths N(12)–Li(1) = 2.035(8) Å and N(22)–Li(1) = 2.055(8) Å are comparable to those in the related compound [Li(thf)L¹] (N–Li = 2.023(4), 2.034(4) Å).⁴² However, we note that a change of the bridging element from [pz]⁻ to [OB(Ph)O]²⁻ causes a widening of the N–Li–N' angle from 115.9(2)° to 125.3(4)°. The opposite is true for the O–Li bonds and the corresponding Li–O–B angles: while the bond is significantly shorter in [Li(thf)L²]⁻ than in the pyrazolide-bridged [Li(thf)L¹] (1.892(7) Å vs 1.940(4) Å), the angles remain largely the same in both molecules.⁴² The B–O–B' angle increases by 7.2(2)° upon going from [Li(thf)L¹] to the boroxine derivative [Li(thf)L²]⁻ (B(1)–O(1)–B(2) = 123.1(2)°).

As in the case of $[\text{Li}(\text{thf})\text{L}^1]$, the coordination sphere around the Li^+ ion of $[\text{Li}(\text{thf})\text{L}^2]^-$ is completed by one THF molecule (O(61)-Li(1) = 1.939(7) Å). The geometry

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index $\tau_4 = 0.77^{76}$ for the corresponding coordination polyhedron indicates that the ligand sphere of the Li⁺ ion more closely approaches a trigonal-pyramidal ($\tau_4 = 0.85$) than a tetrahedral ($\tau_4 = 1.00$) configuration (cf. [Li(thf)L¹]: $\tau_4 = 0.83$).

In comparison to $Ph_3B_3O_3 \cdot Hpz$, it is interesting to see that the N-B bond lengths of $[Li(thf)L^2]^-$ (N(11)-B(1) = 1.605(4) Å, N(21)-B(2) = 1.611(4) Å) lie in the same range as in the pyrazole monoadduct (1.613(4) Å) and that the boroxine ring of $[Li(thf)L^2]^-$ is also practically planar. As expected, the shortest O-B bonds in $[Li(thf)L^2]^-$ are those involving the sp²-hybridized boron atom (O(2)-B-(3) = 1.347(4) Å, O(3)-B(3) = 1.353(4) Å; cf. Ph₃B₃O₃ (O-B)_{av} = 1.382 Å).⁷⁷ The longest bond lengths are observed for O(2)-B(2) = 1.464(4) Å and O(3)-B(1) = 1.469(4) Å, while the O-B bonds between the Li⁺-coordinated oxygen atom O(1) and the sp³-hybridized boron centers possess intermediate lengths (O(1)-B(1) = 1.443-(4) Å, O(1)-B(2) = 1.447(4) Å).

For the targeted synthesis of $[(p\text{-cym})\text{Ru}(\text{L}^2)]$ (Scheme 4), we treated a mixture of Lipz and Ph₃B₃O₃ (2:1) in THF with 0.5 equiv of $[(p\text{-cym})\text{Ru}Cl_2]_2$. Importantly, the yield of $[(p\text{-cym})\text{Ru}(\text{L}^2)]$ (33%) depends strongly on the amount of Lipz used and reduces to 0% when 3 equiv of Lipz are employed.

 $[(p\text{-cym})\text{Ru}(\mathbf{L}^2)]$ is readily soluble in THF and CH₂Cl₂ but only moderately soluble in acetone and CH₃CN, the solutions being air-stable at least for several hours (NMR spectroscopic control).

Similar to the case for Li[Li(thf)L²], the ¹¹B NMR spectrum (CDCl₃) of [(*p*-cym)Ru(L²)] is characterized by a broad signal at ca. 28 ppm and a sharp signal at 5.0 ppm, confirming the presence of three- and four-coordinate boron atoms in the complex^{61,62} (note that the integral ratio of the two signals is less than 1:2, which we attribute to difficulties in the determination of the integral value of the broad signal ($h_{1/2} = 870$ Hz)). The ¹H and ¹³C NMR spectra of [(*p*-cym)Ru(L²)] show resonances of two magnetically equivalent pyrazolyl rings (δ (¹H) 6.20 (H-4), 7.48, 7.62 (H-3,5)) and two sets of signals for the three phenyl groups.

