

Dinuclear N-heterocyclic carbene copper(I) complexes

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Abstract

Copper(I) species exhibit various coordination modes as a function of surrounding ligands. Complexes bearing N-heterocyclic carbenes as ligands are usually monomeric species with the copper adopting a linear geometry. Contrarily to the parent phosphine complexes, in which the presence of species of higher nuclearity is well established, fewer examples of such copper(I)-NHC species are reported and, interestingly, their number is growing. Moreover, these are no longer a mere curiosity from a coordination perspective since they have been shown successful in catalysis. The aim of this review is to present a summary of the synthesis and structural properties of dinuclear copper(I)-NHC complexes. It is our hope that by centralizing all information available on such species, future efforts aimed at exploiting their full potential can be facilitated.

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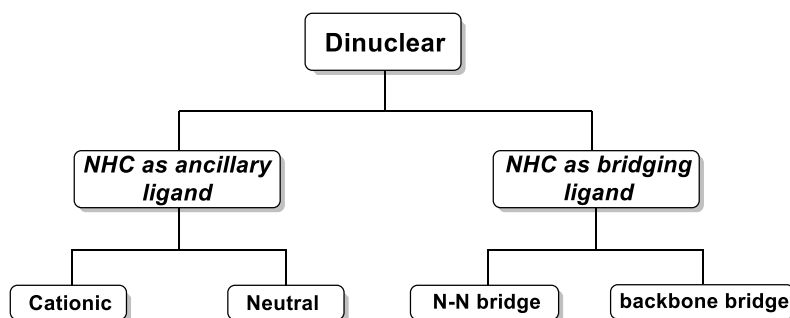
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Abbreviations: Bn, benzyl; CAAC, Cyclic Alkyl Amino Carbene; catB-Bcat, bis(cathecolato)diboron; CuAAC, Cu-catalyzed Azide/Alkyne Cycloaddition; DFT, Density Functional Theory; dipp, diisopropylphenyl; Et₃N·3HF, triethylamine trihydrofluoride; HBpin, pinacolborane; HMDS, hexamethyldisilazane; IMe, *N,N'*-(dimethyl)imidazol-2-ylidene; IMes, *N,N'*-bis-[2,4,6-(trimethyl)phenyl]imidazol-2-ylidene; ⁱPr, isopropyl; IPr, *N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; IPr*, *N,N'*-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene; ⁱPr₂-bimy, *N,N'*-bis(isopropyl)benzimidazolin-2-ylidene; IXy, *N,N'*-bis-(2,6-methylphenyl)imidazol-2-ylidene; Mbim = methylene bisimidazole, Me₂biim, bis(3-methylimidazol-2-ylidene)methane; (Me₂HSi)₂O, (1,1,3,3-tetramethyldisiloxane); Me₂IMe, 1,3,4,5-tetramethylimidazol-2-ylidene; Mes, mesityl; NCMe, acetonitrile; NCS, thiocyanate; NHC, N-heterocyclic carbene; NMR, Nuclear Magnetic Resonance; OAc, acetate; OTf, Trifluoromethanesulfonate; RT, room temperature; SiCy, *N,N'*-(dicyclohexyl)imidazolidin-2-ylidene; SiMes, *N,N'*-bis[2,4,6-(trimethyl)phenyl]imidazolidin-2-ylidene; SiⁱPr, *N,N'*-(di-*iso*-propyl)imidazolidin-2-ylidene, SiPr, *N,N'*-bis(2,6-di-*iso*-propylphenyl)imidazolidin-2-ylidene; ^tBu, tert-butyl; ^tBu-mbim, bis(3-*tert*-butylimidazole-2-ylidene)methane; trz, 1,2,4 triazole; X, anionic ligand; Y, counteranion.

1. Introduction

N-heterocyclic carbene (NHC) ligands have been widely used during the last decades to stabilize numerous metals, generating important complexes utilized in various aspects of synthetic [1], material [2] and medicinal chemistry [3]. Among the plethora of metal-NHC complexes (NHC = N-heterocyclic carbene), copper(I)-NHC species remain one of the most extensively studied class of compounds in this field. These complexes have been widely applied as catalysts in several catalytic transformations [4], as transmetallating reagents for the synthesis of other NHC-metal complexes [5] and as anti-tumor agents [6]. In the literature, copper(I)-NHC complexes are most commonly reported as mononuclear species, usually di-coordinated bearing a second anionic or neutral ligand. Cationic complexes arise from neutral ligands (e.g., NHC, PR₃) [7], whereas neutral complexes derive from anionic ligands (e.g., halogens, alcohols, thiols) [8]. Dinuclear species are also described, although in fewer numbers, and recently examples of catalysis in which they were identified as the active species have been reported. On the other hand, copper(I)-NHC complexes possessing more than two metallic centers have also been reported, but their multinuclearity has not been shown yet to influence catalytic transformations. At the moment, dinuclear species are the best candidates among polynuclear copper(I)-NHC compounds for the development of transformations in which the two metal centers cooperate, resulting in an enhancement of the catalytic activity. In this context, we envisioned to describe herein dinuclear copper(I)-NHC species reported to date, hoping that this review will increase interest in the work on this class of complexes. With this goal in mind, a summary of the species synthesized up to date and their crystal structures are presented here. In this work, the classification within this family is based on the bridge used to couple the two copper atoms. The first class consists of having the NHC as an ancillary ligand and a separate moiety as a bridge, whereas in the second class the NHC ligand itself acts as a bridge (Scheme 1). For the sake of simplicity, the former class is further divided with respect to the nature of the dinuclear complex, namely cationic or neutral. Within each subclass, the species are organized as a function of the bridging ligand. The second class is divided with respect to the position of the bridge between the imidazole moieties, which either links two nitrogen atoms or two carbon atoms (C⁴ or C⁵) from the NHC backbone [9].



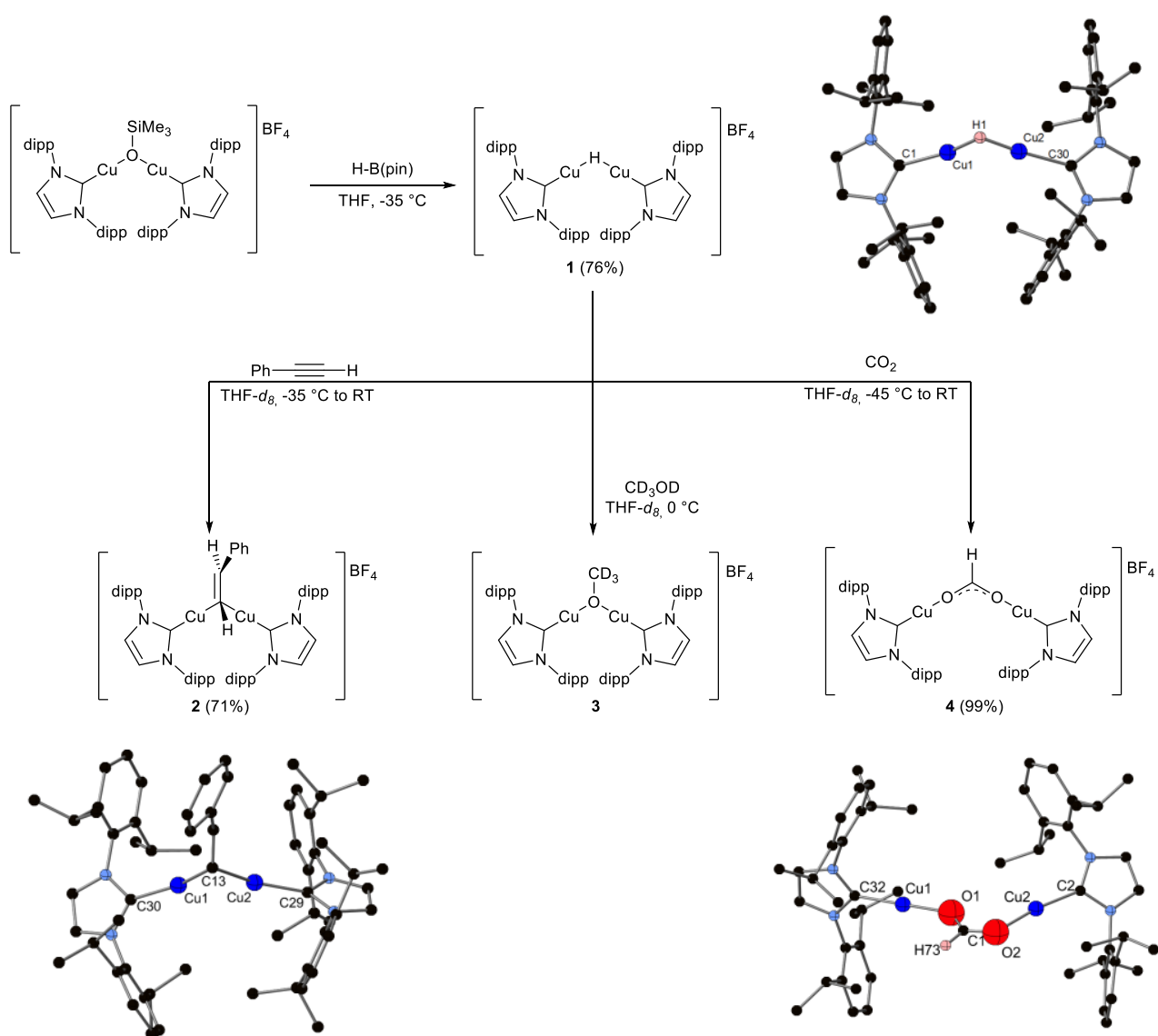
Scheme 1. Classification of the dinuclear copper(I)-NHC complexes used in this review.

2. NHCs as ancillary ligand

2.1 Cationic complexes

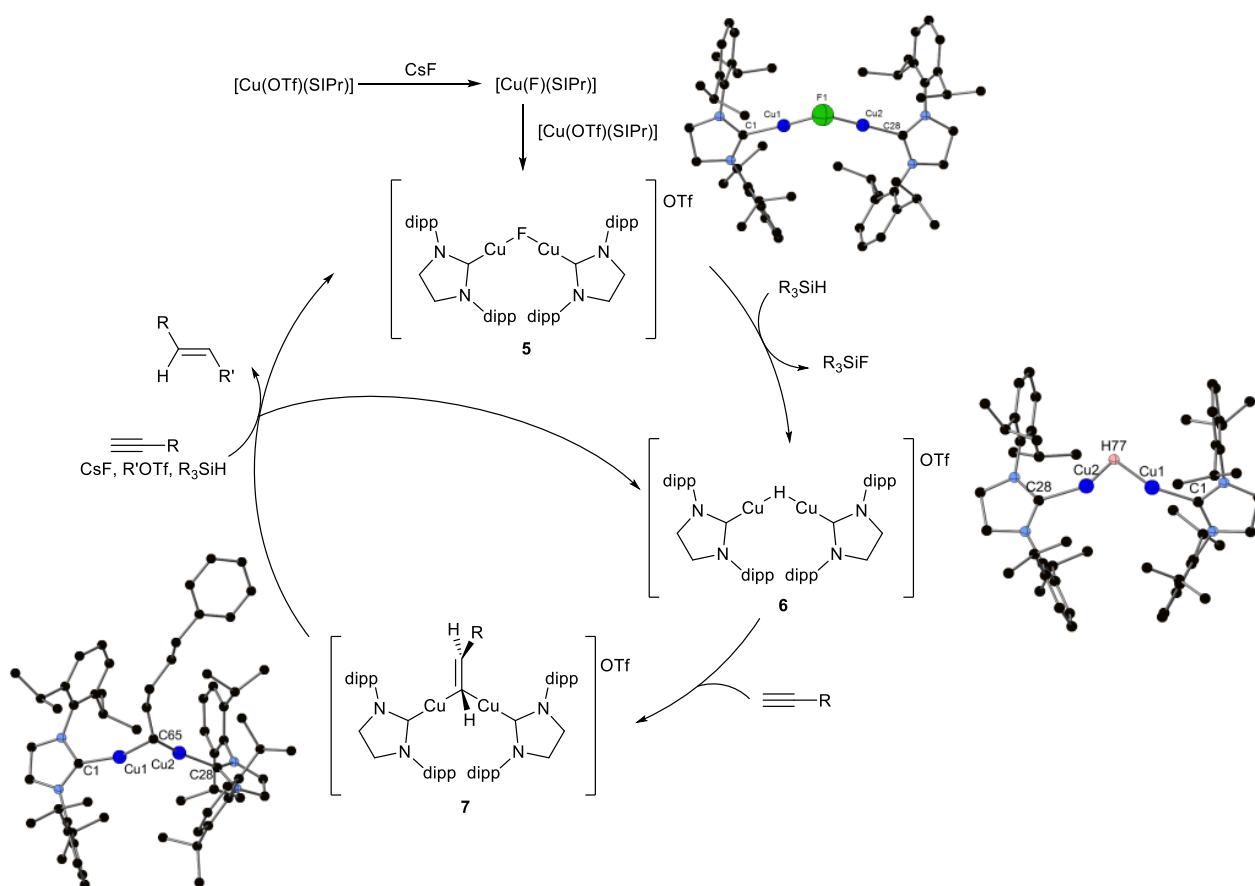
2.1.1. Hydride

Copper hydride complexes are widely used reagents in organic synthesis, mainly in copper-catalyzed hydrosilylation and hydrogenation reactions [10]. The first preparation of a copper hydride dates back to 1844 [11], but its structure was not elucidated until 1926 [12]. One of the best known species is the cluster $[\text{Cu}(\text{H})(\text{PPh}_3)]_6$, Stryker's reagent, whose structure consists of hexameric clusters [13]. In 2013, Sadighi and co-workers employed IPr (IPr = *N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) to stabilize the first reported dinuclear cationic copper(I)-NHC hydride complex $[\{\text{Cu}(\text{IPr})_2(\mu\text{-H})\}^+\text{BF}_4^-]$ (**1**) (Scheme 2) [14]. It was synthesized by the reaction of the siloxide-bridged dicopper $[\{\text{Cu}(\text{IPr})_2(\mu\text{-OSiMe}_3)\}^+\text{BF}_4^-]$ with HBpin and isolated as a colorless solid, with the bridging hydride detected by ^1H NMR at -4.13 ppm in THF-*d*₈. The crystal structure of **1** revealed that each copper atom adopts an almost linear geometry with $\text{C}_{\text{NHC}}\text{-Cu-H}$ angles of $167.4(16)^\circ$ and $174.4(16)^\circ$. The bridging core consists of a triangular $[\text{Cu}_2\text{H}]$ with $\text{Cu}(1)\text{-H}(1)\text{-Cu}(2)$ angle of $122(3)^\circ$ and the two copper atoms separated by $2.5331(15)$ Å. The authors used DFT calculations to obtain the electronic properties of **1**, finding that $[\{\text{Cu}(\text{IPr})_2(\mu\text{-H})\}^+]$ is an example of an open three-center interaction [15]. Moreover, a charge of -0.123 was calculated for the $[\text{Cu}_2\text{H}]$ core, indicating a hydridic character, in spite of its overall positive charge. This hydridic character is reflected in its reactivity with electrophiles such as phenylacetylene, CD_3OD and CO_2 to form the dinuclear species $[\{\text{Cu}(\text{IPr})_2(\mu\text{-trans-CHCHPh})\}^+\text{BF}_4^-]$ (**2**), $[\{\text{Cu}(\text{IPr})_2(\mu\text{-OCD}_3)\}^+\text{BF}_4^-]$ (**3**) and $[\{\text{Cu}(\text{IPr})_2(\mu\text{-O}_2\text{CH})\}^+\text{BF}_4^-]$ (**4**) respectively (Scheme 2). Species **2** was formed upon hydrocupration of phenylacetylene; its crystal structure shows a trigonal $[\text{Cu}_2\text{C}_{\text{vinyl}}]$ core where the two copper atoms again adopt an almost linear geometry, although more distorted with respect to **1**, with $\text{C}_{\text{NHC}}\text{-Cu-C}_{\text{vinyl}}$ angle of $154.3(2)^\circ$ and $151.2(2)^\circ$. In a similar manner to **1**, DFT calculations described that the $[\{\text{Cu}(\text{IPr})_2(\mu\text{-trans-CHCHPh})\}^+]$ cation presented an open three-center interaction. When **1** was reacted with CO_2 , hydrocupration of the C=O bond afforded the dicopper-formato species **4**, with each of the two copper atoms binding to an oxygen of the formato group. In the solid-state, the two copper atoms possess a linear geometry with $\text{C}_{\text{NHC}}\text{-Cu-O}$ angles of $171.23(7)^\circ$ and $177.69(6)^\circ$.



Scheme 2. Synthesis and reactivity of $[\{\text{Cu}(\text{IPr})\}_2(\mu\text{-H})]\text{BF}_4$ (**1**) with molecular structures determined by X-ray diffraction for **1**, **2** and **4**. Solvent molecules and H atoms are omitted for clarity [15].

As previously mentioned, copper(I)-NHC hydrides are useful reductive species, usually formed *in situ* in catalytic amount. It was postulated that the dinuclear copper hydride **1** was not stable in solution, dissociating into the respective monomer that is the species thought to be directly involved in the catalytic transformation [16]. In 2015, Lalic and co-workers studied the mechanism of the hydroalkylation of alkynes catalyzed by $[\text{Cu}(\text{OTf})(\text{SiPr})]$, using CsF as additive and $(\text{Me}_2\text{HSi})_2\text{O}$ (1,1,3,3-tetramethyldisiloxane) as hydride donor (Scheme 3) [17]. They found that the active species in the catalytic cycle were all dinuclear and cationic complexes with a general formula $[\{\text{Cu}(\text{SiPr})\}_2(\mu\text{-X})]\text{OTf}$. Initially, the mononuclear $[\text{Cu}(\text{OTf})(\text{SiPr})]$ precursor was converted to the corresponding mononuclear fluoride $[\text{Cu}(\text{F})(\text{SiPr})]$, which upon coordination with another $[\text{Cu}(\text{OTf})(\text{SiPr})]$ afforded the dinuclear $[\{\text{Cu}(\text{SiPr})\}_2(\mu\text{-F})]\text{OTf}$ (**5**). After this point all species involved are dinuclear and are similar to the ones previously described, such as $[\{\text{Cu}(\text{SiPr})\}_2(\mu\text{-H})]\text{OTf}$ (**6**) formed by transmetalation with the silane, and $[\{\text{Cu}(\text{SiPr})\}_2(\mu\text{-trans-CHCH}(\text{CH}_2)_3\text{Ph})]\text{OTf}$ (**7**) formed after hydrocupration of the alkyne.



