

# Tris(2-pyridyl) Bismuthines: Coordination Chemistry, Reactivity, and Anion-Triggered Pyridyl Coupling

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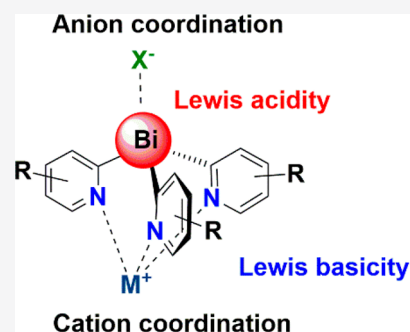


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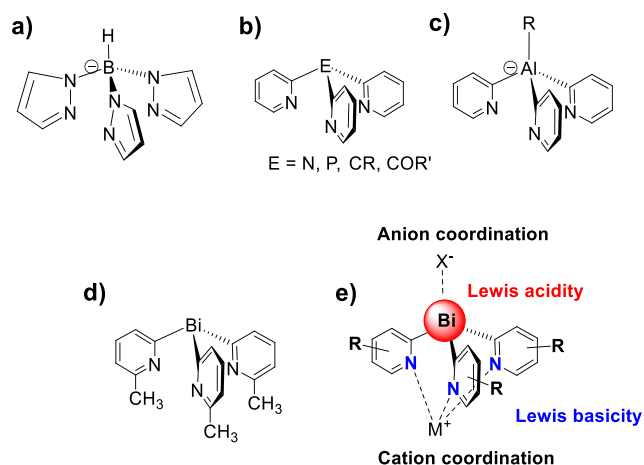
**ABSTRACT:** A series of new *tris*(2-pyridyl) bismuthine ligands of the type  $[\text{Bi}(2\text{-py}')_3]$  have been prepared, containing a range of substituents at various positions within their pyridyl rings ( $\text{py}'$ ). They can act as *intact* ligands or, as a result of the low C–Bi bond energy, exhibit noninnocent reactivity in the presence of metal ions. Structural studies of  $\text{Li}^+$  and  $\text{Ag}^+$  complexes show that the coordination to metal ions using their pyridyl-N atoms and to anions using the Lewis acidity of their Bi(III) centers can be modified by the presence of substituents within the 2-pyridyl rings, especially at the 6- or 3-positions, which can block the donor-N or Lewis acid Bi sites. Electron withdrawing groups (like  $\text{CF}_3$  or Br) can also severely reduce their ability to act as ligands to metal ions by reducing the electron donating ability of the pyridyl-N atoms. Noninnocent character is found in the reactions with  $\text{Cu}^+$  and  $\text{Cu}^{2+}$ , resulting in the coupling of pyridyl groups to form bipyridines, with the rate of this reaction being dependent on the anion present in the metal salts. This leads to the formation of Bi(III)/Cu(I) complexes containing hypervalent  $[\text{X}_2\text{Bi}(2\text{-R-py})]^-$  ( $\text{X} = \text{Cl}, \text{Br}$ ) anions. Alternatively, the *tris*(2-pyridyl) bismuthine ligands can act as 2-pyridyl transfer reagents, transferring 2-py groups to Au(I) and Fe(II).



## INTRODUCTION

Tripodal and facially coordinating ligands have found countless applications in modern coordination, organometallic and bioinorganic chemistry.<sup>1</sup> The ubiquitous *tris*-pyrazolyl borates constitute perhaps the best-known class of this type of ligands (Figure 1a).<sup>2</sup> These popular ligands are extremely versatile, as their steric and electronic characteristics can be easily modified through the introduction of substituents in their pyrazolyl moieties. Although less well-studied, *tris*(2-pyridyl)-based ligands have emerged as another important class of tripodal ligands. Most studies in this area in the last 40 years have focused on ligands of the type  $\text{E}(2\text{-py})_3$  that contain lighter, nonmetallic bridgehead atoms ( $\text{E} = \text{CR}, \text{COR}, \text{CH}, \text{N}, \text{P}, \text{P} = \text{O}$ , etc.; 2-py = 2-pyridyl; Figure 1b).<sup>3</sup> These ligands have found a broad range of applications in similar areas to their *tris*-pyrazolyl borate counterparts in coordination, catalysis, and organometallic and bioinorganic chemistry, including stoichiometric organic transformations and as models for the coordination in enzymatic metal sites.<sup>4</sup>

More recently, attention has turned to *tris*(2-pyridyl) arrangements containing heavier and more metallic bridgehead atoms.<sup>5–20</sup> The introduction of different main group elements as the bridgehead is a simple and emerging strategy for modifying the reactivity and coordination properties of different types of ligands.<sup>21–23</sup> The introduction of larger (more electropositive) *p*-block bridgeheads can be used to modify the electronic (donor) character and the ligand bite of *tris*(2-pyridyl) ligands in a systematic way.<sup>24</sup> This approach has



**Figure 1.** a) The *tris*-pyrazolyl borate ligand, b) “classical” *tris*(2-pyridyl) ligands with nonmetallic bridgeheads, c) *tris*(2-pyridyl) aluminates, and d)  $\text{Bi}[(6\text{-Me-}2\text{-py})_3]$ , the only example of a bismuthine *tris*(2-pyridyl) ligand. e) Introduction of a functional group in the bismuthine framework to modulate Lewis acidity and basicity, which in turn affects the cation and anion coordination ability of the ligand.

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recently been shown to be of value in modulating the catalytic activity of transition metal complexes of Group 15 *tris*(2-pyridyl) ligands.<sup>25</sup>

One further potential consequence of incorporating more electropositive (metallic and semimetallic) bridgehead atoms is an increase in the polarity of the bridgehead atom–C bonds to the pyridyl groups. In contrast to more robust *tris*(2-pyridyl) borate ligands,<sup>26–28</sup> *tris*(2-pyridyl)aluminates [RAL(2-py)<sub>3</sub>]<sup>–</sup> (Figure 1c) react as bases with H<sub>2</sub>O, alcohols, or carboxylic acids in a controlled manner, providing an interesting route to new aluminates containing additional donor functionality.<sup>29–31</sup> This behavior has led to new applications as thermally stable pyridyl-transfer reagents as well as reagents for the rapid NMR spectroscopic determination of the enantiomeric excess (*ee*) of chiral alcohols.<sup>32–34</sup>

Although the coordination chemistry of *tris*(2-pyridyl) ligands E(2-py)<sub>3</sub> of the lighter Group 15 elements (E = N, P, As) has been extensively studied,<sup>35–49</sup> it was only very recently that heavier counterparts containing Sb and Bi have been introduced. Most relevant to the current study, we showed that 6-methyl substitution at the pyridine rings allows the synthesis of the stable ligand [Bi(6-Me-2-py)<sub>3</sub>] (1) (Figure 1d), which is to date the only example of a *tris*(2-pyridyl) bismuthine reported. Our studies on the coordination chemistry of this new ligand were, however, limited to Cu(I) complexes, and very little is known about the coordination characteristics or reactivity of these species.<sup>25</sup>

Due to the low toxicity<sup>50–52</sup> and the highly Lewis acidic character of bismuth, the chemistry of organobismuth compounds is experiencing a resurgence of interest, finding different applications in catalysis, activation reactions, and materials chemistry.<sup>53–61</sup> Nonetheless, bismuthine ligand chemistry remains relatively underdeveloped in comparison to that of lighter Group 15 based ligands, in part due to the weakness of element–Bi bonds, which can make them thermally unstable. Illustrating the potential in this area, Gabbai and Limberg have recently developed amphiphilic bismuthine ligands of the type PBiP (P = phenylenephosphino groups), which utilize the Lewis acidity of Bi(III) to support unusual donor–acceptor transition metal → Bi bonding.<sup>62–65</sup> Our previous study of the *tris*(2-pyridyl) ligand [Bi(6-Me-2-py)<sub>3</sub>] (1) also shows that it can exhibit amphiphilic character (being capable of coordinating anions and cations simultaneously), as revealed in particular by the unusual structure of the Cu(I) dimer [Bi(6-Me-2-py)<sub>3</sub>(CuCl)]<sub>2</sub> in which the separate monomer units associate by Bi⋯Cl interactions.<sup>25</sup>

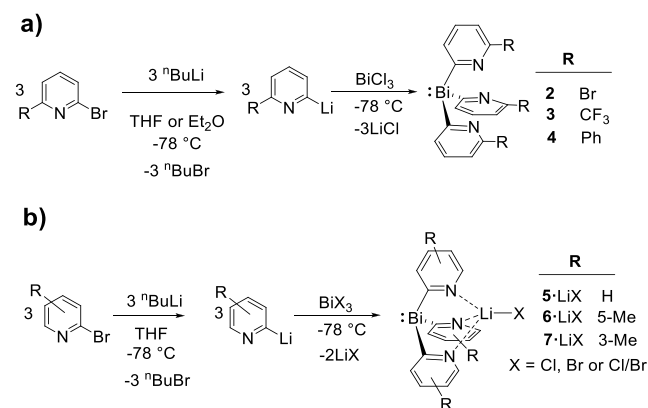
With this background in mind, we present here a study that allows access to a range of *tris*(2-pyridyl) bismuthines containing different functionalities in the pyridyl rings. We explore how the introduction of different substituents on the pyridyl rings (Figure 1e) can be used to control the steric and electronic properties of the bismuthine ligands and thus their reactivity and coordination behavior toward cations and anions.

## RESULTS AND DISCUSSION

Our recent success in the synthesis of [Bi(6-Me-2-py)<sub>3</sub>] (1)<sup>25</sup> motivated us in the initial part of this study to test whether a similar synthetic approach could be used to access a range of related bismuthine ligands. This would be the first step toward fine-tuning their electronic and steric properties by the introduction of substituents in the pyridyl rings. We previously attributed the stability of 1 compared to that of the

unsubstituted bismuthine ligand (which we were unable to obtain) to the presence of 6-Me groups in the pyridyl rings, as their electron-donating nature prevented reductive elimination of 2,2'-bipyridine and the formation of Bi metal. In the current study we first explored the synthesis of other *tris*(2-pyridyl) ligands containing electron-withdrawing substituents at the 6-position of the pyridyl ring in order to assess their stability in comparison to 1. In addition to modifying the donor strength and steric profile of the pyridyl coordination site of the bismuthine ligand, we reasoned that the introduction of electron-withdrawing groups should also result in increased Lewis acidity at the bismuth center. The preparation of the new ligands [Bi(6-R-2-py)<sub>3</sub>] [R = Br (2), CF<sub>3</sub> (3), Ph (4)] was straightforward from the reaction of BiCl<sub>3</sub> and the corresponding 2-lithio-6-substituted-pyridine (2-Li-6-R-py) in THF or Et<sub>2</sub>O at –78 °C (see Scheme 1a). The lithiation time and

**Scheme 1.** a) Synthesis of 6-Substituted *Tris*(2-pyridyl) Ligands 2–4 and b) Synthesis of 3-, 5-, and Unsubstituted *Tris*(2-pyridyl) Ligands 5–7<sup>a</sup>



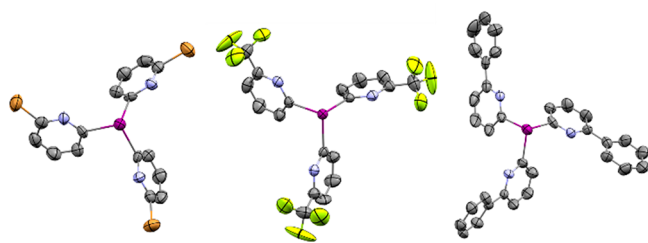
<sup>a</sup>Isolated as their lithium halide complexes.

solvent used in the initial lithiation step were found to be the most critical influences on the yield, with 2–4 being isolated in 60–88% crystalline yields after workup from these reactions (see the Experimental Section).

We also extended this methodology to other 2-pyridyl ligand arrangements *without* 6-substitution (Scheme 1b). In the absence of steric congestion in the proximity of the donor-N atoms of the 2-pyridyl ring units, these new ligands are all isolated as their lithium halide complexes, 5·LiCl, 6·LiX, and 7·LiX, in which X is either Cl or Br, or a mixture of the two (according to X-ray diffraction). To our surprise, although a small amount of black precipitate (presumably Bi metal) is formed in the case of the unsubstituted bismuthine ligand, careful optimization of the reaction conditions allowed us to obtain the unsubstituted ligand [Bi(2-py)<sub>3</sub>] (5), which had previously eluded ourselves and others.<sup>25,66</sup> In addition, the first examples of 3- and 5-methyl substituted ligand frameworks, [Bi(5-Me-2-py)<sub>3</sub>] (6) and [Bi(3-Me-2-py)<sub>3</sub>] (7), were also obtained. The isolated crystalline yields of the halide complexes of 5–7 after workup were in the range 49–74% (see the Experimental Section).

