

The synthesis and structural characterization of bis(mercaptoimidazolyl)hydroborato complexes of lithium, thallium and zinc †

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Bidentate [S₂]-donor bis(mercaptoimidazolyl) ligands, [Bm^{Me}][−] and [Bm^{Mes}][−], have been synthesized by reaction of [BH₄][−] with 2-mercapto-1-methylimidazole and 2-mercapto-1-mesitylimidazole, respectively. Subsequent treatment with ZnX₂ (X = Me, I, NO₃) yields a series of 1 : 1 [Bm^R]ZnX complexes, namely [Bm^{Me}]ZnMe, [Bm^{Me}]ZnI and [Bm^{Mes}]Zn(NO₃), each of which possesses 3-center–2-electron [Zn ⋯ H–B] interactions. The homoleptic complex, [Bm^{Me}]₂Zn, may be obtained by a redistribution reaction of [Bm^{Me}]ZnMe in CHCl₃, and possesses a tetrahedral zinc center which is devoid of a 3-center–2-electron [Zn ⋯ H–B] interaction.

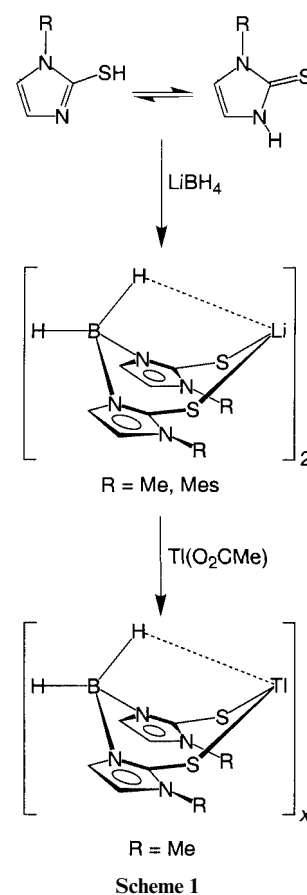
Introduction

Acetylacetonato and bis(pyrazolyl)borato are two of the most commonly employed monoanionic bidentate ligands with a multi-atom linker between the donor atoms, that respectively provide [O₂] and [N₂] coordination to a metal center.¹ In contrast, monoanionic bidentate [S₂] donor ligands of this category have not found much application, although in zinc chemistry thiophosphorylamine ligands {N[PR₂(S)]₂}[−] have been studied in an effort to separate trace quantities of Zn^{II} from aqueous solutions containing Fe^{III}.² In this paper, we report the syntheses of bis(mercaptoimidazolyl)hydroborato ligands and describe their application to zinc chemistry.

Results and discussion

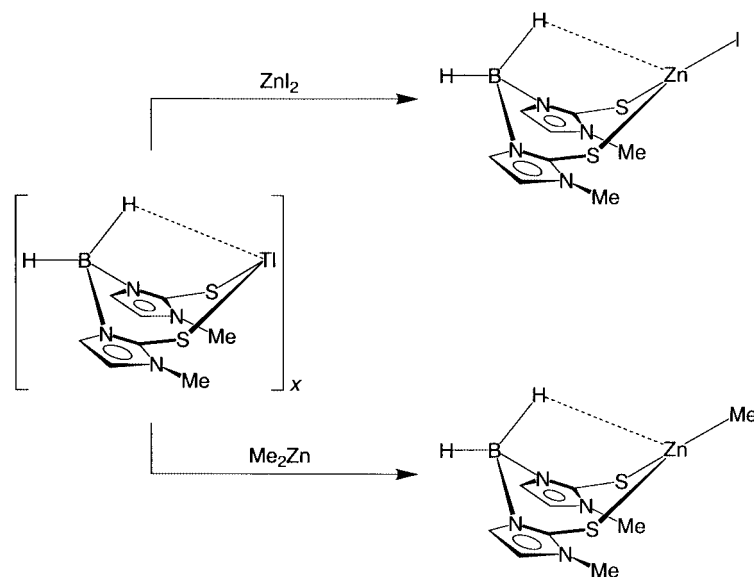
Reglinski and co-workers have recently reported the synthesis of the tripodal [S₃] tris(2-mercapto-1-methylimidazolyl)borate ligand, [Tm^{Me}][−],^{3–5} by reaction of [BH₄][−] with 2-mercapto-1-methylimidazole, a procedure similar to that used in the preparation of tris(pyrazolyl)borato derivatives.⁶ In view of the fact that [S₂] donor analogs of bis(pyrazolyl)borato [Bp^{RR}][−] ligands are not common, we considered it worthwhile to synthesize related bis(mercaptoimidazolyl)borato ligands because they may provide access to an array of interesting chemistry akin to that for the [Bp^{RR}][−] system.⁶

Significantly, the bis(2-mercapto-1-methylimidazolyl)borate ligand [Bm^{Me}][−] may be obtained by reaction of LiBH₄ with 2 equivalents of 2-mercapto-1-methylimidazole in toluene at 50 °C (Scheme 1).⁷ Since thallium derivatives have proved to be useful reagents for transferring bis- and tris-(pyrazolyl)borate ligands,^{6,8} the thallium complex {[Bm^{Me}]Tl}_x was prepared by reaction of [Bm^{Me}]Li with Tl(O₂CMe), from which the zinc methyl and iodide complexes, [Bm^{Me}]ZnMe and [Bm^{Me}]ZnI were obtained by metathesis with Me₂Zn and ZnI₂, respectively (Scheme 2). The more sterically demanding mesityl-substituted [Bm^{Mes}][−] ligand was also obtained in an analogous manner by reaction of LiBH₄ with 2-mercapto-1-mesitylimidazole,⁹ from which the zinc nitrate derivative [Bm^{Mes}]Zn(NO₃) was obtained by treatment with Zn(NO₃)₂ (Scheme 3).

