

# NJC

New Journal of Chemistry

A journal for new directions in chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Shieh, Y. Liu, C. Wang, S. Jian, C. Lin, Y. Chen and C. Huang, *New J. Chem.*, 2019, DOI: 10.1039/C9NJ02051A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

## ARTICLE

## A comparative study of NHC-functionalized ternary Se/Te–Fe–Cu compounds: synthesis, catalysis, and the effect of chalcogens

Minghuey Shieh,\* Yu-Hsin Liu, Chih-Chin Wang, Si-Huan Jian, Chien-Nan Lin, Yen-Ming Chen and Chung-Yi Huang

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

A novel family of N-heterocyclic carbene (NHC)-incorporated Se–Fe–Cu compounds, bis-1,3-dimethylimidazol-2-ylidene (bis-Me<sub>2</sub>-imy)-introduced compound  $[(\mu_4\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-imy})\}_2]$  (**2**), bis-N-methyl- or bis-N-isopropyl-substituted benzimidazol-2-ylidene (bis-Me<sub>2</sub>-bimy or bis-Pr<sub>2</sub>-bimy)-incorporated compounds  $[(\mu_4\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-bimy})\}_2]$  (**3**) or  $[(\mu_4\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{Pr}_2\text{-bimy})\}_2]$  (**4**), and a bis-1,3-dimethyl-4,5-dichloroimidazol-2-ylidene (bis-Me<sub>2</sub>-Cl<sub>2</sub>-imy)-containing compound  $[(\mu_3\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-Cl}_2\text{-imy})\}_2]$  (**5**), were synthesized in moderate yields in facile one-pot reactions of the ternary pre-designed compound  $[(\mu_3\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{MeCN})\}_2]$  (**1**) with the corresponding imidazolium salts and KO<sup>t</sup>Bu in THF in an ice-water bath. Single-crystal X-ray analyses revealed that the Me<sub>2</sub>-imy compound **2** or the Me<sub>2</sub>-bimy compound **3** each exhibited a trigonal bipyramidal SeFe<sub>3</sub>(CO)<sub>9</sub>Cu geometry with an Fe<sub>2</sub>Cu plane further capped by a Cu(Me<sub>2</sub>-imy) or Cu(Me<sub>2</sub>-bimy) fragment, respectively, with one long Cu–Cu covalent bond. In addition, compound **4** also was comprised of a trigonal bipyramidal SeFe<sub>3</sub>(CO)<sub>9</sub>Cu core structure, but the second Cu(Pr<sub>2</sub>-bimy) group bridged the equatorial Fe–Fe edge with the two unbonded Cu atoms, due to the presence of a sterically bulky Pr<sub>2</sub>-bimy fragment. On the other hand, the strong electron-withdrawing chloro-containing NHC compound **5** showed a comparatively open tetrahedral SeFe<sub>3</sub>(CO)<sub>9</sub> metal core, where two Fe–Fe edges each was further bridged by a Cu(Me<sub>2</sub>-Cl<sub>2</sub>-imy) fragment. Due to the nonclassical C–H⋯O(carbonyl) hydrogen bonds between the CO groups of the SeFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub> core and CH moieties of the neighboring NHC ligands, compounds **2** and **3** both were comprised of a one-dimensional network, while compounds **4** and **5** each were made up of a two-dimensional framework in the solid states, which efficiently enhanced the stability of these Se–Fe–Cu NHC compounds. Importantly, all of these synthesized Se–Fe–Cu NHC compounds **2–5** had pronounced catalytic activities for the homocoupling of arylboronic acids with high catalytic yields. Finally, these Se-containing Fe–Cu NHC compounds further represented excellent models for chalcogen effects in comparison with their Te analogs, as demonstrated by their catalytic performances and electrochemical behaviors, as well as by DFT calculations.

## 1. Introduction

The chemistry of heterometallic carbonyl clusters has attracted widespread interest, due to their versatile structures, distinct reactivities, and numerous applications in magnetism, catalysis, conductivity, and nanotechnology.<sup>1–5</sup> The introduction of chalcogen atoms into heterometallic complexes not only stabilize the resulting clusters but also can be used to fine tune their physical and chemical properties.<sup>2–5</sup> For example, it has been reported that E–Mn–Cr complexes (E = S, Se, Te) had rich electrochemical behaviors,<sup>3</sup> and Te–Fe–Cu-based coordination polymers were reported to display semiconducting properties with ultra-narrow energy gaps.<sup>4</sup> In

our previous studies, a series of NHC Te–Fe–Cu-based carbonyl compounds showed pronounced catalytic activities toward the Suzuki homocoupling reaction, due to the incorporation of the effective electron-donating and bulky inorganic ligand  $[\text{TeFe}_3(\text{CO})_9]^{2-}$ .<sup>5</sup> In spite of several reported NHC-containing heterometallic carbonyl telluride compounds,<sup>5</sup> only one example of a NHC-stabilized heterometallic selenide compound has been reported,<sup>6</sup> presumably due to the lack of the systematic syntheses in the Se system. It should also be noted that no examples of NHC heterometallic selenide compounds were used as catalysts for organic reactions.

Prompted by these facts, we attempted to synthesize a new class of Se-containing dimetallic NHC compounds. For this purpose, we were drawn back to our previous research and found that the pre-designed  $[(\mu_3\text{-Te})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{MeCN})\}_2]$  compound acted as an important starting material for preparing a series of monodentate-, bidentate-, and functionalized-NHC-containing Te–Fe–Cu compounds.<sup>5</sup> In this work, we not only successfully isolated an unstable ternary

Department of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan (Republic of China). E-mail: mshieh@ntnu.edu.tw

\* Electronic Supplementary Information (ESI) available: Compounds characterization and supplementary data. CCDC 1909685, 1909691, 1909692, 1909693, and 1909694. See DOI: 10.1039/x0xx00000x

ARTICLE

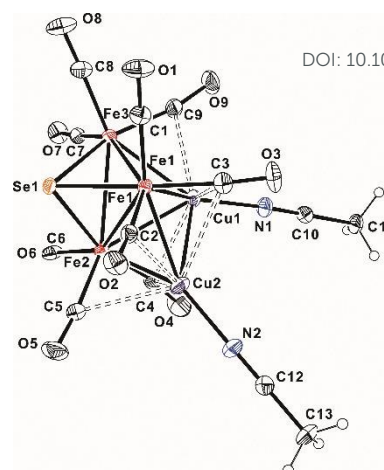
Journal Name

pre-designed  $[(\mu_3\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{MeCN})\}_2]$  cluster but also provided three types of functionalized-NHC  $\text{SeFe}_3\text{Cu}_2$ -based compounds, i.e. the structurally analogous  $\text{Cu}(\text{Me}_2\text{-imy})$ - or  $\text{Cu}(\text{Me}_2\text{-bimy})$ -capped trigonal bipyramidal  $\text{SeFe}_3(\text{CO})_9\text{Cu}$ -based compounds,  $[(\mu_4\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-imy})\}_2]$  (**2**) or  $[(\mu_4\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-bimy})\}_2]$  (**3**) ( $\text{Me}_2\text{-imy}$  = 1,3-dimethylimidazol-2-ylidene;  $\text{Me}_2\text{-bimy}$  = 1,3-dimethylbenzimidazol-2-ylidene), the  $\text{Cu}(\text{Pr}_2\text{-bimy})$ -bridged trigonal bipyramidal  $\text{SeFe}_3(\text{CO})_9\text{Cu}$ -based compound,  $[(\mu_4\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{Pr}_2\text{-bimy})\}_2]$  (**4**) ( $\text{Pr}_2\text{-bimy}$  = 1,3-diisopropylbenzimidazol-2-ylidene), and the bis- $\text{Cu}(\text{Me}_2\text{-Cl}_2\text{-imy})$ -bridged tetrahedral  $\text{SeFe}_3(\text{CO})_9$ -based compound,  $[(\mu_3\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-Cl}_2\text{-imy})\}_2]$  (**5**) ( $\text{Me}_2\text{-Cl}_2\text{-imy}$  = 1,3-dimethyl-4,5-dichloroimidazol-2-ylidene), from facile one-pot reactions of compound **1** with the corresponding imidazolium salts and  $\text{KO}^t\text{Bu}/\text{THF}$  in moderate yields. Importantly, these synthesized compounds **2–5** could be used as efficient catalysts in the homocoupling of 4-bromophenylboronic acid and showed high turnover numbers (TONs). In addition, the chalcogen effects of the structurally analogous  $\text{E-Fe-Cu}$  NHC compounds ( $\text{E} = \text{Se}, \text{Te}$ ) were further studied in terms of their catalytic performances and electrochemical behavior, supported by DFT calculations.

## 2. Results and discussion

### 2.1 One-pot synthesis of a novel family of the NHC-incorporated ternary Se-Fe-Cu carbonyl compounds

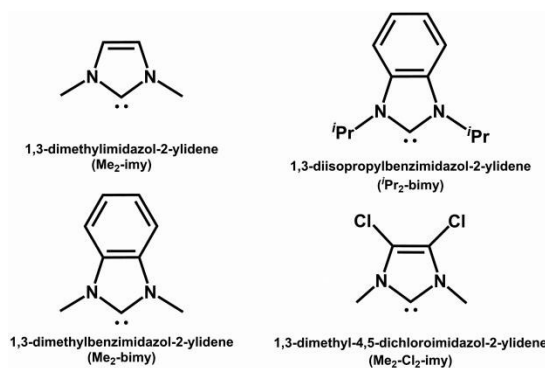
Only a few studies of the NHC heterometallic chalcogenide compounds have been reported,<sup>5–7</sup> probably owing to a lack of methods for the systematic syntheses. In our previous study, a series of  $\text{TeFe}_3(\text{CO})_9$  dicopper NHC compounds were synthesized and found to act as efficient catalysts in the Suzuki homocoupling reactions of arylboronic acid.<sup>5</sup> Given our interest in chalcogen-containing metal carbonyl compounds,<sup>2c,2f,2i,2k,3–5</sup> this prompted us to wonder whether the electronic demands and steric hindrances of chalcogens and NHCs in these chalcogen-iron-copper NHC compounds might play an important factor in influencing their catalytic performance. For this purpose, by mimicking previously reported synthetic routes in the Te system,<sup>4a</sup> we attempted to synthesize the pre-synthesized Se-containing Fe-Cu starting material,  $[(\mu_3\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{MeCN})\}_2]$ , but this method was complicated and was accompanied with a large quantity of decomposition, presumably due to the steric bulk between the  $\text{Fe}_3(\text{CO})_9$  ring and the incoming  $\text{Cu}(\text{MeCN})$  fragments caused by the smaller-sized Se atom. To address this issue, the reaction was carried out at 0 °C to decrease the extent of the