According to CV measurements, $[(p-cym)Ru(L^2)]$ undergoes one partially reversible reduction process at $E_{1/2} = -2.09$ V (vs FcH/FcH⁺, $i_a/i_c = 0.64$; cf. the Supporting Information for more details). This electrochemical feature is observed at a more cathodic potential value than in the case of $[(p-cym)Ru(L^1)]PF_6(E_{1/2} = -1.78$ V vs FcH/FcH⁺). Given that $[(p-cym)Ru(L^2)]$ and $[(p-cym)Ru(L^1)]PF_6$ have practically the same coordination environment at the ruthenium center, these differences in the redox potentials are most likely due to the fact that $[(p-cym)Ru(L^2)]$ contains a dianionic and $[(p-cym)Ru(L^1)]PF_6$ a monoanionic (pyrazol-1-yl)borate ligand. In contrast to $[(p-cym)Ru(L^1)]PF_6$, $[(p-cym)Ru(L^2)]$ did not undergo oxidation under the measurement conditions applied.

The molecular structure of $[(p-cym)Ru(L^2)]$ is shown in Figure 6 (cf. also Table 4S in the Supporting Information). $[(p-cym)Ru(L^2)]$ is one of very few examples⁷⁸ of complexes



Figure 6. Molecular structure of $[(p-cym)Ru(L^2)]$. H atoms are omitted for clarity; displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)-O(1) = 2.142(1), Ru(1)-N(2) = 2.078(2), Ru(1)-N(12) =2.079(2), $Ru(1) \cdots COG(p-cym) = 1.690$, O(1)-B(1) = 1.502(3), O(1)-B(2) = 1.500(3), O(2)-B(2) = 1.453(3), O(2)-B(3) =1.365(3), O(3)-B(1)=1.455(3), O(3)-B(3)=1.364(3); O(1)-Ru(1)-N(2) = 78.3(1), O(1)-Ru(1)-N(12) = 79.5(1), N(2)-Ru(1)-N(12) = 82.7(1), B(1)-O(1)-B(2) = 121.3(2), O(1)-B(1)-O(3)=113.9(2), O(1)-B(2)-O(2)=113.9(2). COG(p-cym)denotes the centroid of the *p*-cymene ring.

in which a transition-metal ion is coordinated to a discrete boroxine ring. The Ru–O interaction is stabilized by two bridging pyrazolide rings. All bond lengths and angles within the coordination environment of the Ru^{II} ion are almost identical with those in $[(p-cym)Ru(L^1)]PF_6$; the largest difference is observed for the N(2)–Ru(1)–N(12) angle, which is more acute in $[(p-cym)Ru(L^2)]$ (82.7(1)°) than in $[(p-cym)Ru(L^1)]PF_6$ (86.5(2)°).

Most of the key structural parameters of the $[L^2]^{2-}$ part of $[(p\text{-cym})\text{Ru}(L^2)]$ closely resemble those of $[\text{Li}(\text{thf})L^2]^-$, with the remarkable exception of the O–B bonds involving the metal-coordinated oxygen atom, which are, on average, 0.056 Å longer in $[(p\text{-cym})\text{Ru}(L^2)]$ (O(1)–B(1) = 1.502(3) Å, O(1)–B(2) = 1.500(3) Å) than in the lithium complex. Moreover, the boroxine ring of $[(p\text{-cym})\text{Ru}(L^2)]$ is slightly nonplanar and adopts a shallow chair conformation with dihedral angles B(1)O(1)B(2)//B(1)B(2)O(2)O(3) and O(2)B-(3)O(3)//B(1)B(2)O(2)O(3) of 14.7 and 12.4°, respectively (in $[\text{Li}(\text{thf})L^2]^-$, the corresponding angles amount to 9.5 and 2.5°).

Similar to the case for $[\text{Li}(\text{thf})\text{L}^2]^-$ vs $[\text{Li}(\text{thf})\text{L}^1]$, the B(1)-O(1)-B(2) angle of $[(p\text{-cym})\text{Ru}(\text{L}^2)]$ (121.3(2)°) is larger by 5.8(2)° than that of $[(p\text{-cym})\text{Ru}(\text{L}^1)]\text{PF}_6$ (115.5(4)°).

