Uncovering a copper(II) alkynyl complex in C−C bond forming reactions

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Abstract

Copper(II) alkynyl species are proposed as key intermediates in numerous Cu−catalysed C−C coupling reactions. Supported by a β−diketiminate ligand, the three coordinate copper(II) alkynyl [Cu^{II}]−C≡CAr (Ar = 2,6−$Cl_2C_6H_3$) forms upon reaction of the alkyne H−C≡CAr with the copper(II) *tert*−butoxide complex [Cu^{II}]−O^{t}Bu. In solution, this [Cu^{II}]−C≡CAr species cleanly transforms the to the Glaser coupling product ArC≡C−C≡CAr and [Cu^{I}](solvent). Addition of nucleophiles R′C≡CLi (R′ = aryl, silyl) and Ph–Li to [Cu^{II}]−C≡CAr affords the corresponding C_{sp}−C_{sp} and C_{sp}−C_{sp2} coupled products RC≡C−C≡CAr and Ph–C≡CAr with concomitant generation of [Cu^{I}](solvent) and {[Cu^{I}]−C≡CAr}$^-$. Supported by DFT calculations, redox disproportionation forms [Cu^{III}](C≡CAr)(R) species that reductively eliminate R−C≡CAr products. [Cu^{II}]−C≡CAr also captures the trityl radical Ph_3C• to give Ph_3C−C≡CAr. Radical capture represents the key C_{sp}−C_{sp3} bond forming step in the copper catalysed C-H functionalization of benzylic substrates R−H with alkynes H−C≡CR′ (R′ = (hetero)aryl, silyl) that provide C_{sp}−C_{sp3} coupled products R−C≡CR via radical relay with ^{t}BuOO^{t}Bu as oxidant.

Introduction

Transition metal mediated carbon–carbon bond formation represents one of the most fundamental transformations in chemical and material synthesis.[1] 150 years ago, Carl Glaser developed the first copper mediated oxidative coupling of terminal alkynes, suggesting copper organometallic intermediates in the C_{sp}–C_{sp} coupling of phenylacetylene (H–C≡C–Ph) to give the diyne Ph–C≡C–C≡C–Ph via reaction of ammoniacal cuprous chloride with oxygen as oxidant (Fig. 1a).[2] Glaser suggested that copper(I) acetylide dimer forms that undergoes oxidation by O_2 to ultimately release Ph–C≡C–C≡C–Ph.[2]

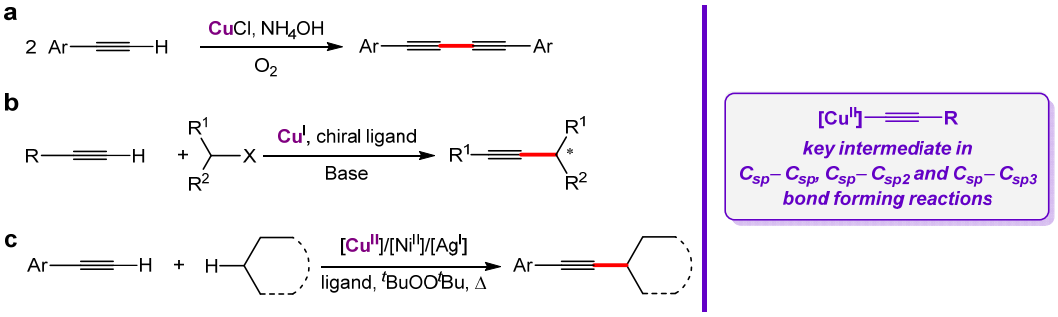


Fig. 1 | Proposed Cu–alkynyl intermediates in C_{sp}–C_{sp}, C_{sp}–C_{sp2} and C_{sp}–C_{sp3} bond forming reactions.

A number of mechanistic proposals have evolved to explain the Glaser C_{sp}–C_{sp} coupling (Fig. 1a). Salkind and Fundyler offered an early proposition that involved alkyne deprotonation followed by oxidation by copper(II) to form an alkynyl radical that dimerizes to give the 1,3–diyne product (Fig 2a).[3] Based on combination of kinetic studies and the prevalence of selective homocoupling in mixtures of alkynes, Bohlman discounted a radical mechanism and put forth dimeric copper(II) acetylides as key species in C-C coupling (Fig. 2b).[4] As part of a detailed mechanistic study of the Glaser–Hay reaction that enables catalytic dimerization of terminal alkynes with O_2 as a terminal oxidant, Vilhelmsen and Nielsen suggested a new role for

a discrete copper(II) acetylide complex (Fig 2c).[5-6] They proposed that a copper(I) acetylide (formed upon deprotonation of the alkyne in the presence of copper(I) source)[7] is aerobically oxidized to the corresponding copper(II) acetylide.[5] Redox disproportionation of this copper(II) acetylide generates a cationic copper(III) acetylide and a nucleophilic copper(I) acetylide that can combine to give a copper(III) bis(acetylide) species susceptible to reductive elimination to give the C−C coupled 1,3−diyne product.

