Dalton
Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Zhang and W. Bie, *Dalton Trans.*, 2016, DOI: 10.1039/C6DT03016E.

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/dalton

View Article Online
DOI: 10.1039/C6DT03016E

Ligand-Dependent Formation of Ion-Pair Cu^I/Cu^{III} Trifluoromethyl Complexes Containing Bisphosphines†

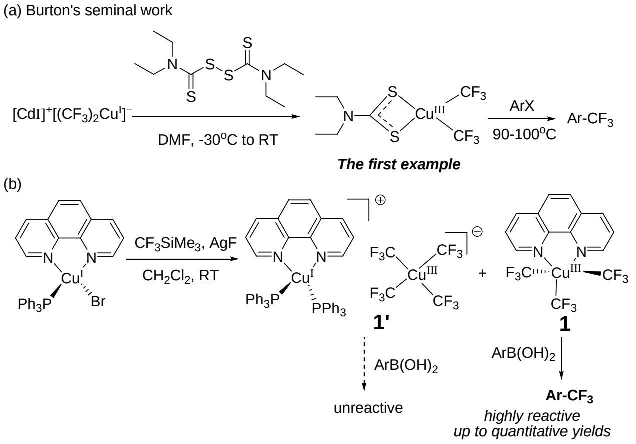
Song-Lin Zhang* and Wen-Feng Bie

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

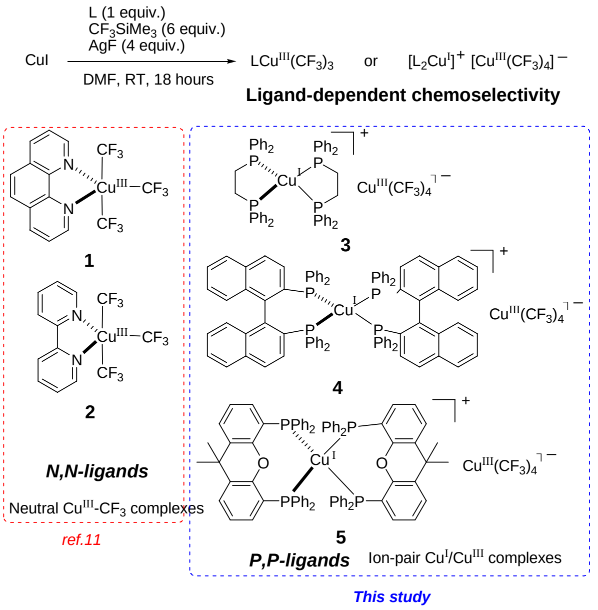
We report novel ion-pair bisphosphine Cu^I/Cu^{III} trifluoromethyl complexes $[(P_2)_2Cu]^+[Cu(CF_3)_4]^-$ (P_2 = DPPE, BINAP or Xantphos) that are prepared via oxidative trifluoromethylation of CuI with CF_3SiMe_3 in the presence of AgF. The bisphosphine Cu^I/Cu^{III} CF_3 complexes are highly reactive for aerobic trifluoromethylation of arylboronic acids to produce trifluoromethylated arenes in good to quantitative yields, which is in sharp contrast to the Cu^I/Cu^{III} complex with phen/PPh_3 ligands (1′). These results not only provide strong evidence that both the neutral and ion-pair Cu^{III} CF_3 complexes are competent catalytic species for Cu-mediated oxidative trifluoromethylation reactions, but also have important mechanistic implications that the active catalyst and reaction mechanism should be distinct and ligand-dependent for trifluoromethylation reactions with different types of ancillary ligands.