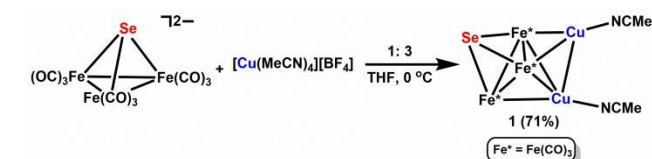
**Fig. 1** An ORTEP diagram (30% thermal ellipsoids) showing the structure and atom labeling for **1**.

decomposition and to stabilize the thermally unstable cluster  $[(\mu_3\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{MeCN})\}_2]$ . After considerable efforts, we were able to successfully synthesize the new Se-Fe-Cu cluster  $[(\mu_3\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{MeCN})\}_2]$  (**1**) in a moderate yield of 71% by reacting  $[\text{SeFe}_3(\text{CO})_9]^{2-}$  with 3 equiv. of  $[\text{Cu}(\text{MeCN})_4]^+$  in THF at 0 °C (Scheme 1). It was notable that compound **1** was very temperature-sensitive, hence, the reaction, purification, and crystallization must be carried out at 0 °C. X-ray analysis showed that compound **1** possessed a distorted  $(\mu_3\text{-Se})\text{Fe}_3(\text{CO})_9\text{Cu}(\text{MeCN})$ -based trigonal bipyramidal core with the  $\text{Fe}_3$  ring residing in the equatorial plane, and the  $\text{Fe}_2\text{Cu}$  plane was further capped by a  $\text{Cu}(\text{MeCN})$  fragment with two Cu atoms covalently bonded (2.6682(5) Å) (Fig. 1). Although the structure of compound **1** was similar to its Te analog, the  $\text{SeFe}_3(\text{CO})_9\text{Cu}(\text{MeCN})$  metal core in **1** was more extensively distorted than its Te congener, mainly due to the larger atomic size difference between the Se, Fe, and Cu atoms. In addition, the Cu-Cu bond distance in **1** (2.6682(5) Å) was much longer than that of  $[(\mu_3\text{-Te})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{MeCN})\}_2]$  (2.605(1) Å)<sup>4a</sup> and also much longer than those of most previously reported Se-Fe-Cu complexes,

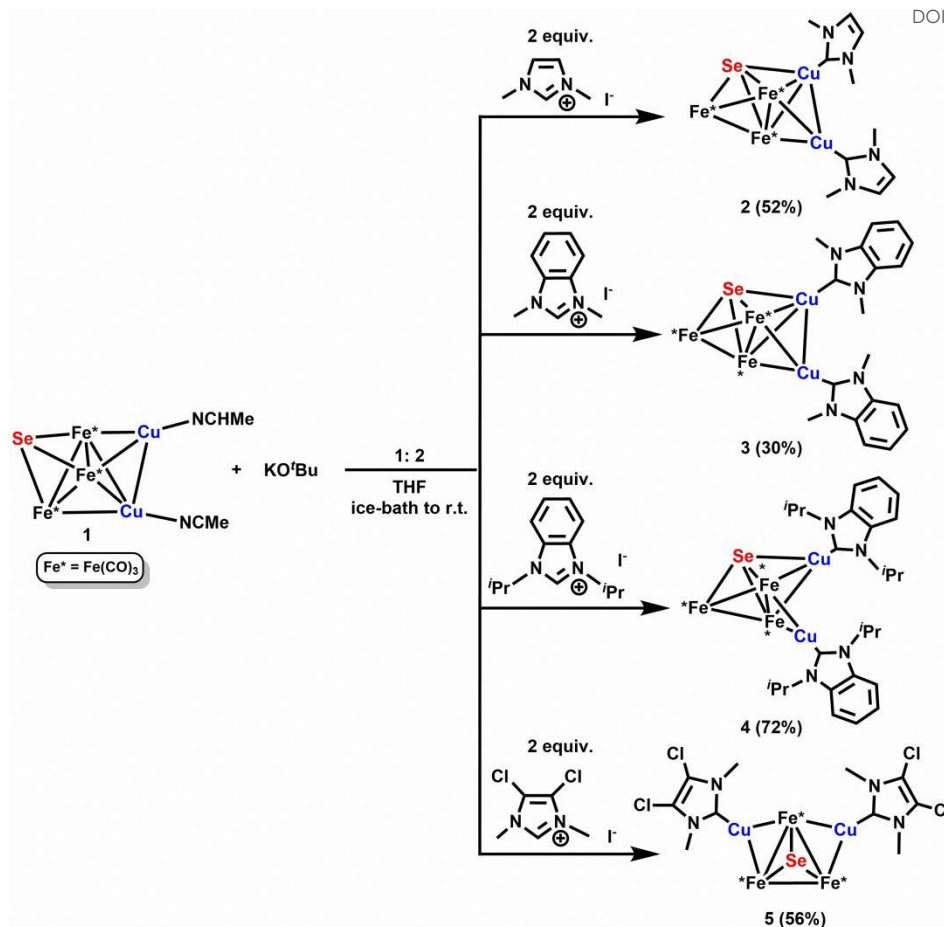
$\text{Cu}_2(\mu_2\text{-}\eta^2\text{-fcSe}_2)(\text{P}^t\text{Pr}_3)_2$	2.6155(8)	Å, <sup>9a</sup>
$\text{Cu}_{20}\text{Se}_6(\text{fcSe}_2)_4(\text{P}^n\text{Pr}_3)_{10}$	2.60(3)	Å, <sup>9a</sup>
$\text{Cu}_{36}(\text{fcSe}_2)_6\text{Se}_{12}(\text{P}^n\text{Pr}_3)_{10}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{SH})_2$	2.62(6)	Å, <sup>9a</sup>



**Chart 1.** Structures and abbreviations of the N-heterocyclic carbenes reported in this work.



**Scheme 1** Synthesis of the ternary Se-Fe-Cu cluster.

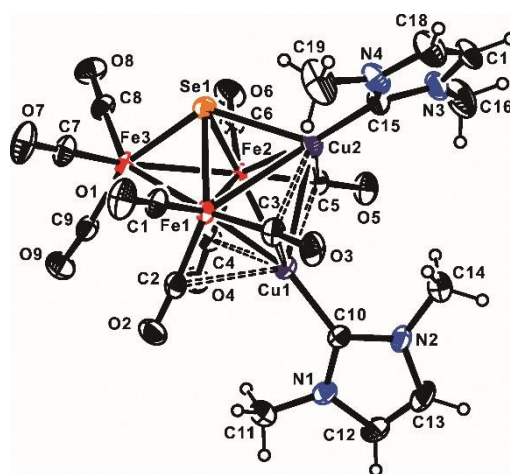


**Scheme 2** One-pot synthesis of a novel family of  $\text{SeFe}_3\text{Cu}_2$ -based NHC compounds 2–5.

$\text{Cu}_{36}\text{Se}_{12}(\text{fcSe}_2)_6(\text{P}^n\text{Pr}_2\text{Ph})_{12}$  (2.65(8) Å) ( $\text{fc} = \text{FeCp}_2$ ),<sup>9a</sup>  $[\{\text{SeFe}_3(\text{CO})_9\}_2\text{Cu}_4\text{Cl}_2]^{2-}$  (2.583(1) Å),<sup>9b</sup>  $[\{\text{SeFe}_3(\text{CO})_9\}_2\text{Cu}_4\text{Br}_2]^{2-}$  (2.5930(7) Å),<sup>9b</sup> and  $\text{Cu}_{40}\text{Se}_{12}(\text{Se}_2\text{fc})_8(\text{PPh}_3)_9$  (2.532(5) Å),<sup>9c</sup> indicating that the Cu–Cu bond in **1** was weak and much more sterically hindered.

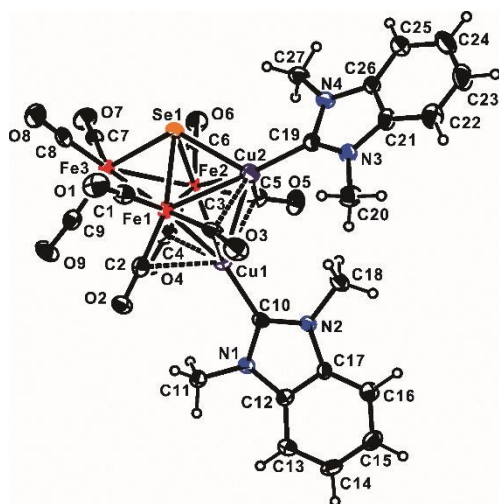
With the reactive Se–Fe–Cu precursor **1** in hand, we treated **1** with various imidazolium salts, including 1,3-dimethylimidazolium iodide ( $\text{Me}_2\text{-imy}\cdot\text{HI}$ ), 1,3-dimethylbenzimidazolium iodide ( $\text{Me}_2\text{-bimy}\cdot\text{HI}$ ), 1,3-diisopropylbenzimidazolium iodide ( $i\text{Pr}_2\text{-bimy}\cdot\text{HI}$ ), and 1,3-dimethyl-4,5-dichloroimidazolium iodide ( $\text{Me}_2\text{-Cl}_2\text{-imy}\cdot\text{HI}$ ) were carried out. As shown in Scheme 2, four bis-NHC Se–Fe–Cu compounds,  $[(\mu_4\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-imy})\}_2]$  (**2**),  $[(\mu_4\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-bimy})\}_2]$  (**3**),  $[(\mu_4\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(i\text{Pr}_2\text{-bimy})\}_2]$  (**4**), and  $[(\mu_3\text{-Se})\text{Fe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-Cl}_2\text{-imy})\}_2]$  (**5**), were obtained in moderate yields directly *via* one-pot stoichiometric reactions of **1**, imidazolium salts, and  $\text{KO}^t\text{Bu}$  in THF in an ice-water bath. As shown in Figs. 2 and 3, compounds **2** and **3** both exhibited a trigonal bipyramidal  $\text{SeFe}_3(\text{CO})_9\text{Cu}$  geometry with an  $\text{Fe}_2\text{Cu}$  plane capped by one Cu atom, in which each Cu atom was coordinated by a  $\text{Me}_2\text{-imy}$  or  $\text{Me}_2\text{-bimy}$  fragment. Although compounds **2** and **3** and their parent compound **1** exhibited the similar trigonal pyramidal  $\text{SeFe}_3(\text{CO})_9\text{Cu}$ -based

metal core, the equatorial  $\text{Fe}_3$  ring in **1** was converted into the  $\text{SeFe}_2$  ring in **2** and **3** to produce a  $\mu_4\text{-Se}$  atom, which presumably weakens the repulsion between the COs and the incoming bulky  $\text{Me}_2\text{-imy}$  and  $\text{Me}_2\text{-bimy}$  ligands. It should be noted, however, that the two  $\text{Me}_2\text{-imy}$ - or  $\text{Me}_2\text{-}$