Conclusion

The reaction of the tripodal [N,O,N] (pyrazol-1-yl)borate ligand $[Ph(pz)B(\mu-O)(\mu-pz)B(pz)Ph]^-$ ($[L^1]^-$) with $[Cp^*Ru-Cl]_4$ and $[(p-cym)RuCl_2]_2$ leads to the pseudo-octahedral Ru^{II} complexes $[Cp^*Ru(L^1)]$ and $[(p-cym)Ru(L^1)]Cl$, respectively (pz = pyrazolyl, Cp^{*} = pentamethylcyclopentadienyl, p-cym = p-cymene). $[(p-cym)Ru(L^1)]Cl$ slowly

⁽⁷⁶⁾ Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955–964. The geometry index $\tau_4 = \{360^\circ - (\alpha + \beta)\}/141^\circ$ is defined for four-coordinate complexes, with α and β being the two largest bond angles around the central atom.

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decomposes in solution but can be stabilized by exchanging the Cl^{-} anion for PF_{6}^{-} .

Attempts to remove the Cl⁻ ions by addition of 4 equiv of TlPF₆ already at the initial stage of the reaction did not lead to $[(p\text{-cym})\text{Ru}(\mathbf{L}^1)]\text{PF}_6$, but resulted in a mixture of other products. The most abundant constituents of this mixture were the dinuclear complex $[(p\text{-cym})\text{Ru}(\mu\text{-Cl})(\mu\text{-pz})_2\text{Ru}(\mu\text{-cym})]\text{PF}_6$ and the mononuclear species $[(p\text{-cym})\text{Ru}(\mathbf{L}^2)]$ ($[\mathbf{L}^2]^{2-} = [\text{Ph}(\text{pz})\text{B}(\mu\text{-O})(\mu\text{-OB}(\text{Ph})\text{O})\text{B}(\text{pz})\text{Ph}]^{2-}$). $[(p\text{-cym})\text{Ru}(\mathbf{L}^2)]$ contains a promising new [N, O, N] (pyrazol-1-yl)borate ligand with a phenylboroxine backbone. In a subsequent targeted synthesis, we prepared the lithium salt Li[Li(thf)\mathbf{L}^2] from Ph_3B_3O_3 and 2 equiv of Lipz and successfully transformed it into $[(p\text{-cym})\text{Ru}(\mathbf{L}^2)]$ by treatment with $[(p\text{-cym})\text{Ru}\text{Cl}_2]_2$.

Our preliminary experience with $[L^1]^-$ and $[L^2]^{2^-}$ indicates the latter ligand to be less prone to hydrolysis and more tolerant to strongly Lewis acidic transition metal complex fragments. Since the substitution pattern of the boroxine backbone and/or the pyrazolyl rings can easily be varied, the straightforward synthesis procedure developed for $[L^2]^{2^-}$ should also make a broad selection of custom-tailored derivatives readily accessible. Moreover, $[L^1]^-$ and $[L^2]^{2^-}$ provide very similar coordination environments but differ in their electronic charge, thereby offering another set screw for the gradual adjustment of the properties of a chelated metal center (cf. the electrode potential required for the partly reversible reduction of $[(p-cym)Ru(L^2)]$, which is more cathodic by -0.31 V than that of $[(p-cym)Ru(L^1)]PF_6$).

In summary, we suggest L^1 - and L^2 -type ligands as viable alternatives to more conventional mixed-donor bis(pyrazol-1-yl)borates [RB(OR')pz₂]⁻, because they are comparatively easy to prepare and show a higher conformational flexibility together with a lower tendency to substituent scrambling.

