



Coinage Metal Complexes | Very Important Paper |

Coinage Metal (Bisfluorosulfonyl)imide Complexes: Preparation, Characterization, and Catalytic Applications

Yu Tang^[a] and Biao Yu^{*[a]}

Abstract: Triflate ($^{-}$ OTf) and triflimide ($^{-}$ NTf₂) represent two most widely used weakly coordinating counteranions in transition metal catalysis, yet their high price hinders large-scale application. Herein, we report the preparation, characterization, and catalytic applications of silver(I), gold(I), and copper(II) (bisfluoro-sulfonyl)imide ($^{-}$ FSI) complexes, showing $^{-}$ FSI as a low cost alternative of $^{-}$ OTf and $^{-}$ NTf₂. These complexes, including AqFSI-2MeCN (**1**), AqFSI-MeCN (**2**), AqFSI-H₂O (**3**), (AqFSI)₆•(H₂O)₄

(4), AgFSI (5), LAuFSI (6a–6e), and CuFSI₂·4H₂O (7), are prepared conveniently starting from KFSI, an inexpensive chemical, and shown interesting structural features and some unprecedented coordination modes. In comparison with the corresponding coinage metal triflimides, the FSI complexes have exhibited comparable or better catalytic performance in a series of the model chemical transformations.

Introduction

The choice of a proper counteranion is critically important in the development of a successful transition metal catalyst,^[1] which influences the structure and catalytic activity of the catalyst,^[2,3] and the kinetics^[4] and selectivity of the catalyzed reactions.^[5,6] Compared to the various types of ligands developed, the types of counteranions that are commonly employed in transition metal catalysis are limited.^[1a,1f,7] Among these counteranions, anions based on the $[E(SO_2R^F)_n]^-$ motif (where E = O, N, or C), especially triflate (-OSO2CF3 or -OTf) and triflimide $(-N(SO_2CF_3)_2 \text{ or } -NTf_2)$, represent the most widely used types of counteranions (Figure 1).^[8,9] In the category of weakly coordinating counteranions, -OTf and -NTf₂ have many advantages in terms of high stability, low nucleophilicity and easy availability. A large number of transition metal-catalyzed reactions developed during the past two decades employed -OTf or -NTf₂ as the counteranion of the catalysts in the optimal catalytic systems,^[9] which were usually established after extensive screening of a series of catalysts with difference only in the counteranions. Despite the excellent performance and numerous applications of metal triflates and metal triflimides as catalysts, a major and inherent drawback of these counteranions lies in their high cost.^[10] The production of triflic acid (HOTf) and triflylimide (HNTf₂), the starting reagents for the preparation of metal triflates and triflimides, requires electrochemical fluorination to introduce the -CF₃ moiety,^[8] which is a high-cost

 [a] State Key Laboratory of Bioorganic and Natural Products Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China E-mail: byu@sioc.ac.cn http://biaoyu.sioc.ac.cn
 Supporting information and ORCID(s) from the author(s) for this article are

available on the WWW under https://doi.org/10.1002/ejic.201901058.

and high energy consuming process. Thus, developing inexpensive counteranions and exploiting their metal complexes as catalysts comparable to or even better than the corresponding metal triflates and triflimides becomes an important task for the future development and application of transition metal catalysis.^[11]



Figure 1. Representative counteranions based on the $[\mathrm{E}(\mathrm{SO}_2\mathrm{R}^f)_n]^-$ motif and the present work.

(Bisfluorosulfonyl)imide (~N(SO₂F)₂ or ~FSI) anion was firstly reported by Ruff in 1965,^[12] but has received little attention during the subsequent four decades.^[13,14] Recently, alkali metal FSI salts, i.e., MFSI (M = Li, Na, K), has received an increasing attention as energy storage materials,^[15] which have been produced on industrial scale and become the inexpensive commercial FSI source. Other types of the FSI derivatives have so far been reported scarcely.^[16] Thus, trimethylsilyl (bisfluorosulfonyl)imide (TMSFSI) has found applications as Lewis acid catalyst in a few organic transformations.^[17] Transition metal FSI complexes, other than Ruff's sliver(I) FSI complexes, have not vet been exploited. In 2014, Sharpless and Dong et al. reported a new click reaction based on sulfur(VI) fluoride exchange.^[18] Recently, they disclosed a stable fluorosulfuryl imidazolium salt,^[19] showing that the sulfonyl fluoride motif is considerably stable under various conditions. In continuation of our own research on the gold(I)-catalyzed glycosylation reaction,^[20] we en-





visaged that replacing \neg OTf or \neg NTf₂ with FSI in the commonly used gold(I) catalysts might be able to reduce the cost and improve the efficiency.

Summarized in Figure 2 are some basic aspects of the FSI motif.^[12,21] The current procedure for the large-scale preparation of FSI salts is through the reaction of alkali metal (bischlorosulfuryl)imide salt with KF in apolar solvent (such as CH_2Cl_2) at reflux temperature,^[21] which is a much safe and economical process than the electrochemical fluorination required for the preparation of triflate and triflimide salts. The pK_a of HFSI in water at 25 °C is 1.28, whereas the corresponding HNTf₂ is 1.7, indicating that FSI has weaker basicity and coordination ability than ⁻NTf₂. Stability is another important property of a counteranion to be used in catalysis, and -FSI shows satisfactory stability in aqueous solutions, which remains stable in neutral or acidic solutions and proceeds slow hydrolysis in 30 % aqueous KOH at 100 °C. With these salient features, we expected that transition metal FSI complexes would have potentials as a new type of catalysts. Herein, we report the synthesis, characterization, and catalytic applications of coinage metal FSI complexes.



Stable in neutral or acidic aqueous solutions
 N-M
 Slowly hydrolyzed in 30% aqueous KOH at 100 °C

Figure 2. Some basic aspects of the FSI compounds.

Results and Discussion

Synthesis and Characterization of Silver(I) FSI Complexes

In Ruff's original work,^[12] Ag(I) FSI complexes were prepared by reaction of HFSI and Ag₂O in CF₃COOH or benzene. Several drawbacks exist in this procedure: HFSI is corrosive and not yet commercially available, and the solvent used is also corrosive or toxic. We thus sought to develop a new method to prepare Ag(I) FSI complexes. The alkali metal FSI salts are now commercially available and the potassium salt is the cheapest one. Solubility test indicated that KFSI easily dissolved in MeCN while KNO₃ is insoluble in MeCN. We thus planed to prepare Aq(I) FSI complexes through metathesis reaction of KFSI and AgNO₃ in MeCN. To our delight, mixing a MeCN solution of KFSI with an equimolar MeCN solution of AqNO₃ led to immediate precipitation of KNO₃, which was removed by filtration. Evaporation of the resulting colorless solution followed by vacuum drying to constant weight afforded a colorless liquid, which was identified to be $AgFSI(MeCN)_2$ (1) by gravimetric, elemental, and NMR analysis (Scheme 1). Surprisingly, complex 1 remained as a liguid even at -30 °C. In fact, several silver-containing ionic liquids have been reported recently, wherein the counteranions are usually $^{-}NTf_{2}$ or $^{-}OTf.^{[22]}$ Complex **1** represents the first low melting silver-containing ionic liquid bearing FSI as the counteranion.





Scheme 1. Synthesis of AgFSI(MeCN)_n complexes 1 and 2.

Complex **1** was readily dissolved in CH₂Cl₂, evaporation of the solvent followed by vacuum drying to constant weight afforded colorless crystals. The structure of the resulting crystals was identified to be AgFSI-MeCN (**2**) by single-crystal X-ray analysis (CCDC 1909180), and was also supported by gravimetric, elemental, and NMR analysis. In the crystals (Figure 3), half of the Ag(I) ions are coordinated by two MeCN molecular in a linear nitrogen-bound fashion, while the other half of Ag(I) ions are coordinated by two FSI anion in a linear nitrogen-bound fashion. Ag(I) disulfonylamide acetonitrile complexes have been synthesized and characterized by Jones and Blaschette et al.^[23] Four coordination modes were observed in these previous complexes; Ag(I) ion could be coordinated by up to four MeCN molecules or to two linear disulfonylamides.^[23] The structure of



Figure 3. Crystal structure of complex **2** at 30 % probability ellipsoids (hydrogen atoms are omitted for clarity).



Scheme 2. Synthesis of Ag(I)FSI hydrates 3 and 4.







Δ











Figure 4. (A) Crystal structure of complex 4 at 30 % probability ellipsoids. (B) Coordination modes of the Ag(I) ions (the outer-sphere Ag(I) atoms and hydrogen atoms are omitted for clarity).





complex 2 represents a new coordination mode in Ag(I) disulfonylamides nitrile complexes. The Ag-N bond length in the previous MeCN-Ag(I) cation range from 209.5 to 232.6 pm, while in complex 2, the length is 210.5(4) pm. The Ag-N bond length in disulfonylamides coordinated Ag(I) ion range from 212.7 to 230.0 pm, and in complex 2, the length is 220.2(3) pm. In both MeCN and disulfonylamides dicoordinated Ag(I) ion, the angles of N-Ag-N are 180°. Linear two acetonitrile coordinated Ag(I) ion has previously been observed in Ag(I) complex $[Aq(NCCH_3)_2][B\{C_6H_3(CF_3)_2\}_4]$ by Kühn et al.^[24] Two slightly different linear coordination geometry was observed, the Ag-N bond length are 209.7(2) pm and 206.6(4) pm, and the angles of N-Ag-N are 180°, similar to that in complex 2. Very interestingly, in those complexes, the C-N-Ag angles are 171.9(3)° and 177.2(2)°, indicating a slightly bent geometry, while in complex 2 the C-N-Ag angles are 179.9(4)°, indicating that the two MeCN ligand and Ag(I) ion are arrayed in a perfect linear geometry.

Both complexes **1** and **2** were easily dissolved in water, evaporation of the solvent followed by vacuum drying to constant weight afforded colorless crystals, which were identified to be AgFSI·H₂O (**3**) by gravimetric, elemental, and NMR analysis (Scheme 2). It is noteworthy that the hydrate forms of AgFSI and AgNTf₂ have not been reported previously,^[25] and complex **3** represents the first AgFSI hydrate characterized to date.