Scheme 3. Catalytic cycle of the hydroalkylation of alkynes catalyzed by $[\{\text{Cu}(\text{SIPr})\}_2(\mu\text{-F})]\text{OTf}$ (**5**) with molecular structures determined by X-ray diffraction of the isolated catalytic intermediates **5-7**. Solvent molecules and H atoms are omitted for clarity [17].

The synthesis of the tetrafluoroborate analogue of complex **5**, $[\{\text{Cu}(\text{SIPr})\}_2(\mu\text{-F})]\text{BF}_4$ (**8**), was reported by Sadighi and co-workers *via* reaction of $[\text{Cu}(\text{O}^t\text{Bu})(\text{SIPr})]$ with $\text{Et}_3\text{N}\cdot 3\text{HF}$ or benzoyl fluoride [18]. Comparing the two species **5** and **8**, no significant differences in bond lengths were found. However, slight deviations in bond angles were observed, possibly indicating that the counter-anion affects, to some extent, their solid-state properties (Table 1).

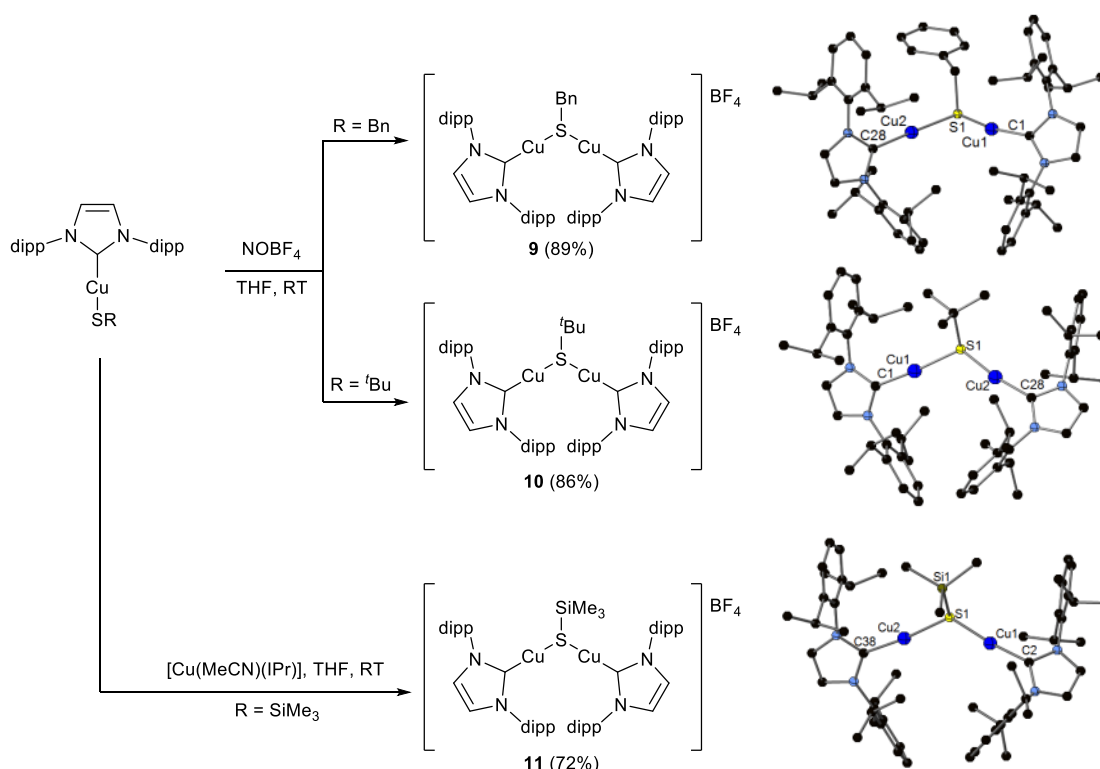
	$\text{C}_{\text{NHC}}\text{-Cu}$ (Å)	Cu-F (Å)	$\text{C}_{\text{NHC}}\text{-Cu-F}$ (°)	Cu-F-Cu (°)
$[\{\text{Cu}(\text{SIPr})\}_2(\mu\text{-F})]\text{OTf}$ (5)	1.869(3), 1.856(3)	1.836(2), 1.841(2)	171.8(1), 175.7(1)	136.5(1)
$[\{\text{Cu}(\text{SIPr})\}_2(\mu\text{-F})]\text{BF}_4$ (8)	1.877(3), 1.868(4)	1.843(3), 1.862(2)	176.5(1), 172.5(1)	143.0(2)

Table 1. Comparison of the bond lengths and angles of $[\{\text{Cu}(\text{SIPr})\}_2(\mu\text{-F})]\text{OTf}$ (**5**) and $[\{\text{Cu}(\text{SIPr})\}_2(\mu\text{-F})]\text{BF}_4$ (**8**) [17,18].

2.1.2. Sulfur

Another explored bridge is the thiolate group ($\mu\text{-SR}$), obtained *via* several approaches starting from the mononuclear copper thiolate complex $[\text{Cu}(\text{SR})(\text{NHC})]$ (Scheme 4). In 2009, Warren and co-workers synthesized two dinuclear thiolate bridged complexes by reacting the mononuclear precursor $[\text{Cu}(\text{SR})(\text{IPr})]$ ($\text{R} = \text{Bn}$, ^tBu), with nitrosonium tetrafluoroborate (NOBF_4) [19]. Upon addition of the latter, the reaction mixture becomes colored indicating the formation of the corresponding *S*-nitrosothiols, concomitantly with

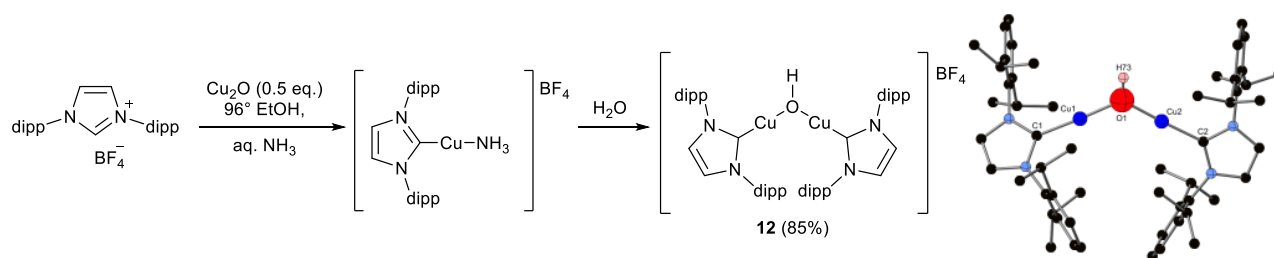
the dinuclear species $[\{\text{Cu}(\text{IPr})\}_2(\mu\text{-SBn})]\text{BF}_4$ (**9**) or $[\{\text{Cu}(\text{IPr})\}_2(\mu\text{-S}^t\text{Bu})]\text{BF}_4$ (**10**). The authors proposed that the reaction with NO^+ forms *S*-nitrosothiol RSNO in the coordination sphere of copper then RSNO is displaced by another copper thiolate affording **9** or **10**. Unfortunately, no evidence for the $[\text{Cu}(\text{S-nitrosothiol})(\text{NHC})]$ was observed. The complexes show an almost linear coordination around each copper atom with $\text{C}_{\text{NHC}}\text{-Cu}$ and Cu-S distances similar to the mononuclear precursor. The bridging $[\text{Cu}_2\text{S}]$ core possesses angles of $112.34(7)^\circ$ for **9** and $118.19(18)^\circ$ for **10**. Later, the Zhai group synthesized another dinuclear copper thiolate complex, $[\{\text{Cu}(\text{IPr})\}_2(\mu\text{-SSiMe}_3)]\text{BF}_4$ (**11**), as intermediate for a Cu_3S cluster [20]. It was achieved by reacting $[\text{Cu}(\text{SSiMe}_3)(\text{IPr})]$ with $[\text{Cu}(\text{NCMe})(\text{IPr})]\text{BF}_4$ *via* displacement of acetonitrile by the SSiMe_3 group. The two metal centers possess a quasi-linear geometry with $\text{C}_{\text{NHC}}\text{-Cu-S}$ angles of $172.47(18)^\circ$ and $172.17(18)^\circ$. While in the case of dimers **9** and **10**, the Cu-S bond distances are comparable to those found in the corresponding monomers, in **11** the Cu-S bond lengths are slightly longer than the Cu-S bond length found in the monomer (2.1423(19) and 2.1410(17) *versus* 2.1147(15) Å).



Scheme 4. Synthesis of dinuclear copper(I)-NHC complexes bridged by a thiolate moiety with molecular structures determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [19,20].

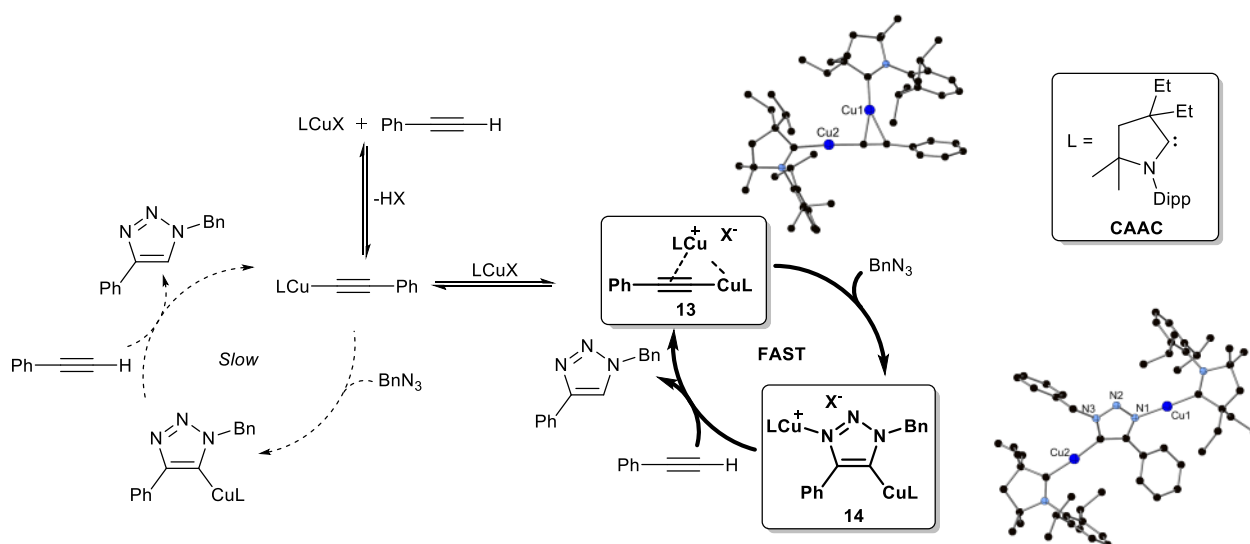
2.1.3. Other bridges

The Gautier group in 2014 discovered serendipitously the synthesis of $[\{\text{Cu}(\text{IPr})\}_2(\mu\text{-OH})]\text{BF}_4$ (**12**) while studying an ammonia-based metalation in ethanol [21]. A possible explanation for its formation is the displacement of NH_3 from $[\text{Cu}(\text{NH}_3)(\text{IPr})]^+$ by H_2O , to form $[\text{Cu}(\text{H}_2\text{O})(\text{IPr})]^+$, which is in turn deprotonated to form $[\text{Cu}(\text{OH})(\text{IPr})]$, which displaces NH_3 from another $[\text{Cu}(\text{NH}_3)(\text{IPr})]^+$ to form **12** (Scheme 5). Its crystal structure shows similar features with respect to the aforementioned cationic species, such as an almost linear coordination of the copper atoms and a triangular $[\text{Cu}_2\text{OH}]$ core. The structure of **12** is similar to the corresponding gold species [22].



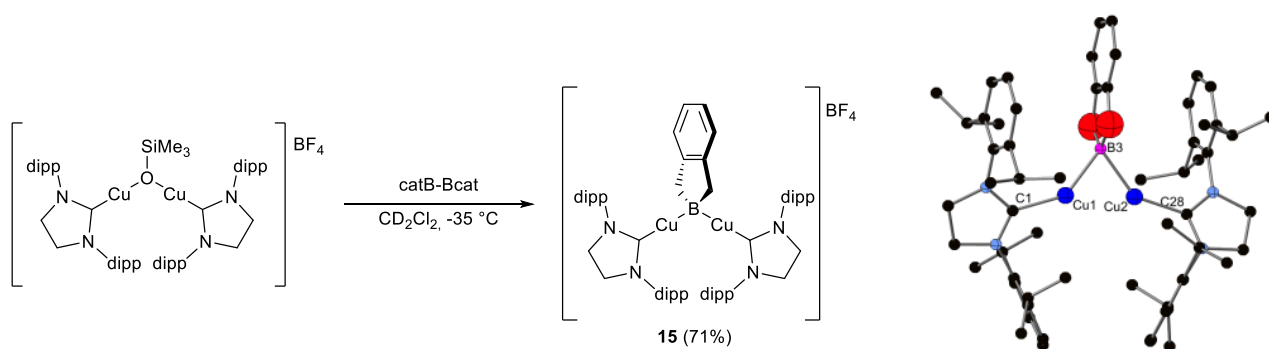
Scheme 5. Synthesis of $[\{\text{Cu}(\text{IPr})\}_2(\mu\text{-OH})]\text{BF}_4$ (**12**) and its molecular structure determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [21].

The following year Bertrand and co-workers isolated two intermediates of the CuAAC (Cu-catalyzed Azide/Alkyne Cycloaddition) reaction between alkynes and organic azides to afford 1,2,3-triazoles [23]. These species proved to be dinuclear and their existence was supported by previous kinetics [24] and computational studies [25]. The first species is the π,σ -bis(copper) (**13**), synthesized in high yield by reacting $[\text{Cu}(\text{C}\equiv\text{CPh})(\text{CAAC})]$ (CAAC = Cyclic Alkyl Amino Carbene) with $[\text{Cu}(\text{OTf})(\text{CAAC})]$. The second is the 3,5-bis(metallated) triazole (**14**), which was accessed cleanly from **13** and benzyl azide. Both complexes are air stable. Experiments showed a more kinetically favored pathway involving the latter species (**13** and **14**) as active catalytic intermediates compared to the mononuclear-based catalytic cycle (Scheme 6).



Scheme 6. Catalytic cycle of the CuAAC reaction; mononuclear pathway (left) and dinuclear pathway (right). The molecular structures determined by X-ray diffraction of the isolated catalytic intermediates **13-14** are also shown. Solvent molecules and H atoms are omitted for clarity [23].

The most recently reported cationic dinuclear complex was synthesized by Sadighi and co-workers in 2016. $[\{\text{Cu}(\text{SIPr})\}_2(\mu\text{-Bcat})]\text{BF}_4$ (**15**) was obtained by the reaction of $[\{\text{Cu}(\text{SIPr})\}_2(\mu\text{-OSiMe}_3)]\text{BF}_4$ with bis(catecholato)diboron (catB-Bcat) (Scheme 7) [26]. A bent geometry of the copper atoms was observed, with $\text{C}_{\text{NHC}}\text{-Cu-B}$ angles of $143.7(2)^\circ$ and $142.7(2)^\circ$ and Cu-B-Cu of $72.1(2)^\circ$. The boryl ligand is perpendicular to the NHC plane in order to minimize steric repulsions, and the boron center has a tetrahedral geometry. DFT calculations revealed a three-center bond order of the two copper and boron centers. Complex **15** did not react with CO_2 in the same manner as $[\text{Cu}(\text{Bpin})(\text{IPr})]$ [27], but can deprotonate phenyl acetylene as the boryl ligand acts as a Brønsted base, whereas the mononuclear $[\text{Cu}(\text{Bpin})(\text{IPr})]$ acted as a nucleophile, affording vinyl copper species *via* borocupration of the alkynes.

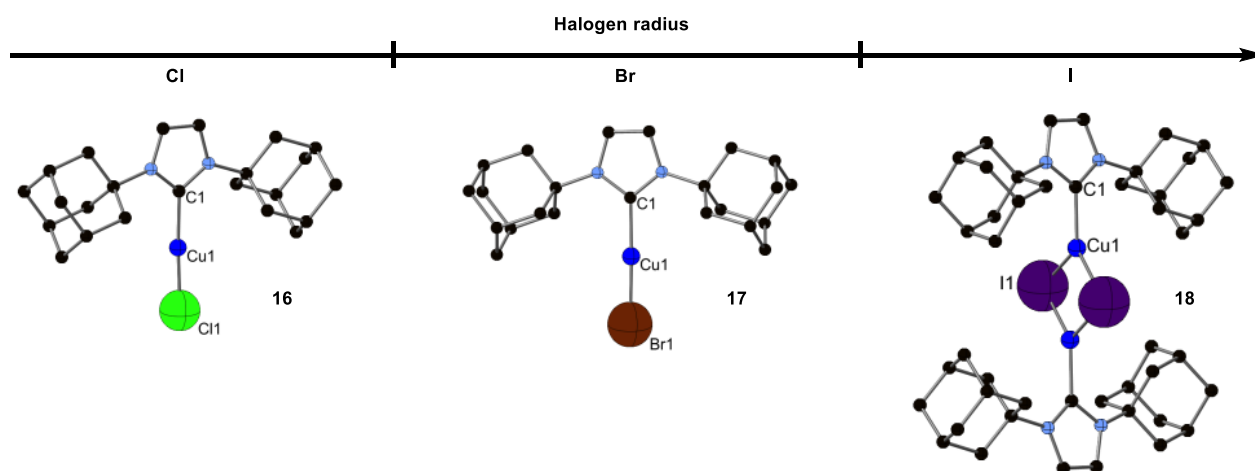


Scheme 7. Synthesis of $[\{\text{Cu}(\text{SIPr})\}_2(\mu\text{-Bcat})]\text{BF}_4$ (**15**) and its molecular structure determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [26].