**Fig. 2** An ORTEP diagram (30% thermal ellipsoids) showing the structure and atom labeling for **2**.

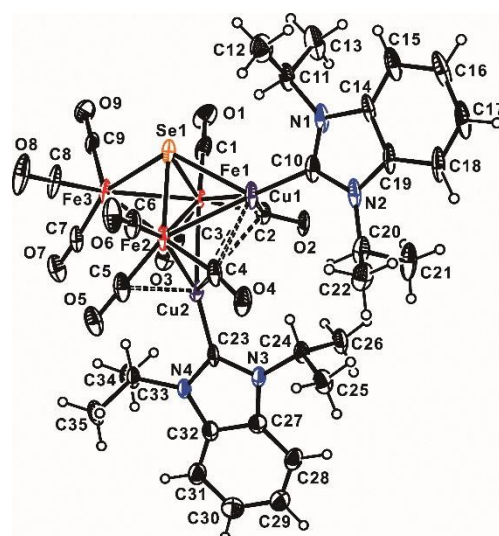




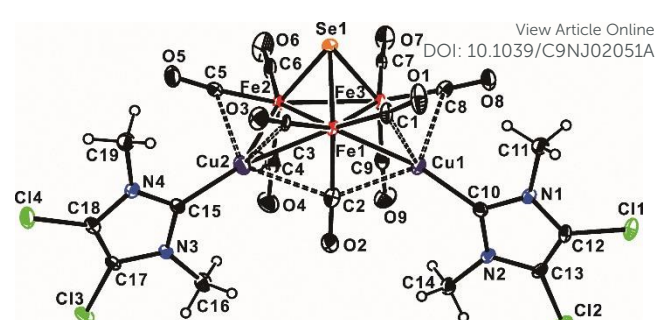
**Fig. 3** An ORTEP diagram (30% thermal ellipsoids) showing the structure and atom labeling for **3**.

bimyl-coordinated Cu atoms in **2** and **3** still remained covalently bonded (2.869(1) Å for **2**; 2.832(1) Å for **3**), suggesting that the ( $\mu_4$ -Se)Fe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub> metal core could tolerate the introduction of the additional NHC ligands.

On the other hand, compound **4** also displayed a ( $\mu_4$ -Se)Fe<sub>3</sub>(CO)<sub>9</sub>Cu-based trigonal bipyramidal metal core, where the equatorial Fe-Fe edge was bridged by the second Cu(<sup>i</sup>Pr<sub>2</sub>-bimy) with two nonbonded Cu atoms (3.385(2) Å), owing to the sterically bulky <sup>i</sup>Pr<sub>2</sub>-bimy fragment (Fig. 4). In addition, compound **5** was composed of a comparatively wide-open tetrahedral SeFe<sub>3</sub>(CO)<sub>9</sub> core with two Fe-Fe edges each of which was linked by a Cu(Me<sub>2</sub>-Cl<sub>2</sub>-imy) fragment, where two Cu(Me<sub>2</sub>-Cl<sub>2</sub>-imy) groups were oriented in a *cis* configuration (Fig. 5). It is important to note that these NHC Se-Fe-Cu compounds **2**–**5** were not temperature-sensitive, indicating that the introduction of the NHC ligands into the SeFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub> cores efficiently enhanced their thermal stability. In addition, all of these structures basically obeyed



**Fig. 4** An ORTEP diagram (30% thermal ellipsoids) showing the structure and atom labeling for **4**.



**Fig. 5** An ORTEP diagram (30% thermal ellipsoids) showing the structure and atom labeling for **5**.

Wade's rule. While SeFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub>-based clusters **1**–**4** each had six skeletal electron pairs for a trigonal bipyramidal SeFe<sub>3</sub>(CO)<sub>9</sub>Cu structure with a capping fragment Cu(MeCN) or Cu(NHC) (NHC = Me<sub>2</sub>-imy and Me<sub>2</sub>-bimy) or a bridging Cu(<sup>i</sup>Pr<sub>2</sub>-bimy) group, cluster **5** is a standard *nido*-type of SeFe<sub>3</sub>(CO)<sub>9</sub>-based tetrahedral cluster with six skeletal electron pairs. Until now, no other NHC-incorporated ternary Se-Fe-Cu carbonyl compounds have been reported to date. In this study, we discovered a new effective synthon **1** for constructing a novel family of SeFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub>-based NHC compounds.

## 2.2 X-ray structural comparison of compounds 2–5

For further a comparison of the steric effect of the introduced NHC ligands of compounds **2**–**5**, the distances between the two Cu atoms in these compounds are listed in Table 1. As shown in Table 1, when MeCN ligands in **1** were substituted by the incoming Me<sub>2</sub>-imy ligands, the Cu–Cu bond in **2** became elongated compared that in **1** due to steric effects. In addition, when 1,3-dimethylbenzimidazol-2-ylidene (Me<sub>2</sub>-bimy) was introduced, the distance between the Cu–Cu bond in **3** was found to be shorter than that of **2**, implying that the slightly electron-withdrawing Me<sub>2</sub>-bimy fragments may have reduced the extent of repulsion between the two Cu atoms. In addition, the average Cu–C<sub>carbene</sub> bond distances of compounds **2**–**5** (1.91–1.96 Å) (Table 1) were within the range of the Cu–C<sub>carbene</sub> bond (*ca.* 1.80–2.20 Å) in the related NHC-containing Cu(I) complexes.<sup>5,10</sup> It also was interesting to note that the bond distance of the average Cu–C<sub>carbene</sub> bond in **5** (1.96(2) Å) was the longest, followed by **3** (1.94(1) Å), **2** (1.927(1) Å), and **4** (1.918(1) Å), suggesting that the strong electron-withdrawing chloro-containing NHC in **5** efficiently weakens the Cu–C<sub>carbene</sub> bonds, even though compound **5** exhibited a comparatively open tetrahedral structure. In contrast, the bulkiest <sup>i</sup>Pr<sub>2</sub>-bimy-containing compound **4** displayed the shortest Cu–C<sub>carbene</sub> bond, probably because of the relief of steric restraint caused by the two unbound Cu atoms.

In addition, we hypothesized that intra-/intermolecular interactions within these structures might help stabilize these bulky NHC-introduced highly strained SeFe<sub>3</sub>Cu<sub>2</sub>-based compounds. In compounds **2**–**5**, the distances between the copper atoms and carbon atoms of the adjacent COs were less than the sum of their van der Waals radii (3.10 Å) and

**Table 1** Average bond distances (Å) for **1**, **2**, **3**, **4**, and **5**

Compound	Se–Fe <sup>a</sup>	Fe–Fe <sup>a</sup>	Fe–Cu <sup>a</sup>	Cu–Cu	Cu–X	Se–Cu
[SeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(MeCN)} <sub>2</sub> ] ( <b>1</b> ) (X = N)	2.31(2)	2.70(6)	2.51(4)	2.6682(5)	1.926(2) <sup>b,g</sup> 1.891(2) <sup>c,f</sup>	
[SeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(Me <sub>2</sub> -imy)} <sub>2</sub> ] ( <b>2</b> ) (X = C)	2.34(3)	2.65(3)	2.6(1)	2.869(1)	1.926(7) <sup>b,e</sup> 1.928(6) <sup>c,f</sup>	2.429(1)
[SeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(Me <sub>2</sub> -bimy)} <sub>2</sub> ] ( <b>3</b> ) (X = C)	2.34(2)	2.64(5)	2.6(1)	2.832(1)	1.946(6) <sup>b,e</sup> 1.929(6) <sup>c,f</sup>	2.469(1)
[SeFe <sub>3</sub> (CO) <sub>9</sub> {Cu( <sup>i</sup> Pr <sub>2</sub> -bimy)} <sub>2</sub> ] ( <b>4</b> ) (X = C)	2.33(1)	2.65(6)	2.54(5)		1.919(6) <sup>b,e</sup> 1.917(6) <sup>d,h</sup>	2.501(2)
[SeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(Me <sub>2</sub> -Cl <sub>2</sub> -imy)} <sub>2</sub> ] ( <b>5</b> ) (X = C)	2.313(9)	2.65(3)	2.53(4)		1.96(2) <sup>a,d,h</sup>	

<sup>a</sup> Average bond distances.  
<sup>b</sup> Five-coordinated Cu atom.  
<sup>c</sup> Four-coordinated Cu atom.  
<sup>d</sup> Three-coordinated Cu atom.

<sup>f</sup> The Cu–NHC fragment capped the SeFe<sub>2</sub> triangle.  
<sup>g</sup> The Cu–NHC fragment capped the Fe<sub>2</sub>Cu triangle.  
<sup>h</sup> The Cu–NHC fragment capped the Fe<sub>3</sub> triangle.  
<sup>i</sup> The Cu–NHC fragment bridged the Fe<sub>2</sub> edge.

significantly longer than the sum of their covalent radii (2.01 Å).<sup>11a,11b</sup> The corresponding Fe–C–O angles were slightly bent from 180°, indicative of weak Cu/C interactions in these ternary Se–Fe–Cu NHC clusters (Figs. 2–5). Although the COs had slightly different environments in the solid states, only one resonance of the COs in these compounds was observed in the <sup>13</sup>C NMR, due to the fast exchange of the COs.

Notably, the 1D networks of **2** and **3** and 2D frameworks of **4** and **5** are revealed in their solid-state packings, *via* nonclassical C–H⋯O(carbonyl) hydrogen bonds<sup>11c,11d</sup> between the COs of the SeFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub> core and the CH moieties of the neighboring NHC ligands (Figs. S1 and S2 and Table S1, ESI<sup>†</sup>). With these nonclassical C–H⋯O(carbonyl) forces<sup>11c,11d</sup> within their infinite 1D- or 2D-frameworks, compounds **2–5** would be predicted to have very great stability and to be stored for extended times in the solid state. To further examine the stability of these compounds, **2** was examined for its air- and water-stability. Compared with the slightly air-sensitive compound **1**, compound **2** was stable in air or water for more than 5 days, as confirmed by powder X-ray diffraction (PXRD) (Fig. S3, ESI<sup>†</sup>), indicating that these nonclassical C–H⋯O(carbonyl) forces<sup>11c,11d</sup> between the COs and NHC ligands further stabilized these SeFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub>-based NHC catalysts.

### 2.3 Suzuki homocoupling reactions using **2–5** as catalysts

With these synthesized Se–Fe–Cu NHC compounds in hand, we examined the roles of the incorporated cluster, [SeFe<sub>3</sub>(CO)<sub>9</sub>]<sup>2–</sup>, and NHC ligands in catalytic reactions. For this purpose, they were examined as catalysts in the Suzuki homocoupling reaction<sup>12</sup> of 4-bromophenylboronic acid, in which the reaction condition was controlled so as to include 1.0 mol% of Cu loading, a MeOH solvent system, an O<sub>2</sub> atmosphere, ambient

temperature, and importantly, with no additive agents such as ligands, bases, or other oxidants (Table 2).