A sample of complex **3** was sealed in a flask and stayed at room temperature for 6 months, colorless block shaped crystals and a clear solution were formed. The crystals were collected and determined to be $(AgFSI)_{6^{+}}(H_2O)_4$ (**4**), which represents the first AgFSI hydrate characterized by X-ray diffraction analysis (CCDC 1909185).

Shown in Figure 4 is the crystal structure of complex 4, which is rather complex, containing six types of Aq(I) ions in six different coordination modes (modes 1-6). Selected bond lengths and angles are summarized in Table 1. In these structures, the Ag(I) ion are five-, six-, or seven-coordinated. Four types of Ag(I) ions (modes 1, 2, 4, and 6) are bridged by two µ2-oxygen of water ligands to form an unprecedented dimeric core $[Ag_2(\mu 2-H_2O)_2]^{2+}$ structure,^[25] and the remaining coordination sites are coordinated by the FSI anion acting as O-donor or N-donor ligand. Interestingly, in mode 4, the FSI anion acts an F-donor ligand (Ag-F distance 273.75 pm),^[27] highlighting the versatile coordination behavior of FSI anion as a multidentate O, N, or F ligand. In the remaining two non-water coordination modes (modes 3 and 5), each Ag(I) ion is coordinated by four FSI anions acting as bidentate O-donor or monodentate Ndonor, and only slight differences are observed between these two modes. The Ag-N bond lengths of the Ag-FSI coordination structure in di-nitrogen coordinated modes 3 and 5 range from 241.6(12) to 244.3(13) pm, longer than in mono N-coordinated mode 1 [228.1(14) pm] and mode 6 [232.6(15) pm], whereas in complex 2 the distance is 220.2(3) pm. The N-Ag-N angles are nearly perpendicular (89.7° in mode 3 and 92.0° in mode 5); such a perpendicular two N-coordination mode has not been observed in coinage metal NTf₂ complexes. In silver chemistry, it is well known that the coordination interaction between the soft Ag(I) cation and the hard water ligand is relatively low,^[28]

thus Ag(I) cation rarely coordinates directly with water in crystal structures.^[26] In fact, nearly all crystalline inorganic silver salts are anhydrous with few exceptions, such as AgClO₄ and AgF, and complex **4** represents a rare example of well characterized hydrated inorganic Ag(I) salt. Herein, the in-depth characterization of this complex yet fascinating structure furthers our understanding of the coordination interaction of the FSI anion with coinage metal ions.

Table 1. Selected bond lengths [pm] and angles (°) for the six coordination modes of Ag(I) ions in complex ${\bf 4}$.

Mode 1	Ag(1)-O(1W)#3 252.6(12) Ag(1)-O(1W) 236.2(12)				
	Ag(1)-O(19) 262.23 Ag(1)-O(21) 257.6(11)				
	Ag(1)-N(1) 228.1(14)				
	$O(1W)-Ag(1)-O(1W) \times 3$ 82.4(4) $O(1W)-Ag(1)-O(21)$ 82.3(4)				
	O(1W)#3-Ag(1)-O(21) 135.0(4) N(1)-Ag(1)-O(1W)#3 97.1(5)				
	N(1)-Ag(1)-O(1W) 178.0(5) N(1)-Ag(1)-O(21) 99.4(4)				
Mode 2	Ag(2)-O(2W) 238.0(12) Ag(2)-O(2W)#4 247.2(11)				
	Ag(2)-O(4) 287.40 Ag(2)-O(5) 257.1(14)				
	Ag(2)-O(7) 252.4(14) Ag(2)-O(9) 252.5(12)				
	Ag(2)-O(16) 261.17				
	O(2W)-Ag(2)-O(2W)#4 82.8(4) O(2W)#4-Ag(2)-O(5) 84.3(4)				
	O(2W)-Ag(2)-O(5) 142.2(4) O(2W)-Ag(2)-O(7) 145.8(4)				
	O(2W)#4-Ag(2)-O(7) 106.1(4) O(2W)#4-Ag(2)-O(9)133.4(4)				
	O(2W)-Ag(2)-O(9) 82.7(4) O(7)-Ag(2)-O(5) 72.0(4)				
	O(7)-Ag(2)-O(9) 110.6(4) O(9)-Ag(2)-O(5) 80.8(4)				
Mode 3	Ag(3)-N(3) 241.6(12) Ag(3)-N(4) 244.2(13)				
	Ag(3)-O(10) 269.27 Ag(3)-O(12) 260.71				
	Ag(3)-O(22) 264.85 Ag(3)-O(24) 262.44				
	N(3)-Ag(3)-N(4) 89.7(4)				
Mode 4	Ag(4)-O(2) 261.93 Ag(4)-O(3)#5 256.0(14)				
	Ag(4)-O(3W) 242.4(11) Ag(4)-O(3W)#6 247.9(11)				
	Ag(4)-O(11) 257.1(12) Ag(4)-O(13) 253.7(12)				
	Ag(4)-F(3) 273.75				
	O(3)#5-Ag(4)-O(11) 78.9(4) O(3W)-Ag(4)-O(3)#5 102.3(4)				
	O(3W)#6-Ag(4)-O(3)#5 154.5(4) O(3W)-Ag(4)-O(3W)#6 83.0(4)				
	O(3W)-Ag(4)-O(11) 130.2(4) O(3W)#6-Ag(4)-O(11) 78.8(4)				
	O(3W)#6-Ag(4)-O(13) 78.7(4) O(3W)-Ag(4)-O(13) 143.2(4)				
	O(13)-Ag(4)-O(3)#5107.9(4) O(13)-Ag(4)-O(11) 76.9(4)				
Mode 5	Ag(5)-O(14) 272.10 Ag(5)-O(15) 257.6(11)				
	Ag(5)-O(17) 270.06 Ag(5)-O(20) 260.50 Ag(5)-N(5) 243.2(14) Ag(5)-N(6) 244.3(13) N(5)-Ag(5)-O(15) 84.0(4) N(5)-Ag(5)-N(6) 92.0(5)				
	N(6)-Ag(5)-O(15) 149.2(4)				
Mode 6	Ag(6)-O(1) 266.64 Ag(6)-O(18) 261.28				
	Ag(6)-O(4W) 243.9(11) Ag(6)-O(4W)#1 249.7(11)				
	Ag(6)-O(23)#2 259.6(12) Ag(6)-N(2) 232.6(15) O(4W)-Ag(6)-O(4W)#1 80.9(4) O(4W)-Ag(6)-O(23)#2 76.8(4)				
	O(4W)#1-Ag(6)-O(23)#2 125.4(4) N(2)-Ag(6)-O(4W)#1 98.8(4)				
	N(2)-Ag(6)-O(4W) 174.5(4) N(2)-Ag(6)-O(23)#2 107.5(5)				

With hydrate **3** in hand, we attempted to prepare anhydrous AgFSI through dehydration. Heating hydrate **3** in air at 105 °C for 2 h led to partial decomposition, as observed by NMR. After many attempts, we managed to remove the water molecule in hydrate **3** by azeotropic distillation with toluene followed by vacuum drying to constant weight (Scheme 3). The water content in the prepared sample could be measured by ¹H NMR analysis in CD₃CN using internal standards and no external water signal was observed. Several grams of the anhydrous AgFSI





(5) were prepared via this procedure. Compared to the original route for the preparation of AgFSI complexes, the present procedure is safe and convenient, and suitable for large-scale preparation.



Scheme 3. Preparation of anhydrous AgFSI (5).

The stability of the above prepared Ag(I)FSI complexes were evaluated. AgFSI-(MeCN)₂ (1), AgFSI-MeCN (2), and (AgFSI)₆· (H₂O)₄ (4), were found stable at room temperature under air atmosphere for a long time; heating these complexes to 100 °C led to slow decomposition. Anhydrous AgFSI (5) was very hygroscopic and should be stored under dry and inert atmosphere. The aqueous solution of AgFSI was rather stable at room temperature; in fact, an aqueous solution of AgFSI (0.082 M) remained intact in a brown reagent bottle for 6 months as measured by ¹⁹F-NMR.

Synthesis and Characterization of Ligand Stabilized Gold(I) FSI Complexes

Having established a convenient approach to the preparation of the Aq(I) FSI complexes, we set out to prepare ligand stabilized gold(I) FSI complexes. A straightforward procedure for the preparation of this type of complexes would via reaction of ligand stabilized gold(I) chlorides with the anhydrous AgFSI (5). Indeed, treatment of chloro(triphenylphosphine)gold(I) with 5 led to the corresponding Ph₃PAuFSI complex (6a) in high yield. However, a major drawback of this procedure lies in the inconvenience in handing the hygroscopic anhydrous silver salt 5. To avoid this problem, we attempted to use air-stable Ag(I)FSI acetonitrile complexes 1 or 2 as the FSI precursor. To our delight, mixing a CH_2Cl_2 solution of complex **1** or **2** with an equimolar CH₂Cl₂ solution of LAuCl led to immediate precipitation of AgCl; filtration and evaporation of the solvent afforded the LAuFSI complexes. Gravimetric, elemental, and NMR analysis indicated that an equimolar MeCN always existed in the product, which could not be removed by vacuum drying or coevaporation with hexane. Gratifyingly, evaporation of the crude samples in a mixture of CH_2CI_2 and toluene (v/v = 2:1) led to the corresponding acetonitrile-free products, as confirmed by NMR analysis. Using this method, ligand-stabilized gold(I) FSI complexes 6a-e were prepared in high yields (Scheme 4).

