

Bulky tris(mercaptoimidazolyl)borates: synthesis and molecular structures of the Group 12 metal complexes $[Tm^{tBu}]MBr$ ($M = Zn, Cd, Hg$)

Jennifer L. White,^a Joseph M. Tanski^b and Daniel Rabinovich^{*a}

^a Department of Chemistry, The University of North Carolina at Charlotte, 9201 University City Boulevard, Charlotte, North Carolina 28223, USA

^b Department of Chemistry, Columbia University, New York, New York 10027, USA

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An improved preparation of the bulky tris(mercaptoimidazolyl)borate ligand $[Tm^{tBu}]^-$ is reported together with convenient high yield syntheses of the Group 12 metal derivatives $[Tm^{tBu}]MBr$ ($M = Zn, Cd, Hg$). The molecular structures of the three new complexes have been determined by single-crystal X-ray diffraction and together constitute the first complete triad of Tm^R compounds in the periodic table to be structurally characterized. The isostructural complexes display in the solid state distorted tetrahedral structures, with the heavier members of the group exhibiting larger $Br-M-S$ and smaller $S-M-S$ angles.

Introduction

Tris(pyrazolyl)borates (Fig. 1) are among the most versatile and

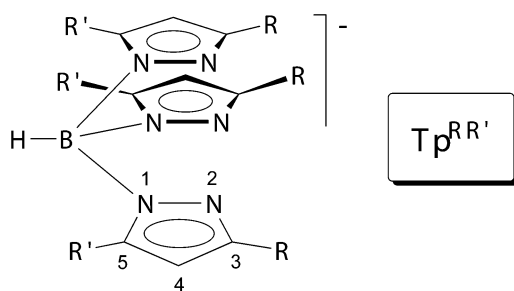


Fig. 1 Tris(pyrazolyl)borate ligands, $Tp^{RR'}$.

useful ligands in modern coordination chemistry.^{1,2} Since their inception,³ and for more than 20 years, most of the research based on this ligand system relied on the parent Tp ligand or its dimethylpyrazolyl analogue (Tp^{Me_2}). The subsequent introduction of a second generation of ligands bearing bulkier alkyl or aryl substituents (e.g., Bu^t , Ph) in the 3-position of the pyrazole rings thus provided a much needed impetus to the field.⁴ Marking a turning point in the development of Tp chemistry, the new so-called “tetrahedral enforcer” ligands proved to be remarkably successful in organometallic and bioinorganic chemistry and found applications ranging from the isolation of well-defined main group metal alkyl derivatives to the synthesis of elegant model compounds for copper and zinc enzymes.⁵ More recently, interest in the design of soft analogues of the Tp ligands has resulted in the syntheses of novel tripodal sulfur donor ligand families, most notably Riordan’s phenyltris-[(alkylthio)methyl]borates⁶ and Reglinski’s tris(mercaptoimidazolyl)borates⁷ (Fig. 2). Although several transition and main group metal complexes of $[Tm^{Me}]^-$ have been synthesized,^{8†} those with more sterically demanding ligands such

† Note added at proof: The syntheses and structures of the methyl substituted complexes $[Tm^{Me}]MBr$ ($M = Zn, Cd, Hg$) were reported after this manuscript was submitted (I. Cassidy, M. Garner, A. R. Kennedy, G. B. S. Potts, J. Reglinski, P. A. Slavin and M. D. Spicer, *Eur. J. Inorg. Chem.*, 2002, 1235).