Copper-mediated trifluoromethylation reactions of aryl halides, boronic acids and other reagents with various CF_3 sources (formally divided into CF_3^-, CF_3^+ and $CF_3\bullet$ precursors) have been intensively studied.[1-6] In contrast to the flourishing achievements in the development of reaction methodologies, the mechanisitc aspects have been far less elucidated. The identity and reactivity properties of the active copper CF_3 species remains elusive for many trifluoromethylation reactions, which are however essential to the understanding and design of trifluoromethylation chemistry.[7,8] Particularly, the isolation, characterization and reactivity properties of high-valent Cu^{III}-CF_3 complexes, catalytically relevant intermediates proposed in oxidative or electrophilic trifluoromethylation reactions, present a challenge awaiting to be addressed.[9,10] Among the sporadic examples of well-characterized Cu^{III}-CF_3 complexes,[10] Burton et al. described a poineering study on the preparation of a dithiocarbamato Cu^{III} bis-CF_3 complex by oxidation of Cu^I-CF_3 precursors with thiuramdisulphide and its reactivity toward aryl iodides to produce trifluoromethylated arenes at 90-100°C (Scheme 1a).[10a] This seminal work represents the first example of isolation, characeterization and reactivity properties of Cu^{III}-CF_3 complexes proposed in trifluoromethylation chemistry.

More recently, we reported a room-temperature preparation and characterization of both neutral Cu^{III}-CF_3 complexes **1** and ion-pair **1′** containing representative phen ligand (Scheme 1b). Our method involves formally oxidative transmelation of phenCuBr with CF_3SiMe_3 in the presence of AgF in CH_2Cl_2 (Scheme 1b).[11] By using a sligthly different method starting from CuI and change of the solvent to more polar DMF, we could access selectively neutral phen$Cu^{III}(CF_3)_3$ (**1**) and (bpy)$Cu^{III}(CF_3)_3$ (**2**) in much higher yields (Scheme 2, red box). Complexes **1** and **2** were found to be highly efficient for the trifluoromethylation of arylboronic acids under mild conditions, but the ion-pair **1′** was unreactive under similar conditions. These findings provide fundamental information about the structures and reactivity of phen-containing Cu^{III}-CF_3 complexes that are closely relevant to a rich branch of trifluoromethylation reactions promoted by Cu/phen system.



Scheme 1 Synthesis and reactivity of isolated Cu^{III} CF_3 complexes.



Scheme 2 A general and ligand-dependent method for selective synthesis of either neutral Cu^{III} or ion-pair Cu^I/Cu^{III} trifluoromethyl complexes **1-5**.

View Article Online
DOI: 10.1039/C6DT03016E

In an attempt to broaden this Cu^{III}-CF_3 chemistry and to establish potential ligand-reactivity relationship, other ancillary ligands need to be investigated. Considering the popular use of bisphosphine ligands in trifluoromethylation and also other transition metal catalysis,[12] it should be of broad interest to isolate possible bisphosphine-containing Cu^{III}-CF_3 complexes and to study their structural and reactivity properties.[1] Thus we studied typical bisphosphine ligands DPPE, BINAP and Xantphos under the reaction conditions in Scheme 2. To our surprise, ion-pair Cu^{I}/Cu^{III} trifluoromethyl complexes **3-5** (Scheme 2, blue box) were selectively obtained in high yields without significant amounts of neutral Cu^{III}-CF_3 complexes detected.

Complexes **3-5** were prepared by reaction of CuI with 1 equivalent of bisphosphine (DPPE, BINAP and Xantphos), 6 equivalents of CF_3SiMe_3 as the CF_3 source in the presence of AgF in DMF at room temperature under N_2 atmosphere (Scheme 2). After workup, recrystallization and column chromatography, ion-pair Cu^{I}/Cu^{III} CF_3 complexes **3-5** with DPPE, BINAP and Xantphos were isolated and purified in good to excellent yields of 65%, 93% and 90% (see ESI for more details of synthesis and purification).†

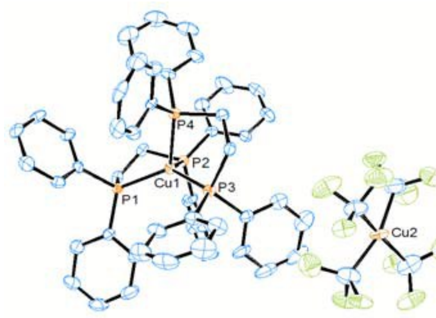
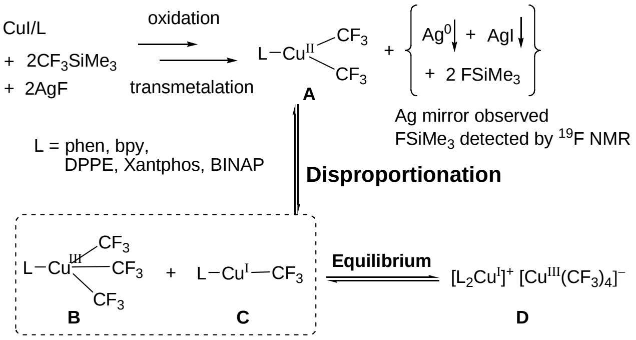


Fig. 1 ORTEP drawing of complex **3** with thermal ellipsoids at 50% probability. All the hydrogen atoms, one solvent molecule and disorders of carbon and fluorine atoms of CF_3s are removed for clarity.