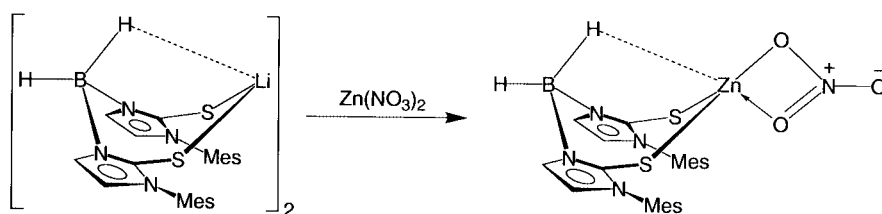


The molecular structures of {[Bm^{Mes}]Li}₂, {[Bm^{Me}]Tl}_x, [Bm^{Me}]ZnMe, [Bm^{Me}]ZnI and [Bm^{Mes}]ZnNO₃ have been determined by X-ray diffraction, as illustrated in Figs. 1–6.¹⁰ A common feature of each of these structures is that the bidentate coordination of the two sulfur donor atoms is supplemented, to varying degrees, by interaction with one of the B–H ligands (Table 1). For comparison, Zn ⋯ H–B interactions listed in the Cambridge Structural Database are observed in the range 1.78–1.98 Å.¹¹ Such 3-center–2-electron [M ⋯ H–B] interactions are analogous to those observed in the structures of several bis(pyrazolyl)hydroborato complexes.^{12,13} Furthermore,

† Dedicated to Professor Heinrich Vahrenkamp, a connoisseur and practitioner of fine zinc chemistry, on the occasion of his 60th birthday. Happy birthday, Heinrich!



Scheme 2



Scheme 3

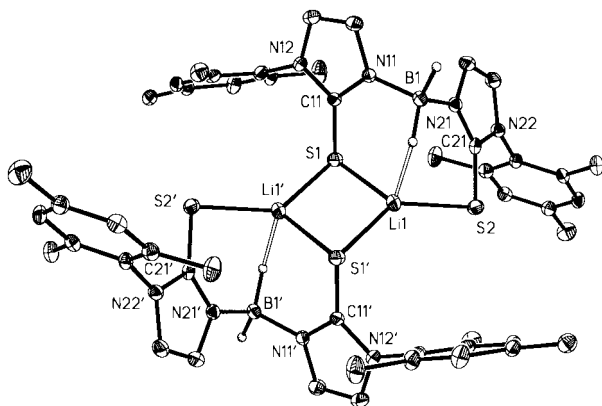


Fig. 1 Selected bond lengths (Å) and angles (°) for $\{[Bm^{Mes}]Li\}_2$: Li(1)–S(1) 2.448(7), Li(1)–S(2) 2.356(7), Li(1)–S(1') 2.413(7), Li(2)–S(3) 2.389(8), Li(2)–S(4) 2.491(8), Li(2)–S(4') 2.518(8), S(1)–C(11) 1.708(4), S(2)–C(21) 1.702(4), S(3)–C(81) 1.696(4), S(4)–C(91) 1.707(4), Li(1)–H(1b) 1.86(3), Li(1)⋯Li(1') 3.03(1), Li(2)⋯Li(2') 3.50(2); S(1)–Li(1)–S(2) 113.6(3), Li(1)–S(1)–Li(1') 77.0(3), S(3)–Li(2)–S(4) 129.0(3), Li(2)–S(4)–Li(2') 88.7(3).

a $[Ag \cdots H-B]$ interaction has been reported for the tris(2-mercapto-1-methylimidazolyl)borate complex $[Tm^{Me}]AgPCy_3$, within which only *two* of the sulfur atom donors coordinate to silver.^{5a,b}

While the zinc complexes $[Bm^R]ZnX$ are strictly monomeric in the solid state, the lithium and thallium complexes $\{[Bm^{Mes}]Li\}_2$ and $\{[Bm^{Me}]Tl\}_x$ are oligonuclear, with the metal centers being bridged by sulfur atoms of the mercaptoimidazolyl groups (Figs. 1–3). The lithium and thallium complexes have similar four membered $[M_2S_2]$ cores, but one of the sulfur atoms on each of the $[Bm^{Me}]$ ligands in the dinuclear thallium fragment also interacts with another thallium center, thereby resulting in a polynuclear structure (Fig. 3). Clearly, the structural motifs adopted by $\{[Bm^{Mes}]Li\}_2$ and $\{[Bm^{Me}]Tl\}_x$ are

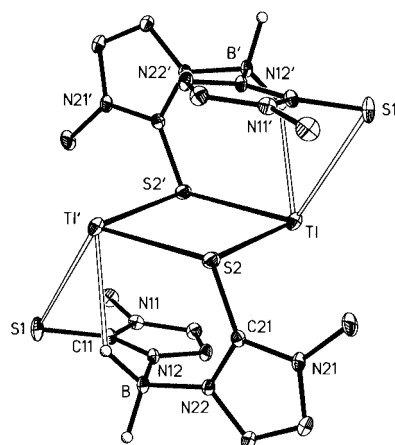


Fig. 2 Selected bond lengths (Å) and angles (°) for $\{[Bm^{Me}]Tl\}_x$, emphasizing the dinuclear $[Tl_2S_2]$ core: Tl–S(2) 3.141(2), Tl(1')–S(2) 3.043(1), S(1)–C(11) 1.707(5), S(2)–C(21) 1.712(5); S(2)–Tl–S(2') 90.10(4), Tl(1)–S(2)–Tl(1') 89.90(4).

different from those of bis(pyrazolyl)hydroborato counterparts since the nitrogen atom of the pyrazolyl group is incapable of bridging in such a manner. Thus, $[Bp^{RR}]Tl$ complexes typically adopt monomeric structures.¹² $\{[Bp]Tl\}_2$, however, is a notable exception in that it is dimeric in the solid state,¹⁴ although the dinuclear nature is a result of a weak $Tl \cdots Tl$ interaction, and not due to a bridging pyrazolyl group. The $Tl \cdots Tl$ separation in $\{[Bm^{Me}]Tl\}_x$ (4.37 Å) is thus significantly greater than that in $\{[Bp]Tl\}_2$ (3.70 Å).