2.2 Neutral complexes

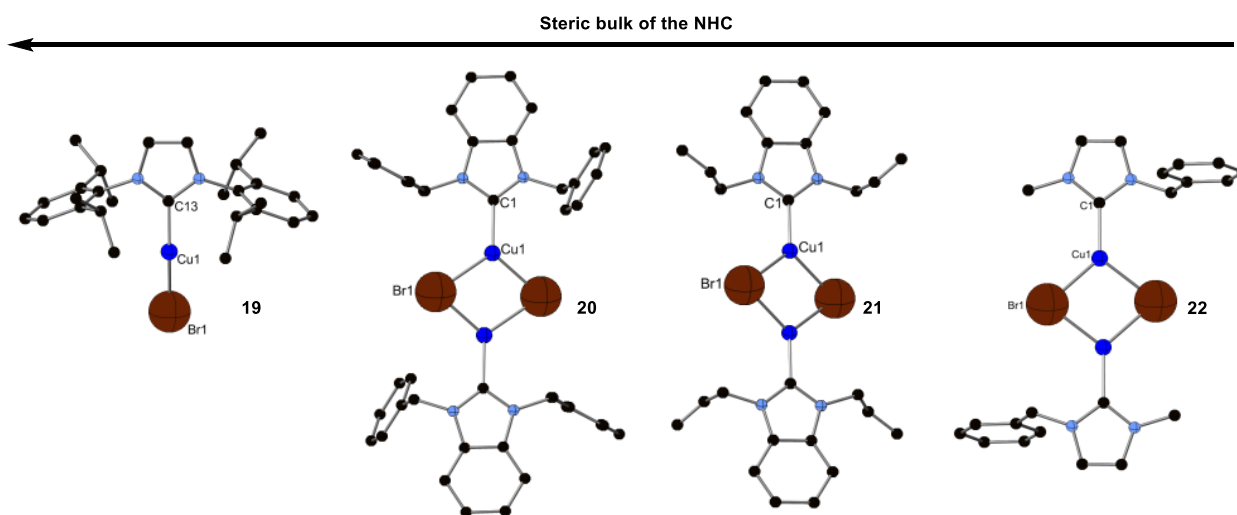
2.2.1. Halide and alkoxide

Copper(I)-NHC halides species are common in the literature and usually employed as a platform for subsequent design and functionalization in order to access a wide range of Cu-NHC derivatives [8a, 8d and 8e]. Their nuclearity is determined by both the steric bulk of the NHC ligand and the atomic radius of the halide [Cl (100 pm) < Br (115 pm) < I (140 pm)] (Scheme 8). This concept is well illustrated with the case of the ligand IAd; the corresponding chloro (**16**) and bromo (**17**) copper-IAd complexes are monomers, whereas the iodo analogue (**18**) is a dimer in the solid state [28]. In comparison, the copper complex bearing the smaller ICy is a monomer only in its chloro form, whereas the bromo and the iodo analogues present trinuclear distorted $[\text{Cu}_3\text{X}_3]$ cores with bridging NHCs.



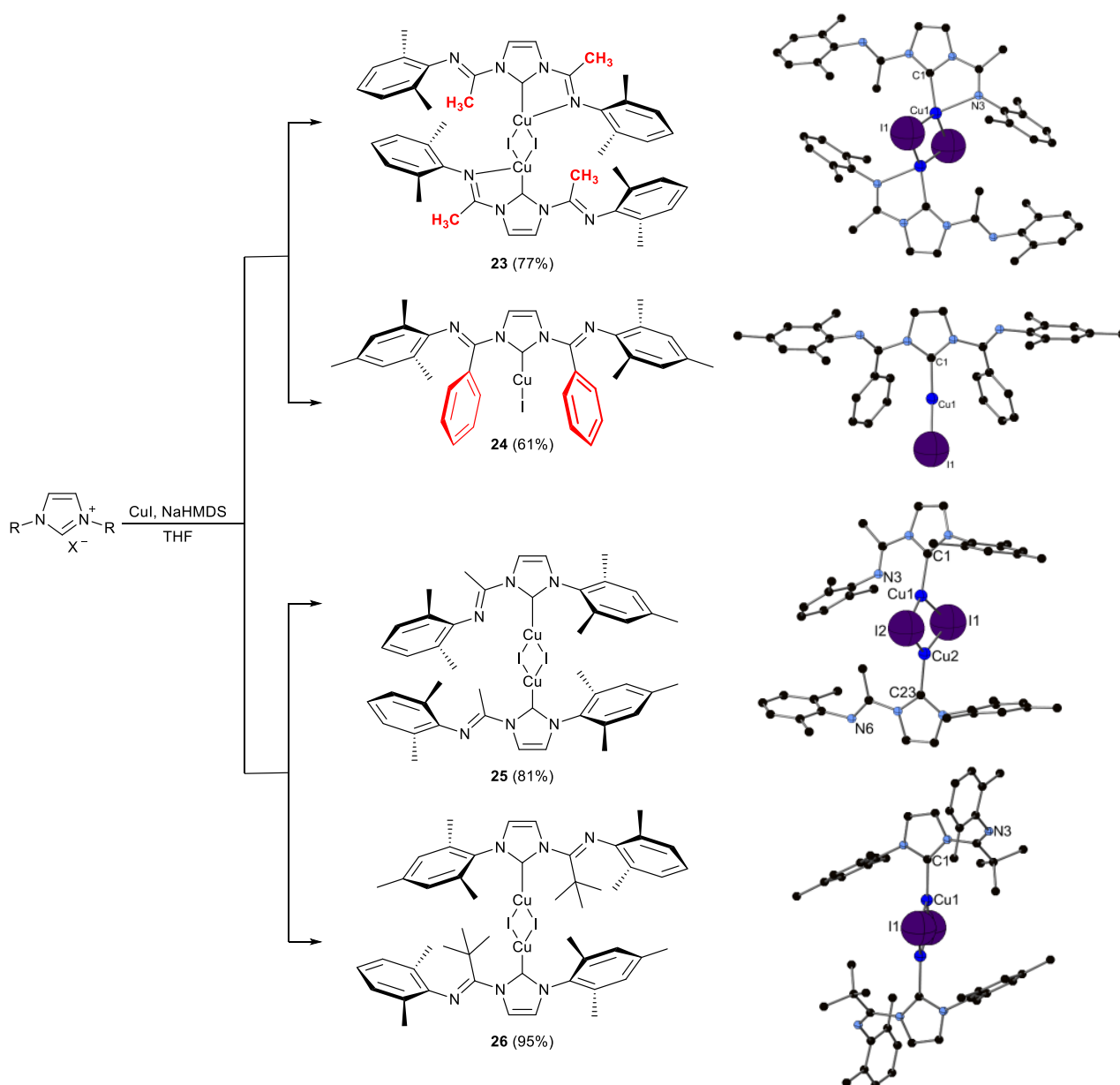
Scheme 8. Relationship between halide atomic radius and nuclearity with molecular structures determined by X-ray diffraction of **16-18**. Solvent molecules and H atoms are omitted for clarity [28].

Regarding the bulkiness of the NHC ligand, bromo-based copper complexes bearing sterically different NHCs were evaluated; it was shown that monomers were obtained with complexes bearing bulky ligands, such as IPr (**19**), whereas complexes bearing smaller ligands such as (1,3-dibenzylbenzimidazol-2-ylidene) (**20**), (1,3-diallylbenzimidazol-2-ylidene) (**21**) and (1-methyl-3-benzylimidazol-2-ylidene) (**22**) lead to dinuclear structures (Scheme 9) [29]. All these dinuclear complexes have a $[\text{C}_2\text{X}_2]$ core with each copper possessing a trigonal geometry binding one C_{NHC} and the two halogens.



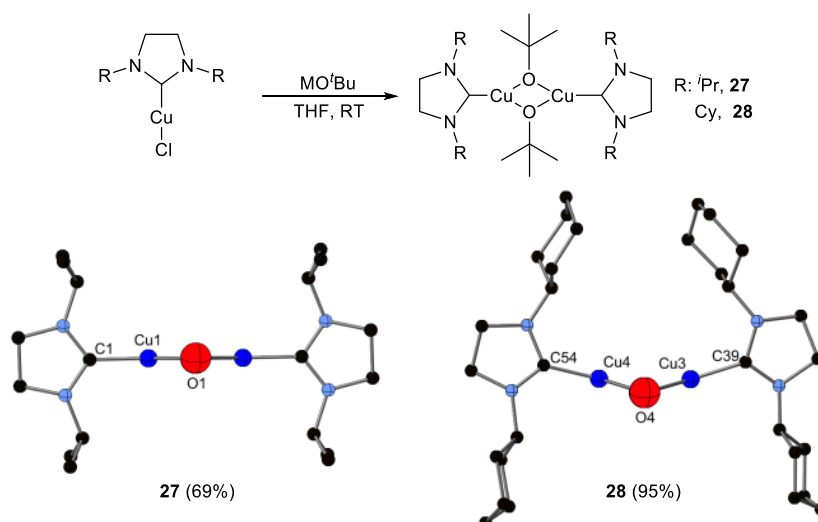
Scheme 9. Relationship between steric bulk of the NHC ligand and nuclearity with molecular structures determined by X-ray diffraction of **19–22**. Solvent molecules and H atoms are omitted for clarity [29].

Another example of the steric bulk/nuclearity correlation is manifested by a family of copper iodide complexes bearing different NCN ligands reported by Lavoie and co-workers (Scheme 10) [30]. The two NCN ligands used in this report differed only by the imminic substituent, which clearly influences the nuclearity of the derived copper iodide complexes in the solid state. In this manner, dinuclear copper complex **23** bearing the small methyl-substituted ligand is obtained, whereas the bulkier phenyl-substituted ligand leads to the mononuclear complex **24**. Interestingly, the copper atom in **23** exhibits a distorted tetrahedral geometry due to the added coordination of the imine nitrogen atom with a C(1)–Cu(1)–N(3) bite angle of 77.86(15)°, whereas the other angles around the metal center are C(1)–Cu(1)–I(1) of 124.85(12)° and N(3)–Cu(1)–I(1) of 102.89(9)°. On the other hand, in **24** the ligand binds to the metal only with the C_{NHC} carbene in a monodentate fashion, affording a dicoordinated linear arrangement around the copper atom with C_{NHC}–Cu–I angle of 169.35(17)°. Later on, the same group reported copper iodide complexes of imino-N-heterocyclic carbenes, [Cu(μ-I)(C[^]Imine_{Me})]₂ (**25**) and [Cu(μ-I)(C[^]Imine_{tBu})]₂ (**26**) (Scheme 10) [31]. Both species are dimeric, possessing a slightly distorted trigonal-planar geometry around each metal center due to the lack of N-coordination of the ligand. However, an imminic nitrogen in complex **25** is located near one of the copper atoms resulting in a more distorted geometry with respect to **26**, in which the nitrogen atoms are both far from the metal center. The degree of distortion was identified by the sum of all the three angles which is 356.0(3)° in **25** and 359.9(2)° in **26**.



Scheme 10. Copper(I) complexes bearing NCN ligands reported by Lavoie and co-workers with molecular structures determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [30,31].

By reacting a copper(I)-NHC halide complex with an alkoxide base, usually *tert*-butoxide, the corresponding $[\text{Cu}(\text{OR})(\text{NHC})]$ is formed (Scheme 11). The nuclearity of these complexes is once again governed by the steric bulk of the NHC ligand. In this context, dinuclear complexes are obtained using smaller ligands such as SiCy and SiⁱPr, resulting in $[\text{Cu}(\mu\text{-O}^t\text{Bu})(\text{Si}^i\text{Pr})]_2$ (**27**) and $[\text{Cu}(\mu\text{-O}^t\text{Bu})(\text{SiCy})]_2$ (**28**) [32,33]. They are highly air- and moisture-sensitive due to the lower stabilization of the NHC. Nevertheless, they are highly reactive species typically used as precursors for other complexes or as catalysts in several organic transformations. Concerning their solid-state structure, they both present a $[\text{Cu}_2\text{O}_2]$ core with each copper atom exhibiting a trigonal geometry. The NHC-Cu-Cu-NHC organization depends on the NHC ligand; complex **27** has an almost linear arrangement due to the smaller SiⁱPr, whereas the bulkier SiCy prompts complex **28** to adopt a bent geometry.



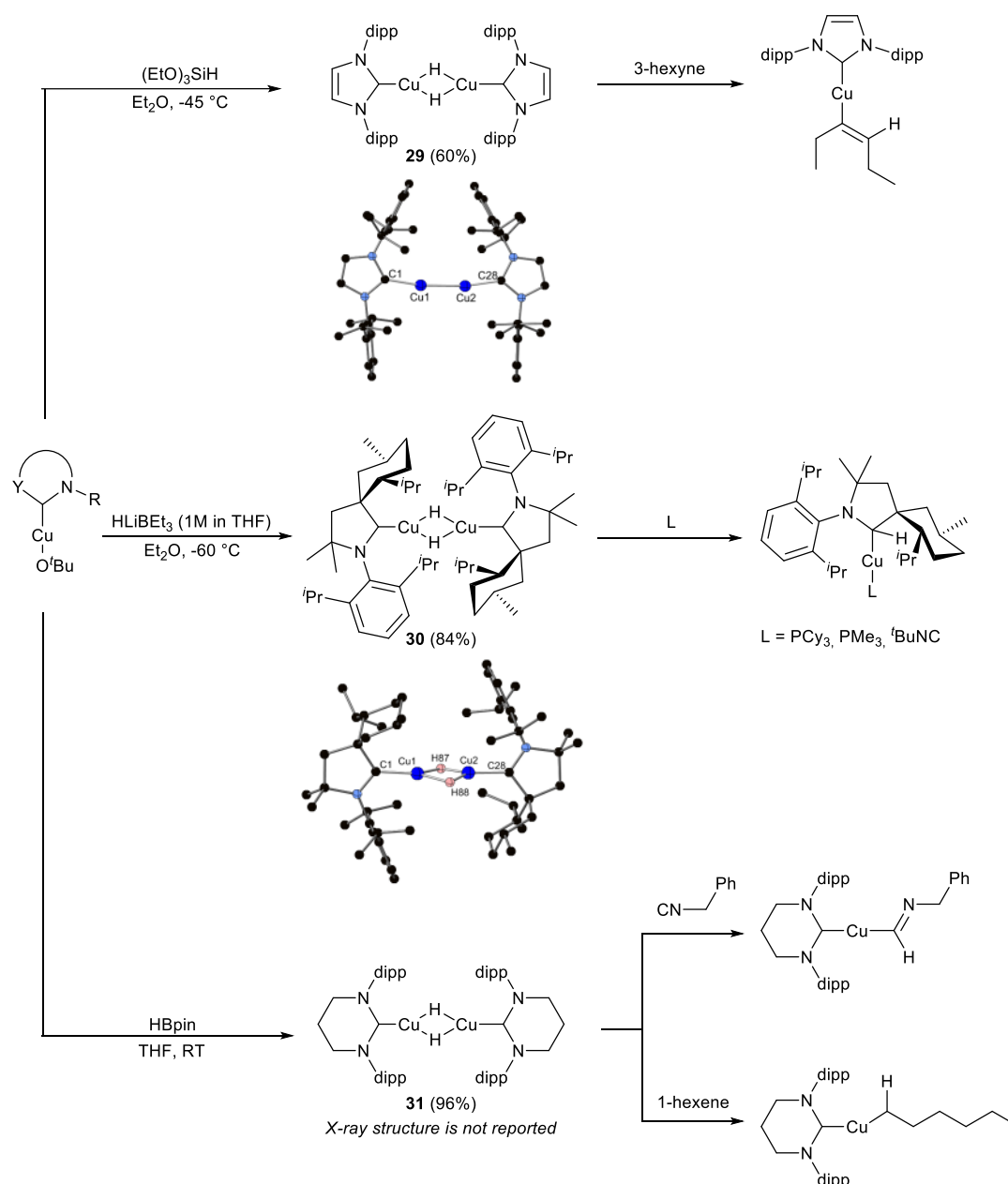
Scheme 11. General synthesis of copper(I)-NHC alkoxide complexes with molecular structures determined by X-ray diffraction. Solvent molecules, H atoms and *tert*-butyl moieties are omitted for clarity [32,33].

2.2.2. Hydride

Only three neutral dinuclear copper(I)-NHC hydride species have been reported in the literature to date (Scheme 12). The first was reported by Sadighi and co-workers in 2004, namely $[\text{Cu}(\mu\text{-H})(\text{IPr})_2]$ (**29**), which was obtained by the reaction of $[\text{Cu}(\text{O}^t\text{Bu})(\text{IPr})]$ with triethoxysilane (Scheme 12, top) [34]. The formation of **29** is accompanied by the appearance of an intense yellow color in C_6D_6 solution and its ^1H NMR spectrum reveals the hydridic peak at 2.67 ppm. This complex decomposes in solution after 1 h and in the solid state after several days. It presents an almost linear NHC-Cu-Cu-NHC geometry with $\text{C}_{\text{NHC}}\text{-Cu-Cu}$ angles of $169.4(2)$ and $170.33(19)$. Interestingly, a short Cu-Cu distance of $2.3059(11)$ Å is observed in **29** indicating a possible interaction between the two metal centers mainly due to the small radius of the hydride and the resulting Cu-H bonds. This complex readily reacts with the triple bond of 3-hexyne *via* hydrocupration to afford the corresponding vinyl copper species.