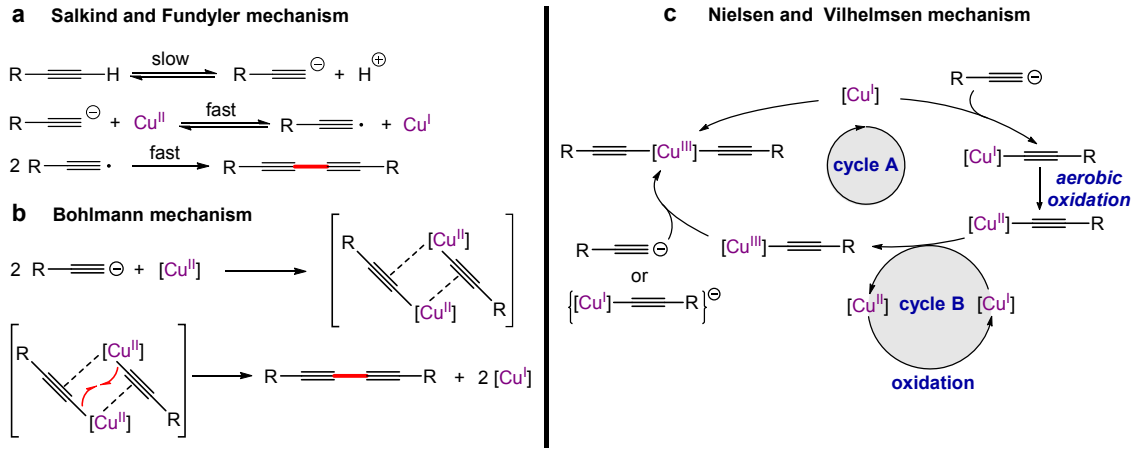


Fig. 2 | Mechanistic proposals for copper(II) promoted C_{sp}-C_{sp} coupling. **a,** Salkind & Fundyler: homocoupling of alkynyl radicals. **b,** Bohlmann: dimerization of Cu^{II}-alkynyl intermediates. **c,** Nielsen & Vilhelmsen: redox disproportionation of Cu^{II}-acetylide to $[Cu^{III}](C{\equiv}CR)_2$ intermediate that undergoes C-C reductive coupling.

Such copper(II) alkynyl intermediates are also envisioned in several copper catalysed organic transformations such as the Pd−free Sonogashira C_{sp}–C_{sp3} coupling of terminal alkynes with primary, secondary, or tertiary alkyl halides (Fig. 1b),[8] trifluoromethylalkynylation of alkenes,[9] [3+2] cycloaddition with azides,[10] oxidative C_{sp3}–H/C_{sp}–H cross-coupling (Fig. 1c),[11-13] oxidative coupling of terminal alkynes,[14-15] deacetylative coupling of ynones,[16] and oxidative amidation of terminal alkynes.[17-18] For instance, recent Pd−free Sonogashira type reactions that form C_{sp}–C_{sp3} or C_{sp}–C_{sp2} bonds have been proposed to proceed through the intermediacy of copper(II) alkynyl species.[8,19-20] Such cupric acetylides were also proposed by Liu as

intermediates in the enantioselective trifluoromethylalkynylation of alkenes under very mild conditions.[8] Recently, Lei *et al.* reported the cross-dehydrogenative coupling of terminal alkynes with unactivated alkanes using a multi-metal catalysed reaction strategy to prepare internal alkynes (Fig. 1c) also proposed to proceed via copper(II) alkynyl intermediates.[11-14]

Despite numerous examples of well−characterized copper(I) acetylide complexes,[21] copper(II) alkynyls, and in general any structurally well-defined organocopper(II) complexes, are extremely rare.[22] In 2017, Tilley and co-workers described the mixed−valent Cu(I)Cu(II) μ−alkynyl complex $\{[DPFN]Cu_2(\mu-\eta^1:\eta^1-C{\equiv}CAr^{p\text{-}Me})\}^{2+}$ (Ar^{p-Me} = 4-MeC_6H_4) stable towards diyne formation (Fig. 3a).[23] Inspired by a β−diketiminato mononuclear copper(II) aryl complex isolated in our laboratory (Fig. 3b),[24] we targeted a discrete, mononuclear copper(II) alkynyl $[Cu^{II}]-C{\equiv}CAr$.