Complexes **6a**, **6b**, **6c**, and **6e** were readily crystallized from a mixture solvent of CH_2Cl_2 /hexane, whereas complex **6d** was highly soluble. The X-ray crystal structures of complexes **6a** (CCDC 1909182), **6b** (CCDC 1909184), **6c** (CCDC 1909183), and **6e** (CCDC 1909181) are shown in Figure 5. In these complexes, the gold(I) center is nearly linear coordinated by a FSI anion and the phosphine or NHC ligand. The $^{-}NTf_2$ counterparts (**6a**'-**e**') of **6a**,^[29a] **6c**,^[30] and **6e**^[29b] have been characterized by X-ray diffraction analysis, while that of **6b** (i.e., **6b**') has not.^[31] We newly prepared **6b**' (Ad₃PAuNTf₂) through the reaction of



Scheme 4. Synthesis of ligand-stabilized gold(I)FSI complexes 6a-e.

Ad₃PAuCl^[32] with AgNTf₂ and raised single crystals for X-ray diffraction analysis (CCDC 1909394). Thus, a full comparison of the structures of the present FSI complexes with their ¬NTf₂ counterparts became possible, and the representative bond lengths (pm) and angles (°) are listed in Table 2.

It is observed that both the Au-P (or Au-C in complex 6e) and Au-N bonds in the FSI complexes are slightly shorter (0.5-1.4 pm) than in the corresponding ⁻NTf₂ series, indicating that the coordination of FSI anion to the Au center is stronger that the ⁻NTf₂ anion. Near linear two-coordination mode of Au(I) center are observed in complexes 6a, 6e, and 6e', whereas in complexes 6a', 6b, 6b', 6c, and 6c', a slightly bent geometry are observed that the bond angles of P-Au-N range from 173.03(16)° to 176.45(17)°. A dramatic difference of coordination geometry between complex 6e and 6e' is observed; in complex 6e', the planes of the -NTf₂ anion (S–N–S plane) and NHC ligand (N–C–N plane) are nearly coplanar,^[29b] whereas in complex **6e**, these planes are nearly perpendicular. This interesting phenomenon might be caused by the C-H--F interaction of the F atom in the FSI anion with the methyl group of the adjacent IPr ligand in complex 6e. The F-H distance is 227.58 pm, indicating a strong C-H--F interaction,^[33] whereas in **6e**', no such interaction is observed. This dramatic difference clearly demonstrates the distinct coordination properties of FSI anion compared to its fluoroalkyl disulfonylamides counterparts.

We have previously studied the coordination of water with LAu⁺ cation, which could be conveniently measured by ¹H NMR in that the coordination led to a downfield shift of the water signal. We found that for LAuOTf complexes hydration was a ready process, while for LAuNTf₂ complexes the hydration process was greatly inhibited by the strong coordination of Au(I) with the nitrogen.^[20e] Herein, the behavior of LAuFSI complexes in aqueous solutions was examined. In fact, the water signal in the solution of complexes **6a–6e** all occurred at 1.55 ppm, close to "free" water signal (1.52 ppm in CD₂Cl₂), suggesting that the coordination of LAu⁺ cation and FSI anion was hardly interrupted by water.











Figure 5. Crystal structures of LAuFSI complexes **6a**, **6b**, **6c**, **6e**, and LAuNTf₂ complex **6b**' at 30 % probability ellipsoids (hydrogen atoms are omitted for clarity).

Table 2. Representative bond lengths [pm] and angles (°) in the LAuFSI and LAuNTf_2 complexes.

6e

	6a/6a'	6b/6b'	6c/6c'	6e/6e'
Au-P(C)	222.35(10)/223.06(7)	224.37(18)/224.78(8)	222.64(18)/222.88(8)	196.4(4)/196.9(2)
Au-N	209.7(3)/210.1(2)	210.8(6)/212.2(3)	210.2(6)/211.3(3)	208.4(4)/209.1(2)
P(C)-Au-N	179.67(11)/174.20(7)	173.03(16)/176.37(7)	176.45(17)/174.06(10)	179.85(16)/178.0(1)

Synthesis and Characterization of Copper(II) FSI Complexes

Copper(II) salts bearing weakly coordinating counteranions, such as $CuSO_4$ and $Cu(OTf)_2$, have been widely used as precatalyst in transition metal catalysis.^[34] The commercially available $Cu(II)(NTf_2)_2$, firstly reported by Sonoda et al. in 1997, exhibited excellent catalytic activities in several copper catalyzed reactions.^[35] With the well characterized Ag(I) FSI complexes in hand, we investigated the preparation of Cu(II) FSI complexes through metathesis of Ag(I) FSI complex **1** with CuCl₂ in water (Scheme 5). The reaction proceeded smoothly as indicated by the immediate precipitate of AgCl. Filtration followed by evaporation and vacuum drying afforded Cu(II) FSI complex **7** as blue crystals. The structure of this complex was unambiguously characterized to be Cu(FSI)₂-4H₂O by X-ray diffraction analysis (CCDC 1909186, Scheme 5).

In the crystal structure of complex **7**, the Cu(II) ion is coordinated by four water molecules and two FSI anions in an elongated tetragonal octahedral geometry.^[36] Four water molecules are at the corner of the square plane, with two Cu(II)–O bond lengths at 195.4(4) pm and two at 195.1(4) pm, and O–Cu(II)–O angles at 92.24(17)° and 177.6(2)°. The two nitrogen atoms of the FSI anions are weakly coordinated with the Cu(II) center at distant axial positions, with Cu(II)–N distances at 253.56(60) and 270.31(60) pm. It is noted that Cu(II) dimesylamide tetrahydrates Cu[N(SO₂CH₃)₂·4H₂O has been synthesized and char-







Scheme 5. Synthesis and crystal structure of Cu(II) FSI complex 7.

acterized by Blaschette and Jones et al.,^[37] which consists of a centrosymmetric trans-octahedral molecule and is similar to complex **7**. However, the $(CH_3SO_2)_2N^-$ anion acts as a monodentate O-donor rather than N-donor. This dramatic difference demonstrates again the distinct coordination properties of FSI anion as compared to its alkyl disulfonylamides counterparts.

The stability of CuFSl₂·4H₂O (**7**) was evaluated. Either the crystals of this complex or its aqueous solution remained stable at room temperature for several weeks, while heating to 100 °C led to slow decomposition. A blue crystal sample of complex **7** was stored at room temperature for 3 months, the sample turned to white-blue fuming slurry and a new signal was observed in ¹⁹F NMR spectrum (δ = 55.4 ppm in H₂O). Thus, it is recommended that this complex should be used in time.

Catalytic Applications

The catalytic performance of the above synthesized coinage metal FSI complexes, in comparison to that of the known coinage NTf₂ complexes, were examined in a variety of model reactions. The preliminary results are summarized in Scheme 6.

The gold(I)-catalyzed organic transformations have been developed rapidly in the past two decades, wherein the ligand stabilized Au(I)NTf₂ complexes become one of the most widely used gold(I) catalysts.^[38,39] The propargyl ester hydration reaction, originally reported by Shi et al.,^[40] has been selected as a benchmark for the evaluation of gold(I) catalysis, wherein nitrogen ligand stabilized gold(I) catalyst such as **6a**' exhibited optimal performances.^[40] A comparison between the catalytic performances of **6a** and **6a**' in this reaction at 1.26 mmol scale under identical conditions revealed similar catalytic activity (Scheme 6, Reaction A).

We next chose gold(I)-catalyzed glycosylation of glycosyl *o*alkynylbenzoates as a model reaction, which was developed by our group and has found wide applications.^[20,41] The glycosylation reactions of perbenzyl glucopyranosyl *o*-alkynylbenzoate **10** α /**10** β and adamantanol **11** proceeded smoothly in the presence of either complex **6a** or **6a**', delivering the glycoside product **12** in high yields (93 %–100 %) as a mixture of α - and β anomers (Scheme 6, Reaction B). The use of the α -donor (**10** α) favored the formation of the β product (**12** β), in contrast, the α product (**12** α) was favorably formed when starting with the β Reaction A: Gold(I)-Catalyzed Propargyl Ester Hydration

Reaction B: Gold(I)-Catalyzed Glycosylation



Reaction C: Gold(I)-Catalyzed Electrophilic Aromatic Substitution with α-Diazoester



Reaction D: Gold(I)-Catalyzed Intermolecular Cyclization of Ynamides and Propargylic Carboxylates



Reaction E: Ir-Catalyzed C-H Hydroarylation with 2-Pyridyl as a Directing Group



Reaction F: Cu(II)-Catalyzed O-Acetylation



Scheme 6. Catalytic applications of the coinage metal FSI complexes.

donor (**10** β). Indeed, the different counteranions in the catalysts brought about a slightly different α/β selectivities. Such a difference reflects again the involvement of the counteranion in the glycosylation reactions,^[20b,20d] which warrants further studies.

The catalytic potential of the Au(I)FSI complexes was further examined in two more gold(I)-catalyzed reactions (Reactions C and D). The gold(I)-catalyzed electrophilic aromatic substitution with α -diazoester represents an efficient C–C bond forming reaction via gold-carbenoids, and complex **6d**' has been identified as an optimal catalyst.^[42] A comparison between the catalytic performance of **6d** and **6d**' in the reaction of diazoester **13** with phenol derivative **14** under otherwise identical conditions





revealed that complex **6d** exhibited slightly better catalytic activity than the conventional **6d**' (72 % vs. 66 %). The intermolecular cyclization of ynamides and propargylic carboxylates catalyzed by **6e**', developed by Hashmi et al.,^[43] provided a facile method for the preparation of highly substituted cyclopentadienes. A comparison between the catalytic performance of **6e** and **6e**' at 1.25 mmol scale under otherwise identical conditions revealed that complex **6e** exhibited slightly better catalytic activity than **6e**' (69 % vs. 64 %; Reaction D). The outcomes of these two reactions demonstrate that FSI complexes could be better catalysts than the corresponding NTf₂ complexes which have been used previously.