The new compounds 2–4 and the lithium halide complexes of 5–7 were characterized by a range of NMR spectroscopic and analytical techniques prior to their structural characterization by single-crystal X-ray diffraction (see the SI). As expected, the solid-state structures of 2, 3, and 4 all show

pyramidal Bi(III) centers (Figure 2). All the N-pyridyl atoms and 6-substituents are oriented “upwards”, approximately



**Figure 2.** Molecular structures of **2** (left), **3** (center), and **4** (right), showing displacement ellipsoids at 50% probability. H atoms and the disorder of one of the CF<sub>3</sub> groups in **3** are omitted for clarity. Selected bond lengths (Å) and angles (deg): **2**, Bi–C<sub>py</sub> 2.252(12); C<sub>py</sub>–Bi–C<sub>py</sub> 93.7(4). **3**, Bi–C<sub>py</sub> 2.257(7); C<sub>py</sub>–Bi–C<sub>py</sub> 93.2(2). **4**, Bi–C<sub>py</sub> 2.26(1)–2.23(1); C<sub>py</sub>–Bi–C<sub>py</sub> 94.7(4)–92.3(4). Color key: C (gray), Bi (purple), N (blue), Br (brown), F (yellow). See also Table S1 in the SI.

toward the bismuth lone pair. The presence of electron-withdrawing groups in **2–4** has no significant effect on the bridgehead C–Bi–C angles compared to those of **1** (range 93.2(2)–94.7(4)° in **2–4**, cf. 95.0(3)° in **1**). Previous studies have indicated that such acute angles indicate p-character in the C–Bi bonds and accordingly s-character in the metal lone pair.<sup>67</sup>

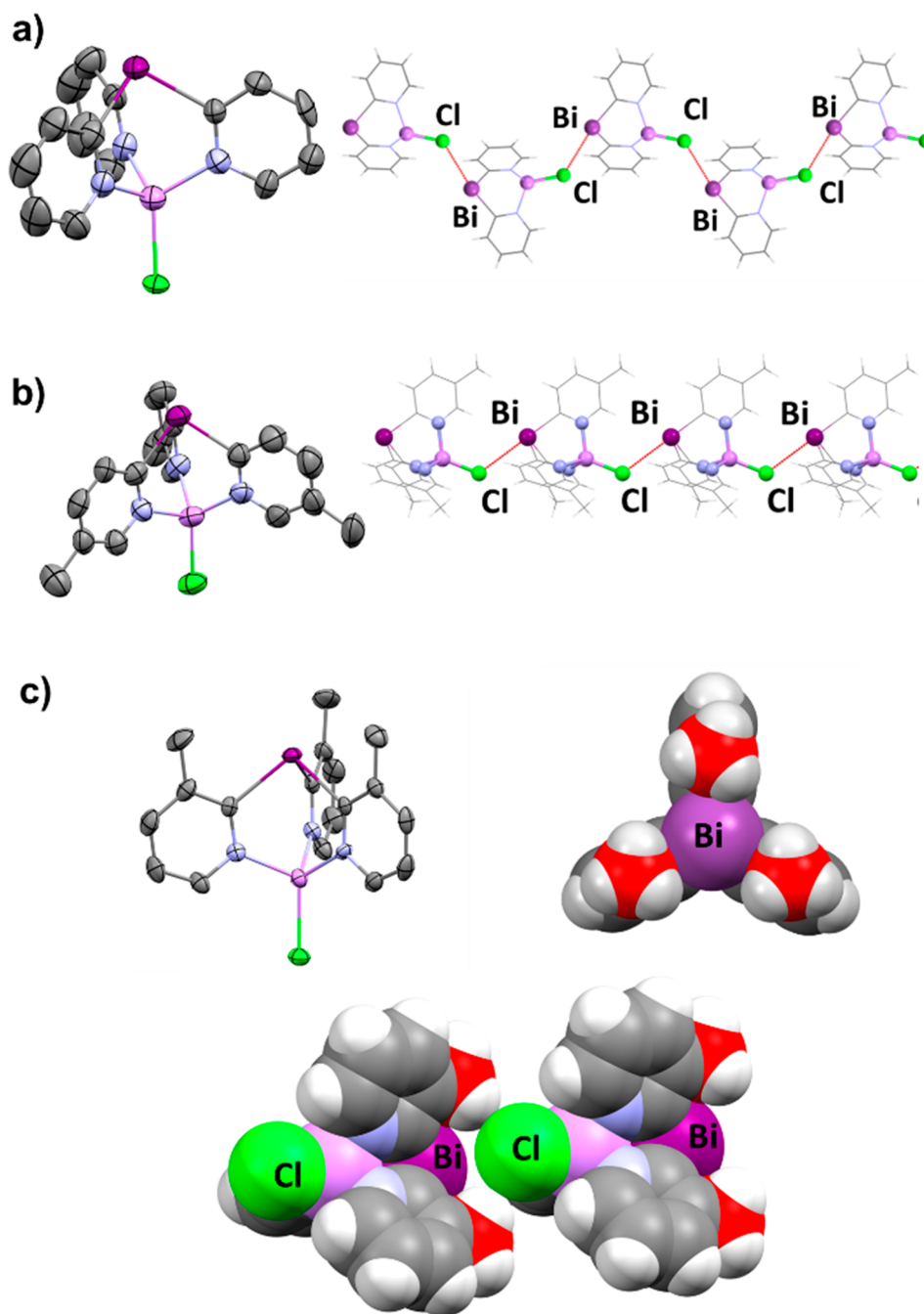
The solid-state structures of the crystalline complexes **5**·LiCl, **6**·LiX·CH<sub>2</sub>Cl<sub>2</sub>, and **7**·LiX·CH<sub>2</sub>Cl<sub>2</sub> are shown in Figure 3. While the single-crystal analysis of **5**·LiCl indicated that Cl<sup>−</sup> was the only halide ion present, crystals of **6**·LiX and **7**·LiX were observed with site-disordered mixtures of Cl<sup>−</sup> and Br<sup>−</sup>. Similar LiX coordination and site disordering of Cl<sup>−</sup> and Br<sup>−</sup> have been observed during the synthesis of a number of other *tris*(2-pyridyl) ligands and result from the *in situ* generation of LiBr by Cl/Br exchange from the byproduct <sup>n</sup>BuBr.<sup>9,24</sup> Molecules of each of these complexes consist of LiX units (X = Cl/Br) in which the Li<sup>+</sup> cation is *tris*-coordinated by the three N atoms of the pyridyl rings of the *tris*(2-pyridyl) bismuthine ligands. The presence of Li<sup>+</sup> in bulk samples of the complexes was confirmed by solution <sup>7</sup>Li NMR spectroscopy. Bulk samples of pure LiCl coordination complexes can be obtained by the reactions of the mixed halide complexes with tetrabutyl ammonium chloride. Mixed halide composition can also be avoided by employing BiBr<sub>3</sub> as the bismuth source instead of BiCl<sub>3</sub>. This allowed us to prepare **6**·LiBr and **7**·LiBr without Cl<sup>−</sup> inclusion (see the Experimental Section and SI).

In **5**·LiCl (Figure 3a) and **6**·LiX (Figure 3b), in which the Bi(III) centers of the *tris*(2-pyridyl) ligands are exposed, short intermolecular Bi⋯X contacts<sup>67,68</sup> clearly link the molecules together into a 1-D polymeric arrangement. The coordination geometry around Bi becomes effectively disphenoidal (see-saw), with the intermolecular contact occupying an axial position. Comparable interactions are seen in **7**·LiX (Bi⋯Br = 3.833(2) Å), but they are considerably longer on account of the steric hindrance caused by the 3-Me groups flanking the Bi(III) center (Figure 3c). This shows that substitution at the 3-position of the pyridyl ring can be used to modulate anion coordination to Bi(III) in a similar manner to the way in which 6-substitution can be employed to control cation coordination of the *tris*(2-pyridyl) bismuthine N atoms (see later).

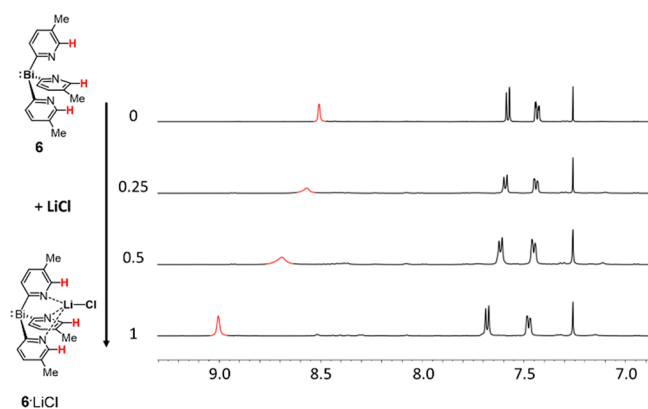
Ligands **2–4** and the complexes **5**·LiCl, **6**·LiX, and **7**·LiX are all thermally stable and can be stored indefinitely in solid form under a N<sub>2</sub> atmosphere. They are also remarkably stable toward moisture. With the exception of **7**, which slowly decomposes in the presence of excess H<sub>2</sub>O to generate free 3-Me-2-py-H, the remaining compounds are stable toward moisture, and no hydrolysis was observed 2 days after the addition of ca. 15 equiv of H<sub>2</sub>O in toluene-d<sub>8</sub> or CDCl<sub>3</sub>, as monitored by <sup>1</sup>H NMR spectroscopy. In fact, decoordination of LiX from ligands **5** and **6** can be accomplished by extraction with toluene/H<sub>2</sub>O (Experimental Section). Nominally halide-free ligands **5** and **6** were obtained in this manner, and in the case of **6**, its structure was confirmed by X-ray crystallography (see the SI).

The isolation of ligands **5**, **6**, and **7** as lithium halide complexes reflects their higher affinity for Li<sup>+</sup>, in contrast to the 6-pyridyl substituted ligands **1–4**, in which the donor-N atoms of the pyridyl groups are more sterically congested. Upon the addition of increasing amounts of LiCl to CDCl<sub>3</sub> solutions of free ligands **5** and **6**, a shift in the pyridyl signals is observed in their <sup>1</sup>H NMR spectra indicative of LiCl coordination. This shift is largest for H-6 (i.e., next to the pyridyl nitrogen), which is deshielded by around 0.5 ppm (see Figure 4). These changes are accompanied by the appearance of a singlet at 6.2 ppm in their <sup>7</sup>Li NMR spectra resulting from coordination of LiCl to the ligand. In contrast, addition of LiCl to solutions of **1–4** under the same conditions did not result in coordination to LiCl, as evidenced by <sup>1</sup>H and <sup>7</sup>Li NMR spectroscopy. This indicates that 6-substitution of the pyridyl ring completely blocks the coordination of LiCl. This may be due in part to the poorer donor ability of the pyridyl N atoms in the bismuthine ligands **2** and **3** (as a result of the presence of electron-withdrawing Br and CF<sub>3</sub> groups), but it is also likely to be steric in origin.

With the new ligands **1** and **2–7** in hand, we next explored their coordination to a range of metals. Reactions of **1** with equimolar amounts of AgOTf, AgBF<sub>4</sub> or AgPF<sub>6</sub> in MeCN give the new complexes [Bi(6-Me-2-py)<sub>3</sub>Ag(MeCN)]OTf (**8**·OTf), [Bi(6-Me-2-py)<sub>3</sub>Ag(MeCN)]BF<sub>4</sub> (**8**·BF<sub>4</sub>), and [Bi(6-Me-2-py)<sub>3</sub>Ag(MeCN)]PF<sub>6</sub> (**8**·PF<sub>6</sub>) (Scheme 2). Similar reaction of **4** with AgBF<sub>4</sub> in MeCN gives [Bi(6-Ph-2-py)<sub>3</sub>Ag(MeCN)]BF<sub>4</sub> (**9**·BF<sub>4</sub>). In contrast to ligands **1** and **4**, no coordination was observed between bismuthine ligands **2** or **3** and AgX salts (X = OTf, BF<sub>4</sub>, PF<sub>6</sub>). Bearing in mind that the van der Waals radius of CH<sub>3</sub> (2.23 Å) is intermediate between those of CF<sub>3</sub> (2.74 Å) and Br (1.85 Å),<sup>69,71</sup> the inability of ligands **2** and **3** to coordinate Ag<sup>+</sup> most likely arises from the electron-withdrawing nature of the substituents (i.e., reducing the donor ability) rather than just steric hindrance of the coordination site. This point is emphasized by the fact that despite its sterically hindering groups, **4** readily forms the Ag(I) complex [Bi(6-Ph-2-py)<sub>3</sub>Ag(MeCN)][BF<sub>4</sub>] (**9**·BF<sub>4</sub>) with AgBF<sub>4</sub>. The lithium halide complexes **5**·LiX, **6**·LiX, and **7**·LiX proved to be very poor sources of the ligands **5**, **6**, and **7** since the halide ions interfered significantly in the transmetalation reactions with Ag<sup>+</sup> salts. For example, reactions with AgOTf in acetonitrile resulted in halogen/OTf anion exchange with the precipitation of AgCl and formation of LiOTf complexes, as shown by multinuclear NMR studies and the solid-state characterization of the LiOTf complex of **6** (see the SI). The reaction between lithium-halide-free ligand **5** and Ag(OTf) in acetonitrile resulted in the precipitation of a white