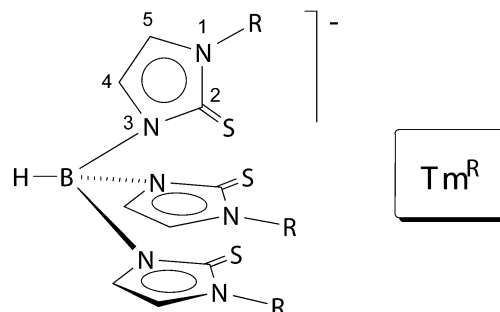


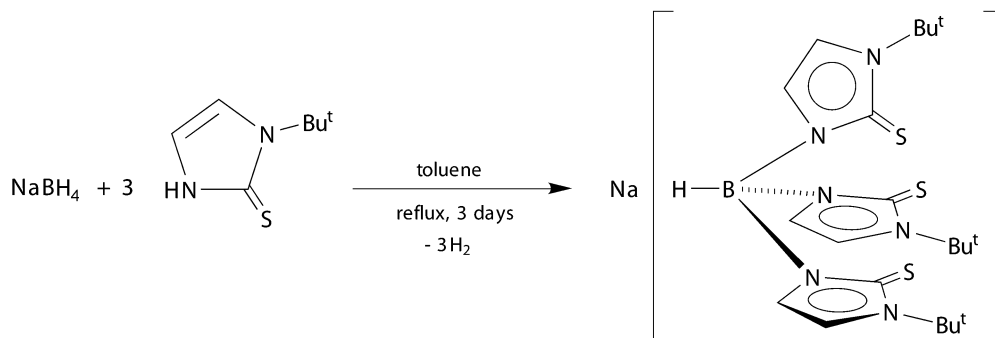
Fig. 2 Tris(mercaptoimidazolyl)borate ligands, Tm^R .

as $[Tm^{Ph}]^-$ and $[Tm^{Mes}]^-$ are limited to some derivatives of iron, cobalt, zinc, thallium, and lead, all of which have been prepared by Parkin.⁹ In addition, we have recently prepared the benzyl- and *p*-tolyl-substituted ligands $[Tm^{Bz}]^-$ and $[Tm^{p-Tol}]^-$ and their corresponding zinc and cadmium complexes $[Tm^R]MBr$ ($M = Zn, Cd$).¹⁰ Extending our efforts to an even bulkier ligand, we report in this paper the convenient preparation of the *tert*-butyl-substituted derivative $Na[Tm^{tBu}]$ and the synthesis and characterization of its corresponding Group 12 metal derivatives $[Tm^{tBu}]MBr$ ($M = Zn, Cd, Hg$). While this manuscript was in preparation, Vahrenkamp and co-workers reported the preparation of the potassium salt $K[Tm^{tBu}]$ and the synthesis and structures of several zinc complexes thereof, including $[Tm^{tBu}]ZnX$ ($X = F, Cl, ONO_2, OClO_2$) and $Zn[Tm^{tBu}]_2$,¹¹ and thus our results will be discussed in this context.

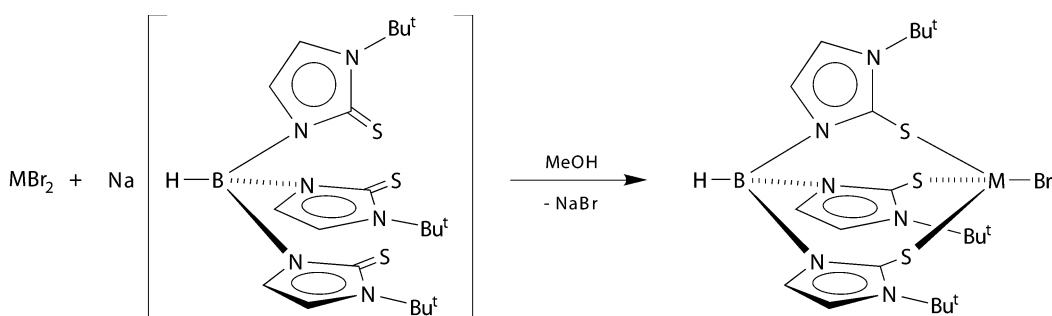
Results and discussion

Synthesis of $Na[Tm^{tBu}]$

The sodium salt of the tris(2-mercapto-1-*tert*-butylimidazolyl)borate anion $[Tm^{tBu}]^-$ was readily obtained (84% yield) from the reaction of $NaBH_4$ with three molar equivalents of the corresponding mercaptoimidazole in refluxing toluene for 3 days, as illustrated in Scheme 1.¹² The desired product tends to retain variable amounts of toluene, which prolonged exposure to vacuum or repeated washings with hydrocarbon solvents such as pentane or benzene failed to completely eliminate. However, treatment of crude $Na[Tm^{tBu}]$ with anhydrous diethyl



