A new family of flexible scorpionate ligands based on 2-mercaptopyridine†

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A new family of flexible scorpionate ligands based on 2-mercaptopyridine is reported. The tris- and bis-substituted ligands, K[HB(mp)$_3$] (**1**) and Na[H$_2$B(mp)$_2$] (**2**) (mp = 2-mercaptopyridine) have been prepared and fully characterised. The structural characterisation of **1** reveals an unprecedented μ_3-κ^3-*SS′H*-$\eta^1\eta^1\eta^2$-κ^2-*S″C*-$\eta^1\eta^1$-κ^1-*S′*-η^1 coordination mode. The coordination of both **1** and **2** to copper(I) complexes containing triphenylphosphine and tricyclohexylphosphine co-ligands is investigated suggesting κ^3-*SSS* coordination modes for [Cu{HB(mp)$_3$}(PR$_3$)] {where R = Ph (**3**); R = Cy, (**4**)} and κ^3-*SSH* coordination modes for [Cu{H$_2$B(mp)$_2$}(PR$_3$)] {where R = Ph (**5**); R = Cy (**6**)} the latter confirmed by structural characterisation of **5**. A structural comparison with the sulfur based scorpionates, HB(mt)$_3$ and H$_2$B(mt)$_2$ (mt = methyl-2-mercaptoimidazole) is made in terms of the degree of tautomerisation of the heterocyclic rings.

Introduction

Ever since Trofimenko reported the first scorpionate ligand[1] in 1966, **Tp** [hydrotris(pyrazolyl)borate] (Fig. 1), there has been great interest in their chemistry and application.[2–4] Since then, there has been a vast array of derivative and further generation ligands.[1c,1d,5] For a long time, scorpionate ligands were generally thought of as inert spectator ligands that could easily be tuneable in terms of their steric and electronic properties.[6] Such ligands could be used to alter the properties of the transition metal centre without getting directly involved in its reactivity.

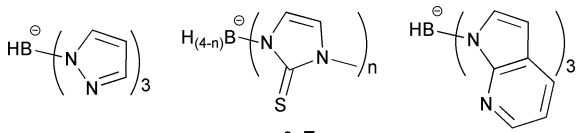

Fig. 1 **Tp** and the flexible scorpionates **Tm**, **Bm** and **Tai**.

This outlook changed following the introduction of a new more flexible scorpionate ligand, **Tm** [hydrotris(methylimidazolyl)-borate], which is based upon a *N*-methyl-2-mercaptoimidazol-1-yl ring system (Fig. 1).[7] This new generation ligand had two major differences when compared to Trofimenko's original scorpionates. The **Tm** ligand was based on soft sulfur donor atoms and perhaps more significantly, greater flexibility had been incorporated into the ligand by addition of an extra atom between the boron and the donor atom. The greater flexibility of this ligand structure opened up the potential for activation at the boron bridgehead and formation of metal–borane (metallaboratrane) complexes[8] giving rise to reactivity not observed in the analogous **Tp** compounds.[9]

The bis-substituted version of this ligand, **Bm** [dihydro-bis(methylimidazolyl)borate], was later reported in 1997.[10] Following the publication of these flexible scorpionate ligands, there have been a number of other bis-substituted[11] and tris-substituted[12] flexible scorpionates reported.

Our interests lie in the potential reversibility of hydride migration between transition metal and boron centres and the application of this process to metal mediated transformations. During the course of our investigations we isolated a compound where a hydride was observed at an intermediate point between the metal and boron centres (Fig. 2).[13] Crossley and Hill have also provided an example where the position of the hydride (*i.e.* at either the boron or metal centre) could be controlled by judicious choice of co-ligand.[14] We have further exploited hydride migration reactivity within the relatively unexplored ligand, **Tai** [hydrotris(azaindoyl)borate] (Fig. 1), providing the first nitrogen based metallaboratrane complexes.[15] Additionally, we reported a series of group nine transition metal complexes containing **Tai** and highlighted their catalytic application in the transfer hydrogenation of ketones.[16]

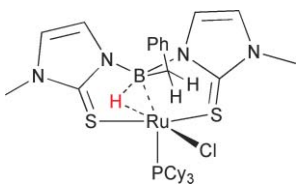

Fig. 2 Previously reported complex where the hydride is found at an intermediate point between the ruthenium and boron centres.

It was of interest to us to provide other examples of flexible scorpionate ligands in order to further explore and exploit potential B–H activation. We wondered what effect changing the heterocycle would have on the electronic properties of the ligand. We aimed at

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providing a more electron rich donor system and therefore targeted scorpionate ligands containing 2-mercaptopyridine heterocycles.

Similar to the methyl-2-mercaptoimidazol-1-yl and 7-azaindolyl ligand "arms" within **Tm** and **Tai**, respectively, the 2-mercaptopyridine unit can undergo tautomerisation between pyridine-2-thionate and 2-thiopyridone forms (Fig. 3). It has been shown that although the thione–thiolate tautomeric equilibrium generally favours the thione form, there is a strong dependence on its environment with only a small difference in the energy between the two tautomeric forms.[17]

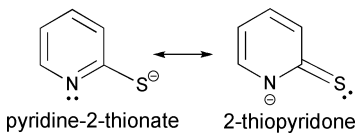


Fig. 3 Tautomerisation between pyridine-2-thionate and 2-thiopyridone forms.