The second dimeric hydride species is $[\text{Cu}(\mu\text{-H})(\text{CAAC})_2]$ (**30**), obtained by Bertrand and co-workers in 2011 from the reaction of its copper *tert*-butoxide precursor and HLiBEt_3 (Scheme 12, middle) [35]. Unlike the IPr analogue, **30** is stable in solution and in the solid state at room temperature for weeks. The authors attributed this increased stability to the steric bulk and rigidity of the CAAC ligand used; the same reaction using a more flexible and smaller ligand did not yield the corresponding dimer. The crystal structure of **30** unambiguously revealed the bridging hydrides, with a $[\text{Cu}_2\text{H}_2]$ core and a quasi-linear CAAC-Cu-Cu-CAAC geometry ($\text{C}_{\text{CAAC}}\text{-Cu-Cu}$ angles of 175.27° and 178.13°). Each copper atom possesses a distorted trigonal geometry. The Cu-Cu distance of $2.3058(5)$ Å is comparable with **29**. Reacting **30** with additional neutral ligands, such as phosphines or *tert*-butylisocyanide, results in a migratory insertion of the CAAC ligand into the Cu-H bond instead of the expected mononuclear tricoordinated copper hydride species.

The third dimeric hydride complex is $[\text{Cu}(\mu\text{-H})(6\text{Dipp})_2]$ (**31**) (6Dipp = *N,N'*-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene), synthesized by Sadighi and co-workers in 2016 *via* the reaction of its copper *tert*-butoxide precursor with HBpin (Scheme 12, bottom) [36]. This complex is stable in solution and in the solid state for days due to the steric encumbrance derived from the expanded NHC backbone which tilts the *N*-aryl moieties closer to the hydrides. This feature is illustrated by the upfield shift of the hydride signal in the proton NMR with respect to **29** ($\delta = 0.77$ ppm for **31**, compared to 2.67 ppm for **29**), due to the major anisotropic shielding of the hydrides by the *N*-aryl and by the higher σ -donation of 6Dipp. The crystal structure of **31** was not reported, but when the complex is reacted with benzyl isocyanide, the 1,1-insertion product was successfully characterized by X-ray analysis.

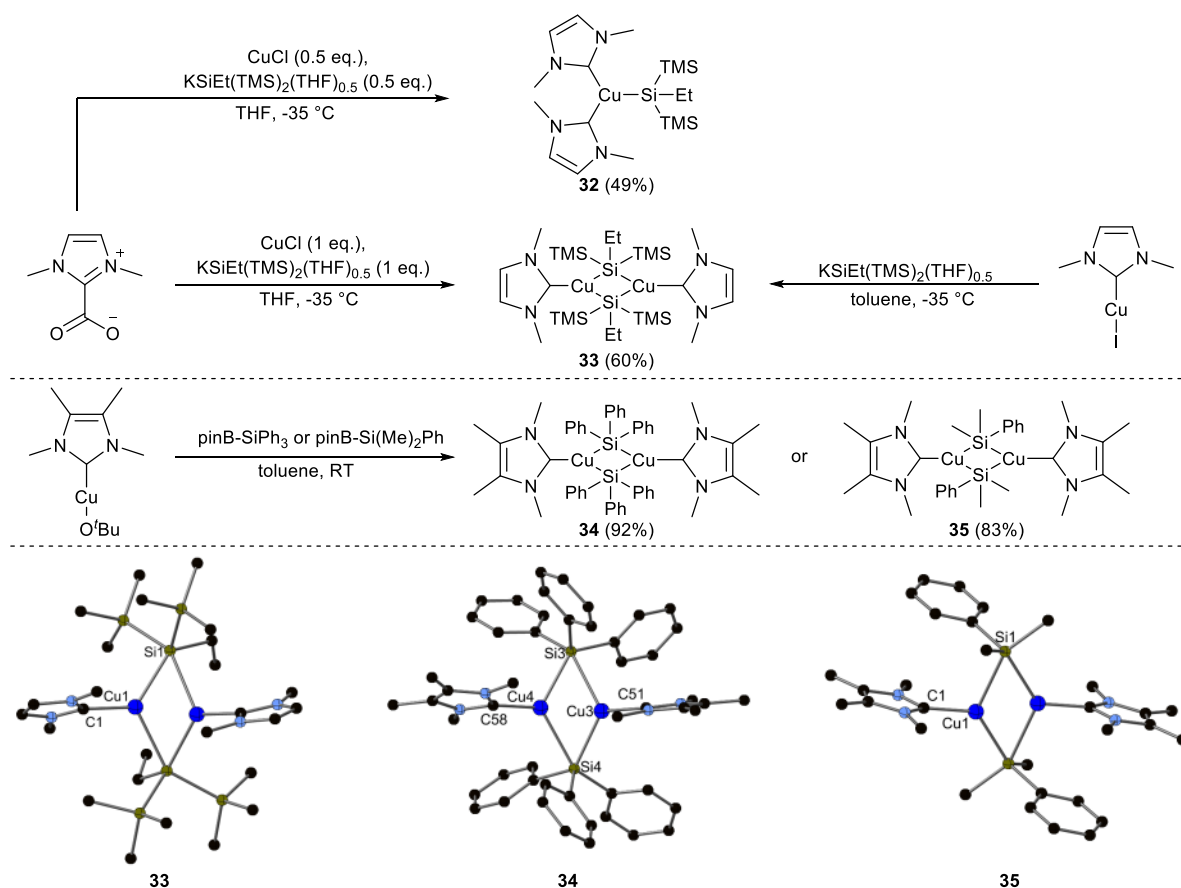


Scheme 12. Synthesis and reactivity of the neutral dinuclear copper hydride species **29-31** with molecular structures determined by X-ray diffraction for **29** and **30**. Solvent molecules and H atoms are omitted for clarity [34-36].

2.2.3. Silicon

The first dimeric complex of the type $[\text{Cu}(\mu\text{-SiR}_3)(\text{NHC})]_2$ was reported in 2015 by Piers and co-workers, supported by a bulky $\text{SiEt}(\text{SiMe}_3)_2$ bridge and a small NHC (IMe) ligand (Scheme 13) [37]. The use of IMe and tuning of reaction conditions ($\text{NHC}/\text{CuCl}/\text{KSiEt}(\text{SiMe}_3)_2$ stoichiometry) allow access to monomeric and dimeric complexes. The use of a 2:1:1 ratio of the reagents yielded the mononuclear complex $[\text{Cu}\{\text{SiEt}(\text{SiMe}_3)_2\}(\text{IMe})_2]$ (**32**), whereas a ratio of 1:1:1 gave the dinuclear complex $[\text{Cu}\{\mu\text{-SiEt}(\text{SiMe}_3)_2\}(\text{IMe})]_2$ (**33**). Analyzing the crystal structure of **33**, a $[\text{Cu}_2\text{Si}_2]$ core is observed with a trigonal planar geometry around the copper atoms. When compared with a mononuclear analogue $[\text{Cu}\{\text{Si}(\text{SiMe}_3)_3\}(\text{IMe})]$, possessing a larger silicon group, the $\text{C}_{\text{NHC}}\text{-Cu}$ distance is longer for **33**, as well as the Cu-Si distances, due to the different coordination mode of the copper. Later on, Kleeberg and co-workers used Me_2IMe as NHC to synthesize the silyl bridged species $[\text{Cu}(\mu\text{-SiPh}_3)(\text{Me}_2\text{IMe})]_2$ (**34**) and $[\text{Cu}(\mu\text{-SiMe}_2\text{Ph})(\text{Me}_2\text{IMe})]_2$ (**35**) from the corresponding *tert*-butoxide complexes and pinB-SiR₃ (Scheme 13) [38]. In these complexes the copper

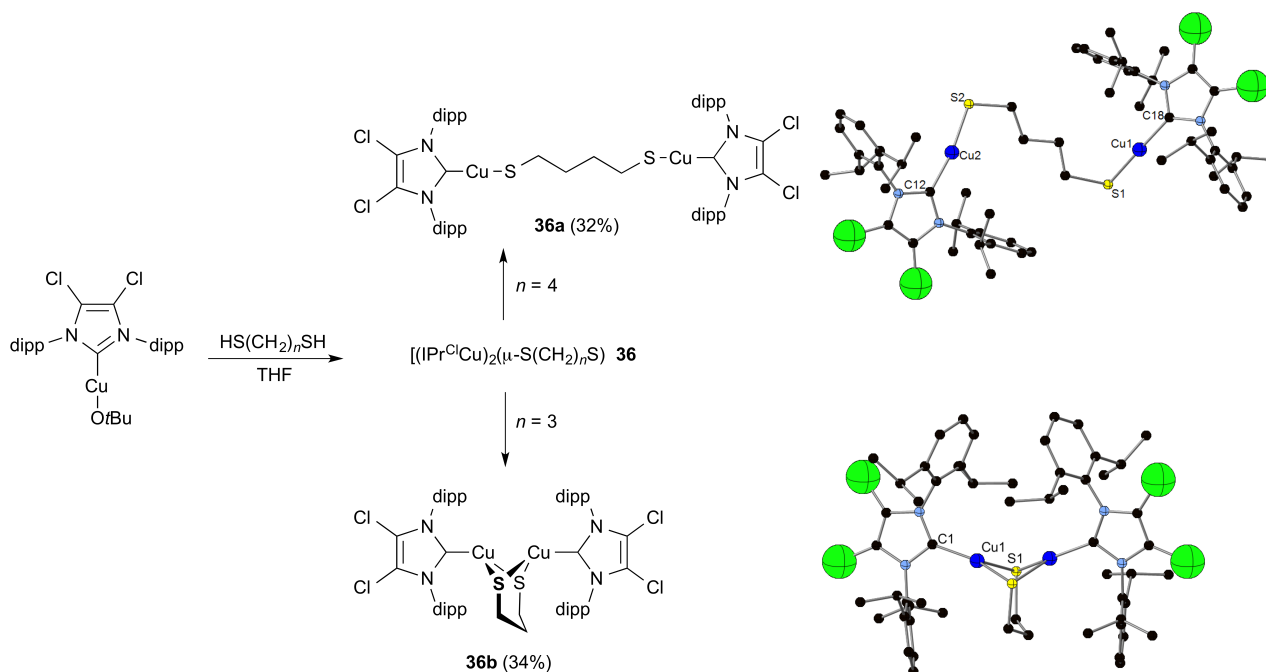
is tri-coordinated with one NHC ligand and two bridging silyl ligands, giving an almost planar $[\text{Cu}_2\text{Si}_2]$ core similar to the one observed in **33**.



Scheme 13. Synthesis of neutral dinuclear copper(I)-NHC complexes possessing a silyl bridge with molecular structures determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [37,38].

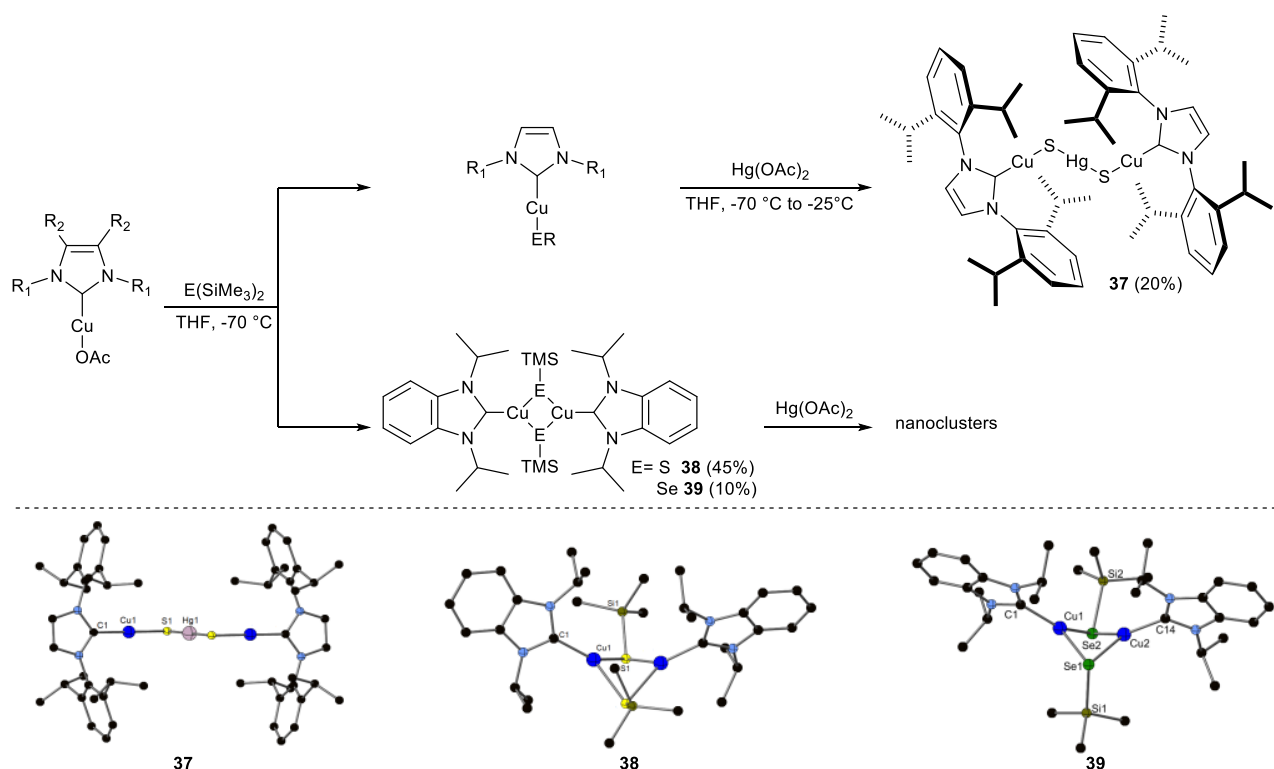
2.2.4. Sulfur and selenium

The first neutral dimeric copper(I)-NHC sulfido, $[\{\text{Cu}(\text{IPr}^{\text{Cl}})\}_2\{\mu\text{-S}(\text{CH}_2)_3\text{S}\}]$ (**36b**), was reported by Warren and co-workers in 2013 aiming to model the Cu_A electronic-transfer site present in important metalloenzymes such as cytochrome C oxydase (CcO) and bacterial nitrous oxide reductase (Scheme 14) [39]. In Nature, the copper atoms in Cu_A show a trigonal planar geometry and **36b** was the first accurate model for this coordination. Complex **36b** crystallized with a $[\text{Cu}_2\text{S}_2]$ diamond core with each metal coordinating to one C_{NHC} and two sulfur atoms, resulting in the desired trigonal planar geometry with $\text{C}_{\text{NHC}}\text{-Cu-S}$ angles of $143.02(18)^\circ$ and $122.56(18)^\circ$ and S-Cu-S angle of $93.76(7)^\circ$. This is in agreement with the original Cu_A structure, although a smaller S-Cu-S angle is observed in the model with respect to the natural Cu_A site in CcO ($110.87\text{-}114.38^\circ$) [40]. Interestingly, when a 4-carbon dithiol bridge $\text{-S}(\text{CH}_2)_4\text{S-}$ was used, an “open” structure was obtained as evidenced by the molecular structure of $[\{\text{Cu}(\text{IPr}^{\text{Cl}})\}_2\{\text{S}(\text{CH}_2)_4\text{S}\}]$ **36a**. In this case, the two copper(I)-NHC moieties did not interact and are connected through the 1,4-butanedithiolate ligand. The copper atoms are coordinated to one C_{NHC} and one sulfur in an almost linear geometry, with $\text{C}_{\text{NHC}}\text{-Cu-S}$ angles of $171.89(10)^\circ$ and $170.06(12)^\circ$.



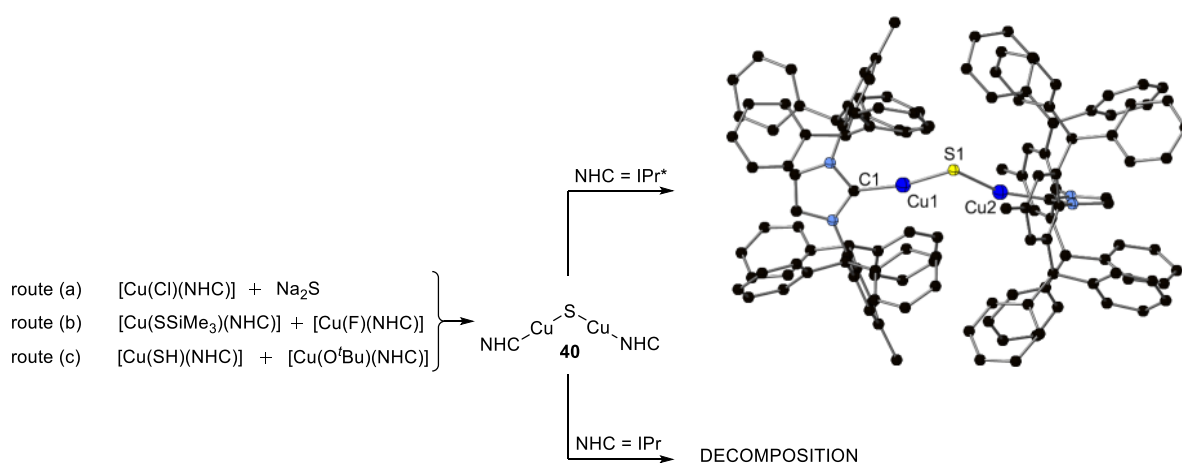
Scheme 14. Synthesis of $[\{\text{Cu}(\text{IPr}^{\text{Cl}})\}_2\{\mu\text{-S}(\text{CH}_2)_n\text{S}\}]$ (**36a** and **36b**) and their corresponding molecular structures determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [39].

