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# Synthesis and Structural Characterization of the Tetrakis(methimazoly)borates Li[Bmt4] and [Ru(p-cymene)(Bmt4)][PF6]

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**Synthesis and Structural Characterization of the  
Tetrakis(methimazolyl)borates Li[Bmt4] and [Ru(p-  
cymene)(Bmt4)][PF6]**

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Keywords:	Scorpionate, Methimazolylborate, Ruthenium, X-ray structure analysis



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14 **Synthesis and Structural Characterization of the**  
15 **Tetrakis(methimazolyl)borates Li[Bmt<sub>4</sub>] and [Ru(*p*-cymene)(Bmt<sub>4</sub>)]PF<sub>6</sub>]**  
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24 Frankfurt, Institut für Anorganische Chemie der Goethe-Universität  
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30 Received XX.YY.2008.  
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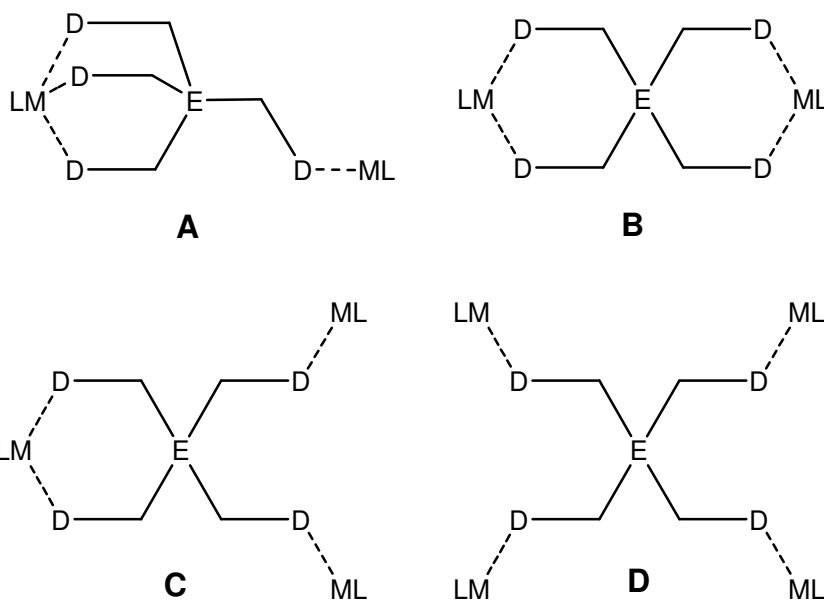
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6 **Abstract.** The lithium tetrakis(methimazolyl)borate Li[Bmt<sub>4</sub>] is accessible from the  
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8 reaction of Li[BH<sub>4</sub>] with four equivalents of methimazole. The crystal structure of Li[Bmt<sub>4</sub>]  
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10 supported by four water molecules is described. Reaction of Li[Bmt<sub>4</sub>] with [Ru(*p*-  
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12 cymene)Cl<sub>2</sub>]<sub>2</sub> and subsequent treatment with NH<sub>4</sub>PF<sub>6</sub> in CH<sub>3</sub>CN results in the formation of  
13  
14 the complex [Ru(*p*-cymene)(Bmt<sub>4</sub>)]PF<sub>6</sub>. In addition, we report the result of the X-ray  
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16 structure analysis of the chiral Ru complex [Ru(*p*-cymene)(Bmt<sub>4</sub>)]PF<sub>6</sub>.  
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25 **Keywords:** Scorpionate; Methimazolylborate; Ruthenium; X-ray structure analysis  
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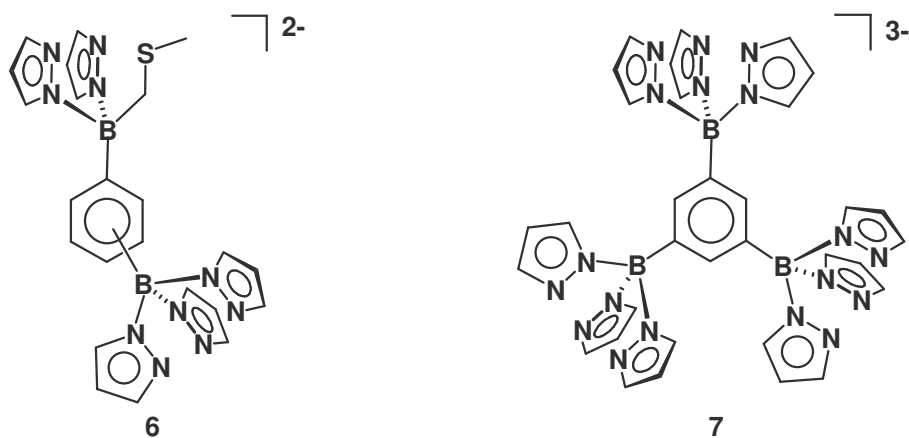
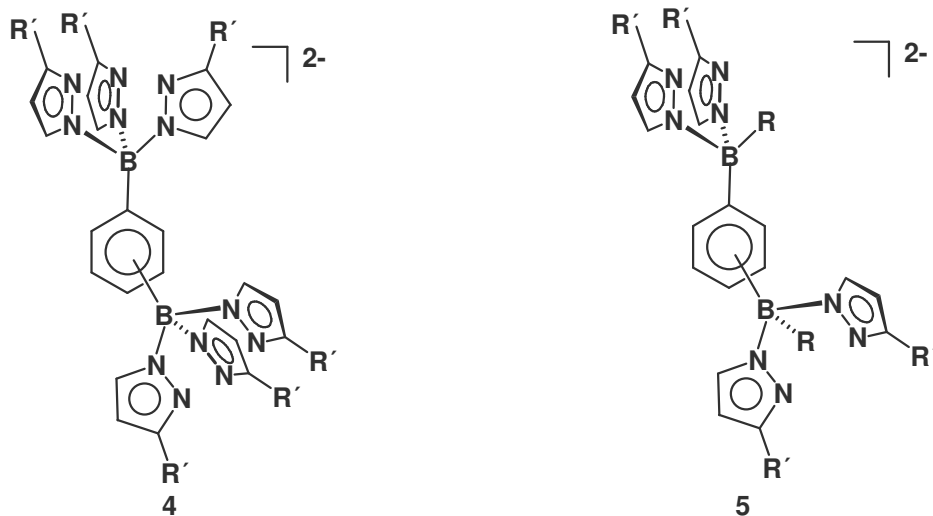
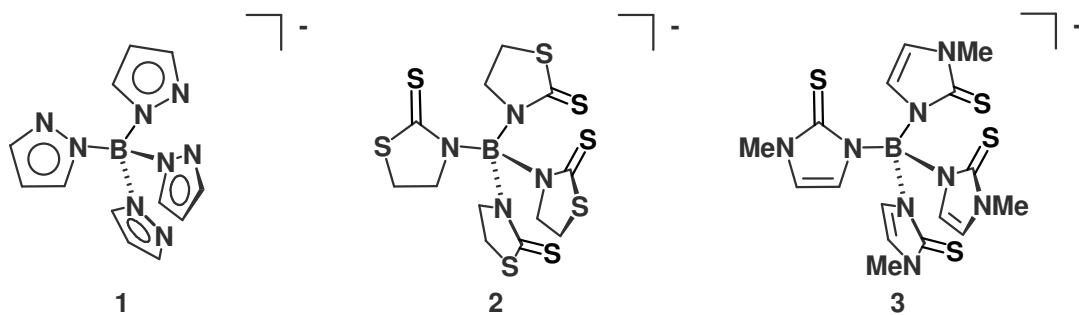
## Introduction

