

## Furan- and thiophene-functionalised bis-carbene ligands: Synthesis, silver(I) complexes, and catalysis

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### Abstract

New furan- and thiophene-functionalised nucleophilic heterocyclic carbene (NHC) complexes of Ag(I) were prepared via the reaction of novel furan- and thiophene-functionalised bis-imidazolium salts with Ag<sub>2</sub>O. Samples of both the *N*-methyl substituted furan- and thiophene-functionalised Ag(I) complexes suitable for single crystal X-ray studies were obtained following anion metathesis to the tetrafluoroborate salts. The structural characterisations revealed dinuclear [Ag<sub>2</sub>(MeCEC)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (E = O, S) formulations with discrete twenty-membered dimetallacycles present in both instances; however, the overall molecular conformation varies considerably, notably in the orientations of the two bridging furan or thiophene heterocycles to the silver coordination plane. The functionalised bis-imidazolium salts were tested as in situ additives in a Pd(0)-catalysed aryl amination coupling reaction, with the best observed activities around 20% of those seen with 1,3-bis(2,6-di-*iso*-propylphenyl)imidazolium chloride under identical conditions. The bulkier *N*-<sup>t</sup>Bu and *N*-mesityl substituted salts were found to be more active than the *N*-methyl substituted analogues.

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**Keywords:** Imidazolium salts; Functionalised; NHC; Silver carbenes; X-ray structures; Amination

### 1. Introduction

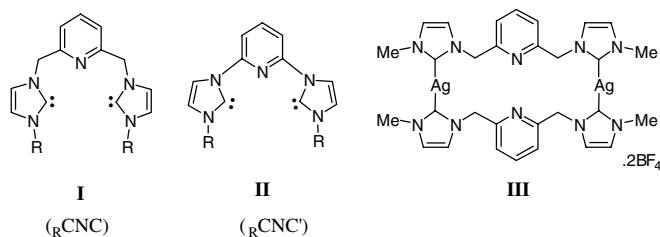
Nucleophilic heterocyclic carbene (NHC) ligands have enjoyed wide applicability as ligands for transition and main group elements since they were first isolated in 1991 [1]. NHC complexes of Ag(I) have proven popular due to a combination of their ready accessibility through a number of synthetic routes (most notably through the reaction of an imidazolium salt with Ag<sub>2</sub>O by the method of Wang and Lin [2]), stability and functional group tolerance, and their usefulness as facile transmetallation reagents. The latter property has notably seen their application in the synthesis of NHC complexes of late transition metals such as

Pd, Rh, Ru, and Ir of interest for catalytic and fundamental studies [3]. Thus, Ag<sup>I</sup>(NHC) complexes have played an important part in the rapid development of functionalised NHC ligands and their application in homogeneous catalysis; despite the first Ag<sup>I</sup>(NHC) report appearing as recently as 1998 the subject has already been reviewed [3,4].

The concept of two NHC groups separated by a weaker donor ligand has been explored by several groups; most interest has focused on the incorporation of pyridine functionalities [5–7] with the structural characterisation of several Ag(I) complexes of <sub>R</sub>CNC' (**I**) and <sub>R</sub>CNC' (**II**) (R = various alkyl/aryl) ligands reported, e.g., **III** [5]. More recently, Ag(I) complexes of more flexible bis-NHC ligands bearing linkages incorporating amino/amido [8], and ether [9] functionalities have been reported, the latter structurally characterised and found to be dinuclear [10], as well as ligands with chiral linker groups [11].

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We were motivated to produce potentially tridentate functionalised bis-NHC ligands for Pd(II) with similar geometries to **I** but with the pyridine donor replaced by weaker furan and thiophene moieties, and report here some examples of Ag(I) complexes of these ligands.

In recent years the number of crystallographically characterised Ag<sup>I</sup>(NHC) complexes has increased considerably with a rich structural diversity revealed, especially when halide ions are present in the compound [4,12,13]. However, when non-coordinating anions are present the complexes invariably adopt a quasi-linearly dicoordinated Ag(I) cation [2,12,14,15]; bis-NHC ligands typically yield dinuclear [Ag<sub>2</sub>(bis-NHC)<sub>2</sub>]<sup>2+</sup> complexes [5,16–18], sometimes stabilised by Ag...Ag interactions in the solid state [16,18]. Syntheses conducted in the presence of excess Ag<sub>2</sub>O or Ag<sup>+</sup> may yield products incorporating additional silver ions that participate in metal–metal interactions [15,19]. Notably, Ag(I) has little affinity for additional nucleophilic functional groups when ligated by two NHC ligands so these have little structural influence [5,15–17,20]. This lack of interaction may, at least in part, explain the compatibility of the ‘Ag<sub>2</sub>O route’ to complexes of functionalised NHC ligands, although it would seem that the tolerance of Ag<sub>2</sub>O towards activated hydrogens adjacent to functional groups is key to its versatility.

## 2. Results and discussion

### 2.1. Furan- and thiophene-functionalised bis-imidazolium salts

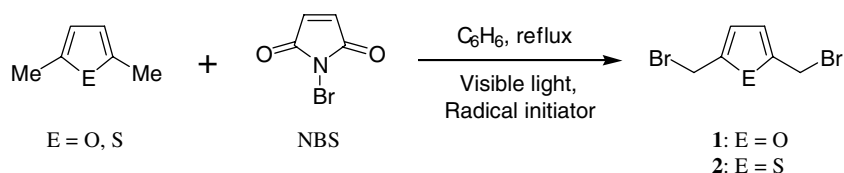
Methodology similar to that used for the preparation of the pyridine-functionalised bis-imidazolium salt analogues [5] was employed to prepare a range of furan- and thiophene-functionalised bis-imidazolium salts. The precursors 2,5-bis(bromomethyl)thiophene, **1**, and 2,5-bis(bromomethyl)furan, **2**, were obtained as colourless, crystalline, temperature sensitive solids in moderate yields from 2,5-dimethylfuran and 2,5-dimethylthiophene, respectively, using a modification of Offermann’s [21] radical bromination methodology, Scheme 1.

Reaction of **1** and **2** with *N*-methyl-, *N*-mesityl- and *N*-*tert*-butylimidazole gave functionalised bis-imidazolium salts **3–8** as colourless to pale tan coloured solids in good yields, Scheme 2. Extended reaction times were required to ensure complete disubstitution of halogenated precursors **1** and **2**.

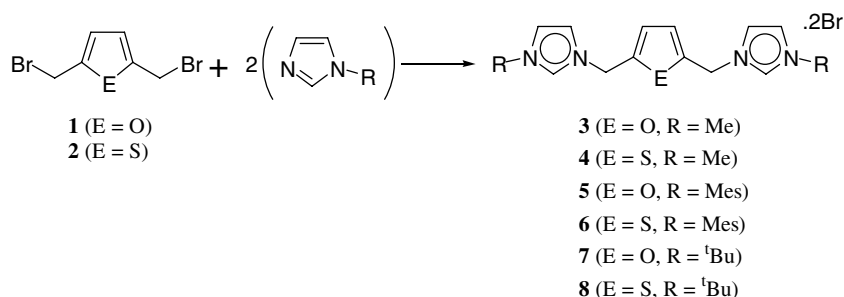
Bis-imidazolium salts **3–8** were characterised by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and by mass spectrometry; simple spectra consistent with the proposed structures were observed in all cases. A comparison of the <sup>1</sup>H NMR spectra of the furan- and thiophene-functionalised bis-imidazolium salts shows that variation of the functional group has a negligible effect on the chemical shifts of the imidazolium ring imC<sub>2,4,5</sub>-H protons although replacing the *N*-methyl groups of **3** and **4** with bulkier *N*-mesityl or *N*-<sup>t</sup>Bu groups consistently shifts the signals of all imidazolium ring protons to lower field.