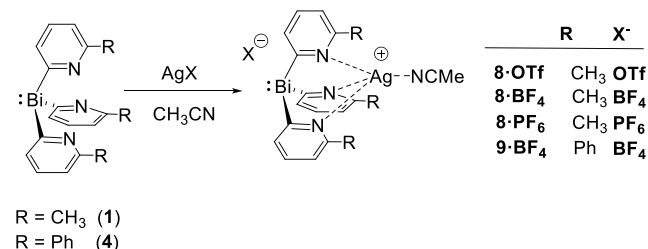


**Figure 3.** (a, left) Molecular structure of the monomeric unit of 5-LiCl; displacement ellipsoids at 50% probability. (a, right) View along the *b* axis and formation of a zigzag type structure through Bi...Cl interactions between the monomeric units. (b, left) Molecular structure of 6-LiX; displacement ellipsoids at 50% probability. Cl/Br disorder is present, with a partial occupancy of 0.6 for Cl and 0.4 for Br. H atoms and the Br component of the disorder, as well as one molecule of CH<sub>2</sub>Cl<sub>2</sub> present in the asymmetric unit, are omitted for clarity. See the SI for the structure of the pure 6-LiBr coordination complex. (b, right) View of 6-LiX along the *a* axis and formation of a zigzag type structure through Bi...Cl interactions of the monomeric units. The Br component of the disorder is omitted for clarity. Both the Bi...Cl contacts in 5-LiCl (3.455(2) Å) and the Bi...Br contacts in 6-LiBr (3.525(8) Å) are well below the sum of the relevant van der Waals radii ( $\Sigma_{\text{VDW}}(\text{Bi}-\text{Cl}) = 3.82$ ,  $\Sigma_{\text{VDW}}(\text{Bi}-\text{Br}) = 3.90$  Å).<sup>69,70</sup> (c, left) Molecular structure of the monomeric unit of 7-LiX; displacement ellipsoids at 50% probability. Cl/Br disorder is present, with a partial occupancy of 0.7 for Cl and 0.3 for Br. See the SI for the pure LiCl and LiBr coordination complexes. H atoms and the Br component of the disorder, as well as one molecule of CH<sub>2</sub>Cl<sub>2</sub> present in the asymmetric unit, are omitted for clarity. See the SI for the structures of 7-LiCl and 7-LiBr. (c, right) Space-filling view of 7 down the Bi...Li axis with the Li-X unit omitted and the 3-methyl groups highlighted in red. (c, bottom) Space-filling representation of two adjacent 7-LiX molecules. The Br component of the disorder is omitted for clarity, and the 3-methyl groups are highlighted in red. Selected bond lengths (Å) and angles (deg) for 5-LiCl: Bi-C<sub>py</sub> 2.266(8)–2.289(10), N–N 3.13(1)–3.154(9); C<sub>py</sub>–Bi–C<sub>py</sub> 92.3(4)–93.4(3), Cl–Bi–C<sub>11py</sub> 170.4(2) for 6-LiCl<sub>0.6</sub>Br<sub>0.4</sub>: Bi–C<sub>py</sub> 2.287(8)–2.257(8), N–N 3.174(8)–3.110(8); C<sub>py</sub>–Bi–C<sub>py</sub> 92.6(3)–93.2(3), for 7-LiCl<sub>0.7</sub>Br<sub>0.3</sub>: Bi–C<sub>py</sub> 2.281(6)–2.296(8), N–N 3.115(9)–3.077(9). Color key: C (gray), Bi (purple), N (blue), Li (pink), Cl (green). See also Table S1 in the SI.



**Figure 4.**  $^1\text{H}$  NMR spectra of the successive addition of LiCl to a solution of free ligand **6**. LiCl coordination is evident from the observed shifts of the signals. H-6 (i.e., next to the pyridyl nitrogen, highlighted in red) exhibits the largest shift of around 0.5 ppm. The spectrum for 1 equiv of LiCl is identical to that of **6**·LiCl in  $\text{CDCl}_3$ . No further changes to the spectrum were observed when  $>1$  equiv of LiCl was added.

### Scheme 2. Synthesis of the Silver Complexes **8**·X and **9**·BF<sub>4</sub>



solid, suggesting the formation of a silver complex. However, this was highly insoluble and could not be characterized.

The room-temperature  $^1\text{H}$  NMR spectra of the Ag<sup>+</sup> complexes **8** and **9** in acetonitrile-*d*<sub>3</sub> both show the presence of only one pyridyl environment. The pyridyl resonances are shifted downfield with respect to those of the free ligands **1** and **4**, indicating coordination to Ag. In the case of complex **8**, the presence of different anions (OTf<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, and PF<sub>6</sub><sup>-</sup>) does not substantially affect the  $^1\text{H}$  chemical shifts of the pyridyl resonances.

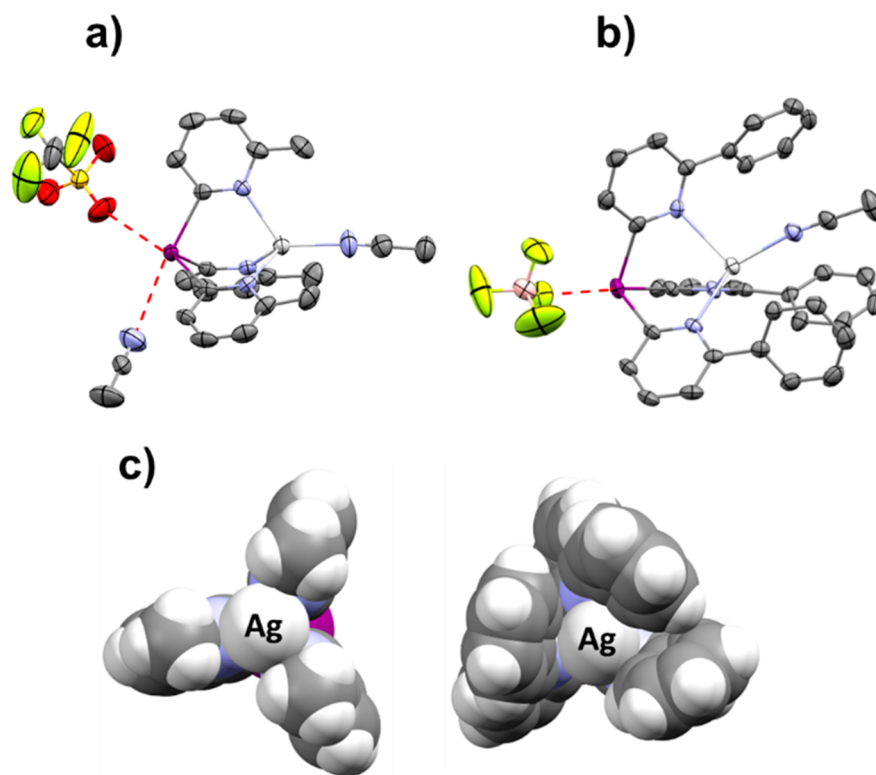
The solid-state structures of the crystalline complexes **8**·OTf·MeCN, **8**·BF<sub>4</sub>, **8**·PF<sub>6</sub>·2CH<sub>3</sub>CN, and **9**·BF<sub>4</sub> have ion-separated arrangements consisting of  $[\{\text{Bi}(\text{6-Me-2-py})\}_3\text{AgCH}_3\text{CN}]^+$  or  $[\{\text{Bi}(\text{6-Ph-2-py})\}_3\text{AgCH}_3\text{CN}]^+$  cations and the corresponding anions. Their complex cations contain Ag<sup>+</sup> centers that are coordinated by the three pyridyl-N atoms of the ligands and by a molecule of MeCN (Figure 5). The structural arrangement of these silver complexes is related to that found previously for the ion-separated Cu(I) complexes  $[\{\text{E}(\text{6-Me-2-py})_3\}\text{Cu}\cdot\text{CH}_3\text{CN}]^+\text{PF}_6^-$  (E = As, Sb, Bi).<sup>25</sup> However, it differs from that of the silver complex  $[\text{Ag}@\text{Ag}_4(\text{2-py}_3\text{P})_4(\text{OTf})_4](\text{OTf})$  cluster, in which the tris(2-pyridyl) phosphine ligand  $[\text{P}(\text{2-Py})_3]$  coordinates Ag(I) through the pyridines and the phosphorus lone pair.<sup>72</sup> In the bismuthine silver complexes **8**·X (X = OTf<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, and PF<sub>6</sub><sup>-</sup>) and **9**·BF<sub>4</sub><sup>-</sup> the low energy of the 6s orbitals of the lone pairs of the bismuthine ligands results in no coordination to the soft Ag(I) centers. Instead, the greater Lewis acidity at the bismuth bridgehead atoms can result in solvent···Bi and anion···Bi interactions (as also observed in the LiX complexes of **5**–**7**).

Varying degrees of cation–anion interactions are found in **8**·OTf, **8**·BF<sub>4</sub><sup>-</sup>, and **8**·PF<sub>6</sub><sup>-</sup>. In **8**·OTf (Figure 5a), the Bi(III) bridgehead is involved in an additional long-range interaction with one O atom of a OTf<sup>-</sup> anion and with the N atom of an MeCN ligand. The Bi–N (3.309(6) Å) and Bi–O (3.326(6) Å) distances involved are longer than expected for donor–acceptor or coordination bonds but significantly shorter than the sum of their van der Waals radii (3.62 and 3.59 Å, respectively). Moving to the less coordinating anions BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>, the Bi(III)···anion interactions are no longer present (see the SI). In **8**·PF<sub>6</sub><sup>-</sup>·2CH<sub>3</sub>CN the Bi(III) bridgehead is coordinated by two MeCN ligands only, and in **8**·BF<sub>4</sub><sup>-</sup> no secondary interaction is found with BF<sub>4</sub><sup>-</sup> (see the SI).

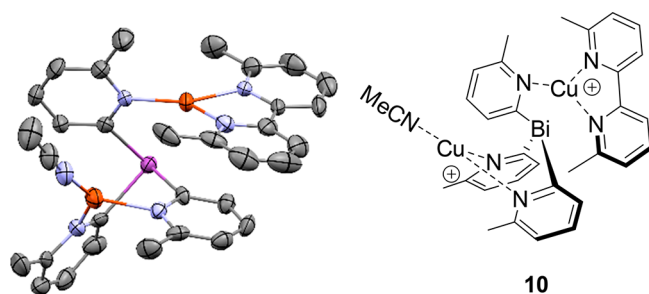
The use of the more sterically congested bismuthine ligand **4** results in the significantly distorted cation **9**·BF<sub>4</sub><sup>-</sup> (Figure 5b). An indication of this is seen in the coordination of the molecule of MeCN to the Ag center, which is tilted away from the Bi···Ag···N axis (Bi–Ag–N angle 162.4(1)°), unlike in the cations  $[\mathbf{8}]^+$  in which the Bi···Ag···N fragment is almost linear (Bi···Ag···N range 176.1(2)–175.3(2)°). No expansion of the C<sub>py</sub>–Bi–C<sub>py</sub> angles is observed in the cation  $[\mathbf{9}]^+$  (94.9(2)–96.7(2), cf. 93.3(2)–100.4(2) for cations  $[\mathbf{8}]^+$ ), and therefore the coordination of the MeCN molecule to Ag<sup>+</sup> must be accomplished by distortion of the pyridyl coordination environment. A large twist of 49.2° in one of the Py units with respect to the Bi···Ag axis occurs, which in turn results in the elongation of the coordinating N–Ag bonds (2.464(3) Å, cf. N–Ag distances in the range 2.307(5)–2.380(4) Å for the cations  $[\mathbf{8}]^+$ ). Figure 5c shows the cations  $[\mathbf{8}]^+$  and  $[\mathbf{9}]^+$  along their Ag–acetonitrile axes and illustrates the more sterically constrained nature of the coordination environment around the Ag(I) center in cation  $[\mathbf{9}]^+$  as compared to cations  $[\mathbf{8}]^+$ . Recently, there has been great interest in closed-shell metal–Bi interactions.<sup>48,65,73–75</sup> In this regard, seemingly short Bi···Ag contacts are present in the cations  $[\mathbf{8}]^+$  and  $[\mathbf{9}]^+$  (range 3.6746(6)–3.7291(4), cf. 3.79 Å for  $\Sigma_{\text{VDW}}$ ). However, it is likely that these interactions are weak at best in this case.

Further investigations of the coordination behavior of these bismuthine ligands toward the other coinage metals, copper and gold, illustrate the noninnocent nature of some of these ligands, which are subject to either 2-pyridyl ligand transfer or reductive elimination. While the silver complexes **8**·X (X = OTf<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>) and **9**·BF<sub>4</sub><sup>-</sup> are stable in rigorously dried CH<sub>3</sub>CN in an N<sub>2</sub> atmosphere, the corresponding Cu(I) complexes of ligands **1** and **4** were found to be less stable. Prolonged storage of the 1:1 reaction between  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$  and bismuthine ligand **1** at room temperature in MeCN led to a gradual color change from pale yellow to orange, with the formation of a few red and yellow crystals and a black precipitate. X-ray analysis shows that the red crystals are the copper(I) complex  $[\text{Cu}(\text{Me-bpy})_2]\text{BF}_4$  (Me-bpy = 6,6′-dimethyl-2,2′-bipyridyl),<sup>76</sup> while the yellow crystals are the unusual Bi(III)/Cu(I) complex  $[\{\text{Bi}(\text{6-Me-2-py})_3\text{Cu}\}\text{Cu}(\text{Me-bpy})](\text{BF}_4)_2$  (**10**·(BF<sub>4</sub>)<sub>2</sub>). The  $[\{\text{Bi}(\text{6-Me-2-py})_3\text{Cu}\}\text{Cu}(\text{Me-bpy})]^{2+}$  dication **10**<sup>2+</sup> (Figure 6) consists of a  $[\text{Bi}(\text{6-Me-2-py})_3\text{Cu}]$  subunit in which the Cu(I) center is only coordinated by two of the three 2-pyridyl N atoms, with the third pyridyl-N atom coordinating the Cu(I) center of a  $[\text{Cu}(\text{Me-bpy})]^+$  unit, giving rise to two trigonal planar Cu(I) environments. No  $\pi$ -arene–Cu(I) interactions are present in this arrangement.