Scheme 1



Scheme 2

ether, followed by drying under vacuum for 4 h, effectively provides analytically pure, solvent-free product without a significant sacrifice in overall yield for the reaction. This method compares favorably with Vahrenkamp's preparation of the closely related potassium salt $K[Tm^{tBu}]$,¹¹ which was isolated in 51% yield as the ethyl acetate solvate after recrystallization from EtOAc–cyclohexane (1 : 1). $Na[Tm^{tBu}]$ is a white, thermally robust, air-stable solid, only sparingly soluble in toluene but more so in dichloromethane, chloroform, acetonitrile, dimethylsulfoxide (DMSO), methanol, and water. It has been characterized by a combination of analytical and spectroscopic techniques. Its 1H NMR spectrum (in $CDCl_3$) shows a singlet and two doublets, corresponding to the *tert*-butyl and imidazolyl protons, respectively, implying the magnetic equivalence of the three mercaptoimidazolyl groups in solution on the NMR time scale. Although the B–H proton is only observed as a very weak and broad peak in the 1H NMR spectrum of $Na[Tm^{tBu}]$, its presence is also verified in its IR spectrum (KBr pellet), which shows a distinctive band (ν_{B-H}) at 2503 cm^{-1} . While this value is almost identical to those observed for $Na[Tm^{Bz}]$ and $Na[Tm^{p-Tol}]$ (2503 and 2500 cm^{-1} , respectively),¹⁰ it is unexpectedly some 50 cm^{-1} lower than that reported for $K[Tm^{tBu}]$ (2554 cm^{-1}).¹¹

Synthesis of $[Tm^{tBu}]MBr$ ($M = Zn, Cd, Hg$)

The divalent Group 12 metal complexes $[Tm^{tBu}]MBr$ ($M = Zn, Cd, Hg$) were readily prepared by mixing equimolar methanolic solutions of the corresponding anhydrous metal bromides and the ligand (Scheme 2), and isolated in 85–90% yield after appropriate work-up. It is important to note that while several $[Tm^R]ZnX$ complexes have been prepared in recent years,¹³ related cadmium and mercury derivatives are still rare.^{10,14} The desired products are all air-, light-, and water-stable white (Zn, Cd) or ivory (Hg) solids, only slightly soluble in benzene or toluene but more so in dichloromethane, chloroform, tetrahydrofuran, acetonitrile, and dimethylsulfoxide (DMSO). Satisfactory analytical data have been obtained for the three new complexes, which have also been characterized by standard spectroscopic methods. Their 1H and ^{13}C NMR spectra are not only virtually identical to each other but are also qualitatively similar to those of $Na[Tm^{tBu}]$, with most of the ligand signals

exhibiting typical downfield chemical shifts relative to the corresponding values obtained for the free ligand in the same solvent. For example, the chemical shifts of the imidazolyl carbons in the ^{13}C NMR spectra are shifted between 4.6 and 5.0 ppm as a result of complexation. An exception to this trend is observed for the thione carbons, for which upfield chemical shifts of *ca.* 9 ppm are observed in the ^{13}C NMR spectra. This phenomenon may be ascribed to a number of factors, including the reduction in π -electron density and concomitant weakening of the carbon–sulfur linkages upon coordination to the metal centers. While preceded for other thione complexes,¹⁵ we note, however, that these arguments should be used with caution when discussing chemical shift variations since magnetic shielding in nuclei having a non-symmetrical or anisotropic distribution of valence electrons (*e.g.*, ^{13}C) is dominated by the paramagnetic contribution, which does not necessarily correlate with electron density.