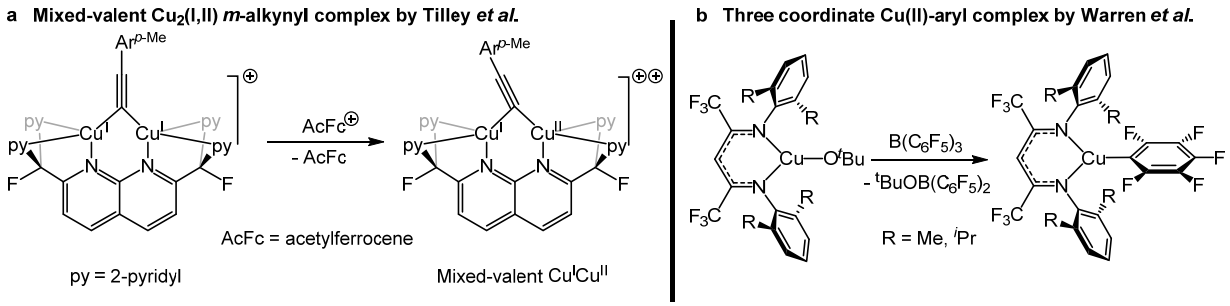


Fig. 3 | Structurally well-defined organocopper(II) compounds. a, Isolation of mixed-valent Cu(I)Cu(II)−μ−alkynyl complex by Tilley *et al*. **b**, Isolation of three coordinate Cu(II)−aryl complex by Warren *et al*.

Results and Discussion

Synthesis, characterization and reactivity of a copper(II) alkynyl complex. Reaction of the copper(I) β-diketiminate complex [^{i}Pr$_2$NN]Cu(NCMe)[25] (**1−NCMe**) with ^{t}BuOO^{t}Bu at RT gives [^{i}Pr$_2$NN]Cu^{II}−O^{t}Bu (**2**). This three coordinate Cu(II) alkoxide is similar in structure to several related [Cu^{II}]−O^{t}Bu species (Fig. S20) and possesses closely related spectroscopic parameters.[26-28] Addition of H−C≡CAr^{Cl2} (Ar^{Cl2} = 2,6−Cl$_2$C$_6$H$_3$) to **2** in pentane at RT results in a colour change from brown to dark violet. Crystallization from pentane affords dark violet crystals of [^{i}Pr$_2$NN]Cu−C≡CAr^{Cl2} (**3**) in 41% yield (Fig. 4a). The X−ray structure of **3** reveals two nearly identical, yet crystallographically independent molecules featuring trigonal planar, three coordinate Cu centers (Σ(angles about Cu) = 359.72(7) and 359.60(8)°). The Cu−C$_{alkynyl}$ distances of 1.887(5) and 1.872(6) Å are on the low end of those reported for Cu(I) acetylide complexes (1.87 - 1.98 Å).[21] The large disparity of the two N−Cu−C angles in **3** (Molecule 1: 142.5(2) and 122.0(2)°; Molecule 2: 150.6(2) and 112.9(2)°) and shortened Cu-N distance distal to the Cu-C unit (Cu-N distances: Molecule 1: 1.907(4) and 1.859(4) Å; Molecule 2: 1.903(4) and 1.861(4) Å) results in a Y−shaped geometry around Cu atom. In the solid state there is a π−stacking interaction between an electron−rich *N*−aryl ring of molecule 1 and the electron−deficient alkynyl dichlorophenyl ring of molecule 2 (Fig. 4a).

