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

Synthesis and Structural Characterization of the Tetrakis(methimazolyl)borates Li[Bmt_4] and [Ru(*p*-cymene)(Bmt_4)][PF_6]

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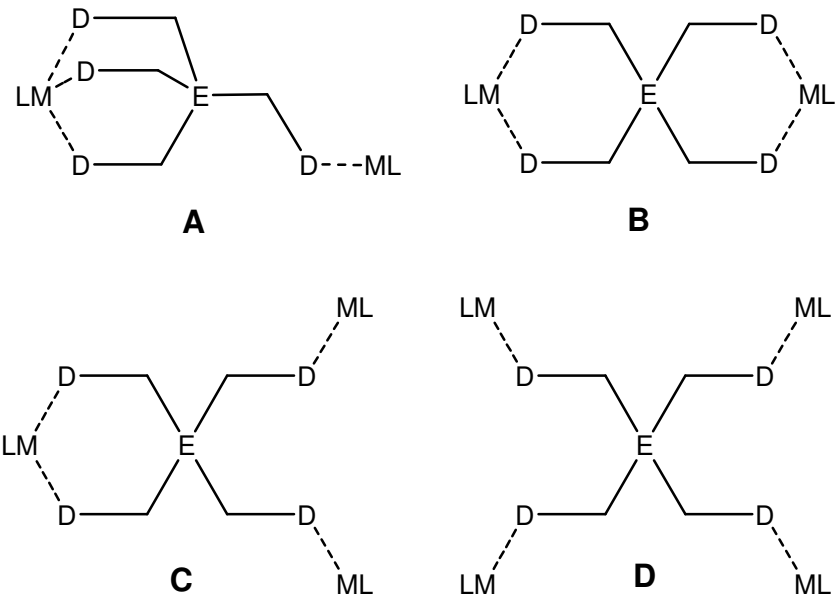
Abstract. The lithium tetrakis(methimazolyl)borate Li[Bmt_4] is accessible from the reaction of Li[BH_4] with four equivalents of methimazole. The crystal structure of Li[Bmt_4] supported by four water molecules is described. Reaction of Li[Bmt_4] with [Ru(*p*-cymene)Cl_2]$_2$ and subsequent treatment with NH_4PF_6 in CH_3CN results in the formation of the complex [Ru(*p*-cymene)(Bmt_4)][PF_6]. In addition, we report the result of the X-ray structure analysis of the chiral Ru complex [Ru(*p*-cymene)(Bmt_4)][PF_6].

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

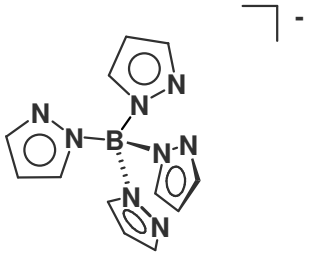
Introduction

Multidentate ligand systems have attracted considerable interest in the last decades [1, 2]. As mentioned in Figure 1, the "classical" tetradentate ligand systems $E(CH_2D)_4$ (E = C, Si, Sn; D = OR, SR, NR_2, 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 $RE(CH_2D)_3$ and $E(CH_2D)_4$ (E = C, Si, Sn; D = OR, SR, NR_2, PR_2) with "podand topology" can be achieved by implementing

group 13 elements as ligand centers E (e.g. E = B) and heterocycles (e.g. pyrazole = pz) as their chelating donors. Due to the Coulomb attraction between ligand and cation, very stable complexes will be formed thereby. Prominent examples of this class of ligands are the pyrazolylborates (scorpionates) $[R_nBpz_{4-n}]^-$ (R = H, alkyl, aryl; n = 2, 1, 0; pz = pyrazolyl) which have found applications in a wide range of chemistry, from modelling the active site of metaloenzymes, through analytical chemistry and organic synthesis to catalysis and materials science [3].