Molecular structures of $[Tm^{tBu}]MBr$ ($M = Zn, Cd, Hg$)

The molecular structures of $[Tm^{tBu}]MBr$ ($M = Zn, Cd, Hg$) were determined by single-crystal X-ray diffraction, as illustrated in Figs. 3–5, with selected bond lengths and angles for the three complexes included in Table 1. While the zinc and cadmium compounds are isomorphous and were crystallized as the

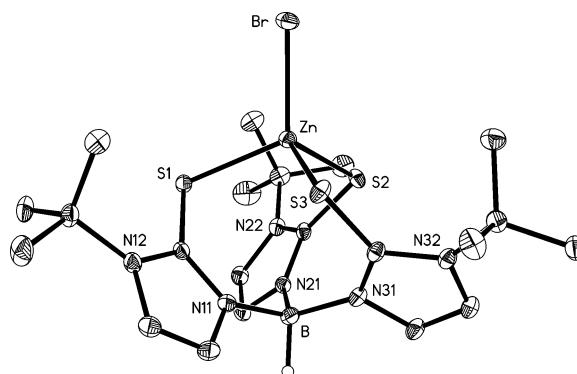


Fig. 3 Molecular structure of $[Tm^{tBu}]ZnBr$.

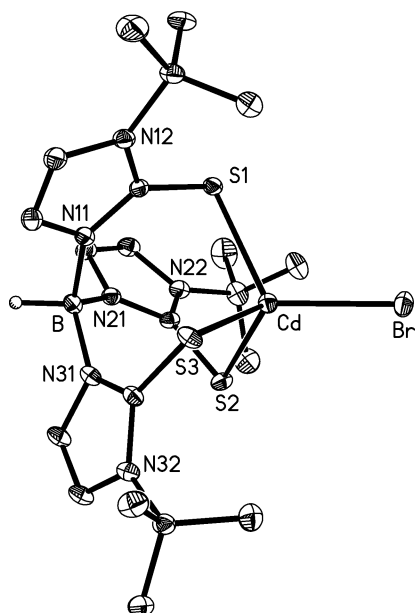


Fig. 4 Molecular structure of [Tm^{tBu}]CdBr.

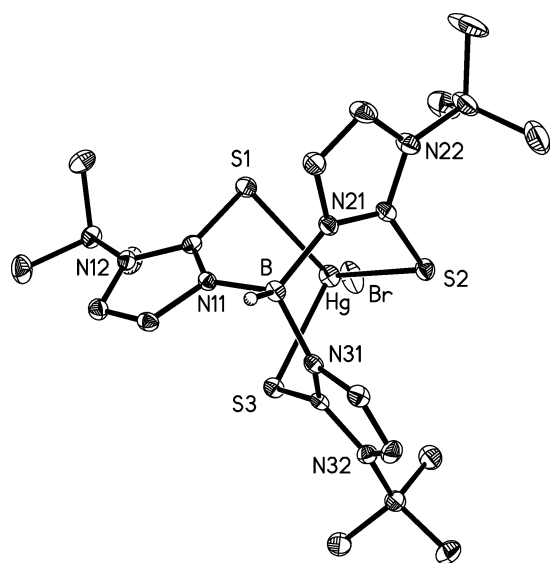


Fig. 5 Molecular structure of [Tm^{tBu}]HgBr showing the propeller-like arrangement of mercaptoimidazolyl groups.