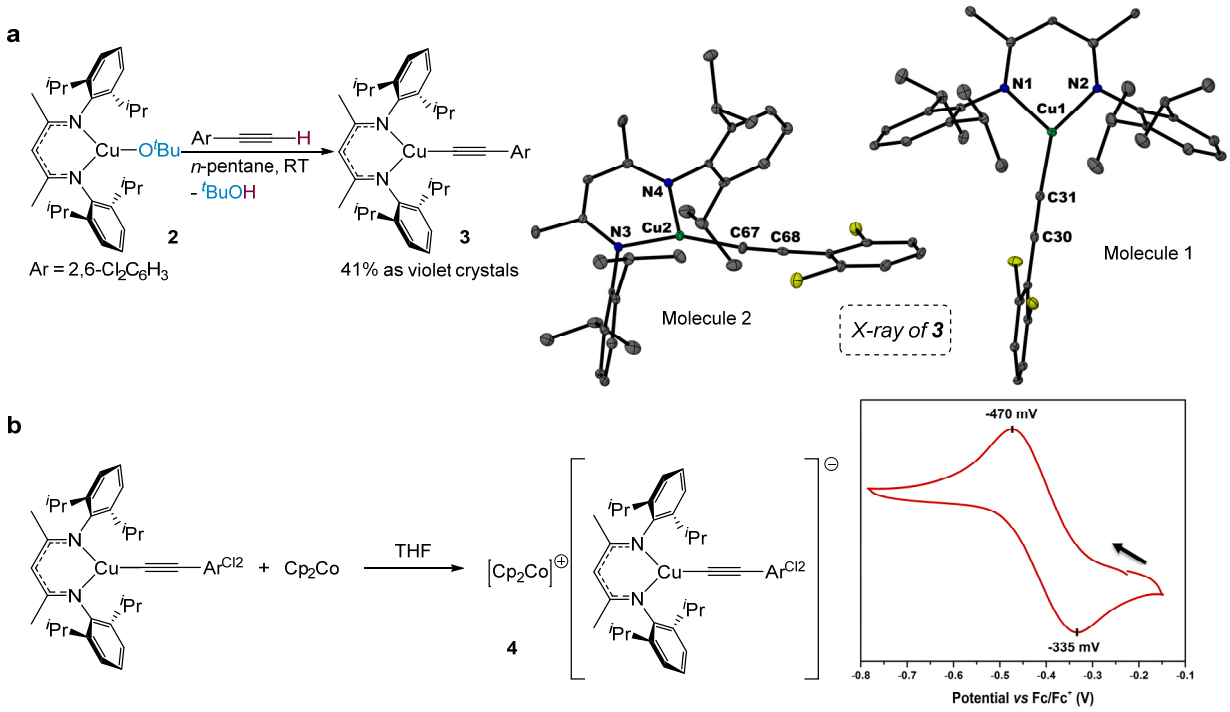


Fig. 4 | Synthesis and isolation of the three-coordinate Cu(II)−alkynyl. a, Synthesis and X-ray crystal structure of **3**. **b,** One-electron reduction of [^{i}Pr$_2$NN]Cu−C≡CAr^{Cl2} (**3**) with cobaltocene to generate [Cp$_2$Co]$^+${[^{i}Pr$_2$NN]Cu−C≡CAr^{Cl2}}$^-$ (**4**). Cyclic voltammogram at 20 mV/s of [^{i}Pr$_2$NN]Cu−C≡CAr^{Cl2} (**3**) in fluorobenzene (1.8 mM) at 23 °C with 0.1 M NaBAr$^F{}_4$ (Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$) as supporting electrolyte.

The isotropic X−band EPR spectrum of **3** in toluene at 200 K shows a four−line signal characteristic of a mononuclear Cu(II) center (Fig. S5). Simulation of the isotropic EPR spectrum provides g_{iso} = 2.097 with A_{iso}(Cu) = 210 and A_{iso}(N) = 40 MHz. The frozen glass EPR spectrum of **3** in toluene at 80 K provides is axially biased with g_1 = 2.178, g_2 = 2.040, g_3 = 2.050 with A_1(Cu) = 130, A_2(Cu) = 290, A_3(Cu) = 130 MHz (Fig. S6). These data are in good agreement with previously reported axially biased three coordinate [Cu^{II}]−X species (X = amide, alkoxide, thiolate, halide) with $g_1 \approx 2.20$ and $g_{2,3} \approx 2.05$.[24] The IR spectrum of **3** exhibits $\nu_{(C\equiv C)}$ at 2187 cm^{-1} (Fig. S7), while the optical spectrum of **3** in toluene shows a strong band at λ_{max} = 580 nm (4300 M^{-1}cm^{-1}) (Fig. S4).

Cyclic voltammetry of [^{i}Pr$_2$NN]Cu−C≡CAr^{Cl2} (**3**) in fluorobenzene (PhF) at RT exhibits a quasi-reversible reduction wave centered at −470 mV vs Fc^{+}/Fc (Fig. 4b). Encouraged by this observation, reduction of **3** by cobaltocene (Cp_2Co) in C_6D_6 allows for *in situ* formation of the corresponding copper(I) acetylide $[Cp_2Co]^{+}\{[^{i}Pr_2NN]Cu{-}C{\equiv}CAr^{Cl2}\}^{-}$ (**4**). Unfortunately, this species decays in solution over a matter of minutes to form an insoluble yellow solid preventing characterization by X−ray crystallography. Nonetheless, ^{1}H NMR analysis of the reaction mixture in THF−d_8 fully supports the diamagnetic nature of anionic **4**. These spectroscopic signatures include a sharp, distinct doublet at δ 6.60 ppm and a triplet at δ 6.17 ppm that represents *meta*−H and *para*−H resonances of the Ar^{Cl2} ring on the acetylide ligand, respectively, along with a diagnostic signal for the β−diketiminate backbone C−H methine at δ 4.75 ppm (Fig. S9).

Mechanism for C_{sp}−C_{sp} and C_{sp}-C_{sp2} Coupling via [^{i}Pr$_2$NN]Cu−C≡CAr^{Cl2}: Experiment and Theory. The copper(II) alkynyl [^{i}Pr$_2$NN]Cu−C≡CAr^{Cl2} (**3**) is unstable in solution at RT, transforming to yield ^{Cl2}ArC≡C−C≡CAr^{Cl2} (**5**) and [^{i}Pr$_2$NN]Cu(solvent) over hours to minutes, depending on the solvent (Fig. 5a). Surprisingly, the use of polar solvents such as MeCN accelerates diyne formation from [^{i}Pr$_2$NN]Cu−C≡CAr^{Cl2} (**3**) to form ^{Cl2}ArC≡C−C≡CAr^{Cl2} and [Cu^{I}]−NCMe (**1−NCMe**) in 88% and 98% yields, respectively within 5 minutes (Fig. 5a). These observations run counter to the Bohlmann mechanism[4] that requires a bimolecular interaction between [Cu^{II}]−C≡CR species to form a less polar dimer $\{[Cu^{II}]_2(\mu{-}C{\equiv}CR)_2\}$. Moreover, spontaneous loss of •C≡CAr^{Cl2} radical from [Cu^{II}]−C≡CAr^{Cl2} (**3**) as required by the Salkind and Fundyler mechanism[3] (Fig. 4a) is unlikely due to the high BDFE of the copper(II) acetylide bond calculated at 73.1 kcal/mol (BP86/6-311+G(d)/gas//BP86+GD3BJ/6-311++G(d,p)/SMD-acetonitrile).

