C–H Amination

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Elusive Terminal Copper Arylnitrene Intermediates

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In memory of Gregory L. Hillhouse

Abstract: *We report herein three new modes of reactivity between arylazides N_3Ar with a bulky copper(I) β-diketiminate. Addition of N_3Ar^{X3} ($Ar^{X3} = 2,4,6\text{-}X_3C_6H_2$; X = Cl or Me) to $[^iPr_2NN]Cu(NCMe)$ results in triazenido complexes from azide attack on the β-diketiminato backbone. Reaction of $[^iPr_2NN]Cu(NCMe)$ with bulkier azides N_3Ar leads to terminal nitrenes $[^iPr_2NN]Cu{=}NAr$ that dimerize via formation of a C–C bond at the arylnitrene p-position to give the dicopper(II) diketimide* ***4*** *($Ar = 2,6\text{-}^iPr_2C_6H_3$) or undergo nitrile insertion to give diazametallocyclobutene* ***8*** *($Ar = 4\text{-Ph-}2,6\text{-}iPr_2C_6H_2$). Importantly, reactivity studies reveal both* ***4*** *and* ***8*** *to be "masked" forms of the terminal nitrenes $[^iPr_2NN]Cu{=}NAr$ that undergo nitrene group transfer to PMe_3, ^tBuNC, and even into a benzylic sp^3 C–H bond of ethylbenzene.*

Terminal imido/nitrene species of the first row transition metals have been suggested as key intermediates in catalytic C–H amination[1] as well as aziridination[2] of olefins. Despite the important role of copper catalysis in these nitrene transfer reactions,[1b,g] terminal copper nitrenes [Cu]=NR remain elusive synthetic targets,[3] even after nearly 50 years since their first suggestion by Kwart and Kahn.[4]

Employing β-diketiminato copper(I) complexes [Cu^I], our group first reported dicopper nitrenes $[Cu]_2(\mu\text{-NAr})$ ($Ar = 3,5\text{-}Me_2C_6H_3$) which incorporate chemically distinct [Cu^I] fragments in solution to give unsymmetric [Cu](μ-NAr)[Cu′] species that suggest terminal [Cu]=NAr intermediates (Figure 1a).[3f] Stoichiometric, catalytic, and kinetic studies on C–H amination with sp^3 substrates (R-H) employing N_3R' (R′ = 1-Ad or ^{t}Bu) with $[Cl_2NN]Cu$ suggested the presence of $[Cu^{II}]{=}NR'$ intermediates capable of H-atom abstraction to give copper(II) amides $[Cu^{II}]$-NHR′ and R$^\bullet$, which subsequently combine to give C–H functionalization products R-NHR′ (Figure 1a).[3c,e,f] Employing a novel, isolable singlet phosphinonitrene N-P(NR″),[5] Bertrand and coworkers reported a bridged dicopper nitrene adduct with CuOTf which disproportionates in solution to give a bis(nitrene) $\{Cu({=}NP(NR'')_2)\}^+$ (Figures 1b and c).[3b] Ray and co-workers employed a Lewis acid to trap a reactive copper-tosylnitrene intermediate as its $Sc(OTf)_3$ adduct, which was identified through spectrocopic studies at −90 °C and which engages in sp^3 C–H bond amidation (Figure 1d).[3d] Most recently, Ribas, Ray, Company and co-workers have used a macrocycle possessing an azide functionality, which leads to a spectroscopically copper-nitrene species at room temperature that participates in H-atom transfer (HAT) with weak C–H bonds (Figure 1e).[3a]

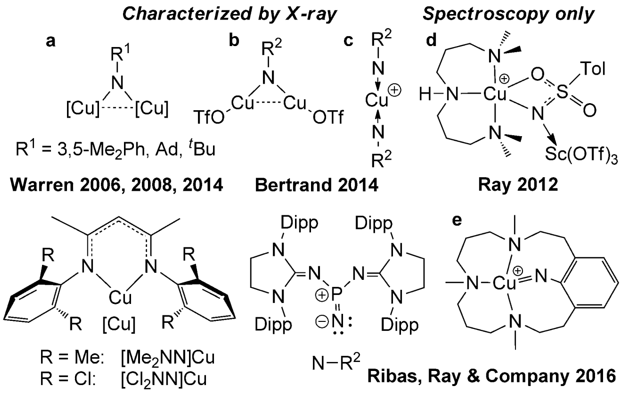

Figure 1. Previously reported copper nitrenes.