Various transition metal NTf₂ complexes are commonly prepared through halide abstraction of the corresponding metal halides with AgNTf₂.^[44] The application of Ag(I) FSI complexes as halide abstractor was thus investigated. The Ir(III)-catalyzed C-H hydroarylation with 2-pyridyl group as a directing group was selected as a model reaction (Reaction E).^[45] Previous studies revealed that the optimal counteranion for this reaction was -NTf₂, which was introduced by halide abstraction of $[IrCp^*Cl_2]_2$ (Cp^{*} = 1,2,3,4,5-pentamethylcyclopentadienyl) with AgNTf₂. The Ag(I)FSI complexes, including AgFSI-2MeCN (1), AgFSI-MeCN (2), and AgFSI, together with AgNTf₂, were examined herewith. Under the previously established optimal conditions, comparable yields and ratios of the hydroarylation products 20 and 21 were obtained (ca. 36 % for 20 and ca. 15 % for 21) when Ag(I)FSI complexes 1, 2, or 5 were employed; the yields of 20 were slightly better than that with AgNTf₂ (30 % for 20).

Finally, the catalytic potential of Cu(II)FSI complex **7** was tested, with per-O-acetylation of glucose being chosen as a model reaction (Reaction F). Yadav et al. have screened a variety of Cu(II) salts as catalysts for this reaction and found Cu(ClO₄)₂·6H₂O to be the optimal.^[46] In the presence of 1.0 mol-% Cu(ClO₄)₂·6H₂O, the reaction completed within 0.5 h to provide per-O-acetyl glucose **23** in 97 % yield. Many other Cu(II) complexes, such as Cu(OAc)₂·H₂O, Cu(NO₃)₂·3H₂O, CuCl₂·2H₂O, and CuSO₄·5H₂O led to poor results. To our delight, CuFSl₂·4H₂O (**7**) was found to be an efficient catalyst for this reaction, which completed in 14 h in the presence of 1.0 mol-% of **7** to give **23** in 95 % yield.

Conclusion

We have developed convenient procedures for the preparation of a series of the coinage metal FSI complexes, those include AgFSI-2MeCN (1), AgFSI-MeCN (2), AgFSI-H₂O (3), (AgFSI)₆--(H₂O)₄ (4), AgFSI (5), LAuFSI (**6a–6e**), and Cu(FSI)₂-4H₂O (7). Novel and interesting structural features and coordination modes were observed in these complexes. In the crystal of AgFSI-MeCN (2), half of the Ag(I) ions are coordinated by two MeCN in a linear fashion while the other half of Ag(I) ions are coordinated by two FSI anion in a linear nitrogen-bound fashion. (AgFSI)₆-(H₂O)₄ (4) contains six types of Ag(I) ions in six different coordination modes (modes 1–6), wherein ⁻FSI can behave as bidentate O-donor, monodentate N-donor, or even Fdonor. The R₃PAuFSI complexes (**6a–6c**) show similar geometry as their NTf₂ counterparts (6a'-6c'); however, in IPrAuFSI (6e), the planes of the -NTf₂ anion (S-N-S plane) and NHC ligand (N-C-N plane) are nearly perpendicular, whereas in IPrAuNTf₂ (**6e**'), these two planes are nearly coplanar. In Cu(FSI)₂·4H₂O (**7**), the Cu(II) ion is coordinated by four water molecules and two FSI anions in an elongated tetragonal octahedral geometry. These distinct coordination properties of FSI anion compared to that of -NTf₂ (and other fluoroalkyl disulfonylamides) indicates FSI anion as a potentially unconventional weakly coordinating counteranion in transition metal chemistry. Brief evaluation of these complexes in a series of Au(I), Ir(III)/Ag(I), and Cu(II) catalyzed reactions has revealed that the FSI complexes could serve as efficient and versatile catalysts. Compared to the widely used coinage metal NTf₂ catalysts, the FSI catalysts are cost-effective, readily accessible, and exhibit comparable or slightly better catalytic performances. With these promising features, this series of fundamentally important FSI complexes shall find wide applications in the future development of transition metal chemistry.

Experimental Section

General. The syntheses of coinage metal FSI complexes were preformed under ambient atmosphere unless specialized. Analytical grade commercial reagents were used without further purification unless specialized. Thin layer chromatography (TLC) was performed on TLC Silica Gel 60 F254 (Merck). The TLC plates were visualized with UV light and/or by staining with EtOH/H₂SO₄ (8 %, v/v). Flash column chromatography was performed on Silica Gel 60 (40–64 µm, Fluka, Canada). NMR spectra were measured on Varian Mercury 300, Bruker AM 400, NEO 500 and Agilent 500 MHz NMR spectrometer at 25 °C. ¹H and ¹³C NMR signals were calibrated to the residual proton and carbon resonance of the solvent (CDCl₃: $\delta_{\rm H}$ = 7.26 ppm; $\delta_{\rm C}$ = 77.16 ppm or CD₂Cl₂: $\delta_{\rm H}$ = 5.32 ppm; $\delta_{\rm C}$ = 54.00 ppm). Elemental analysis was obtained on a Vario EL III elemental analyzer.

X-ray Crystallography

Single crystal X-ray data were collected on Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo K_{α} radiation ($\lambda = 0.71073$ Å) at 133 K.

CCDC 1909180 (for **2**), 1909185 (for **4**), 1909182 (for **6a**), 1909184 (for **6b**), 1909183 (for **6c**), 1909181 (for **6e**), 1909394 (for **6b**'), and 1909186 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of AgFSI-2MeCN (1). To a mixture of KFSI (6.529 g, 29.8 mmol) and AgNO₃ (5.059 g, 29.8 mmol) in a 250 mL roundbottomed flask equipped with a Teflon-coated magnetic stir bar was added MeCN (HPLC grade, 80 mL). The mixture was stirred for 1 h, and then filtered through a sand core funnel (G4 type with 3– 4 µm cores). The resulting KNO₃ cake was washed with MeCN (HPLC grade, 20 mL × 2). The filtrate was combined and concentrated in vacuo to afford a colorless liquid, which was further dried under high vacuum to constant weight to afford complex **1** as a colorless liquid (10.99 g, 99.7 % yield). ¹H NMR (500 MHz, CD₂Cl₂): δ = 2.23 (s, 6H). ¹³C NMR (126 MHz, CD₂Cl₂): δ = 119.74, 2.83. ¹⁹F NMR (282 MHz, CD₂Cl₂): δ = 49.32 (s). Elemental analysis calcd. (%) for C₄H₆AgF₂N₃O₄S₂: C 12.98, H 1.63, N 11.35; found C 13.34, H 2.02, N 11.49.





Synthesis of AgFSI-MeCN (2). Complex **1** (852 mg, 2.30 mmol) was dissolved in CH₂Cl₂ (20 mL), the resulting solution was filtered and concentrated in vacuo to afford a colorless liquid, which was further dried under high vacuum to constant weight to afford complex **2** as colorless crystals (755 mg, 99.7 % yield). ¹H NMR (500 MHz, CD₂Cl₂): δ = 2.25 (s, 3H). ¹³C NMR (126 MHz, CD₂Cl₂): δ = 119.94, 2.84. ¹⁹F NMR (282 MHz, CD₂Cl₂): δ = 49.45 (s). Elemental analysis calcd. (%) for C₂H₃AgF₂N₂O₄S₂: C 7.30, H 0.92, N 8.51; found C 7.74, H 1.40, N 8.09.

Synthesis of AgFSI-H₂O (3). Complex **1** (4.290 g, 11.60 mmol) was dissolved in deionized H₂O (40 mL) under sonication. The resulting solution was concentrated in vacuo and again dissolved in deionized H₂O (40 mL). The solution was concentrated in vacuo and further dried under high vacuum to constant weight, affording complex **3** as a white solid (3.60 g, 100 % yield): ¹⁹F NMR (282 MHz, H₂O) δ = 49.31 (s); elemental analysis calcd. (%) for AgF₂H₂NO₅S₂ H 0.66, N 4.58, found H 0.88, N 4.55.

Isolation and Characterization of (AgFSI)₆·(**H**₂**O**)₄ (4). Complex **3** was stored in a 100 mL round-bottomed flask for 6 months, colorless block shaped crystals and colorless solution were formed. The crystals were isolated and characterized by X-ray diffraction analysis to be (AgFSI)₆·(H₂O)₄ (complex **4**): ¹⁹F NMR (282 MHz, H₂O) δ = 49.31 (s).

Synthesis of AgFSI (5). Complex 1 (878 mg, 2.37 mmol) was dissolved in deionized H₂O (15 mL) under sonication in a 50 mL roundbottomed flask. The resulting solution was concentrated in vacuo and again dissolved in deionized H₂O (10 mL). The solution was concentrated in vacuo and further dried under high vacuum to afford a white solid, toluene (25 mL) was added and the mixture was distilled under atmospheric pressure using a Dean-Stark apparatus to remove water. After all the water was removed, the resulting mixture was cooled to room temperature and concentrated in vacuo to afford a white solid, which was further dried under high vacuum at 100 °C for 2 min to afford anhydrous AgFSI (5) as a white solid (718 mg, theoretical amount: 683 mg). Salt 5 was very hygroscopic and should be stored under dry and inert atmosphere. ¹H NMR analysis of a CD₃CN solution of **5** using 1-bromo-4-iodobenzene as internal standard indicated that the sample contains trace amount of toluene, and no external water could be detected. ¹⁹F NMR (282 MHz, CD₃CN) δ = 45.90; elemental analysis calcd. (%) for AgF₂NO₄S₂ N 4.86, found N 4.44.

Synthesis of Ph₃PAuFSI (6a). To a mixture of Complex 1 (91.3 mg, 0.247 mmol) and Ph₃PAuCl (122.0 mg, 0.247 mmol) in a 25 mL round-bottomed flask equipped with a Teflon-coated magnetic stir bar was added CH₂Cl₂ (2.0 mL). The mixture was stirred for 15 min and filtered through a sand core funnel (G4 type with 3–4 μ m cores). The resulting AgCl precipitate was washed with CH₂Cl₂ (2 mL \times 2). The filtrate was combined, toluene (2 mL) was added and the resulting solution was concentrated in vacuo to afford a white solid, which was further dissolved in CH₂Cl₂ (4.0 mL), and petroleum ether (2.0 mL) was added. The resulting solution was concentrated in vacuo and then dried under high vacuum to constant weight to afford complex 6a as a white solid (155 mg, 98.7 % yield). ¹H NMR (500 MHz, CD₂Cl₂): δ = 7.65–7.47 (m, 15H). ¹³C NMR (126 MHz, CD_2CI_2): δ = 134.72 (d, J = 13.8 Hz), 133.22 (d, J = 2.8 Hz), 130.13 (d, J = 12.4 Hz), 127.68 (d, J = 66.7 Hz). ¹⁹F NMR (282 MHz, CD_2CI_2): $\delta = 51.24$ (s). ³¹P NMR (121 MHz, CD_2CI_2): $\delta = 31.27$ (s). Elemental analysis calcd. (%) for C₁₈H₁₅AuF₂NO₄PS₂: C 33.81, H 2.36, N 2.19; found C 33.62, H 2.36, N 2.22.