It was envisaged that the aromaticity of the thiolate tautomer might provide greater electron density upon the sulfur atoms thus furnishing more electron rich ligands (Fig. 4). Herein, we wish to report the synthesis and characterisation of this new family of flexible scorpionate ligands together with a preliminary investigation of their coordination chemistry to a series of copper(I) complexes.

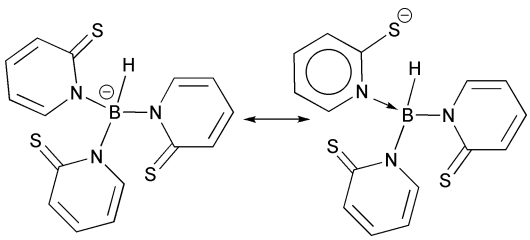
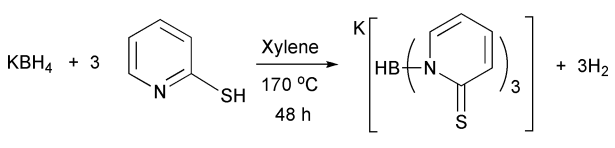


Fig. 4 Tautomerisation of tris-substituted ligand resulting in a greater negative charge at sulfur.

Results and discussion

Synthesis and characterisation of ligands

The syntheses of our target ligands were performed by similar methods to those used for other scorpionate ligands.[7,11,12] The tris-substituted ligand potassium hydrotris(2-thiopyridone)borate, K[HB(mp)3] (mp = 2-mercaptopyridine), K[**Tmp**] (**1**) was readily prepared by heating a xylene suspension of KBH_4 in the presence of an excess of 2-mercaptopyridine (4 equivalents) at 170 °C under a nitrogen atmosphere (Scheme 1). The extent of the reaction could be followed by taking aliquots from the reaction mixture and recording their $^{11}B\{^1H\}$ NMR spectra (in DMSO-d_6). A single broad peak at 4.4 ppm (h.h.w. = 560 Hz) was observed after a period of *ca.* 48 h. The solid product (**1**) was obtained in high yield



Scheme 1 Synthesis of **1**.

as a yellow powder and characterised by ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ NMR, IR spectroscopies and ESI^- mass spectrometry. The ^1H NMR spectrum was particularly broad, however it revealed four signals between 7.83 and 6.46 ppm each integrating to three protons corresponding to the ring protons. A very broad signal centred at 4.83 ppm which integrated to one proton was assigned as the B–H proton. This assignment was further confirmed following a boron decoupled proton NMR experiment where a sharp singlet signal was observed in place of the broad signal. The $^{13}C\{^1H\}$ NMR spectrum of **1** also gave broad signals, nevertheless it showed five signals in the low field region of the spectrum. The chemical shift corresponding to the *C*=S group was found at 182.5 ppm. It has previously been shown that ^{13}C NMR spectroscopy can provide a means of estimating the equilibrium composition of the two tautomeric forms and the observed chemical shift is indicative of a high degree of the thiopyridone tautomeric form as expected.[18]

The formation of **1** was further confirmed by an X-ray single crystal diffraction study. Crystals suitable for X-ray diffraction were grown when diethyl ether was allowed to diffuse into a saturated tetrahydrofuran solution of **1**. ORTEP representations of **1** are presented in Fig. 5 and 6. Selected bond distances and angles, and crystallographic parameters are given in Tables 1 and 2 respectively.†

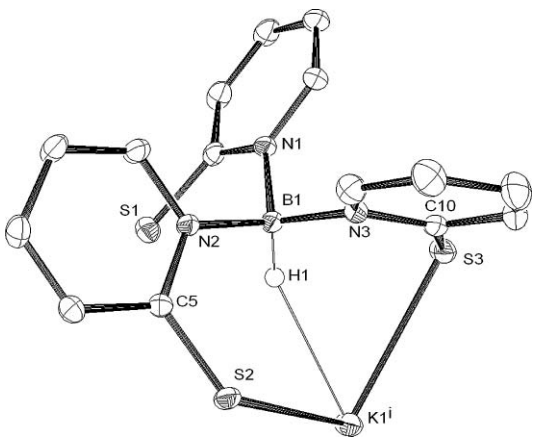


Fig. 5 Structure of K[**Tmp**] (**1**). Hydrogen atoms (except for H_1) have been omitted for clarity (thermal ellipsoids drawn at the 50% level).

The X-ray solution of **1** revealed an extended structure involving an unprecedented μ_3-κ^3-*SS′H*-$\eta^1\eta^1\eta^2$-κ^2-*S″C*-$\eta^1\eta^1$-κ^1-*S′*-η^1 coordination mode of the ligand to the potassium centres. Two sulfur atoms (*S*,*S′*) and the B–H functionality coordinate and interact with one of the potassium atoms. The ligand bridges to further potassium atoms in two different ways. Firstly, one of the indicated sulfur groups (*S′*) bridges to a second potassium centre. Secondly, a third sulfur donor (*S″*) coordinates to a third potassium. The latter potassium interacts with a carbon in the 5-position of the mercaptopyridine ring which is bridging the two former potassium centres. Each potassium atom is coordinated to three sulfur atoms, a B–H group, a carbon atom of a mercaptopyridine ring and one molecule of tetrahydrofuran.[19] The structure also reveals that the thione tautomeric form predominates for the thiopyridyl units (Table 1).