The structural characterization of the heteroleptic 1:1 $[Bm^R]ZnX$ complexes is of interest in light of the fact that only homoleptic L_2Zn complexes have been previously structurally characterized¹¹ using related anionic bidentate $[S_2]$ donors, namely $[MeC(S)CH_2C(S)OEt]_2Zn$ ¹⁵ and $\{N[PPt_2(S)]_2\}_2Zn$.¹⁶ In this regard, the corresponding homoleptic complex, $[Bm^{Me}]_2Zn$,

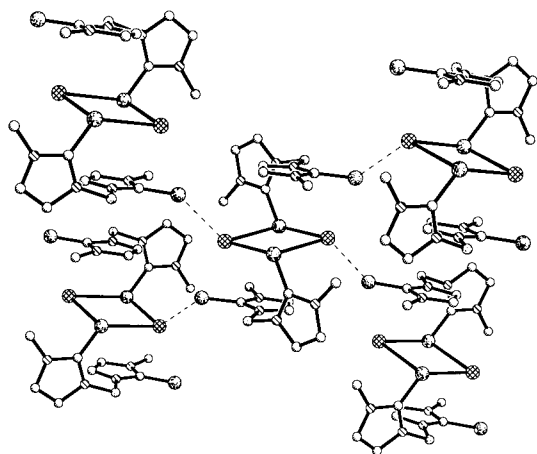


Fig. 3 A portion of the polymeric structure of {[Bm^{Me}]Tl}_x.

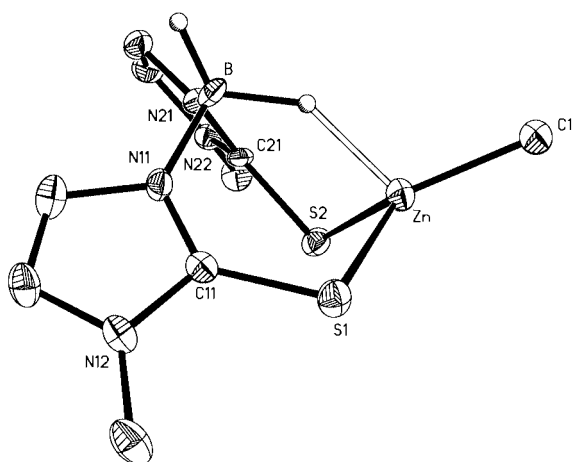


Fig. 4 Selected bond lengths (Å) and angles (°) for [Bm^{Me}]ZnI: Zn–S(1) 2.287(2), Zn–S(2) 2.292(2), Zn–I 2.548(1), S(1)–C(11) 1.719(5), S(2)–C(21) 1.723(5); S(1)–Zn–S(2) 118.0(1), S(1)–Zn–I 116.6(1), S(2)–Zn–I 124.9(1).

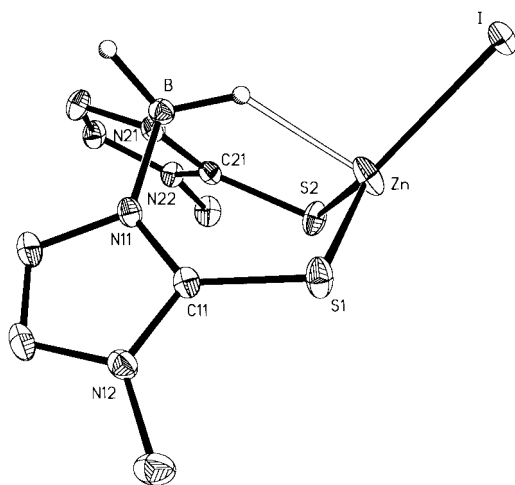


Fig. 5 Selected bond lengths (Å) and angles (°) for [Bm^{Me}]ZnMe: Zn–S(1) 2.342(3), Zn–S(2) 2.382(3), Zn–C(1) 1.97(1), S(1)–C(11) 1.724(10), S(2)–C(21) 1.693(9); S(1)–Zn–S(2) 105.9(1), S(1)–Zn–C(1) 123.0(3), S(2)–Zn–C(1) 125.3(4).

may be obtained by a redistribution reaction of [Bm^{Me}]ZnMe in CHCl₃ (Scheme 4). The molecular structure of [Bm^{Me}]₂Zn is illustrated in Fig. 7 and, as would be expected for a tetrahedral zinc center, the complex does not possess a 3-center–2-electron [Zn···H–B] interaction; thus, the Zn···B separation of 3.78 Å is substantially greater than those in the above [Bm^R]ZnX complexes (2.82–2.94 Å). The principal distinction between

Table 1 [M···H–B] interactions in {[Bm^R]M} derivatives

| | $d(\text{M}\cdots\text{B})/\text{Å}$ | $d(\text{M}\cdots\text{H})/\text{Å}$ |
|--|--------------------------------------|--------------------------------------|
| {[Bm ^{Mes}]Li} ₂ | 2.80, 3.09 ^a | 1.86, 2.34 ^a |
| {[Bm ^{Me}]Tl} _x | 3.50 | 2.69 |
| [Bm ^{Me}]ZnI | 2.94 | 2.06 |
| [Bm ^{Me}]ZnMe | 2.88 | 1.77 |
| [Bm ^{Mes}]Zn(NO ₃) | 2.82 | 1.93 ^b |
| [Bm ^{Me}] ₂ Zn | 3.78 | 3.51 |

^a Values for two independent molecules. ^b H atom not refined.