^{19}F NMR spectra of **3-5** show only one singlet resonance around -34.7 ppm, which corresponds to four equivalent CF_3 groups in $[Cu^{III}(CF_3)_4]^-$. ^1H NMR spectra of **3-5** show characteristic resonances and splittings of protons of coordinating DPPE, BINAP and Xantphos that are significantly low-field shifted in the aromatic region compared to the free ligands (see ESI for more details).† Most remarkable are the ^{31}P NMR behaviour of **3-5**. **3** shows only one resonance of broad singlet at +4.7 ppm, consistent with the tetrahedral geometry where all the four P atoms are totally equivalent. In constrast, ^{31}P NMR spetrum of **4** shows two major doublet singnals at +15.9 and +14.4 ppm with coupling constants of 17.4 Hz in a ratio of 1:1. This may be caused by the P-P coupling of R- and S-enantiomer of the racemic BINAP used in our study. In ^{31}P NMR of **5**, there are also two resonances at -8.2 and -9.7 ppm with doublet splittings (coupling constants of 18.0 Hz). This can be rationalized that the presence of endo/exo face of one Xantphos distinguishes the two P atoms of another Xantphos in the tetrahedral geometry of $[(Xantphos)_2Cu]^+$ moiety.

The structure of **3** was further confirmed by X-ray diffraction analysis (Fig 1).[13] A square planar $[Cu(CF_3)_4]^-$ anion and a tetrahedral $[Cu(DPPE)_2]^+$ counterion are unambugously observed in the crystal structure. The average Cu-CF_3 bond lengths are *ca* 1.952(5) Å, which are disturbed by the disorders of the carbon atoms of CF_3 ligands.

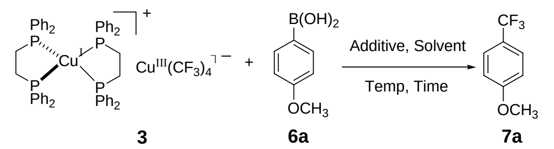


Scheme 3 Plausible mechanism for the formation of **1-5**.

As proposed in our previous study,[11] Cu^{II}-CF_3 intermediates **A** should probably be generated initially via oxidation and transmetalation (Scheme 3). The observation of Ag mirror and some green impurity during workup, and the detection of $FSiMe_3$ at *ca* -157 ppm in ^{19}F NMR supports this proposal. **A** could disproportionate into $LCu^{III}(CF_3)_3$ (**B**) and $LCu^{I}CF_3$ (**C**) that is in equilibrium with $[L_2Cu^{I}]^+[Cu^{III}(CF_3)_4]^-$ (**D**) after L/CF_3 ligand exchange between **B** and **C** (Scheme 3). Due to the much stronger coordinating ability of bisphosphines than phen or bpy and the polar solvent, this equilibrium should be irreversibly driven to the side of ion-pair complexes **D** for bisphosphines. In constrast, for less electron-rich N,N-chelates phen and bpy, the left side **B** + **C** should instead be dominant. Moreover, the presence of excess AgF and CF_3SiMe_3 may further enable iterative oxidation of **C** to **A** and disproportionation of **A** to **B+C**, resulting in the accumulation of **B**. This well rationalizes the selective formation of neutral type **B** for phen and bpy while ion-pair **D** type complexes for bisphosphines. The proposal of the equilibrium between **B+C** and **D**, and the effect of ancillary ligand-coordinaing ability on the equilibrium are supported by the observation that addition of excess phen to the solution of ion-pair **4** allow the access of neutral **1** in an isolated yield of 60% (please see ESI for more details)†. Possibly, ligand exchange between **4** and phen results in the formation of transient $[(phen)(BINAP)Cu^{I}]^+[Cu^{III}(CF_3)_4]^-$ (which parallels closely to complex **1′**) that is unstable and equilibriates preferentially to the neutral $phenCu^{III}(CF_3)_3$ (**1**) in the presence of excess phen. Similar conversion of **1′** to **1** in the presence of excess phen has already been observed in our previous study.[11]