Table 1 Selected bond distances (Å) and angles (°) for **1**

S(1)–K(1)	3.294(5)
S(2)–K(1)	3.271(5)
S(3)–K(1)	3.216(5)
H(1)–K(1)	2.748(18)
H(1)–B(1)	1.051(18)
C(1)–S(1)	1.703(15)
C(5)–S(2)	1.705(14)
C(10)–S(3)	1.695(16)
N(1)–B(1)	1.573(18)
N(2)–B(1)	1.567(19)
N(3)–B(1)	1.579(19)
K(1)–C(8)	3.312(16)
N(2)–B(1)–N(1)	109.55(10)
N(1)–B(1)–N(3)	110.14(11)
N(3)–B(1)–N(2)	108.76(11)
C(10)–S(3)–K(1)	96.00(5)
C(1)–S(1)–K(1)	162.17(5)
C(5)–S(2)–K(1)	121.59(5)
K(1)–H(1)–B(1)	149.64(12)

Table 2 Crystallographic data and parameters for **1** and **5**

Complex	**1**	**5**
Chemical formula	$C_{19}H_{21}BKN_3OS_3$	$C_{28}H_{25}BCuN_2PS_2$
Formula weight	453.48	558.94
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	7.5891(3)	14.8949(7)
b/Å	10.2493(4)	8.9263(4)
c/Å	14.4333(6)	19.1954(8)
α/°	96.181(2)	90
β/°	94.557(2)	92.750(2)
γ/°	105.418(2)	90
Z	2	4
V	1069.11(7)	2549.2(2)
T/K	173	173
D_c/Mg m^{-3}	1.409	1.456
μ/mm^{-1}	0.557	1.104
No. of data collected	33 398	75 804
No. of unique data	6548	7807
Goodness of fit on F^2	1.143	1.067
R_{int}	0.0289	0.0590
Final $R(\|F\|)$ for $F_o > 2\sigma(F_o)$	0.0338	0.0295
Final $R(F^2)$ for all data	0.1057	0.0821

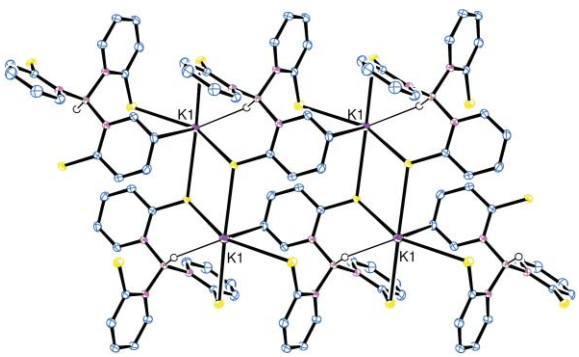
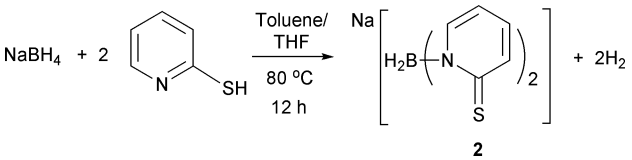


Fig. 6 ORTEP representation of the extended solid state structure of **1**. One molecule of tetrahydrofuran is coordinated to each potassium atom. Hydrogen atoms (except for H_1) have been omitted for clarity. (Colours representing atoms are: yellow: sulfur; blue: carbon; brown: boron; pink: nitrogen; white: hydrogen).

The preparation of the bis-substituted ligand sodium dihydrobis(2-thiopyridone)borate, Na[$H_2B(mp)_2$] (mp = 2-mercaptopyridine), Na[**Bmp**] (**2**) required some optimisation. It was found that the best conditions for the preparation of this ligand involved heating $NaBH_4$ and two equivalents of 2-mercaptopyridine in a 3 : 1 mixture of toluene and tetrahydrofuran at 80 °C for 12 h (Scheme 2). The sodium borohydride salt gave much better selectivity for the desired product over the corresponding potassium salt in this case. The product was isolated in good yield, as a pale yellow solid by filtration of the reaction mixture and washing the solid with a further quantity of toluene. The bis-substituted ligand was also characterised by NMR, IR spectroscopy and mass spectrometry.



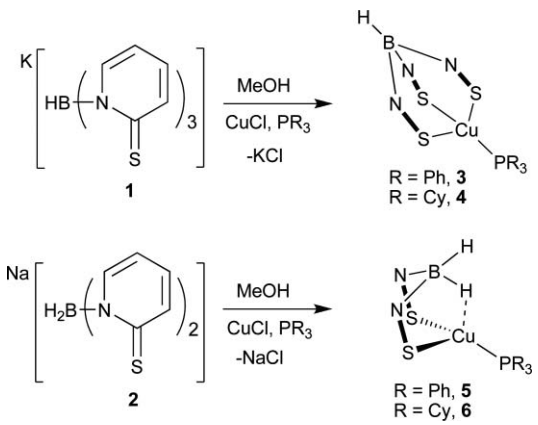
2

Scheme 2 Synthesis of **2**.