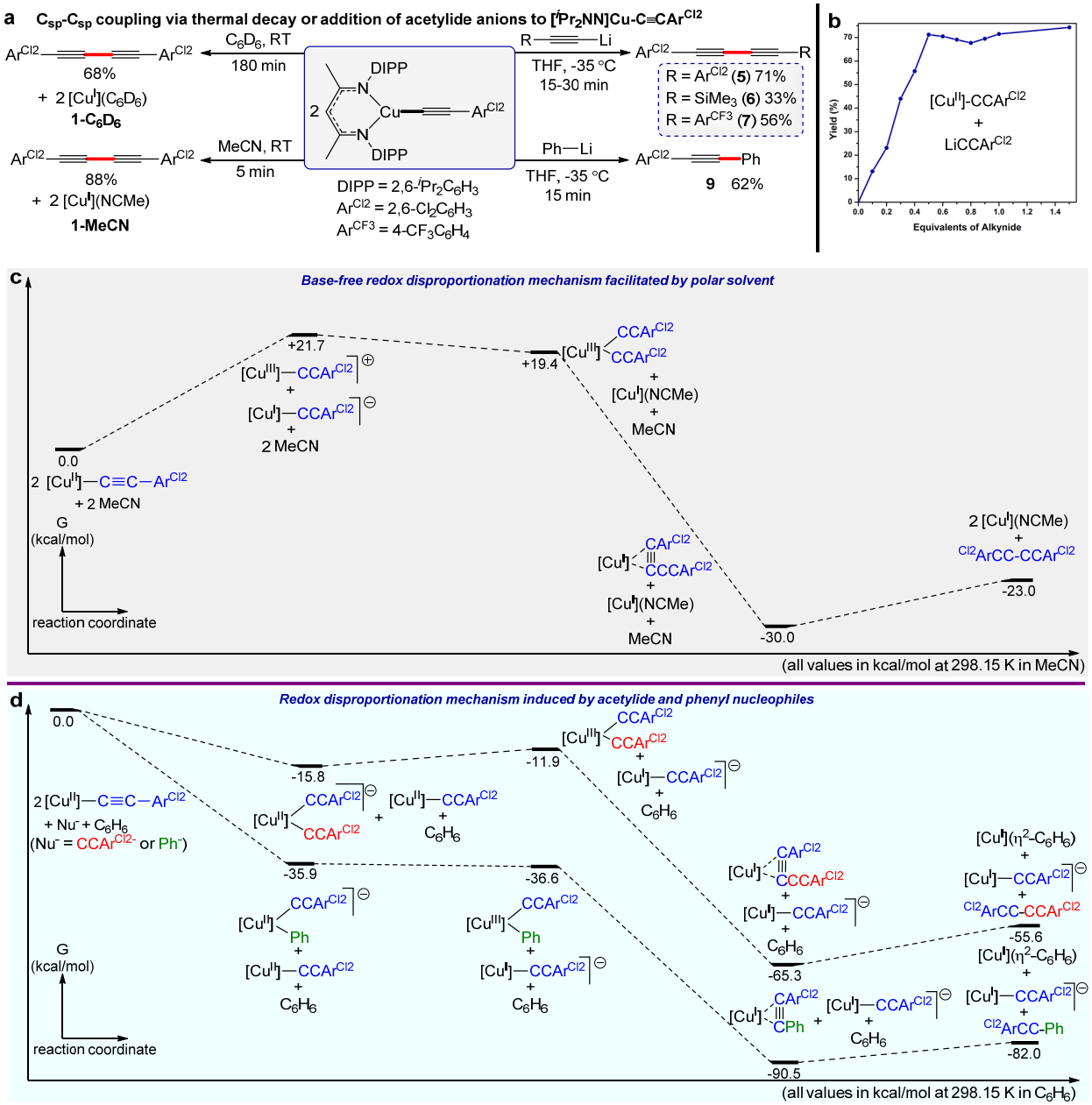


Fig. 5 | Mechanistic studies of Cu(II)-alkynyl mediated C_{sp}-C_{sp} and C_{sp}-C_{sp2} coupling reactions. a, C_{sp}-C_{sp} and C_{sp}-C_{sp2} coupling promoted by polar solvents (left) or organolithium nucleophiles (right) mediated by Cu(II) alkynyl complex **3**. **b,** Yield of diyne **5** vs. equivalents $LiC{\equiv}CAr^{Cl2}$ added to **3**, reaching a maximum yield with a 2 $[Cu^{II}]$-$C{\equiv}CAr^{Cl2}$: $LiC{\equiv}CAr^{Cl2}$ stoichiometry. **c,** DFT calculated thermodynamic values for C_{sp}-C_{sp} and C_{sp}-C_{sp2} coupling mediated by **3** that involve redox disproportionation / nucleophile transmetallation pathways.