Next, reactivity properties of complexes **3-5** were studied by reaction with arylboronic acids.[14] For ion-pair complex **3**, DMF is ineffective for trifluoromethylation of arylboronic acid **6a** (Table 1, entries 1,2). In nonpolar toluene, it was exciting to see that reaction of complex **3** with **6a** gave the trifluoromethylated product **7a** in 76% yield at 80°C for 18 hours, without the assistance of any additive (entry 3). The great promotion effect of non-polar toluene implies that neutral type **B** and/or **C** may also be involved in the aerobic trifluoromethylation since less polar solvent is expected to favor their generation from the equilibrium in Scheme 3.

Table 1 Reactivity studies of **3** with arylboronic acid **6a** [ab]

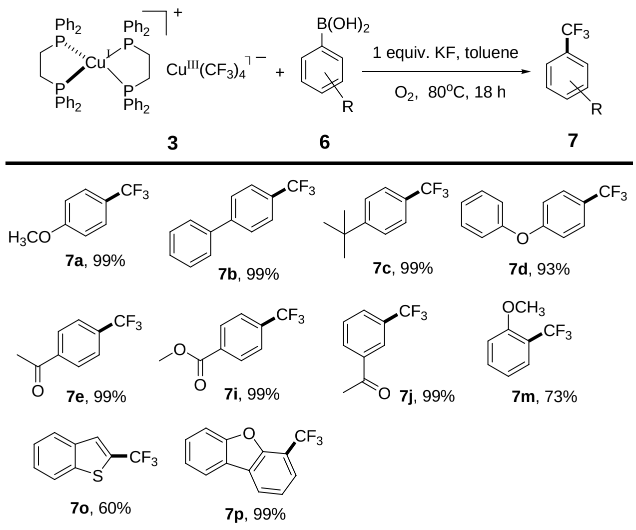


Entry	Additive	Solvent	Time (h)	T (℃)	Yield[%]
1	KF	DMF	18	80	7
2	K_3PO_4	DMF	18	80	6
3	**--**	**Toluene**	**18**	**80**	**76**
4	AgF	Toluene	18	80	84
5	KI	Toluene	18	80	55
6	Cs_2CO_3	Toluene	18	80	42
7	**KF**	**Toluene**	**18**	**80**	**99**
8	KF	Toluene	10	80	50
9	KF	Toluene	18	50	47

[a] Reaction conditions: **3** (0.1 mmol), **6a** (0.2 mmol), additive (0.2 mmol), 4,4′-difluorobiphenyl (0.2 mmol, internal standard, *ca* -117.0 ppm in ^{19}F NMR), solvent (1 mL), under dry O_2 atmosphere. [b] Yields determined by ^{19}F NMR spectroscopy relative to **6a**.

Further examination of additive effect (entries 4-7), such as AgF, KI, Cs_2CO_3 and KF shows that addition of KF led to the quantitative trifluoromethylation of **6a** in toluene (entry 7). AgF also shows some promoting effect, but are less efective than KF (entry 4). Both the reaction temperature and time are also important for achieving quantitative yields since reduced temperature and time led to much lower yields (entries 8,9). This finding achieves for the first time quantitative trifluoromethylation of arylboronic acids by isolated ion-pair Cu^I/Cu^{III} trifluoromethyl complexes.