Multidentate ligand systems have attracted considerable interest in the last decades [1, 2]. As mentioned in Figure 1, the “classical” tetradentate ligand systems  $E(\text{CH}_2\text{D})_4$  ( $E = \text{C}, \text{Si}, \text{Sn}; \text{D} = \text{OR}, \text{SR}, \text{NR}_2, \text{PR}_2$ ) can coordinate in different modes: (i) in a ditopic monodentate tripodate (**A**), (ii) in a ditopic bidentate-chelating (**B**), (iii) in a tritopic bis-monodentate bidentate-chelating (**C**), and (iv) in a tetratopic monodentate mode (**D**).



A modification of “classical” chelating ligand systems  $\text{RE}(\text{CH}_2\text{D})_3$  and  $\text{E}(\text{CH}_2\text{D})_4$  ( $E = \text{C}, \text{Si}, \text{Sn}; \text{D} = \text{OR}, \text{SR}, \text{NR}_2, \text{PR}_2$ ) with “podand topology” can be achieved by implementing

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6 group 13 elements as ligand centers E (e.g. E = B) and heterocycles (e.g. pyrazole = pz) as  
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8 their chelating donors. Due to the Coulomb attraction between ligand and cation, very  
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10 stable complexes will be formed thereby. Prominent examples of this class of ligands are  
11  
12 the pyrazolylborates (scorpionates)  $[R_nBpz_{4-n}]^-$  (R = H, alkyl, aryl; n = 2, 1, 0; pz =  
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14 pyrazolyl) which have found applications in a wide range of chemistry, from modelling the  
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16 active site of metalloenzymes, through analytical chemistry and organic synthesis to  
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18 catalysis and materials science [3].  
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8 In 1967 *Trofimenko* reported the synthesis of a tetradentate scorpionate, the  
9 tetrakis(pyrazolyl)borate **1** (Figure 2) [4]. More than 30 years later, in 2004, a sulfur  
10 analogue of **1**, the tetrakis(2-mercaptothiazolyl)borate **2**, was synthesized for the first time  
11 by *Silva* and coworkers [5]. The synthesis was achieved from potassiumborohydride  
12  $K[BH_4]$  and 2-mercaptothiazole. However, the preparation of the first  
13 hydrotris(methimazolyl)borate  $M[HBmt_3]$ , a tridentate ligand with sulfur donor, was  
14 reported earlier in 1996 by *Reglinski* and coworkers [6]. In contrast to pyrazolyl based  
15 scorpionates, which usually form six-membered  $B(N_2)_2M$ -rings in solid state, the structural  
16 motif in soft analogues of the pyrazolylborates, the mercaptoimidazolylborates, is generally  
17 an eight-membered  $B(NCS)_2M$ -heterocycle. Normally, S,N borate ligands such as  
18 tetrakis(2-mercaptothiazolyl)borate **2** [5] or hydrotris(methimazolyl)borate  $Na[HBmt_3]$  [6]  
19 are softer than the pyrazolyl analogues and as such are more useful to be used as supporting  
20 ligands with soft transition metals.  
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39 In previous studies we had described the synthesis and structural characterization of several  
40 di- and tritopic ligands with a phenylene linker **4**, **5**, **6**, and **7**, as shown in Figure 2 [7, 8, 9,  
41 10]. Now we are interested in mononuclear soft ligand systems with binding modes **A** and  
42 **B**, as depicted in Figure 1. Recently, we have synthesized and characterized the soft ligands  
43  $Sn(CH_2SMe)_4$  and  $Sn(CH_2PPh_2)_4$  [2]. However, the solid-state structure of the coordination  
44 polymer  $\{Zn[Sn(CH_2SMe)_4]_{0.5}Cl_2\}_n$  features Zn centers which are coordinated by the  
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6 tetradentate ligand  $\text{Sn}(\text{CH}_2\text{SCH}_3)_4$  in the tritopic bis-monodentate bidentate-chelating mode  
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8 **C** [2].  
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10 Herein we report the synthesis of the tetradentate tetrakis(methimazolyl)borate ligand  
11  $[\text{Bmt}_4]^-$  (**3**) and its coordination behavior. In addition, we describe the result of the X-ray  
12 structure analysis of  $[\text{Li}(\text{H}_2\text{O})_4][\text{Bmt}_4]$   $\{[\text{Li}(\text{H}_2\text{O})_4][\mathbf{3}]\}$  and the synthesis of the complex  
13  $[\text{Ru}(p\text{-cymene})(\text{Bmt}_4)][\text{PF}_6]$   $\{\mathbf{8}[\text{PF}_6]\}$  which can be obtained by reaction of  $\text{Li}[\mathbf{3}]$  with  
14  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  in the presence of  $\text{NH}_4\text{PF}_6$  in  $\text{CH}_3\text{CN}$ .  