### 2.2. Ag(I) complexes

Bis-imidazolium salts **3–6** were reacted with Ag<sub>2</sub>O in DCM–MeOH solutions giving the Ag<sup>I</sup>(NHC) complexes



Scheme 1. Synthesis of **1** and **2** via radical bromination.



Scheme 2. Synthesis of thiophene- and furan-functionalised bis-imidazolium salts.

**9–12** as pale grey to pale tan solids in reasonable yields, Scheme 3.  $^1\text{H}$  NMR spectra of **9–12** were consistent with symmetrical  $\text{Ag}^{\text{I}}(\text{NHC})$  complexes, but mass spectrometry data for **11** and **12** suggested different metal–ligand associations. Thus, while LSIMS of **11** showed exclusively signals due to mononuclear  $[\text{Ag}(\text{MesCOC})]^+$  species, the thiophene-substituted analogue **12** showed a small peak cluster at  $m/z = 1255.2$  corresponding to the association of a dinuclear  $[\text{Ag}_2(\text{MesCSC})_2]^{2+}$  cation and a bromide ion, together with a strong signal corresponding to  $[\text{Ag}(\text{MesCSC})]^+$ . Limited solubility in common organic solvents precluded LSIMS results being obtained for **9** and **10**; similar problems have been encountered before in  $\text{Ag}(\text{I})$  complexes of bis-NHC ligands with *N*-Me substituents [5,9]. Furthermore, elemental analysis of **11** and **12** gave less than optimal results, perhaps stemming from compositional uncertainty with regards to the putative  $[\text{AgBr}_2]^-$  anion. Elemental analysis results for **11** led to the anionic component being formulated as an equal mixture of  $[\text{AgBr}_2]^-$  and bromide ions, while **12** yielded compositional data close to that required by a  $[\text{Ag}_2(\text{MesCSC})_2] \cdot 2[\text{AgBr}_2]$  formulation, albeit with an unsatisfactorily high %H value.

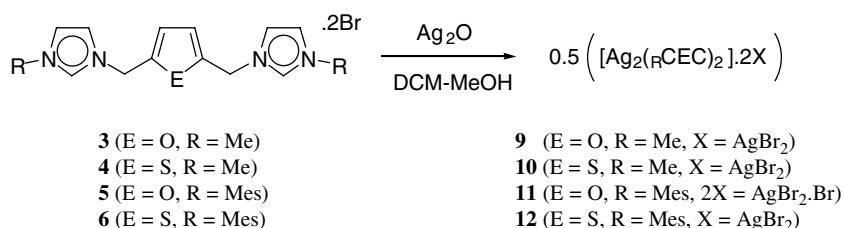
Anion substitution yielding tetrafluoroborate complexes of  $\text{Ag}(\text{bis-NHC})$  complexes has proved useful in preparing crystalline samples with well-defined compositions, notably with the pyridine analogue of the title furan- and thiophene-functionalised bis-NHC ligands [5]. Thus, **9** and **10** were treated with  $\text{AgBF}_4$  in MeCN to obtain  $\text{Ag}(\text{I})$  complexes **13** and **14** containing the  $\text{MeCOC}$  and  $\text{MeCSC}$  ligands, respectively, as colourless, crystalline tetrafluoroborate salts, Scheme 4.

The  $^1\text{H}$  NMR spectra of **13** and **14** closely resembled those of **9** and **10**, respectively, suggesting that the  $[\text{Ag}_2(\text{MeCEC})_2]^{2+}$  association (vide infra) was unaffected by the anion substitution. However, while **14** showed a peak cluster in the MS due to a dinuclear association, the spectra

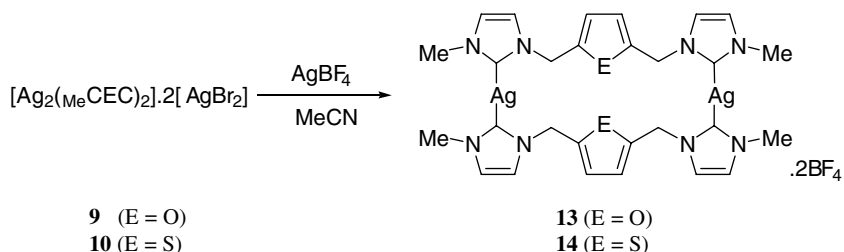
of **13** showed only signals attributable to mononuclear species. Nonetheless, the  $^1\text{H}$  NMR spectrum of **13** mirrors that of **14** with respect to the  $\text{imC}_{4,5}\text{-H}$  signals; chemical shift discrepancies about the functionalised cores of the ligands are consistent with those observed in the precursor imidazolium salts **3** and **4**.

When  $\text{Ag}(\text{NHC})$  complexes **9–14** are divided into furan- and thiophene-functionalised examples it is apparent that the nature of the anion and the *N*-substituent have little impact on the  $^1\text{H}$  and  $^{13}\text{C}$  NMR shifts common across each set. Thus, when those signals due to the *N*-substituents are excluded, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the *N*-methyl substituted **9** and **13** closely resemble that of the *N*-mesityl substituted **11**, and **10** closely resembles both **12** and **14**. However, signals in the  $^{13}\text{C}$  NMR due to  $\text{imC}_2$  were only observed in the *N*-methyl substituted **13** and **14**, at  $\delta$  180.6 and 180.1, respectively. These observations suggest that a dinuclear  $[\text{Ag}_2(\text{RCEC})_2]^{2+}$  association such as that found in **13** and **14** (vide infra) is present in all of the furan- and thiophene-functionalised  $\text{Ag}(\text{NHC})$  complexes described herein. However, NMR data cannot distinguish between the two different  $\text{MeCEC}$  ligand orientations described below.

Complex **14** was crystallised from MeCN and the proposed dinuclear structure of two  $\text{Ag}(\text{I})$  ions bridged by two NHC ligands binding in a *C, C'* mode confirmed by a single crystal X-ray crystallographic investigation, Fig. 1. Compound **14** crystallises in the triclinic system accompanied by two molecules of MeCN per dinuclear  $[\text{Ag}_2(\text{MeCSC})_2]^{2+}$  cation; one half of the cation, a tetrafluoroborate anion and a molecule of MeCN comprise the asymmetric unit. The centrosymmetric dinuclear  $[\text{Ag}_2(\text{MeCSC})_2]^{2+}$  motif in **14** is similar to that seen in the pyridine-functionalised **III** [5]. The preferred *quasi*-linear orientation of  $\text{Ag}(\text{I})$  bridging between two NHC moieties is observed, with  $\text{C}(22)\text{-Ag-C}(22')$  ( $1 - x, 1 - y, \bar{z}$ ) =  $173.05(8)^\circ$ ; the  $\text{Ag-C}(22,22')$



Scheme 3. Syntheses of  $\text{Ag}(\text{I})$  complexes of thiophene- and furan-functionalised bis-NHC ligands.



Scheme 4. Synthesis of tetrafluoroborate complexes.