Addition of alkynyl anion equivalents Li−C≡CR to [^{i}Pr$_2$NN]Cu−C≡CAr^{Cl2} (**3**) results in rapid diyne formation according to the stoichiometry 2 [Cu^{I}]−C≡CAr^{Cl2} : 1 Li−C≡CR (Fig 5b). Addition of 1 equiv. Li−C≡CAr^{Cl2} (Ar^{Cl2} = 2,6−Cl$_2$C$_6$H$_3$) to 2 equiv. **3** in THF at −35 °C provides the symmetric diyne ^{Cl2}ArC≡C−C≡CAr^{Cl2} (**5**) in 71% yield (Fig. 5a). Interestingly, addition of 1 equiv. LiC≡CTMS (TMS = trimethylsilyl) or LiC≡CAr^{CF3} (Ar^{CF3} = 4−CF$_3$C$_6$H$_4$) to 2 equiv. **3** in cold THF results in immediate colour change from violet to bright orange and formation of the corresponding unsymmetric 1,3−diynes TMSC≡C−C≡CAr^{Cl2} (**6**) or ^{CF3}ArC≡C−C≡CAr^{Cl2} (**7**) in 33% and 56% yields, respectively (Fig. 5b). In each case, the homocoupled 1,3−diyne ^{Cl2}ArC≡C−C≡CAr^{Cl2} (**5**) also forms in 36% and 13% yields. This coupling reaction of the copper(II) acetylide with incoming nucleophiles may be general. For instance, reaction of PhLi (1 equiv.) with **3** (2 equiv.) in cold THF afforded PhC−C≡CAr^{Cl2} (**9**) in 62% yield.

DFT studies support reaction pathways that proceed through redox disproportionation of the copper(II) acetylide into copper(III) and copper(I) acetylide complexes. In the absence of an added nucleophile (Fig. 5c), [^{i}Pr$_2$NN]Cu−C≡CAr^{Cl2} disproportionates to {[^{i}Pr$_2$NN]Cu^{III}−C≡CAr^{Cl2}}$^{+}$ (**8**) and {[^{i}Pr$_2$NN]Cu^{I}−C≡CAr^{Cl2}}$^{-}$ (**4**). This reaction is facilitated by a polar solvent that stabilizes these charged species, explaining the dramatic rate acceleration in MeCN vs. benzene. In the next step, anionic acetylide **4** attacks cationic acetylide **8** to form [^{i}Pr$_2$NN]Cu^{III}(C≡CAr^{Cl2})$_2$ followed by reductive elimination that furnishes the homocoupled product ^{Cl2}ArC≡C−C≡CAr^{Cl2} (**5**). In the presence of a nucleophile R^{-} modelled as either ^{Cl2}ArC≡C^{-} or Ph^{-}, [Cu^{II}]−C≡CAr^{Cl2} (**3**) binds the nucleophile to form the four coordinate {[Cu^{II}](C≡CAr^{Cl2})R}$^{-}$ species (Fig 5d). Owing to their negative charge, electron-rich {[Cu^{II}](C≡CAr^{Cl2})R}$^{-}$ complexes are especially unstable towards redox disproportionation in the

presence of $[Cu^{II}]-C\equiv CAr^{Cl2}$ (**3**) to give $[Cu^{III}](C\equiv CAr^{Cl2})R$ along with $\{[Cu^{I}]-C\equiv CAr^{Cl2}\}^-$ (**4**). Facile reductive elimination from $[Cu^{III}](C\equiv CAr^{Cl2})R$ provides the corresponding C−C coupled products $R-C\equiv CAr^{Cl2}$ (Fig. 5b). This mechanism is related to a report on Cu−mediated C_{sp2}–O bond formation via a $[Cu^{II}]-C_6F_5$ intermediate (Fig. 3b) that undergoes attack by a phenolate nucleophile PhO^- that triggers redox disproportionation between $\{[Cu^{II}](C_6F_5)(OPh)\}^-$ and $[Cu^{II}]-C_6F_5$ to give $[Cu^{III}](C_6F_5)(OPh)$ that rapidly reductively eliminates the diaryl ether $PhO-C_6F_5$.[24]