The formation of a bipyridine molecule as a ligand in the cation of **10** must result from reductive elimination, presumably from the initially formed  $[\text{Bi}(\text{6-Me-2-py})_3\text{Cu}$



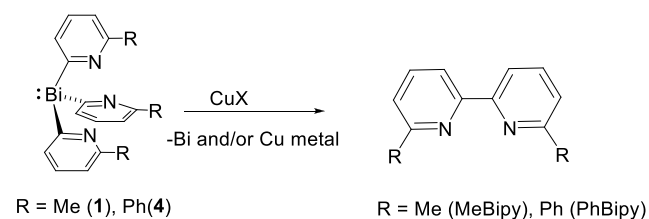
**Figure 5.** (a) Molecular structure of complex **8**·OTf([Bi(6-Me-2-py)<sub>3</sub>Ag(MeCN)]OTf); displacement ellipsoids at 50% probability. (b) Molecular structure of complex **9**·BF<sub>4</sub> [Bi(6-Ph-2-py)<sub>3</sub>Ag(MeCN)] [BF<sub>4</sub>]; displacement ellipsoids at 50% probability. H atoms are omitted for clarity. (c) Space-filling views of the cations [Bi(6-Me-2-py)<sub>3</sub>Ag(MeCN)]**[8]<sup>+</sup>** (left) and [Bi(6-Ph-2-py)<sub>3</sub>Ag(MeCN)]**[9]<sup>+</sup>** (right) down the Ag...Bi vector. Selected bond lengths (Å) and angles (deg) for **8**·OTf: Bi–C<sub>py</sub> 2.274(5)–2.288(5), N–Ag 2.307(5)–2.380(4); C<sub>py</sub>–Bi–C<sub>py</sub> 93.3(2)–99.0(2), O–Bi–C<sub>11py</sub> 168.7(2), N<sub>acetonitrile</sub>–Bi–C<sub>21py</sub> 168.6(2) for **9**·BF<sub>4</sub>: Bi–C<sub>py</sub> 2.258(5)–2.273(4), N–Ag 2.337(3)–2.464(3); C<sub>py</sub>–Bi–C<sub>py</sub> 94.9(2)–96.7(2), F–Bi–C<sub>21py</sub> 175.7(1). Color key: C (gray), Bi (purple), N (blue), Ag (light gray), F (yellow), B (pink), O (red).



**Figure 6.** (left) Solid-state structure and (right) line drawing of complex dication **[10]<sup>2+</sup>**. Displacement ellipsoids shown at 50% probability; H atoms and two BF<sub>4</sub><sup>−</sup> anions omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi–C<sub>py</sub> 2.259(6)–2.291(9), C<sub>py</sub>–Bi–C<sub>py</sub> 90.4(3)–91.7(3). Color key: C (gray), Bi (purple), N (blue), Cu (orange).

(MeCN)]<sup>+</sup> cation in the manner illustrated in **Scheme 3**. This was proved by *in situ* <sup>1</sup>H NMR spectroscopic investigation of the 1:1 reactions of **1** and **4** with [Cu<sup>I</sup>NCMe]BF<sub>4</sub> or Cu<sup>I</sup>Cl in acetonitrile-d<sub>3</sub> under N<sub>2</sub> at room temperature. Upon mixing [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> and the bismuthine ligands **1** or **4**, immediate formation of the complexes [Bi(6-Me-2-py)<sub>3</sub>CuNCMe]BF<sub>4</sub> and [Bi(6-Ph-2-py)<sub>3</sub>CuNCMe]BF<sub>4</sub> was observed (see the SI). After 7 and 5 days, respectively, very small amounts of the corresponding bipyridines Me-bpy and 6,6′-diphenyl-2,2′-dipyridyl (Ph-bpy) were formed. Much faster reaction occurs using CuCl instead of [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub>. The reaction of **4** and CuCl (1:1) in MeCN immediately

### Scheme 3. Reductive Elimination from the 2-Pyridyl Ligands of **1** and **4** (X = Cl<sup>−</sup>, BF<sub>4</sub><sup>−</sup>)



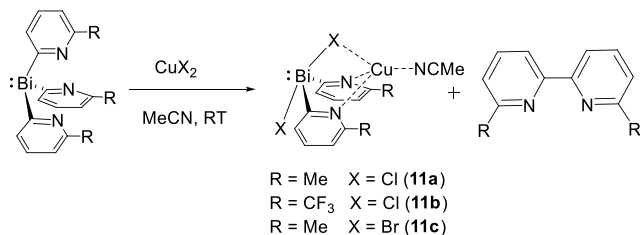
turned red, and the <sup>1</sup>H NMR spectrum showed the formation of Ph-bpy within the first 10 min. After 24 h at room temperature, the <sup>1</sup>H NMR spectrum shows the almost exclusive formation of Ph-bpy, together with unidentified minor products and with the appearance of a black precipitate (see later discussion). Similar observations were made in the reaction between **1** and CuCl. In this case, however, the formation of Me-bpy proceeded more slowly, and after 5 days at room temperature *ca.* 80% conversion had occurred.

An intriguing observation in these reactions is the marked effect of the anion on the rate of these coupling reactions. As seen in our previous study of the coordination chemistry of [Bi(6-Me-2-py)<sub>3</sub>] with CuX (X = Cl<sup>−</sup>, PF<sub>6</sub><sup>−</sup>)<sup>25</sup> as well as in the current study with Ag(I) and Li salts, the Bi(III) bridgehead atom is sufficiently Lewis acidic to interact with anions. The presence of the more strongly coordinating chloride ligand in CuCl (as compared to weakly coordinating BF<sub>4</sub>) could potentially trigger ligand coupling by the transfer of the

halogen to the Bi(III) center, forming more reactive hypervalent bismuthate species which facilitate the transfer of the 2-pyridyl groups and reductive elimination to bipyridines.

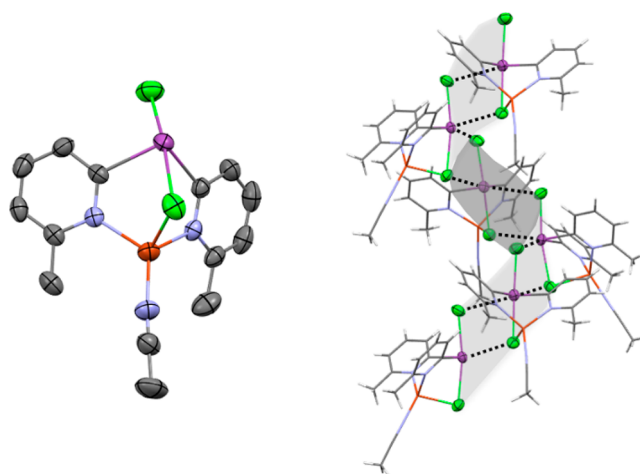
The black precipitate formed in these reactions could be Bi(0) and/or Cu(0). In this regard, Cu(II)-mediated coupling of pyridyl anions to bipyridines is a well-established synthetic protocol, and one plausible mechanism for the coupling of the pyridyl groups in our study involves the disproportionation of Cu(I) into Cu(0) and Cu(II), with subsequent Cu(II)-mediated coupling.<sup>77,78</sup> To explore this possibility further, CuCl<sub>2</sub> was reacted with ligand **1** (1:1 equiv) in acetonitrile at room temperature. The solution immediately turned red, and orange crystals of the product [Cu<sup>I</sup>(MeCN)(μ-Cl)(6-Me-2-Py)<sub>2</sub>Bi<sup>III</sup>Cl] (**11a**) were obtained in 40% yield. The reaction of ligand **3** with CuCl<sub>2</sub> under the same conditions gave the closely related complex [Cu<sup>I</sup>(MeCN)(μ-Cl)(6-CF<sub>3</sub>-2-Py)<sub>2</sub>Bi<sup>III</sup>Cl]·MeCN (**11b**·MeCN), although in this case three equivalents of CuCl<sub>2</sub> were required and unreacted ligand **3** was still present in the reaction mixture. The analogous complex [Cu<sup>I</sup>(MeCN)(μ-Cl)(6-Me-2-Py)<sub>2</sub>Bi<sup>III</sup>Br]·CH<sub>2</sub>Cl<sub>2</sub> (**11c**·CH<sub>2</sub>Cl<sub>2</sub>) was obtained from the reaction of ligand **2** with CuBr<sub>2</sub> in 24% crystalline yield. *In situ* <sup>1</sup>H NMR spectroscopy confirmed the formation of the corresponding bipyridine products in each of the reactions producing **11a–11c** (Scheme 4). Compounds **11a–11c** are stable in MeCN

#### Scheme 4. Formation of **11a**, **11b**, and **11c**



solution even in the presence of aerial oxygen for several days, after which slow formation of the free pyridines was observed by <sup>1</sup>H NMR spectroscopy. Significantly, no formation of the bipyridines was observed, proving that the coupling reaction does not result from the effect of adventitious oxygen or moisture on **11a–11c** (i.e., they are not intermediates in the coupling reaction). Although organobismuth compounds can mediate different carbon–carbon bond forming reactions, bismuthine ligand **1** is thermally stable, and no decomposition or coupling reaction to produce Me-bpy was observed after heating a sample of **1** in acetonitrile at 80 °C for 24 h.<sup>79</sup>

Complexes **11a–11c** are isostructural, having a Bi(III)/Cu(I) arrangement which consists of an ion-pair between hypervalent [X<sub>2</sub>Bi(2-R-py)<sub>2</sub>]<sup>−</sup> (X = Cl, Br) anions and the Cu(MeCN)<sup>+</sup> cation, nicely illustrating the ability of the newly-formed pyridine bismuthine ligands to simultaneously coordinate anions and cations. Figure 7a shows the structure of **11a**. As expected, the Bi(III) centers within these anions adopt similar distorted trigonal-bipyramidal geometries with the Bi lone pair formally occupying an equatorial position and the (most electronegative) halogen ligands axial (consistent with VSEPR theory). The Cu(I) centers are coordinated by the two pyridyl-N atoms of the [X<sub>2</sub>Bi(2-R-py)<sub>2</sub>]<sup>−</sup> anions and by one of the halogen atoms. Support for the conclusion that these complexes contain hypervalent [X<sub>2</sub>Bi(2-R-py)<sub>2</sub>]<sup>−</sup> anions is seen in a comparison in the Bi–X bond lengths within the



**Figure 7.** (a) Solid-state structure of complex **11a**. Compounds **11b** and **11c** are isostructural (see the SI). Displacement ellipsoids shown at 50% probability; H atoms and one molecule of MeCN are omitted for clarity. (b) Association of molecules of **11a** in the lattice (the right-handed helix present in *P*<sub>4</sub><sub>1</sub> is shown; for details of the helical arrangement with the opposite handedness, see the SI). Selected bond lengths (Å) and angles (deg): Bi–C<sub>py</sub> 2.30(1)–2.28(1), N–Cu 2.03(1)–2.05(1); C<sub>py</sub>–Bi–C<sub>py</sub> 92.1(4), Cl–Bi–Cl 169.19(13), Cl–Bi–C<sub>py</sub> 165.9(3). Color key: C (gray), Bi (purple), N (blue), Cu (orange), Cl (green).

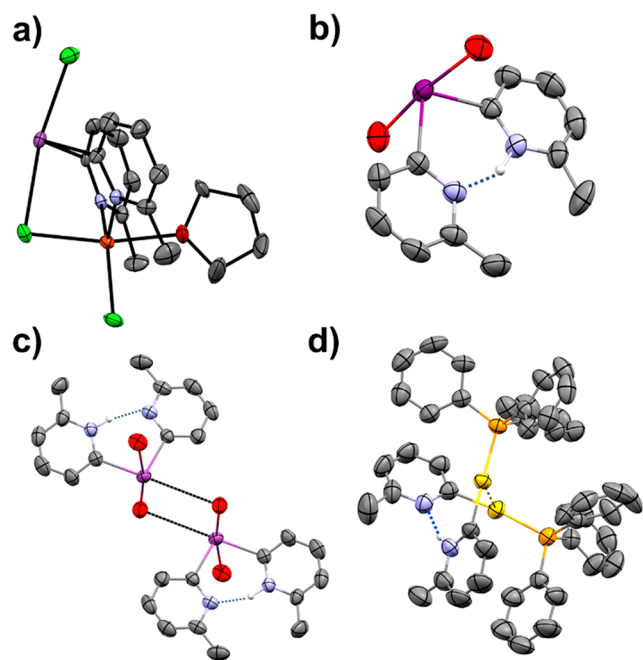
Cu–(μ-X)–Bi bridges, these bonds being similar to those seen previously in the few known examples of structurally characterized [X<sub>2</sub>BiR<sub>2</sub>]<sup>−</sup> anions, e.g., Bi–Cl 2.688(3) and 2.773(3) Å in **11a**, cf. 2.674(2) Å and 2.800(2) Å in [Cl<sub>2</sub>BiAr<sub>2</sub>]<sup>−</sup> (Ar = 2-methylphenyl).<sup>80</sup> Overall, two important points are illustrated by the formation and structures of **11a–11c**: the coupling reaction of the 2-pyridyl groups is likely (at least in part) to involve Cu(II) (via disproportionation of 2Cu(I) → Cu(0) + Cu(II)), and that pyridyl-bismuthine ligands of this type can indeed function as fully fledged amphiphilic ligands.