[SeFe<sub>3</sub>(CO)<sub>9</sub>]<sup>2–</sup> was initially examined as a catalyst in this homocoupling reaction. However, [SeFe<sub>3</sub>(CO)<sub>9</sub>]<sup>2–</sup> exhibited no activity toward 4-bromophenylboronic acid, even though the time for this catalytic reaction was extended to 1 day (Table 2). Furthermore, [Cu(MeCN)<sub>4</sub>][BF<sub>4</sub>] and [Cu<sub>2</sub>(Melm(CH<sub>2</sub>)<sub>2</sub>ImMe)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> both showed catalytic activity,<sup>5a</sup> revealing that Cu was essential for catalytic performance. However, the turnover frequency (TOF) of [Cu<sub>2</sub>(Melm(CH<sub>2</sub>)<sub>2</sub>ImMe)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (TOF = 10.6 h<sup>–1</sup>) was significantly higher than that of the non-NHC-containing Cu(I) complex [Cu(MeCN)<sub>4</sub>][BF<sub>4</sub>] (TOF = 0.8 h<sup>–1</sup>), indicating the importance of the NHC ligands in catalysis. Surprisingly, these SeFe<sub>3</sub>(CO)<sub>9</sub>-based dicopper NHC catalysts **2–5** possessed even much higher TOFs (TOF = 18.2 ~ 21.8 h<sup>–1</sup>) than that of [Cu<sub>2</sub>(Melm(CH<sub>2</sub>)<sub>2</sub>ImMe)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (TOF = 10.6 h<sup>–1</sup>) (Table 2). These results demonstrate that [SeFe<sub>3</sub>(CO)<sub>9</sub>]<sup>2–</sup> acts as an excellent and suitable ligand to efficiently enhance the catalytic performance of these NHC-dicopper complexes. For further comparison, compound **2** (TOF = 21.8 h<sup>–1</sup>) had a slightly higher TOF compared to for the N-methyl- or N-isopropyl-substituted benzimidazol-2-ylidene compound **3** (TOF = 21.2 h<sup>–1</sup>) or **4** (TOF = 20.0 h<sup>–1</sup>), indicating that the presence of benzimidazol-2-ylidene slightly retarded the catalytic reaction (Table 2). In addition, the TOF of the Me<sub>2</sub>-Cl<sub>2</sub>-imy compound **5** (TOF = 18.2 h<sup>–1</sup>) was lower than the corresponding values for compounds **2–4** (TOF = 20.0–21.8 h<sup>–1</sup>) but much higher than that of the parent compound **1** (TOF = 13.3 h<sup>–1</sup>), indicating that the catalytic performance of the most structurally open and strong electron-withdrawing NHC-containing, namely, compound **5** was least effective compared to compounds **2–4** but still better than that of the non-NHC-containing compound **1**.

**Table 2** Homocoupling of 4-bromophenylboronic acid with different catalysts<sup>a</sup>

View Article Online  
DOI: 10.1039/C9NJ02051A

Entry	Catalyst	Cu (mol%)	Time (h)	Yield (%) <sup>b,c</sup>	TON <sup>d</sup>	TOF (h <sup>-1</sup> ) <sup>e</sup>	Ref.
1	[Et <sub>4</sub> N] <sub>2</sub> [SeFe <sub>3</sub> (CO) <sub>9</sub> ]	0 <sup>g</sup>	24	0	–	–	<i>f</i>
2	[Cu(MeCN) <sub>4</sub> ][BF <sub>4</sub> ]	1.0	60	47	47	0.8	5a
3	[Cu <sub>2</sub> (MeIm(CH <sub>2</sub> ) <sub>2</sub> ImMe) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>	1.0	8	85	85	10.6	5a
4	[SeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(MeCN)} <sub>2</sub> ] ( <b>1</b> )	1.0	6	80	80	13.3	<i>f</i>
5	[TeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(MeCN)} <sub>2</sub> ]	1.0	3	85	85	28.3	5a
6	[SeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(Me <sub>2</sub> -imy)} <sub>2</sub> ] ( <b>2</b> )	1.0	4	87	87	21.8	<i>f</i>
7	[TeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(Me <sub>2</sub> -imy)} <sub>2</sub> ]	1.0	2	88	88	44.0	5a
8	[SeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(Me <sub>2</sub> -bimy)} <sub>2</sub> ] ( <b>3</b> )	1.0	4	85	85	21.2	<i>f</i>
9	[TeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(Me <sub>2</sub> -bimy)} <sub>2</sub> ]	1.0	4.5	82	82	18.2	5b
10	[SeFe <sub>3</sub> (CO) <sub>9</sub> {Cu( <sup>i</sup> Pr <sub>2</sub> -bimy)} <sub>2</sub> ] ( <b>4</b> )	1.0	4	80	80	20.0	<i>f</i>
11	[TeFe <sub>3</sub> (CO) <sub>9</sub> {Cu( <sup>i</sup> Pr <sub>2</sub> -bimy)} <sub>2</sub> ]	1.0	3	80	80	26.7	5b
12	[SeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(Me <sub>2</sub> -Cl <sub>2</sub> -imy)} <sub>2</sub> ] ( <b>5</b> )	1.0	4.5	82	82	18.2	<i>f</i>
13	[TeFe <sub>3</sub> (CO) <sub>9</sub> {Cu(Me <sub>2</sub> -Cl <sub>2</sub> -imy)} <sub>2</sub> ]	1.0	2.2	81	81	36.8	5b

<sup>a</sup> Reaction conditions: 4-bromophenylboronic acid (1.0 mmol), MeOH (3.0 mL), 25 °C, O<sub>2</sub> (1 atm, balloon). <sup>b</sup> The isolated yield as an average of three runs. <sup>c</sup> All reactions were monitored by TLC. <sup>d</sup> Turnover number per copper for the 4-bromophenylboronic acid consumed. <sup>e</sup> TON per hour. <sup>f</sup> This work. <sup>g</sup> 1.5 mol% of Fe loading.

To further understand the chalcogen effect of compounds **2–5** in the catalytic reaction, we were drawn back to the catalytic performance of our previously reported Te–Fe–Cu NHC compounds.<sup>5</sup> As shown in Table 2, the catalytic performance of these EFe<sub>3</sub>Cu<sub>2</sub>-based catalysts (E = Se, Te) was all high (80–88%), however, the TOFs for the Se–Fe–Cu NHC compounds (18.2–21.8 h<sup>-1</sup>) were somehow lower than those of the Te–Fe–Cu NHC compounds (18.2–44 h<sup>-1</sup>),<sup>5</sup> suggesting that these Se-containing Fe–Cu NHC compounds would be less efficient for a transmetalation with 4-bromophenylboronic acid through a proposed Cu(I)/Cu(III) catalytic cycle.<sup>13</sup> In addition, it was also interesting to note that while the more structurally open Me<sub>2</sub>-Cl<sub>2</sub>-imy compound **5** had a lower catalytic efficiency than that of the bulky Me<sub>2</sub>-bimy or <sup>i</sup>Pr<sub>2</sub>-bimy group-containing compounds **3** or **4** in the Se system, the analogous Me<sub>2</sub>-Cl<sub>2</sub>-imy Te compound, [(μ<sub>3</sub>-Te)Fe<sub>3</sub>(CO)<sub>9</sub>{Cu(Me<sub>2</sub>-Cl<sub>2</sub>-imy)}<sub>2</sub>], had the highest TOF compared to those of [(μ<sub>4</sub>-Te)Fe<sub>3</sub>(CO)<sub>9</sub>{Cu(Me<sub>2</sub>-bimy)}<sub>2</sub>] and [(μ<sub>4</sub>-Te)Fe<sub>3</sub>(CO)<sub>9</sub>{Cu(<sup>i</sup>Pr<sub>2</sub>-bimy)}<sub>2</sub>] in the Te cases.<sup>5b</sup> Based on the catalytic efficiency of these E–Fe–Cu NHC catalysts (E = Se, Te), the steric hindrance of the NHC ligands of the Te-containing catalysts appeared to play an important role in their catalytic

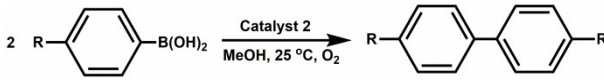
performance, however, the electronic demand of the NHC ligands of these Se-containing catalysts was considered to be a key factor in affecting their catalytic efficiency.

To expand the scope of the catalytic reaction, the homocoupling of two different *para*-substituted arylboronic acids, 4-nitrophenylboronic acid and 4-methoxyphenylboronic acid, by catalyst **2** was examined and the results are summarized in Table 3. As shown in Table 3, the catalytic yield (66%) from the 4-nitrophenylboronic acid bearing a stronger electron-withdrawing nitro group was higher than that of phenylboronic acid with an electron-donating methoxy group (32%). However, the yield of 4-nitrophenylboronic acid was still lower than that of phenylboronic acid with a weak electron-withdrawing bromo group (87%). These results reveal that the SeFe<sub>3</sub>(CO)<sub>9</sub>-based NHC-dicopper **2** exhibited catalytic selectivity toward these arylboronic acids, in which phenylboronic acid with the weak electron-withdrawing Br group showed the highest catalytic yields.

## 2.4 Computational studies and electrochemical properties of **2–5**

To better understand the nature of these Se–Fe–Cu NHC

**Table 3** Substrate scope of arylboronic acids using catalyst **2**<sup>a</sup>

				
Entry	R	Cu (mol%)	Time (h)	Yield (%) <sup>b,c</sup>
1	<i>para</i> -Br	1.0	4	87
2	<i>para</i> -OMe	1.0	4.5	32
3	<i>para</i> -NO <sub>2</sub>	1.0	52.5	66 <sup>d</sup>

<sup>a</sup> Reaction conditions: arylboronic acid (1.0 mmol), MeOH (3.0 mL), 25 °C, O<sub>2</sub> (1 atm, balloon). <sup>b</sup> The isolated yield as an average of three runs. <sup>c</sup> All reactions were monitored by TLC. <sup>d</sup> An addition–elimination side product 4-nitrophenol was isolated in 10% yield due to the presence of H<sub>2</sub>O in the reaction and the major product 4,4'-dinitrobiphenyl was obtained in 56% yield. Therefore, the yield of 4,4'-dinitrobiphenyl was considered as 66%.

compounds and their catalytic performance, density functional theory (DFT) calculations were carried out at the B3PW91 functional<sup>14</sup> with a Def2-TZVP basis set.<sup>15</sup> The details of the natural population analysis (NPA) and natural bond orbital (NBO) analysis are summarized in Table 4 and Fig. 6.