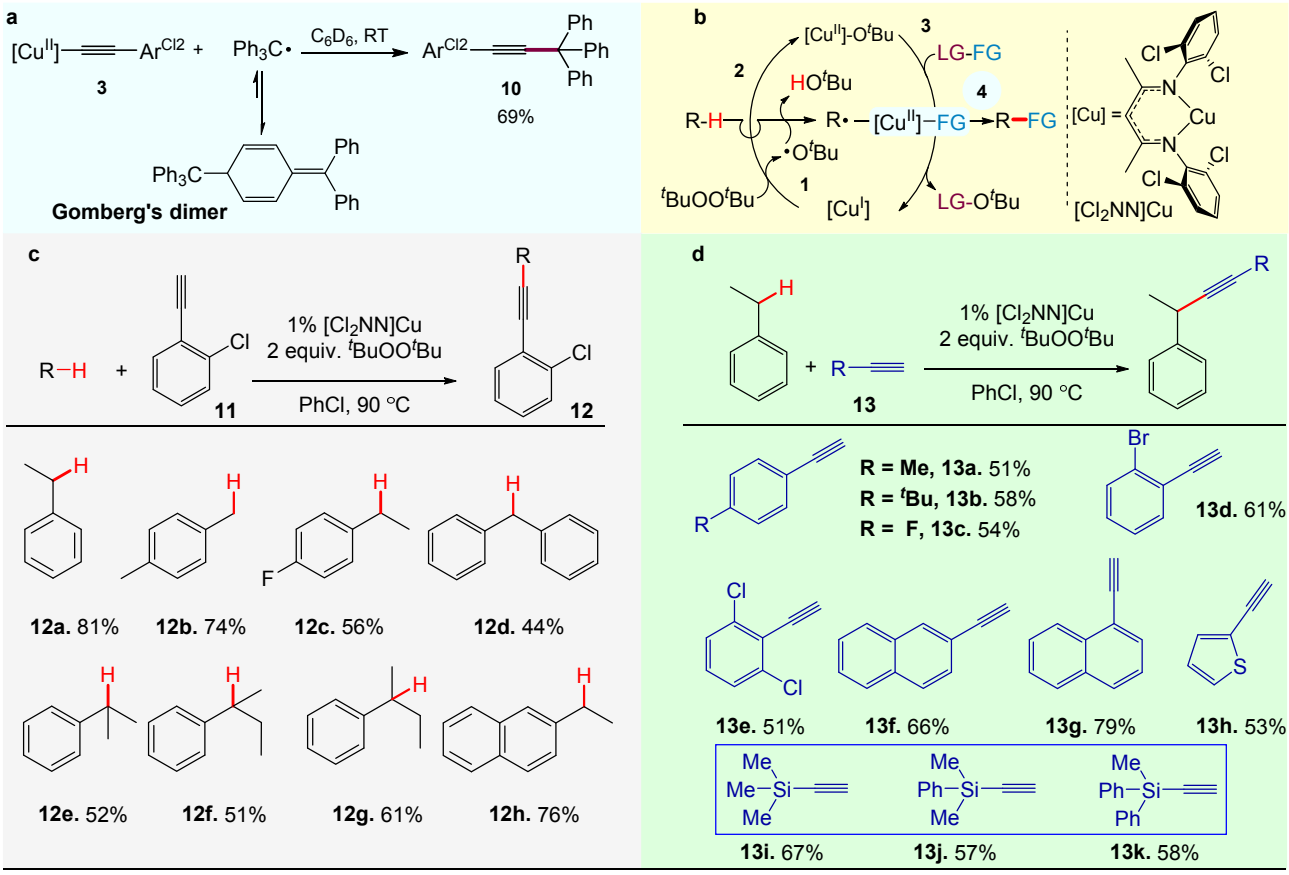
$C_{sp}-C_{sp3}$ Coupling Mediated by $[^iPr_2NN]Cu-C\equiv CAr^{Cl2}$ (3) and Catalytic C-H Alkynylation.

$[^iPr_2NN]Cu-C\equiv CAr^{Cl2}$ (**3**) captures the radical $Ph_3C\bullet$ (formed in the equilibrium dissociation of the Gomberg's dimer $\{Ph_3C\}_2$[29] to form $Ph_3C-C\equiv CAr^{Cl2}$ (**10**) within 5 min at RT in 69% yield along with $[^iPr_2NN]Cu(C_6D_6)$ in 78% yield (Fig. 6a). Since capture of radicals R• by $[Cu^{II}]-FG$ (FG = anilide, phenoxide) to give R−FG is the key C−FG bond forming step in radical relay mechanisms for C_{sp3}-H functionalization (Fig. 6b; step 4),[25,30-33] we explored the possibility of $C_{sp3}-H$ alkynylation mediated by copper(II) alkynyls $[Cu^{II}]-C\equiv CR$ generated by acid-base reaction of terminal alkynes $H-C\equiv CR$ with $[Cu^{II}]$-O^{t}Bu intermediates readily formed upon reaction of β−diketiminato catalysts $[Cu^{I}]$ with ^{t}BuOO^{t}Bu (Fig. 6b).[31]

We embarked on catalytic $C_{sp}-C_{sp3}$ coupling[11−13] by examining a model reaction of ethylbenzene ($PhCH_2Me$) with $H-C\equiv CAr^{CF3}$ (Ar^{CF3} = $4-CF_3-C_6H_4$) to form $PhCH(C\equiv CAr^{CF3})Me$ under various conditions (Supporting Information, Tables S3−S6). Several types of Cu(I) β−diketiminate catalysts were extensively screened in combination with various catalyst loadings, different oxidants as well as different solvents (Supporting Information, Tables S3−S6). The desired C−H alkynylation product $PhCH(C\equiv CAr^{CF3})Me$ forms along with

^{CF3}ArC≡C−C≡CAr^{CF3} and an alkene byproduct (Supporting Information, Table S3).[34] While the [^{i}Pr$_2$NN]Cu(NCMe) (**1−NCMe**) catalyst provides a moderate yield of PhCH(C≡CAr^{CF3})Me, the closely related [Cl$_2$NN]Cu catalyst enhances the C−H alkynylation yield, especially when the catalyst loading is reduced from 5% to 1% that effectively suppresses the Glaser homocoupled product ^{CF3}ArC≡C−C≡CAr^{CF3} (Supporting Information, Table S4).