In the crystal lattices of the solvates **11b**·CH<sub>3</sub>CN and **11c**·CH<sub>2</sub>Cl<sub>2</sub> (which crystallize in the nonchiral space groups *P*<sub>2</sub><sub>1</sub>/*c* and *P*-1, respectively), the monomer units are linked via Bi···Cl or Bi···Br interactions. Molecules of **11b** associate into zigzagged polymers via Bi···Cl interactions (3.458 Å, cf. Σ<sub>VDW</sub> = 3.82 Å), while in **11c** this association only occurs to form very loosely linked dimers in which the Bi···Br distance is at the very limit of the van der Waals distance [(Bi···Br 3.872, cf. 3.9 Å for Σ<sub>VDW</sub>(Br–Bi)] (see the SI). The Bi atoms of **11b**·CH<sub>3</sub>CN are also involved in long-range Bi···N interactions with the lattice CH<sub>3</sub>CN molecules.

In contrast, **11a**·CH<sub>3</sub>CN, which, like **11b** and **11c**, is an achiral complex, crystallizes in the tetragonal chiral space group *P*<sub>4</sub><sub>1</sub> (Figure 7a) in which the molecules associate via Bi···Cl interactions into chiral helical polymers formed by four molecules of **11a** around crystallographic 4<sub>1</sub> screw axes. This leads to the formation of a right-handed helix (anticlockwise looking down the crystallographic *c* axis). Whereas only the terminal Cl atom is involved in the Bi···Cl interactions in **11b**, both the terminal and μ-Cl atoms are involved in the intermolecular interactions in **11a** (Bi···Cl mean 3.589 Å). Further analysis of samples of **11a** allowed us to obtain the crystal structure of the other enantiomorph, which crystallizes in space group *P*<sub>4</sub><sub>3</sub> in crystals containing solely the left-handed

helix (see the SI). Compound **11a** is an example of crystalline enantiomorphism emerging from an achiral complex.<sup>81,82</sup>

A related structural arrangement to **11a–11c** is formed in the 1:1 reaction of **1** with FeCl<sub>2</sub> to give the heterometallic Bi(III)/Fe(II) complex [ClBi(6-Me-2-Py)<sub>2</sub>FeCl<sub>2</sub>] (**12**) (Figure 8a). This reaction results in significant decomposition and



**Figure 8.** (a) Molecular structure of [ClBi(6-Me-2-Py)<sub>2</sub>FeCl<sub>2</sub>] (**12**). H atoms have been omitted for clarity. Thermal ellipsoids at 50% probability. (b) Solid-state structure of **13** and (c) its association into dimers through Bi–I intermolecular interactions. Displacement ellipsoids shown at 50% probability. H atoms (except H1) are omitted for clarity. (d) Solid-state structure of the gold pyridyl cation [((6-Me-2-Py)Au(PPh<sub>3</sub>))<sub>2</sub>H]<sup>+</sup> (**14**)<sup>+</sup>. H atoms (except H1) and the OTf<sup>−</sup> anion are omitted for clarity. Displacement ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): **12**, Bi–C<sub>py</sub> 2.298(8)–2.287(7), N–Fe 2.144(6)–2.151(6); C<sub>py</sub>–Bi–C<sub>py</sub> 92.1(2), Cl–Bi–Cl 170.13(6), Cl–Bi–C<sub>1py</sub> 164.18(6). **13**, Bi–C<sub>py</sub> 2.286(6), 2.281(7), C<sub>py</sub>–Bi–C<sub>py</sub> 94.3(2), I–Bi–C<sub>11py</sub> 170.5(2). Owing to difficulties with the structure refinement, no bond lengths or angles are quoted for compound **14-OTf**. Color key: C (gray), Bi (purple), N (blue), Au (yellow, P (light orange), Fe (dark orange), O (dark red), Cl (green), I (red).

the formation of a black precipitate, presumably of Bi and/or Fe metal or even Bi–Fe intermetallic compounds. The observation of the formation of black precipitates throughout these studies could be due to the formation of Bi–transition metal intermetallics, which could echo recent findings by Vela in the synthesis of 10–14, 10–15, and 11–15 binary intermetallics from heterobimetallic single-source precursors.<sup>83,84</sup> The low isolated yield of **12** meant that it was only characterized by X-ray crystallography. The formation of **12** presumably results from metal–halogen transfer from Fe(II) to Bi(III). However, because of the paramagnetic nature of the reaction solution, we were not able to determine the presence of Me-bpy in solution, and it is therefore unknown whether any pyridyl coupling occurs in this case. In the structure of **12**, the Fe<sup>II</sup> and Bi<sup>III</sup> atoms are bridged by 6-Me-2-py groups and by a  $\mu$ -Cl atom, with both Bi(III) and Fe(II) having trigonal bipyramidal geometries (in the case of Bi(III), the fifth

position is formally occupied by the lone pair). Compound **12** forms a 1-D zigzagged polymer in the crystal lattice via Bi $\cdots$ Cl interactions between the monomer units (see the SI).

Metal–halogen transfer is also observed in the reaction of FeI<sub>2</sub> with **1**, from which a few crystals of Bi[(6-Me-2-py)<sub>2</sub>HI<sub>2</sub>] (**13**) were isolated and structurally characterized by X-ray crystallography. Like **12**, **13** contains a hypervalent Bi(III) center (Figure 8b) and can be regarded as an advanced state of the situation seen in the structure of **12**, in which full transfer of the halogen (iodine) from the Fe(II) to the Bi(III) center has occurred. This leads to the formation of an anionic bismuthate complex [I<sub>2</sub>Bi(6-Me-2-Py)<sub>2</sub>]<sup>−</sup>, which is then protonated at one of the pyridyl-N atoms in the reaction medium to give **13** (with the resulting formation of a relatively strong N–H $\cdots$ N hydrogen bond between the two pyridyl groups). Dimerization of these units occurs in the solid state via intermolecular Bi–I $\cdots$ Bi interactions (3.7988(6) Å, cf. 4.05 Å for the sum of their VdW radii) (Figure 8c).

The ability for *tris*(2-pyridyl) ligands to act as pyridyl transfer reagents has been seen previously in the case of the highly reactive and moisture-sensitive [MeAl(2-py)<sub>3</sub>]<sup>−</sup> anion<sup>33,61</sup> and is symptomatic of low bond energy of the C-bridgehead bonds in ligands containing more electropositive (metallic) bridgehead atoms. The ability for **1** to act in a similar way is seen in the example of its reaction with Au(I) salts. While the reaction of **1** and ClAu(tht) (tht = tetrahydrothiophene) in THF led to the formation of an intractable yellow precipitate that could not be further investigated due to its marked insolubility, reaction of (OTf)AuPPh<sub>3</sub> with **1** in acetone resulted in a mixture of compounds as shown by <sup>1</sup>H NMR, including the appearance of an unexpected broad resonance at  $\delta$  = ca. 12 ppm. After storing the reaction mixture for 48 h at −25 °C, a few crystals of the new compound [((6-Me-2-Py)Au(PPh<sub>3</sub>))<sub>2</sub>H][OTf] (**14-OTf**) were formed. Despite difficulties in its collection and refinement (due to modeling of disordered triflate; see SI), the single-crystal X-ray data of **14-OTf** define its structure unambiguously. The solid-state structure shows that **14-OTf** has an ion-separated arrangement containing the cation [((6-Me-2-Py)Au(PPh<sub>3</sub>))<sub>2</sub>H]<sup>+</sup> (**14**) (Figure 8d) and OTf<sup>−</sup> anions. The cation consists of a (pyridyl)Au–Au(pyridyl) bonded dimer arrangement in which one of the pyridyl-N atoms is protonated, resulting in an overall positive charge and the formation of a relatively strong N–H $\cdots$ N hydrogen bond (similar to **13**). The pyridyl transfer from bismuthine **1** to Au(I) is consistent with previous observations by Schmidbaur, in which the coordination of tertiary bismuthanes (R<sub>3</sub>Bi:) to Au(I) was prevented by rapid transmetalation, leading to the formation of organogold compounds.<sup>85</sup>

## CONCLUSIONS

The particular interest in *tris*-pyridyl bismuthine ligands of the type [Bi(2-py')<sub>3</sub>] is their ability to behave as amphiphilic ligands that are capable of coordinating anions at the Lewis acid Bi(III) bridgehead and at the same time coordinating cations at the donor-N atoms. Our study has provided a range of bismuthine ligands of this type beyond the single example previously reported, illustrating that a range of electron-donating and -withdrawing groups can be introduced into the pyridyl frameworks at various positions. Importantly, we find that 6-Me substitution is not essential for the stabilization of these ligands and that even the unsubstituted ligand **5** is thermally stable. The nature of the substituents (electron-



donating or -withdrawing and the steric effects) has a significant impact on the ligand properties. For example, the introduction of 6-Br and 6-CF<sub>3</sub> groups in the ligands **2** and **3** severely curtails the donor ability. Conversely, substitution at the 3-position in the ligand **6** sterically shields the Bi(III) center and reduces its ability to coordinate anions. These features allow control of the coordination ability of the ligand regarding both cation and anion coordination.

The weakness of the C–Bi bonds in these ligands is expressed in their reactions with Cu(I/II), Fe(II), and Au(I). In the case of Cu(I), coupling of the pyridyl groups to the corresponding bipyridines is observed, the rate of which is dependent on the anion present in the Cu(I) salt used. This reaction most probably involves disproportionation of Cu(I) to Cu(II) and Cu(0), as illustrated by the reactions of 6-substituted **1** and **3** with Cu<sup>I</sup>X<sub>2</sub> (X = halide) which results in both pyridyl coupling and the formation of Cu(I) complexes containing hypervalent Bi(III) [X<sub>2</sub>Bi(2-R-py)]<sup>−</sup> species. A related characteristic is the ability of the bismuthine frameworks to exchange ligands, undergoing metal–halogen or pyridyl transfer with Fe(II) and Au(I) salts.

Overall, this study provides a range of *tris*(2-pyridyl) bismuthines and reveals their interesting coordination and reaction characteristics (as well as their limitations) as ligands. We are continuing our studies in this area, particularly with respect to the use of p-block *tris*(2-pyridyl) species as reagents for chiral discrimination, in supramolecular chemistry and catalysis.

## EXPERIMENTAL SECTION

**General Experimental Techniques.** All syntheses were carried out on a vacuum line under a N<sub>2</sub> atmosphere. Products were isolated and handled under a N<sub>2</sub> atmosphere. Liquid pyridines, NMR solvents, and reaction solvents were stored over molecular sieves and degassed by three freeze–pump–thaw cycles under N<sub>2</sub> prior to use. [Bi(6-Me-2-py)]<sup>+</sup> (**1**) was synthesized as described previously. NMR spectra were recorded on 500 MHz Agilent DD2 instruments equipped with a cold probe and a 400 MHz Agilent instrument equipped with a ONEPROBE in the Laboratory of Instrumental Techniques (LTI) Research Facilities, University of Valladolid. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm). <sup>1</sup>H and <sup>13</sup>C NMR are referenced to TMS. <sup>7</sup>Li and <sup>19</sup>F NMR experiments are referenced to a solution of LiCl/D<sub>2</sub>O and CCl<sub>3</sub>F, respectively. Coupling constants (*J*) are reported in Hz. Standard abbreviations are used to indicate multiplicity: s = singlet, d = doublet, t = triplet, and m = multiplet. <sup>1</sup>H and <sup>13</sup>C peak assignments were performed with the help of additional 2D NMR experiments (<sup>1</sup>H–<sup>1</sup>H COSY, <sup>1</sup>H–<sup>1</sup>H NOESY, <sup>1</sup>H–<sup>13</sup>C HSQC, and <sup>1</sup>H–<sup>13</sup>C HMBC). High-resolution mass spectra were recorded at the mass spectrometry service of the Laboratory of Instrumental Techniques (LTI) of the University of Valladolid and the Centros de Apoyo a la Investigación (CAI) of the University of Alcalá. A MALDI-TOF system (MALDI-TOF) and a Bruker autoflex speed (N<sub>2</sub> laser: 337 nm, pulse energy: 100  $\mu$ J, 1 ns; acceleration voltage: 19 kV, reflector positive mode) were used. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) was used as the matrix. Elemental analysis was obtained using a CHNS-932 Elemental Analyzer at the CAI of the University of Alcalá. In cases where we have been unable to obtain satisfactory elemental analysis, the formulations of the compounds are either supported by X-ray structure determination or high-resolution mass spectroscopy (in addition to NMR spectroscopy).

**X-ray Diffraction Studies.** Diffraction data were collected using an Oxford Diffraction Supernova diffractometer equipped with an Atlas CCD area detector and a four-circle kappa goniometer. For the data collection, Mo or Cu microfocused sources with multilayer optics were used. When necessary, crystals were mounted directly from

solution using perfluorohydrocarbon oil to prevent atmospheric oxidation, hydrolysis, and solvent loss. Data integration, scaling, and empirical absorption correction were performed using the CrysAlisPro software package. The structure was solved by direct methods and refined by full-matrix-least-squares against *F*<sup>2</sup> with SHELX in OLEX2. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at idealized positions and refined using the riding model. Graphics were made with OLEX2 and MERCURY. In the case of **11**, data was collected on a Bruker D8 QUEST diffractometer with an Incoatec I $\mu$ S Cu microfocus source.