As shown in Table 4, the natural charges of the SeFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub> in the NHC-incorporated compounds **2–5** were significantly more negative than that of their parent compound **1**, revealing that the electron density of these SeFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub> cores was dramatically increased as the result of introducing the NHC ligands. This result explains our experimental results showing that compounds **2–5** all had much better TOFs than **1** in the catalytic reaction, mainly because the more electron-rich metal core in **2–5** was predicted to be more efficient to proceed the Cu(I)/Cu(III) catalytic processes.<sup>13</sup> Although the natural charges of the metal cores in compounds **2–5** were similar to those of their Te analogues,<sup>5</sup> the natural charges of the chalcogen atoms were very clearly different. The selenium atoms in **2–5** were negatively charged (−0.039~−0.242), in contrast, the tellurium atoms in these Te congeners were positively charged (0.283~0.570), indicating that the more electronegative Se atom significantly reduced the electron density on the Fe and Cu atoms thus resulting in the less easier oxidation of our Cu(I) catalysts with a somehow lower efficiency.

To further understand the oxidative behavior of these synthesized Se–Fe–Cu NHC compounds **2–5**, differential pulse voltammetry (DPV) experiments were conducted in MeCN under N<sub>2</sub>. The DPVs revealed that compounds **2–5** all exhibited two quasi-reversible oxidations and one quasi-reversible reduction, as evidenced by the detection of two oxidation potential peaks between 0.042 and 0.270 V vs. SCE (Fig. S4 and Table S2, ESI<sup>†</sup>). In addition, their HOMO and LUMO each received a major contribution from the d and p orbitals of the three Fe atoms with a significant contribution from the d orbitals of Cu atoms contained in the SeFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub> core.

**Table 4** Results of natural population analyses of **1**, **2**, **3**, **4**, and **5**

Compound	Natural charge			
	Se	Fe <sup>a</sup>	Cu <sup>a</sup>	SeFe <sub>3</sub> (CO) <sub>9</sub> Cu <sub>2</sub>
<b>1</b>	−0.013	−0.593	0.665	−0.086
<b>2</b>	−0.238	−0.537	0.636	−0.374
<b>3</b>	−0.242	−0.538	0.638	−0.341
<b>4</b>	−0.210	−0.555	0.657	−0.319
<b>5</b>	−0.039	−0.544	0.642	−0.363

<sup>a</sup> Average natural charge.

According to the Cu(I)/Cu(III) catalytic cycle,<sup>13</sup> the ease of oxidation of these compounds should be related to their catalytic performances. As a consequence, the ease of the first oxidation of these Se–Fe–Cu NHC compounds **2–5** was found to be perfectly parallel to their catalytic efficiency. In addition, the redox patterns of **2–5** were also similar to those of their analogous Te compounds,<sup>5</sup> but the first oxidation in the Se cases (0.042–0.192 V) was shifted more anodically in comparison to the Te cases (0.015–0.084 V),<sup>5</sup> due to the more electronegative Se vs. Te, indicating that compounds **2–5** were somehow more difficult to oxidize compared to their Te congeners, which is consistent with the lower HOMO energy levels found for the Se cases. Lastly, we not only discovered a facile synthetic route for constructing a series of the NHC-functionalized ternary Se–Fe–Cu compounds but also provided excellent models for the comprehensive comparison of chalcogen effects in the E–Fe–Cu NHC systems (E = Se, Te) in catalytic performance for the homocoupling reactions of 4-bromophenylboronic acid.

### 3. Conclusions

In conclusion, we report on the facile synthesis of a novel series of the functionalized-NHC Se–Fe–Cu compounds starting from the pre-synthesized cluster [(μ<sub>3</sub>-Se)Fe<sub>3</sub>(CO)<sub>9</sub>{Cu(MeCN)}<sub>2</sub>] (**1**) with different types of the imidazolium salts and KO<sup>t</sup>Bu in stoichiometric amounts. In the solid state, these Se–Fe–Cu–NHC compounds are comprised of 1D cluster-chain polymers or 2D planar-like frameworks, stabilized by C–H...O hydrogen bonds between the COs moieties of the SeFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub>-based clusters and CH moieties of the neighboring NHC ligands, which enhance their stability and long time storage characteristics. Importantly, these SeFe<sub>3</sub>(CO)<sub>9</sub>Cu<sub>2</sub>-based NHC compounds were all found to efficiently catalyze the homocoupling of arylboronic acids with high turnovers (80–87) under mild conditions. The TONs for these Se–Fe–Cu NHC compounds were similar to those of their Te analogs but their catalytic affinities were dependent on the functionalized NHC ligand. In the highly strained Se system, the electronic properties of the NHC ligands appear to play an important role in tuning catalytic performance, while in the Te system, the steric hindrance of the NHC ligands was a key factor in controlling their catalytic activities. Finally, the catalytic efficiency of both the Se and Te systems can be perfectly



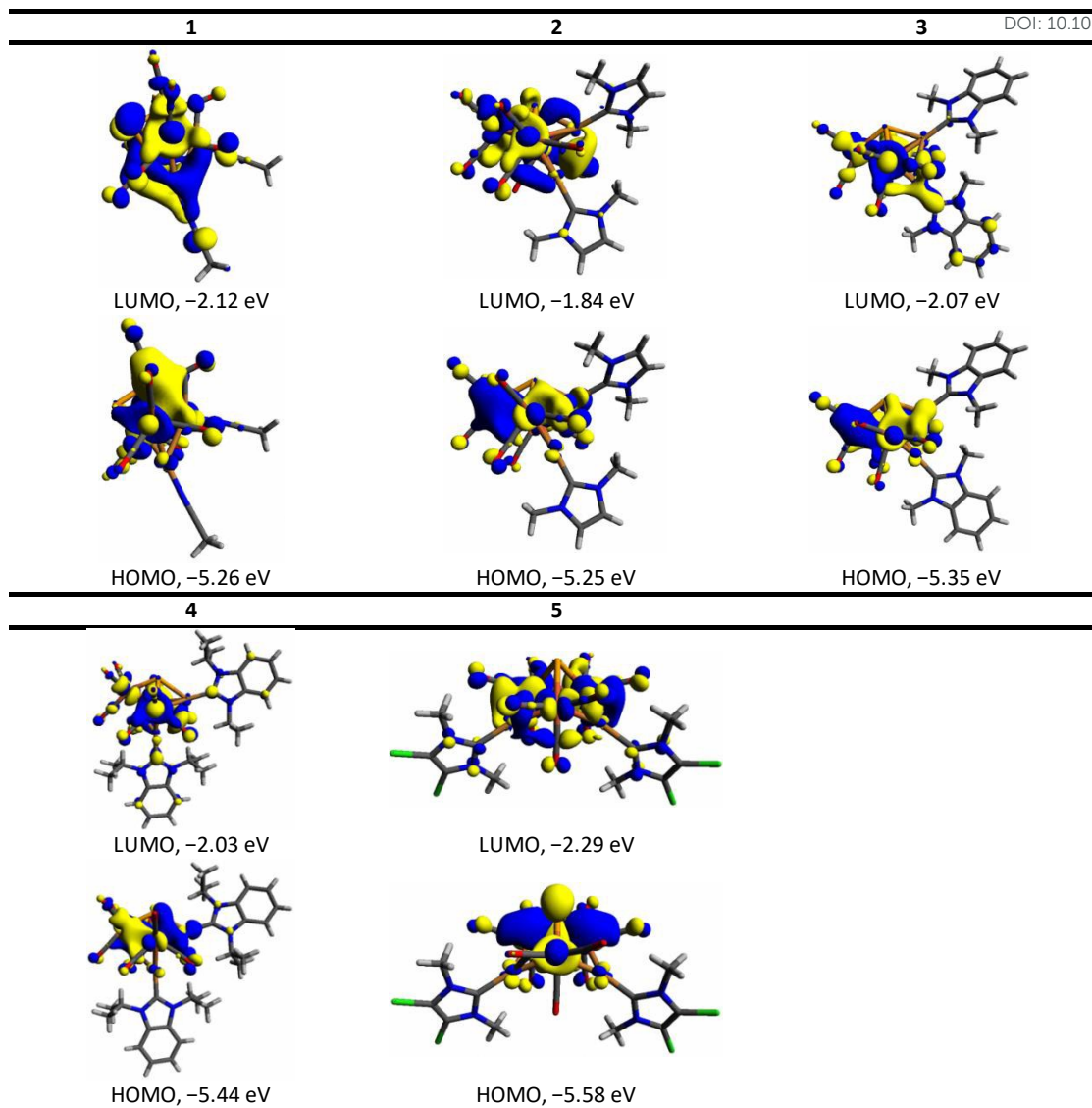


Fig. 6 The spatial graphs (isovalue = 0.03–0.04) of the frontier molecular orbitals and their associated calculated energies of **1**, **2**, **3**, **4**, and **5**.

probed in terms of the ease of their first oxidation potential. In this work, we not only discovered a new strategy for achieving a novel family of the  $\text{SeFe}_3(\text{CO})_9\text{Cu}_2$ -based NHC compounds but also carried out a comprehensive study of the chalcogen effects of the E–Fe–Cu NHC systems (E = Se, Te) *via* investigating their catalytic and electrochemical behaviors, the findings of which were further supported by DFT calculations.

## 4. Experimental section

### 4.1 General procedures

All synthetic reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.<sup>16</sup> Solvents were purified, dried, and distilled under nitrogen prior to use.  $\text{KO}^t\text{Bu}$  (ACROS) and 4-bromophenylboronic acid (Lancaster) were used as received.  $[\text{Et}_4\text{N}]_2[\text{SeFe}_3(\text{CO})_9]$ ,<sup>8</sup>

$[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ ,<sup>17</sup> and the imidazolium salts, 1,3-dimethylimidazolium iodide ( $\text{Me}_2\text{-imy-HI}$ ),<sup>18a</sup> 1,3-dimethylbenzimidazolium iodide ( $\text{Me}_2\text{-bimy-HI}$ ),<sup>18b</sup> 1,3-diisopropylbenzimidazolium iodide ( $\text{Pr}_2\text{-bimy-HI}$ ),<sup>18c</sup> and 1,3-dimethyl-4,5-dichloro-imidazolium iodide ( $\text{Me}_2\text{-Cl}_2\text{-imy-HI}$ ),<sup>18d</sup> were prepared according to previously published methods. Compounds were purified by chromatography on Merck 60 silica gel (40–63 mm) and analytical thin layer chromatography (TLC) was performed on Silica Gel 60 F254 precoated plates. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 or 500 IR spectrometer as solutions in  $\text{CaF}_2$  cells. The NMR spectra were obtained on a Bruker AV 400 at 400.13 MHz for  $^1\text{H}$  and 100.61 MHz for  $^{13}\text{C}$  or on a Bruker AV 500 at 500.13 MHz for  $^1\text{H}$  and 125.76 MHz for  $^{13}\text{C}$ .  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported in parts per million and were calibrated relative to  $\text{DMSO}-d_6$  ( $^1\text{H}$ : 2.49 ppm,  $^{13}\text{C}$ : 39.51 ppm) as the internal