Table 2 Substrate scope for reaction of **3** with various arylboronic acids [a]

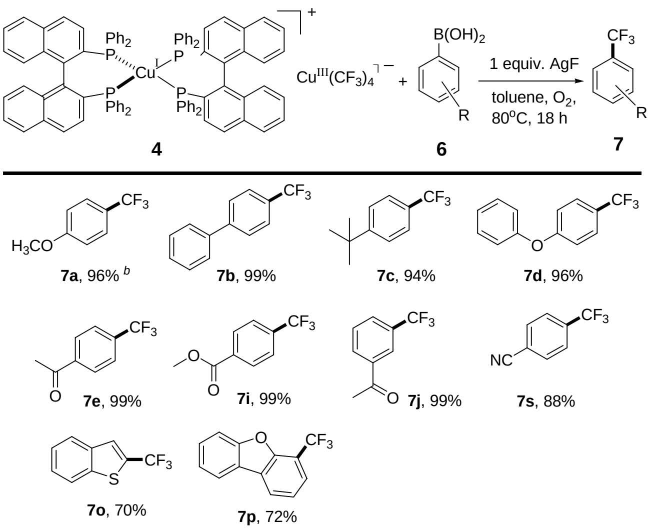


[a] Reaction yields were determined by ^{19}F NMR spectroscopy using 4,4′-difluorobiphenyl as internal standard (*ca* -117.0 ppm).

With the optimized reaction conditions identified, we next examined reaction of **3** with a variety of substituted aryl boronic acids **6** with diverse electronic properties (Table 2). Trifluoromethylated arenes **7** were thus prepraed in generally good to quantitative yields regardless of the electronic properties of the substituents. However, the reaction exhibits a significant steric effect for *ortho*-substituted arylboronic acid. For example, **7m** with an *ortho*-OMe was obtained in only 73%, which is much lower than the quantitative yied of regiomer **7a** with a *para*-OMe.

Similarly, complexes **4** and **5** also show up to quantitative reactivity toward aerobic trifluoromethylation of arylboronic acids under mild conditions. Some selected examples are summarized in Table 3 and 4 (see ESI for more details).† These results on the reactivity properties strongly imply that **3-5** are competent as reactive intermediates in oxidative trifluoromethylation reactions. Furthermore, the reactivity of ion-pari Cu^{III}-CF_3 complexes **3-5** are also in sharp contrast to the ion-pair complex **1′** containing phen which is unreactive toward trifluoromethylation of arylboronic acids.

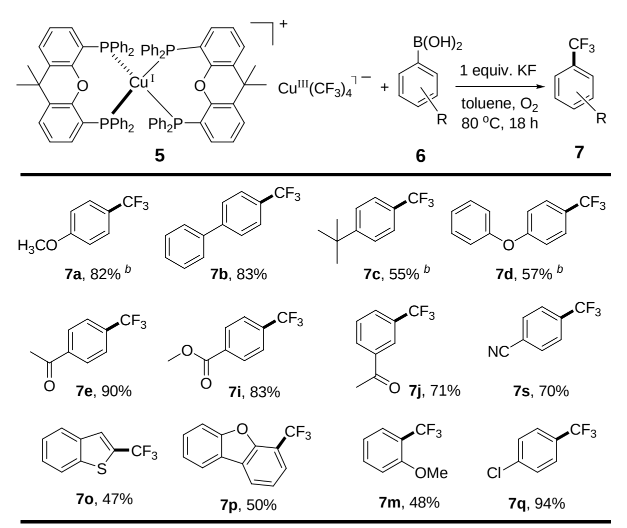
Table 3 Substrate scope for reaction of **4** with various arylboronic acids [a]



[a] Reaction yields were determined by ^{19}F NMR spectroscopy using 4,4′-difluorobiphenyl as internal standard (*ca* -117.0 ppm).[b] Using KF in DMF.

The ligand-dependent coordinating structures and distinct reactivity propreties of Cu^{III}-CF_3 complexes **1-5** as well as **1′** have important mechanistic implications as to the identity and reactivity patterns of active catalytic species for oxidative trifluoromethylation reactions. First, it implies that in the presence of different ancillary ligands, distinct copper CF_3 intermediates with totally different coordinating structures may be involved as the active catalytic species (or catalyst resting state). Second, the distinct reactivity propreties of **3-5** from that of phen-containing complex **1′** suggest that ancillary ligand has a crucial effect on the reactivity of Cu^{III}-CF_3 complexes. The structures of complexes **3-5** versus **1′** differ only in the Cu(I) cation with different ancillary ligands. Therefore, the Cu(I) cation must be responsible for the differences in reactivity of these complexes. Considering the fact the reactions of **3-5** with arylboronic acids are benefited in the nonpolar toluene solvent, this may suggest that neural bisphosphine-ligated $Cu^{III}(CF_3)_3$ complexes may probably be the real active species under the reaction conditions, although