Employing a sterically demanding copper(I) β-diketiminate $[^iPr_2NN]Cu$, we sought to discourage the formation of bridged dicopper nitrenes $[Cu]_2(\mu\text{-NAr})$ to enable the direct observation of terminal nitrenes [Cu]=NAr. Reaction of $[^iPr_2NN]Cu(NCMe)$ (**1**) with N_3Ar^{Cl3} ($Ar^{Cl3} = 2,4,6\text{-}Cl_3C_6H_2$) in ether at −35 °C results in a rapid color change from pale yellow to purple to orange (Scheme 1). Crystallization from ether:*n*-pentane yields orange crystals of the dicopper(I) aryltriazenido species **2** in 71 % yield (Figure 2). While 1,3-diaryltriazenido complexes are known,[6] **2** is a novel example of a monoaryltriazenide directly from the reduction of the corresponding arylazide. We propose that the aryltriazenido complex forms by nucleophilic attack of the α-carbon of one β-diketiminato moiety at the terminal N atom of an azide coordinated to another $[^iPr_2NN]Cu$ moiety (Scheme 1). Repeating this reaction with mesityl azide similarly results in the isolation of the corresponding aryltriazenido complex **3** in 36 % yield. Both **2** and **3** possess short Cu⋯Cu separations of 2.5974(5) and 2.5978(3) Å, respectively. ^{1}H NMR studies of **2** clearly reveals it to be a diamagnetic copper(I) complex.

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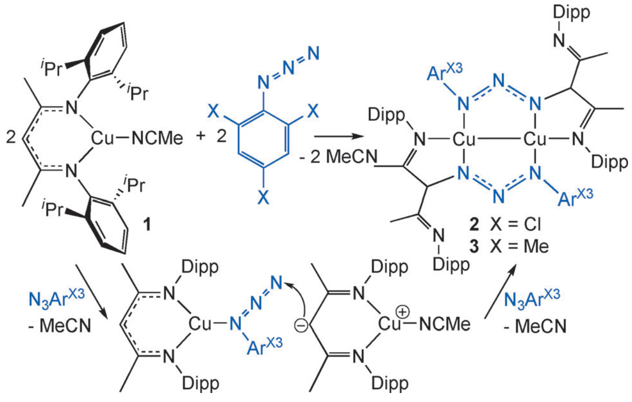


Scheme 1. Formation of dicopper triazenide complexes.

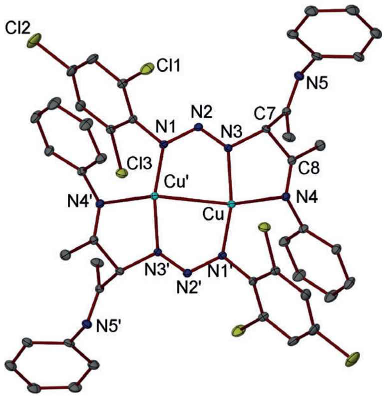
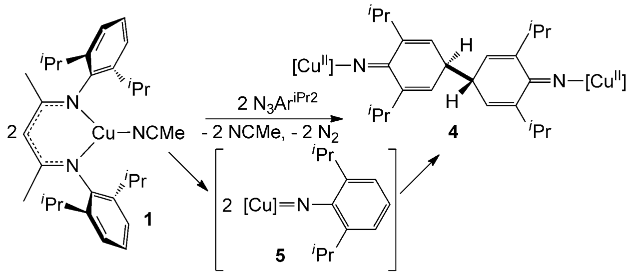


Figure 2. X-ray structure of dicopper triazenide **2** (^{i}Pr groups omitted).