More recently, the Corrigan group used an S-Hg-S bridge to connect two copper-NHC fragments (Scheme 15) [41]. The synthetic route consists of reacting the mononuclear $[\text{Cu}(\text{SSiMe}_3)(\text{NHC})]$ precursor with 0.5 equivalent of $\text{Hg}(\text{OAc})_2$ at low temperature, affording $[\{\text{Cu}(\text{S})(\text{IPr})\}_2(\mu\text{-Hg})]$ (**37**). The S-Hg-S bridge has a linear geometry with Hg-S bond lengths of 2.309(2) Å with the inversion center of the complex located at the Hg atom. Each copper atom is coordinated with one C_{NHC} and a sulfur atom, showing an almost linear arrangement with $\text{C}_{\text{NHC}}\text{-Cu-S}$ angle of 177.4(3)°. In a following work, the same group explored the consequence of employing different ligands on the nuclearity of $[\text{Cu}(\text{ER})(\text{NHC})]$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) species [42]. In this context, mononuclear species were obtained upon reacting the $[\text{Cu}(\text{OAc})(\text{IPr})]$ precursor with $\text{E}(\text{SiMe}_3)_2$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$). Using the same protocol, but replacing the sterically demanding IPr by a smaller ${}^i\text{Pr}_2\text{-bimy}$ (${}^i\text{Pr}_2\text{-bimy} = N,N'$ -bis(isopropyl)benzimidazol-2-ylidene) [% V_{Bur} (IPr) = 44.5 *versus* % V_{Bur} (${}^i\text{Pr}_2\text{-bimy}$) = 27.9; % V_{Bur} = percentage of a sphere, centered on the metal, which is occupied by the ligand], dinuclear complexes containing a chalcogenide bridge were obtained, namely $[\text{Cu}(\mu\text{-SSiMe}_3)({}^i\text{Pr}_2\text{-bimy})_2]$ (**38**) and $[\text{Cu}(\mu\text{-SeSiMe}_3)({}^i\text{Pr}_2\text{-bimy})_2]$ (**39**) (Scheme 15). Complex **38** is thermally stable and melts at 91-93°, whereas complex **39** decomposes above -25 °C. Crystal structures show a butterfly shaped $[\text{Cu}_2\text{E}_2]$ core, with Cu-S-Cu and Cu-Se-Cu angles of 119° and 138.04(4)° respectively. The copper centers in both species exhibit a distorted trigonal planar geometry, each coordinating a C_{NHC} and two $\mu\text{-ESiMe}_3$ groups. The main difference between the molecular structures of **38** and **39** lies in the orientation of the TMS groups; these are on the same side (*cis*) of the central ring in **38**, whereas in **39**, they reside on opposite sides (*trans*). Moreover, the use of a smaller ligand in **38** and **39** has a significant effect on reactivity; this was highlighted when these complexes were reacted with 0.5 equivalent of $\text{Hg}(\text{OAc})_2$, affording nanoclusters instead of the expected dimers.



Scheme 15. Synthesis and reactivity of **37-39** and their molecular structures determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [41,42].

As noticed for copper halides, there is a correlation between smaller ligands and higher nuclearity and larger ligands with low nuclearity. This concept was used by Zhai and co-workers, who employed the bulkier IPr^* ($\text{IPr}^* = N,N'$ -bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene) to stabilize a naked Cu_2S , thus avoiding the condensation of unsaturated Cu-S units into clusters (Scheme 16) [43]. Different approaches were developed to achieve the final complex $[\{\text{Cu}(\text{IPr}^*)\}_2(\mu\text{-S})]$ (**40**), obtaining an overall yield of *ca.* 65%. Attempts to synthesize the IPr analogue complex were unsuccessful due to the lower steric bulk of the NHC ligand.

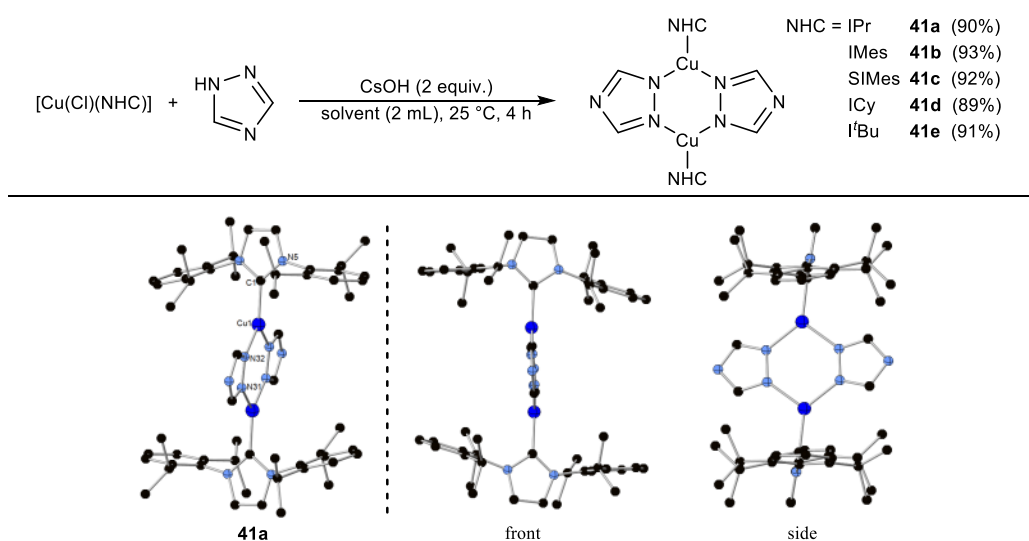


Scheme 16. Different routes for the synthesis of $[\{\text{Cu}(\text{IPr}^*)\}_2(\mu\text{-S})]$ (**40**) and its molecular structure determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [43].

2.2.5. Azole

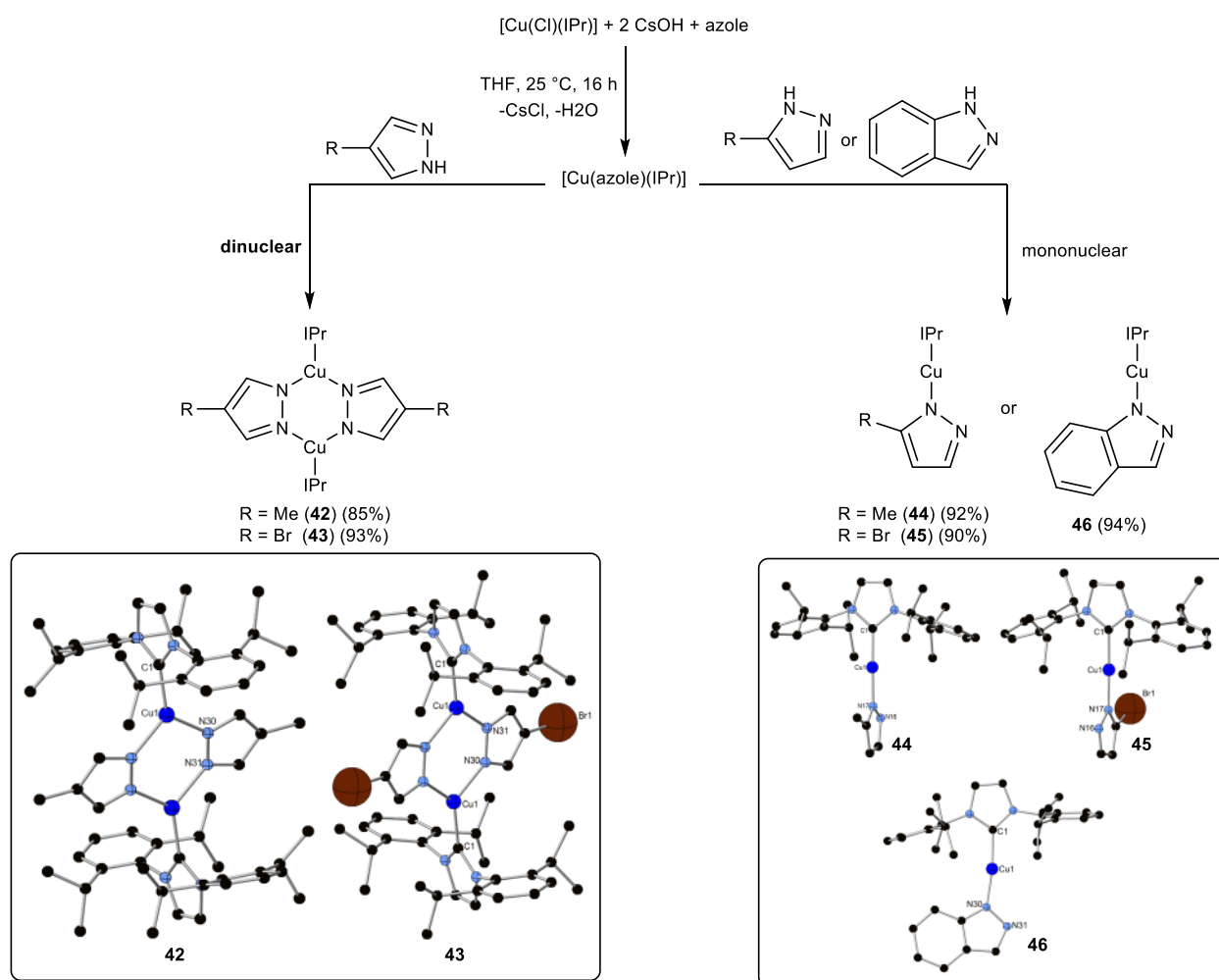
The Cazin group reported a family of neutral dinuclear copper(I)-NHC complexes bearing 1,2,4-triazole (trz) as a bridging ligand, namely $[\text{Cu}(\mu\text{-trz})(\text{NHC})]_2$ (**41a-e**), derived from the reaction between the

corresponding $[\text{Cu}(\text{Cl})(\text{NHC})]$ precursor, CsOH and 1,2,4-triazole (Scheme 17) [44]. During the course of the reaction $[\text{Cu}(\text{OH})(\text{IPr})]$ is generated *in situ*, then deprotonates the azole molecule, yielding the dimeric complex with the concomitant liberation of water. High yields and straightforward purification were systematically achieved using this procedure. $[\text{Cu}(\mu\text{-trz})(\text{IPr})]_2$ (**41a**) shows a distorted trigonal geometry around each metal center with $\text{C}_{\text{NHC}}\text{-Cu-N31}$, $\text{C}_{\text{NHC}}\text{-Cu-N32}^1$ and N31-Cu-N32^1 angles of $119.15(10)^\circ$, $134.57(10)^\circ$ and $106.17(9)^\circ$, respectively. Two different Cu-N bond distances ($\text{Cu-N31} = 2.001(2) \text{ \AA}$; $\text{Cu-N32}^1 = 1.964(2) \text{ \AA}$) were found. The main characteristic of these complexes is the six-membered ring formed by the two copper atoms and the four nitrogen of the bridging triazolate. This ring is almost perpendicular to the NHC-Cu-Cu-NHC plane ($\text{N31-Cu1-C1-N5} = 99.3(2)^\circ$) in order to minimize steric repulsions. Changing the steric bulk of the NHC did not affect the nuclearity, but a deviation in linearity between the two NHC fragments was observed. These complexes were shown to be highly efficient catalysts for the hydrosilylation of various ketones without the need for additional external base.



Scheme 17. Synthesis of $[\text{Cu}(\mu\text{-trz})(\text{NHC})]_2$ complexes. The molecular structure determined by X-ray diffraction of $[\text{Cu}(\mu\text{-trz})(\text{IPr})]_2$ (**41a**) is shown. Solvent molecules and H atoms are omitted for clarity [44].

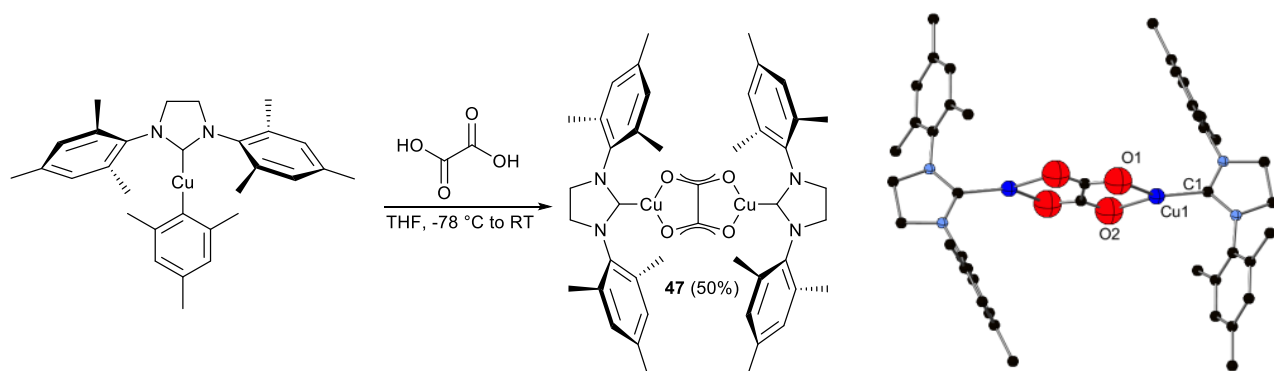
Recently, the same group expanded this family to include a range of azole groups, showing the dependence of the nuclearity with respect to the azole substituents (Scheme 18) [45]. In particular, the use of a 4-substituted pyrazole results in the formation of dinuclear species **42** and **43**, whereas the 3-substituted pyrazoles and the indazole all lead to mononuclear complexes (**44-46**). This outcome derived from steric reasons; changing the electronics of the azole, ranging from the electron-withdrawing bromopyrazole to the electron-donating methylpyrazole, did not change the coordination behavior in the solid state.



Scheme 18. Synthesis of $[\text{Cu}(\text{azole})(\text{IPr})]$ **42-46** and their molecular structures as determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [45].

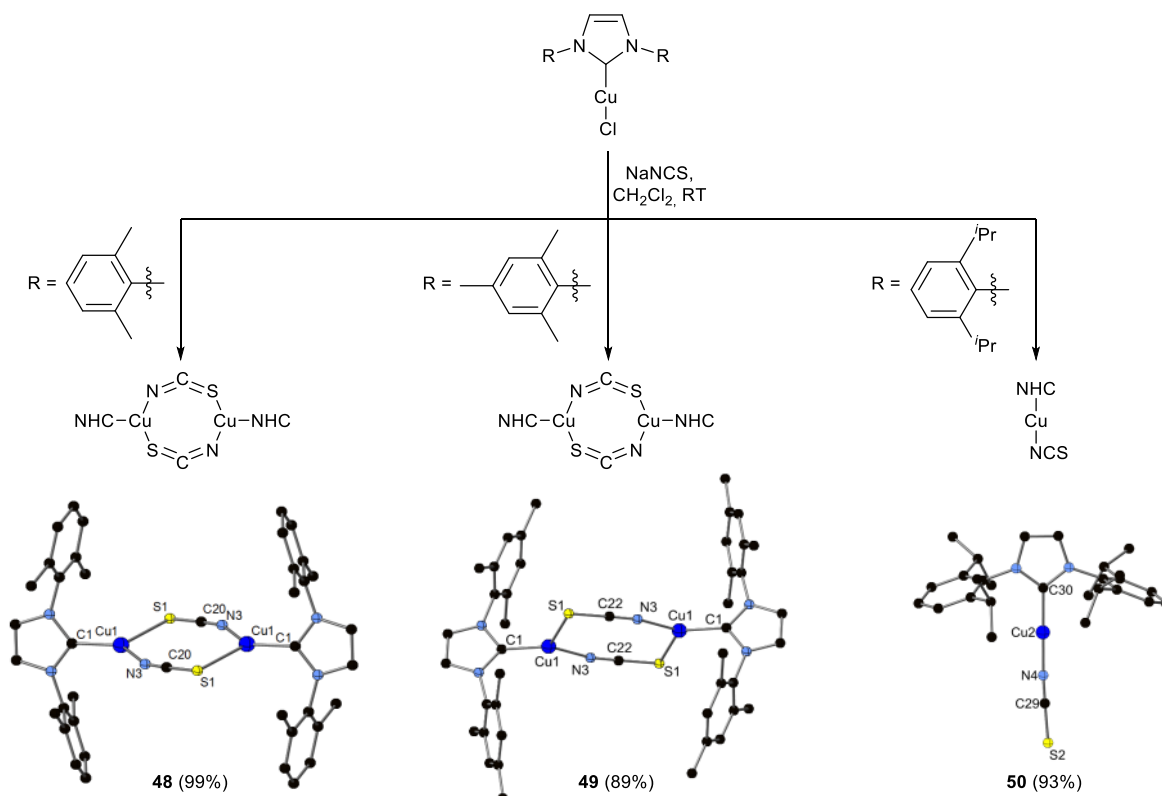
2.2.6. Other neutral dinuclear copper(I)-NHC species

Other neutral dinuclear copper(I)-NHC species include $[\text{Cu}(\mu\text{-C}_2\text{O}_4)(\text{SIMes})]_2$ (**47**), bridged by a dianionic oxalate in a μ -1,2,3,4 fashion (Scheme 19) [46]. This species was synthesized by mixing one equivalent of oxalic acid and two equivalents of $[\text{Cu}(\text{Mes})(\text{SIMes})]$ at low temperature. The crystal structure of **47** shows each copper atom in a distorted trigonal planar coordination, mainly due to the small bite angle of the bridging oxalate [$\text{O-Cu-O} = 81.93(14)^\circ$]. Comparing the Cu-O bond of **47** with other tricoordinate copper complexes bearing an alkyne [47] or isonitrile [48] instead of SIMes, the bond in the former is shown to be longer. This could be ascribed to the π -acceptor character of olefins and alkynes which reduces the electron density on the metal center.