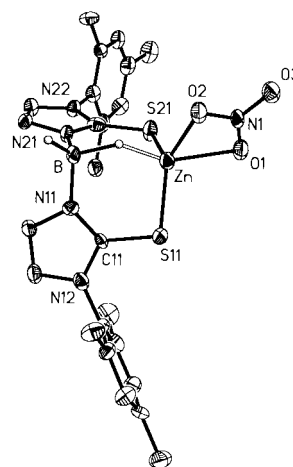
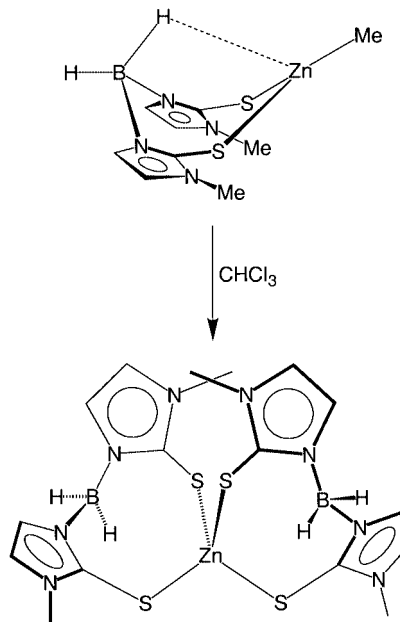


Fig. 6 Selected bond lengths (Å) and angles (°) for [Bm^{Mes}]Zn(NO₃): Zn–S(11) 2.267(3), Zn–S(21) 2.268(3), Zn–O(1) 2.241(5), Zn–O(2) 2.065(5), S(11)–C(11) 1.738(10), S(21)–C(21) 1.645(12); S(11)–Zn–S(21) 127.33(8), O(1)–Zn–O(2) 59.5(2), S(11)–Zn–O(1) 103.1(3), S(11)–Zn–O(2) 119.7(3), S(21)–Zn–O(1) 98.3(3), S(21)–Zn–O(2) 112.7(3).



Scheme 4

[Bm^{Me}]₂Zn and [Bm^R]ZnX is that the [Bm^R] ligand in the former adopts a configuration which results in a “chair-like” eight-membered ring, as opposed to the “boat-like” rings present in [Bm^R]ZnX which allow for a closer proximity between the metal and B–H group. For comparison purposes the Zn–S bond lengths in these complexes are summarized in Table 2.¹⁷ Thus, the average Zn–S bond length in [Bm^{Me}]₂Zn (2.34 Å) is comparable to the mean value for tetrahedral [ZnS₄] coordination geometries listed in the CSD (2.35 Å),¹¹ and also the mean value for the structural site in LADH–NADH–DMSO (2.35 Å).^{20,21}

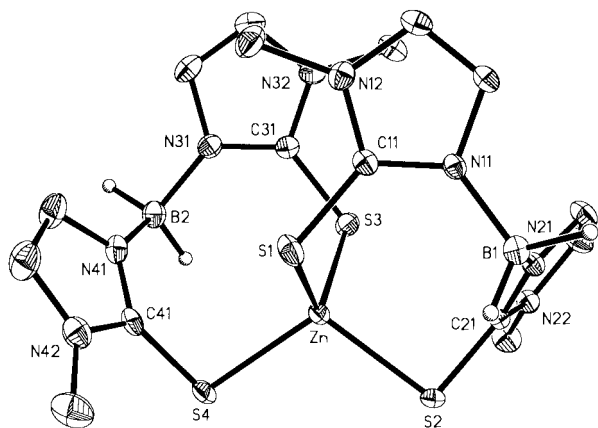


Fig. 7 Selected bond lengths (Å) and angles (°) for $[\text{Bm}^{\text{Me}}]_2\text{Zn}$: Zn–S(1) 2.336(1), Zn–S(2) 2.344(1), Zn–S(3) 2.330(1), Zn–S(4) 2.338(1), S(1)–C(11) 1.732(3), S(2)–C(21) 1.724(3), S(3)–C(31) 1.717(3), S(4)–C(41) 1.726(4); S(1)–Zn–S(2) 115.75(4), S(1)–Zn–S(3) 114.13(4), S(1)–Zn–S(4) 102.74(3), S(2)–Zn–S(3) 100.59(3), S(2)–Zn–S(4) 108.91(3), S(3)–Zn–S(4) 115.16(4).

Table 2 Comparison of Zn–S bond lengths in zinc complexes with bidentate $[\text{S}_2]$ ligands

| | $d(\text{Zn}-\text{S}_{av})/\text{Å}$ | Ref. |
|--|---------------------------------------|-----------|
| $[\text{Bm}^{\text{Me}}]\text{ZnI}$ | 2.29 | This work |
| $[\text{Bm}^{\text{Me}}]\text{ZnMe}$ | 2.36 | This work |
| $[\text{Bm}^{\text{Me}}]\text{Zn}(\text{NO}_3)$ | 2.27 | This work |
| $[\text{Bm}^{\text{Me}}]_2\text{Zn}$ | 2.34 | This work |
| $\{\text{N}[\text{PPr}^i_2(\text{S})]_2\}_2\text{Zn}$ | 2.35 | 18 |
| $[\text{MeC}(\text{S})\text{CH}_2\text{C}(\text{S})\text{OEt}]_2\text{Zn}$ | 2.30 | 19 |

Experimental

General considerations

All manipulations were performed using a combination of glovebox, high-vacuum or Schlenk techniques.²² Solvents were purified and degassed by standard procedures. ^1H NMR spectra were recorded on Varian VXR-400 and Bruker Avance 400 DRX spectrometers. ^{13}C NMR spectra were recorded on Varian VXR-300 (75.43 MHz) and Bruker Avance 300wb DRX (75.47 MHz) spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to SiMe_4 ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity or the ^{13}C resonances, respectively. All coupling constants are reported in Hz. IR spectra were recorded as KBr pellets on Perkin-Elmer 1430 or 1600 spectrophotometers and are reported in cm^{-1} . C, H, and N elemental analyses were measured using a Perkin-Elmer 2400 CHN Elemental Analyzer. 2-mercapto-1-mesitylimidazole was obtained from Aldrich.