Synthesis of Ad₃PAuFSI (6b)

Complex **6b** was prepared by the reaction of complex **1** and $Ad_3PAuCI-CH_2CI_2$, the latter was synthesized according to a slightly

modified literature procedure.^[32] A THF (100 mL, freshly distilled) solution of Ad₃P (400 mg, 0.916 mmol) was added dropwise to a stirred CH₂Cl₂ (25 mL) solution of Me₂SAuCl (400 mg, 1.36 mmol) in a 250 mL round-bottomed flask under argon atmosphere. The mixture was stirred at r.t. for 30 min, and then concentrated under reduced pressure to half volume. EtOH (150 mL) was added, and the product participated as white solids. The mixture was filtered and washed with EtOH (15 mL) to afford a white powder, which was suspended in MeOH (60 mL) and stirred for 1 h. The mixture was filtered and dried under reduced pressure to afford a white powder (452 mg). 397 mg of the powder was suspended in a CH_2CI_2 (5.0 mL) and petroleum ether (7.5 mL) was added. The mixture was filtered and dried under reduced pressure to afford Ad₃PAuCl·CH₂Cl₂ (378 mg, 0.50 mmol) as a white powder. The overall yield based on Ad₃P is 62 %. ¹H NMR (300 MHz, CDCl₃) δ = 5.30 (s, 2H), 2.40 (s, 18H), 2.04 (s, 9H), 1.74 (q, J = 13.0 Hz, 18H).

To a mixture of complex 1 (34.6 mg, 93.5 µmol) and Ad₃PAuCl·CH₂Cl₂ (70.5 mg, 93.5 µmol) in a 25 mL round-bottomed flask equipped with a Teflon-coated magnetic stir bar was added CH₂Cl₂ (5.0 mL). The mixture was stirred for 15 min and filtered through a sand core funnel (G4 type with 3–4 μ m cores). The resulting AgCl precipitate was washed with CH_2Cl_2 (2 mL \times 2). The filtrate was combined, toluene (2 mL) was added and the resulting solution was concentrated in vacuo to afford a white solid, petroleum ether (2.0 mL) was added, and the resulting mixture was concentrated in vacuo and then dried under high vacuum to constant weight to afford complex **6b** as a white solid (76.5 mg, 100 % yield): ¹H NMR (500 MHz, CD_2Cl_2) δ = 2.41 (br, 18H), 2.06 (br, 9H), 1.83–1.70 (m, 18H); ¹³C NMR (126 MHz, CD₂Cl₂) δ = 47.95 (d, J = 17.1 Hz), 43.44 (br), 36.73, 29.69 (d, J = 8.4 Hz); ¹⁹F NMR (471 MHz, CD₂Cl₂) $\delta =$ 53.71 (s); ³¹P NMR (202 MHz, CD₂Cl₂) δ = 82.67 (s); elemental analysis calcd. (%) for C₃₀H₄₅AuF₂NO₄PS₂ C 44.28, H 5.57, N 1.72, found C 44.28, H 5.64, N 1.47.

Synthesis of Ad₃PAuNTf₂ (6b'). To a mixture of AgNTf₂ (24.6 mg, 63.4 µmol) and Ad₃PAuCl (42.5 mg, 63.5 µmol) in a 25 mL roundbottomed flask equipped with a Teflon-coated magnetic stir bar was added CH₂Cl₂ (5.0 mL). The mixture was stirred for 15 min and filtered through a sand core funnel (G4 type with 3–4 µm cores). The AgCl precipitate was washed with CH₂Cl₂ (2 mL × 2). The filtrate was combined and concentrated in vacuo to afford complex **6b'** as a white solid (54.6 mg, 94 % yield): ¹H NMR (500 MHz, CD₂Cl₂) δ = 2.40 (br, 18H), 2.06 (br, 9H), 1.84–1.67 (m, 18H); ¹³C NMR (126 MHz, CD₂Cl₂) δ = 119.89 (q, *J* = 322.8 Hz), 47.93 (d, *J* = 16.3 Hz), 43.49 (br), 36.74, 29.69 (d, *J* = 8.2 Hz); ¹⁹F NMR (471 MHz, CD₂Cl₂) δ = -76.36 (s); ³¹P NMR (202 MHz, CD₂Cl₂) δ = 81.96 (s); elemental analysis calcd. (%) for C₃₂H₄₅AuF₆NO₄PS₂ C 42.06, H 4.96, N 1.53, found C 40.43, H 4.91, N 1.51.

Synthesis of Au₂(FSI)₂(μ -DPPF) (6c). To a mixture of complex 1 (74.0 mg, 0.200 mmol) and Au₂Cl₂(μ -DPPF) (102.0 mg, 0.200 mmol) in a 25 mL round-bottomed flask equipped with a Teflon-coated magnetic stir bar was added CH₂Cl₂ (2.0 mL). The mixture was stirred for 15 min and filtered through a sand core funnel (G4 type with 3–4 μ m cores). The resulting AgCl precipitate was washed with CH₂Cl₂ (2 mL × 2). The filtrate was combined, toluene (1 mL) was added and the resulting solution was concentrated in vacuo to afford an orange solid, which was then dried under high vacuum to constant weight to afford complex **6c** as an orange solid (131.6 mg). ¹H NMR analysis revealed that the product contains ca. 0.4 eq cocrystallized toluene (correspond to 3 % w/w), which could not be removed by washing with petroleum ether and high vacuum drying. The yield is thus calcd. 97 %. ¹H NMR (500 MHz, CD₂Cl₂) δ = 7.67–7.39 (m, 20H), 4.85 (s, 4H), 4.30 (s, 4H); ¹³C NMR (126 MHz,





CD₂Cl₂) δ = 133.91 (d, *J* = 14.3 Hz), 133.21, 129.97 (d, *J* = 12.2 Hz), 128.69 (d, *J* = 68.0 Hz), 76.66, 76.65 (d, *J* = 8.0 Hz), 75.21 (d, *J* = 13.4 Hz); ¹⁹F NMR (471 MHz, CD₂Cl₂) δ = 53.98 (s); ³¹P NMR (202 MHz, CD₂Cl₂) δ = 25.53 (s); elemental analysis calcd. (%) for C₃₄H₂₈Au₂F₄FeN₂O₈P₂S₄ C 31.21, H 2.16, N 2.14, found C 31.58, H 2.32, N 1.99.

Synthesis of (Ar*O)₃PAuFSI (6d). To a mixture of complex 1 (37.2 mg, 0.101 mmol) and (Ar*O)₃PAuCl^[42] (88.4 mg, 0.101 mmol) in a 25 mL round-bottomed flask equipped with a Teflon-coated magnetic stir bar was added CH₂Cl₂ (5.0 mL). The mixture was stirred for 15 min and filtered through a sand core funnel (G4 type with 3-4 µm cores). The resulting AgCl precipitate was washed with CH_2Cl_2 (2 mL \times 2). The filtrate was combined, toluene (2 mL) was added and the resulting solution was concentrated in vacuo to afford a white foam, which was then dissolved in CH₂Cl₂ (2 mL), petroleum ether (5.0 mL) was added. The resulting mixture was concentrated in vacuo and then dried under high vacuum to constant weight to afford complex 6d as a white foam (104.4 mg, 100 % yield): ¹H NMR (500 MHz, CD₂Cl₂) δ = 7.49 (dd, J = 2.5, 1.5 Hz, 2H), 7.39 (dd, J = 8.5, 1.6 Hz, 2H), 7.20 (dd, J = 8.6, 2.5 Hz, 2H), 1.44 (s, 27H), 1.30 (s, 27H); ¹³C NMR (126 MHz, CD₂Cl₂) δ = 149.50, 147.61 (d, J = 6.7 Hz), 139.87 (d, J = 6.8 Hz), 126.34, 124.90, 119.82 (d, J = 9.1 Hz), 35.53, 35.16, 31.58, 30.82; ¹⁹F NMR (471 MHz, CD₂Cl₂) δ = 53.76 (s); ³¹P NMR (202 MHz, CD₂Cl₂) δ = 90.83 (s); elemental analysis calcd. (%) for C₄₂H₆₃AuF₂NO₇PS₂ C 49.26, H 6.20, N 1.37, found C 49.72, H 6.28, N 1.30.

Synthesis of IPrAuFSI (6e). To a mixture of complex 1 (101.1 mg, 0.273 mmol) and IPrAuCl (170.0 mg, 0.273 mmol) in a 25 mL roundbottomed flask equipped with a Teflon-coated magnetic stir bar was added CH₂Cl₂ (3.0 mL). The mixture was stirred for 15 min and filtered through a sand core funnel (G4 type with 3-4 µm cores). The resulting AqCl precipitate was washed with CH_2Cl_2 (2 mL \times 2). The filtrate was combined, toluene (2 mL) was added and the resulting solution was concentrated in vacuo to afford a white solid, which was then dried under high vacuum to constant weight to afford complex **6e** as a white solid (204.0 mg, 97 %): ¹H NMR (500 MHz, CD_2Cl_2) δ = 7.57 (t, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 4H), 7.32 (s, 2H), 2.50 (hept, J = 6.9 Hz, 4H), 1.31 (d, J = 6.9 Hz, 12H), 1.23 (d, J = 6.9 Hz, 12H); ¹³C NMR (126 MHz, CD₂Cl₂) $\delta = 167.68$, 146.26, 134.00, 131.47, 124.82, 124.57, 29.40, 24.42; ¹⁹F NMR (471 MHz, CD₂Cl₂) δ = 53.33 (s); elemental analysis calcd. (%) for C₂₇H₃₆AuF₂N₃O₄S₂ C 42.35, H 4.74, N 5.49, found C 42.18, H 4.75, N 5.46.