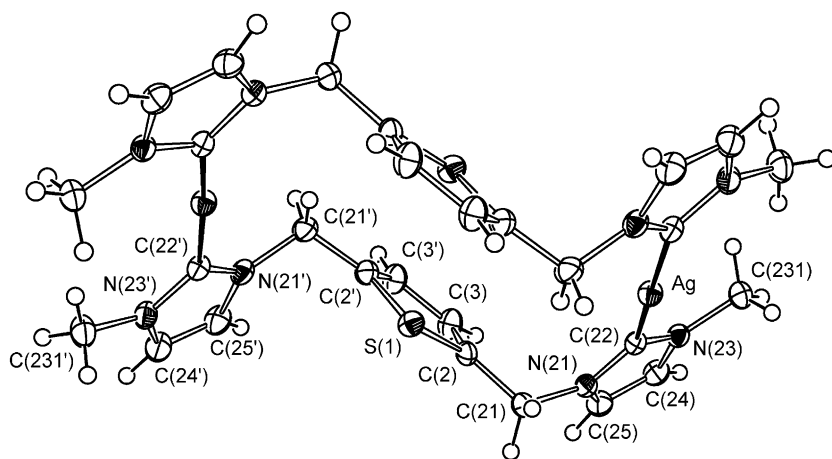


Fig. 1. Projection of the cation of **14** oblique to the plane of the NHC rings, showing the zig-zag conformation and the atom labelling scheme.

distances (2.079(1), 2.086(1) Å) are similar to those in **III** [5], Table 1. In the solid state **14** shows no significant silver–sulphur interactions, but *quasi*-planar (NHC)Ag(NHC) arrays stack, inversion-related, up *a* yielding successive

Table 1  
Bond distances and angles about the  $\text{imC}_2\text{-Ag-imC}'_2$  units of  $[\text{Ag}_2(\text{MeCEC})_2](\text{BF}_4)_2$  (E = O, S) complexes **13** and **14**, and previously reported  $[\text{Ag}_2(\text{MeCNC})_2](\text{BF}_4)_2$  **III**

Complex <sup>a</sup>	$\text{imC}_2\text{-Ag}$ distance (Å) <sup>b</sup>	$\text{imC}_2\text{-Ag-imC}'_2$ angle (°)
<b>13</b> $[\text{Ag}_2(\text{MeCOC})_2](\text{BF}_4)_2$	2.081(1)	176.3(3)
<b>14</b> $[\text{Ag}_2(\text{MeCSC})_2](\text{BF}_4)_2$	2.079(1), 2.086(1)	173.05(8)
<b>III</b> <sup>c</sup> $[\text{Ag}_2(\text{MeCNC})_2](\text{BF}_4)_2$	2.088(4), 2.093(4)	176.78(9)

<sup>a</sup> Solvent of crystallisation omitted.

<sup>b</sup> Data for  $\text{imC}_2(\text{unprimed, primed})$ , respectively, where not crystallographically identical.

<sup>c</sup> Ref. [5].

Ag...Ag distances of 3.5420(6) Å, slightly greater than the sum of the van der Waals radii (3.40 Å) [22]. The NHC ring planes have an interplanar dihedral angle of 4.95(8)°, and angles of 77.90(8)° and 82.78(8)° to the central thiophene ring.

Vapour diffusion of Et<sub>2</sub>O into an MeCN–CHCl<sub>3</sub> solution of **13** yielded a sample of lower crystallinity than that of **14**; nevertheless, single crystal X-ray diffraction showed that the dinuclear  $[\text{Ag}_2(\text{MeCOC})_2]^{2+}$  motif is also present in **13**, Fig. 2. The cation has *mm* symmetry, and the complex crystallises together with half a molecule of chloroform and one molecule of MeCN, one quarter of the formula unit being crystallographically independent. Complex **13** shows no close inter- or intra-molecular contacts to Ag or O(1), but in a significant deviation from the structures observed for **14** and **III**, the furan rings of **13** are disposed to the same side of the plane defined by the two Ag and the four C(22,22') atoms. The pair of NHC rings within the MeCOC ligand are inclined at 27.7(3)° to each other and at 78.7(4)°

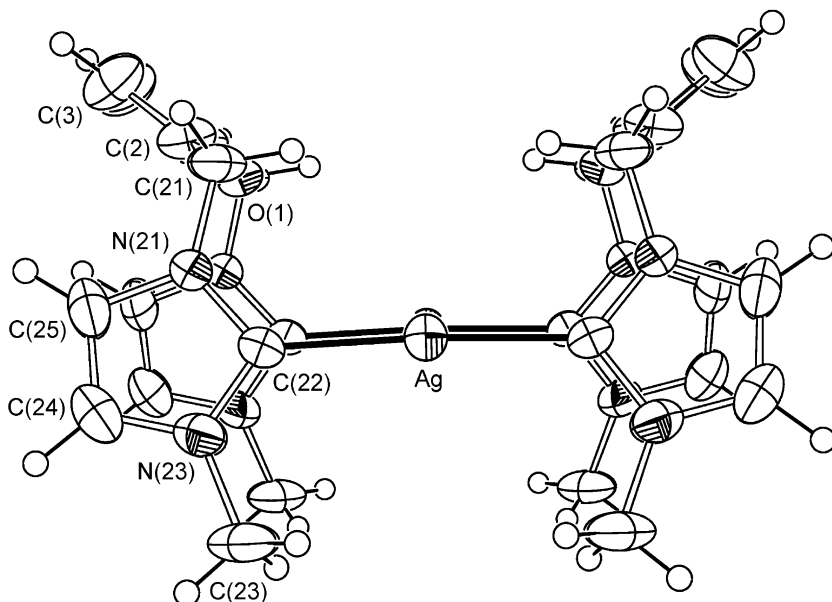


Fig. 2. Projection of the cation of **13** along the Ag–Ag' axis. Labelled non-hydrogen atoms are those included in the asymmetric unit.

to the furan ring plane, Table 2. Apart from this gross structural disparity the dimensions about the silver atoms in **13** are comparable to those in **14**, Table 1. However, the larger size of the sulphur atom in **14** compared to the oxygen atom in **13** results in an increased span across the heterocycle  $\alpha$ -methylene groups, i.e., C(21)–C(21'), of almost 0.5 Å in the former complex. It is thus possible for the furan and thiophene functionalities to influence the disparate conformations of **13** and **14** wholly through geometric factors; however, the greater size and reduced electronegativity of S compared to O should make the  $\text{MeCSC}$  ligand more suitable for 'pincer' complexation of the late transition metals.

### 2.3. Catalytic testing – aryl amination

The furan- and thiophene-functionalised bis-imidazolium salts, together with the previously reported pyridine-functionalised analogues [5,7,23], were applied in conjunction with Pd(dba)<sub>2</sub> and KO<sup>t</sup>Bu to the aryl amination of morpholine with 4-bromotoluene, Scheme 5. The results of these catalytic trials are given in Table 3, benchmarked against the highly active 1,3-bis(dipp)imidazolium chloride [24].

Compared to 1,3-bis(dipp)imidazolium chloride (Entry 16, 91% conversion) all of the functionalised bis-imidazolium salts tested show low activity. Significant amounts of toluene, a product of the hydrodehalogenation of 4-bromotoluene, was observed for the runs employing furan- and thiophene-functionalised bis-imidazolium salts (Entries 4–9) but not for those using the pyridine-functionalised examples or 1,3-bis(dipp)imidazolium chloride. Under conditions identical to that of Entry 13 the best conversions were shown by **4** (Entry 6, 19% conversion with 11% toluene by-product), and (MesCNC)(HBr)<sub>2</sub> (Entry 3, 18% conversion). Both of these salts feature bulky N-Mes substituents, and the furan-functionalised analogue **5** also performed relatively well over a longer reaction time (Entry 9, 30% conversion), albeit with significant formation of toluene byproduct. Increasing the reaction temperature for the pyridine-functionalised salts from 100 to 120 °C, Entries 10–12, gave little improvement. It is of interest to note that the N-<sup>t</sup>Bu substituted furan-functionalised **7** outperforms the N-Mes substituted **5** (Entry 9, 30% conversion with 10% toluene), the opposite result to that observed for the pyridine- and thiophene-functionalised salts at 100 °C.