Scheme 19. Synthesis of $[\text{Cu}(\mu\text{-C}_2\text{O}_4)(\text{SIMes})_2]$ (**47**) with its molecular structure determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [46].

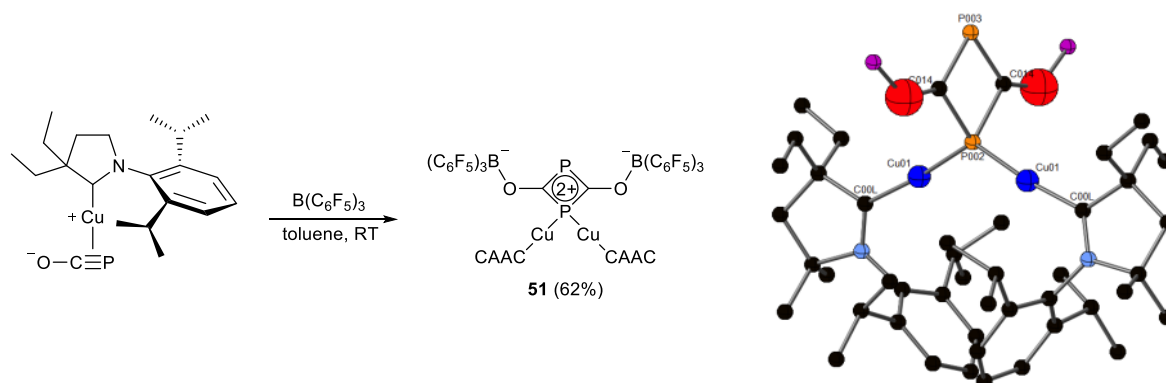
Other species include $[\text{Cu}(\text{NCS})(\text{IXy})_2]$ **48** and $[\text{Cu}(\text{NCS})(\text{IMes})_2]$ **49**, that contain a thiocyanate bridge [49]. Their synthesis was achieved by reacting the corresponding copper chloride precursor with NaNCS in dichloromethane at room temperature (Scheme 20). Once more, a trigonal planar environment around each copper atom was observed, with $\text{C}_{\text{NHC}}\text{-Cu-S}$, $\text{C}_{\text{NHC}}\text{-Cu-N}$, N-Cu-S angles of $121.51(9)^\circ$, $136.84(11)^\circ$ and $101.64(7)^\circ$. When the same procedure was performed using the bulkier IPr ligand, the monomeric $[\text{Cu}(\text{NCS})(\text{IPr})]$ **50** was formed. As noticed earlier, this is mainly due to difference in steric hindrance. In **50**, the thiocyanate anion is bound through the nitrogen with a Cu-N bond length of $1.815(4)$ Å, which is shorter than the one observed in **48** and **49** due to the lower coordination number. Moreover, the copper atom is dicoordinated in a nearly linear arrangement with $\text{C}_{\text{NHC}}\text{-Cu-N}$ angle of $179.42(18)^\circ$.



Scheme 20. Synthesis of copper(I)-NHC thiocyanate complexes **48-50** and their molecular structures determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [49].

The last complex in this series, complex **51**, consists of two copper atoms bridged by a phosphorus atom belonging to a four member P_2C_2 heterocycle (Scheme 21). It was obtained from the reaction of $[\text{Cu}(\text{PCO})(\text{CAAC})]$ with the strong Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ [50]. This exotic heterocycle originates from the

coordination of the borane to the oxygen of PCO, followed by dimerization and finally migration of one [Cu(CAAC)] fragment from one phosphorus center to the other.



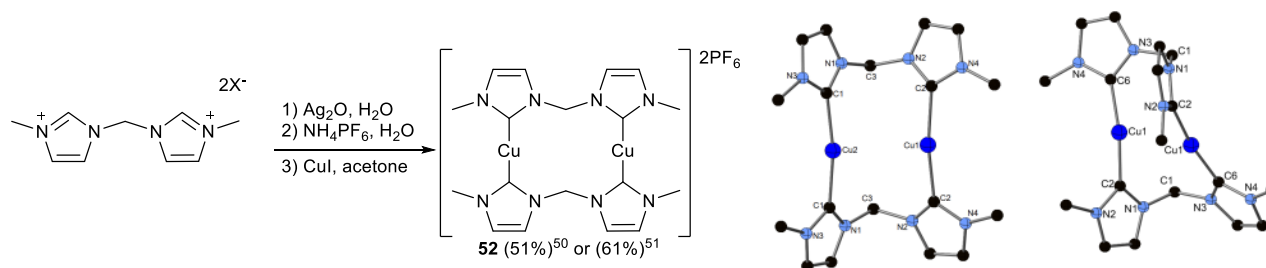
Scheme 21. Synthesis of **51** and its molecular structure determined by X-ray diffraction. Solvent molecules, H atoms and $(\text{C}_6\text{F}_5)_3$ groups are omitted for clarity [50].

3. NHCs as bridging ligands

3.1. Bis-NHCs connected through the *N* atoms

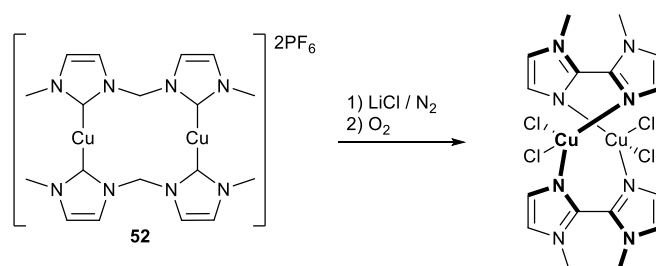
3.1.1. Methylene bridge

Various methylene-linked copper(I)-bis(NHC) complexes were synthesized by different research groups. The main difference regarding the ligand lies in the substituents on the nitrogen atoms of the NHC moiety. The methyl-substituted copper(I)-bis(NHC) complex **52**, $[\text{Cu}(\mu\text{-Me-mbim})_2][\text{PF}_6]_2$ was obtained *via* a transmetallation route and its crystal structures **52-1** [51] and **52-2** [52] revealed a similar coordination structure concerning the copper atoms and the two bridged NHC cores of the Me-mbim ligand as shown in Scheme 22; however, their bond lengths and angles differed considerably due to the high degree of freedom of the bridging ligand, allowing different accessible conformations (Scheme 22).



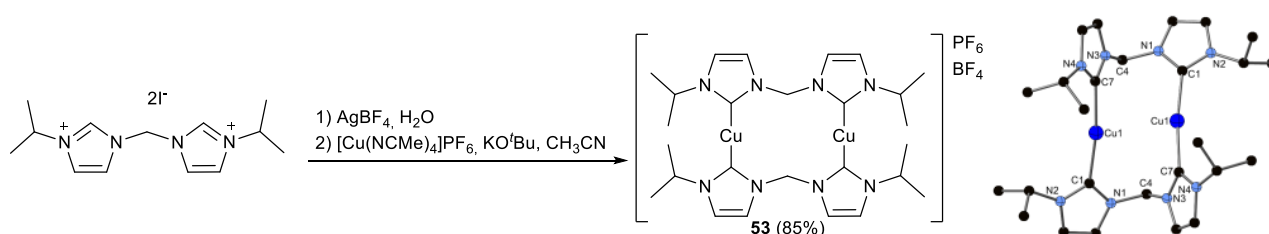
Scheme 22. Synthesis of $[\text{Cu}(\mu\text{-Me-mbim})_2][\text{PF}_6]_2$ (**52**) and its molecular structures **52-1** and **52-2** determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [51,52].

This complex is relatively air and moisture stable, however when reacted with LiCl and then exposed to oxygen atmosphere, it undergoes C-N bond cleavage of the methylene bridge and concomitant C-C coupling of the two imidazole fragments at the C^2 position (Scheme 23). The change of counter-anion from PF_6 to Cl leads to a highly air sensitive complex which decomposed to $[\text{Cu}_2(\text{Cl})_4(\text{Me}_2\text{biim})_2]$ and formaldehyde. This pathway was not observed with the ethylene-bridged analogue, indicating that the acidic methylene protons might have played a significant role during this process.



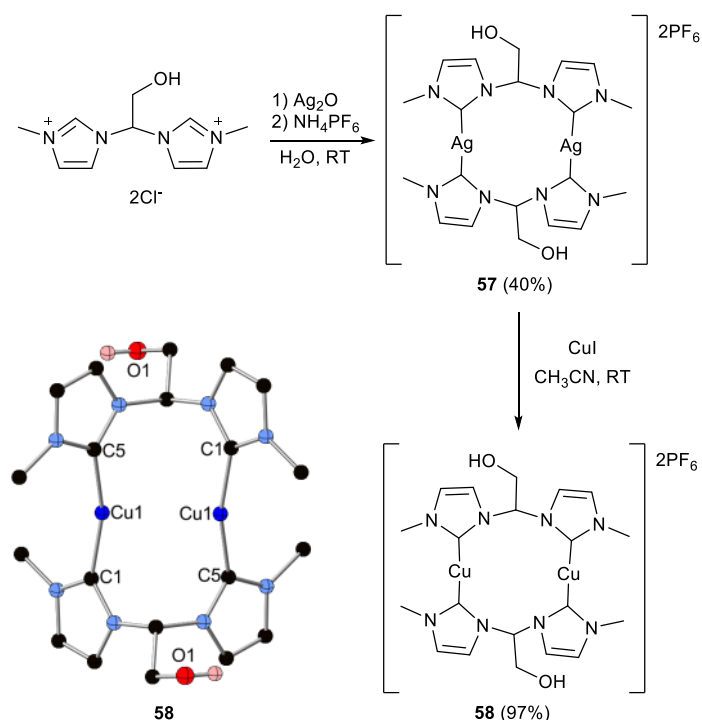
Scheme 23. Decomposition of $[\text{Cu}(\mu\text{-Me-mbim})_2][\text{PF}_6]_2$ [52].

The isopropyl-substituted copper(I)-bis(NHC) complex **53** was synthesized by Albrecht and co-workers using the transmetalation route [53]. Its structure is reminiscent of the methyl analogue **52**, with both carbenes bound to a different metal center forming a 12-membered macrocyclic structure (Scheme 24). The two imidazolium units are twisted of $44.9(11)^\circ$, calculated by $\text{N}(1)\text{-C}(1)\text{-C}(7)\text{-N}(3)$ torsional angle, thus minimizing any π -bond overlap with the metal center. This lack of π character might explain the long $\text{C}_{\text{NHC}}\text{-Cu}$ distances measured in this species, namely $\text{C}(1)\text{-Cu} = 2.076(9) \text{ \AA}$ and $\text{C}(7)\text{-Cu} = 2.112(8) \text{ \AA}$.



Scheme 24. Synthesis of **53** and its molecular structure determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [53].

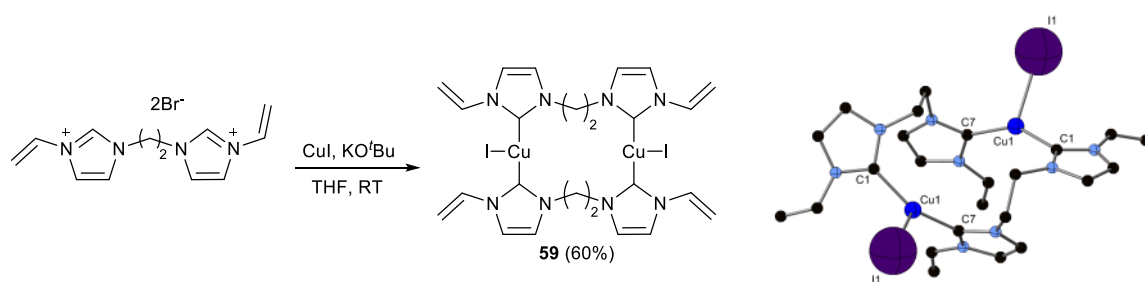
The more sterically hindered *tert*-butyl-substituted copper(I)-bis(NHC) complex was also reported. Hofmann and co-workers showed that the organometallic polymer $[(\text{CuBr})_2(\text{}^t\text{Bu-mbim})_2]_n$ can be obtained by reacting $[\text{}^t\text{Bu-mbim-H}_2]\text{Br}_2$ with CuBr and *n*-BuLi as base [54]. Interestingly, it can be depolymerized upon treatment with a nitrogen nucleophile, such as *N-tert*-butyl imidazole or piperidine, yielding the dinuclear copper complexes $[(\text{CuBr})_2(\text{}^t\text{Bu-mbim})(N\text{-tert-butylimidazole})]$ **54** and $[(\text{CuBr})_2(\text{piperidine})(\text{}^t\text{Bu-mbim})]$ **55** respectively (Scheme 25). In these complexes, each copper possesses a trigonal planar geometry in which one copper atom is coordinated to one C_{NHC} , one bromine and the nitrogen of the amine; whereas the other copper is coordinated to a C_{NHC} and two bromine atoms. The distance between $\text{Cu-N}(\text{imidazole})$ in **54** ($\text{Cu1-N5} = 1.969(9) \text{ \AA}$) is shorter with respect to the $\text{Cu-N}(\text{piperidine})$ in **55** ($\text{Cu1-N5} = 2.036(3) \text{ \AA}$), which accounts for the higher stability of the former, whereas the latter easily loses the coordinated amine. Later on, the same group showed that changing the anion of the ligand from bromine to hexafluorophosphate allows the synthesis of the 12-membered macrocyclic complex **56**, upon deprotonation of the ligand by $n\text{-BuLi}$ or KO^tBu and addition of $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ as the copper source [55]. The two NHC rings attached to the same copper center are almost perpendicular to each other possessing N-C-C-N angle of 75° .



Scheme 26. Synthesis of **58** and its molecular structure as determined by X-ray diffraction. Solvent molecules and H atoms (apart from OH) are omitted for clarity [56].

3.1.2. Ethylene bridge

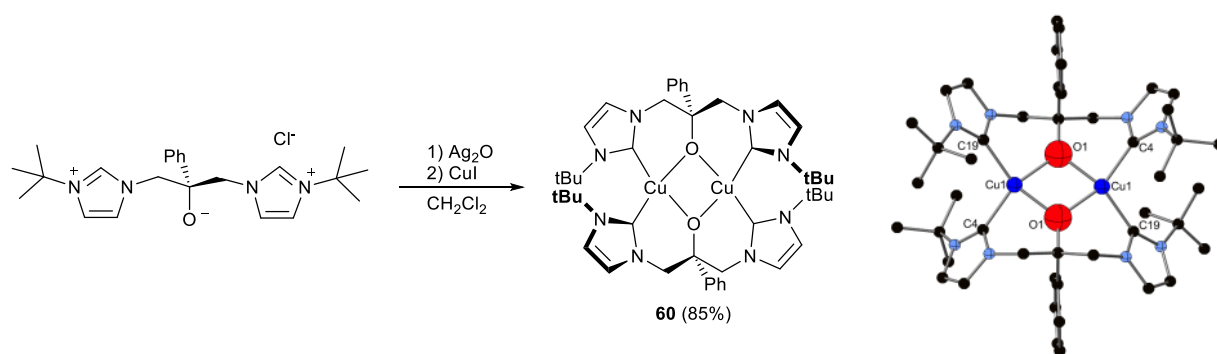
An ethylene-linked copper(I)-bis(NHC) complex **59** was reported by Prabusankar and co-workers in 2014 and was obtained by reaction of the corresponding ligand with potassium *tert*-butoxide and copper iodide (Scheme 27) [57]. Its crystal structure showed a folded form in which each copper center possesses a distorted trigonal geometry, binding two NHCs and one iodine with $C_{NHC}-Cu-C_{NHC}$ angle of $145.0(5)^\circ$ and $C_{NHC}-Cu-I$ angles of $110.5(3)^\circ$ and $104.5(4)^\circ$. The hydrogen belonging to the bridge of another molecule fills a vacant coordination site, forming a tetranuclear assembly sustained by $Cu \cdots H-C$ hydrogen bonding type interactions.



Scheme 27. Synthesis of ethylene-linked copper(I)-bis(NHC) complex **59** and its molecular structure determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [57].

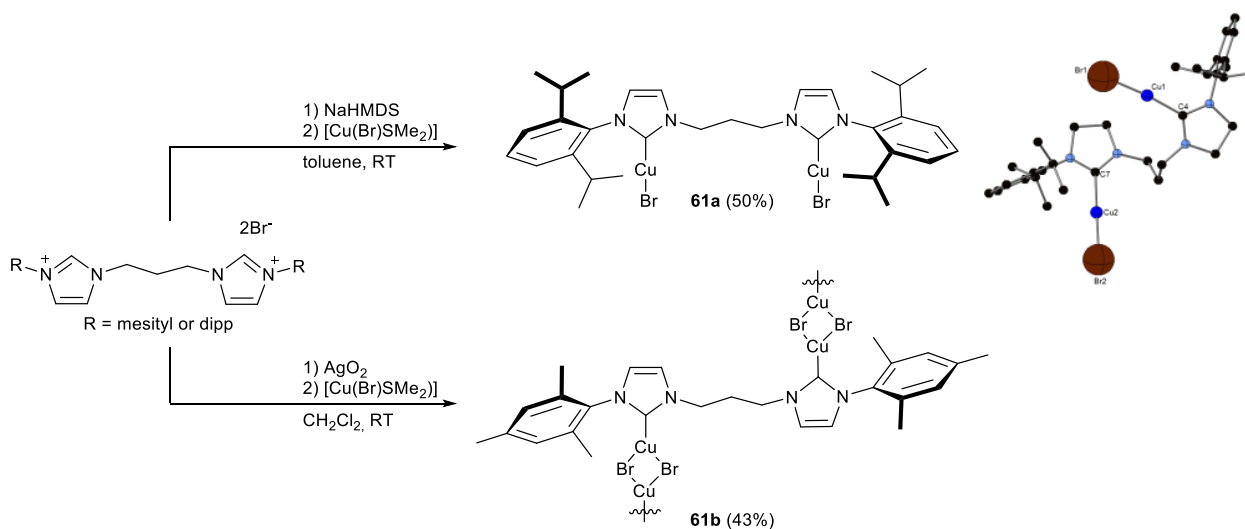
3.1.3. Propylene bridge

The first example of a propylene-linked copper(I)-bis(NHC) complex was reported by Arnold and co-workers in 2001 (Scheme 28) [58]. Treatment of the ligand with Ag_2O followed by transmetalation using CuI as the copper source provided the dinuclear species **60** where the copper center is coordinated by the two carbenes and the alkoxide. Its crystal structure revealed a nearly square planar geometry around each metal along with a Cu_2O_2 core.