Synthesis of 2-mercapto-1-mesitylimidazole

2-Mercapto-1-mesitylimidazole was prepared using a general procedure.²³ Specifically, a mixture of MesNCS ²⁴ ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) (15 g, 0.085 mol) and amino acetaldehyde diethyl acetal $[\text{H}_2\text{NCH}_2\text{CH}(\text{OEt})_2]$ (12.3 mL, 0.085 mol) in toluene (*ca.* 60 mL) was stirred at room temperature for 3 hours. After this period, $\text{HCl}(\text{aq})$ (3.2 mL of 14 M, 0.045 mol) was added and the mixture was refluxed for 7 hours. The volatile components were removed *in vacuo* and water (*ca.* 300 mL) was added to the residue. The pH was adjusted to 8 by the addition of NaOH (0.1 M), resulting in the formation of a precipitate. The mixture was filtered and the precipitate was dried, extracted into CHCl_3 (*ca.* 500 mL), and filtered. The volatile components were removed *in vacuo*, and the residue obtained was washed with Et_2O giving 2-mercapto-1-mesitylimidazole as a pale peach colored powder (13.6 g, 74%) (Calc. for $\text{C}_3\text{H}_3\text{N}_2(\text{S})[\text{C}_6\text{H}_2\text{-}$

$(\text{CH}_3)_3$: C, 66.0; H, 6.5; N, 12.8. Found: C, 65.7; H, 6.4; N, 12.1%). ^1H NMR (CDCl_3): δ 2.08 [s, 2 *ortho*- CH_3], 2.33 [s, *para*- CH_3], 6.63 [d, $^3J_{\text{H-H}} = 2$, 1 H of $\text{C}_3\text{H}_3\text{N}_2\text{S}$], 6.84 [d, $^3J_{\text{H-H}} = 2$, 1 H of $\text{C}_3\text{H}_3\text{N}_2\text{S}$], 6.99 [s, $\text{C}_6\text{H}_2\text{Me}_3$], 11–12 [br, 1 H of $\text{C}_3\text{H}_3\text{N}_2\text{S}$].

Synthesis of $\{[\text{Bm}^{\text{Me}}]\text{Li}\}_2$

A mixture of 2-mercapto-1-mesitylimidazole (10.0 g, 87.6 mmol) and LiBH_4 (0.795 g, 36.5 mmol) in toluene (50 mL) was heated overnight at 50 °C. After this period, the volatile components were removed *in vacuo* giving a white solid which was washed with Et_2O (2×50 mL) and with CHCl_3 (30 mL) to remove excess 2-mercapto-1-mesitylimidazole. Yield of $\{[\text{Bm}^{\text{Me}}]\text{Li}\}_2 \cdot \text{CHCl}_3$: 6.0 g, 54% (Calc. for $\{[\text{Bm}^{\text{Me}}]\text{Li}\}_2 \cdot \text{CHCl}_3$: C, 33.4; H, 4.1; N, 18.3. Found: C, 33.6; H, 4.5; N, 18.4%). IR (KBr disk, cm^{-1}): 3121 (s), 2945 (m), 2399 (m), 2379 (m), 2276 (w), 1654 (w), 1628 (w), 1560 (m), 1525 (vw), 1510 (vw), 1458 (s), 1412 (s), 1380 (vs), 1303 (m), 1193 (s), 1119 (vs), 1086 (m), 1040 (w), 1015 (vw), 959 (vw), 884 (vw), 755 (m), 727 (s), 699 (m), 678 (m), 615 (w), 512 (m), 460 (w). NMR spectroscopic data are listed in Table 3. Crystals for X-ray diffraction were obtained from chloroform.

Synthesis of $\{[\text{Bm}^{\text{Me}}]\text{Ti}\}_x$

A suspension of $\{[\text{Bm}^{\text{Me}}]\text{Li}\}_2 \cdot \text{CHCl}_3$ (7.0 g, 28.4 mmol) and $\text{Ti}(\text{O}_2\text{CMe})$ (12.4 g, 47.1 mmol) in MeOH (85 mL) was stirred at room temperature for 1 hour. After this period, the volatile components were removed *in vacuo* giving a sticky white solid which was washed with water (2×100 mL) and dried *in vacuo*. Yield of $\{[\text{Bm}^{\text{Me}}]\text{Ti}\}_x$: 7.23 g, 71% (Calc. for $\{[\text{Bm}^{\text{Me}}]\text{Ti}\}_x$: C, 21.7; H, 2.7; N, 12.6. Found: C, 21.6; H, 2.5; N, 12.0%). IR (KBr disk, cm^{-1}): 3144 (w), 3116 (m), 3077 (w), 2934 (w), 2665 (vw), 2371 (s), 2078 (vw), 1547 (m), 1453 (s), 1402 (s), 1373 (vs), 1297 (s), 1203 (s), 1181 (s), 1165 (s), 1109 (vs), 1082 (s), 983 (m), 888 (m), 848 (vw), 828 (vw), 749 (s), 728 (s), 701 (m), 678 (m), 651 (w), 606 (vw), 518 (w), 502 (w), 458 (w). NMR spectroscopic data are listed in Table 3. Crystals for X-ray diffraction were obtained from chloroform.