CCDC 1981115–1981137 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center.

**Synthesis of 2.** <sup>n</sup>BuLi (8 mL, 20 mmol, 2.5 M in hexane) was dissolved in THF (40 mL). 6-Dibromopyridine (4.74 g, 20 mmol) in THF (28 mL) was added dropwise over 30 min at –78 °C. The resulting dark green solution was stirred for 70 min at –78 °C. A suspension of BiCl<sub>3</sub> (2.1 g, 6.66 mmol) in THF (6 mL) was added dropwise to the lithiated species, and the resulting light green mixture was stirred for 2 h. Subsequently, the resulting white mixture was allowed to reach room temperature. After overnight stirring, all volatiles were removed under vacuum, and the resulting white solid residue was extracted with warm toluene (40 mL). The suspension was filtered through Celite to yield a pale-yellow solution, which was concentrated under vacuum until the precipitation of a white solid was observed, which was redissolved by gentle heating. Storage overnight at –24 °C yielded **2** as white blocks suitable for X-ray crystallography. Yield 2.94 g (4.34 mmol, 65%). <sup>1</sup>H NMR (298 K, toluene-d<sub>8</sub>, 500 MHz):  $\delta$  = 7.60 (d, *J* = 6.9 Hz, 3H, H<sub>3</sub> py), 6.78–6.72 (m, 6H, H<sub>4</sub>+H<sub>5</sub> py). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, toluene-d<sub>8</sub>, 100.6 MHz):  $\delta$  = 196.2 (br, C<sub>2</sub> py), 132.2 (C<sub>3</sub> py), 145.7 (C<sub>6</sub> py), 138.1 (C<sub>4</sub> py), 126.1 (C<sub>5</sub> py). These resonances were observed and unambiguously assigned through <sup>1</sup>H–<sup>13</sup>C HMBC and <sup>1</sup>H–<sup>13</sup>C HMQC experiments. HR-MS [ESI, positive ion mode ESI-TOF]: *m/z* for C<sub>15</sub>H<sub>9</sub>BiBr<sub>3</sub>N<sub>3</sub> [2+H]<sup>+</sup> calcd: 679.8203. Found: 679.8238 (–5.06 ppm error).

**Synthesis of 3.** 2-Bromo-6-(trifluoromethyl)pyridine (4.520 g, 20 mmol) was dissolved in diethyl ether (40 mL). To this was added dropwise <sup>n</sup>BuLi (8 mL, 20 mmol, 2.5 M in hexane) over 30 min at –78 °C. The resulting orange solution was stirred for 3 h at –78 °C. A suspension of BiCl<sub>3</sub> (2.1 g, 6.66 mmol) in THF (6 mL) was added dropwise to the dark orange lithiated species, and the resulting pale brown mixture was allowed to reach room temperature. After overnight stirring, a dark brown solution with a brown precipitate was observed. All volatiles were removed under vacuum, and the resulting solid residue was extracted with warm toluene (40 mL). The suspension was filtered through Celite to yield a brown solution, which was concentrated under vacuum until the precipitation of a white solid was observed, which was redissolved by gentle heating. Storage overnight at –24 °C yielded **3** as white blocks suitable for X-ray crystallography. Yield 3.80 g (5.87 mmol, 88%). <sup>1</sup>H NMR (298 K, toluene-d<sub>8</sub>, 400 MHz):  $\delta$  (ppm) = 7.95 (d, *J* = 7.75 Hz, 3H, H<sub>3</sub> py), 7.03 (t, *J* = 7.75 Hz, 3H, H<sub>4</sub> py), 6.94 (d, *J* = 7.75 Hz, 3H, H<sub>5</sub> py). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, toluene-d<sub>8</sub>, 100.5 MHz):  $\delta$  = 195.7 (br, C<sub>2</sub> py), 150.8 (q, *J*<sub>C–F</sub> = 34 Hz, C<sub>6</sub> py), 136.5 (C<sub>4</sub> py), 135.5 (C<sub>3</sub> py), 122.2 (q, *J*<sub>C–F</sub> = 272 Hz, C<sub>7</sub> py), 118.5 (q, *J*<sub>C–F</sub> = 3 Hz, C<sub>5</sub> py). <sup>19</sup>F NMR (298 K, toluene-d<sub>8</sub>, 376 MHz):  $\delta$  = –62.62 (s, 9F, CF<sub>3</sub>). Elemental analysis (%) calcd for **3** (C<sub>18</sub>H<sub>9</sub>BiF<sub>9</sub>N<sub>3</sub>): C 33.4, H 1.4, N 6.5. Found: C 33.2, H 1.6, N 6.4. HR-MS [ESI, positive ion mode ESI-TOF]: *m/z* for C<sub>18</sub>H<sub>9</sub>BiF<sub>9</sub>N<sub>3</sub> [3+H]<sup>+</sup> calcd: 648.0529. Found: 648.0532 (–0.35 ppm error).

**Synthesis of 4.** 2-Bromo-6-(phenyl)pyridine (1.170 g, 5 mmol) was dissolved in THF (20 mL). To this was added dropwise <sup>n</sup>BuLi (2 mL, 5 mmol, 2.5 M in hexane) over 30 min at –78 °C. The resulting red solution was stirred for 1 h at –78 °C. A suspension of BiCl<sub>3</sub> (0.525 g, 1.66 mmol) in THF (5 mL) was added dropwise to the dark red lithiated species, and the resulting pale red mixture was allowed to reach room temperature. After overnight stirring, a clear red solution was observed. All volatiles were removed under vacuum, and the resulting solid residue was extracted with warm toluene (15 mL). The suspension was filtered through Celite to yield a red solution, which

was concentrated under vacuum until the precipitation of a white solid was observed, which was redissolved by gentle heating. Storage overnight at  $-24\text{ }^{\circ}\text{C}$  yielded 4 as white needles suitable for X-ray crystallography. Yield 0.663 g (0.99 mmol, 60%).  $^1\text{H}$  NMR (298 K, toluene- $d_8$ , 500 MHz):  $\delta$  = 8.09 (d,  $J$  = 7.8 Hz, 6H,  $\text{H}_8$  Ph), 7.82 (d,  $J$  = 7.6 Hz, 3H,  $\text{H}_3$  py), 7.27–7.22 (m, 9H,  $\text{H}_5$ + $\text{H}_9$  py+Ph), 7.21–7.16 (m, 6H,  $\text{H}_4$ + $\text{H}_{10}$  py+Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K, toluene- $d_8$ , 100.6 MHz):  $\delta$  = 195.42 ( $\text{C}_2$  py), 159.66 ( $\text{C}_6$  py), 139.82 ( $\text{C}_7$ -Ph), 137.08 ( $\text{C}_4$  py), 133.14 ( $\text{C}_3$  py), 128.97 ( $\text{C}_{10}$ Ph), 128.78 ( $\text{C}_5$  py), 127.26 ( $\text{C}_8$ Ph), 118.45 ( $\text{C}_9$ Ph). Elemental analysis (%) calcd for 4 ( $\text{C}_{33}\text{H}_{24}\text{BiN}_3$ ): C 59.0, H 3.6, N 6.3. Found: C 59.1, H 3.7, N 6.4. HR-MS [ESI, positive ion mode ESI-TOF]:  $m/z$  for  $\text{C}_{18}\text{H}_{19}\text{BiF}_9\text{N}_3$  [ $4+\text{H}$ ] $^+$  calcd: 672.1847. Found: 672.1856 ( $-1.41$  ppm error).

**Synthesis of 5-LiCl-CH<sub>2</sub>Cl<sub>2</sub>.** 2-Bromopyridine (1.90 mL, 20 mmol) was dissolved in THF (40 mL). To this was added dropwise  $^n\text{BuLi}$  (8 mL, 20 mmol, 2.5 M in hexane) over 30 min at  $-78\text{ }^{\circ}\text{C}$ . The resulting green suspension was stirred for 2.5 h at  $-78\text{ }^{\circ}\text{C}$ . A suspension of  $\text{BiCl}_3$  (2.1 g, 6.66 mmol) in THF (6 mL) was added dropwise to lithiated species, and the resulting gray mixture was allowed to reach room temperature. After overnight stirring, a gray solution with a white precipitate was observed. All volatiles were removed under vacuum, and the resulting solid residue was extracted with DCM (40 mL). The suspension was filtered through Celite to yield a red solution, which was concentrated under vacuum, and slow diffusion of *n*-hexane (20 mL) at  $-24\text{ }^{\circ}\text{C}$  yielded 5-LiCl-CH<sub>2</sub>Cl<sub>2</sub> as white needles suitable for X-ray crystallography. Yield (calculated as 5-LiCl-CH<sub>2</sub>Cl<sub>2</sub>): 2.35 g (4.11 mmol, 61%).  $^1\text{H}$  NMR (298 K, DMSO- $d_6$ , 500 MHz):  $\delta$  = 8.60 (m, 3H,  $\text{H}_6$  py), 7.80–7.72 (m, 6H,  $\text{H}_4$ + $\text{H}_5$  py), 7.29 (m, 3H,  $\text{H}_3$  py).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K, DMSO- $d_6$ , 100.6 MHz):  $\delta$  = 194.53 ( $\text{C}_2$  py), 152.45 ( $\text{C}_6$  py), 136.75 ( $\text{C}_4$  py), 134.30 ( $\text{C}_5$  py), 122.29 ( $\text{C}_3$  py).  $^7\text{Li}$  NMR (298 K, DMSO- $d_6$ , 194.2 MHz):  $\delta$  =  $-1.07$ .  $^7\text{Li}$  NMR (298 K,  $\text{CDCl}_3$ , 194.2 MHz):  $\delta$  = 6.25. Elemental analysis (%) calcd for 5-LiCl-CH<sub>2</sub>Cl<sub>2</sub>( $\text{C}_{16}\text{H}_{14}\text{BiCl}_3\text{LiN}_3$ ): C 33.7, H 2.5, N 7.4. Found: C 34.0, H 2.7, N 8.2. HR-MS [ESI, positive ion mode ESI-TOF]:  $m/z$  for  $\text{C}_{15}\text{H}_{12}\text{BiLiN}_3$  [ $5+\text{Li}$ ] $^+$  calcd: 450.0990. Found: 450.0981 (2.07 ppm error).

**Synthesis of 6-LiBr-CH<sub>2</sub>Cl<sub>2</sub>.** 2-Bromo-5-(methyl)pyridine (1.72 g, 10 mmol) was dissolved in THF (20 mL). To this was added dropwise  $^n\text{BuLi}$  (4 mL, 10 mmol, 2.5 M in hexane) over 30 min at  $-78\text{ }^{\circ}\text{C}$ . The resulting red solution was stirred for 2.5 h at  $-78\text{ }^{\circ}\text{C}$ . A solution of  $\text{BiBr}_3$  (1.49 g, 3.33 mmol) in THF (5 mL) was added dropwise to the dark red lithiated species. The resulting pale brown mixture was allowed to reach room temperature. After overnight stirring, a brown solution with a white precipitate was observed. All volatiles were removed under vacuum, and the resulting solid residue was extracted with DCM (20 mL). The suspension was filtered through Celite to yield a brown solution, which was concentrated under vacuum, and slow diffusion of *n*-hexane (20 mL) at  $-24\text{ }^{\circ}\text{C}$  yielded 6-LiBr-CH<sub>2</sub>Cl<sub>2</sub> as white needles suitable for X-ray crystallography. Yield (calculated as 6-LiBr-CH<sub>2</sub>Cl<sub>2</sub>): 1.59 g (2.42 mmol, 73%).  $^1\text{H}$  NMR (298 K, DMSO- $d_6$ , 500 MHz):  $\delta$  = 8.45 (s, 3H,  $\text{H}_6$  py), 7.58 (s, 6H,  $\text{H}_3$ + $\text{H}_4$  py), 2.23 (s, 3H,  $\text{H}_7$  Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K, DMSO- $d_6$ , 100.6 MHz):  $\delta$  = 189.57 ( $\text{C}_2$  py), 152.78 ( $\text{C}_6$  py), 137.36 ( $\text{C}_4$  py), 133.80 ( $\text{C}_3$  py), 131.35 ( $\text{C}_5$  py), 18.01 ( $\text{C}_7$  Me).  $^7\text{Li}$  NMR (298 K, DMSO- $d_6$ , 194.2 MHz):  $\delta$  =  $-1.16$ . Elemental analysis (%) calcd for 6-LiBr-CH<sub>2</sub>Cl<sub>2</sub> ( $\text{C}_{19}\text{H}_{20}\text{BiBrCl}_2\text{LiN}_3$ ): 34.7, H 3.1, N 6.4. Found: C 34.0, H 3.2, N 6.5.