Table 4 Substrate scope for reaction of **5** with various arylboronic acids [a]



[a] Reaction yields were determined by ^{19}F NMR spectroscopy using 4,4′-difluorobiphenyl as internal standard (*ca* -117.0 ppm). [b] Using AgF.

the concentrations should be very low. Therefore, a possible mechanistic scheme is that the ion-pair Cu^{I}/Cu^{III} CF$_3$ complexes constitute the Cu-CF$_3$ resting state, but the real active species are the neutral (P$_2$)Cu^{III}(CF$_3$)$_3$ species that are equilibrium with the resting state. Although the concentrations are low, the high reactivity of these (P$_2$)Cu^{III}(CF$_3$)$_3$ complexes renders the steady conversion of the ion-pair complexes to the neutral complexes to maintain such an equilibrium (Scheme 3). However, for complex **1′**, the conversion to neutral **1** requires the presence of additional excess phen which is absent in the aerobic trifluoromethylation reactions. More, the conditions (90°C in HOAc solvent) required for the conversion of **1′** to **1** as shown in our previous study[11] are also different from the aerobic trifluoromethylation conditions. Therefore, the unreactive **1′** should be unable to convert to the active neutral **1** under the aerobic trifluoromethylation reactions. This may rationalize the cation effect on the reactivity differences of **3-5** versus **1′**. Finally, the solvent polarity should impart significant effects on both the active catalyst forms and their reactivity properties. Further efforts on the elucidation of the detailed mechanisms for reaction of both the neutral and ion-pair Cu^{III}-CF$_3$ complexes are desirable to clearly resolve these fundamental issues.

In summary, ion-pair Cu^{I}/Cu^{III} CF$_3$ complexes **3-5** containing bisphospine ligands DPPE, BINAP and Xantphos are efficiently and selectively prepared following a general and mild method. Complexes **3-5** are composed of a tetrahedral [(bisphosphine)$_2$Cu^{I}]$^{+}$ and a square planar [Cu^{III}(CF$_3$)$_4$]$^{-}$. Their strucutres have been well characterized by ^{1}H, ^{19}F, ^{31}P NMR spectroscopy and X-ray crystallography for **3**. Under similar conditions neutral (L)Cu^{III}(CF$_3$)$_3$ complexes with N,N-bidentante ligands such as phen and bpy were determined previously. Furthermore, all these ion-pair complexes **3-5** are highly reactive toward arylboronic acids to produce trifluoromethylated arenes in up to quantitative yields under mild conditions. This is also in sharp contrast to the ion-pair complex **1′** that is unreactive toward arylboronic acids. The ligand-dependent formation, coordinating structures and reactivity properties of the N,N-bidentate and bisphosphine-containing Cu^{III} CF$_3$ complexes have important mechanistic implications that distinct reactive Cu^{III} CF$_3$ species and reaction mechanisms may be involved for trifluoromethylation reactions using different ancillary ligands.

This study was supported by the National Natural Science Foundation of China (21472068 and 21202062) and the Natural Science Foundation of Jiangsu Province (BK2012108).

Notes and references

[a] *The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, Jiangsu Province, China. Fax/Tel: +86-510-85917763; E-mail: slzhang@jiangnan.edu.cn*

† Electronic Supplementary Information (ESI) available: Experimental details, spectroscopic characterization data. See DOI: 10.1039/b000000x/

1 (a) P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, Germany, **2004**; (b) S. Purser, P. R. Moore, S. Swallow and V. V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320; (c) Y. Jiang, H. Yu, Y. Fu and L. Liu, *Sci. China Chem.*, 2015, **58**, 673.

2 (a) M. Schlosser, *Angew. Chem., Int. Ed.*, 2006, **45**, 5432; (b) J.-A. Ma and D. Cahard, *Chem. Rev.*, 2008, **108**, PR1; (c) V. V. Grushin, *Acc. Chem. Res.*, 2010, **43**, 160; (d) T. Furuya, A. S. Kamlet and T. Ritter, *Nature*, 2011, **473**, 470; (e) T. Liang, C. N. Neumann and T. Ritter, *Angew. Chem., Int. Ed.*, 2013, **52**, 8214.