Table 2  
Selected bond lengths and angles in [Ag<sub>2</sub>(MeCEC)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (E = O, S) complexes **13** and **14**, and previously reported [Ag<sub>2</sub>(MeCNC)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, **III**

Complex <sup>a,b</sup>	[Ag <sub>2</sub> (MeCOC) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> ( <b>13</b> )	[Ag <sub>2</sub> (MeCSC) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> ( <b>14</b> )	[Ag <sub>2</sub> (MeCNC) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> ( <b>III</b> ) <sup>c</sup>
<i>Bond distance (Å)</i>			
N(21)–C(22)	1.355(9)	1.353(2), 1.351(3)	1.350(3), 1.354(3)
C(22)–N(23)	1.352(10)	1.351(3), 1.354(3)	1.353(4), 1.354(4)
N(23)–C(24)	1.332(13)	1.381(2), 1.383(2)	1.381(5), 1.382(5)
C(24)–C(25)	1.352(14)	1.343(3), 1.339(4)	1.347(4), 1.344(4)
C(25)–N(21)	1.380(11)	1.382(2), 1.390(2)	1.385(5), 1.383(5)
C(21)–N(21)	1.439(9)	1.464(3), 1.469(3)	1.468(4), 1.475(4)
C(21)–C(2)	1.507(2)	1.503(2), 1.497(2)	–
E(1)–C(2)	1.353(9)	1.7269(17), 1.726(2)	–
C(2)–C(3)	1.342(13)	1.360(3), 1.361(3)	–
C(3)–C(3')	1.411(14)	1.419(2)	–
<i>Bond angles (°)</i>			
N(21)–C(22)–N(23)	104.0(7)	104.32(13), 104.57(13)	104.3(3), 104.2(3)
C(22)–N(23)–C(24)	112.0(7)	111.28(17), 110.95(18)	111.1(2), 111.3(2)
N(23)–C(24)–C(25)	107.6(8)	106.59(17), 106.96(17)	107.0(3), 106.6(3)
C(24)–C(25)–N(21)	105.9(8)	106.75(15), 106.64(17)	106.1(3), 106.8(3)
C(22)–N(21)–C(25)	110.5(7)	111.06(18), 110.88(18)	111.5(3), 111.2(2)
C(21)–N(21)–C(22)	125.4(6)	124.02(13), 124.16(13)	124.3(3), 123.0(3)
N(21)–C(21)–C(2)	112.1(6)	111.55(19), 112.13(15)	–
E(1)–C(2)–C(21)	117.8(7)	121.04(16), 121.45(16)	–
E(1)–C(2)–C(3)	110.1(7)	110.73(12), 111.02(12)	–
C(2)–E(1)–C(2')	106.8(7)	92.09(9)	–
C(2)–C(3)–C(3')	106.5(9)	113.36(18), 112.8(2)	–
Ag–C(22)–N(21)	128.7(5)	131.68(15), 131.18(14)	125.5(2), 130.2(2)
Ag–C(22)–N(23)	127.2(5)	123.99(13), 124.25(14)	129.4(2), 125.6(2)
<i>Interplanar dihedral angles (°)<sup>d</sup></i>			
Funct./MeIm	78.7(4)	77.90(8), 82.78(8)	74.4(1), 70.5(1)
MeIm/MeIm'	27.7(3)	4.95(8)	9.2(1)
Coord./MeIm	76.2(3)	32.81(6), 36.21(6)	77.55(9), 75.17(10)
Coord./Funct.	39.2(3)	54.25(5)	50.36(9)

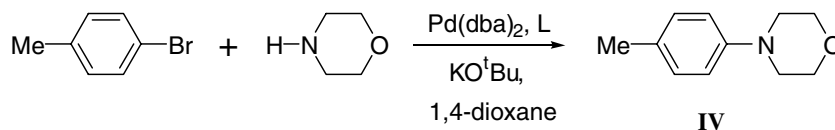
<sup>a</sup> Solvent of crystallisation omitted.

<sup>b</sup> Data for Ag(unprimed, primed), respectively, where not crystallographically identical.

<sup>c</sup> Ref. [5].

<sup>d</sup> Funct. = furan, thiophene, or pyridyl ring; MeIm = C<sub>3</sub>N<sub>2</sub> ring of imidazolin-2-ylidene; Coord. = the plane described by the four C atoms coordinated to the two Ag atoms.





Scheme 5. Pd(0)/imidazolium salt aryl amination coupling protocol. L = functionalised bis-imidazolium salt.

Table 3

Results of the aryl amination reaction of morpholine with 4-bromotoluene catalysed by Pd(dba)<sub>2</sub> and functionalised bis-imidazolium salts

Entry	Imidazolium salt	Time (h)	Temperature (°C)	Conversion (%) <sup>a</sup>	Toluene (%) <sup>b</sup>
1	(MeCNC)(HBr) <sub>2</sub>	24	100	14	–
2	( <i>t</i> -BuCNC)(HBr) <sub>2</sub>	24	100	11	–
3	(MesCNC)(HBr) <sub>2</sub>	24	100	18	–
4	<b>4</b> (MeCSC)(HBr) <sub>2</sub>	24	100	8	7
5	<b>8</b> ( <i>t</i> -BuCSC)(HBr) <sub>2</sub>	24	100	10	5
6	<b>6</b> (MesCSC)(HBr) <sub>2</sub>	24	100	19	11
7	<b>3</b> (MeCOC)(HBr) <sub>2</sub>	48	100	24	4
8	<b>7</b> ( <i>t</i> -BuCOC)(HBr) <sub>2</sub>	48	100	36	7
9	<b>5</b> (MesCOC)(HBr) <sub>2</sub>	48	100	30	10
10	(MeCNC)(HBr) <sub>2</sub>	24	120	14	–
11	( <i>t</i> -BuCNC)(HBr) <sub>2</sub>	24	120	14	–
12	(MesCNC)(HBr) <sub>2</sub>	24	120	12	–
13 <sup>c</sup>	1,3-bis(dipp)Im · Cl	24	100	91	–

Reaction conditions: 1.0 mmol 4-bromotoluene, 1.2 mmol morpholine, 1.5 mmol KO<sup>t</sup>Bu, 2.0 mol% Pd(dba)<sub>2</sub>, 2.0 mol% imidazolium salt, 3 mL dioxane.

<sup>a</sup> GC yields.

<sup>b</sup> Hydrodehalogenation side product; yield relative to substrate.

<sup>c</sup> Pd:L ratio = 1:2. 1,3-bis(dipp)Im · Cl = 1,3-bis(2,6-di-*iso*-propylphenyl)imidazole.

Nonetheless, the provision of steric bulk at the N-substituents is clearly of benefit to the overall activity of the system, and similar behaviour should follow in preformed catalyst systems [25].