	1	2	3	4	5
empirical formula	C <sub>13</sub> H <sub>6</sub> Cu <sub>2</sub> Fe <sub>3</sub> N <sub>2</sub> O <sub>9</sub> Se	C <sub>19</sub> H <sub>16</sub> Cu <sub>2</sub> Fe <sub>3</sub> N <sub>4</sub> O <sub>9</sub> Se	C <sub>27</sub> H <sub>20</sub> Cu <sub>2</sub> Fe <sub>3</sub> N <sub>4</sub> O <sub>9</sub> Se	C <sub>35</sub> H <sub>36</sub> Cu <sub>2</sub> Fe <sub>3</sub> N <sub>4</sub> O <sub>9</sub> Se	C <sub>19</sub> H <sub>12</sub> C <sub>4</sub> Cu <sub>2</sub> Fe <sub>3</sub> N <sub>4</sub> O <sub>9</sub> Se
formula weight	707.79	817.95	918.06	1030.27	955.72
crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
crystal size, mm	0.57 × 0.23 × 0.12	0.40 × 0.38 × 0.22	0.16 × 0.12 × 0.10	0.58 × 0.52 × 0.34	0.18 × 0.08 × 0.02
<i>a</i> , Å	8.8011(9)	13.8056(3)	10.211(2)	12.115(5)	8.3228(5)
<i>b</i> , Å	10.775(1)	13.7351(3)	18.962(4)	12.288(6)	23.245(2)
<i>c</i> , Å	12.165(1)	14.3112(4)	16.852(3)	15.442(7)	15.4952(7)
$\alpha$ , deg	85.346(2)			107.607(5)	
$\beta$ , deg	79.733(2)	101.793(1)	105.308(6)	99.965(6)	103.387(3)
$\gamma$ , deg	68.143(2)			108.614(4)	
<i>V</i> , Å <sup>3</sup>	1053.4(2)	2656.4(1)	3147(1)	1982(2)	2916.3(3)
<i>Z</i>	2	4	4	2	4
<i>D</i> (calc), g/cm <sup>−3</sup>	2.231	2.045	1.938	1.726	2.177
$\mu$ , mm <sup>−1</sup>	5.777	4.599	3.893	3.102	4.560
color, habit	black, prism	black, prism	black, prism	black, prism	black, prism
diffractometer	Apex II CCD	Kappa CCD	Apex II CCD	Apex II CCD	Apex II CCD
radiation ( $\lambda$ ), Å	0.71073	0.71073	0.71073	0.71073	0.71073
temperature, K	200(2)	293(2)	200(2)	200(2)	200(2)
$\theta$ range for data collection, deg	2.52–25.00	2.04–25.03	2.30–21.56	2.58–25.61	2.52–24.97
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.14/0.54	0.30/0.51	0.06/0.70	0.27/0.42	0.49/0.91
no. of independent reflections ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	3211 ( <i>R</i> <sub>int</sub> = 0.0217)	4008 ( <i>R</i> <sub>int</sub> = 0.1211)	3334 ( <i>R</i> <sub>int</sub> = 0.0833)	4493 ( <i>R</i> <sub>int</sub> = 0.0619)	3919 ( <i>R</i> <sub>int</sub> = 0.0326)
no. of parameters	273	343	415	487	379
goodness of fit	1.040	1.359	0.907	0.988	1.092
<i>R</i> <sub>1</sub> <sup>a</sup> / <i>wR</i> <sub>2</sub> <sup>a</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.022/0.046	0.055/0.143	0.041/0.088	0.050/0.106	0.080/0.215
<i>R</i> <sub>1</sub> <sup>a</sup> / <i>wR</i> <sub>2</sub> <sup>a</sup> (all data)	0.027/0.048	0.072/0.167	0.086/0.099	0.089/0.124	0.100/0.230

<sup>a</sup> The functions minimized during least-squares cycles were  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ .

standard. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 2400 analyzer at the MOST Regional Instrumental Center at National Taiwan University, Taipei, Taiwan.

#### 4.2 Synthesis of [SeFe<sub>3</sub>(CO)<sub>9</sub>{Cu(MeCN)}<sub>2</sub>] (**1**)

A 20 mL of a THF solution was added to a mixture of [Et<sub>4</sub>N]<sub>2</sub>[SeFe<sub>3</sub>(CO)<sub>9</sub>] (1.00 g, 1.30 mmol) and [Cu(MeCN)<sub>4</sub>][BF<sub>4</sub>] (1.24 g, 3.90 mmol), and the mixture was stirred at 0 °C for 3 h. The resulting reddish-purple solution was filtered and removed under a vacuum. The residue was washed with de-ionized water and *n*-hexane several times and then extracted with Et<sub>2</sub>O and then recrystallized from Et<sub>2</sub>O/*n*-hexane to give a purplish sample of [SeFe<sub>3</sub>(CO)<sub>9</sub>{Cu(MeCN)}<sub>2</sub>] (**1**) (0.65 g, 0.92 mmol) (71% based on [Et<sub>4</sub>N]<sub>2</sub>[SeFe<sub>3</sub>(CO)<sub>9</sub>]). IR ( $\nu_{CO}$ , THF): 2035 (w), 2000 (vs), 1985 (s), 1952 (m), 1911 (s) cm<sup>−1</sup>. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 300 K, ppm):  $\delta$  2.08 (s, 3H; NCH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, 300 K, ppm):  $\delta$  217.97 (Fe-CO), 117.83 (NCCH<sub>3</sub>), 1.00 (NCCH<sub>3</sub>). Anal. Calcd for **1**: C, 22.06; H, 0.85; N, 3.99. Found: C, 21.97; H, 0.82; N, 4.07. Mp: 78 °C dec. Crystals of **1** suitable for X-ray diffraction were grown from *n*-hexane/Et<sub>2</sub>O/THF.

#### 4.3 Synthesis of [SeFe<sub>3</sub>(CO)<sub>9</sub>{Cu(Me<sub>2</sub>-imy)}<sub>2</sub>] (**2**)

A 20 mL of a THF solution of **1** (0.40 g, 0.57 mmol), Me<sub>2</sub>-imy·HI (0.25 g, 1.13 mmol), and KO<sup>t</sup>Bu (0.13 g, 1.13 mmol) was stirred in an ice-water bath overnight. The resulting solution was filtered, and the solvent was removed under a vacuum. The residue was extracted with Et<sub>2</sub>O to give a purplish-brown solution and the solvent was removed under a vacuum. The residue was washed with deionized water several times and then extracted with CH<sub>2</sub>Cl<sub>2</sub> and then recrystallized from *n*-hexane/MeOH/CH<sub>2</sub>Cl<sub>2</sub> to give a purplish-black sample of [SeFe<sub>3</sub>(CO)<sub>9</sub>{Cu(Me<sub>2</sub>-imy)}<sub>2</sub>] (**2**) (0.24 g, 0.30 mmol) (52% based on **1**). IR ( $\nu_{CO}$ , CH<sub>2</sub>Cl<sub>2</sub>): 2036 (m), 1983 (vs), 1923 (w) cm<sup>−1</sup>. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 300 K, ppm):  $\delta$  7.31 (br, 4H; NCH), 3.77 (br, 12H; NCH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, 300 K, ppm):  $\delta$  217.98 (Fe-CO), 177.72 (C<sub>carbene</sub>), 122.06 (NCH), 37.21 (NCH<sub>3</sub>). Anal. Calcd for **2**: C, 27.90; H, 1.97; N, 6.86. Found: C, 27.80; H, 2.21; N, 7.06. Mp: 128 °C dec. Crystals of **2** suitable for X-ray diffraction were grown from *n*-hexane/MeOH/CH<sub>2</sub>Cl<sub>2</sub>.

#### 4.4 Synthesis of [SeFe<sub>3</sub>(CO)<sub>9</sub>{Cu(Me<sub>2</sub>-bimy)}<sub>2</sub>] (**3**)

A 20 mL of a THF solution of **1** (0.40 g, 0.57 mmol), Me<sub>2</sub>-bimy·HI (0.31 g, 1.13 mmol), and KO<sup>t</sup>Bu (0.13 g, 1.13 mmol) was stirred in an ice-water bath overnight. The resulting solution was filtered, and the solvent was removed under a vacuum. The residue was extracted with Et<sub>2</sub>O to give a

purplish-brown solution and the solvent was removed under a vacuum. The residue was washed with deionized water several times and then extracted with  $\text{CH}_2\text{Cl}_2$  and then recrystallized from *n*-hexane/MeOH/ $\text{CH}_2\text{Cl}_2$  to give a purplish-brown sample of  $[\text{SeFe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-bimy})\}_2]$  (**3**) (0.16 g, 0.17 mmol) (30% based on **1**). IR ( $\nu_{\text{CO}}$ ,  $\text{CH}_2\text{Cl}_2$ ): 2032 (m), 1993 (vs), 1981 (vs), 1959 (m), 1924 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ , 300 K, ppm):  $\delta$  7.69 (dd, 4H; Ar-H), 7.43 (dd, 4H; Ar-H), 4.03 (s, 12H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ , 300 K, ppm):  $\delta$  218.06 (Fe-CO), 186.89 ( $\text{C}_{\text{carbene}}$ ), 133.68, 123.46, 111.34 (Ar-C), 34.46 ( $\text{CH}_3$ ). Anal. Calcd for **3**: C, 35.32; H, 2.20; N, 6.10. Found: C, 35.30; H, 2.21; N, 6.27. Mp: 142 °C dec. Crystals of **3** suitable for X-ray diffraction were grown from *n*-hexane/MeOH/ $\text{CH}_2\text{Cl}_2$ .

#### 4.5 Synthesis of $[\text{SeFe}_3(\text{CO})_9\{\text{Cu}(\text{Pr}_2\text{-bimy})\}_2]$ (**4**)

A 20 mL of a THF solution of **1** (0.40 g, 0.57 mmol),  $\text{Pr}_2\text{-bimy-HI}$  (0.37 g, 1.13 mmol), and  $\text{KO}^t\text{Bu}$  (0.13 g, 1.13 mmol) was stirred in an ice-water bath overnight. The resulting solution was filtered, and the solvent was removed under a vacuum. The residue was extracted with  $\text{Et}_2\text{O}$  to give a purplish-brown solution and the solvent was removed under a vacuum. The residue was washed with deionized water several times and then extracted with  $\text{CH}_2\text{Cl}_2$  and then recrystallized from *n*-hexane/MeOH/ $\text{CH}_2\text{Cl}_2$  to give a purplish-brown sample of  $[\text{SeFe}_3(\text{CO})_9\{\text{Cu}(\text{Pr}_2\text{-bimy})\}_2]$  (**4**) (0.42 g, 0.41 mmol) (72% based on **1**). IR ( $\nu_{\text{CO}}$ ,  $\text{CH}_2\text{Cl}_2$ ): 2037 (m), 1982 (vs), 1961 (m), 1924 (w), 1900 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ , 300 K, ppm):  $\delta$  7.88 (dd, 4H; Ar-H), 7.39 (dd, 4H; Ar-H), 5.20 (m, 4H,  $\text{NCH}(\text{CH}_3)_2$ ), 1.67 (d, 24H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ , 300 K, ppm):  $\delta$  218.25 (Fe-CO), 182.23 ( $\text{C}_{\text{carbene}}$ ), 132.31, 123.37, 112.78 (Ar-C), 51.94 ( $\text{NCH}(\text{CH}_3)_2$ ), 21.99 ( $\text{CH}_3$ ). Anal. Calcd for **4**: C, 40.80; H, 3.52; N, 5.44. Found: C, 40.85; H, 3.54; N, 5.50. Mp: 108 °C dec. Crystals of **4** suitable for X-ray diffraction were grown from *n*-hexane/MeOH/ $\text{CH}_2\text{Cl}_2$ .