3 (a) O. A. Tomashenko and V. V. Grushin, *Chem. Rev.*, 2011, **111**, 4475; (b) S. Roy, B. T. Gregg, G. W. Gribble, V.-D. Le and S. Roy, *Tetrahedron*, 2011, **67**, 2161; (c) T. Liu and Q. Shen, *Eur. J. Org. Chem.*, 2012, 6679; (d) X. Liu and X. Wu, *Synlett*, 2013, 1882; (e) P. Chen and G. Liu, *Synthesis*, 2013, 2919; (f) J. Xu, X. Liu and Y. Fu, *Tetrahedron Lett.*, 2014, **55**, 585; (g) X. D. Zhang, P. Huang, Y. M. Li and C. Y. Duan, *Org. Biomol. Chem.*, 2015, **13**, 10917.

4 For examples of copper-promoted trifluoromethylation of aryl and heteroaryl halides, please refer to ref. 3 and references cited therein.

5 For copper trifluoromethylation of ArB(OH)$_2$, see: (a) L. Chu and F.-L. Qing, *Org. Lett.*, 2010, **12**, 5060; (b) T. D. Senecal, A. T. Parsons and S. L. Buchwald, *J. Org. Chem.*, 2011, **76**, 1174; (c) T. Liu and Q. Shen, *Org. Lett.*, 2011, **13**, 2342; (d) J. Xu, D.-F. Luo, B. Xiao, Z.-J. Liu, T.-J. Gong, Y. Fu and L. Liu, *Chem. Commun.*, 2011, **47**, 4300; (e) C.-P. Zhang, J. Cai, C.-B. Zhou, X.-P. Wang, X. Zheng, Y.-C. Gu and J.-C. Xiao, *Chem. Commun.*, 2011, **47**, 9516; (f) X. Jiang, L. Chu and F.-L. Qing, *J. Org. Chem.*, 2012, **77**, 1251; (g) B. A. Khan, A. E. Buba and L. J. Goossen, *Chem. Eur. J.*, 2012, **18**, 1577; (h) N. D. Litvinas, P. S. Fier and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 2012, **51**, 536; (i) P. Nova′k, A. Lishchynskyi and V. V. Grushin, *Angew. Chem., Int. Ed.*, 2012, **51**, 7767; (j) Y. Ye and M. S. Sanford, *J. Am. Chem. Soc.*, 2012, **134**, 9034.

6 Copper-mediated trifluoromethylation of *arenes*, see: (a) R. Koller, K. Stanek, D. Stolz, R. Aardoom, K. Niedermann and A. Togni, *Angew. Chem., Int. Ed.*, 2009, **48**, 4332; (b) L. Chu and F.-L. Qing, *J. Am. Chem. Soc.*, 2012, **134**, 1298; (c) R. Shimizu, H. Egami, T. Nagi, J. Chae, Y. Hamashima and M. Sodeoka, *Tetrahedron Lett.*, 2010, **51**, 5947; (d) M. S. Wiehn, E. V. Vinogradova and A. Togni, *J. Fluorine Chem.*, 2010, **131**, 951; (e) S. Cai, C. Chen, Z. Sun and C. Xi, *Chem. Commun.*, 2013, **49**, 4552. For *alkene* trifluoromethylation reactions, see: (f) H. Egami and M. Sodeoka, *Angew. Chem., Int. Ed.*, 2014, **53**, 8293; (g) E. Merino and C. Nevado, *Chem. Soc. Rev.*, 2014, **43**, 6598. Copper-mediated trifluoromethylation of *alkynes*, see: (h) L. Chu and F.-L. Qing, *J. Am. Chem. Soc.*, 2010, **132**, 7262.

7 D. M. Wiemers and D. J. Burton, *J. Am. Chem. Soc.*, 1986, **108**, 832.

8 For isolated Cu^{I}-CF$_3$ complexes, see: (a) G. G. Dubinina, H. Furutachi and D. A. Vicic, *J. Am. Chem. Soc.*, 2008, **130**, 8600; (b) G. G. Dubinina, J. Ogikubo and D. A. Vicic, *Organometallics*, 2008, **27**, 6233; (c) H. Morimoto, T. Tsubogo, N. D. Litvinas and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 2011, **50**, 3793; (d) O. A. Tomashenko, E. C.