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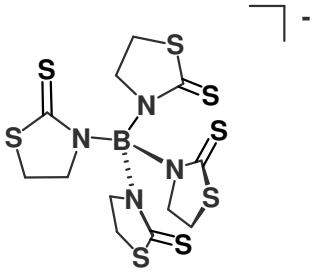

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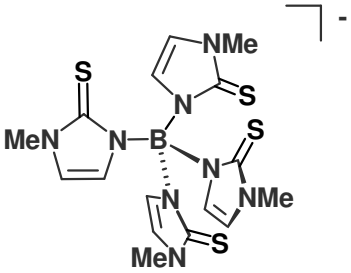

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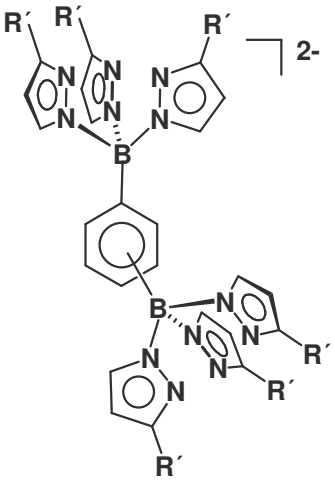

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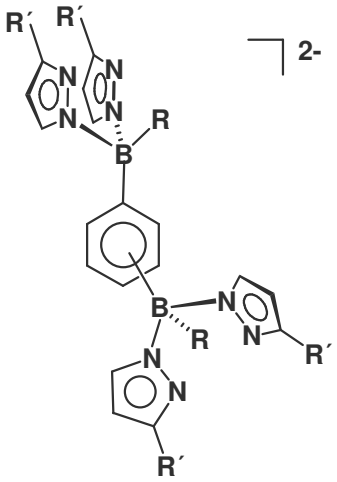

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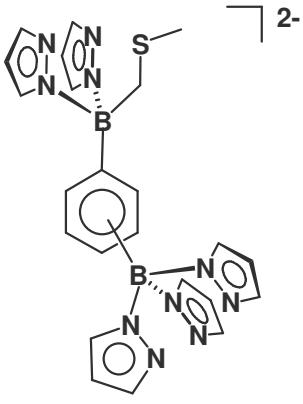

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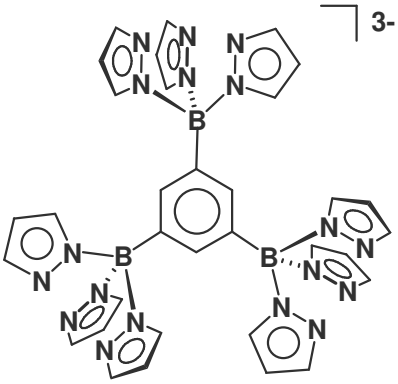

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In 1967 *Trofimenko* reported the synthesis of a tetradentate scorpionate, the tetrakis(pyrazolyl)borate **1** (Figure 2) [4]. More than 30 years later, in 2004, a sulfur analogue of **1**, the tetrakis(2-mercaptothiazolyl)borate **2**, was synthesized for the first time by *Silva* and coworkers [5]. The synthesis was achieved from potassiumborohydride $K[BH_4]$ and 2-mercaptothiazole. However, the preparation of the first hydrotris(methimazolyl)borate $M[HBmt_3]$, a tridentate ligand with sulfur donor, was reported earlier in 1996 by *Reglinski* and coworkers [6]. In contrast to pyrazolyl based scorpionates, which usually form six-membered $B(N_2)_2M$-rings in solid state, the structural motif in soft analogues of the pyrazolylborates, the mercaptoimidazolylborates, is generally an eight-membered $B(NCS)_2M$-heterocycle. Normally, S,N borate ligands such as tetrakis(2-mercaptothiazolyl)borate **2** [5] or hydrotris(methimazolyl)borate $Na[HBmt_3]$ [6] are softer than the pyrazolyl analogues and as such are more useful to be used as supporting ligands with soft transition metals.

In previous studies we had described the synthesis and structural characterization of several di- and tritopic ligands with a phenylene linker **4**, **5**, **6**, and **7**, as shown in Figure 2 [7, 8, 9, 10]. Now we are interested in mononuclear soft ligand systems with binding modes **A** and **B**, as depicted in Figure 1. Recently, we have synthesized and characterized the soft ligands $Sn(CH_2SMe)_4$ and $Sn(CH_2PPh_2)_4$ [2]. However, the solid-state structure of the coordination polymer $\{Zn[Sn(CH_2SMe)_4]_{0.5}Cl_2\}_n$ features Zn centers which are coordinated by the

tetradentate ligand $Sn(CH_2SCH_3)_4$ in the tritopic bis-monodentate bidentate-chelating mode **C** [2].