**Synthesis of 6-LiCl.** 2-Bromo-5-(methyl)pyridine (3.44 g, 20 mmol) was dissolved in THF (40 mL). To this was added dropwise  $^n\text{BuLi}$  (8 mL, 20 mmol, 2.5 M in hexane) over 30 min at  $-78\text{ }^{\circ}\text{C}$ . The resulting red solution was stirred for 2.5 h at  $-78\text{ }^{\circ}\text{C}$ . A suspension of  $\text{BiCl}_3$  (2.1 g, 6.66 mmol) in THF (6 mL) was added dropwise to the dark red lithiated species. The resulting pale brown mixture was allowed to reach room temperature. After stirring overnight, a brown solution with a white precipitate was observed. All volatiles were removed under vacuum, and the resulting solid residue was extracted with DCM (40 mL). The suspension was filtered through Celite to yield a red solution, which was concentrated under vacuum, and slow diffusion of *n*-hexane (20 mL) at  $-24\text{ }^{\circ}\text{C}$  yielded 6-LiX-CH<sub>2</sub>Cl<sub>2</sub> as white needles suitable for X-ray crystallography. Elemental analysis

was hampered by salt metathesis resulting in LiX (where X is a mixture of Cl and Br, leading to  $\text{X} = \text{Cl}_{0.6}\text{Br}_{0.4}$  as determined from single crystal X-ray crystallography). This problem was avoided in the preparation of the analogous 6-LiBr described above. Yield (calculated as 6-LiCl<sub>0.6</sub>Br<sub>0.4</sub>-CH<sub>2</sub>Cl<sub>2</sub>): 2.4 g (3.80 mmol, 57.05%).  $^1\text{H}$  NMR (298 K, DMSO- $d_6$ , 500 MHz):  $\delta$  = 8.45 (s, 3H,  $\text{H}_6$  py), 7.58 (s, 6H,  $\text{H}_3$ + $\text{H}_4$  py), 2.23 (s, 3H,  $\text{H}_7$  Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K, DMSO- $d_6$ , 100.6 MHz):  $\delta$  = 189.57 ( $\text{C}_2$  py), 152.78 ( $\text{C}_6$  py), 137.36 ( $\text{C}_4$  py), 133.80 ( $\text{C}_3$  py), 131.35 ( $\text{C}_5$  py), 18.01 ( $\text{C}_7$  Me).  $^7\text{Li}$  NMR (298 K, DMSO- $d_6$ , 194.2 MHz):  $\delta$  =  $-1.02$ .  $^7\text{Li}$  NMR (298 K,  $\text{CDCl}_3$ , 194.2 MHz):  $\delta$  = 6.21. HR-MS [Maldi, positive ion mode Maldi-TOF]:  $m/z$  for  $\text{C}_{18}\text{H}_{18}\text{BiN}_3$  [ $6+\text{H}$ ] $^+$  calcd: 486.1377. Found: 486.1388 (1.1 ppm error).

**Synthesis of 6-OTf.** 6-LiX (X = Cl or Br, 0.294 mmol) was dissolved in DCM (10 mL). To this was added AgOTf (75.5 mg, 0.294 mmol). The resulting white suspension was stirred for 1 h at rt. The suspension was filtered through Celite to yield a colorless solution which was concentrated under vacuum, and slow diffusion of *n*-hexane (5 mL) at  $-24\text{ }^{\circ}\text{C}$  yielded 6-OTf as white needles suitable for X-ray crystallography. Yield 48 mg (0.082 mmol, 41%).  $^1\text{H}$  NMR (298 K,  $\text{CDCl}_3$ , 500 MHz):  $\delta$  = 8.83 (d,  $J$  = 2.0 Hz, 3H,  $\text{H}_6$  py), 7.72 (d,  $J$  = 7.70 Hz, 3H,  $\text{H}_3$ ), 7.51 (dd,  $J$  = 2.0/7.70 Hz, 3H,  $\text{H}_4$ ), 2.26 (s, 9H,  $\text{H}_7$  Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K,  $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  = 181.4 ( $\text{C}_2$  py), 154.7 ( $\text{C}_6$  py), 137.8 ( $\text{C}_4$  py), 134.7 ( $\text{C}_3$  py), 134.1 ( $\text{C}_5$  py), 18.7 ( $\text{C}_7$  Me).  $^7\text{Li}$  NMR (298 K,  $\text{CDCl}_3$ , 194.2 MHz):  $\delta$  = 5.35.  $^{19}\text{F}$  NMR (298 K, MeCN- $d_3$ , 376 MHz):  $\delta$  =  $-78.02$  (s, 3F, OTf $^-$ ).

**Synthesis of 7-LiBr-0.5CH<sub>2</sub>Cl<sub>2</sub>.** 2-Bromo-3-(methyl)pyridine (1.11 mL, 10 mmol) was dissolved in THF (20 mL). To this was added dropwise  $^n\text{BuLi}$  (4 mL, 10 mmol, 2.5 M in hexane) (30 min) at  $-78\text{ }^{\circ}\text{C}$ . The resulting dark red solution was stirred for 2 h at  $-78\text{ }^{\circ}\text{C}$ . A solution of  $\text{BiBr}_3$  (1.49 g, 3.33 mmol) in THF (5 mL) was added dropwise to the dark red lithiated species. The resulting brown mixture was allowed to reach room temperature. After overnight stirring, a colorless solution with a white precipitate was observed. All volatiles were removed under vacuum, and the resulting solid residue was extracted with DCM (20 mL). The suspension was filtered through Celite to yield a red solution, which was concentrated under vacuum, and slow diffusion of *n*-hexane (20 mL) at  $-24\text{ }^{\circ}\text{C}$  yielded 7-LiBr-CH<sub>2</sub>Cl<sub>2</sub> as white crystals suitable for X-ray crystallography. Yield (calculated as 7-LiBr-0.5CH<sub>2</sub>Cl<sub>2</sub>): 1.44 g (2.34 mmol, 75%).  $^1\text{H}$  NMR (298 K, DMSO- $d_6$ , 500 MHz):  $\delta$  = 8.29 (d,  $J$  = 4.65 Hz, 3H,  $\text{H}_6$  py), 7.66 (d,  $J$  = 7.5 Hz, 6H,  $\text{H}_4$  py), 7.20–7.23 (m, 3H,  $\text{H}_5$  py), 2.22 (s, 3H,  $\text{H}_7$  Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K, DMSO- $d_6$ , 100.6 MHz):  $\delta$  = 195.92 ( $\text{C}_2$  py), 149.71 ( $\text{C}_6$  py), 142.89 ( $\text{C}_3$  py), 136.39 ( $\text{C}_4$  py), 121.99 ( $\text{C}_5$  py), 22.56 ( $\text{C}_7$  Me).  $^7\text{Li}$  NMR (298 K, DMSO- $d_6$ , 194.2 MHz):  $\delta$  =  $-1.15$ . Elemental analysis (%) Calcd for 7-LiBr-0.5CH<sub>2</sub>Cl<sub>2</sub>( $\text{C}_{18.5}\text{H}_{19}\text{BiBrClLiN}_3$ ): C 36.2, H 3.1, N 6.8. Found: C 36.5, H 3.3, N 7.3.

**Synthesis of 7-LiX.** 2-Bromo-3-(methyl)pyridine (2.22 mL, 20 mmol) was dissolved in THF (30 mL). To this was added dropwise  $^n\text{BuLi}$  (8 mL, 20 mmol, 2.5 M in hexane) over 30 min at  $-78\text{ }^{\circ}\text{C}$ . The resulting dark red solution was stirred for 2 h at  $-78\text{ }^{\circ}\text{C}$ . A suspension of  $\text{BiCl}_3$  (2.1 g, 6.66 mmol) in THF (6 mL) was added dropwise to the dark red lithiated species. The resulting brown mixture was allowed to reach room temperature. After overnight stirring, a colorless solution with a white precipitate was observed. All volatiles were removed under vacuum, and the resulting solid residue was extracted with DCM (40 mL). The suspension was filtered through Celite to yield a red solution, which was concentrated under vacuum, and slow diffusion of *n*-hexane (20 mL) at  $-24\text{ }^{\circ}\text{C}$  yielded 7-LiCl<sub>0.7</sub>Br<sub>0.3</sub>-CH<sub>2</sub>Cl<sub>2</sub> as white needles suitable for X-ray crystallography. When the samples were left under persistent vacuum, an amorphous material that was found to contain no CH<sub>2</sub>Cl<sub>2</sub> solvation was obtained, corresponding to 7-LiCl<sub>0.7</sub>Br<sub>0.3</sub>. Yield (calculated as 7-LiCl<sub>0.7</sub>Br<sub>0.3</sub>): 1.78 g (3.28 mmol, 49.2%).  $^1\text{H}$  NMR (298 K, DMSO- $d_6$ , 500 MHz):  $\delta$  = 8.29 (d,  $J$  = 4.65 Hz, 3H,  $\text{H}_6$  py), 7.66 (d,  $J$  = 7.5 Hz, 6H,  $\text{H}_4$  py), 7.20–7.23 (m, 3H,  $\text{H}_5$  py), 2.22 (s, 3H,  $\text{H}_7$  Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR (298 K, DMSO- $d_6$ , 100.6 MHz):  $\delta$  = 195.92 ( $\text{C}_2$  py), 149.71 ( $\text{C}_6$  py), 142.89 ( $\text{C}_3$  py), 136.39 ( $\text{C}_4$  py), 121.99 ( $\text{C}_5$  py), 22.56 ( $\text{C}_7$  Me).  $^7\text{Li}$  NMR (298 K, DMSO- $d_6$ , 194.2 MHz):  $\delta$  =  $-0.91$ .  $^7\text{Li}$  NMR (298 K,

CDCl<sub>3</sub>, 194.2 MHz):  $\delta$  = 6.73. HR-MS [Maldi, positive ion mode Maldi-TOF]:  $m/z$  for C<sub>18</sub>H<sub>18</sub>BiLiN<sub>3</sub> [7+Li]<sup>+</sup> calcd: 492.1460. Found: 492.1485 (2.5 ppm error). HR-MS [Maldi, positive ion mode Maldi-TOF]:  $m/z$  for C<sub>18</sub>H<sub>18</sub>BiN<sub>3</sub> [7+H]<sup>+</sup> calcd: 486.1377. Found: 486.1405 (2.8 ppm error). We found that when samples were left to crystallize for long periods, salt metathesis can occur, leading to the formation of crystals of 7LiX (X = Cl, Br) containing variable amounts of LiBr. When this happens, bulk samples of pure 7-LiCl can be obtained by treatment with an excess of tetrabutyl ammonium chloride (TBACl) as follows. Typically, 100 mg of LiX and TBACl (415 mg, 3.79 mmol) was dissolved in DCM (4 mL). After overnight stirring, the colorless solution was concentrated under vacuum, and slow diffusion of *n*-hexane (3 mL) at -24 °C yielded 7-LiCl·CH<sub>2</sub>Cl<sub>2</sub> as colorless crystals suitable for X-ray crystallography. Yield (calculated as 7-LiCl·CH<sub>2</sub>Cl<sub>2</sub>): 62.8 mg (0.11 mmol, 58%). Elemental analysis (%) Calcd for 7-LiCl (C<sub>18</sub>H<sub>18</sub>BiClLiN<sub>3</sub>): C 41.0, H 3.4, N 8.00. Found: C 41.8, H 4.0, N 8.1.

**Decoordination of LiX from Ligands 5 and 6.** A suspension of 5-LiX or 6-LiX (0.20 mmol) in toluene (10 mL) was extracted with water (3 × 2 mL). The extract was dried over anhydrous magnesium sulfate and then filtered through Celite. The solvent was removed by evaporation under reduced pressure to give a white oil, which yielded crystalline samples of halide-free 5 and 6 as colorless needles overnight at -24 °C. The absence of LiX in the samples was verified by <sup>7</sup>Li NMR spectroscopy. Compound 5. Yield: 65.7 mg (0.148 mmol, 72%). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 8.68 (m, 3H, H<sub>6</sub> py), 7.73 (m, 6H, H<sub>5</sub> py), 7.65 (m, 3H, H<sub>4</sub> py), 8.21 (m, 3H, H<sub>3</sub> py). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, CDCl<sub>3</sub>, 100.6 MHz):  $\delta$  = 194.3 (C<sub>2</sub> py), 152.9 (C<sub>6</sub> py), 137.2 (C<sub>4</sub> py), 134.0 (C<sub>5</sub> py), 122.3 (C<sub>3</sub> py). HR-MS [Maldi, positive ion mode Maldi-TOF]:  $m/z$  for C<sub>15</sub>H<sub>12</sub>BiN<sub>3</sub> [M + H]<sup>+</sup> calcd: 444.0908. Found: 444.0919 (1.1 ppm error). Compound 6. Yield 59.2 mg (0.12 mmol, 64%). <sup>1</sup>H NMR (298 K, CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 8.51 (br, 3H, H<sub>6</sub> py), 7.58 (d, *J* = 7.70 Hz, 3H, H<sub>3</sub>), 7.43 (dd, *J* = 2.0/7.70 Hz, 3H, H<sub>4</sub>), 2.26 (s, 9H, H<sub>7</sub> Me). HR-MS [Maldi, positive ion mode Maldi-TOF]:  $m/z$  for C<sub>18</sub>H<sub>18</sub>BiN<sub>3</sub> [M + H]<sup>+</sup> calcd: 486.1377. Found: 486.1388 (1.1 ppm error).