In contrast to N_3Mes and N_3Ar^{Cl3}, reaction of the bulkier 2,6-diisopropylphenyl azide N_3Ar^{iPr2} ($Ar^{iPr2}=2,6\text{-}^{i}Pr_2C_6H_3$) with **1** at −35 °C leads to a rapid color change from pale yellow to dark violet with effervescence of N_2 gas and formation of dicopper(II) ketimide complex **4** in 59 % yield (Scheme 2). The X-ray structure of **4** (Figure 3) shows a centrosymmetric dimer connected by a long sp^3–sp^3 C–C bond (C33–C33′ = 1.586(4) Å) formed by dimerization of the NAr^{iPr2} rings at the *p*-position, resulting in a bridging diketimide ligand. The trigonal planar Cu center possesses a much shorter $Cu–N_{ketimide}$ bond length of 1.7661(17) Å as compared to its nearly identical $Cu–N_{\beta\text{-dik}}$ distances of 1.9128(16) and 1.9142(16) Å. Interestingly, the $Cu\text{-}N_{ketimide}\text{-}C$ angle approaches linearity at 161.78(15)° suggesting the possibility of extended interaction with the π-system. Careful investigation of the C–C bond lengths of the ketimide aromatic ring clearly reveal dearomatization with corresponding alternating bond lengths. For instance, the C30–C31 bond length is 1.501(3) Å whereas the C31–C32 bond distance is 1.331(3) Å (Figure 3 and Figure S14 in the Supporting Information). It is noteworthy that **4** is isostructural with a dinickel(II) diketimide obtained from the reaction of $\{[^{i}Pr_2NN]Ni\}_2(\mu\text{-toluene})$ with N_3Ar^{iPr2} as reported in 2007 by Bai and Stephan.[7] While the steric bulk of the azide N_3Ar^{iPr2} apparently directs reaction with $[^{i}Pr_2NN]Cu$ towards a nitrene intermediate $[^{i}Pr_2NN]Cu{=}NAr^{iPr2}$ (**5**), a few crystals of a triazenide similar to **2** and **3** were isolated as a minor product (**11**, Figure S18).



Scheme 2. Synthesis of dicopper(II) diketimide **4** via terminal nitrene **5**.

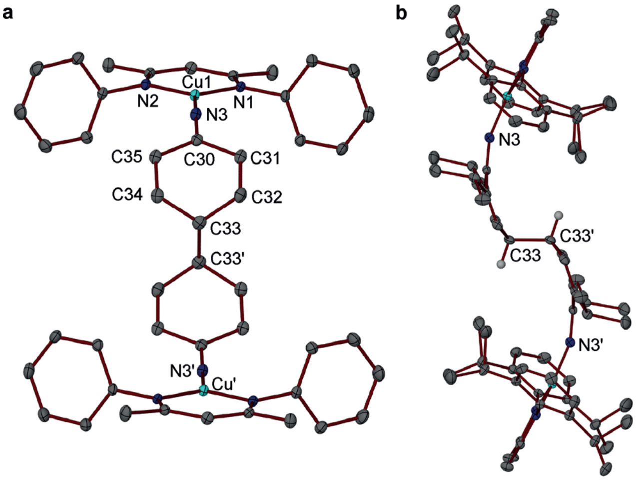


Figure 3. a) X-ray structure of dicopper(II) diketimide **4** (^{i}Pr groups not shown). b) Side view of **4**.

The dark violet ($\lambda_{max}=560$ nm ($5600\,M^{-1}cm^{-1}$), 639 nm ($3500\,M^{-1}cm^{-1}$)) paramagnetic dicopper(II) complex **4** exhibits an X-band EPR spectrum typical of a triplet biradical.[8] Coupling to both Cu^{II} centers results in a seven-line pattern ($A(2Cu)=99.5$ MHz) centered at $g=2.0548$ in its isotropic X-band EPR spectrum at room temperature in *n*-pentane (Figure 4). Complex **4** is paramagnetic with a solution molec-

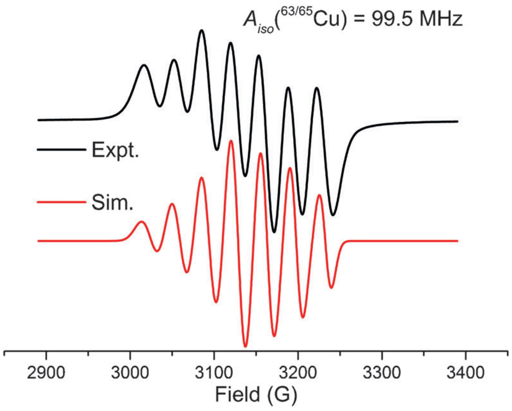
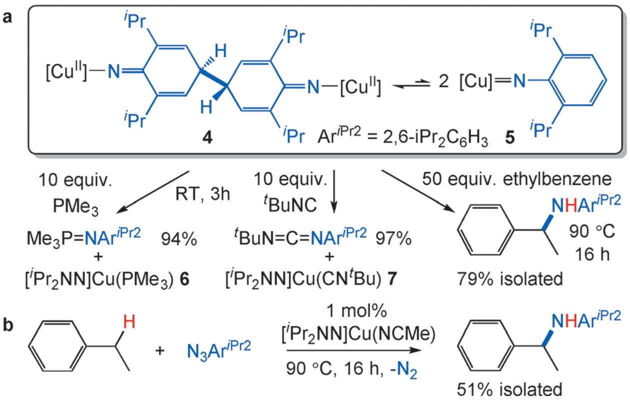