Herein we report the synthesis of the tetradentate tetrakis(methimazolyl)borate ligand $[Bmt_4]^-$ (**3**) and its coordination behavior. In addition, we describe the result of the X-ray structure analysis of $[Li(H_2O)_4][Bmt_4]$ {$[Li(H_2O)_4]$**[3]**} and the synthesis of the complex [Ru(*p*-cymene)$(Bmt_4)][PF_6]$ {**8**$[PF_6]$} which can be obtained by reaction of Li**[3]** with $[Ru(p\text{-cymene})Cl_2]_2$ in the presence of NH_4PF_6 in CH_3CN.

Results and discussion

Recently *Bailey* and coworkers have reported the synthesis of the ligands [B(N-methylimidazolyl)$(mt)_3]^-$ [11, 12]. Now we were able to prepare the lithium tetrakis(methimazolyl)borate Li**[3]** in the melt by reaction of one equivalent of $Li[BH_4]$ with four equivalents of methimazole, as shown in Scheme 1. In contrast to the preparation of Li**[3]** the syntheses of hydrotris(methimazolyl)borates $M[HBmt_3]$ (M = Li, Na, K) and dihydrobis(methimazolyl)borate $M[H_2Bmt_2]$ were achieved at lower temperatures by the reaction of $M[BH_4]$ (M = Li, Na, K) with 3 or 2 equivalents of methimazole [6, 13, 14, 15]. Single crystals of $[Li(H_2O)_4]$**[3]** suitable for X-ray diffraction were obtained from a solution

of methanol and water at room temperature. The colorless methimazolyl borate Li**[3]** is stable against air and moisture. However, Li**[3]** can easily be transformed to the corresponding transition metal complexes by salt metathesis.

--- Scheme 1---

First of all the Ru(II) complex **8**[Cl] was generated by the reaction of Li**[3]** with [Ru(*p*-cymene)Cl_2]$_2$ in CH_3CN (Scheme 1). Subsequent treatment with NH_4PF_6 led to the formation of the corresponding complex **8**[PF_6]. Recrystallization from methylene chloride yielded large red single crystals of **8**[PF_6] suitable for X-ray diffraction.

The tetrakis(methimazolyl)borate [Li(H_2O)$_4$]**[3]** crystallizes in the triclinic space group *P*-1 with four molecules in the asymmetric unit (Figures 3 and 4). The Li cation in [Li(H_2O)$_4$]**[3]** is coordinated by four molecules of water. The angles around the boron atom are with 109.5(1)° very close to the ideal tetrahedral angle (109.5°). As is to be expected for the donor-supported lithium atoms in [Li(H_2O)$_4$]**[3]**, no short Li-S contacts are found in this structure. In consequence the Li-S-distance of 4.506 - 9.171 Å in the solvent separated ion pair [Li(H_2O)$_4$]**[3]** is significantly longer than the sum of the atomic radii.

--- Figure 3 and 4---

The ruthenium complex **8**[PF_6] crystallizes together with one molecule of methylene chloride (Figure 5). Due to the chiral nature tetrakis(methimazolyl)borates exist as a pair of two mirror-image forms. As expected the unit cell of **8**[PF_6] contains two molecules one of each enantiomer (Figure 6). The structural parameters of the tetrakis(methimazolyl)borate ligand in **8**[PF_6] are comparable to those of the anion in [$Li(H_2O)_4$]**[3]**. The Ru atom which is coordinated by three sulfur atoms of the tetrakis(methimazolyl)borate ligand [Ru-S distances: 2.4253(10) – 2.4601(10) Å], form relatively short contacts to the carbon atoms of the cymene ligand. The Ru atom displays Ru-C distances of 2.201(4) – 2.246(4) Å to the carbon atoms of the cymene rings. This is, in essence, the same situation as in [Ru(*p*-cymene)(B(N-methylimidazolyl)$(mt)_3$)] [Cl] [11], where the anion has been exchanged.