View Article Online
DOI: 10.1039/C6DT03016E

Escudero-Adan, M. M. Belmonte and V. V. Grushin, *Angew. Chem., Int. Ed.*, 2011, **50**, 7655; (e) Z. Weng, R. Lee, W. Jia, Y. Yuan, W. Wang, X. Feng and K.-W. Huang, *Organometallics*, 2011, **30**, 3229; (f) A. I. Konovalov, J. Benet-Buchholz, E. Martin and V. V. Grushin, *Angew. Chem., Int. Ed.*, 2013, **52**, 11637; (g) L. I. Panferova, F. M. Miloserdov, A. Lishchynskyi, M. M. Belmonte, J. Benet-Buchholz and V. V. Grushin, *Angew. Chem., Int. Ed.*, 2015, **54**, 5218.

9 (a) A. J. Hickman and M. S. Sanford, *Nature*, 2012, **484**, 177; (b) A. Casitas and X. Ribas, *Chem. Sci.*, 2013, **4**, 2301.

10 For Cu^{III}-CF_3 complexes, see: (a) M. A. Willert-Porada, D. J. Burton and N. C. Baenziger, *J. Chem. Soc. Chem. Commun.*, 1989, 1633; (b) D. Naumann, T. Roy, K.-F. Tebbe and W. Crump, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1482; (c) A. M. Romine, N. Nebra, A. I. Konovalov, E. Martin, J. Benet-Buchholz and V. V. Grushin, *Angew. Chem., Int. Ed.*, 2015, **54**, 2745; (d) J. A. Schlueter, U. Geiser, J. M. Williams, J. D. Dudek, D. Naumann, T. Roy, J. E. Schirber and W. R. Bayless, *J. Chem. Soc. Chem. Commun.*, 1994, 1599.

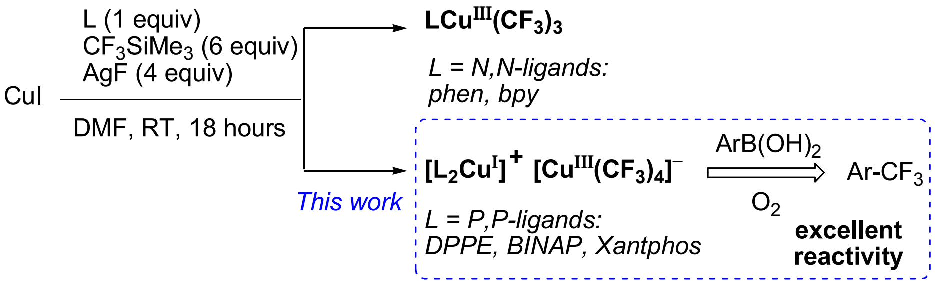
11 S.-L. Zhang and W.-F. Bie, *RSC Adv.*, 2016, **6**, 70902.

12 (a) E. J. Cho, T. D. Senecal, T. Kinzel, Y. Zhang, D. A. Watson and S. L. Buchwald, *Science*, 2010, **328**, 1679; (b) E. J. Cho and S. L. Buchwald, *Org. Lett.*, 2011, **13**, 6552; (c) V. V. Grushin and W. J. Marshall, *J. Am. Chem. Soc.*, 2006, **128**, 12644; (d) M. C. Nielsen, K. J. Bonney and F. Schoenebeck, *Angew. Chem., Int. Ed.*, 2014, **53**, 5903.

13 CCDC 1441928 (**3**) contains the supplementary crystallographic data which can be obtained free of charge from Cambridge Crystallographic Data Centre.

14 For detailed reaction procedures, please refer to ESI.†

View Article Online
DOI: 10.1039/C6DT03016E



Novel ion-pair Cu^{I}/Cu^{III} trifluoromethyl complexes with representative bisphosphines are isolated and fully characterized to feature square planar $[Cu^{III}(CF_3)_4]^{-}$ and tetrahedral $[L_2Cu]^{+}$ units. They show unprecedented excellent reactivity for aerobic trifluoromethylation of arylboronic acids in generally good to quantitative yields.