Synthesis of $[\text{Bm}^{\text{Me}}]\text{ZnI}$

A mixture of $\{[\text{Bm}^{\text{Me}}]\text{Ti}\}_x$ (660 mg, 1.48 mmol Ti) and ZnI_2 (485 mg, 1.52 mmol) in CH_2Cl_2 was stirred at room temperature for *ca.* 3 hours, resulting in the formation of a yellow precipitate. After this period, the mixture was filtered. Removal of the volatile components from the filtrate *in vacuo* gave $[\text{Bm}^{\text{Me}}]\text{ZnI}$ as a white solid. Yield of $[\text{Bm}^{\text{Me}}]\text{ZnI}$: 220 mg, 34% (Calc. for $[\text{Bm}^{\text{Me}}]\text{ZnI}$: C, 22.3; H, 2.8; N, 13.0. Found: C, 22.3; H, 2.8; N, 12.5%). IR (KBr disk, cm^{-1}): 3155 (m), 3125 (m), 3087 (w), 2948 (w), 2865 (vw), 2708 (vw), 2439 (m), 2224 (m), 2067 (w), 1559 (s), 1463 (vs), 1439 (m), 1420 (s), 1390 (vs), 1326 (m), 1299 (m), 1261 (w), 1195 (vs), 1156 (m), 1130 (s), 1088 (s), 1049 (m), 1017 (m), 963 (m), 878 (m), 836 (w), 802 (w), 725 (s), 694 (s), 678 (w), 643 (w), 593.4 (w), 514 (m), 464 (vw). NMR spectroscopic data are listed in Table 3. Crystals for X-ray diffraction were obtained from chloroform.

Synthesis of $[\text{Bm}^{\text{Me}}]\text{ZnMe}$

A suspension of $\{[\text{Bm}^{\text{Me}}]\text{Ti}\}_x$ (0.75 g, 1.70 mmol Ti) in benzene (25 mL) was treated with a solution of ZnMe_2 (0.29 g, 3.0 mmol) in toluene (1.5 mL), thereby resulting in the slow formation of a black precipitate. The mixture was stirred for 2 hours, filtered and the volatile components were removed *in vacuo*. Yield of $[\text{Bm}^{\text{Me}}]\text{ZnMe}$ 0.45 g (83%). IR (KBr, cm^{-1}): 3122 (vs), 2938 (s), 2409 (vs), 2293 (s), 2068 (m), 1578 (w), 1561 (s), 1460 (vs), 1418 (s), 1381 (vs), 1322 (m), 1304 (m), 1227 (m), 1198 (vs), 1120 (vs), 1087 (s), 1043 (m), 1017 (m), 957 (m), 878 (w), 749 (s), 732 (vs), 697 (s), 678 (s), 663 (m), 526 (s), 502 (m), 484 (m), 455 (m). NMR spectroscopic data are listed in Table 3. Crystals for X-ray diffraction were obtained from benzene.

Table 3 NMR spectroscopic data for {[Bm^{Me}]M} derivatives

| | {[Bm ^{Me}]Li} ₂ ^a | {[Bm ^{Me}]Ti} _x ^a | [Bm ^{Me}]ZnI ^b | [Bm ^{Me}]ZnMe ^b | [Bm ^{Me}]Zn ^c |
|---------------------|--|--|--|---|--|
| ¹ H NMR | 3.32, s 6.69, d, ³ J _{H-H} = 2 [2H] 6.97, d, ³ J _{H-H} = 2 [2H] 3.19, br | 3.42, s 6.74, d, ³ J _{H-H} = 2 [2H] 7.00, d, ³ J _{H-H} = 2 [2H] 3.94, br | 3.62, s 6.81, d, ³ J _{H-H} = 2 [2H] 6.90, d, ³ J _{H-H} = 2 [2H] 3.54, br | 3.59, s 6.72, d, ³ J _{H-H} = 2 [2H] 6.84, d, ³ J _{H-H} = 2 [2H] 3.35, br -0.43, s, Zn-CH ₃ | 3.51, s 6.94, d, ³ J _{H-H} = 2 [2H] 7.02, d, ³ J _{H-H} = 2 [2H] 3.60, br |
| ¹³ C NMR | 33.7, q, ¹ J _{C-H} = 139 115.2, d, ¹ J _{C-H} = 192 [2C] 123.7, d, ¹ J _{C-H} = 193 [2C] 163.3, s | 34.1, q, ¹ J _{C-H} = 140 118.4, d, ¹ J _{C-H} = 195 [2C] 122.5, d, ¹ J _{C-H} = 193 [2C] 160.2, s | 35.4, q, ¹ J _{C-H} = 142 120.4, d, ¹ J _{C-H} = 194 [2C] 123.2, d, ¹ J _{C-H} = 197 [2C] 156.3, s | 35.1, q, ¹ J _{C-H} = 141 119.6, d, ¹ J _{C-H} = 195 [2C] 123.0, d, ¹ J _{C-H} = 202 [2C] 157.1, s -10.7, q, ¹ J _{C-H} = 121, Zn-CH ₃ | 36.0, q, ¹ J _{C-H} = 142 121.3, d, ¹ J _{C-H} = 195 [2C] 124.6, d, ¹ J _{C-H} = 196 [2C] 155.1, s |

^a In d⁶-Me₂SO. ^b In CDCl₃. ^c In CD₃CN.

Synthesis of [Bm^{Me}]₂Zn

A solution of [Bm^{Me}]ZnMe (100 mg, 0.19 mmol) in CHCl₃ (*ca.* 5 mL) was allowed to stand at room temperature for 4 days, depositing [Bm^{Me}]₂Zn as an off-white precipitate which was separated by filtration, washed with pentane (*ca.* 5 mL) and dried. Yield of [Bm^{Me}]₂Zn: 54 mg (65%). IR data (KBr, cm⁻¹): 3147 (s), 3120 (s), 2946 (s), 2492 (m), 2393 (s), 2291 (m), 1687 (w), 1556 (s), 1459 (s), 1412 (s), 1379 (s), 1326 (m), 1302 (m), 1188 (s), 1171 (s), 1128 (s), 1087 (s), 1042 (m), 1014 (m), 909 (w), 886 (w), 804 (vw), 763 (m), 751 (s), 725 (s), 698 (s), 647 (w), 618 (vw), 601 (vw), 548 (vw), 507 (w), 450 (vw). NMR spectroscopic data are listed in Table 3. Crystals for X-ray diffraction were obtained from CHCl₃.