--- Figure 5 and 6 ---

--- Table 1 ---

Conclusion

The lithium tetrakis(methimazolyl)borate Li[**3**] is accessible from the reaction of $Li[BH_4]$ with four equivalents of methimazole in the melt. X-ray quality crystals of Li[**3**] supported by four water molecules were obtained from a solution of methanol and water at ambient temperature. Reaction of Li[**3**] with $[Ru(p\text{-cymene})Cl_2]_2$ and subsequent treatment with NH_4PF_6 in CH_3CN results in the formation of the complex **8**$[PF_6]$. In addition, we report the result of the X-ray structure analysis of the chiral Ru complex **8**$[PF_6]$. As expected the unit cell of **8**$[PF_6]$ contains two molecules one of each enantiomer.

Experimental Section

General Remarks: All experiments were carried out under dry argon or nitrogen using standard Schlenk and glove box techniques. Solvents were distilled from Na/benzophenone (toluene), Na/Pb alloy (pentane), CaH_2 (CH_2Cl_2, $CHCl_3$) and molecular sieve (CH_3CN) under a dry argon atmosphere prior to use. Starting materials were purchased from commercial sources and used without further purification. NMR: Bruker Avance 300.

Chemical shifts are referenced to residual solvent signals (^{1}H, ^{13}C) or external $BF_3{\cdot}Et_2O$ (^{11}B). Abbreviations: s = singlet, d = doublet, sept = septet, n.r. = multiplet expected in the ^{1}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]: $LiBH_4$ 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°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 $CHCl_3$ (10 mL). The solid was suspended in 10 mL H_2O and centrifuged. The supernatant was discarded and the solid was washed with pentane (5 mL) and dried *in vacuo*. Colorless crystals of $[Li(H_2O)_4]$**[3]** were formed at room temperature by evaporation of a MeOH/H_2O (1:1) solution. Yield: 0.76 g (30%).

^{1}H NMR (300 MHz, [D_6]DMSO, 297.3 K): δ 3.33 (s, 12H, NMe), 6.66, 6.81 (1 × d, 1 × n.r., 2 × 4H, $^{3}J_{HH}$ = 2.4 Hz, CH). – **^{13}C{^{1}H} NMR** (75.5 MHz, [D_6]DMSO, 298.7 K): δ 34.0 (NMe), 115.3, 124.3 (CH), 164.0 (CS), n.o. (CB). – **^{11}B{^{1}H} NMR** (96.3 MHz, [D_6]DMSO, 297.1 K): δ 0.5 ($h_{1/2}$ = 9 Hz). **Anal. Calcd** for $C_{16}H_{20}BLiN_8S_4$ (470.40) × 4 H_2O (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) $[Bmt_4]^-$, **calcd for** $[Bmt_4]^-$ 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_6]: [Ru(*p*-cymene)Cl_2]$_2$ (0.23 g, 0.38 mmol) was stirred in 35 mL of CH_3CN for 1 h. [Li(H_2O)$_4$]**[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_4PF_6 (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_6] were formed upon slow diffusion of **8**[PF_6] in CH_2Cl_2 in pentane.

^{1}H NMR (300 MHz, CD_2Cl_2, 299.6 K): δ 1.21, 1.23 (2 × d, 2 × 3H, $^3J_{HH}$ = 4.8 Hz, CH_3-^{i}Pr), 2.21 (s, 3H, CH_3), 2.95 (sept, 1H, CH-^{i}Pr), 3.52 (s, 3H, NMe*), 3.69 (s, 9H, NMe), 5.29-5.41 (n.r., 4H, Ar-H), 6.86 (d, 1H, $^3J_{HH}$ = 2.7 Hz, CH*), 6.92 (d, 3H, $^3J_{HH}$ = 2.4 Hz, CH), 6.99 (d, 1H, $^3J_{HH}$ = 2.4 Hz, CH*), 7.08 (br, 3H, CH). – **^{13}C{^{1}H} NMR** (100.6 MHz, CD_2Cl_2, 298.0 K): δ 18.9 (CH_3), 22.5, 22.7 (CH_3 ^{i}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). – **^{11}B{^{1}H} NMR** (96.3 MHz, CD_2Cl_2, 299.5 K): δ 0.7 ($h_{1/2}$ = 10 Hz). **Anal. Calcd** for $C_{26}H_{34}BF_6N_8PRuS_4$ (843.71): C, 37.01; H, 4.06; N, 13.28. **Found**: C, 36.80; H, 4.10; N, 13.01. MS (ESI$^+$): *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_4]$^-$, **calcd for** [Bmt_4]$^-$ 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).