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## 32 **Results and discussion**

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36 Recently *Bailey* and coworkers have reported the synthesis of the ligands  $[\text{B}(\text{N}$ -  
37 methylimidazolyl)(*mt*) $_3]^-$  [11, 12]. Now we were able to prepare the lithium  
38 tetrakis(methimazolyl)borate  $\text{Li}[\mathbf{3}]$  in the melt by reaction of one equivalent of  $\text{Li}[\text{BH}_4]$   
39 with four equivalents of methimazole, as shown in Scheme 1. In contrast to the preparation  
40 of  $\text{Li}[\mathbf{3}]$  the syntheses of hydrotris(methimazolyl)borates  $\text{M}[\text{HBmt}_3]$  ( $\text{M} = \text{Li, Na, K}$ ) and  
41 dihydrobis(methimazolyl)borate  $\text{M}[\text{H}_2\text{Bmt}_2]$  were achieved at lower temperatures by the  
42 reaction of  $\text{M}[\text{BH}_4]$  ( $\text{M} = \text{Li, Na, K}$ ) with 3 or 2 equivalents of methimazole [6, 13, 14, 15].  
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53 Single crystals of  $[\text{Li}(\text{H}_2\text{O})_4][\mathbf{3}]$  suitable for X-ray diffraction were obtained from a solution  
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6 of methanol and water at room temperature. The colorless methimazolyl borate Li[**3**] is  
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8 stable against air and moisture. However, Li[**3**] can easily be transformed to the  
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10 corresponding transition metal complexes by salt metathesis.  
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20 First of all the Ru(II) complex **8**[Cl] was generated by the reaction of Li[**3**] with [Ru(*p*-  
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22 cymene)Cl<sub>2</sub>]<sub>2</sub> in CH<sub>3</sub>CN (Scheme 1). Subsequent treatment with NH<sub>4</sub>PF<sub>6</sub> led to the  
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24 formation of the corresponding complex **8**[PF<sub>6</sub>]. Recrystallization from methylene chloride  
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26 yielded large red single crystals of **8**[PF<sub>6</sub>] suitable for X-ray diffraction.  
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30 The tetrakis(methimazolyl)borate [Li(H<sub>2</sub>O)<sub>4</sub>][**3**] crystallizes in the triclinic space group *P*-1  
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32 with four molecules in the asymmetric unit (Figures 3 and 4). The Li cation in  
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34 [Li(H<sub>2</sub>O)<sub>4</sub>][**3**] is coordinated by four molecules of water. The angles around the boron atom  
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36 are with 109.5(1)° very close to the ideal tetrahedral angle (109.5°). As is to be expected for  
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38 the donor-supported lithium atoms in [Li(H<sub>2</sub>O)<sub>4</sub>][**3**], no short Li-S contacts are found in this  
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40 structure. In consequence the Li-S-distance of 4.506 - 9.171 Å in the solvent separated ion  
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42 pair [Li(H<sub>2</sub>O)<sub>4</sub>][**3**] is significantly longer than the sum of the atomic radii.  
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49 --- Figure 3 and 4---  
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6 The ruthenium complex **8**[PF<sub>6</sub>] crystallizes together with one molecule of methylene  
7 chloride (Figure 5). Due to the chiral nature tetrakis(methimazolyl)borates exist as a pair of  
8 two mirror-image forms. As expected the unit cell of **8**[PF<sub>6</sub>] contains two molecules one of  
9 each enantiomer (Figure 6). The structural parameters of the tetrakis(methimazolyl)borate  
10 ligand in **8**[PF<sub>6</sub>] are comparable to those of the anion in [Li(H<sub>2</sub>O)<sub>4</sub>][**3**]. The Ru atom which  
11 is coordinated by three sulfur atoms of the tetrakis(methimazolyl)borate ligand [Ru-S  
12 distances: 2.4253(10) – 2.4601(10) Å], form relatively short contacts to the carbon atoms of  
13 the cymene ligand. The Ru atom displays Ru-C distances of 2.201(4) – 2.246(4) Å to the  
14 carbon atoms of the cymene rings. This is, in essence, the same situation as in [Ru(*p*-  
15 cymene)(B(N-methylimidazolyl)(mt)<sub>3</sub>)] [Cl] [11], where the anion has been exchanged.  
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31 --- Figure 5 and 6 ---  
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## 14 Conclusion