acetonitrile adducts, the mercury derivative was obtained as the benzene solvate. Most significantly, this triad is the first complete series of tris(mercaptoimidazolyl)borate metal complexes to be structurally characterized for any group in the periodic table. The isostructural four-coordinate complexes exhibit, in the solid state, distorted tetrahedral geometries that resemble those of other complexes of general formula [Tm^R]MX (M = Zn, Cd)^{10,13,14} and, as such, contain the three mercaptoimidazolyl groups in a propeller-like arrangement around the approximate three-fold axis containing the B–H and M–Br groups. Whereas the average Br–M–S angles (112.4, 115.9 and 117.4° for M = Zn, Cd and Hg, respectively) steadily increase in that same order, the average S–M–S angles (106.3, 102.1 and 100.4°, respectively) follow the opposite trend and thus result in a progressive elongation of the tetrahedral molecules along the pseudo-C₃ axis for the heavier group congeners. The Zn–Br and average Zn–S bond lengths in [Tm^{tBu}]ZnBr (2.372 and 2.359 Å, respectively) are only slightly longer than those observed in either [Tm^{Me}]ZnBr (2.364 and 2.355 Å)⁷ or [Tm^{Bz}]ZnBr (2.334 and 2.350 Å).¹⁰ Similarly, the Cd–Br and average Cd–S bond distances in [Tm^{tBu}]CdBr (2.536 and 2.543 Å, respectively) are virtually identical to the corresponding values reported for

Table 1 Selected bond lengths (Å) and angles (°) for [Tm^{tBu}]MBr (M = Zn, Cd, Hg)

	M = Zn	M = Cd	M = Hg
M–Br	2.3720(4)	2.5364(4)	2.5330(6)
M–S(1)	2.3517(7)	2.5380(8)	2.5782(15)
M–S(2)	2.3663(8)	2.5548(8)	2.5349(13)
M–S(3)	2.3578(8)	2.5363(8)	2.6067(13)
S(1)–C(11)	1.730(3)	1.732(3)	1.753(5)
S(2)–C(21)	1.728(2)	1.723(3)	1.733(5)
S(3)–C(31)	1.724(3)	1.732(3)	1.723(5)
Br–M–S(1)	111.65(2)	114.10(2)	118.46(4)
Br–M–S(2)	107.93(2)	108.62(2)	121.91(3)
Br–M–S(3)	117.75(2)	125.01(2)	111.86(3)
S(1)–M–S(2)	105.58(2)	101.13(2)	101.24(4)
S(1)–M–S(3)	105.12(3)	101.05(3)	101.57(4)
S(2)–M–S(3)	108.13(3)	104.07(3)	98.28(4)
M–S(1)–C(11)	97.14(9)	95.94(10)	95.63(17)
M–S(2)–C(21)	95.36(9)	94.12(9)	97.49(17)
M–S(3)–C(31)	96.74(9)	94.84(9)	97.17(15)

[Tm^{Bz}]CdBr (2.534 and 2.543 Å).¹⁰ Since [Tm^{tBu}]HgBr is the first tris(mercaptoimidazolyl)borate complex of mercury to be structurally characterized, analogous compounds are not available for direct comparison. However, its Hg–S bond lengths, in the range 2.533 to 2.578 Å, are comparable to those observed in the bis(*N,N*-dimethylthioformamide) adducts L₂HgX₂ (X = Cl, Br, I)¹⁶ and the Hg–Br bond distance (2.533 Å) is very close to the mean value (2.528 Å) found in the Cambridge Structural Database for such terminal groups.¹⁷ It is also interesting to note that the average S–C bond lengths for all three [Tm^{tBu}]MBr complexes (*ca.* 1.73 Å in each case) are only slightly longer than the corresponding distances observed in 2-mercapto-1-*tert*-butylimidazole (1.70 Å)¹⁸ or those found in the uncoordinated [Tm^{Me}][−] ligand (average = 1.70 Å)^{8d} or in a variety of other free heterocyclic thiones, typically in the range 1.67 to 1.70 Å.¹⁹ In this regard, the lengthening of the exocyclic C–S bonds in the [Tm^{tBu}]MBr complexes is consistent with a 10–15% reduction in the π-character of the bonds upon coordination to the metal centers,²⁰ a situation that is in line with previous observations, as discussed above.¹⁵