Synthesis of Cu(FSI)₂**·4H**₂**O (7).** To a mixture of complex **1** (3.70 g, 10.0 mmol) and CuCl₂ (672 mg, 5.0 mmol) in a 100 mL roundbottomed flask equipped with a Teflon-coated magnetic stir bar was added deionized H₂O (40 mL). The mixture was stirred for 1 h, and filtered through a sand core funnel (G4 type with 3–4 µm cores). The resulting AgCl cake was washed with deionized H₂O (20 mL × 2). The filtrate was combined and concentrated in vacuo to afford a blue liquid, which was further dried under high vacuum at 100 °C for 2 min to afford Cu(FSI)₂·4H₂O (**7**) as a blue crystal (2.44 g, 98 %): ¹⁹F NMR (282 MHz, H₂O) δ = 49.55; elemental analysis calcd. (%) for CuF₄HN₂O₈S₄ H 0.24, N 6.59, found H 2.88, N 5.65.

Catalytic Applications – Reaction A: Gold(I)-catalyzed propargyl ester hydration. To a solution of **8** (220 mg, 1.26 mmol) in acetone (12.5 mL, 0.1 M) were added Au(I) catalyst (8.1 mg **6a** or 9.3 mg **6a**', 12.6 µmol, 1.0 mol-%) and H₂O (67 µL, 3.7 mmol) at r.t. under argon atmosphere. The reaction mixture was stirred at r.t. for 6 h, TLC indicated the reaction was complete. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 12.5:1) to give **9**^[40] (233 mg, 96 % for **6a** and 229 mg, 94 % for **6a**') as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ = 7.46–7.35 (m, 5H), 5.97 (s, 1H), 2.19 (s, 3H), 2.11 (s, 3H).

Reaction B: Gold(I)-catalyzed glycosylation reaction. To a mixture of 10α or 10β (150 mg, 0.206 mmol), 11 (25.0 mg, 0.164 mmol), and 5Å MS was added dry CH₂Cl₂ under argon atmosphere. The mixture was stirred at r.t. for 1 h and then cooled to 0 °C, Au(I) catalyst (13.4 mg 6a or 15.5 mg 6a', 21.0 µmol, 10 mol-%) was added, and the reaction mixture was stirred at 0 °C for 2 h, TLC indicated the reaction was complete. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1 to 20:1 to 17:1) to give **12**^[47] as a white solid, the yields and α/β ratio were shown in Scheme 6. Data of product **12** prepared starting from **10**^β catalyzed by **6a**: ¹H NMR (500 MHz, CDCl₃) δ = 7.41–7.23 (m, 30.1H), 7.22-7.19 (m, 1.95H), 7.17-7.14 (m, 1.89H), 5.30 (d, J = 3.6 Hz, 1.00H), 5.02 (t, J = 10.5 Hz, 2.01H), 4.93 (d, J = 10.9 Hz, 1.10H), 4.87-4.81 (m, 2.83H), 4.79 (d, J = 10.9 Hz, 1.08H), 4.76-4.69 (m, 3.68H), 4.65 (d, J = 12.1 Hz, 1.10H), 4.63-4.54 (m, 3.09H), 4.50-4.44 (m, 1.96H),4.07-4.00 (m, 1.90H), 3.81-3.72 (m, 2.12H), 3.70-3.60 (m, 3.84H), 3.59-3.42 (m, 4.21H), 2.21-2.10 (m, 5.41H), 2.00-1.92 (m, 2.99H), 1.91-1.79 (m, 8.07H), 1.70-1.56 (m, 11.44H); ¹³C NMR (126 MHz, $CDCl_3$) $\delta = 139.20, 138.83, 138.72, 138.55, 138.50, 138.46, 138.34,$ 138.24, 128.49, 128.47, 128.46, 128.42, 128.40, 128.35, 128.26, 128.10, 128.07, 128.01, 127.96, 127.86, 127.83, 127.78, 127.70, 127.69, 127.66, 127.58, 127.57, 96.38, 89.97, 85.26, 82.48, 82.22, 80.23, 78.36, 78.28, 75.83, 75.66, 75.43, 75.22, 75.04, 74.70, 74.66, 73.57, 73.49, 72.98, 69.81, 69.66, 68.92, 42.93, 42.59, 36.43, 30.84, 30.79.

Reaction C: Gold(I)-catalyzed electrophilic aromatic substitution with α-**diazoester.** To a mixture of **13** (177 mg, 1.0 mmol), **14** (610 mg, 5.0 mmol), and wet CH₂Cl₂ (5.0 mL) in a 25 mL round bottomed flask was added Au(I) catalyst (51.2 mg **6d** or 56.0 mg **6d**', 50.0 mmol, 5.0 mol-%) under air atmosphere. The reaction mixture was stirred at r.t. for 1 h, TLC indicated the reaction was complete. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100:0 to 50:1) to give **15**^[42] (195 mg, 72 % for **6d** and 178 mg, 66 % for **6d**') as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ = 7.33–7.25 (m, 5H), 6.82 (s, 1H), 6.76 (s, 1H), 5.93 (s, 2H), 4.95 (s, 1H), 3.74 (s, 3H).

Reaction D: Gold(I)-catalyzed intermolecular cyclization of ynamides and propargylic carboxylates. To a mixture of **8** (217.2 mg, 1.25 mmol) and **16** (331.5 mg, 1.25 mmol) in dry CH₂Cl₂ (10.0 mL) was added Au(I) catalyst (48.0 mg **6e** or 54.0 mg **6e**', 62.5 µmol, 5 mol-%) under argon atmosphere. The mixture was stirred at r.t. for 24 h, TLC indicated the reaction was complete. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate = 10:1) to give **17**^[43] (380 mg, 69 % for **6e** and 360 mg, 64 % for **6e**') as a white solid: ¹H NMR (500 MHz, CDCl₃) δ = 7.63 (d, *J* = 7.9 Hz, 2H), 7.31–7.20 (m, 5H), 7.04–6.94 (m, 2H), 6.20 (s, 1H), 4.54 (s, 1H), 2.62 (s, 3H), 2.43 (s, 3H), 2.04 (s, 3H), 1.88–1.80 (m, 1H), 1.74–1.65 (m, 1H), 1.37–1.05 (m, 4H), 0.82 (t, *J* = 7.1 Hz, 3H).

Reaction E: Ir(III)-catalyzed C-H hydroarylation. To a mixture of **18** (310.4 mg, 2.00 mmol), **2** (0.270 mL, 2.40 mmol), $[IrCp^*Cl_2]_2$ (80.0 mg, 0.10 mmol), Ag(I) complex (**1**, **2**, **5**, or AgNTf₂, 0.40 mmol, 20 mol-%) in a 25 mL sealed Schlenk tube equipped with a Teflon stirbar was added dry CICH₂CH₂Cl (5.0 mL) under atmospheric conditions. The tube was sealed and the reaction mixture was stirred in a pre-heated oil bath at 120 °C for 6 h. The reaction was cooled to room temperature, filtered through a plug of celite and then



washed with ethyl acetate (20 mL × 3). The solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to give **20**^[45] and **21** as yellow oil. The yields and ratios were shown in Scheme 6. Data for **20**: ¹H NMR (300 MHz, CDCl₃) δ = 8.77–8.56 (m, 1H), 7.76 (td, *J* = 7.7, 1.9 Hz, 1H), 7.55–7.13 (m, 6H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.05 (t, *J* = 8.0 Hz, 2H), 2.53 (dd, *J* = 8.8, 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). Data for **21**: ¹H NMR (300 MHz, CDCl₃) δ = 8.84–8.56 (m, 1H), 7.79 (td, *J* = 7.6, 1.9 Hz, 1H), 7.40–7.22 (m, 3H), 7.17–7.15 (m, 2H), 4.04 (q, *J* = 7.2 Hz, 4H), 2.65 (m, 4H), 2.41 (m, 4H), 1.18 (t, *J* = 7.1 Hz, 6H).

Reaction F: Cu(II)-catalyzed per-O-acetylation of glucose. To a mixture of glucose 22 (1.80 g, 10 mmol) and Ac₂O (5.20 mL, 55 mmol) was added complex 7 (50.0 mg, 0.10 mmol, 1.0 mol-%). The mixture was stirred at r.t. for 14 hour, TLC indicated the reaction was complete. The mixture was diluted with CH₂Cl₂ (50 mL) and the mixture was washed with aqueous NaHCO₃ followed by brine. The organic phase was dried with anhydrous Na₂SO₄, and was then filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1) to afford product **23**^[46] as a white solid (3.72 g, 95 %, α/β = 3.2:1): ¹H NMR (500 MHz, CDCl₃) δ = 6.32 (d, J = 3.6 Hz, 1.00H), 5.71 (d, J = 8.3 Hz, 0.31H), 5.46 (t, J = 9.9 Hz, 1.05H), 5.28–5.21 (m, 0.39H), 5.17-5.04 (m, 2.62H), 4.32-4.22 (m, 1.40H), 4.15-4.04 (m, 2.53H), 3.83 (ddd, J = 10.1, 4.6, 2.2 Hz, 0.35H), 2.17 (s, 2.92H), 2.11 (s, 0.89H), 2.08 (s, 2.70H), 2.08 (s, 1.25H), 2.03 (s, 2.82H), 2.02 (s, 1.33H), 2.02 (s, 2.88H), 2.01 (s, 3.46H); ¹³C NMR (126 MHz, CDCl₃) δ = 170.73, 170.70, 170.33, 170.20, 169.76, 169.50, 169.35, 169.06, 168.85, 91.83, 89.19, 72.92, 72.86, 70.36, 69.96, 69.32, 68.02, 67.88, 61.59, 21.00, 20.94, 20.82, 20.79, 20.69, 20.68, 20.57.