### 3. Conclusions

New furan- and thiophene-functionalised bis-imidazolium salts have been synthesised, characterised, and reacted with Ag<sub>2</sub>O to give Ag<sup>I</sup>(NHC) complexes of functionalised bis-NHC ligands. Single crystal X-ray structures of dinuclear [Ag<sub>2</sub>L<sub>2</sub>]<sup>2+</sup> complexes bearing the MeCOC and MeCSC ligands are presented in which the ligands adopt similar geometries but for the positions of the functional group rings relative to the Ag<sub>2</sub>C<sub>4</sub> plane. Notably, Ag atoms from successive molecules in the complex containing MeCSC approach close to the sum of the van der Waals radii and it is possible that a weak Ag(I)···Ag(I) bonding interaction contributes to the stability of the observed structure. The described Ag(NHC) complexes are expected to find use as transmetallation reagents to catalytically interesting metals such as Pd(II). Although the described furan- and thiophene-functionalised bis-imidazolium salts performed relatively poorly in catalytic testing in combination with a Pd(0) source for a model aryl amination reaction, the addition of bulky N-substituents showed increased product yield. Furthermore, increased product yields when extended reaction times were used suggests that although the catalytically active species exhibit poor performance, they are stable over the long term. However, it is likely that

preformed complexes of the reported bis-NHC ligands with catalytically interesting metals such as Pd(II) will yield better insights into the influences of the donor group, N-substituent steric bulk, and potentially chelating nature of these ligands in a catalytic situation.

### 4. Experimental

#### 4.1. General

All reactions were performed under an atmosphere of dry dinitrogen or argon using standard Schlenk techniques. Solvents were purified and dried by usual methods [26], unless otherwise indicated. N-substituted imidazoles bearing *tert*-butyl [27] and mesityl [28] substituents were prepared according to literature procedures; *N*-(2,6-di-*iso*-propylphenyl)imidazole was prepared by modification of the procedure for *N*-mesitylimidazole. All other reagents were used as received. <sup>1</sup>H and <sup>13</sup>C (proton decoupled) NMR spectra were run on Varian Gemini 200, Unity Inova 400, Bruker DPX 400, or JEOL Eclipse 300 instruments at ambient temperature and referenced to residual solvent signals [29]. <sup>13</sup>C DEPT spectra were used to aid assignments where necessary. Elemental analyses (Carlo Erba EA1108 or ThermoFinnigan Flash 1112 Series EA) and Liquid Secondary Ion Mass Spectrometry (LSIMS, Kratos Concept ISQ) were performed by the Central Science Laboratory, University of Tasmania. Electrospray Mass Spectrometry (ESMS) was performed at Cardiff University. All reactions involving silver compounds were performed with the exclusion of light.

#### 4.1.1. 2,5-Bis(bromomethyl)furan (**1**)

This compound was prepared in 46% yield in an identical manner to **2** and showed similar decomposition behaviour.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.36 (s, 2H, furC<sub>3,4</sub>-H), 4.48 (s, 4H, CH<sub>2</sub>).

#### 4.1.2. 2,5-Bis(bromomethyl)thiophene (**2**)

*N*-bromosuccinimide (15.47 g, 86.9 mmol) was suspended in benzene (150 mL) and 2,5-dimethylthiophene (4.5 mL, 39.5 mmol) added, followed by 1,1'-azobis(cyclohexanecarbonitrile) (0.2 g) as radical initiator. The resulting mixture was refluxed under a 150 W incandescent bulb for 6 h, yielding a red solution. On cooling the supernatant was decanted off and washed with saturated NaHCO<sub>3</sub> solution (3 × 50 mL) and water (50 mL) then dried over MgSO<sub>4</sub>. The solvent was removed in vacuo and the residue extracted with hot hexanes (3 × 50 mL). Colourless crystals of **2** (6.34 g, 59%) deposited on cooling at 0 °C. Compound **2** blackens and generates HBr during storage at -20 °C; however, pure material may be obtained by extracting the partially decomposed mass with Et<sub>2</sub>O and removing the solvent (and HBr) in vacuo.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.94 (s, 2H, thioC<sub>3,4</sub>-H), 4.67 (s, 4H, CH<sub>2</sub>).

### 4.2. Furan-functionalised bis-imidazolium salts

#### 4.2.1. 2,5-Bis[(3-methylimidazolium-1-yl)methyl]furan dibromide (**3**) $\equiv$ (*Me*COC)(HBr)<sub>2</sub>

Compound **1** (0.70 g, 2.76 mmol) and *N*-methylimidazole (0.8 mL, 10.0 mmol) were dissolved in THF (20 mL) and stirred at room temperature for 12 days, then refluxed for 24 h. The solvent was removed in vacuo and the residue washed with hexanes (3 × 20 mL) and Et<sub>2</sub>O (20 mL) and dried in vacuo giving **3** (1.08 g, 94%) as a cream powder. MS (ESMS):  $m/z$  337.3 and 339.3 [M - Br]<sup>+</sup>, 257.4 [M - 2Br - H]<sup>+</sup>.  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO,  $\delta$ ): 9.34 (s, 2H, imC<sub>2</sub>-H), 7.82 and 7.77 (m × 2, each 2H, imC<sub>4,5</sub>-H), 6.69 (s, 2H, furC<sub>3,4</sub>-H), 5.55 (s, 4H, CH<sub>2</sub>), 3.89 (s, 6H, N-Me).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO,  $\delta$ ): 148.6 (furC<sub>2,5</sub>), 136.6 (imC<sub>2</sub>), 124.0 and 122.3 (imC<sub>4,5</sub>), 112.1 (furC<sub>3,4</sub>), 44.7 (CH<sub>2</sub>), 36.0 (N-Me).

#### 4.2.2. 2,5-Bis[(3-mesitylimidazolium-1-yl)methyl]furan dibromide (**5**) $\equiv$ (*Mes*COC)(HBr)<sub>2</sub>

Compound **1** (0.40 g, 1.6 mmol) and *N*-mesitylimidazole (0.65 g, 3.5 mmol) were dissolved in THF (20 mL) and refluxed for 72 h, giving incomplete substitution. The solvent was removed in vacuo, the residue stirred in acetone (30 mL) for 72 h and then refluxed a further 24 h. The solvent was removed in vacuo and the residue washed with acetone (3 × 4 mL) giving **5** (0.56 g, 57%) as a tan powder. MS (ESMS):  $m/z$  547.6 [M - Br]<sup>+</sup>.  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO,  $\delta$ ): 9.66 (s, 2H, imC<sub>2</sub>-H), 8.11 and 8.00 (t × 2,  $J$  = 1.6 Hz, each 2H, imC<sub>4,5</sub>-H), 7.14 (s, 4H, MesC<sub>3,5</sub>-H), 6.78 (s, 2H, furC<sub>3,4</sub>-H), 5.67 (s, 4H, CH<sub>2</sub>), 2.33 (s, 6H, MesC<sub>4</sub>-Me), 1.98 (s, 12H, MesC<sub>2,6</sub>-Me).  $^{13}\text{C}$  NMR

(100 MHz,  $d_6$ -DMSO,  $\delta$ ): 148.4 (furC<sub>2,5</sub>), 140.3 (MesC<sub>1</sub>), 137.7 (imC<sub>2</sub>), 134.2 (MesC<sub>2,6</sub>), 131.1 (MesC<sub>4</sub>), 129.3 (MesC<sub>3,5</sub>), 124.2 and 123.1 (imC<sub>4,5</sub>), 112.4 (furC<sub>3,4</sub>), 45.4 (CH<sub>2</sub>), 20.6 (MesC<sub>4</sub>-Me), 17.0 (MesC<sub>2,6</sub>-Me).