Experimental

1. General considerations

All reactions were performed under dry oxygen-free nitrogen in an Innovative Technology System One-M-DC glove box or under argon using a combination of high-vacuum and Schlenk techniques.²¹ Solvents were purified and degassed by standard procedures and all commercially available reagents were used as received. 2-Mercapto-1-*tert*-butylimidazole was prepared as published.²² ¹H and ¹³C NMR spectra were obtained on General Electric QE 300 or Varian Gemini (300 MHz) FT spectrometers. Chemical shifts are reported in ppm relative to SiMe₄ (δ = 0 ppm) and were referenced internally with respect to the solvent resonances [¹H: δ 7.24 for CHCl₃; ¹³C: δ 39.5 for (CD₃)₂SO]; coupling constants are given in Hz. IR spectra were recorded as KBr pellets on a Bio-Rad 175C FT spectrophotometer and are reported in cm^{−1}; relative intensities of the absorptions are indicated in parentheses (vs = very strong, s = strong, m = medium, w = weak). Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, GA).

2. Synthesis of Na[Tm^{tBu}]

A suspension of NaBH₄ (0.242 g, 6.397 mmol) and 2-mercapto-1-*tert*-butylimidazole (3.0 g, 19.20 mmol) in toluene (40 mL) was heated to reflux for 3 days under an atmosphere of argon. The reaction mixture was allowed to cool to room temperature and concentrated under reduced pressure to *ca.* 20 mL. The

Table 2 Crystallographic data for [Tm^{tBu}]MBr (M = Zn, Cd, Hg)

Formula	C ₂₁ H ₃₄ BBrN ₆ S ₃ Zn·CH ₃ CN	C ₂₁ H ₃₄ BBrCdN ₆ S ₃ ·CH ₃ CN	C ₂₁ H ₃₄ BBrHgN ₆ S ₃ ·C ₆ H ₆
Formula weight	663.87	710.90	836.14
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)
<i>a</i> /Å	9.6992(8)	9.8222(7)	17.7024(10)
<i>b</i> /Å	33.035(3)	32.991(2)	10.8838(6)
<i>c</i> /Å	10.2817(8)	10.4059(7)	35.013(2)
β /°	109.407(2)	110.769(1)	96.7900(10)
<i>V</i> /Å ³	3107.2(4)	3152.9(4)	6698.6(7)
<i>Z</i>	4	4	8
<i>T</i> /K	238(2)	243(2)	243(2)
Radiation (λ /Å)	0.71073	0.71073	0.71073
μ (Mo-K α)/mm ⁻¹	2.303	2.183	6.002
No. of data	6938	7056	7692
No. of parameters	330	330	358
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0427	0.0339	0.0364
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1074	0.1295	0.0751

white product was isolated by filtration, washed with anhydrous diethyl ether (2 × 20 mL), and dried *in vacuo* for 4 h (2.675 g, 84%). Mp = 270 °C (dec). ¹H NMR data (in CDCl₃): δ 1.74 [s, 27 H, C(CH₃)₃], 6.03 (d, ³*J*_{H-H} = 2.6, 3 H, imidazole H), 6.78 (d, ³*J*_{H-H} = 2.1, 3 H, imidazole H), *BH* not observed. ¹³C NMR data (in d₆-DMSO): δ 28.0 [q, ¹*J*_{C-H} = 127, 9 C, C(CH₃)₃], 56.7 [s, 3 C, C(CH₃)₃], 113.3 (dd, ¹*J*_{C-H} = 193, ²*J*_{C-H} = 13, 3 C, imidazole C), 119.0 (dd, ¹*J*_{C-H} = 191, ²*J*_{C-H} = 9, 3 C, imidazole C), 162.4 (s, 3 C, C=S). IR data: 3146 (w), 2972 (s), 2926 (m), 2503 (w), 1635 (w), 1561 (w), 1477 (m), 1407 (s), 1398 (s), 1360 (vs), 1269 (s), 1223 (s), 1199 (vs), 1164 (vs), 1101 (vs), 1055 (s), 1046 (s), 981 (m), 820 (m), 745 (m), 718 (s), 677 (s). Analysis calculated for C₂₁H₃₄BN₆NaS₃: C, 50.4; H, 6.9; N, 16.8. Found: C, 50.0; H, 6.7; N, 16.6%.