#### 4.6 Synthesis of $[\text{SeFe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-Cl}_2\text{-imy})\}_2]$ (**5**)

A 20 mL of a THF solution of **1** (0.40 g, 0.57 mmol),  $\text{Me}_2\text{-Cl}_2\text{-imy-HI}$  (0.33 g, 1.13 mmol), and  $\text{KO}^t\text{Bu}$  (0.13 g, 1.13 mmol) was stirred in an ice-water bath overnight. The resulting solution was filtered, and the solvent was removed under a vacuum. The residue was extracted with  $\text{Et}_2\text{O}$  to give a reddish-brown solution and the solvent was removed under a vacuum. The residue was washed with deionized water several times and then extracted with  $\text{CH}_2\text{Cl}_2$  and then recrystallized from *n*-hexane/MeOH/ $\text{CH}_2\text{Cl}_2$  to give a reddish-brown sample of  $[\text{SeFe}_3(\text{CO})_9\{\text{Cu}(\text{Me}_2\text{-Cl}_2\text{-imy})\}_2]$  (**5**) (0.30 g, 0.31 mmol) (56% based on **1**). IR ( $\nu_{\text{CO}}$ ,  $\text{CH}_2\text{Cl}_2$ ): 2034 (m), 1992 (s), 1981 (vs), 1960 (m), 1925 (w), 1900 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ , 300 K, ppm):  $\delta$  3.79 (s, 12H;  $\text{NCH}_3$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ , 300 K, ppm):  $\delta$  217.89 (Fe-CO), 179.39 ( $\text{C}_{\text{carbene}}$ ), 116.06 (C-Cl), 36.36 ( $\text{NCH}_3$ ). Anal. Calcd for **5**: C, 23.88; H, 1.27; N, 5.86. Found: C, 24.17; H, 1.31; N, 5.97. Mp: 114 °C dec. Crystals of **5** suitable for X-ray diffraction were grown from *n*-hexane/MeOH/ $\text{CH}_2\text{Cl}_2$ .

#### 4.7 Homocoupling of 4-bromophenylboronic acid with catalysts 1–5

DOI: 10.1039/C9NJ02051A

A 3 mL of a MeOH solution of catalyst **1**, **2**, **3**, **4**, or **5** and 4-bromophenylboronic acid (1.00 mmol) was stirred at 25 °C in an  $\text{O}_2$  atmosphere. After the reaction reached completion, as determined by the disappearance of the starting material by TLC, 4-bromophenylboronic acid, the resulting reaction mixture was evaporated to dryness under a vacuum. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and purified by column chromatography on silica gel using *n*-hexane as the eluent to afford the biaryl product which was confirmed by NMR spectroscopy. To compare the activities of all of the catalysts, all of the homocoupling reactions described herein were carried out repeatedly and carefully to ensure accuracy.

#### 4.8 Homocoupling of 4-methoxyphenylboronic acid with catalyst 2

A solution of catalyst **2** (0.0050 mmol) and 4-methoxyphenylboronic acid (1.00 mmol) in MeOH (3 mL) was stirred at 25 °C. The resulting reaction mixture was evaporated to dryness under a vacuum. The residue was purified by flash chromatography on a silica gel column (petroleum ether/ethyl acetate, 5: 1) to afford biaryl derivatives. To compare the activities of the catalysts, all the homocoupling reactions described herein were carried out repeatedly and carefully to ensure accuracy.

#### 4.9 Homocoupling of 4-nitrophenylboronic acid with catalyst 2

A solution of catalyst **2** (0.0050 mmol) and 4-nitrophenylboronic acid (1.00 mmol) in MeOH (3 mL) was stirred at 25 °C. The resulting reaction mixture was evaporated to dryness under a vacuum. The residue was purified by flash chromatography on a silica gel column (petroleum ether/ethyl acetate, 5: 1) to afford 4,4'-dinitrobiphenyl (0.27 mmol, 56 %) and 4-nitrophenol (0.09 mmol, 10 %). To compare the activities of the catalysts, the homocoupling reaction described herein was carried out repeatedly and carefully to ensure accuracy.

#### 4.10 X-ray structural characterization of 1–5

Selected crystallographic parameters for **1**, **2**, **3**, **4**, and **5** are given in Table 5. All crystals were mounted on glass fibers with epoxy cement. Data collection for **1**, **3**, **4**, and **5** were carried out on a Bruker Apex II CCD diffractometer with graphite-monochromated  $\text{MoK}_\alpha$  radiation. Compound **2** was examined on a Bruker-Nonius Kappa CCD diffractometer with graphite-monochromated  $\text{MoK}_\alpha$  radiation. An empirical absorption correction by the multi-scan method was applied to the data using SADABS.<sup>19</sup> All structures were solved by a combination of direct methods and difference Fourier syntheses and refined with the SHELXL-2014 program.<sup>20</sup> All of the non-hydrogen atoms for **1**, **2**, **3**, **4**, and **5** were refined with anisotropic temperature factors. The selected distances and angles for **1**, **2**, **3**, **4**, and **5** are listed in Table S3 in ESI†. CCDC reference numbers 1909685 for **1**, 1909691 for **2**, 1909692 for **3**,

1909693 for **4**, and 1909694 for **5** contain the supplementary crystallographic data for this paper.

#### 4.11 Computational Details

The calculations reported in this study were performed *via* density functional theory (DFT) using the Gaussian 09 series of packages.<sup>21</sup> The geometries of compounds **1**, **2**, **3**, **4**, and **5** were taken from single-crystal X-ray diffraction data. All calculations were performed using the hybrid B3PW91 functional<sup>14</sup> with the large basis set Def2-TZVP.<sup>15</sup> Natural charges<sup>22</sup> were evaluated using the Weinhold NBO method.<sup>23</sup> For orbital contributions, the molecular orbital compositions were analyzed using the AOMix program.<sup>24</sup> Graphical representations of the molecular orbitals were obtained using Avogadro.<sup>25</sup>

#### 4.12 Electrochemical Studies

Electrochemical measurements were performed at room temperature under a nitrogen atmosphere and recorded using a CHI 621D electrochemical potentiostat. A glassy carbon working electrode, a platinum wire auxiliary electrode, and a non-aqueous Ag/Ag<sup>+</sup> electrode were used in a three-electrode configuration. Tetra-*n*-butylammonium perchlorate (TBAP) was used as the supporting electrolyte, and the solute concentration was  $\sim 10^{-3}$  M. The redox potentials were calibrated with a ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple in the working solution and were referenced to SCE. Electrochemical measurements of **2**, **3**, **4**, and **5** were carried out by differential pulse voltammetry (DPV). Because of the interference of irreversible desorption of Cu ( $-0.33$  to  $-0.38$  V)<sup>26</sup> and the reported one-electron oxidation of Cu(I) ( $0.45$ – $0.36$  V),<sup>27</sup> the DPV profiles were only discussed between  $0.30$  and  $-0.20$  V. The DPV data are summarized in Table S2 in ESI<sup>†</sup>. For the DPV analysis, the peak width at half height ( $W_{1/2}$ ) was used to determine electron stoichiometry.<sup>28</sup> Compounds **2**–**5** and their Te congeners<sup>5</sup> each showed two one-electron quasi-reversible oxidations ( $0.042 \sim 0.192$  V and  $0.252 \sim 0.270$  V) and a one-electron quasi-reversible reduction ( $-0.090 \sim -0.126$  V) (Table S2, ESI<sup>†</sup>). The widths of the DPV peaks at the half-height ( $W_{1/2}$ ) of these compounds were a bit greater or lower than the expected value ( $W_{1/2} = 90$  mV) for one-electron reversible redox couples, indicating that these DPV responses were quasi-reversible.<sup>28</sup>

#### Conflicts of interest

The authors declare no conflicts of interest.

#### Acknowledgements

This work was supported by the Ministry of Science and Technology of Taiwan (Grant No. 107-2113-M-003-006 to M. Shieh). We wish to thank the NCHC of Taiwan for providing the computer time and the facilities. Our gratitude also goes to the Academic Paper Editing Clinic, NTNU.