We next surveyed a range of C−H substrates that undergo C−H alkynylation with 1−chloro−2−ethynylbenzene (**11**). While a range alkylbenzenes with benzylic C−H bonds provide good yields (Fig. 6c), we observed little success with substrates that possess only stronger, unactivated sp^3 C−H bonds. This may result from slower generation of R• radicals that allow ArC≡C−C≡CAr formation from [Cu^{II}]−C≡CAr intermediates that competes with radical capture by R• to give the desired C−H alkynylation product R−C≡CAr.



Conditions: 0.5 mmol alkyne, 10 equiv. ethylbenzene, 2 equiv. ^{t}BuOO^{t}Bu, 90 °C in PhCl, 24 h. Isolated yields shown.

Fig. 6 | Catalytic C_{sp3}-H alkynylation via copper(II) alkynyls. a, Capture of the trityl radical Ph_3C• (via Gomberg's dimer) by $[Cu^{II}]$−C≡CAr^{Cl2} (**3**) to form Ph_3C−C≡CAr^{Cl2} (**10**). **b**, Radical relay mechanism for catalytic C−N, C−O, and C−C bond formation. **c,** Substrate scope of terminal alkyne alkylation catalysed by $[Cl_2NN]Cu$. **d,** C−H alkynylation of ethylbenzene with various terminal alkynes, including silyl−protected alkynes **13h** − **13j**.

A range of terminal alkynes participate in the C−H alkynylation of ethylbenzene (Fig. 6d). Commercially available electron−rich (**13a**−**13b**) or electron−poor (**13c**−**13e**) aryl alkynes afforded good yields (51−66%). 1− and 2−ethynylnaphthalene were also subjected to this C−H alkynylation protocol and gave corresponding alkylated products **13g** and **13f** in 79% and 66% isolated yields, respectively. Gratifyingly, this methodology could also be applied in the alkylation of silyl−protected alkynes (**13h – 13j**). For instance, use of TMS−C≡CH affords trimethyl(3−phenylbut−1−yn−1−yl)silane (**13h**) in 65% yield. Silyl−protected alkyne products

R′−C≡C−SiR_3 are broadly useful as they can be directly deployed in cross-coupling reactions or easily deprotected to synthetically versatile terminal alkynes R′−C≡C−H.[35]

Conclusions and Summary

[$^{i}Pr_2$NN]Cu]−C≡CAr^{Cl2} (**3**) represents the first crystallographically characterized mononuclear copper(II) alkynyl complex, representing a key intermediate in the valuable C_{sp}−C_{sp} Glaser coupling reaction. Mechanistic studies reveal that such coupling is assisted by polar solvents such as MeCN, supporting a redox disproportionation pathway via charged {[Cu^{III}]−C≡CR}$^{+}$ and {[Cu^{I}]−C≡CR}$^{-}$ intermediates. Furthermore, addition of ½ equiv. nucleophiles R^{-} such as Ar′C≡CLi or PhLi to [$^{i}Pr_2$NN]Cu]−C≡CAr^{Cl2} results in immediate formation of ^{Cl2}ArC≡C−R with concomitant reduction to Cu(I) as both [Cu^{I}](solvent) and the Cu(I) alkynylate {[Cu^{I}]−C≡CAr^{Cl2}}$^{-}$. These observations shed light on other C_{sp}−C_{sp2} bond forming reactions such as the Pd−free Sonogashira reactions.[8,19-20] Additionally, [Cu^{II}]−C≡CAr^{Cl2} cleanly reacts with Gomberg's dimer to provide Ph_3C−C≡CAr^{Cl2} (**10**) indicating the ability of [Cu^{II}]−C≡CAr^{Cl2} to capture alkyl radicals R•. Based on this observation, a Cu−catalysed method was developed for alkynylation of unactivated alkanes. Significantly, silyl–acetylenes were shown to undergo alkynylation for the first time that can be further optimized for drug discover and late−stage functionalization of organic molecules.

These findings are expected to be broadly applicable to the development of versatile Cu-based catalysts to construct C_{sp}-C bonds for synthetic, medicinal and material applications, providing a mechanistic rationale the interaction of both nucleophiles and radicals with copper(II) organometallic species.

Acknowledgements

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Data availability

The X–ray crystallographic data for **2**, **3**, and **10** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC 1938189−1938191, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif). All the other data supporting the findings of this study are available within the article and its Supplementary Information, or from the corresponding author upon reasonable request.

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