Synthesis and characterisation of copper complexes

The coordination chemistry of **Tp**, **Tm** and their derivatives has been extensively investigated using a wide range of transition metal centres. In particular, the coordination to copper has been reported in a number of examples.[1,20,21] The coordination chemistry of ligands **1** and **2** with copper was investigated.

The complexes [({HB(mp)$_3$})Cu(PR$_3$)] {where R = Ph (**3**); R = Cy (**4**)} and [({$H_2B(mp)_2$})Cu(PR$_3$)] {where R = Ph$_3$ (**5**); R = Cy$_3$ (**6**)} were readily prepared by the addition of one equivalent of either K[**Tmp**] or Na[**Bmp**] to methanol solutions containing CuCl and the corresponding phosphine ligand (Scheme 3). One equivalent of the phosphine was added to furnish complexes **3**–**6**. The same products were also obtained in the presence of two equivalents of phosphine. Yellow solids precipitated from the reaction mixtures within a few minutes. The products were isolated in high yields and fully characterised by NMR and IR spectroscopy, mass spectrometry and elemental analysis.



1

2

Scheme 3 Synthesis of copper complexes **3**–**6**.

The $^{31}P\{^1H\}$ NMR spectra of **3** and **5** revealed broad signals at –2.4 ppm (h.h.w. = 85 Hz) and 1.7 ppm (h.h.w. = 265 Hz)

respectively. In contrast, the $^{31}P\{^{1}H\}$ NMR spectra of the tricyclohexylphosphine complexes **4** and **6** revealed relatively sharp signals at 17.4 ppm and 19.0 ppm. This is consistent with a more labile coordination of the aryl phosphine relative to the alkyl phosphine ligands. Similar observations have been recorded in other examples.[20,21]

The $^{11}B\{^{1}H\}$ NMR spectra of complexes **3** and **4** revealed single broad peaks at –0.1 ppm (h.h.w. = 412 Hz) and –0.5 ppm (h.h.w. = 331 Hz), respectively [upfield from the free ligand (**1**), 4.4 ppm (h.h.w. = 560 Hz)]. The ^{1}H and $^{13}C\{^{1}H\}$ NMR data for both **3** and **4** suggested the formation of $[Cu\{\kappa^3\text{-}SSS\text{-}HB(mp)_3\}(PPh_3)]$ and $[Cu\{\kappa^3\text{-}SSS\text{-}HB(mp)_3\}(PCy_3)]$ since signals corresponding to only one chemical environment for the thiopyridone units were observed in both cases. A variable temperature investigation was carried out on complex **4** in CD_2Cl_2. At –90 °C, the signals corresponding to the ring protons became broad. At this temperature however, the spectrum still indicated one chemical environment for these protons. It was not possible to locate the B*H* resonance for complex **3**, however, the corresponding signal for **4** was located as a singlet at 5.86 ppm in a $^{1}H\{^{11}B\}$ NMR experiment (in $CDCl_3$). The downfield shift of this signal in comparison to the free ligand [δ (DMSO) 4.83 ppm] suggested no significant interaction of the BH group with the metal centre in solution. Infrared spectroscopy gave no evidence of a BH–Cu interaction in the solid state for complex **3**. The spectrum showed a band at 2458 cm^{-1} characteristic of a non-coordinated B–H stretching frequency, while no B–H band was observed in the case of complex **4**. All of the spectroscopic data is therefore consistent with a κ^3-*SSS* coordination mode of **Tmp** in complexes **3** and **4**.

The coordination mode κ^3-*NNN* is observed in all structurally characterised mono-phosphine copper complexes containing either **Tp** or its derivatives.[20] This is with the exception of one example, where a coordination mode κ^2-*NN* was observed,[20g] resulting from the use of particularly large sterically hindered ligands. The sulfur based scorpionates, on the other hand, are more flexible than the pyrazole based ligands, the former ligands forming eight-membered rings upon coordination (Fig. 7). The B–H–metal interaction therefore has a particular stabilising effect in the flexible scorpionates since it leads to the formation of two six-membered rings rather than one eight-membered ring.[16] As a result of this, both κ^3-*SSS* and κ^3-*SSH* coordination modes are commonly observed within complexes containing the **Tm** ligand.[1,5]

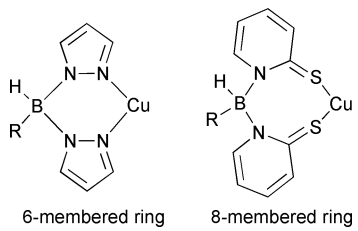


Fig. 7 Comparison of chelation sizes for the pyrazole and 2-mercaptopyridine based scorpionates.

The $^{11}B\{^{1}H\}$ NMR spectra of complexes **5** and **6** revealed single broad (albeit sharper than in the cases of **3** and **4**) peaks at 0.7 ppm (h.h.w. = 265 Hz) and –0.7 ppm (h.h.w. = 248 Hz), respectively [upfield from the free ligand (**2**), –3.7 ppm (h.h.w. = 211 Hz)]. The BH_2 resonances for complexes **5** and **6** were located as singlets at 4.12 ppm and 3.99 ppm respectively in the $^{1}H\{^{11}B\}$ NMR spectra (in $CDCl_3$). The equivalence of the BH_2 protons in the NMR spectrum, suggest no significant interaction of the B–H group with the metal centre in solution. The ^{1}H NMR data therefore suggests the formation of $[Cu\{\kappa^2\text{-}SS\text{-}H_2B(mp)_2\}(PR_3)]$ [R = Ph (**5**); Cy (**6**)] in solution. The IR spectra, on the other hand, showed two bands at 2425 cm^{-1} and 2374 cm^{-1} (solid state) and 2417 and 2393 cm^{-1} (dichloromethane solution) for **5** and **6** respectively, for the B–H stretching frequencies suggesting κ^3-*SSH* coordination both in solution and solid state. The presence of a BH–Cu interaction was confirmed by a X-ray diffraction study on **5** (Fig. 8). Single crystals were obtained by layering a tetrahydrofuran solution containing the complex with hexane.