Experimental Section

General Considerations. All reactions were carried out under nitrogen using standard Schlenk techniques. All solvents were dried and distilled prior to use. Starting materials $[Cp*RuCl]_4$,⁵⁴ PhB(NMe₂)₂,⁵¹ 2,4,6-Ph₃B₃O₃,⁵² and $[Li(thf)L^I]^{42}$ were prepared as published in the literature. [(p-cym)Ru(µ-Cl)₃-(p-cym)]PF₆ was synthesized by adapting a synthesis protocol previously reported for the synthesis of the analogous benzene derivative.⁶⁸ Compounds $[Cp_2Fe]PF_6$ and $[(p-cym)RuCl_2]_2$ were obtained from commercial sources. ¹H, ¹³C{¹H}, and ¹¹B{¹H} NMR spectra were recorded with Bruker AMX 300 or Avance 400 spectrometers at room temperature. Abbreviations: s =singlet, d = doublet, t = triplet, sept = septet, vt = virtualtriplet, dd = doublet of doublets, m = multiplet, br = broad; pz = pyrazolide, Tos = tosylate; Tfl = triflate; p-cym = p-cymene. Cyclic voltammograms were recorded using an EG&G Princeton Applied Research 263A potentiostat. UV/ vis spectra were recorded on a Varian Cary 50 UV/vis spectrophotometer. For spectroelectrochemical measurements, the spectrometer was equipped with a Hellma 661.500 guartz immersion probe. Elemental analyses were performed by the microanalytical laboratory of the Goethe University Frankfurt.

Synthesis of $[Cp*Ru(L^{I})]$. A mixture of $[Li(thf)L^{1}]$ (96 mg, 0.20 mmol) and $[Cp*Ru(Cl]_{4}$ (55 mg, 0.05 mmol) was stirred in THF (10 mL) for 12 h. The solvent was removed under vacuum and the orange residue extracted into hexane (20 mL). The extract was concentrated to a volume of 3 mL under reduced pressure and kept at -30 °C overnight, whereupon yellow-orange crystals precipitated that were suitable for an X-ray analysis. Yield: 81 mg (64%). ¹H NMR (300 MHz, CDCl₃): δ

1.26 (s, 15H; CH₃), 6.24 (vt, 2H; pzH-4), 6.44 (t, 1H, ${}^{3}J_{HH} = 2.4$ Hz; μ -pzH-4), 7.13–7.17 (m, 4H; PhH), 7.24–7.28 (m, 8H; PhH/pzH-3 or 5), 7.51 (d, 2H, ${}^{3}J_{HH} = 2.4$ Hz; μ -pzH-3,5), 7.61 (br, 2H; pzH-3 or 5). ${}^{11}B{}^{1}H{}$ NMR (96.3 MHz, CDCl₃): δ 5.7. ${}^{13}C{}^{1}H{}$ NMR (100.6 MHz, CDCl₃): δ 9.9 (CH₃), 73.3 (CCH₃), 106.2 (pzC-4), 109.7 (μ -pzC-4), 127.1 (PhC), 127.3 (PhC-p), 130.2 (br, pzC-3 or 5), 130.4 (μ -pzC-3,5), 132.8 (PhC), 139.2 (br, pzC-3 or 5). Anal. Calcd for C₃₁H₃₄B₂N₆ORu [629.33]: C, 59.16; H, 5.45; N, 13.35. Found: C, 59.11; H, 5.53; N, 13.21.

Synthesis of $[Cp*Ru(L^1)]PF_6$. A mixture of $[Cp*Ru(L^1)]$ (82 mg, 0.13 mmol) and $[Cp_2Fe]PF_6$ (36 mg, 0.11 mmol) was stirred in CH₂Cl₂ (10 mL) overnight. The solvent was evaporated under vacuum to give a dark red solid, which was extracted with pentane to remove ferrocene and excess $[Cp*Ru(L^1)]$. The crude product was redissolved in CH₂Cl₂ (3 mL) and layered with pentane (15 mL), whereupon dark red crystals grew near the interface of the two liquids. The crystals were suitable for X-ray analysis. Yield: 75 mg (88%). Anal. Calcd for C₃₁H₃₄-B₂F₆N₆OPRu [774.30]: C, 48.09; H, 4.43; N, 10.85. Found: C, 48.35; H, 4.48; N, 10.99.