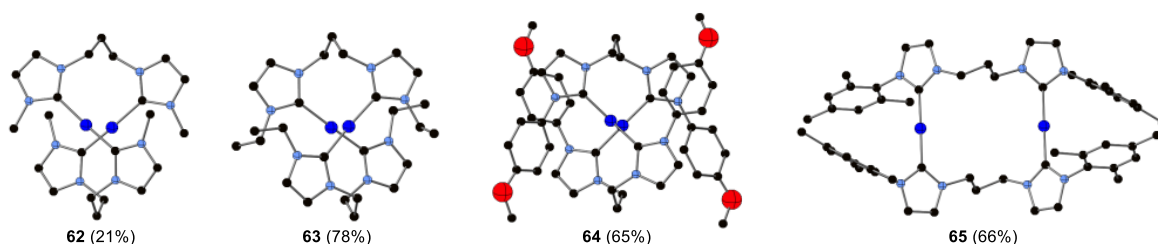
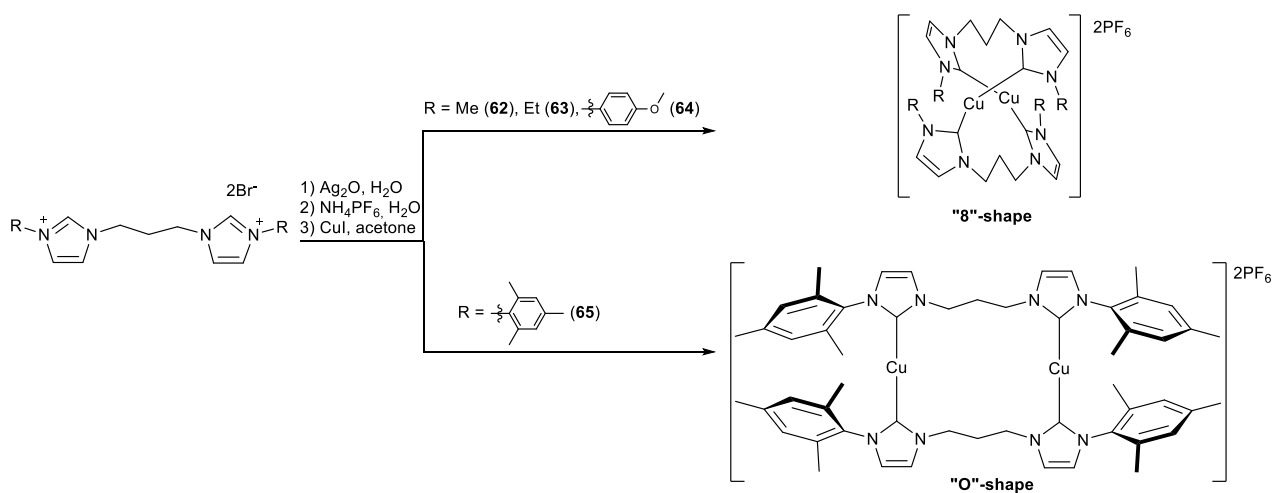
Scheme 28. Synthesis of **60** and its molecular structure determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [58].

Later on, Straub and co-workers developed the synthesis of unsubstituted propylene-bridged bis-(NHC) ligands and their related copper halides complexes using NaHMDS/[Cu(Br)(SMe₂)] or the transmetallation route, depending on the nitrogen substituents of the imidazolium ring (Scheme 29) [59]. These moieties dictated the coordination of the copper species; with a dimeric species (**61a**) being obtained with the ligand bearing the bulkier dipp group, whereas the smaller mesityl-substituted derivative leads to a coordination polymer (**61b**). The solid-state structure of **61a** showed that each copper is bound to a NHC and one bromide in an almost linear arrangement with C_{NHC}-Cu-Br angles of 174.4° and 179.2°.



Scheme 29. Synthesis of **61a** and **61b** and molecular structure of **61a** determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [59].

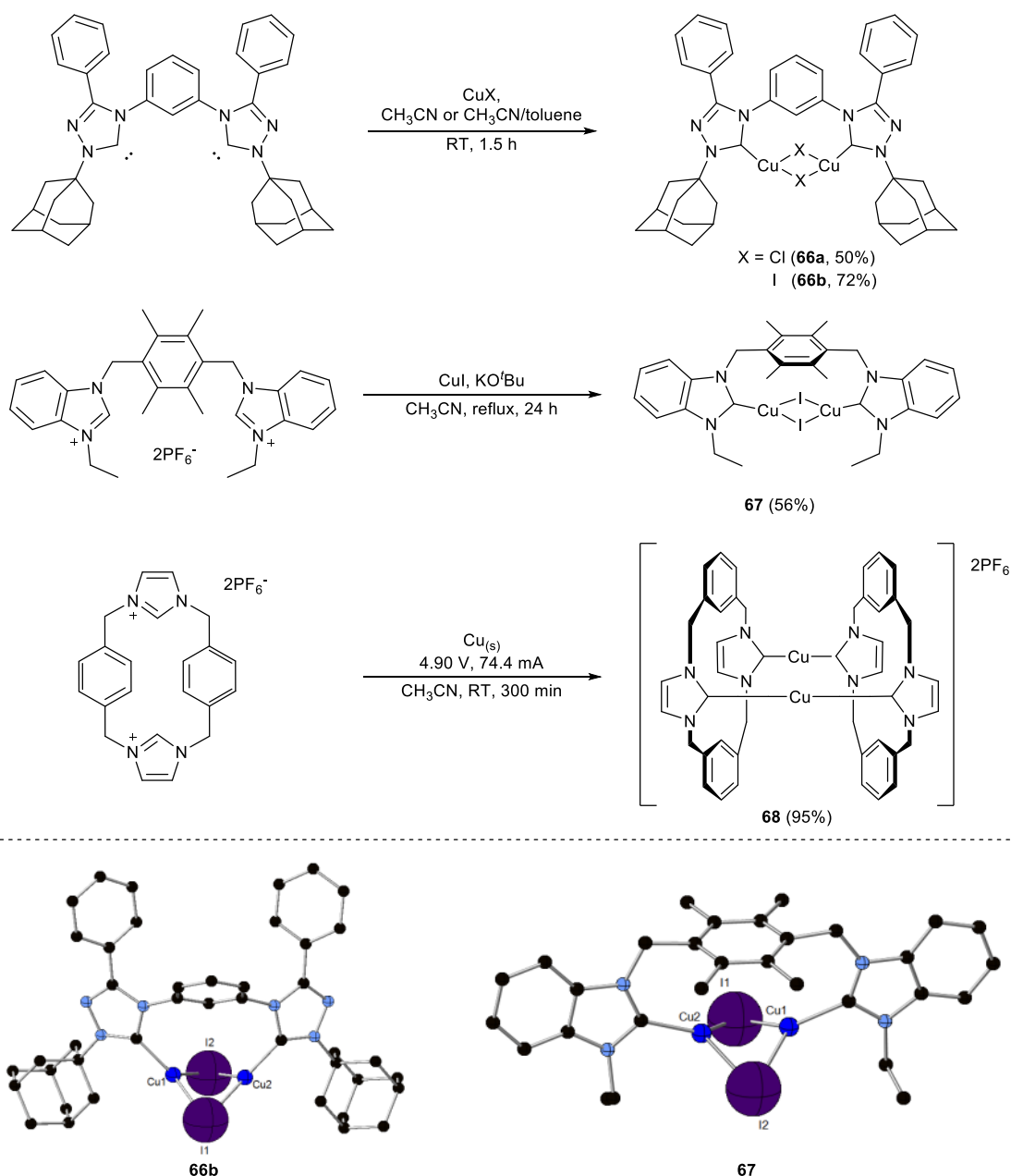
Recently, this family of complexes was further extended by Tsubomura and co-workers (Scheme 30) [60]. The copper complexes were again accessed *via* transmetallation from the corresponding silver species. Each copper in this family of compounds is chelated by two NHCs due to the use of a non-coordinating anion. The metal center lies in an almost linear environment, but the 16-membered macrocycle's shape depends on the bulkiness of the *N*-substituents; in particular, complexes bearing ligands with small *N*-substituents such as methyl (**62**), ethyl (**63**) and *p*-methoxyphenyl (**64**) lead to "8"-shape complexes, whereas the ones bearing the bigger mesityl group (**65**) provided an "O-shape" complex.



Scheme 30. Library of propylene-linked copper(I)-bis(NHC) complexes **62-65** and their molecular structure determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [60].

3.1.4. Phenyl-based bridge

Few examples appeared in the literature reporting dinuclear copper(I)-bis(NHC) complexes in which the two NHCs are connected through a phenyl based-bridge (Scheme 31). Cowley and co-workers have reported the synthesis of **66** from the corresponding free carbene and CuX [X = Cl (**66a**), I (**66b**)]. The crystal structure of **66b** is depicted in Scheme 31 [61]; It shows an asymmetric Cu₂I₂ core with Cu1-I2 distance (2.827(1) Å) longer than the Cu1-I1 (2.580(1) Å). Similar features are detected in **67**, which has a durene as linker between two benzimidazole moieties. It was achieved by reaction of the bis(benzimidazolium) salt with CuI and potassium *tert*-butoxide [62]. Finally, compound **68** was synthesized using an electrochemical flow-cell in high yield starting from the corresponding bis(imidazolium) salt and copper powder [63].

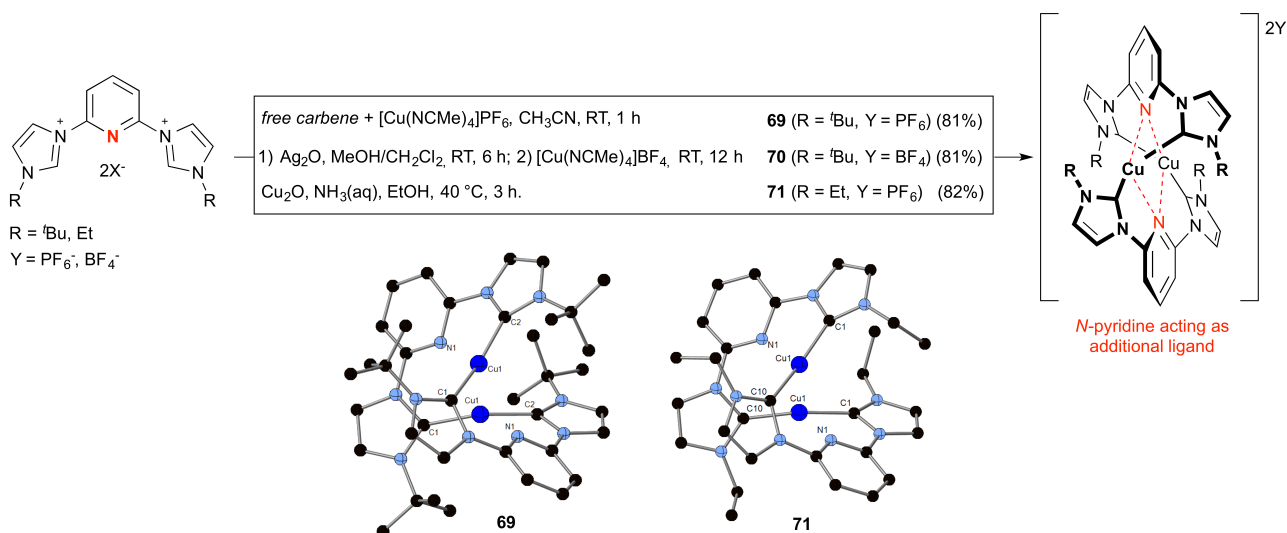


Scheme 31. Synthesis of complexes **66-68** and molecular structure of **66b** and **67** determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [61-63].

3.1.5. Pyridine bridge (CNC ligands)

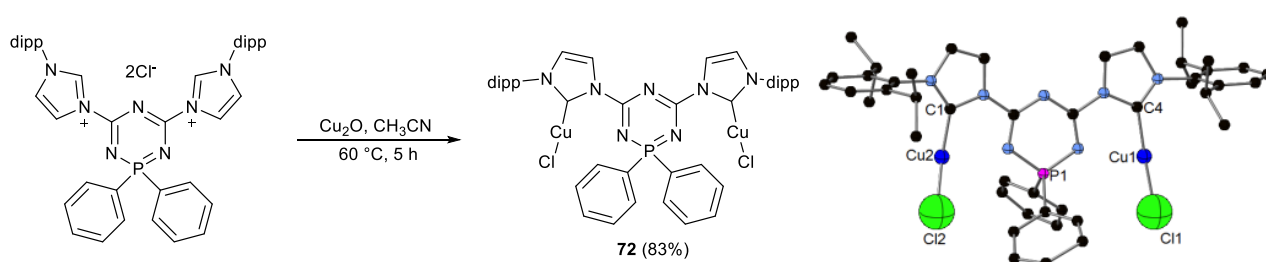
Only a few examples of such complexes have been reported to date, differing mainly by the substituent on the nitrogen atom of the imidazole ring (Scheme 32). The first examples contain a *tert*-butyl group as *N*-substituent and were obtained by different routes, such as the reaction of the free carbene ligand with $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ [64], or transmetalation from the silver analogue to $[\text{Cu}(\text{NCMe})_4]\text{BF}_4$ [65], affording the respective $[\text{Cu}(\text{CNC})]_2(\text{Y})_2$ complexes [$\text{Y} = \text{PF}_6$ (**69**) or BF_4 (**70**)]. The crystal structure of these complexes showed each copper atom bound to two NHCs of different ligands in a quasi-linear conformation. The overall shape of these complexes is reminiscent of the aforementioned “8”-shape, with the two NCN ligand components being intertwined with each other forming a double helical geometry. Similar observations were made with the copper complex (**71**) possessing the *N*-ethyl-substituted version of the ligand, obtained by direct reaction of the ligand with Cu_2O and an excess of ammonia [66]. Interestingly, **71** is chiral in the solid-state in its twisted form due to axial chirality. This chirality is also maintained in solution as revealed by the non-equivalence of the *N*-

ethyl CH₂ protons in its ¹H NMR spectrum. In all species, the nitrogen atoms of the pyridine are directed towards the metal centers and their distances, ranging from 2.4220(18) Å to 2.8298(18) Å, reveal a weak interaction between these two atoms. Recently, Tahsini and co-workers demonstrated that the formation of this type of dinuclear complexes is only possible when the NHCs are directly bound to the pyridine ring, whereas mononuclear complexes are formed when a methylene spacer between the two moieties is present [67].



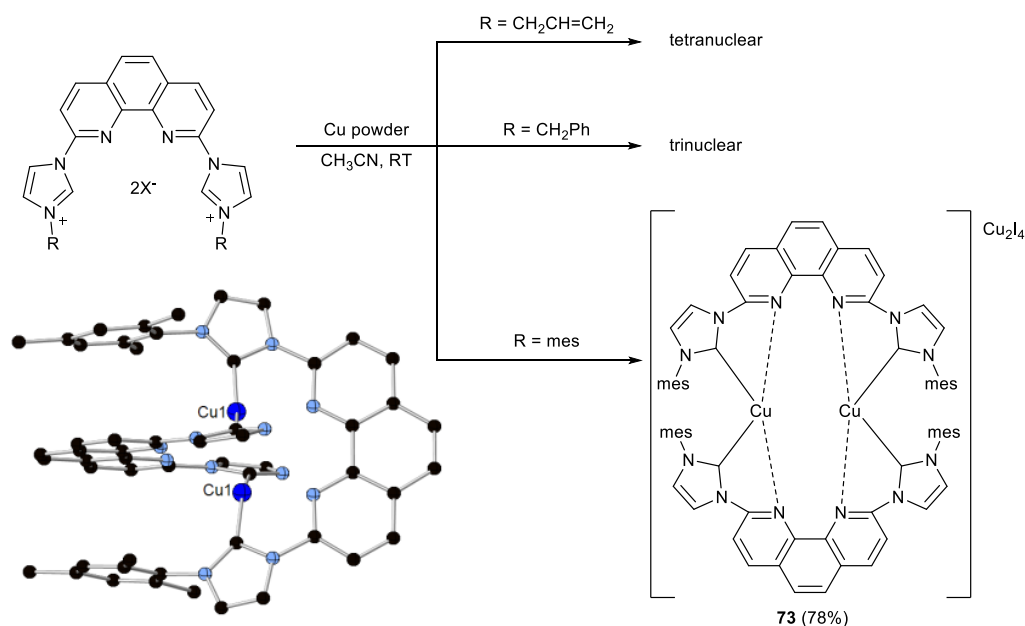
Scheme 32. Pyridine-linked copper(I)-bis(NHC) complexes **69–71** with molecular structures determined by X-ray diffraction of **69** (R = ^tBu, Y = PF₆) and **71** (R = Et, Y = BF₄). Solvent molecules and H atoms are omitted for clarity [64–66].

Reddy and co-workers further extended this family of complexes by reporting carbaphosphazene derivatives (Scheme 33) [68]. The related copper complex **72** was synthesized using Cu₂O. Each copper atom was shown to be coordinated to one NHC of the NCN ligand and to one bromine in an almost linear fashion with C_{NHC}-Cu-Cl angles of 176.1(2)° and 166.1(2)°.