X-ray structure determination. Data collection: Stoe-IPDS-II diffractometer, graphite monochromated Mo K_α radiation; T = 173 K. Empirical absorption correction using MULABS [16], structure solution by direct methods [17], structure refinement by full-matrix least-squares on F^2 with SHELXL-97 [18]. Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 711110 {$[Li(H_2O)_4]$**[3]**} and CCDC 711111 {**8**$[PF_6]$}. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (Telefax : +1223/336 033; e-mail: deposit@ccdc.cam.ac.uk).

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Figure 1 Tetradentate ligand systems for polymetallic coordination chemistry.

Figure 2 Di- and tritopic boron-based ligands.

Figure 3 Structure of $[Li(H_2O)_4]$**[3]** in the crystal; thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths / Å and angles / °: B(1)-N(1) 1.5699(19); N(1)-B(1)-N(1)#2 108.52(14), N(1)#1-B(1)-N(1) 109.95(7). Symmetry transformations used to

generate equivalent atoms: -y+3/4,x-1/4,-z+3/4 (#1), -x+1,-y+1/2,z+0 (#3).

Figure 4 Crystal packing diagram of $[Li(H_2O)_4]$**[3]**.

Figure 5 Structure of **8**$[PF_6]$ in the crystal; thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths / Å, atom···atom distances / Å and angles / °: B(1)-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) 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) 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), 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)-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)-S(11)-Ru(1) 104.75(12), C(21)-S(21)-Ru(1) 111.09(13).

Figure 6 Mirror image pair of the complex cation **8**.

Scheme 1 Synthesis of lithium tetrakis(methimazolyl)borate $[Li(H_2O)_4]$**[3]**, and the Ruthenium *para*-cymene complex **8**$[PF_6]$. (i) melt, (ii) toluene, (iii) $[Ru(p\text{-cymene})Cl_2]_2$, CH_3CN, (iv) NH_4PF_6, EtOH.

Table 1 Crystal data and refinement details for $[Li(H_2O)_4]$**[3]**and **8**$[PF_6]$.

	[Li(H$_2$O)$_4$][**3**]	**8**[PF$_6$] (CH$_2$Cl$_2$)
empirical formula	$C_{16}H_{28}BLiN_8O_4S_4$	$C_{27}H_{36}BCl_2F_6N_8PRuS_4$
formula weight	542.45	928.63
T / K	173(2)	173(2)
wavelenght	MoK_α, 0.71073 Å	MoK_α, 0.71073 Å
crystal system	tetragonal	triclinic
space group	$I4_1/a$	P-1
a / Å	13.9830(14)	11.4919(8)
b / Å	13.9830(14)	13.1799(11)
c / Å	12.7265(12)	13.8989(11)
α / °	90	78.370(6)
β / °	90	71.105(6)
γ / °	90	69.822(6)
V / Å^3	2488.3(4)	1859.9(3)
Z	4	2
density calculated g cm^{-3}	1.448	1.658
F(000)	1136	940
μ mm^{-1}	0.422	0.897
index ranges	-16≤h≤16	-13≤h≤13
	-14≤k≤16	-15≤k≤15
	-15≤l≤15	-16≤l≤16
crystal size / mm^3	0.17 × 0.17 × 0.17	0.29 × 0.13 × 0.09
no. of reflections collected	8253	18616
R1, wR2 [I>2σ(I)]	0.0400, 0.0787	0.0395, 0.0930
data / restraints / parameter	1097 / 0 / 86	6900 / 423 / 514
GOOF on F^2	0.982	1.003
R1, wR2 (all data)	0.0665, 0.0861	0.0542, 0.0984
largest diff peak and hole / eÅ^{-3}	0.224, -0.240	0.971, -0.705