3. Synthesis of [Tm^{tBu}]ZnBr

A solution of Na[Tm^{tBu}] (0.200 g, 0.400 mmol) in methanol (6 mL) was added to a stirred solution of ZnBr₂ (0.090 g, 0.400 mmol) in the same solvent (4 mL), resulting in the formation, within 3 min, of a white precipitate. The suspension was stirred for an additional 30 min, treated with water (5 mL), and the product was isolated by filtration and dried *in vacuo* for 1.5 h (0.216 g, 87%). Mp = 270 °C (dec.). ¹H NMR data (in CDCl₃): δ 1.75 [s, 27 H, C(CH₃)₃], 6.82 (d, ³*J*_{H-H} = 2.1, 3 H, imidazole H), 6.98 (d, ³*J*_{H-H} = 2.1, 3 H, imidazole H), *BH* not observed. ¹³C NMR data (in d₆-DMSO): δ 28.4 [q, ¹*J*_{C-H} = 127, 9 C, C(CH₃)₃], 59.0 [s, 3 C, C(CH₃)₃], 118.2 (dd, ¹*J*_{C-H} = 197, ²*J*_{C-H} = 12, 3 C, imidazole C), 123.6 (dd, ¹*J*_{C-H} = 196, ²*J*_{C-H} = 10, 3 C, imidazole C), 153.5 (s, 3 C, C=S). IR data: 3190 (w), 3155 (w), 3137 (w), 3095 (w), 2967 (m), 2929 (w), 2886 (w), 2869 (w), 2445 (w), 2413 (w), 2363 (w), 2344 (w), 2295 (w), 2231 (w), 1567 (m), 1542 (w), 1509 (w), 1482 (w), 1458 (w), 1419 (m), 1399 (m), 1364 (vs), 1308 (m), 1258 (w), 1230 (m), 1195 (vs), 1173 (s), 1147 (w), 1131 (w), 1070 (m), 1030 (w), 931 (w), 821 (w), 760 (m), 740 (m), 725 (m), 687 (m), 589 (w), 553 (w), 496 (w), 456 (w). Analysis calculated for C₂₁H₃₄BBrN₆S₃Zn: C, 40.5; H, 5.5; N, 13.5. Found: C, 39.9; H, 5.6; N, 13.2%.

4. Synthesis of [Tm^{tBu}]CdBr

A solution of Na[Tm^{tBu}] (0.195 g, 0.390 mmol) in methanol (6 mL) was added to a stirred solution of CdBr₂ (0.106 g, 0.389 mmol) in the same solvent (6 mL). The resulting colorless solution was stirred for 1 h and concentrated under reduced pressure to *ca.* 4 mL, leading to the formation of a white precipitate. After addition of water (5 mL), the product was isolated by filtration and dried *in vacuo* for 16 h (0.223 g, 85%). Mp = 260 °C (dec.). ¹H NMR data (in CDCl₃): δ 1.75 [s, 27 H, C(CH₃)₃], 6.82 (d, ³*J*_{H-H} = 2.1, 3 H, imidazole H), 6.99 (d, ³*J*_{H-H} = 2.1, 3 H, imidazole H), *BH* not observed. ¹³C NMR data (in d₆-DMSO): δ 28.4 [q, ¹*J*_{C-H} = 127, 9 C, C(CH₃)₃], 59.0