**Synthesis of Silver Complexes 8-X (X = OTf, BF<sub>4</sub>, PF<sub>6</sub>).** The corresponding silver salt (0.144 mmol) (36.99 mg, 28.03 mg, and 36.40 mg for AgOTf, AgBF<sub>4</sub>, and AgPF<sub>6</sub>, respectively) was dissolved in MeCN (5 mL) in the dark. After stirring the mixture for 1 h, all volatiles were removed under vacuum, and the resulting white solid was dissolved in THF (5 mL). Bi(6-Me-2-py)<sub>3</sub> (1) (70 mg, 0.144 mmol) in THF (3 mL) was added to give a white precipitate. The solvents were evaporated, the residue was dissolved in MeCN (5 mL), and the solution was concentrated until the formation of a white precipitate was observed, which was redissolved by gentle heating. Storage at -24 °C yielded 8-OTf·CH<sub>3</sub>CN, 8-BF<sub>4</sub>, and 8-PF<sub>6</sub>·2CH<sub>3</sub>CN as colorless crystals suitable for X-ray crystallography. Crystalline yield (calculated for all crystals): 62.6 mg (0.076 mmol, 53%), 60.5 mg (0.084 mmol, 60%), and 58.5 mg (0.068 mmol, 47%), respectively. The crystals were found to be very unstable toward light and moisture, resulting in loss of crystallinity and the rapid formation of a black amorphous solid, which hampered elemental analysis. <sup>1</sup>H and <sup>13</sup>C NMR spectra for 8-X were found to be identical within the experimental error. <sup>1</sup>H NMR (298 K, MeCN-*d*<sub>3</sub>, 500 MHz):  $\delta$  = 7.83 (d, *J* = 7.40 Hz, 3H, H<sub>3</sub> py), 7.76 (t, *J* = 7.40 Hz, 3H, H<sub>4</sub> py), 7.32 (d, *J* = 7.40 Hz, 3H, H<sub>5</sub> py), 2.74 (s, 9H, H<sub>7</sub> Me). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, MeCN-*d*<sub>3</sub>, 100.6 MHz):  $\delta$  = 194.2 (br, C<sub>2</sub> py), 161.9 (C<sub>6</sub> py), 137.9 (C<sub>4</sub> py), 133.5 (C<sub>3</sub> py), 124.0 (C<sub>5</sub> py), 25.8 (C<sub>7</sub> Me). 8-OTf: <sup>19</sup>F NMR (298 K, MeCN-*d*<sub>3</sub>, 376 MHz):  $\delta$  = -79.25 (s, 3F, OTf<sup>-</sup>). 8-BF<sub>4</sub>: <sup>19</sup>F NMR (298 K, MeCN-*d*<sub>3</sub>, 376 MHz):  $\delta$  = -151.71 (br, <sup>10</sup>BF<sub>4</sub><sup>-</sup>), -151.76 (br, <sup>11</sup>BF<sub>4</sub><sup>-</sup>). 8-PF<sub>6</sub>: <sup>19</sup>F NMR (298 K, MeCN-*d*<sub>3</sub>, 376 MHz):  $\delta$  = -72.8 (d, 6F, *J*<sub>PF</sub> = 707 Hz, PF<sub>6</sub><sup>-</sup>). HR-MS [Maldi, positive ion mode Maldi-TOF]:  $m/z$  for C<sub>18</sub>H<sub>18</sub>AgBiN<sub>3</sub> [8-CH<sub>3</sub>N]<sup>+</sup> calcd: 592.035. Found: 592.0349 (-0.1 ppm error).

**Synthesis of 9-BF<sub>4</sub>.** AgBF<sub>4</sub> (14.49 mg, 0.074 mmol) was dissolved in MeCN (2 mL) in the dark. After 30 min of stirring, all volatiles were removed under vacuum, and the resulting white solid was redissolved in THF (2 mL). Then, Bi(6-Ph-2-py)<sub>3</sub> (4) (50 mg, 0.074 mmol) in THF (2 mL) was added to give a white precipitate.

Subsequently, the solvents were evaporated, and the residue was redissolved in MeCN (5 mL). The colorless solution was concentrated under vacuum until the precipitation of a white precipitate was observed. Storage at -24 °C yielded 9-BF<sub>4</sub> as colorless crystals suitable for X-ray crystallography. The product was isolated by filtration. Yield 45 mg (0.049 mmol, 66%). Similarly to 8-X, the crystals of 9-BF<sub>4</sub> were found to be very unstable toward light and moisture, resulting in rapid loss of crystallinity and formation of a black amorphous solid, which hampered elemental analysis. <sup>1</sup>H NMR (298 K, MeCN-*d*<sub>3</sub>, 500 MHz):  $\delta$  = 8.00–7.96 (m, 6H, H<sub>3</sub>+H<sub>4</sub> py), 7.71 (m, 3H, H<sub>5</sub> py), 7.59 (d, *J* = 7.10 Hz, 6H, H<sub>8</sub> Ph), 7.39 (t, *J* = 7.10 Hz, 6H, H<sub>10</sub> Ph), 7.31 (t, *J* = 7.10 Hz, 6H, H<sub>9</sub> Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, MeCN-*d*<sub>3</sub>, 100.6 MHz):  $\delta$  = 198.3 (br, C<sub>2</sub> py), 163.19 (C<sub>6</sub> py), 141.9 (C<sub>7</sub> Ph), 139.3 (C<sub>4</sub> py), 135.6 (C<sub>3</sub> py), 130.2 (C<sub>10</sub> Ph), 129.4 (C<sub>9</sub> Ph), 128 (C<sub>8</sub> Ph), 123.2 (C<sub>5</sub> Ph). <sup>19</sup>F NMR (298 K, MeCN-*d*<sub>3</sub>, 376 MHz):  $\delta$  = -151.97 (s, <sup>10</sup>BF<sub>4</sub><sup>-</sup>), -152.03 (s, <sup>11</sup>BF<sub>4</sub><sup>-</sup>). HR-MS [Maldi, positive ion mode Maldi-TOF]:  $m/z$  for C<sub>33</sub>H<sub>24</sub>AgBiN<sub>3</sub> [9-CH<sub>3</sub>CN]<sup>+</sup> calcd: 778.0820. Found: 778.0824 (0.4 ppm error).

**Synthesis of 10.** Bi(6-Me-2-py)<sub>3</sub> (150 mg, 0.30 mmol) was dissolved in MeCN (2 mL)/THF (2 mL). To this solution was added [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> (97.1 mg, 0.30 mmol). The resulting pale-yellow solution was stirred for 24 h at room temperature. The solution was filtered through Celite to yield a red solution, which was concentrated under vacuum. Storage at -24 °C for several weeks yielded 10 as a few orange crystals suitable for X-ray crystallography, along with the red crystals of [Cu(Me-bpy)<sub>2</sub>]BF<sub>4</sub> (Me-bpy = 6,6'-dimethyl-2,2'-bipyridyl; see the SI) and a black precipitate.

**Synthesis of 11a·CH<sub>3</sub>CN.** Bi(6-Me-2-py)<sub>3</sub>(1) (100 mg, 0.20 mmol) was dissolved in MeCN (5 mL). To this solution was added CuCl<sub>2</sub> (27.7 mg, 0.20 mmol). The resulting red solution was stirred for 15 min at rt. The solution was filtered through Celite to yield a red solution, which was concentrated under vacuum, and slow diffusion of diethyl ether (5 mL) at -24 °C yielded 11a·CH<sub>3</sub>CN as red pale crystals suitable for X-ray crystallography. 11a·CH<sub>3</sub>CN yield (calculated as 11a·CH<sub>3</sub>CN): 48 mg (0.078 mmol, 40%). <sup>1</sup>H NMR (298 K, MeCN-*d*<sub>3</sub>, 500 MHz):  $\delta$  = 8.20 (d, *J* = 7.70 Hz, 2H, H<sub>3</sub> py), 7.91 (t, *J* = 7.70 Hz, 2H, H<sub>4</sub> py), 7.32 (d, *J* = 7.70 Hz, 2H, H<sub>5</sub> py), 2.79 (s, 6H, H<sub>7</sub> Me). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, MeCN-*d*<sub>3</sub>, 100.6 MHz):  $\delta$  = 216.6 (br, C<sub>2</sub> py), 163.5 (C<sub>6</sub> py), 139.0 (C<sub>4</sub> py), 135.4 (C<sub>3</sub> py), 124.4 (C<sub>5</sub> py), 26.0 (C<sub>7</sub> Me). Elemental analysis (%) calcd for 11a·CH<sub>3</sub>CN (C<sub>16</sub>H<sub>18</sub>BiCl<sub>2</sub>CuN<sub>4</sub>): C 31.5, H 3.0, N 9.2. Found C 31.0, H 2.9, N 8.6. HR-MS [Maldi, positive ion mode Maldi-TOF]:  $m/z$  for C<sub>12</sub>H<sub>12</sub>BiCl<sub>2</sub>Cu [M-Cl-CH<sub>3</sub>CN]<sup>+</sup> calcd: 490.9783. Found: 490.9762 (-2.1 ppm error).

**Synthesis of 11b.** Bi(6-CF<sub>3</sub>-2-py)<sub>3</sub> (3) (200 mg, 0.30 mmol) was dissolved in MeCN (5 mL). To this solution was added CuCl<sub>2</sub> (124.6 mg, 0.90 mmol). The resulting pale-yellow solution was stirred overnight at rt. The solution was filtered through Celite to yield a yellow solution, which was concentrated under vacuum, and slow diffusion of diethyl ether (5 mL) at -24 °C yielded 11b as yellow blocks suitable for X-ray crystallography. Samples were found to contain variable amounts of the ligand Bi(6-CF<sub>3</sub>-2-py)<sub>3</sub> as demonstrated by crystallography and NMR studies. For this reason, a specific yield cannot be provided. <sup>1</sup>H NMR (298 K, MeCN-*d*<sub>3</sub>, 500 MHz):  $\delta$  = 8.47 (d, *J* = 7.80 Hz, 2H, H<sub>3</sub> py), 8.20 (t, *J* = 7.80 Hz, 2H, H<sub>4</sub> py), 7.76 (d, *J* = 7.80 Hz, 2H, H<sub>5</sub> py).

**Synthesis of 11c·CH<sub>2</sub>Cl<sub>2</sub>.** Bi(6-Me-2-py)<sub>3</sub> (100 mg, 0.20 mmol) was dissolved in MeCN (5 mL). To this solution was added CuBr<sub>2</sub> (46 mg, 0.20 mmol). The resulting red solution was stirred for 15 min at rt. The solution was filtered through Celite to yield a red solution, which was concentrated under vacuum. Slow diffusion of diethyl ether (5 mL) at -24 °C yielded 11c·CH<sub>2</sub>Cl<sub>2</sub> as pale red crystals suitable for X-ray crystallography. Yield (calculated as 11c·CH<sub>2</sub>Cl<sub>2</sub>) 36.8 mg (0.049 mmol, 24%). <sup>1</sup>H NMR (298 K, MeCN-*d*<sub>3</sub>, 500 MHz):  $\delta$  = 8.35 (d, *J* = 7.80 Hz, 2H, H<sub>3</sub> py), 7.88 (t, *J* = 7.80 Hz, 2H, H<sub>4</sub> py), 7.35 (d, *J* = 7.80 Hz, 2H, H<sub>5</sub> py), 2.79 (s, 6H, H<sub>7</sub> Me). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, MeCN-*d*<sub>3</sub>, 100.6 MHz):  $\delta$  = 212.2 (br, C<sub>2</sub> py), 163.6 (C<sub>6</sub> py), 139.0 (C<sub>4</sub> py), 137.0 (C<sub>3</sub> py), 124.5 (C<sub>5</sub> py), 25.9 (C<sub>7</sub> Me). HR-MS

[Maldi, positive ion mode Maldi-TOF]:  $m/z$  for  $C_{12}H_{12}BiBrN_2Cu$  [ $M-Br-CH_3CN$ ] $^+$  calcd: 536.9259. Found: 536.926 (0.1 ppm error).

**Synthesis of 12.** Inside a  $N_2$  filled glovebox, a Schlenk tube was charged with  $Bi(6-Me-2-py)_3$  (**1**) (200 mg, 0.41 mmol) and  $FeCl_2$  (52 mg, 0.41 mmol) and transferred to a Schlenk line. Twenty milliliters of THF was added. The resulting pale orange solution was stirred overnight at room temperature. An orange solution with a small amount of brown precipitate formed overnight and was removed by filtration. The clear orange filtrate was concentrated under vacuum to approximately 5 mL. Storage at  $-20$  °C yielded a few yellow crystals suitable for X-ray crystallography.

**Synthesis of 13.**  $FeI_2$  (92.8 mg, 0.30 mmol) was dissolved in THF (5 mL). To this black solution was added  $Bi(6-Me-2-py)_3$  (**1**) (150 mg, 0.30 mmol). The resulting brown suspension was stirred overnight at room temperature. All volatiles were removed under vacuum, and the resulting solid residue was redissolved in MeCN (5 mL). This suspension was filtered through Celite, which was redissolved by gentle heating. Storage overnight at  $-24$  °C yielded **13** as a few yellow crystals suitable for X-ray crystallography.

**Synthesis of 14-OTf.**  $(PPh)_3AuOTf$  (15.9 mg, 0.032 mmol) and  $Bi(6-Me-2-py)_3$  were dissolved in acetone (2 mL). Then, a solution of  $Bi(6-Me-2-py)_3$  (**1**) (20 mg, 0.032 mmol) was added. After stirring for 30 min at room temperature, the colorless solution was concentrated under vacuum. Storage at  $-24$  °C yielded **14** as a few colorless blocks suitable for X-ray crystallography.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00579>.

NMR spectra, additional X-ray structures, details and information, and HR-MS data (PDF)

### Accession Codes

CCDC 1981115–1981137 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors.

### Notes

The authors declare no competing financial interest.

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