Acknowledgments

Financial support from the National Natural Science Foundation of China (21432012 and 21621002), the Strategic Priority Research Program of CAS (XDB20020000), the K. C. Wong Education Foundation, the Shanghai Sailing Program (17YF1424000), and the China Postdoctoral Science Foundation (2017LH038) is acknowledged. We are grateful to Mr. Jie Sun and Xuebing Leng for their help in X-ray diffraction analysis.

Keywords: Coinage metals · Silver · Gold · Structure elucidation · Homogeneous catalysis

- a) I. M. Riddlestone, A. Kraft, J. Schaefer, I. Krossing, Angew. Chem. Int. Ed.
 2018, *57*, 13982–14024; Angew. Chem. **2018**, *130*, 14178; b) T. A. Engesser, M. R. Lichtenthaler, M. Schleep, I. Krossing, Chem. Soc. Rev. **2016**, *45*, 789–899; c) I. Krossing, I. Raabe, Angew. Chem. Int. Ed. **2004**, *43*, 2066–2090; Angew. Chem. **2004**, *116*, 2116; d) E. Y.-X. Chen, T. J. Marks, Chem. Rev. **2000**, *100*, 1391–1434; e) S. H. Strauss, Chem. Rev. **1993**, *93*, 927–942; f) Z. Lu, J. Han, O. E. Okoromoba, N. Shimizu, H. Amii, C. F. Tormena, G. B. Hammond, B. Xu, Org. Lett. **2017**, *19*, 5848–5851; g) L. Biasiolo, A. D. Zotto, D. Zuccaccia, Organometallics **2015**, *34*, 1759–1765; h) Y. Li, M. Cokoja, F. E. Kühn, Coord. Chem. Rev. **2011**, *255*, 1541–1557; i) J. Schießl, J. Schulmeister, A. Doppiu, E. Wörner, M. Rudolph, R. Karch, A. S. K. Hashmi, Adv. Synth. Catal. **2018**, *360*, 3949–3959.
- [2] a) D. Zuccaccia, L. Belpassi, F. Tarantelli, A. Macchioni, J. Am. Chem. Soc.
 2009, 131, 3170–3171; b) A. Zhdanko, M. E. Maier, ACS Catal. 2014, 4,
 2770–2775; c) K. E. Aldrich, B. S. Billow, D. Holmes, R. D. Bemowski, A. L. Odom, Organometallics 2017, 36, 1227–1237; d) R. M. P. Veenboer, A. Collado, S. Dupuy, T. Lebl, L. Falivene, L. Cavallo, D. B. Cordes, A. M. Z. Slawin, C. S. J. Cazin, S. P. Nolan, Organometallics 2017, 36, 2861–2869;



e) A. Bihlmeier, M. Gonsior, I. Raabe, N. Trapp, I. Krossing, *Chem. Eur. J.* **2004**, *10*, 5041–5051.

- [3] a) E. P. Farney, S. J. Chapman, W. B. Swords, M. D. Torelli, R. J. Hamers, T. P. Yoon, J. Am. Chem. Soc. 2019, 141, 6385–6391; b) T. Zhou, L. Xu, Y. Xia, Org. Lett. 2013, 15, 6074–6077; c) G. Ciancaleoni, L. Belpassi, D. Zuccaccia, F. Tarantelli, P. Belanzoni, ACS Catal. 2015, 5, 803–814; d) R. M. E. Brooner, T. J. Brown, M. A. Chee, R. A. Widenhoefer, Organometallics 2016, 35, 2014–2021; e) M. Jia, M. Bandini, ACS Catal. 2015, 5, 1638– 1652; f) R. Agahi, A. J. Challinor, N. B. Carter, S. P. Thomas, Org. Lett. 2019, 21, 993–997; g) F. Jaroschik, A. Simonneau, G. Lemière, K. Cariou, N. Agenet, H. Amouri, C. Aubert, J.-P. Goddard, D. Lesage, M. Malacria, Y. Gimbert, V. Gandon, L. Fensterbank, ACS Catal. 2016, 6, 5146–5160.
- [4] a) M. R. Kennedy, L. A. Burns, C. D. Sherrill, J. Phys. Chem. A 2015, 119, 403–409; b) D. Marcoux, P. Bindschädler, A. W. H. Speed, A. Chiu, J. E. Pero, G. A. Borg, D. A. Evans, Org. Lett. 2011, 13, 3758–3761.
- [5] a) X. H. Yang, R. T. Davison, S.-Z. Nie, F. A. Cruz, T. M. McGinnis, V. M. Dong, J. Am. Chem. Soc. **2019**, *141*, 3006–3013; b) D. Frejka, J. Ulč, E. A. B. Kantchev, I. Císarŏvá, M. Kotora, ACS Catal. **2018**, *8*, 10290–10299; c) R. Chung, A. Vo, V. V. Fokin, J. E. Hein, ACS Catal. **2018**, *8*, 7889–7897; d) C. Xu, W. Du, Y. Zeng, B. Dai, H. Guo, Org. Lett. **2014**, *16*, 948–951.
- [6] a) M. Bandini, A. Bottoni, M. Chiarucci, G. Cera, G. P. Miscione, J. Am. Chem. Soc. 2012, 134, 20690–20700; b) M. Mahlau, B. List, Angew. Chem. Int. Ed. 2013, 52, 518–533; c) G. L. Hamilton, E. J. Kang, M. Mba, F. D. Toste, Science 2007, 317, 496–499; d) S. Mukherjee, B. List, J. Am. Chem. Soc. 2007, 129, 11336–11337.
- [7] a) C. A. Reed, Acc. Chem. Res. **1998**, *31*, 133–139; b) S. P. Fisher, A. W. Tomich, S. O. Lovera, J. F. Kleinsasser, J. Guo, M. J. Asay, H. M. Nelson, V. Lavallo, Chem. Rev. **2019**, DOI: https://doi.org/10.1021/acs.chemrev. 8b00551.
- [8] a) J.-F. Gal, C. lacobucci, I. Monfardini, L. Massi, E. Duñach, S. Olivero, J. Phys. Org. Chem. 2013, 26, 87–97; b) S. Antoniotti, V. Dalla, E. Duñach, Angew. Chem. Int. Ed. 2010, 49, 7860–7888; Angew. Chem. 2010, 122, 8032; c) B. A. Shainyan, L. L. Tolstikova, Chem. Rev. 2013, 113, 699–733; d) W. Zhao, J. Sun, Chem. Rev. 2018, 118, 10349–10392; e) M. Hong, J. Min, S. Wang, Chin. J. Org. Chem. 2018, 38, 1907–1916; f) R. D. Howells, J. D. M. Cown, Chem. Rev. 1977, 77, 69–92.
- [9] a) G. Lemière, E. Duñach, Chem. Eur. J. 2013, 19, 3270–3280; b) G. Fang,
 X. Bi, Chem. Soc. Rev. 2015, 44, 8124–8173; c) Z. Xu, H. Chen, Z. Wang,
 A. Ying, L. Zhang, J. Am. Chem. Soc. 2016, 138, 5515–5518.
- [10] The current price of reagent grade (98 %) HOTf from Sigma-Aldrich is \$148/100 g, and $\rm HNTf_2$ (> 95.0 %) is \$104/5g.
- [11] For recently developed weakly coordinating anions, see: a) I. M. Riddlestone, S. Keller, F. Kirschenmann, M. Schorpp, I. Krossing, *Eur. J. Inorg. Chem.* 2019, 2019, 59–67; b) J. F. Kögel, T. Linder, F. G. Schröder, J. Sundermeyer, S. K. Goll, D. Himmel, I. Krossing, K. Kütt, J. Saame, I. Leito, *Chem. Eur. J.* 2015, 21, 5769–5782; c) F. A. LeBlanc, A. Decken, T. S. Cameron, J. Passmore, J. M. Rautiainen, T. K. Whidden, *Inorg. Chem.* 2017, 56, 974–983.
- [12] J. K. Ruff, Inorg. Chem. 1965, 4, 1446–1449.
- [13] A. Vij, R. L. Kirchmeier, J. M. Shreeve, R. D. Verma, Coord. Chem. Rev. 1997, 158, 413–432.
- [14] For the sulfur-based fluorine containing reagents, see: C. Ni, M. Hu, J. Hu, Chem. Rev. 2015, 115, 765–825.
- [15] a) S. Terada, K. Ikeda, K. Ueno, K. Dokko, M. Watanabe, Aust. J. Chem. 2019, 72, 70–80; b) K. Ueno, K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko, M. Watanabe, J. Phys. Chem. B 2012, 116, 11323–11331.
- [16] a) B. Krumm, A. Vij, R. L. Kirchmeier, J. M. Shreeve, *Inorg. Chem.* **1998**, *37*, 6295–6303; b) O. Hiemisch, D. Henschel, A. Blaschette, P. G. Jones, *Z. Anorg. Allg. Chem.* **1997**, *623*, 324–332; c) J. K. Ruff, *Inorg. Chem.* **1966**, *5*, 732–735.
- [17] a) A. Trehan, A. Vij, M. Walia, G. Kaur, R. D. Verma, S. Trehan, *Tetrahedron Lett.* **1993**, *34*, 7335–7338; b) H. Kaur, G. Kaur, S. Trehan, *Synth. Commun.* **1996**, *26*, 1925–1929.
- [18] J. Dong, L. Krasnova, M. G. Finn, K. B. Sharpless, Angew. Chem. Int. Ed. 2014, 53, 9430–9448; Angew. Chem. 2014, 126, 9584.
- [19] T. Guo, G. Meng, X. Zhan, Q. Yang, T. Ma, L. Xu, K. B. Sharpless, J. Dong, Angew. Chem. Int. Ed. 2018, 57, 2605–2610; Angew. Chem. 2018, 130, 2635.
- [20] a) B. Yu, Acc. Chem. Res. 2018, 51, 507–516; b) Y. Zhu, B. Yu, Chem. Eur.
 J. 2015, 21, 8771–8780; c) J. Li, Y. Dai, W. Li, S. Laval, P. Xu, B. Yu, Asian





J. Org. Chem. 2015, 4, 756–762; d) Y. Tang, J. Li, Y. Zhu, Y. Li, B. Yu, J. Am. Chem. Soc. 2013, 135, 18396–18405; e) Y. Tang, B. Yu, RSC Adv. 2012, 2, 12686–12689; f) S. Wang, Q. Zhang, Y. Zhao, J. Sun, W. Kang, F. Wang, H. Pan, G. Tang, B. Yu, Angew. Chem. Int. Ed. 2019, 58, 10558–10562; Angew. Chem. 2019, 131, https://doi.org/10.1002/ange.201907849.