Synthesis of {[Bm^{Mes}]Li}₂

A stirred mixture of 2-mercapto-1-mesitylimidazole (500 mg, 2.29 mmol) and LiBH₄ (50 mg, 2.29 mmol) in toluene, was heated at *ca.* 115 °C for two days in an ampoule (**CARE!**). The mixture was allowed to cool to room temperature and filtered. The volatile components were removed from the filtrate *in vacuo* and the white product was washed with pentane (*ca.* 20 mL) and dried to give {[Bm^{Mes}]Li}₂ as a white powder (365 mg, 70%). IR (KBr disk, cm⁻¹): 2366 (m), 2345 (m), [ν(B-H)]. NMR spectroscopic data are listed in Table 4. Crystals for X-ray diffraction were obtained from benzene.

Synthesis of {[Bm^{Mes}]Ti}_x

A mixture of 2-mercapto-1-mesitylimidazole (7 g, 0.032 mol) and LiBH₄ (1.4 g, 0.07 mmol) in THF (*ca.* 50 mL) was heated at *ca.* 70 °C for 1 day in an ampoule (**CARE!**). The THF was removed *in vacuo* and the product was dissolved in methanol (*ca.* 30 mL). Ti(O₂CMe) (5.15 g, 0.020 mol) was added to the solution and the mixture was stirred for 1 hour, resulting in the formation of a white/beige precipitate. The mixture was stirred for 1 hour, and the supernatant was decanted. The residue was dried *in vacuo*, and washed with diethyl ether, giving {[Bm^{Mes}]Ti}_x as an off-white powder (4.99 g, 68%). IR data (KBr disk, cm⁻¹): 2361 (s), 2212 (m) [ν(B-H)]. ¹H NMR (*d*₆-DMSO, obtained immediately): δ 1.89 (s, 2 × CH₃), 2.27 (s, 1 × CH₃), 6.84 (d, 2H), 6.93 (d, 2H), 6.95 (s, 4H).²⁵

Synthesis of [Bm^{Mes}]ZnNO₃

A mixture of {[Bm^{Mes}]Li}₂ (310 mg, 0.68 mmol) and Zn(NO₃)₂·6H₂O (400 mg, 1.34 mmol) in MeOH (*ca.* 15 mL) was stirred at room temperature for 2 hours. The volatile components were removed *in vacuo* and the residue was extracted into C₆H₆ (10 mL). The mixture was filtered and the filtrate was concentrated. Colorless microcrystals of [Bm^{Mes}]ZnNO₃ were deposited and were isolated by filtration. The volatile components were removed from the filtrate giving [Bm^{Mes}]ZnNO₃ as a white powder (108 mg, 27%) (Calc. for [Bm^{Mes}]ZnNO₃: C, 50.2; H, 4.9; N, 12.2. Found: C, 50.3; H, 4.8; N, 12.0%). NMR spectroscopic data are listed in Table 4. Crystals for X-ray diffraction were obtained from benzene.

X-Ray structure determinations

Crystal data, data collection and refinement parameters are summarized in Table 5. X-Ray diffraction data for [Bm^{Me}]ZnI and [Bm^{Me}]ZnMe were collected on a Siemens P4 diffractometer. The unit cells were determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite monochromated Mo-Kα X-radiation (λ = 0.71073 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization and absorption effects. X-Ray diffraction data for {[Bm^{Me}]Ti}_x, {[Bm^{Mes}]Li}₂, [Bm^{Mes}]Zn(NO₃) and

Table 4 NMR spectroscopic data for $\{[\text{Bm}^{\text{Mes}}]\text{M}\}$ derivatives

| | $\{[\text{Bm}^{\text{Mes}}]\text{Li}\}_2^a$ | $[\text{Bm}^{\text{Mes}}]\text{ZnNO}_3^a$ |
|---|--|--|
| ¹ H NMR | | |
| $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}_6\text{H}_2(\text{CH}_3)_3]\text{S}\}_2$ | 1.95, s, <i>ortho</i> 2.30, s, <i>para</i> | 1.94, s, <i>ortho</i> 2.34, s, <i>para</i> |
| $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}_6\text{H}_2(\text{CH}_3)_3]\text{S}\}_2$ | 6.93, s | 6.99, s |
| $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}_6\text{H}_2(\text{CH}_3)_3]\text{S}\}_2$ | 6.90, d, $^3J_{\text{H-H}} = 2$ [2H] 6.60, d, $^3J_{\text{H-H}} = 2$ [2H] | 6.82, d, $^3J_{\text{H-H}} = 2$ [2H] 7.16, d, $^3J_{\text{H-H}} = 2$ [2H] |
| $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}_6\text{H}_2(\text{CH}_3)_3]\text{S}\}_2$ | Not observed | 3.75, br |
| ¹³ C NMR | | |
| $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}_6\text{H}_2(\text{CH}_3)_3]\text{S}\}_2$ | 17.9, q, $^1J_{\text{C-H}} = 127$ [<i>o</i> -CH ₃] 21.1, q, $^1J_{\text{C-H}} = 127$ [<i>p</i> -CH ₃] | 17.5, q, $^1J_{\text{C-H}} = 128$ [<i>o</i> -CH ₃] 21.1, q, $^1J_{\text{C-H}} = 127$ [<i>p</i> -CH ₃] |
| $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}_6\text{H}_2(\text{CH}_3)_3]\text{S}\}_2$ | 129.0, d, $^1J_{\text{C-H}} = 154$ 134.1, s 135.8, s 138.7, s | 129.4, d, $^1J_{\text{C-H}} = 158$ 132.7, s 135.3, s 140.1, s |
| $\text{H}_2\text{B}\{\text{C}_3\text{N}_2\text{H}_2[\text{C}_6\text{H}_2(\text{CH}_3)_3]\text{S}\}_2$ | 117.8, d, $^1J_{\text{C-H}} = 195$ 123.4, d, $^1J_{\text{C-H}} = 186$ 160.5, s | 119.9, d, $^1J_{\text{C-H}} = 198$ 124.3, d, $^1J_{\text{C-H}} = 197$ 155.6, s |