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18 The lithium tetrakis(methimazolyl)borate Li[**3**] is accessible from the reaction of Li[BH<sub>4</sub>]  
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20 with four equivalents of methimazole in the melt. X-ray quality crystals of Li[**3**] supported  
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22 by four water molecules were obtained from a solution of methanol and water at ambient  
23  
24 temperature. Reaction of Li[**3**] with [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> and subsequent treatment with  
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26 NH<sub>4</sub>PF<sub>6</sub> in CH<sub>3</sub>CN results in the formation of the complex **8**[PF<sub>6</sub>]. In addition, we report  
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28 the result of the X-ray structure analysis of the chiral Ru complex **8**[PF<sub>6</sub>]. As expected the  
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30 unit cell of **8**[PF<sub>6</sub>] contains two molecules one of each enantiomer.  
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## 41 Experimental Section

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44 **General Remarks:** All experiments were carried out under dry argon or nitrogen using  
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46 standard Schlenk and glove box techniques. Solvents were distilled from Na/benzophenone  
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48 (toluene), Na/Pb alloy (pentane), CaH<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>) and molecular sieve (CH<sub>3</sub>CN)  
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50 under a dry argon atmosphere prior to use. Starting materials were purchased from  
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52 commercial sources and used without further purification. NMR: Bruker Avance 300.  
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Chemical shifts are referenced to residual solvent signals ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or external  $\text{BF}_3\cdot\text{Et}_2\text{O}$  ( $^{11}\text{B}$ ). Abbreviations: s = singlet, d = doublet, sept = septet, n.r. = multiplet expected in the  $^1\text{H}$  NMR spectrum but not resolved, n.o. = signal not observed, br = broad. The free methimazolyl substituent is denoted with an asterisk (mt\*).

**Synthesis of Li[3]:**  $\text{LiBH}_4$  in THF (2.33 ml, 4.66 mmol, 2 mol/l) and methimazole (2.18 g, 19.09 mmol) were put together and the solvent was evaporated *in vacuo*. The two colorless solids were heated up (1 h) to  $200^\circ\text{C}$  until they began to turn light yellow. 25 mL of toluene were added and the suspension was refluxed for 11 hours. The colorless precipitate was filtered off and washed one time with  $\text{CHCl}_3$  (10 mL). The solid was suspended in 10 mL  $\text{H}_2\text{O}$  and centrifuged. The supernatant was discarded and the solid was washed with pentane (5 mL) and dried *in vacuo*. Colorless crystals of  $[\text{Li}(\text{H}_2\text{O})_4][\mathbf{3}]$  were formed at room temperature by evaporation of a  $\text{MeOH}/\text{H}_2\text{O}$  (1:1) solution. Yield: 0.76 g (30%).

$^1\text{H}$  NMR (300 MHz,  $[\text{D}_6]\text{DMSO}$ , 297.3 K):  $\delta$  3.33 (s, 12H, NMe), 6.66, 6.81 (1  $\times$  d, 1  $\times$  n.r., 2  $\times$  4H,  $^3J_{\text{HH}} = 2.4$  Hz, CH). –  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $[\text{D}_6]\text{DMSO}$ , 298.7 K):  $\delta$  34.0 (NMe), 115.3, 124.3 (CH), 164.0 (CS), n.o. (CB). –  $^{11}\text{B}\{^1\text{H}\}$  NMR (96.3 MHz,  $[\text{D}_6]\text{DMSO}$ , 297.1 K):  $\delta$  0.5 ( $h_{1/2} = 9$  Hz). **Anal. Calcd** for  $\text{C}_{16}\text{H}_{20}\text{BLiN}_8\text{S}_4$  (470.40)  $\times$  4  $\text{H}_2\text{O}$  (18.02): C, 35.43; H, 5.20; N, 20.66. **Found:** C, 35.77; H, 5.31; N, 20.18. MS (ESI):  $m/z$  (%) = 463.2 (100.00) 464.2 (26.49) 462.1 (22.31) 465.2 (20.04) 466.1 (4.48) 467.1 (1.69)  $[\text{Bmt}_4]^+$ , **calcd for**  $[\text{Bmt}_4]^+$  463.08 (100.0) 464.08 (29.1) 462.08 (25.6) 465.08 (22.4) 466.08 (4.9) 467.07 (1.4).