- [21] M. Beran, J. Příhoda, Z. Anorg. Allg. Chem. 2005, 631, 55-59.
- [22] a) N. R. Brooks, S. Schaltin, K. V. Hecke, L. V. Meervelt, J. Fransaer, K. Binnemans, *Dalton Trans.* 2012, *41*, 6902–6905; b) D. Depuydt, N. R. Brooks, S. Schaltin, L. V. Meervelt, J. Fransaer, K. Binnemans, *ChemPlus-Chem* 2013, *78*, 578–588; c) J. Sniekers, N. R. Brooks, S. Schaltin, L. V. Meervelt, J. Fransaer, K. Binnemans, *Dalton Trans.* 2014, *43*, 1589–1598.
- [23] a) C. Wölper, A. Rodríguez-Gimeno, K. C. Iborra, H. Kuhn, A. K. Lüttig, S. Moll, C. Most, M. Freytag, I. Dix, P. G. Jones, A. Blaschette, Z. Naturforsch. B 2009, 64, 952–968; b) A. Blaschette, P. G. Jones, T. Hamann, M. Naveke, D. Schomburg, H. K. Cammenga, M. Epple, I. Steppuhn, Z. Anorg. Allg. Chem. 1993, 619, 912–922.
- [24] a) Y. Zhang, A. M. Santos, E. Herdtweck, J. Mink, F. E. Kühn, New J. Chem. 2005, 29, 366–370; b) S. F. Rach, E. Herdtweck, F. E. Kühn, Z. Anorg. Allg. Chem. 2011, 637, 499–501.
- [25] M. Stricker, B. Oelkers, C. P. Rosenau, J. Sundermeyer, Chem. Eur. J. 2013, 19, 1042–1057.
- [26] For examples of silver(I)-water coordination in crystals, see: a) S.-Q. Zang, T. C. W. Mak, *Inorg. Chem.* 2008, 47, 7094–7105; b) P. G. Jones, D. Henschel, A. Weitze, A. Blaschette, Z. Anorg. Allg. Chem. 1994, 620, 1514– 1520.
- [27] For Ag(I)-F interaction observed in crystal structures, see: E. Goreshnik, Z. Mazej, Solid State Sci. 2005, 7, 1225–1229.
- [28] T. C. W. Mak, X.-L. Zhao in Silver: Inorganic & Coordination Chemistry. Encyclopedia of Inorganic Chemistry (Ed. R. B. King) Wiley-VCH, Weinheim, 2006, pp. 1–10.
- [29] a) N. Mezailles, L. Ricard, F. Gagosz, Org. Lett. 2005, 7, 4133–4136; b) L. Ricard, F. Gagosz, Organometallics 2007, 26, 4704–4707.
- [30] S. K. Kristensen, S. L. R. Laursen, E. Taarning, T. Skrydstrup, Angew. Chem. Int. Ed. 2018, 57, 13887–13891; Angew. Chem. 2018, 130, 14083.
- [31] For catalytic application of complex 6b' which was prepared in situ without characterization, see: R. Liu, Q. Wang, Y. Wei, M. Shi, *Chem. Commun.* 2018, 54, 1225–1228.
- [32] L. Chen, P. Ren, B. P. Carrow, J. Am. Chem. Soc. 2016, 138, 6392–6395.
- [33] R. Taylor, Cryst. Growth Des. 2016, 16, 4165-4168.
- [34] a) E.-C. Liu, J. J. Topczewski, J. Am. Chem. Soc. 2019, 141, 5135–5138; b)
 Q.-J. Liu, J. Zhu, X.-Y. Song, L. Wang, S. R. Wang, Y. Tang, Angew. Chem. Int. Ed. 2018, 57, 3810–3814; Angew. Chem. 2018, 130, 3872; c) Y. Qiao,
 X.-X. Wu, Y. Zhao, Y. Sun, B. Li, S. Chen, Adv. Synth. Catal. 2018, 360,
 2138–2143; d) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless,
 Angew. Chem. Int. Ed. 2002, 41, 2596–2599; Angew. Chem. 2002, 114,
 2708.
- [35] J. Nie, H. Kobayashi, T. Sonoda, Catal. Today 1997, 36, 81-84.
- [36] B. J. Hathaway, P. G. Hodgson, J. Inorg. Nucl. Chem. 1973, 35, 4071–4081.

- [37] D. Henschel, K. Linoh, K.-H. Nagel, A. Blaschette, P. G. Jones, Z. Anorg. Allg. Chem. 1996, 622, 1065–1075.
- [38] For selected reviews, see: a) M. Rudolph, A. S. K. Hashmi, Chem. Soc. Rev. 2012, 41, 2448–2462; b) T. C. Boorman, I. Larrosa, Chem. Soc. Rev. 2011, 40, 1910–1925; c) N. Krause, C. Winter, Chem. Rev. 2011, 111, 1994–2009; d) A. Corma, A. Leyva Pefez, M. J. Sabater, Chem. Rev. 2011, 111, 1657–1712; e) M. Bandini, Chem. Soc. Rev. 2011, 40, 1358–1367; f) Z. Li, C. Brouwer, C. He, Chem. Rev. 2008, 108, 3239–3265; g) D. J. Gorin, B. D. Sherry, F. D. Toste, Chem. Rev. 2008, 108, 3321–3378; h) A. S. K. Hashmi, M. Rudolph, Chem. Soc. Rev. 2008, 37, 1766–1775; i) E. Jimeńez-Nünéz, A. M. Echavarren, Chem. Rev. 2008, 108, 3326–3350; j) A. Arcadi, Chem. Rev. 2008, 108, 3266–3325; k) A. S. K. Hashmi, Chem. Rev. 2007, 107, 3180–3211; l) A. Fürstner, P. W. Davies, Angew. Chem. Int. Ed. 2007, 46, 3410–3449; Angew. Chem. Int. Ed. 2006, 45, 7896–7936; Angew. Chem. 2006, 118, 8064.
- [39] a) H. Chen, L. Zhang, Angew. Chem. Int. Ed. 2015, 54, 11775–11779; Angew. Chem. 2015, 127, 11941; b) B. Lu, Y. Li, Y. Wang, A. H. Aue, Y. Luo, L. Zhang, J. Am. Chem. Soc. 2013, 135, 8512–8524; c) G. Henrion, T. E. J. Chavas, X. L. Goff, F. Gagosz, Angew. Chem. Int. Ed. 2013, 52, 6277–6282; Angew. Chem. 2013, 125, 6397; d) A.-H. Zhou, Q. He, C. Shu, Y.-F. Yu, S. Liu, T. Zhao, W. Zhang, X. Lu, L.-W. Ye, Chem. Sci. 2015, 6, 1265–1271.
- [40] D. Wang, R. Cai, S. Sharma, J. Jirak, S. K. Thummanapelli, N. G. Akhmedov, H. Zhang, X. Liu, J. L. Petersen, X. Shi, *J. Am. Chem. Soc.* **2012**, *134*, 9012– 9019.
- [41] a) Y. Li, X. Yang, Y. Liu, C. Zhu, Y. Yang, B. Yu, Chem. Eur. J. 2010, 16, 1871–1882; b) Y. Li, Y. Yang, B. Yu, Tetrahedron Lett. 2008, 49, 3604–3608.
- [42] a) Z. Yu, B. Ma, M. Chen, H.-H. Wu, L. Liu, J. Zhang, J. Am. Chem. Soc.
 2014, 136, 6904–6907; b) Y. Xi, Y. Su, Z. Yu, B. Dong, E. J. McClain, Y. Lan,
 X. Shi, Angew. Chem. Int. Ed. **2014**, 53, 9817–9821; Angew. Chem. **2014**, 126, 9975.
- [43] E. Rettenmeier, A. M. Schuster, M. Rudolph, F. Rominger, C. A. Gade,
 A. S. K. Hashmi, *Angew. Chem. Int. Ed.* 2013, *52*, 5880–5884; *Angew. Chem.* 2013, *125*, 5993.
- [44] a) S.-B. Wang, Q. Gu, S.-L. You, Organometallics 2017, 36, 4359–4362; b)
 J. R. Cabrero-Antonino, A. Leyva-Pérez, A. Corma, Chem. Eur. J. 2013, 19, 8627–8633; c) F. Xie, Z. Qi, S. Yu, X. Li, J. Am. Chem. Soc. 2014, 136, 4780–4787; d)
 J. Kim, S. Chang, Angew. Chem. Int. Ed. 2014, 53, 2203–2207; Angew. Chem. 2014, 126, 2235.
- [45] J. Kim, S.-W. Park, M.-H. Baik, S. Chang, J. Am. Chem. Soc. 2015, 137, 13448–13451.
- [46] D. Chatterjee, A. Paul, R. Yadav, S. Yadav, RSC Adv. 2015, 5, 29669–29674.
- [47] X. Chen, D. Shen, Q. Wang, Y. Yang, B. Yu, Chem. Commun. 2015, 51, 13957–13960.

Received: September 30, 2019



Ð



Coinage Metal Complexes
Y. Tang, B. Yu* 1–13

Coinage Metal (Bisfluorosulfonyl)imide Complexes: Preparation, Char-

acterization, and Catalytic Applications



A series of silver(I), gold(I), and copper(II) (bisfluorosulfonyI)imide (¬FSI) complexes are prepared from KFSI, an inexpensive chemical, and shown interesting structural features and some unprecedented coordination modes. They exhibit comparable catalytic performance to the corresponding coinage metal triflimides (¬NTf₂) in a series of the model chemical transformations.

DOI: 10.1002/ejic.201901058