Synthesis of $[(p-cym)Ru(L^1)]PF_6$. A mixture of $[Li(thf)L^1](154)$ mg, 0.33 mmol) and [(p-cym)RuCl₂]₂ (100 mg, 0.16 mmol) was stirred in THF (5 mL) for 2 h. A yellow precipitate formed, which was isolated by filtration, washed with Et₂O, redissolved in CH₂Cl₂ (5 mL), and treated with NH₄PF₆ (53 mg, 0.33 mmol). After 2 h, the mixture was filtered and the filtrate concentrated under reduced pressure to a volume of 2 mL. Addition of Et₂O (20 mL) resulted in the precipitation of a yellow solid, which was collected on a frit, washed with Et₂O, and dried under vacuum. Yield: 171 mg (69%). X-ray-quality crystals were obtained by slow diffusion of hexane into a CH2Cl2 solution of the complex. ¹H NMR (300 MHz, CDCl₃): δ 0.72 $(d, 6H, {}^{3}J_{HH} = 6.9 \text{ Hz}; (CH_{3})_{2}CH), 1.63 (s, 3H; CH_{3}), 1.83 (sept,$ ¹H, ³ $J_{\rm HH} = 6.9$ Hz; (CH₃)₂CH), 5.31, 5.54 (2 × d, 2 × 2H, ${}^{3}J_{\text{HH}} = 6.0 \text{ Hz; } p\text{-cymH}$), 6.31 (vt, 2H; pzH-4), 6.58 (t, 1H, ${}^{3}J_{\text{HH}} = 2.4 \text{ Hz; } \mu\text{-pzH-4}$), 7.27–7.29, 7.39–7.41 (2 × m, 4H, 6H; ³J_{HH} = 2.4 Hz, μ -pzH-3,5), 8.07 (d, 2H, ³J_{HH} = 2.1 Hz; pzH-3 or 5), 7.62 (d, 2H, ³J_{HH} = 2.4 Hz; μ -pzH-3,5), 8.07 (d, 2H, ³J_{HH} = 2.1 Hz; pzH-3 or 5). ¹¹B{¹H} NMR (96.3 MHz, CDCl₃): δ 5.9. ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 18.2 (CH₃), 21.8 ((CH₃)₂CH), 30.6 ((CH₃)₂CH), 81.3, 81.9, 101.1, 106.1 (*p*-cymC), 109.2 (pzC-4), 111.2 (µ-pzC-4), 128.1 (PhC), 129.0 (PhC-p), 131.8 (PhC), 132.1, 132.3 (*µ*-pzC-3,5/pzC-3 or 5), 143.6 (pzC-3 or 5). Anal. Calcd for C₃₁H₃₃B₂F₆N₆OPRu [773.29]: C, 48.15; H, 4.30; N, 10.87. Found: C, 47.89; H, 4.30; N, 10.63.

Synthesis of $[(p-cym)Ru(\mu-Cl)_3Ru(p-cym)]PF_6$. A mixture of $[(p-cym)RuCl_2]_2$ (100 mg, 0.16 mmol) and TIPF₆ (230 mg, 0.65 mmol) in THF (15 mL) was stirred for 2 h. TlCl was removed by filtration, the filtrate was evaporated to dryness under reduced pressure, and the orange solid residue was carefully dried. Yield: 111 mg (95%). ¹H NMR (250.0 MHz, CDCl_3): 1.31 (d, 6H, ³J_{HH} = 7.0 Hz; (CH₃)₂CH), 2.24 (s, 3H; CH₃), 2.78 (sept, 1H, ³J_{HH} = 7.0 Hz; (CH₃)₂CH), 5.48, 5.65 (2 × d, 2 × 2H, ³J_{HH} = 6.3 Hz; *p*-cymH).