**Synthesis of 8[PF<sub>6</sub>]:** [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (0.23 g, 0.38 mmol) was stirred in 35 mL of CH<sub>3</sub>CN for 1 h. [Li(H<sub>2</sub>O)<sub>4</sub>][**3**] (0.40 g, 0.74 mmol) was added and the reaction mixture was stirred for 1 h at 60°C. The solvent was evaporated *in vacuo* and the residue was resolved in 50 mL of EtOH. To the solution was added NH<sub>4</sub>PF<sub>6</sub> (0.12 g, 0.74 mmol) and it was stirred for 2 d at room temperature. The red-brown precipitate was filtered off, washed five times with EtOH (5 mL) and dried *in vacuo*. Yield: 0.18 g (29%). Single crystals of **8**[PF<sub>6</sub>] were formed upon slow diffusion of **8**[PF<sub>6</sub>] in CH<sub>2</sub>Cl<sub>2</sub> in pentane.

**<sup>1</sup>H NMR** (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 299.6 K): δ 1.21, 1.23 (2 × d, 2 × 3H, <sup>3</sup>J<sub>HH</sub> = 4.8 Hz, CH<sub>3</sub>-<sup>*i*</sup>Pr), 2.21 (s, 3H, CH<sub>3</sub>), 2.95 (sept, 1H, CH-<sup>*i*</sup>Pr), 3.52 (s, 3H, NMe\*), 3.69 (s, 9H, NMe), 5.29-5.41 (n.r., 4H, Ar-H), 6.86 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 2.7 Hz, CH\*), 6.92 (d, 3H, <sup>3</sup>J<sub>HH</sub> = 2.4 Hz, CH), 6.99 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 2.4 Hz, CH\*), 7.08 (br, 3H, CH). – **<sup>13</sup>C{<sup>1</sup>H} NMR** (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298.0 K): δ 18.9 (CH<sub>3</sub>), 22.5, 22.7 (CH<sub>3</sub> <sup>*i*</sup>Pr), 30.8. (CH), 35.5 (NMe\*), 35.8 (NMe), 83.7, 84.9, 85.5, 85.6 (Ar-C), 101.6, 106.8 (Ar-*i*C), 119.6, 119.9 (CH\*), 120.9, 124.3 (CH), n.o. (CS), n.o. (CB). – **<sup>11</sup>B{<sup>1</sup>H} NMR** (96.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 299.5 K): δ 0.7 (*h*<sub>1/2</sub> = 10 Hz). **Anal. Calcd** for C<sub>26</sub>H<sub>34</sub>BF<sub>6</sub>N<sub>8</sub>PRuS<sub>4</sub> (843.71): C, 37.01; H, 4.06; N, 13.28. **Found:** C, 36.80; H, 4.10; N, 13.01. MS (ESI<sup>+</sup>): *m/z* (%) = 698.6 (100.00) 699.4 (90.52) 697.6 (77.94) 700.5 (68.55) 701.3 (55.68) 702.4 (20.79) [Bmt<sub>4</sub>]<sup>+</sup>, **calcd for** [Bmt<sub>4</sub>]<sup>+</sup> 699.09 (100.0) 698.09 (76.9) 701.09 (65.5) 697.09 (52.2) 700.09 (50.7) 696.09 (39.9) 702.09 (22.9) 695.09 (14.6) 693.09 (13.3) 703.09 (12.4) 694.10 (5.5) 692.1 (3.0) 704.09 (3.0).

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6 **X-ray structure determination.** Data collection: Stoe-IPDS-II diffractometer, graphite  
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8 monochromated Mo  $K_{\alpha}$  radiation;  $T = 173$  K. Empirical absorption correction using  
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10 MULABS [16], structure solution by direct methods [17], structure refinement by full-  
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12 matrix least-squares on  $F^2$  with SHELXL-97 [18]. Hydrogen atoms were placed on ideal  
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14 positions and refined with fixed isotropic displacement parameters using a riding model.  
15  
16 Crystallographic data (excluding structure factors) for the structures reported in this paper  
17  
18 have been deposited with the Cambridge Crystallographic Data Centre as supplementary  
19  
20 publication nos. CCDC 711110 {[Li(H<sub>2</sub>O)<sub>4</sub>][**3**]} and CCDC 711111 {**8**[PF<sub>6</sub>]}. Copies of the  
21  
22 data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge  
23  
24 CB2 1EZ (Telefax : +1223/336 033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).  
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40 **Figure 1** Tetradentate ligand systems for polymetallic coordination chemistry.

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45 **Figure 2** Di- and tritopic boron-based ligands.