#### 4.2.3. 2,5-Bis[(3-*tert*-butylimidazolium-1-yl)methyl]furan dibromide (**7**) $\equiv$ (*t*-BuCOC)(HBr)<sub>2</sub>

Compound **1** (1.93 g, 7.60 mmol) and *N*-*tert*-butylimidazole (2.08 g, 16.7 mmol) were dissolved in acetone (30 mL) and stirred at room temperature for 30 min, then refluxed for 72 h. The solvent was removed in vacuo and the residue washed with Et<sub>2</sub>O (3 × 25 mL) and hexanes (20 mL) and dried in vacuo giving **7** (3.76 g, 99%) as a cream powder. MS (ESMS):  $m/z$  423.1 [M - Br]<sup>+</sup>, 341.5 [M - 2Br - H]<sup>+</sup>.  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO,  $\delta$ ): 9.59 (s, 2H, imC<sub>2</sub>-H), 8.11 and 7.88 (t × 2,  $J$  = 1.8 Hz, each 2H, imC<sub>4,5</sub>-H), 6.70 (s, 2H, furC<sub>3,4</sub>-H), 5.53 (s, 4H, CH<sub>2</sub>), 1.59 (s, 18H, N-CMe<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO,  $\delta$ ): 148.5 (furC<sub>2,5</sub>), 134.7 (imC<sub>2</sub>), 122.6 and 120.7 (imC<sub>4,5</sub>), 112.0 (furC<sub>3,4</sub>), 59.8 (N-CMe<sub>3</sub>), 44.8 (CH<sub>2</sub>), 29.0 (N-CMe<sub>3</sub>).

### 4.3. Thiophene-functionalised bis-imidazolium salts

#### 4.3.1. 2,5-Bis[(3-methylimidazolium-1-yl)methyl]thiophene dibromide (**4**) $\equiv$ (*Me*CSC)(HBr)<sub>2</sub>

Compound **2** (1.00 g, 3.70 mmol) and *N*-methylimidazole (1.0 mL, 12.5 mmol) were dissolved in THF (20 mL) and stirred at 40 °C for 24 h, then refluxed for 4 h. The solvent was removed in vacuo and the residue washed with Et<sub>2</sub>O (3 × 20 mL) and petroleum (b.p. 40–60 °C, 20 mL) then dried in vacuo giving **4** (1.37 g, 85%) as a white powder. MS (ESMS):  $m/z$  353.3 and 355.3 [M - Br]<sup>+</sup>, 273.3 [M - 2Br - H]<sup>+</sup>.  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO,  $\delta$ ): 9.36 (s, 2H, imC<sub>2</sub>-H), 7.86 and 7.75 (s × 2, each 2H, imC<sub>4,5</sub>-H), 7.29 (s, 2H, thioC<sub>3,4</sub>-H), 5.70 (s, 4H, CH<sub>2</sub>), 3.87 (s, 6H, N-Me).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ ,  $\delta$ ): 138.1 (thioC<sub>2,5</sub>), 136.4 (imC<sub>2</sub>), 129.4 (thioC<sub>3,4</sub>), 124.0 and 122.1 (imC<sub>4,5</sub>), 46.2 (CH<sub>2</sub>), 36.0 (N-Me).

#### 4.3.2. 2,5-Bis[(3-mesitylimidazolium-1-yl)methyl]thiophene dibromide (**6**) $\equiv$ (*Mes*CSC)(HBr)<sub>2</sub>

Compound **2** (1.00 g, 3.70 mmol) and *N*-mesitylimidazole (1.59 g, 8.51 mmol) were dissolved in acetone (25 mL) and refluxed for 48 h. The solvent was removed in vacuo and the residue washed with Et<sub>2</sub>O (4 × 10 mL) and dried in vacuo giving **6** (1.86 g, 78%) as a cream powder. MS (ESMS):  $m/z$  561.4 and 563.4 [M - Br]<sup>+</sup>, 481.0 [M - 2Br - H]<sup>+</sup>.  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO,  $\delta$ ): 9.72 (s, 2H, imC<sub>2</sub>-H), 8.14 and 7.98 (t × 2,  $J$  = 1.8 Hz, each 2H, imC<sub>4,5</sub>-H), 7.37 (s, 2H, thioC<sub>3,4</sub>-H), 7.15 (s, 4H, MesC<sub>3,5</sub>-H), 5.83 (s, 4H, CH<sub>2</sub>), 2.33 (s, 6H, MesC<sub>4</sub>-Me), 1.99 (s, 12H, MesC<sub>2,6</sub>-Me).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO,  $\delta$ ): 140.3 (MesC<sub>1</sub>), 138.2 (thioC<sub>2,5</sub>), 137.6 (imC<sub>2</sub>), 134.2 (MesC<sub>2,6</sub>), 131.1 (MesC<sub>4</sub>), 129.6 (thioC<sub>3,4</sub>), 129.3 (MesC<sub>3,5</sub>), 124.3 and 123.0 (imC<sub>4,5</sub>), 47.1 (CH<sub>2</sub>), 20.6 (MesC<sub>4</sub>-Me), 17.0 (MesC<sub>2,6</sub>-Me).

#### 4.3.3. 2,5-Bis[(3-*tert*-butylimidazolium-1-yl)methyl]thiophene dibromide (**8**) $\equiv$ (<sup>*t*</sup>BuCSC)(HBr)<sub>2</sub>

Compound **2** (1.50 g, 5.56 mmol) and *N-tert*-butylimidazole (1.52 g, 12.22 mmol) were dissolved in acetone (30 mL) and refluxed for 65 h. The solvent was removed in vacuo and the residue washed with Et<sub>2</sub>O (2 × 20 mL) then acetone (4 × 7 mL) until the washes were almost colourless. The product was washed with Et<sub>2</sub>O (15 mL) and dried in vacuo giving **8** (2.08 g, 73%) as a pale tan powder. MS (ESMS): *m/z* 437.4 and 439.2 [M – Br]<sup>+</sup>, 357.7 [M – 2Br – H]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO,  $\delta$ ): 9.73 (s, 2H, imC<sub>2</sub>-H), 8.10 and 7.93 (t × 2, *J* = 1.7 Hz, each 2H, imC<sub>4,5</sub>-H), 7.32 (s, 2H, thioC<sub>3,4</sub>-H), 5.68 (s, 4H, CH<sub>2</sub>), 1.58 (s, 18H, N-CMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO,  $\delta$ ): 138.0 (thioC<sub>2,5</sub>), 134.6 (imC<sub>2</sub>), 129.4 (thioC<sub>3,4</sub>), 122.4 and 120.8 (imC<sub>4,5</sub>), 59.8 (N-CMe<sub>3</sub>), 46.3 (CH<sub>2</sub>), 28.9 (N-CMe<sub>3</sub>).

#### 4.4. Ag(I) complexes

##### 4.4.1. [Ag<sub>2</sub>(MeCOC)<sub>2</sub>][AgBr<sub>2</sub>]<sub>2</sub> (**9**) (MeCOC = *C, C'*-2,5-bis[(3-methylimidazolin-2-yliden-1-yl)methyl]furan)

Compound **3** (0.207 g, 0.495 mmol) was dissolved in 20:3 DCM:MeOH (23 mL) and Ag<sub>2</sub>O (0.117 g, 0.505 mmol) added. The resulting black suspension was stirred overnight at room temperature after which time the Ag<sub>2</sub>O had been replaced by a pale grey powder. The solvent was removed in vacuo and the residue washed with 10:1 DCM:MeOH (3 × 5 mL) giving **9** (0.172 g, 55%) as a pale grey solid. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO,  $\delta$ ): 7.49 and 7.43 (d × 2, *J* = 1.6 Hz, each 4H, imC<sub>4,5</sub>-H), 6.48 (s, 4H, furC<sub>3,4</sub>-H), 5.30 (s, 8H, CH<sub>2</sub>), 3.70 (s, 12H, N-Me). <sup>13</sup>C NMR: insufficient solubility.