Synthesis of Li(thf)([12]-c-4)[Li(thf)L²]. A mixture of Lipz (47 mg, 0.64 mmol), Ph₃B₃O₃ (100 mg, 0.32 mmol), and [12]-crown-4 (113 mg, 0.64 mmol) was stirred in THF (5 mL) for 30 min. Hexane (3 mL) was added, and the solution was cooled to -5 °C overnight. Colorless X-ray-quality crystals formed, which were isolated on a frit, rinsed with hexane (2 × 5 mL), and briefly dried under reduced pressure. Yield: 260 mg (95%). Since the crystals tend to lose THF, most of the crop was kept under vacuum for several hours in order to obtain a well-defined sample for elemental analysis. ¹H NMR (300.0 MHz, THF-*d*₈): δ 3.58 (s, 16H; [12]-c-4), 5.96 (vt, 2H; pzH-4), 6.80–6.87, 7.07–7.10, 7.25–7.27 (3 × m, 6H, 4H, 3H; PhH), 7.28, 7.60 (2 × d, 2 × 2H, ³*J*_{HH} = 1.8 Hz; pzH-3,5), 7.97–8.00 (m, 2H; PhH). ¹¹B{¹H} NMR (96.3 MHz, THF-*d*₈): δ 5.5 (s, 2B), ca. 30 (*h*_{1/2} = 720 Hz, 1B). ¹³C{¹H} NMR (100.6 MHz, CDCl₃): δ 71.6

([12]-c-4), 103.2 (pzC-4), 124.8, 126.6, 127.7, 129.4, 132.4, 132.7, 135.0, 136.5 (PhC/pzC-3,5). Anal. Calcd. for $C_{36}H_{45}B_3Li_2N_4O_8$ [708.06] × 2 H₂O [18.02]: C, 58.11; H, 6.64; N, 7.53. Found: C, 56.83; H, 6.30; N, 7.84.

Synthesis of $[(p-cym)Ru(L^2)]$. Method 1. A mixture of $[\text{Li}(\text{thf})L^1]$ (200 mg, 0.42 mmol), $[(p-cym)RuCl_2]_2$ (130 mg, 0.21 mmol), and TIPF₆ (300 mg, 0.86 mmol) in THF (10 mL) was stirred for 12 h. After TICl had been removed by filtration, the filtrate was first concentrated to a volume of 1 mL under reduced pressure and then layered with hexane (15 mL). Two kinds of crystals, orange plates and yellow plates, were obtained. The crystals were identified by X-ray analysis as $[(p-cym)Ru(\mu-Cl)(\mu-pz)_2Ru(p-cym)]PF_6$ and $[(p-cym)Ru(L^2)]$, respectively. The crystal mixture was dissolved in CH₂Cl₂ and filtered through a thin layer of silica gel (1 × 0.5 cm) using CH₂Cl₂ as the eluent. Evaporation of the solvent from the eluate left $[(p-cym)Ru(L^2)]$ as a yellow solid. Yield: 57 mg (20%).

Method 2. A mixture of Lipz (49 mg, 0.66 mmol) and Ph₃B₃O₃ (102 mg, 0.33 mmol) was stirred in THF (10 mL) for 30 min. [(p-cym)RuCl₂]₂ (100 mg, 0.16 mmol) was added, and stirring was continued for 12 h. The solvent was removed under vacuum to give a yellow-orange solid residue, which was extracted into CH₂Cl₂. The extract was filtered through a thin layer of silica gel $(1 \times 0.5 \text{ cm})$ using CH₂Cl₂ as the eluent. The yellow band was collected and the eluate evaporated to dryness under vacuum. Yield: 72 mg (33%). ¹H NMR (300.0 MHz, CDCl₃): δ 1.05 (d, 6H, ³J_{HH} = 6.9 Hz; (CH₃)₂CH), 1.13 (s, 3H; CH₃), 2.09 (sept, 1H, ${}^{3}J_{\text{HH}} = 6.9$ Hz; (CH₃)₂CH), 4.17, 5.25 (2 × d, 2 × 2H, ${}^{3}J_{\rm HH} = 6.0$ Hz; p-cymH), 6.20 (vt, 2H; pzH-4), 7.16–7.30 (m, 13H; PhH), 7.48, 7.62 (2 × 2H, 2 × d, ${}^{3}J_{HH} = 1.5$ Hz; pzH-3,5), 7.97 (m, 2H; PhH). ${}^{11}B{}^{1}H{}$ NMR (96.3 MHz, CDCl₃): δ 5.0 (s, 2B), ca. 28 ($h_{1/2} = 870$ Hz, 1B). ¹³C{¹H} NMR (75.4 MHz, CDCl₃): δ 17.4 (CH₃), 22.7 ((CH₃)₂CH), 29.9 ((CH₃)₂CH), 80.2, 84.1, 100.2, 104.6 (*p*-cymC), 106.4 (*pz*C-4), 126.1, 126.9, 127.0, 129.1, 131.8 (PhC), 133.2 (pzC-3 or 5), 134.8 (PhC), 138.9 (pzC-3 or 5). Anal. Calcd for $C_{34}H_{35}B_3N_4O_3Ru$ [681.16]: C, 59.95; H, 5.18; N, 8.23. Found: C, 60.07; H, 5.23; N. 7.99%.