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50 **Figure 3** Structure of  $[\text{Li}(\text{H}_2\text{O})_4][\mathbf{3}]$  in the crystal; thermal ellipsoids are drawn at the 50 %  
51 probability level. Selected bond lengths / Å and angles / °: B(1)-N(1) 1.5699(19); N(1)-  
52 B(1)-N(1)#2 108.52(14), N(1)#1-B(1)-N(1) 109.95(7). Symmetry transformations used to  
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6 generate equivalent atoms:  $-y+3/4, x-1/4, -z+3/4$  (#1),  $-x+1, -y+1/2, z+0$  (#3).  
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11 **Figure 4** Crystal packing diagram of  $[\text{Li}(\text{H}_2\text{O})_4][\mathbf{3}]$ .  
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15 **Figure 5** Structure of  $\mathbf{8}[\text{PF}_6]$  in the crystal; thermal ellipsoids are drawn at the 50 %  
16 probability level. Selected bond lengths / Å, atom...atom distances / Å and angles / °: B(1)-  
17 N(1) 1.547(5), B(1)-N(11) 1.556(6), B(1)-N(21) 1.576(5), B(1)-N(31) 1.573(5), C(1)-S(1)  
18 1.730(4), C(11)-S(11) 1.734(4), C(21)-S(21) 1.731(4), Ru(1)-S(1) 2.4253(10), Ru(1)-S(11)  
19 2.4601(10), Ru(1)-S(21) 2.4260(9), Ru(1)-COG(Cym) 1.709; N(1)-B(1)-N(11) 110.1(3),  
20 N(1)-B(1)-N(21) 114.8(3), N(1)-B(1)-N(31) 105.2(3), N(11)-B(1)-N(21) 106.9(3), N(11)-  
21 B(1)-N(31) 110.4(3), N(21)-B(1)-N(31) 109.4(3), C(1)-S(1)-Ru(1) 106.14(14), C(11)-  
22 S(11)-Ru(1) 104.75(12), C(21)-S(21)-Ru(1) 111.09(13).  
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37 **Figure 6** Mirror image pair of the complex cation  $\mathbf{8}$ .  
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6 **Scheme 1** Synthesis of lithium tetrakis(methimazolyl)borate  $[\text{Li}(\text{H}_2\text{O})_4][\mathbf{3}]$ , and the  
7  
8 Ruthenium *para*-cymene complex  $\mathbf{8}[\text{PF}_6]$ . (i) melt, (ii) toluene, (iii)  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ ,  
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10  $\text{CH}_3\text{CN}$ , (iv)  $\text{NH}_4\text{PF}_6$ , EtOH.  
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25 **Table 1** Crystal data and refinement details for  $[\text{Li}(\text{H}_2\text{O})_4][\mathbf{3}]$  and  $\mathbf{8}[\text{PF}_6]$ .  
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	[Li(H <sub>2</sub> O) <sub>4</sub> ][ <b>3</b> ]	<b>8</b> [PF <sub>6</sub> ] (CH <sub>2</sub> Cl <sub>2</sub> )
empirical formula	C <sub>16</sub> H <sub>28</sub> BLiN <sub>8</sub> O <sub>4</sub> S <sub>4</sub>	C <sub>27</sub> H <sub>36</sub> BCl <sub>2</sub> F <sub>6</sub> N <sub>8</sub> PRuS <sub>4</sub>
formula weight	542.45	928.63
T / K	173(2)	173(2)
wavelength	MoK <sub>α</sub> , 0.71073 Å	MoK <sub>α</sub> , 0.71073 Å
crystal system	tetragonal	triclinic
space group	<i>I</i> 4 <sub>1</sub> / <i>a</i>	<i>P</i> -1
<i>a</i> / Å	13.9830(14)	11.4919(8)
<i>b</i> / Å	13.9830(14)	13.1799(11)
<i>c</i> / Å	12.7265(12)	13.8989(11)
<i>α</i> / °	90	78.370(6)
<i>β</i> / °	90	71.105(6)
<i>γ</i> / °	90	69.822(6)
<i>V</i> / Å <sup>3</sup>	2488.3(4)	1859.9(3)
<i>Z</i>	4	2
density calculated g cm <sup>-3</sup>	1.448	1.658
<i>F</i> (000)	1136	940
<i>μ</i> mm <sup>-1</sup>	0.422	0.897
index ranges	-16 ≤ <i>h</i> ≤ 16	-13 ≤ <i>h</i> ≤ 13
	-14 ≤ <i>k</i> ≤ 16	-15 ≤ <i>k</i> ≤ 15
	-15 ≤ <i>l</i> ≤ 15	-16 ≤ <i>l</i> ≤ 16
crystal size / mm <sup>3</sup>	0.17 × 0.17 × 0.17	0.29 × 0.13 × 0.09
no. of reflections collected	8253	18616
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2σ( <i>I</i> )]	0.0400, 0.0787	0.0395, 0.0930
data / restraints / parameter	1097 / 0 / 86	6900 / 423 / 514
GOOF on <i>F</i> <sup>2</sup>	0.982	1.003
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0665, 0.0861	0.0542, 0.0984
largest diff peak and hole / eÅ <sup>-3</sup>	0.224, -0.240	0.971, -0.705