Scheme 1

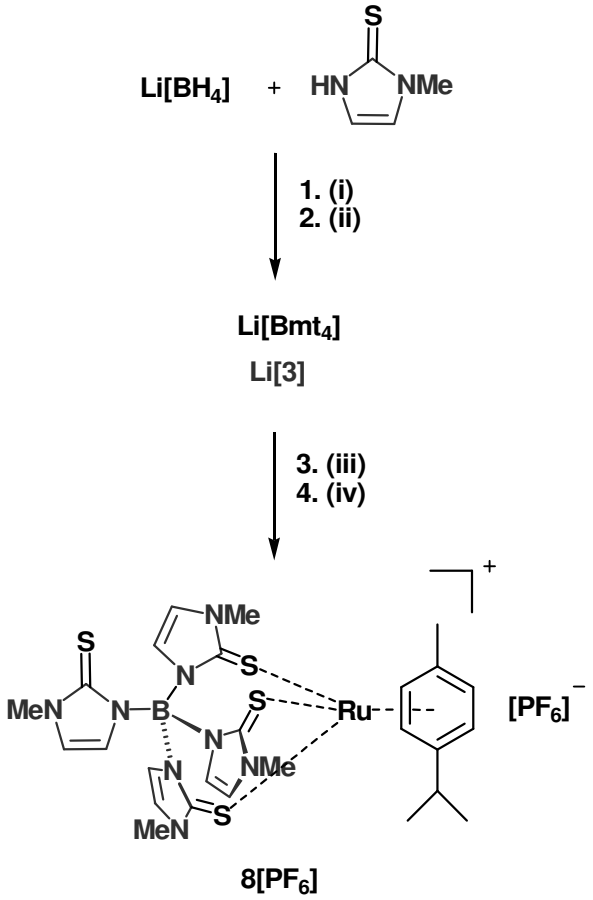
Li[BH4]
+
HN
NMe
S
1. (i)
2. (ii)
Li[Bmt4]
Li[3]
3. (iii)
4. (iv)
MeN
N
B
S
NMe
Ru
[PF6]−
8[PF6]