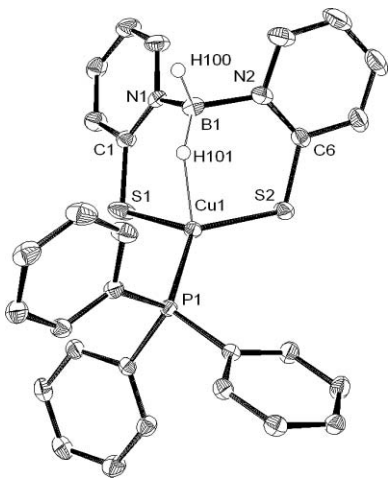


Fig. 8 Molecular structure of $[Cu\{\kappa^3\text{-}SSH\text{-}H_2B(mp)_2\}(PPh_3)]$ (**5**). Hydrogen atoms {except for H(100) and H(101)} have been omitted for clarity (thermal ellipsoids drawn at the 50% level).

The molecular structure of **5** confirmed a κ^3-*SSH* coordination mode for **Bmp**. Selected bond distances and angles and crystallographic parameters are highlighted in Tables 2 and 3.† The geometry at the metal centre is somewhat distorted between tetrahedral and trigonal pyramidal. The sum of the angles defining the trigonal plane, involving the atoms copper, two sulfur atoms and phosphine, is 350.4°. The angles S(1)–Cu–H(101), S_2–Cu–H(101) and P–Cu–H(101) are 88.8(5)°, 92.7(5)° and 117.8(5)°

Table 3 Selected bond distances (Å) and angles (°) for **5**

P(1)–Cu(1)	2.216(3)
Cu(2)–S(2)	2.248(4)
Cu(1)–S(1)	2.255(4)
C(1)–S(1)	1.707(14)
C(6)–S(2)	1.708(14)
B(1)–N(1)	1.592(2)
B(1)–N(2)	1.583(18)
Cu(1)–H(101)	1.832(17)
B(1)–H(101)	1.150(17)
B(1)–H(100)	1.090(18)
S(1)–Cu(1)–P(1)	111.88(15)
S(2)–Cu(1)–P(1)	124.56(14)
Cu(1)–H(101)–B(1)	133.02(13)
S(1)–Cu(1)–S(2)	113.98(18)
N(1)–B(1)–N(2)	109.08(10)
C(6)–S(2)–Cu(1)	109.83(5)
C(1)–S(1)–Cu(1)	106.49(5)

respectively. The BH–Cu, B–H and Cu–B distances are 1.832(17) Å, 1.150(17) Å and 2.748 Å which are close to the analogues values for a closely related complex [Cu{κ³-*SSH*-Ph(H)B(mt^{Ph})$_2$}PPh$_3$] (where mt^{Ph} = phenyl-2-mercaptoimidazole) (**7**).[21b]

Of particular interest to us were the copper–sulfur and boron–nitrogen bond distances within complex **5** in order to determine the extent of tautomerisation of the mercaptopyridine units. To date there are no reported examples of bis-substituted ligands of the type [H$_2$BR$_2$]$^-$ (where R ≠ H) and so it is not possible to make a direct comparison. Nevertheless the aforementioned complex **7** is similar enough to make some comparison. In complex **7**, the copper–sulfur distances are 2.2892(8) Å and 2.3210(8) Å while in complex **5** the corresponding distances are 2.248(4) Å and 2.255(4) Å. The boron–nitrogen distances in complex **7** are 1.567(4) Å and 1.564(4) Å and in the case of **5** the boron–nitrogen distances are 1.583(18) Å and 1.592(2) Å. The copper–sulfur distances are shorter and boron–nitrogen distances longer in complex **5**. Furthermore, the boron–nitrogen distances are larger than those found for all other structurally characterised transition metal complexes containing either the HB(mt^R)$_3$ or H$_2$B(mt^R)$_2$ motifs.[22] The longer boron–nitrogen and shorter copper–sulfur distances indicate that, although the thiopyridone tautomer is still predominant, a higher degree of the thiolate tautomer occurs within the resulting complexes compared to the analogous **Tm** and **Bm** complexes. This suggests a small but increased localisation of the negative charge at the metal centre with **Tmp** and **Bmp** as compared to the other sulfur based scorpionate ligands.