## Scheme 1

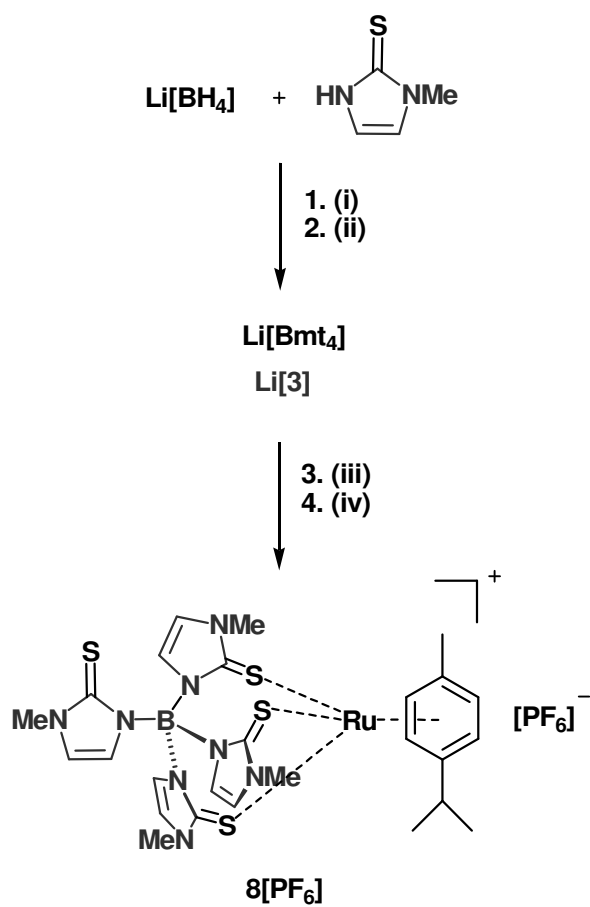


Figure 1

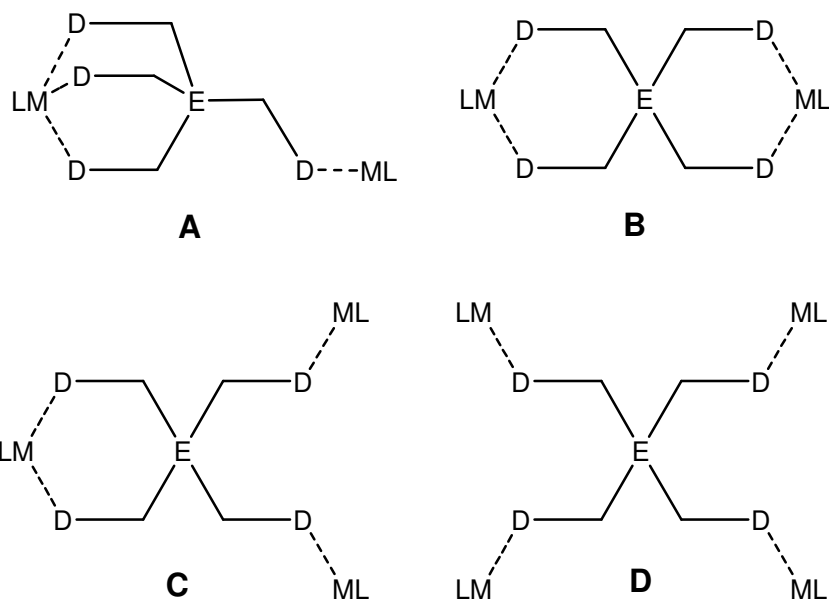


Figure 2

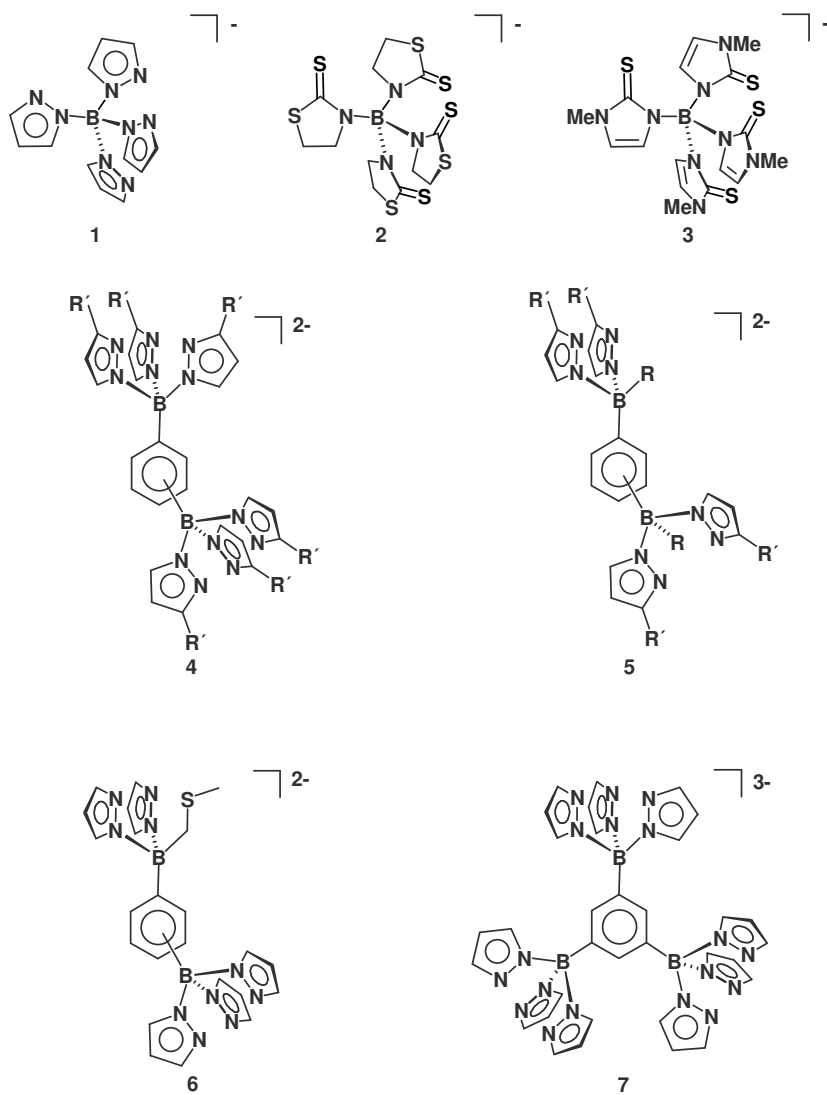