Figure 1

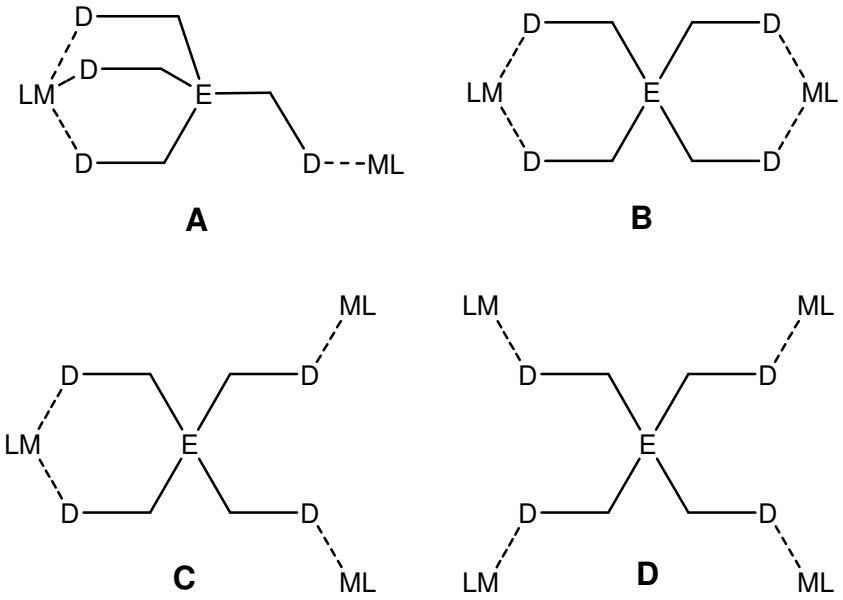

Figure 2

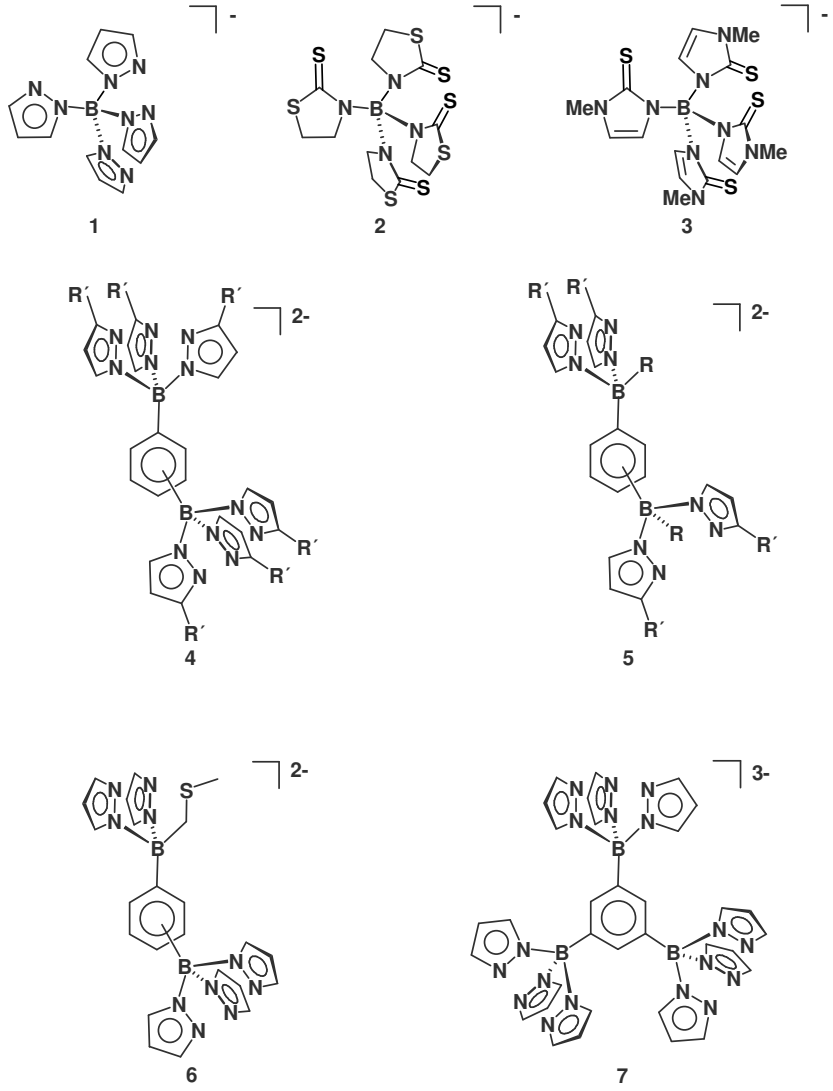

Figure 3

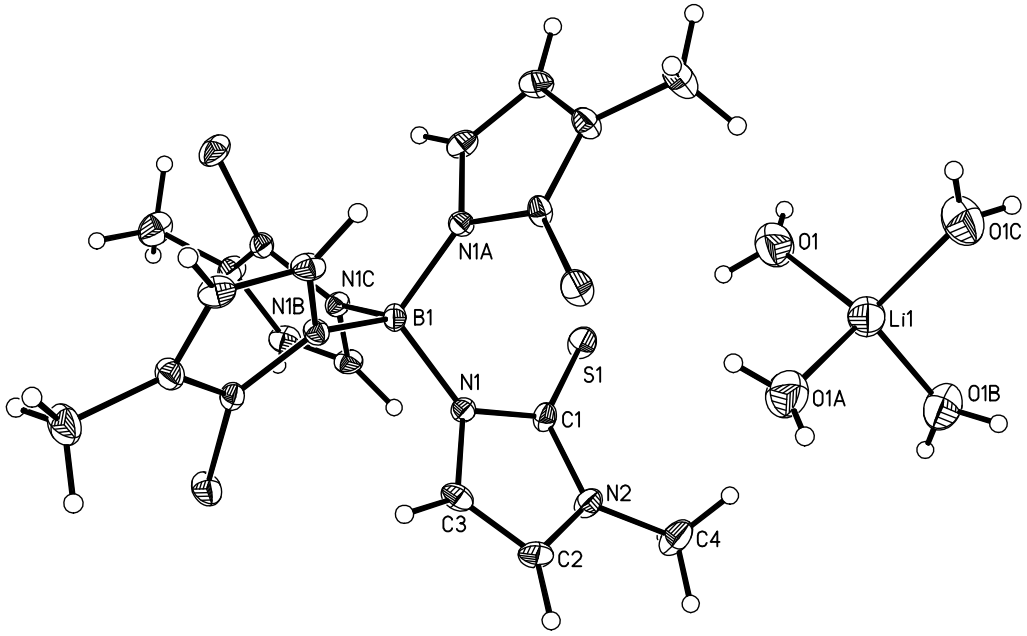

Figure 4

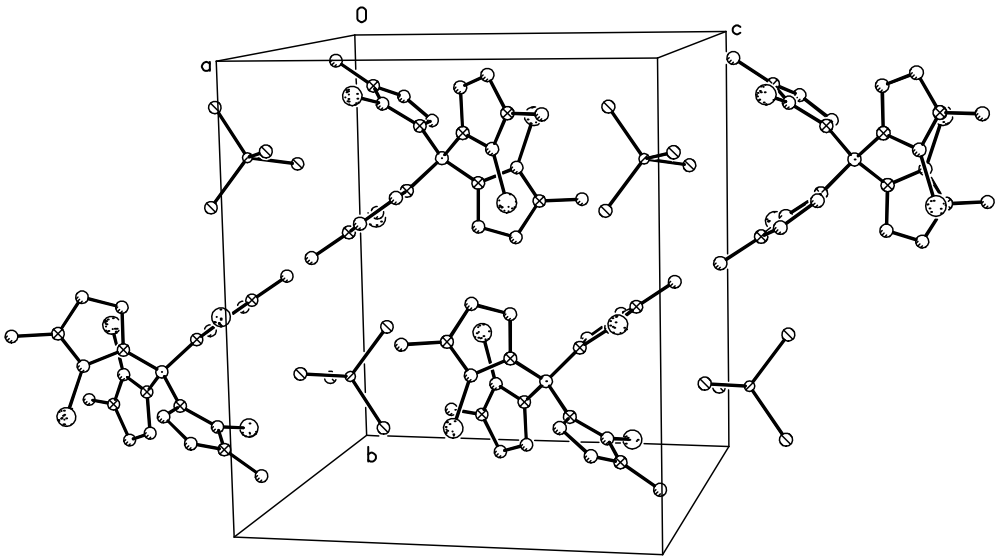