##### 4.4.2. [Ag<sub>2</sub>(MeCSC)<sub>2</sub>][AgBr<sub>2</sub>]<sub>2</sub> (**10**) (MeCSC = *C, C'*-2,5-bis[(3-methylimidazolin-2-yliden-1-yl)methyl]thiophene)

Compound **4** (0.317 g, 0.73 mmol) was dissolved in 20:1 DCM:MeOH (32 mL) and Ag<sub>2</sub>O (0.169 g, 0.73 mmol) added. The resulting black suspension was stirred overnight at room temperature after which time the Ag<sub>2</sub>O had been replaced by a pale tan-grey powder. The solvent was removed in vacuo, the residue suspended in MeOH (30 mL) and the solids filtered off. The filtrate was stripped in vacuo giving **10** (0.31 g, 66%) as a pale grey solid. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO,  $\delta$ ): 7.52 and 7.41 (d × 2, *J* = 1.6 Hz, each 4H, imC<sub>4,5</sub>-H), 7.04 (s, 4H, thioC<sub>3,4</sub>-H), 5.47 (s, 8H, CH<sub>2</sub>), 3.72 (s, 12H, N-Me). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO,  $\delta$ ): 180.2 (imC<sub>2</sub>), 140.4 (thioC<sub>2,5</sub>), 127.1 (thioC<sub>3,4</sub>), 123.3 and 121.9 (imC<sub>4,5</sub>), 48.9 (CH<sub>2</sub>), 38.3 (N-Me).

##### 4.4.3. [Ag<sub>2</sub>(MesCOC)<sub>2</sub>][AgBr<sub>2</sub>]Br (**11**) (MesCOC = *C, C'*-2,5-bis[(3-mesitylimidazolin-2-yliden-1-yl)methyl]furan)

Compound **5** (1.000 g, 1.60 mmol) was dissolved in 10:1 DCM:MeOH (55 mL) and Ag<sub>2</sub>O (0.363 g, 1.57 mmol) added. The resulting black suspension was stirred overnight at room temperature after which time the Ag<sub>2</sub>O had reacted and a little pale grey coloured precipitate remained. The

supernatant was decanted off and stripped in vacuo, the residue washed with acetone (3 × 10 mL) and dried in vacuo giving **11** as a dark cream coloured powder (0.81 g, 69%). Required for C<sub>60</sub>H<sub>64</sub>Ag<sub>3</sub>Br<sub>3</sub>N<sub>8</sub>O<sub>2</sub>: C, 48.28; H, 4.32; N, 7.51. Found: C, 50.48; H, 3.96; N, 7.69%. MS (LSIMS): *m/z* 571.0 and 573.0 [(M – AgBr<sub>2</sub> – Br)/2]<sup>+</sup>, dinuclear ion not observed. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO,  $\delta$ ): 7.67 and 7.44 (d × 2, *J* = 1.6 Hz, each 4H, imC<sub>4,5</sub>-H), 6.96 (s, 8H, MesC<sub>3,5</sub>-H), 6.53 (s, 4H, furC<sub>3,4</sub>-H), 5.41 (s, 8H, CH<sub>2</sub>), 2.54 (s, 12H, MesC<sub>4</sub>-Me), 1.68 (s, 24H, MesC<sub>2,6</sub>-Me). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO,  $\delta$ ): 150.6 (furC<sub>2,5</sub>), 138.4 and 135.6 (MesC<sub>1</sub> and MesC<sub>4</sub>), 134.2 (MesC<sub>2,6</sub>), 128.8 (MesC<sub>3,5</sub>), 123.3 and 122.4 (imC<sub>4,5</sub>), 111.1 (furC<sub>3,4</sub>), 47.0 (CH<sub>2</sub>), 20.7 (MesC<sub>4</sub>-Me), 17.1 (MesC<sub>2,6</sub>-Me), imC<sub>2</sub> not observed.

##### 4.4.4. [Ag<sub>2</sub>(MesCSC)<sub>2</sub>][AgBr<sub>2</sub>]<sub>2</sub> (**12**) (MesCSC = *C, C'*-2,5-bis[(3-mesitylimidazolin-2-yliden-1-yl)methyl]thiophene)

Compound **6** (1.000 g, 1.56 mmol) was dissolved in 20:1 DCM:MeOH (75 mL) and Ag<sub>2</sub>O (0.354 g, 1.53 mmol) added. The resulting black suspension was stirred overnight at room temperature after which time the Ag<sub>2</sub>O had reacted and a little pale grey powder remained. The supernatant was decanted from the precipitate and stripped in vacuo, the residue washed with acetone (3 × 10 mL) and dried in vacuo giving **12** as a pale yellow powder (0.58 g, 44%). Required for C<sub>60</sub>H<sub>64</sub>N<sub>8</sub>Ag<sub>4</sub>Br<sub>4</sub>S<sub>2</sub>: C, 42.08; H, 3.77; N, 6.54. Found: C, 41.94; H, 4.36; N, 7.00%. MS (LSIMS): *m/z* 1255.2 [M – 2(AgBr<sub>2</sub>) + Br]<sup>+</sup>, 587.1 and 589.1 [M/2 – AgBr<sub>2</sub>]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO,  $\delta$ ): 7.76 and 7.42 (d × 2, *J* = 1.6 Hz, each 4H, imC<sub>4,5</sub>-H), 6.97 (br s, 12H, MesC<sub>3,5</sub>-H and thioC<sub>3,4</sub>-H), 5.49 (s, 8H, CH<sub>2</sub>), 2.39 (s, 12H, MesC<sub>4</sub>-Me), 1.62 (s, 24H, MesC<sub>2,6</sub>-Me). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO,  $\delta$ ): 140.5 and 138.5 and 135.4 (thioC<sub>2,5</sub> and MesC<sub>1</sub> and MesC<sub>4</sub>), 134.2 (MesC<sub>2,6</sub>), 128.8 (MesC<sub>3,5</sub>), 127.1 (thioC<sub>3,4</sub>), 123.4 and 122.5 (imC<sub>4,5</sub>), 49.1 (CH<sub>2</sub>), 20.7 (MesC<sub>4</sub>-Me), 17.0 (MesC<sub>2,6</sub>-Me), imC<sub>2</sub> not observed.