^a In CDCl₃.**Table 5** Crystal, intensity collection and refinement data

| | $\{[\text{Bm}^{\text{Me}}]\text{Ti}\}_x$ | $\{[\text{Bm}^{\text{Mes}}]\text{Li}\}_2$ | $[\text{Bm}^{\text{Me}}]\text{ZnI}$ | $[\text{Bm}^{\text{Me}}]\text{ZnMe}$ | $[\text{Bm}^{\text{Mes}}]\text{Zn}(\text{NO}_3)\cdot 3\text{C}_6\text{H}_6$ | $[\text{Bm}^{\text{Me}}]_2\text{Zn}$ |
|-------------------------------------|--|--|--|--|--|---|
| Formula | C ₈ H ₁₂ B ₁ N ₄ S ₂ Tl | C ₄₈ H ₅₆ B ₂ Li ₂ N ₈ S ₄ | C ₈ H ₁₂ BN ₄ S ₂ Zn | C ₉ H ₁₅ BN ₄ S ₂ Zn | C ₄₂ H ₄₆ BN ₅ O ₃ S ₂ Zn | C ₁₆ H ₂₄ B ₂ N ₈ S ₄ Zn |
| Formula weight | 887.03 | 908.75 | 431.2 | 319.6 | 809.14 | 543.66 |
| Crystal symmetry | Monoclinic | Triclinic | Monoclinic | Monoclinic | Orthorhombic | Monoclinic |
| Space group | <i>P</i> ₂ / <i>1</i> (no. 14) | <i>P</i> $\bar{1}$ (no. 2) | <i>P</i> ₂ / <i>1</i> (no. 14) | <i>P</i> ₂ / <i>1</i> / <i>c</i> (no. 14) | <i>Pna</i> 2 ₁ (no. 33) | <i>P</i> ₂ / <i>1</i> / <i>n</i> (no. 14) |
| <i>a</i> /Å | 8.5696(4) | 8.135(1) | 11.362(2) | 7.652(1) | 24.777(5) | 9.327(1) |
| <i>b</i> /Å | 14.1642(7) | 16.526(3) | 9.937(2) | 13.822(3) | 9.451(2) | 14.393(2) |
| <i>c</i> /Å | 11.3006(5) | 20.404(3) | 13.483(3) | 13.469(2) | 18.736(4) | 18.520(3) |
| <i>a</i> /° | 90 | 106.379(3) | 90 | 90 | 90 | 90 |
| <i>β</i> /° | 111.966(1) | 101.143(3) | 110.31(2) | 102.588(7) | 90 | 93.811(2) |
| <i>γ</i> /° | 90 | 97.605(2) | 90 | 90 | 90 | 90 |
| <i>V</i> /Å ³ | 1272.1(1) | 2530.8(6) | 1427.6(5) | 1390.3(4) | 4387(2) | 2480.6(6) |
| <i>Z</i> | 4 | 2 | 4 | 4 | 4 | 4 |
| Temperature/K | 203 | 213 | 293 | 293 | 223 | 228 |
| Radiation, λ/Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| <i>D</i> /g cm ⁻³ | 2.316 | 1.193 | 2.007 | 1.527 | 1.225 | 1.456 |
| μ(Mo-Kα)/mm ⁻¹ | 13.00 | 0.23 | 4.16 | 2.05 | 0.70 | 1.348 |
| θ _{max} /° | 28.3 | 28.3 | 24.0 | 22.5 | 28.3 | 28.2 |
| No. of data | 2865 | 10289 | 2226 | 1783 | 9177 | 5607 |
| No. of parameters | 154 | 606 | 163 | 163 | 459 | 300 |
| <i>R</i> ₁ ^a | 0.0292 | 0.0718 | 0.0353 | 0.0579 | 0.0838 | 0.0416 |
| <i>wR</i> ₂ ^a | 0.0616 | 0.1194 | 0.0799 | 0.1164 | 0.0909 | 0.0919 |
| GOF | 1.128 | 1.038 | 1.042 | 1.014 | 1.066 | 1.000 |

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $[I > 2\sigma(I)]$; $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ for $[I > 2\sigma(I)]$.

$[\text{Bm}^{\text{Me}}]_2\text{Zn}$ were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.03).²⁶ Hydrogen atoms on carbon were included in calculated positions.

CCDC reference number 186/1829.

See <http://www.rsc.org/suppdata/dt/a9/a908411h/> for crystallographic files in .cif format.

Conclusion

In summary, the bidentate [S₂]-donor bis(mercaptoimidazolyl) ligands, $[\text{Bm}^{\text{Me}}]^-$ and $[\text{Bm}^{\text{Mes}}]^-$, have been synthesized by reaction of $[\text{BH}_4]^-$ with 2-mercapto-1-methylimidazole and 2-mercapto-1-mesitylimidazole, respectively. Subsequent treatment with ZnX_2 (X = Me, I, NO₃) yields a series of 1:1 $[\text{Bm}^{\text{R}}]\text{ZnX}$ complexes, namely $[\text{Bm}^{\text{Me}}]\text{ZnMe}$, $[\text{Bm}^{\text{Me}}]\text{ZnI}$ and $[\text{Bm}^{\text{Mes}}]\text{Zn}(\text{NO}_3)$. The isolation of these 1:1 $[\text{Bm}^{\text{R}}]\text{ZnX}$ complexes provides a contrast with the homoleptic L_2Zn derivatives that have previously been obtained using related bidentate [S₂

donor ligands. The $[\text{Bm}^{\text{Me}}]$ ligand is, however, insufficiently bulky to prevent the formation of the homoleptic derivative, $[\text{Bm}^{\text{Me}}]_2\text{Zn}$, which may be obtained by a redistribution reaction of $[\text{Bm}^{\text{Me}}]\text{ZnMe}$ in CHCl_3 .

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