Attempted synthesis of other copper complexes

It was of interest to probe the electronic nature of the new ligands **1** and **2**, so we therefore attempted to prepare complexes containing carbonyl and isocyanide ligands in place of the phosphine groups. The resulting complexes would provide useful information about the electronic nature of the metal centre.[23] Despite a range of examples being reported with the pyrazole based ligands,[23,24] we were unsuccessful in synthesising the analogous complexes. A similar observation was recorded by Reglinski *et al.* in an attempt to prepare the complex [Cu(CO)(**Tm**)].[7]

Conclusions

By comparing the structural properties of complex **5** to previously reported compounds, it has been found that the boron–nitrogen bond distances are longer in our system, while the corresponding copper–sulfur distances are shorter. This is consistent with a more electron rich ligand as compared to other sulfur based scorpionates. This can be ascribed to the greater negative charge of the sulfur atoms *via* tautomerisation of the mercaptopyridine arms as indicated in Fig. 4. Further investigations are currently being carried out in order to explore the effect on tautomerisation on the electronic environment of both the boron and transition metal centres.

Experimental

General remarks

All manipulations were carried out using standard Schlenk techniques or with the use of a M Braun glove box. All reagents were purchased from Aldrich, Alfa Aesar or Acros and used as received. Solvents were dried on a Grubbs column system and stored in Young's Ampoules over 4 Å molecular sieves. ^{1}H, ^{1}H{^{11}B}, ^{13}C{^{1}H}, ^{11}B{^{1}H} and ^{31}P{^{1}H} NMR spectra were acquired on a Jeol ECP 300 MHz, Jeol Lambda 300 MHz, Varian 400 MHz or Varian 500 MHz Spectrometer. Spectra were obtained at ambient temperature and referenced to the residual protio-solvent (^{1}H NMR), the solvent signal (^{13}C{^{1}H} NMR) or referenced internally to BF$_3$.OEt$_2$ (^{11}B{^{1}H} NMR) or H$_3$PO$_4$ (^{31}P{^{1}H} NMR). ESI Mass Spectra were recorded on a Brüker Daltonics Apex IV instrument. Elemental analyses were recorded at the micro-analytical laboratory of the School of Chemistry at the University of Bristol.

Potassium hydrotris(2-thiopyridone)borate, K[Tmp] (1)

A round bottomed flask was charged with KBH$_4$ (0.10 g, 1.85 mmol), 2-mercaptoypyridine (0.82 g, 7.38 mmol) and degassed xylene (50 mL). The mixture was gradually heated to 180 °C over a period of 1 h under a nitrogen atmosphere. H$_2$ gas was observed during the course of the reaction. The reaction mixture was kept at 170 °C for 48 h. The mixture was then allowed to cool and the resulting solid was isolated by filtration, washed further with two portions of cold tetrahydrofuran (2 × 10 mL) and dried under vacuum to give **1** as a yellow powder. Yield = 0.52 g, 74%. Crystals suitable for a X-ray diffraction study were grown by vapour diffusion of diethyl ether into a tetrahydrofuran solution of the compound. IR (cm^{-1}, powder film), 2468 w (B–H), 1613 s, 1527 s; in THF (cm^{-1}) 2455 (B–H), 1618 s, 1527 s. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 4.83 (1H, br, B*H*), 6.46 (3H, br, ^{mp}C*H*), 7.17 (3H, br, ^{mp}C*H*), 7.27 (3H, br, ^{mp}C*H*), 7.83 (3H, br, ^{mp}C*H*). ^{13}C{^{1}H} NMR (DMSO-d_6, 101 MHz) δ 110.1 (br, ^{mp}*C*H), 132.5 (br, ^{mp}*C*H), 135.0 (br, ^{mp}*C*H), 146.9 (br, ^{mp}*C*H), 182.5 (br, *C*=S). ^{11}B{^{1}H} NMR (DMSO-d_6, 96.2 MHz) 4.4 (s, br, h.h.w. = 560 Hz). MS (ESI), m/z = 342 [M – K]$^-$, 100%. HRMS (ESI) [calc. (found)] for C$_{13}$H$_{13}$BN$_3$S$_3$ = 342.0365 (342.0375).

Sodium dihydrobis(2-thiopyridone)borate, Na[Bmp] (2)

A 200 mL Schlenk flask was charged with NaBH$_4$ (224 mg, 5.94 mmol) and mercaptopyridine (1.13 g, 12.0 mmol). A degassed 75 : 25 toluene : tetrahydrofuran mixture (50 mL) was added, and heated to reflux with stirring overnight. The resulting mixture was filtered, the solid was washed with toluene (3 × 20 mL) and dried under vacuum to give **2** as a yellow powder. Yield = 0.88 g, 85%. IR (cm^{-1}, powder film), 2438 w, 2370 w (B–H), 1603 s, 1534 s; in THF (cm^{-1}) 2412, 2354 w (B–H), 1612 s, 1531 s. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.45 [2H, τd, J = 6.5 Hz, $^4J_{HH}$ = 1.5 Hz, ^{mp}C*H*-(5)], 7.04 [2H, ddd, $^3J_{HH}$ = 8.5 and 6.5 Hz, $^4J_{HH}$ = 1.5 Hz, ^{mp}C*H*-(4)], 7.29 [2H, dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = unresolved, ^{mp}C*H*-(3)], 8.44 (2H, dd, $^3J_{HH}$ = 6.5, $^4J_{HH}$ = 1.5 Hz, ^{mp}C*H*-(6)]. ^{1}H{^{11}B} NMR (DMSO-d_6, 400 MHz) δ 3.64 (2H, s, B*H*$_2$). ^{13}C{^{1}H} NMR (CD$_3$CN, 101 MHz) δ 109.8 [^{mp}*C*H-(5)], 133.1 [^{mp}*C*H-(4)], 133.9 [^{mp}*C*H-(3)], 150.6 [^{mp}*C*H-(6)], 182.6 (*C*=S). ^{11}B{^{1}H} NMR (DMSO-d_6, 96.2 MHz) δ –3.7 (h.h.w. = 211 Hz). ^{11}B (CD$_3$CN, 96.2 MHz) δ –0.92 (t, $^1J_{BH}$ = 10.1 Hz). MS (ESI), m/z = 233 [M – Na]$^-$ 100%. HRMS (ESI) [calc. (found)] for C$_{10}$H$_{10}$BN$_2$S$_2$ = 233.0378 (233.0382).