##### 4.4.5. [Ag<sub>2</sub>(MeCOC)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**13**) (MeCOC = *C, C'*-2,5-bis[(3-methylimidazolin-2-yliden-1-yl)methyl]furan)

Compound **3** (0.410 g, 0.981 mmol) was dissolved in 9:1 DCM:MeOH (45 mL) and Ag<sub>2</sub>O (0.232 g, 1.00 mmol) added. The resulting black suspension was stirred overnight at room temperature giving a suspension of pale grey **9**. The solvent was stripped in vacuo, the residue suspended in MeCN (40 mL) and AgBF<sub>4</sub> (0.382 g, 1.96 mmol) added. After stirring at ca. 40 °C for 1 h the precipitated AgBr was removed by filtration and the solvent stripped in vacuo giving a pale grey residue that was washed with MeCN (2 × 2 mL) and recrystallised from warm MeCN by cooling at –20 °C. The product was washed with cold MeCN (2 × 1 mL) and dried in vacuo giving **13** as a very pale grey microcrystalline solid (0.261 g, 59%). X-ray diffraction quality crystals were grown by diffusion of Et<sub>2</sub>O into an MeCN–CHCl<sub>3</sub> solution of **13**. Required for C<sub>28</sub>H<sub>32</sub>Ag<sub>2</sub>B<sub>2</sub>F<sub>8</sub>N<sub>8</sub>O<sub>2</sub>: C, 37.29; H, 3.58; N, 12.42. Found: C, 36.79; H, 3.56; N,



11.27%. MS (LSIMS):  $m/z$  363.0 and 365.0  $[M/2 - BF_4]^+$ , dinuclear ion not observed.  $^1H$  NMR (400 MHz,  $d_6$ -DMSO,  $\delta$ ): 7.51 and 7.45 ( $d \times 2$ ,  $J = 1.8$  Hz, each 4H,  $imC_{4,5-H}$ ), 6.45 (s, 4H,  $furC_{3,4-H}$ ), 5.33 (s, 8H,  $CH_2$ ), 3.58 (s, 12H,  $N-Me$ ).  $^{13}C$  NMR (100 MHz,  $d_6$ -DMSO,  $\delta$ ): 180.6 ( $imC_2$ ), 150.5 ( $furC_{2,5}$ ), 123.2 and 122.2 ( $imC_{4,5}$ ), 110.4 ( $furC_{3,4}$ ), 47.1 ( $CH_2$ ), 37.8 ( $N-Me$ ).

#### 4.4.6. $[Ag_2(MeCSC)_2](BF_4)_2$ (**14**) ( $MeCSC = C, C'-2,5$ -bis[(3-methylimidazolin-2-ylidene-1-yl)methyl]thiophene)

Compound **10** (0.30 g, 0.46 mmol) was suspended in MeCN (30 mL) and  $AgBF_4$  (0.096 g, 0.49 mmol) added. The resulting suspension was stirred at 40 °C for 1 h, then filtered to remove  $AgBr$ . The solvent was removed in vacuo giving **14** (0.16 g, 74%) as an off-white powder. X-ray diffraction quality crystals were grown by slowly cooling a warm MeCN solution of **14**. MS (LSIMS):  $m/z$  847.1  $[M - BF_4]^+$ , 379.0 and 381.0  $[M/2 - BF_4]^+$ .  $^1H$  NMR (400 MHz,  $d_6$ -DMSO,  $\delta$ ): 7.55 and 7.44 ( $d \times 2$ ,  $J = 1.6$  Hz, each 4H,  $imC_{4,5-H}$ ), 7.06 (s, 4H,  $thioC_{3,4-H}$ ), 5.49 (s, 8H,  $CH_2$ ), 3.70 (s, 12H,  $N-Me$ ).  $^{13}C$  NMR (100 MHz,  $d_6$ -DMSO,  $\delta$ ): 180.1 ( $imC_2$ ), 140.5 ( $thioC_{2,5}$ ), 127.1 ( $thioC_{3,4}$ ), 123.4 and 122.0 ( $imC_{4,5}$ ), 49.0 ( $CH_2$ ), 38.2 ( $N-Me$ ).

#### 4.5. Structure determination

Full spheres of 'low-temperature' CCD area-detector diffractometer data were measured (Bruker AXS instrument,  $\omega$ -scans; monochromatic  $Mo K\alpha$  radiation,  $\lambda = 0.71073$  Å;  $T$  ca. 153 K), yielding  $N_{t(otal)}$  reflections, these merging to  $N$  unique ( $R_{int}$  cited) after 'empirical'/multiscan absorption correction (proprietary software),  $N_o$  with  $F > 4\sigma(F)$  being considered 'observed' and used in the full matrix least squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, ( $x, y, z, U_{iso}$ )<sub>H</sub> being constrained at estimates. Conventional residuals  $R, R_w$  (weights:  $(\sigma^2(F) + 0.000nF^2)^{-1}$ ) on  $|F|$  at convergence are cited; neutral atom complex scattering factors were employed within the context of the XTAL 3.7 program system [30]. Pertinent results are given below and in the tables and figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Molecular diagrams were generated using ORTEP-3 for Windows [31].

#### 4.6. Crystal refinement data

##### 4.6.1. $13 \cdot 1/2 CHCl_3 \cdot 2 MeCN \equiv [Ag_2(MeCOC)_2](BF_4)_2 \cdot 1/2 CHCl_3 \cdot 2 MeCN$

$C_{32.5}H_{38.5}Ag_2B_2Cl_{1.5}F_8N_{10}O_2$ ,  $M = 1043.76$ . Orthorhombic, space group  $Pmmn$ ,  $Z = 2$  (dimeric f.u.),  $a = 12.424(2)$ ,  $b = 19.439(2)$ ,  $c = 8.532(3)$  Å,  $V = 2060$  Å<sup>3</sup>.  $D_c = 1.682$  g cm<sup>-3</sup>.  $2\theta_{max} = 55^\circ$ ,  $\mu_{Mo} = 1.13$  mm<sup>-1</sup>; specimen:  $0.16 \times 0.14 \times 0.12$  mm,  $T_{min/max} = 0.75$ .  $N_t = 32,893$ ,  $N = 2284$  ( $R_{int} = 0.075$ ),  $N_o = 1848$ ;  $R = 0.085$ ,  $R_w =$

0.13. CCDC No. 239232. *Variata*: Solvent residues were modeled as a mixture of  $CHCl_3$  and MeCN.

##### 4.6.2. $14 \cdot 2 MeCN \equiv [Ag_2(MeCSC)_2](BF_4)_2 \cdot 2 MeCN$

$C_{32}H_{38}Ag_2B_2F_8N_{10}S_2$ ,  $M = 1016.2$ . Triclinic, space group  $P\bar{1}$ ,  $Z = 1$  (dimeric f.u.),  $a = 10.562(2)$ ,  $b = 10.833(2)$ ,  $c = 11.160(2)$  Å,  $\alpha = 114.459(3)$ ,  $\beta = 116.135(3)$ ,  $\gamma = 94.572(3)^\circ$ ,  $V = 988$  Å<sup>3</sup>.  $D_c = 1.707$  g cm<sup>-3</sup>.  $2\theta_{max} = 76^\circ$ ,  $\mu_{Mo} = 1.17$  mm<sup>-1</sup>; specimen:  $0.25 \times 0.13 \times 0.10$  mm,  $T'_{min/max} = 0.90$ .  $N_t = 20238$ ,  $N = 10137$  ( $R_{int} = 0.026$ ),  $N_o = 7955$ ;  $R = 0.032$ ,  $R_w = 0.033$ . CCDC No. 239231. *Variata*: The fluorine atoms of the anion were modeled as disordered over two sets of sites, occupancies refining to 0.872(3) and complement. All ( $x, y, z, U_{iso}$ )<sub>H</sub> were refined throughout.

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#### Appendix A. Supplementary data

Data files in the .cif format for compounds **13** and **14**, preparation and characterisation data for the  $N$ -<sup>t</sup>Bu substituted pyridine-functionalised bis-imidazolium salt (<sup>t</sup>BuCNC)(HBr)<sub>2</sub>, and procedure for the aryl amination reactions. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.08.023.

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