Scheme 33. Synthesis of **72** and its molecular structure determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [68].

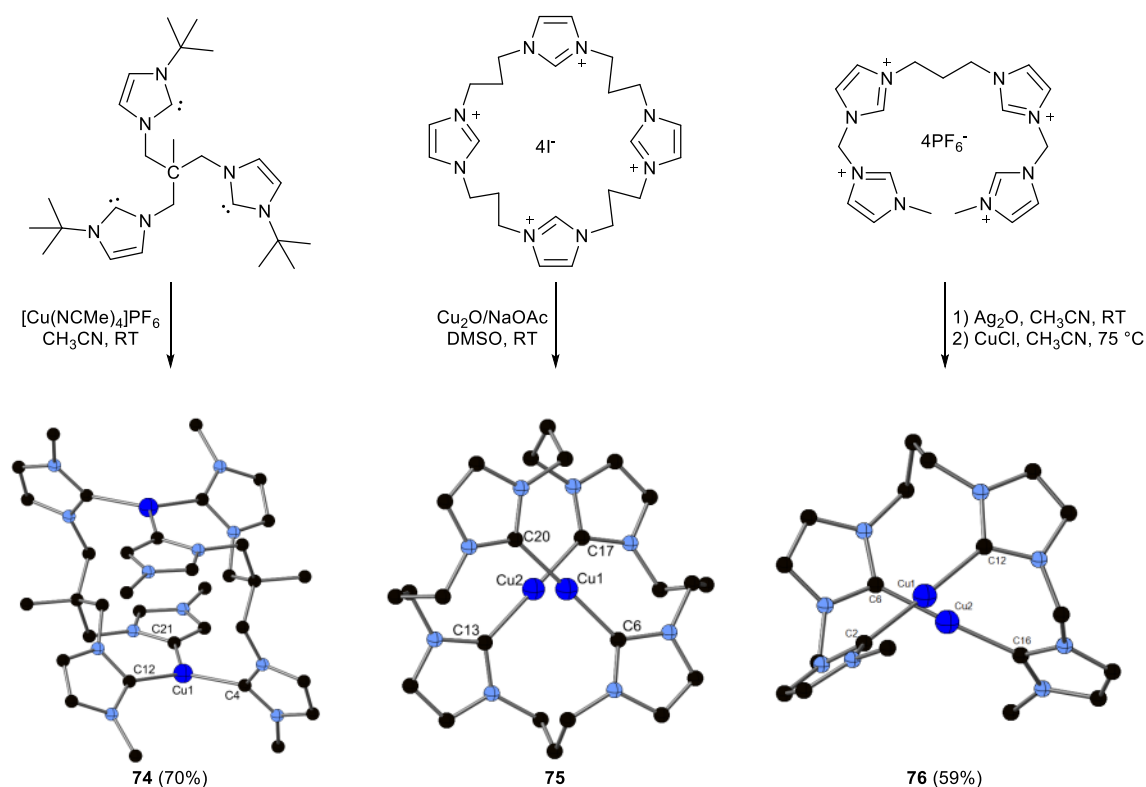
As an extension of the same concept, Chen and co-workers synthesized bis(NHC) salts with 1,10-phenanthroline as bridge (Scheme 34) [69]. They obtained the corresponding copper(I) complexes by reaction of these salts with copper powder at room temperature. Different nuclearities, ranging from dinuclear to tetranuclear, were observed due to the additional coordinating nitrogens of the phenanthroline fragment. Overall, the nuclearity is dictated by the steric bulk of the N-substituents of the NHCs with dinuclear complex **73** arising from the bulky mesityl-substituted ligand.



Scheme 34. Synthesis of **73** and its molecular structure determined by X-ray diffraction. Solvent molecules, H atoms and two mesityl substituents are omitted for clarity [69].

3.1.6. Polycarbene ligands

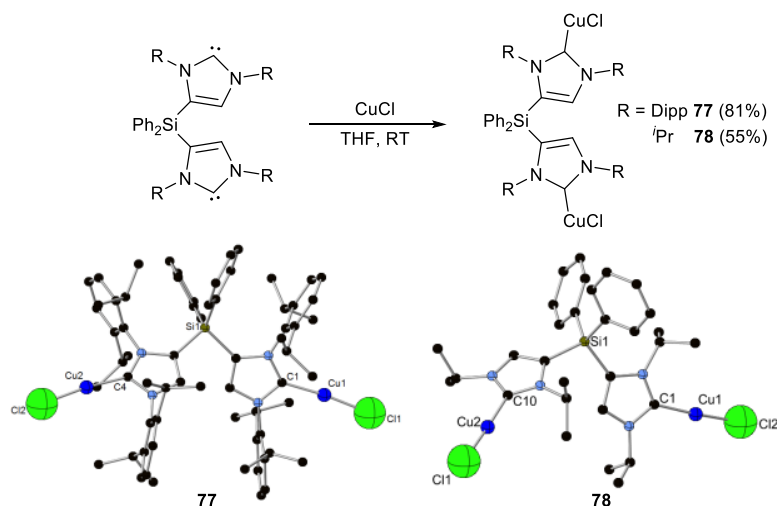
A natural extension of the chemistry of bis-(NHC)-based complexes is the synthesis of polycarbene ligands, possessing three or more NHCs, which can be divided into open chain ligands or macrocyclic ligands (Scheme 35). Few copper complexes supported by these species have been synthesized to date. The first example was reported by Meyer and co-workers in 2003 employing a tripodal tris-carbene ligand that was reacted as a free carbene with [Cu(NCMe)₄]PF₆, leading to the formation of **74** [70]. Its crystal structure shows each metal center in a trigonal planar geometry, coordinating to three carbon centers. Interestingly, two NHCs are coordinated in a “normal” fashion, whereas one is coordinated in an “abnormal” manner, *via* the backbone carbon. This arises from C-H activation at the backbone carbon followed by protonation of the carbene carbon. A second example is the tetra-carbene macrocycle **75** reported by Murphy and Spicer, which yields the corresponding binuclear copper complex upon treatment with Cu₂O [71]. Its formation was possible due to the flexibility of this ligand that allows the incorporation of two metal ions. Each copper center is dicoordinated with two NHC ligands in an almost linear geometry. An open-chain version of a tetra-carbene ligand was reported by Kühn and co-workers, and its dinuclear copper complex **76** was accessed by transmetallation from its silver analogue [72].



Scheme 35. Copper(I) complexes bearing polycarbene ligands **74-76** and their molecular structures determined by X-ray diffraction. Solvent molecules and H atoms are omitted for clarity [70-72].

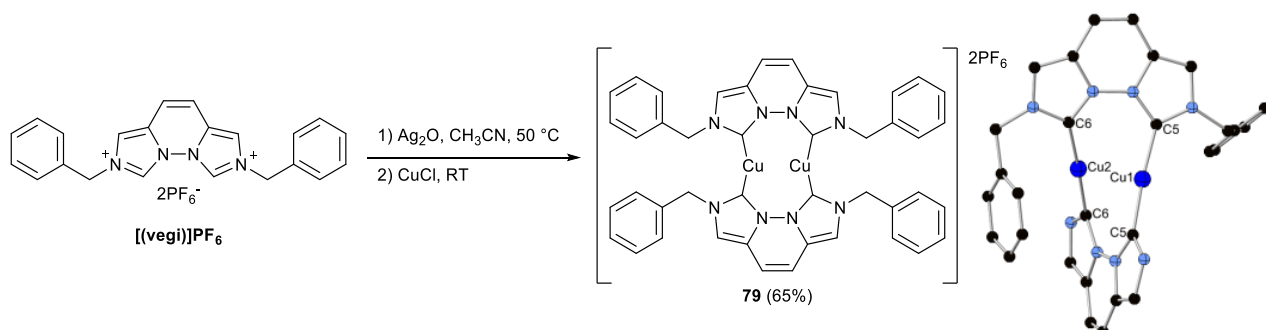
3.2. Bis-NHCs connected through the NHC backbone carbons

A different ligand design for the synthesis of bis-(NHC) ligands consists of merging the two imidazole moieties through their backbone (C^4 , C^5). This approach is not widely used and only two types of complexes have been reported thus far (Scheme 36). The first type is based on Ph_2Si -bridged NHCs, leading to the formation of complexes **77** and **78** from the reaction of the free carbene with CuCl . These complexes are dinuclear species with each copper ligated to one NHC and one chloride [73].



Scheme 36. Copper(I) complexes of silyl-functionalized di-N-heterocyclic carbenes **77-78** and their molecular structures determined by X-ray diffraction. Solvent molecules and H atoms have been omitted for clarity [73].

The other example is a pyridazine annulated bis-(NHC) ligand (vegi) possessing both nitrogen-nitrogen and backbone linkers (Scheme 37) [74]. Treatment of [(vegi)]PF₆ with Ag₂O, followed by addition of CuCl affords the dinuclear copper complex **79** with each copper atom ligated to two NHCs in an almost linear geometry, maintained by a significant twist of the vegi ligand relative to each other by as much as 70 °.



Scheme 37. [Cu(vegi)]₂[PF₆]₂ **79** and its molecular structures determined by X-ray diffraction. Solvent molecules, H atoms and *N*-benzyl substituents of one carbene ligand in **79** have been omitted for clarity [74].

4. Conclusions and outlook

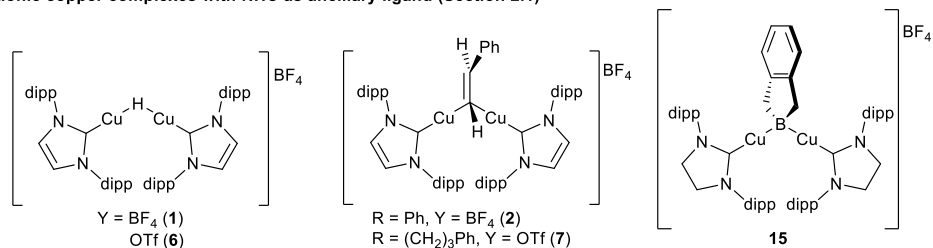
Dinuclear copper(I)-NHC complexes have shown great versatility in terms of coordination environment and geometries through manipulation of the NHC and of the anionic moieties. A common requirement for the assembly of dinuclear complexes appears to be the judicious selection of ligand steric properties. Such constructs lead in some cases to close proximity of the copper centers, thus distances considerably less than twice the van der Waals radius of copper (1.4 Å) [75] are detected (Table 2 and Figure 1).

Table 2. Cu-Cu distances (Å) of the dinuclear copper complexes presented in this review.

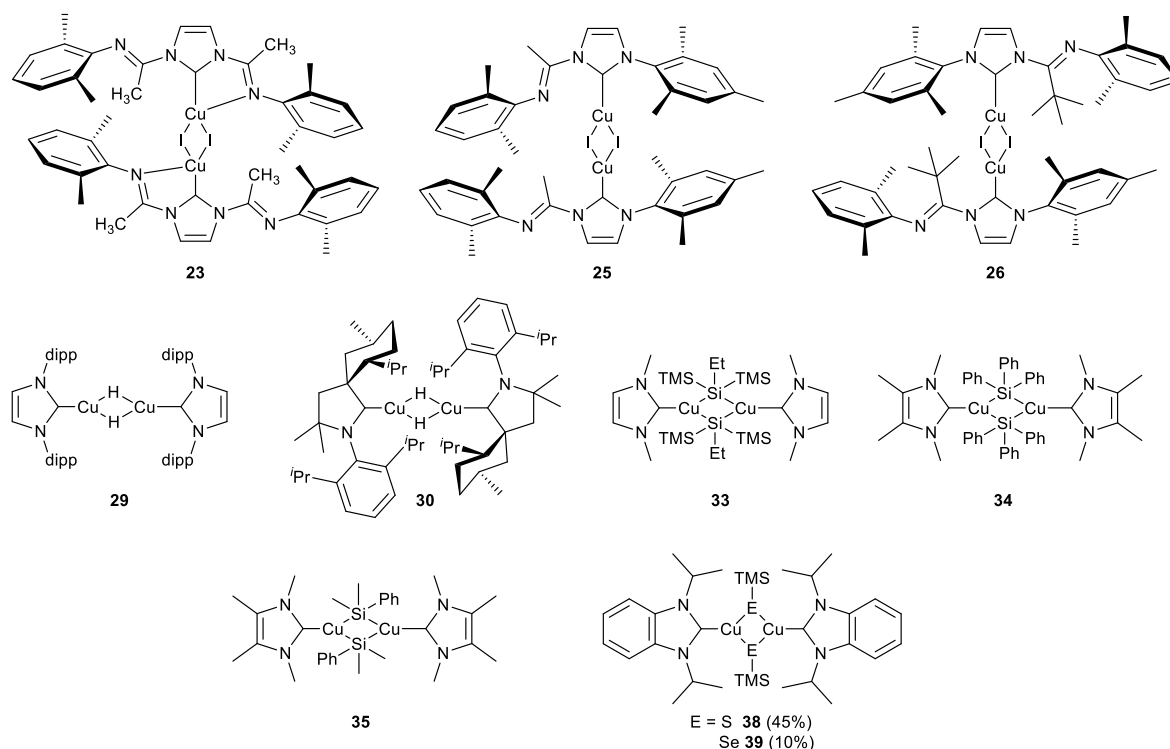
Complex	Cu-Cu distance (Å)	Complex	Cu-Cu distance (Å)	Complex	Cu-Cu distance (Å)
1	2.5331(15)	30	2.3058(5)	54	2.924(2)
2	2.6303(4)	33	2.2857	55	2.8408(6)
4	5.0532(6)	34	2.2692(5)	56	2.8661(3)
5	3.4150(5)	35	2.2504	58	3.192(4)
6	2.541(2)	36a	7.913(1)	59	4.977
7	2.5080(3)	36b	2.8389	60	3.1122
8	3.5130(7)	37	6.088	61a	6.2812(8)
9	3.575(1)	38	2.7074	62	2.694
10	3.731(1)	39	2.6125(9)	63	2.671(1)
11	3.756(1)	40	3.6085(9)	64	2.909
12	3.3077(3)	41a	3.769(1)	65	6.164
13	2.9388(7)	41b	3.757(3)	66b	2.663(1)
14	5.985(1)	41c	3.7734(5)	67	2.640(2)
15	2.4083(9)	41d	3.7599(7)	69	3.2060(5)
18	2.9511	41e	3.7372(4)	71	2.8046
20	2.9972	42	3.7055(6)	72	7.734(1)
21	3.0758	43	3.7455(6)	73	2.9547
22	3.110	47	5.3259	74	5.2249
23	2.6357	48	5.2251	75	2.553(2)
25	2.6341(6)	49	5.2470	76	2.6581(9)
26	2.7210	51	3.9910	77	10.604(1)

27	2.991	52-1	3.353	78	9.8490(9)
28	2.9409(8)	52-2	2.903	79	2.4923
29	2.3059(11)	53	3.2268		

Dinuclear cationic copper complexes with NHC as ancillary ligand (Section 2.1)



Dinuclear neutral complexes with NHC as ancillary ligand (Section 2.2)



Dinuclear complexes with NHC as bridging ligand (Section 3)

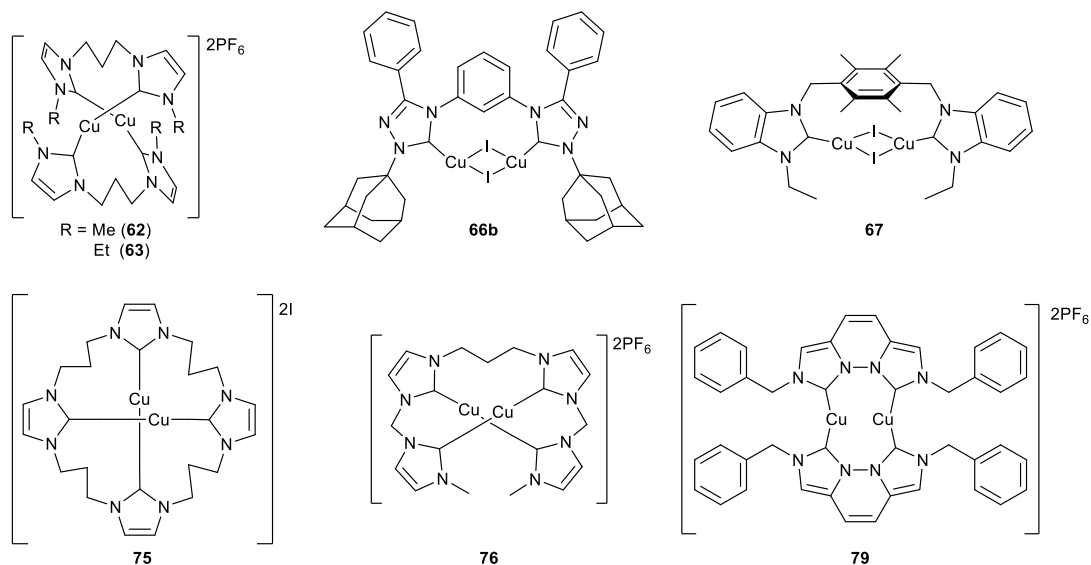


Figure 1. Dinuclear copper complexes with Cu-Cu distances shorter than twice the van der Waals radius of copper.

These species are more than mere structural curiosities as their synthetic access now permits the study of their reactivity. Indeed, such dinuclear species have permitted the investigation of their role in [3+2] cycloaddition reactions and their catalytic behavior in the hydroalkylation of alkynes and in the hydrosilylation of ketones. These recent examples have shown that two-centered catalysts (or pre-catalysts) permitted faster and more efficient reactions. Such dinuclear complexes have become attractive entities enabling the study of their role in established reactions but more excitingly will surely facilitate the discovery and development of novel transformations.

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