[s, 3 C, C(CH₃)₃], 118.3 (dd, ¹*J*_{C-H} = 198, ²*J*_{C-H} = 12, 3 C, imidazole C), 123.7 (dd, ¹*J*_{C-H} = 197, ²*J*_{C-H} = 9, 3 C, imidazole C), 153.3 (s, 3 C, C=S). IR data: 3184 (m), 3141 (m), 3102 (w), 2979 (s), 2927 (s), 2887 (m), 2659 (w), 2497 (w), 2441 (m), 2413 (m), 2296 (w), 2235 (w), 1568 (s), 1482 (s), 1457 (w), 1419 (vs), 1398 (vs), 1361 (vs), 1305 (vs), 1258 (m), 1230 (s), 1196 (vs), 1174 (vs), 1131 (s), 1071 (s), 1030 (m), 980 (w), 929 (w), 846 (w), 821 (s), 757 (vs), 732 (vs), 688 (vs), 632 (w), 589 (m), 552 (m), 542 (w), 493 (m), 454 (w). Analysis calculated for C₂₁H₃₄BBrCdN₆S₃: C, 37.7; H, 5.1; N, 12.6. Found: C, 37.9; H, 5.3; N, 12.3%.

5. Synthesis of [Tm^{tBu}]HgBr

A solution of Na[Tm^{tBu}] (0.200 g, 0.400 mmol) in methanol (6 mL) was added to a stirred solution of HgBr₂ (0.144 g, 0.400 mmol) in the same solvent (6 mL), resulting in the immediate formation of an ivory precipitate, which dissolved within 3 min to give a clear pale yellow solution. After stirring for 45 min, the solution was concentrated under reduced pressure to *ca.* 4 mL, leading to the formation of an ivory solid. After addition of water (5 mL), the product was isolated by filtration and dried *in vacuo* for 16 h (0.268 g, 88%). Mp = 160 °C (dec.). ¹H NMR data (in CDCl₃): δ 1.74 [s, 27 H, C(CH₃)₃], 6.85 (d, ³*J*_{H-H} = 2.1, 3 H, imidazole H), 6.97 (d, ³*J*_{H-H} = 2.1, 3 H, imidazole H), *BH* not observed. ¹³C NMR data (in d₆-DMSO): δ 28.4 [q, ¹*J*_{C-H} = 129, 9 C, C(CH₃)₃], 59.1 [s, 3 C, C(CH₃)₃], 118.2 (dd, ¹*J*_{C-H} = 197, ²*J*_{C-H} = 13, 3 C, imidazole C), 123.8 (dd, ¹*J*_{C-H} = 196, ²*J*_{C-H} = 8, 3 C, imidazole C), 153.5 (s, 3 C, C=S). IR data: 3143 (w), 3095 (w), 2977 (m), 2926 (m), 2882 (w), 2651 (w), 2492 (w), 2415 (w), 2296 (w), 2231 (w), 1564 (m), 1481 (m), 1458 (s), 1419 (s), 1398 (s), 1357 (vs), 1298 (s), 1262 (m), 1228 (m), 1198 (vs), 1163 (vs), 1112 (s), 1060 (m), 1029 (w), 985 (w), 929 (w), 821 (m), 724 (s), 685 (s), 635 (w), 590 (w), 553 (w), 494 (w), 478 (w), 460 (w), 420 (w). Analysis calculated for C₂₁H₃₄BBrHgN₆S₃: C, 33.3; H, 4.5; N, 11.1. Found: C, 33.3; H, 4.6; N, 10.9%.

6. X-Ray structure determinations

X-Ray diffraction data for [Tm^{tBu}]MBr (M = Zn, Cd, Hg) were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. Crystal data, data and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on *F*² using SHELXTL (Version 5.03).²³ Hydrogen atoms on carbon were included in calculated positions.

CCDC reference numbers 176312–176314.

See <http://www.rsc.org/suppdata/dt/b1/b111558h/> for crystallographic data in CIF or other electronic format.

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