Cu(Tmp)(PPh$_3$) (3)

To a methanol (10 mL) suspension of CuCl (22 mg, 2.21×10^{-4} mol) and PPh_3 (116 mg, 2.21×10^{-4} mol) was added K[**Tmp**] (70 mg, 2.21×10^{-4} mol), a precipitate immediately formed and the mixture was stirred for 2 h. This was filtered and the solid washed with methanol (1×5 mL), diethyl ether (2×5 mL) and extracted into DCM to give **3** as a bright yellow solid. Yield = 118 mg, 80%. IR (cm^{-1}, powder film) 2458 w (B–H), 1611 s, 1531 s; in THF (cm^{-1}) 1614 s, 1535 s, B–H not observed. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.66 (3H, τ, $J = 6.0$ Hz, ^{mp}CH), 7.19–7.43 [21H, m, $P(C_6H_5)_3 + 2\times$ ^{mp}CH], 7.72 (3H, d, $^3J_{HH} = 9.0$ Hz, ^{mp}CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz) δ 115.6 (^{mp}CH), 128.6 [d, $J_{CP} = 9.2$ Hz, $P(C_6H_5)_3$], 129.5 [s, $P(C_6H_5)_3$], 134.0 [d, $J_{CP} = 16.1$ Hz, $P(C_6H_5)_3$], 134.4 (^{mp}CH), 146.6 (^{mp}CH), 149.1 (^{mp}CH), 178.3 (C=S). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 96.4 MHz) δ –0.12 (h.h.w. = 413 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 122 MHz) δ –2.4 (s, br, h.h.w. = 85 Hz). Anal. [Found (calc.)] for $C_{33}H_{28}N_3BCuPS_3$.0.2 DCM: C 58.33 (58.20), H 4.18 (4.28), N 6.13 (5.85).

Cu(Tmp)(PCy$_3$) (4)

To a methanol (10 mL) solution of CuCl (39.5 mg, 3.99×10^{-4} mol) and PCy_3 (112 mg, 3.99×10^{-4}) was added K[**Tmp**] (152 mg, 3.99×10^{-4} mol). The solution turned yellow and was stirred for 2 h during which time a yellow/orange precipitate formed. This was filtered and the solid washed with methanol (1×5 mL), hexane (2×5 mL) and dried under vacuum to give **4** as a dark yellow solid. Yield = 87%, 238 mg. IR (cm^{-1}, powder film) 1611 s, 1524 s; in DCM (cm^{-1}) 1615 s, 1534 s. B–H not observed in either solution or solid spectra. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.19–1.87 [33H, m, $P(C_6H_{11})_3$], 6.64 [3H, τd, $J = 8.5$ Hz, $^4J_{HH} = 1.5$ Hz, ^{mp}CH-(5)], 7.13 [3H, d, $^3J_{HH} = 6.5$ Hz, ^{mp}CH-(6)], 7.21 [3H, ddd, $^3J_{HH} = 8.5$ and 7.0 Hz, $^4J_{HH} = 1.5$ Hz, ^{mp}CH-(4)], 7.73 [3H, d, $^3J_{HH} = 8.5$ Hz, ^{mp}CH-(3)]. $^1H\{^{11}B\}$ ($CDCl_3$, 300 MHz) δ 5.86 (1 H, s br, B*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz) δ 26.3 (PCy_3), 27.5 (d, $J_{CP} = 10.7$ Hz, PCy_3), 30.3 (d, $J_{CP} = 3.8$ Hz, PCy_3), 31.9 (d, $^1J_{CP} = 13.1$ Hz, PCy_3), 114.4 [^{mp}CH-(5)] 134.1 [^{mp}CH-(4)], 135.7 [^{mp}CH-(3)], 142.0 [^{mp}CH-(6)], 181.0 (C=S). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 96.4 MHz) δ –0.50 (h.h.w. = 331 Hz). $^{31}P\{^1H\}$ NMR δ 17.4 (s, br, h.h.w. = 40 Hz). MS (ESI), m/z = 684.2 ($[M - H]^+$) 50%. Anal. [Found (calc.)] for $C_{33}H_{46}N_3BCuPS_3$.0.2MeOH: C 57.30 (57.57), H 6.66 (6.81), N 6.03 (6.07).