Figure 5

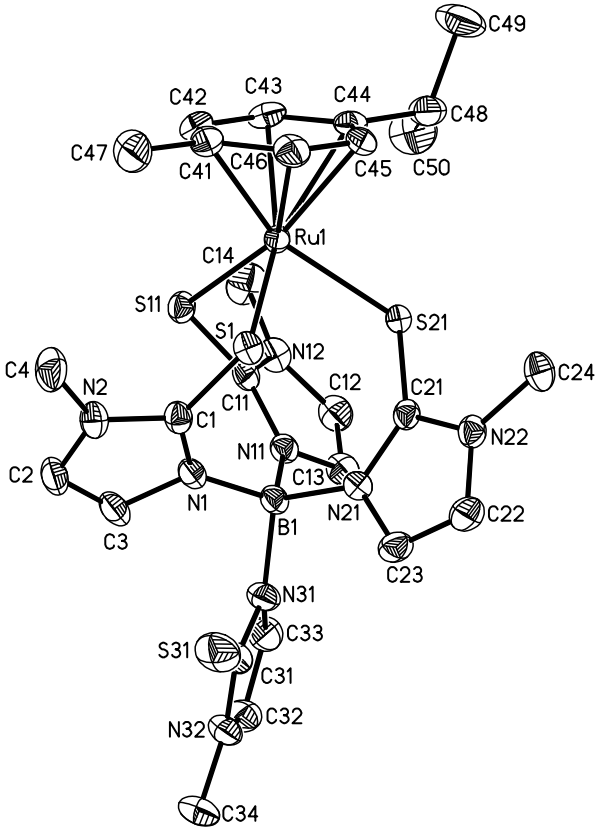
C49
C42
C43
C44
C48
C47
C41
C46
C45
C50
Ru1
C14
S11
S1
N12
S21
C4
N2
C11
C12
C21
C24
C1
N11
N22
C2
C13
N1
N21
C22
B1
C3
C23
N31
C33
S31
C31
N32
C32
C34

Figure 6