X-ray Crystal Structure Analysis. Single crystals were analyzed with a STOE IPDS II two-circle diffractometer with graphite-monochromated Mo K α (0.710 73 Å) radiation. Empirical absorption corrections were performed for all structures, except Ph₃B₃O₃·Hpz and Li(thf)([12]-c-4)[Li(thf)L²], using the MULABS⁷⁹ option in PLATON.⁸⁰ The structures were solved by direct methods using the program SHELXS⁸¹ and refined against F^2 with full-matrix least-squares techniques using the program SHELXL-97.⁸² All non-hydrogen atoms (except the disordered atoms of Li(thf)([12]-c-4)[Li(thf)L²]) were refined with anisotropic displacement parameters. The hydrogen atoms were geometrically positioned and treated as riding on the carbon atoms. The *H*pz-atom in Ph₃B₃O₃·Hpz was freely refined.

The crystal of $[Cp^*Ru(L^1)]$ looks monoclinic but is actually a triclinic twin (twin law: -100/0-10/001) with a ratio of 0.772(1)/0.228(1) for the two twin components.

In the structure $[(p\text{-cym})\text{Ru}(\text{L}^1)]\text{PF}_6$ there are channels containing disordered solvent molecules. However, no reasonable model could be found for refinement. Thus, the contribution of the solvent to the reflections has been suppressed with the SQUEEZE⁸³ option in PLATON.

The crystal lattice of Li(thf)([12]-c-4)[Li(thf)L²] contains 1 equiv of noncoordinating THF molecules, i.e. Li(thf)([12]c-4)[Li(thf)L²] ·THF. Two THF molecules (marked with # in the structure below) and the crown ether ring of Li(thf)([12]c-4)[Li(thf[#])L²] ·THF[#] are disordered over two sites with site occupation factors of the major occupied site of 0.63(1)/0.61(1) for the two THF molecules and 0.62(1) for the crown ether ring. Equivalent bond lengths and angles in the disordered THF molecules were restrained to be equal in order to keep the geometric parameters within a reasonable range.

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Supporting Information Available: CIF files giving crystallographic data for [Cp*Ru(L¹)] (CCDC-735031), [Cp*Ru(L¹)]PF₆ (CCDC-735033), [(*p*-cym)Ru(L¹)]PF₆ (CCDC-735035), [(*p*-cym)- $Ru(\mu-Cl)(\mu-pz)_2Ru(p-cym)]PF_6$ (CCDC-735032), [(p-cym)Ru-(Tos)(\mu-Cl)_2Ru(Tos)(p-cym)] (CCDC-735036), Ph_3B_3O_3 \cdot Hpz (CCDC-735030), Li(thf)([12]-c-4)[Li(thf)L²] (CCDC-735037), and $[(p-cym)Ru(L^2)]$ (CCDC-735034), structure plot of $[Cp*Ru(L^1)]$ -PF₆, structure plots and a compilation of key structural parameters of [(p-cym)Ru(µ-Cl)(µ-pz)₂Ru(p-cym)]PF₆ and [(p-cym)Ru(Tos)- $(\mu$ -Cl)₂Ru(Tos)(*p*-cym)], UV/vis spectra of [Cp*Ru(L¹)] and $[Cp*Ru(L^1)]PF_6$, synthesis and NMR data of $[(p-cym)Ru(L^1)]X$ $(X = [B(C_6F_5)_4], [Tos], [Tfl])$, and details of the electrochemical investigations of [Cp*Ru(L¹)], [(p-cym)Ru(L¹)]PF₆, and [(p-cym)- $Ru(L^2)$]. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data can also be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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