Cu(Bmp)(PPh$_3$) (5)

To a methanol (10 mL) solution of CuCl (49 mg, 4.92×10^{-4} mol) and PPh_3 (258 mg, 4.92×10^{-4} mol) was added Na[**Bmp**] (126 mg, 4.92×10^{-4} mol). The solution turned yellow with a precipitate forming, this was stirred for 2 h. This was filtered and the solid washed with methanol (1×5 mL), diethyl ether (2×5 mL) and dried under vacuum to give **5** as a yellow solid. Yield = 228 mg, 83%. Crystals suitable for X-ray diffraction were grown from a tetrahydrofuran solution layered with hexane. IR (cm^{-1}, powder film), 2425 w (B–H), 1609 s, 1538 s; in DCM (cm^{-1}) 2417 w (B–H), 1610 s, 1538 s. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.75 (2H, m, ^{mp}CH), 7.28–7.44 [17H, m, $P(C_6H_5)_3$ + ^{mp}CH], 7.74 (2H, m, ^{mp}CH), 8.01 (2H, m, ^{mp}CH). $^1H\{^{11}B\}$ ($CDCl_3$, 300 MHz) δ 4.12 (2H, s br, BH_2). $^{13}C\{^1H\}$ ($CDCl_3$, 126 MHz) δ 115.4 (s br, ^{mp}CH), 128.6 [d, $J_{C-P} = 8.3$ Hz, $P(C_6H_5)_3$], 129.8 [s, $P(C_6H_5)_3$], 132.7 (s br, ^{mp}CH), 133.9 [d, $J_{C-P} = 15$ Hz, $P(C_6H_5)_3$], 135.0 (s br, ^{mp}CH), 145.7 (s br, ^{mp}CH), PC_{ipso} and C=S signals not observed. $^{11}B\{^1H\}$ δ 0.71 (h.h.w. = 265 Hz). $^{31}P\{^1H\}$ ($CDCl_3$, 122 MHz) δ 1.71 (s, br, h.h.w. = 265 Hz). Anal. [Found (calc.)] for $C_{28}H_{25}N_2BCuPS_2$: C 60.33 (60.12), H 4.71 (4.51), N 4.92 (5.01).

Cu(Bmp)(PCy$_3$) (6)

To a methanol (10 mL) suspension of CuCl (56.8 mg, 5.74×10^{-4} mol) and PCy_3 (161 mg, 5.74×10^{-4}) was added Na[**Bmp**] (152 mg, 3.99×10^{-4} mol). The solution turned yellow and was stirred for 2 h during which time a yellow/orange precipitate formed. This was filtered and washed with methanol (5 mL) and hexane (2×5 mL) to give **6** as a dark yellow solid. Yield = 278 mg, 84%. IR (powder film, cm^{-1}) 2374 w (B–H), 1611 s, 1533 s; in DCM (cm^{-1}) 2393 w (B–H), 1611 s, 1536 s. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.15–1.42 (15H, m, PCy_3), 1.63–1.87 (18H, m, PCy_3), 6.69 [2H, τd, $J = 6.5$ Hz, $^4J_{HH} = 1.5$ Hz, ^{mp}CH-(5)], 7.19 [2H, ddd, $^3J_{HH} =$ 8.5 and 6.5 Hz, $^4J_{HH} = 1.5$ Hz, ^{mp}CH-(4)], 7.70 [2H, d, $^3J_{HH} =$ 8.5 Hz, ^{mp}CH-(3)], 7.99 [2H, d, $^3J_{HH} = 6.5$ Hz, ^{mp}CH-(6)]. $^1H\{^{11}B\}$ ($CDCl_3$, 300 MHz) δ 3.99 (2H, s br, BH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz) δ 26.3 (PCy_3), 27.5 (d, $J_{CP} = 10.9$ Hz, PCy_3), 30.3 (d, $J_{CP} = 4.7$ Hz, PCy_3), 32.0 (d, $^1J_{CP} = 14.8$ Hz, PCy_3), 114.7 [^{mp}CH-(5)], 133.9 [^{mp}CH-(3)], 134.5 [^{mp}CH-(4)], 145.6 [^{mp}CH-(6)], 178.2 (C=S). ^{11}B ($CDCl_3$, 96.4 MHz) δ –0.7 (s, br, h.h.w. = 248 Hz). $^{31}P\{^1H\}$ ($CDCl_3$, 122 MHz) δ 19.0 (s, br, h.h.w = 67 Hz). MS (ESI), m/z = 583.22 ($[M + Li]^+$) 100%, 599.20 ($[M + Na]^+$) 10%. Anal. [Found (calc.)] for $C_{28}H_{43}N_2BCuPS_2$.0.4MeOH: C 57.53 (57.82), H 7.43 (7.62), N 4.98 (4.76).

Crystallography†

The data for **1** and **5** were collected on a Bruker Kappa Apex II CCD detector diffractometer with a fine-focus sealed tube Mo Kα radiation source and a Cryostream Oxford Cryosystems low temperature device, operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The program used for control and integration were APEX II, SAINT v. 7.34A and XPREP v2005/4.[25] The crystal was mounted on a glass fibre with silicon grease from paraffin oil.

All solutions and refinements were performed using the Bruker SHELTXTL software and all software packages within.[26] All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogen atoms, with the exception of H(100) and H(101), in **5** (which were refined using isotropic thermal parameters), were added using a riding model.

The data collection parameters and refinement information are presented in Table 3. Anisotropic parameters, bond distances and (torsion) angles for **1** and **5** are available from the cif files in the ESI.†

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