Figure 3

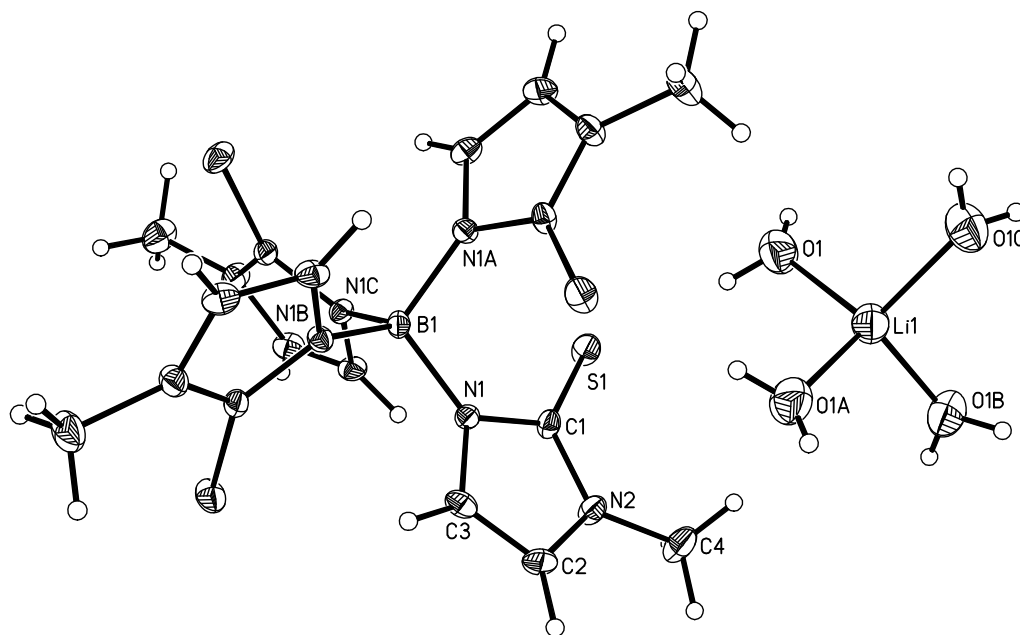




Figure 4

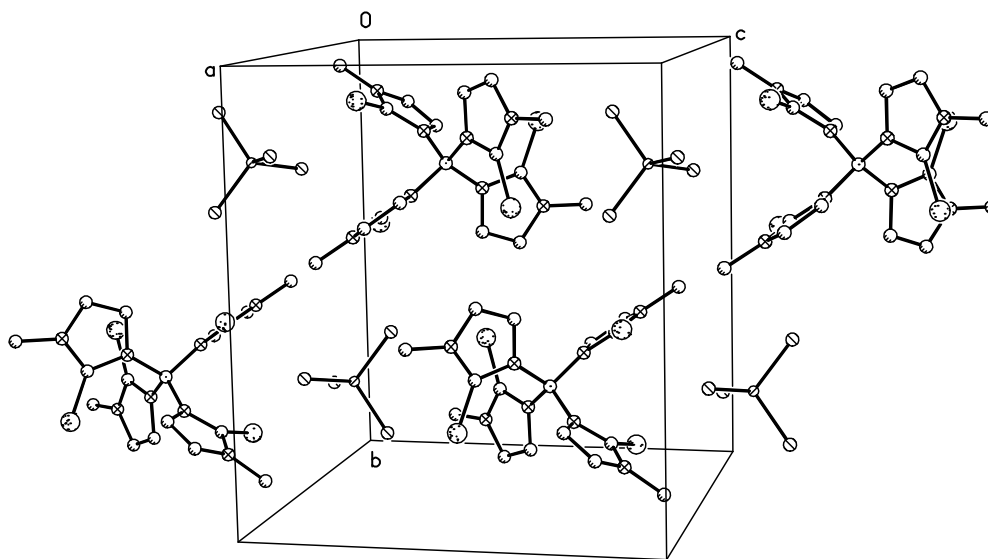




Figure 6