#### Notes and references

- (a) *The Chemistry of Metal Cluster Complexes*, ed. D. F. Shriver, H. D. Kaesz and R. D. Adams, Wiley-VCH Publishers, New York, 1990; (b) *Metal Clusters in Chemistry*, ed. P. Braunstein, L. A. Oro and P. R. Raithby, Wiley-VCH Publishers, Weinheim, 1999; (c) P. Mathur, *Adv. Organomet. Chem.*, 1997, **41**, 243–314; (d) N. A. Compton, R. J. Errington and N. C. Norman, *Adv. Organomet. Chem.*, 1990, **31**, 91–182; (e) S. C. Lee and R. H. Holm, *Chem. Rev.*, 2004, **104**, 1135–1157; (f) M. G. Richmond, *Coord. Chem. Rev.*, 2005, **249**, 2763–2786; (g) R. Ferrando, J. Jellinek and R. L. Johnston, *Chem. Rev.*, 2008, **108**, 845–910; (h) P. Buchwalter, J. Rosé and P. Braunstein, *Chem. Rev.*, 2015, **115**, 28–126; (i) F. Schwyer-Tihay, C. Estournès, P. Braunstein, J. Guille, J.-L. Paillaud, M. Richard-Plouet and J. Rosé, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4018–4028; (j) A. Naitabdi, O. Toulemonde, J. P. Bucher, J. Rosé, P. Braunstein, R. Welter and M. Drillon, *Chem. Eur. J.*, 2008, **14**, 2355–2362; (k) C. Femoni, M. C. Iapalucci, G. Longoni, C. Tiozzo and S. Zacchini, *Angew. Chem. Int. Ed.*, 2008, **47**, 6666–6669.
- (a) M. Hidai, S. Kuwata and Y. Mizobe, *Acc. Chem. Res.*, 2000, **33**, 46–52; (b) R. A. Henderson, *Chem. Rev.*, 2005, **105**, 2365–2437; (c) M. Shieh, C.-Y. Miu, Y.-Y. Chu and C.-N. Lin, *Coord. Chem. Rev.*, 2012, **256**, 637–694; (d) D. T. Tran, L. M. C. Beltran, C. M. Kowalchuk, N. R. Trefiak, N. J. Taylor and J. F. Corrigan, *Inorg. Chem.*, 2002, **41**, 5693–5698; (e) T. C. Deivaraj, J.-H. Park, M. Afzaal, P. O'Brien and J. J. Vittal, *Chem. Mater.*, 2003, **15**, 2383–2391; (f) M. Shieh, R.-L. Chung, C.-H. Yu, M.-H. Hsu, C.-H. Ho, S.-M. Peng and Y.-H. Liu, *Inorg. Chem.*, 2003, **42**, 5477–5479; (g) R. D. Adams, S. Miao, M. D. Smith, H. Farach, C. E. Webster, J. Manson and M. B. Hall, *Inorg. Chem.*, 2004, **43**, 2515–2525; (h) M. W. DeGroot, H. Rösner and J. F. Corrigan, *Chem. Eur. J.*, 2006, **12**, 1547–1554; (i) M. Shieh, M.-H. Hsu, W.-S. Sheu, L.-F. Jang, S.-F. Lin, Y.-Y. Chu, C.-Y. Miu, Y.-W. Lai, H.-L. Liu and J. L. Her, *Chem. Eur. J.*, 2007, **13**, 6605–6616; (j) A. Eichhöfer, J. Olkowska-Oetzel, D. Fenske, K. Fink, V. Mereacre, A. K. Powell and G. Buth, *Inorg. Chem.*, 2009, **48**, 8977–8984; (k) C.-N. Lin, W.-T. Jhu and M. Shieh, *Chem. Commun.*, 2014, **50**, 1134–1136.
- (a) M. Shieh, C.-N. Lin, C.-Y. Miu, M.-H. Hsu, Y.-W. Pan and L.-F. Ho, *Inorg. Chem.*, 2010, **49**, 8056–8066; (b) M. Shieh, C.-Y. Miu, K.-C. Huang, C.-F. Lee and B.-G. Chen, *Inorg. Chem.*, 2011, **50**, 7735–7748; (c) M. Shieh, C.-H. Yu, Y.-Y. Chu, Y.-W. Guo, C.-Y. Huang, K.-J. Hsing, P.-C. Chen and C.-F. Lee, *Chem. Asian J.*, 2013, **8**, 963–973.
- (a) M. Shieh, C.-H. Ho, W.-S. Sheu, B.-G. Chen, Y.-Y. Chu, C.-Y. Miu, H.-L. Liu and C.-C. Shen, *J. Am. Chem. Soc.*, 2008, **130**, 14114–14116; (b) M. Shieh, C.-C. Yu, C.-Y. Miu, C.-H. Kung, C.-Y. Huang, Y.-H. Liu, H.-L. Liu and C.-C. Shen, *Chem. Eur. J.*, 2017, **23**, 11261–11271.
- (a) C.-N. Lin, C.-Y. Huang, C.-C. Yu, Y.-M. Chen, W.-M. Ke, G.-J. Wang, G.-A. Lee and M. Shieh, *Dalton Trans.*, 2015, **44**, 16675–16679; (b) M. Shieh, Y.-H. Liu, Y.-H. Li, C.-N. Lin and C.-C. Wang, *J. Organomet. Chem.*, 2018, **867**, 161–169.
- A. M. Polgar, F. Weigend, A. Zhang, M. J. Stillman and J. F. Corrigan, *J. Am. Chem. Soc.*, 2017, **139**, 14045–14048.
- (a) A. J. Arduengo III, D. Tapu and W. J. Marshall, *Angew. Chem. Int. Ed.*, 2005, **44**, 7240–7244; (b) A. J. Arduengo III, D. Tapu and W. J. Marshall, *J. Am. Chem. Soc.*, 2005, **127**, 16400–16401; (c) Q.-X. Liu, J. Yu, X.-J. Zhao, S.-W. Liu, X.-Q. Yang, K.-Y. Li and X.-G. Wang, *CrystEngComm*, 2011, **13**, 4086–4096; (d) M. A. Fard, T. I. Levchenko, C. Cadogan, W. J. Humenny and J. F. Corrigan, *Chem. Eur. J.*, 2016, **22**, 4543–4550.
- R. L. Holliday, L. C. Roof, B. Hargus, D. M. Smith, P. T. Wood, W. T. Pennington and J. W. Kolis, *Inorg. Chem.*, 1995, **34**, 4392–4401.



- 9 (a) C. Nitschke, D. Fenske and J. F. Corrigan, *Inorg. Chem.*, 2006, **45**, 9394–9401; (b) M. Shieh, C.-Y. Miu, C.-J. Lee, W.-C. Chen, Y.-Y. Chu and H.-L. Chen, *Inorg. Chem.*, 2008, **47**, 11018–11031; (c) A. I. Wallbank, A. Borecki, N. J. Taylor and J. F. Corrigan, *Organometallics*, 2005, **24**, 788–790.
- 10 (a) C. E. Ellul, G. Reed, M. F. Mahon, S. I. Pascu and M. K. Whittlesey, *Organometallics*, 2010, **29**, 4097–4104; (b) B. Liu, Y. Zhang, D. Xu and W. Chen, *Chem. Commun.*, 2011, **47**, 2883–2885; (c) V. J. Catalano, L. B. Munro, C. E. Strasser and A. F. Samin, *Inorg. Chem.*, 2011, **50**, 8465–8476; (d) C. Chen, H. Qiu and W. Chen, *J. Organomet. Chem.*, 2012, **696**, 4166–4172; (e) E. Kühnel, I. V. Shishkov, F. Rominger, T. Oeser and P. Hofmann, *Organometallics*, 2012, **31**, 8000–8011; (f) B. R. M. Lake and C. E. Willans, *Chem. Eur. J.*, 2013, **19**, 16780–16790; (g) B. Liu, C. Chen, Y. Zhang, X. Liu and W. Chen, *Organometallics*, 2013, **32**, 5451–5460 and references therein; (h) B. Liu, S. Pan, B. Liu and W. Chen, *Inorg. Chem.*, 2014, **53**, 10485–10497; (i) A. Sathyanarayana, B. P. R. Metla, N. Sampath and G. Prabusankar, *J. Organomet. Chem.*, 2014, **772–773**, 210–216; (j) R. D. Pergola, A. Sironi, A. Rosehr, V. Colombo and A. Sironi, *Inorg. Chem. Commun.*, 2014, **49**, 27–29; (k) J. Plotzitzka and C. Kleeberg, *Inorg. Chem.*, 2016, **55**, 4813–4823.
- 11 (a) J. E. Huheey, *Inorganic Chemistry*, Harper & Row, New York, 1983; (b) B. Cordero, V. Gomez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán and S. Alvarez, *Dalton Trans.*, 2008, 2832–2838; (c) D. Braga and F. Grepioni, *Acc. Chem. Res.*, 1997, **30**, 81–87; (d) D. Braga, F. Grepioni, K. Biradha, V. R. Pedireddi and G. R. Desiraju, *J. Am. Chem. Soc.*, 1995, **117**, 3156–3166.
- 12 R. N. Dhital and H. Sakurai, *Asian J. Org. Chem.*, 2014, **3**, 668–684 and references therein.
- 13 (a) P. Puthiaraj, P. Suresh and K. Pitchumani, *Green Chem.*, 2014, **16**, 2865–2875; (b) A. S. Demir, Ö. Reis and M. Emrullahoglu, *J. Org. Chem.*, 2003, **68**, 10130–10134.
- 14 (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (b) J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244–13249.
- 15 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
- 16 D. F. Shriver and M. A. Drezdson, *The Manipulation of Air-sensitive Compounds*, Wiley-VCH Publishers, New York, 1986.
- 17 G. J. Kubas, *Inorg. Synth.*, 1979, **19**, 90–92.
- 18 (a) W. A. Herrmann, C. Köcher, L. J. Gooßen and G. R. J. Artus, *Chem. Eur. J.*, 1996, **2**, 1627–1636; (b) B. L. Benac, E. M. Burgess and A. J. Arduengo III, *J. Org. Syn.*, 1986, **64**, 92–96; (c) H. V. Huynh, T. C. Neo and G. K. Tan, *Organometallics*, 2006, **25**, 1298–1302; (d) K. M. Hindi, T. J. Siciliano, S. Durmus, M. J. Panzner, D. A. Medvetz, D. V. Reddy, L. A. Hogue, C. E. Hovis, J. K. Hilliard, R. J. Mallet, C. A. Tessier, C. L. Cannon and W. J. Youngs, *J. Med. Chem.*, 2008, **51**, 1577–1583.
- 19 G. M. Sheldrick, *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, 2003. DOI: 10.1039/C9NJ02051A
- 20 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112–122.
- 21 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A., Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, revision E.01; Gaussian, Inc.: Wallingford, CT, 2009.
- 22 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735–746.
- 23 (a) A. E. Reed and F. Weinhold, *J. Chem. Phys.*, 1983, **78**, 4066–4073; (b) A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.
- 24 S. I. Gorelsky, AOMix. <http://www.sg-chem.net/>.
- 25 (a) Avogadro: An Open-Source Molecular Builder and Visualization Tool, version 1.2.0, <http://avogadro.openmolecules.net/>. (b) M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek and G. R. Hutchison, *J. Cheminf.*, 2012, **4**, 4–17.
- 26 (a) V. W.-W. Yam, W.-K. Lee and T.-F. Lait, *Organometallics*, 1993, **12**, 2383–2387; (b) V. W.-W. Yam, W.-K. Lee, K.-K. Cheung, B. Crystall and D. Phillips, *J. Chem. Soc., Dalton Trans.*, 1996, 3283–3287; (c) V. W.-W. Yam, W. K.-M. Fung and M.-T. Wong, *Organometallics*, 1997, **16**, 1772–1778.
- 27 (a) M. Scheer, A. Schindler, R. Merkle, B. P. Johnson, M. Linseis, R. Winter, C. E. Anson and A. V. Virovets, *J. Am. Chem. Soc.*, 2007, **129**, 13386–13387; (b) X. Xue, X.-S. Wang, R.-G. Xiong, X.-Z. You, B. F. Abrahams, C.-M. Che and H.-X. Ju, *Angew. Chem. Int. Ed.*, 2002, **41**, 2944–2946; (c) M. S. Doescher, J. M. Tour, A. M. Rawlett and M. L. Myrick, *J. Phys. Chem. B*, 2001, **105**, 105–110.
- 28 (a) A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., John Wiley & Sons, New York, 2001, p. 291; (b) T. Nakanishi, H. Murakami, T. Sagara and N. Nakashima, *J. Phys. Chem. B*, 1999, **103**, 304–308.

**Table of contents entry:**

A novel family of highly efficient Se–Fe–Cu–NHC catalysts was synthesized, which were suitable models for studies of the chalcogen effect.