Figure 4. X-band EPR spectra (black trace) of **4** in *n*-pentane at 297 K. Frequency = 8.9951 GHz, power = 0.25 mW, ModWidth = 1.0 mT. Simulation (red trace) provides $g_{iso}=2.0548$ with $A_{iso}(^{63/65}Cu)=99.5$ MHz.

ular magnetic moment of 2.49(2) BM in C_6D_6 at 23 °C (12.5 mM), consistent with a triplet formulation.

Reactivity studies of **4** demonstrate clean nitrene group transfer to nucleophiles such as trimethylphosphine (PMe_3) and *tert*-butylisocyanide (^{t}BuNC) (Scheme 3 a). Reaction of **4** with 10 equiv PMe_3 or ^{t}BuNC at room temperature leads to the rapid discharge of the violet color of **4** with formation of ^{iPr2}ArN=PMe_3 and ^{iPr2}ArN=C=N^{t}Bu in 94 % and 97 % yields, respectively. The use of excess nucleophile traps the [^{i}Pr$_2$NN]Cu fragment as adducts [^{i}Pr$_2$NN]Cu(PMe_3) (**6**) and [^{i}Pr$_2$NN]Cu(CN^{t}Bu) (**7**) (Figures S15 and S16) that may also be prepared independently by addition of PMe_3 or CNBu^t to [^{i}Pr$_2$NN]Cu(NCMe). Importantly, the stoichiometric (1:1) reaction of **4** with ethylbenzene (BDE = 87 kcal mol^{-1})[9] at 90 °C gives C−H amination of the benzylic site in modest yield (31 %) along with 2,6-diisopropylaniline. Increasing the ethylbenzene loading to 50 equiv enhances the isolated yield of the C−H amination product to 79 %. C−H amination with N_3Ar^{iPr2} may also be performed catalytically with 1 mol % **1** in neat ethylbenzene at 90 °C to give a 51 % GC yield (Scheme 3 b).



Scheme 3. a) Reactivity of dicopper diketimide **4** via terminal nitrene **5**. b) Catalytic amination of ethylbenzene catalyzed by [^{i}Pr$_2$NN]Cu-(NCMe).

The reactivity profile of **4** does not fit that of a transition metal-ketimide species. For instance, ketimides have been used to stabilize tetrahedral Mn^{IV},[10a] Fe^{IV},[10b] and Co^{IV}[10c] complexes due to their bonding properties[10d] that render the M−N bond rather inert.[10e] Rather, the reactivity of **4** mirrors that of β-diketiminato copper nitrene intermediates [Cu]=NR that can undergo attack by nucleophiles[3f] as well as participate in C−H amination.[1g,3c,e] Thus, we propose that these nitrene transfer reactions proceed via the intermediacy of the terminal nitrene [^{i}Pr$_2$NN]Cu=NAr^{iPr2} (**5**).

We employed DFT methods to elucidate the electronic structure of the dicopper diketimide **4** as well as to assess the viability of the terminal nitrene intermediate [^{i}Pr$_2$NN]Cu=NAr^{iPr2} (**5**). First, DFT geometry optimization of **4** in the triplet state at (BP86 functional with dispersion and solvent effects)[11] with all-electron basis sets predicted distances of Cu−N$_{ketimide}$ and C−C (C33−C33′) as 1.76 and 1.62 Å, respectively (Figure S41), as compared to the experimentally observed structure of 1.7661(17) and 1.586(4) Å, respectively. The triplet electronic structure has significant spin density predicted at the Cu and ketimide N atoms (Figure 5 a), rationalizing the hyperfine observed to both Cu centers (A(Cu) = 99.5 MHz) in the isotropic EPR spectrum of **4** (Figure 4).

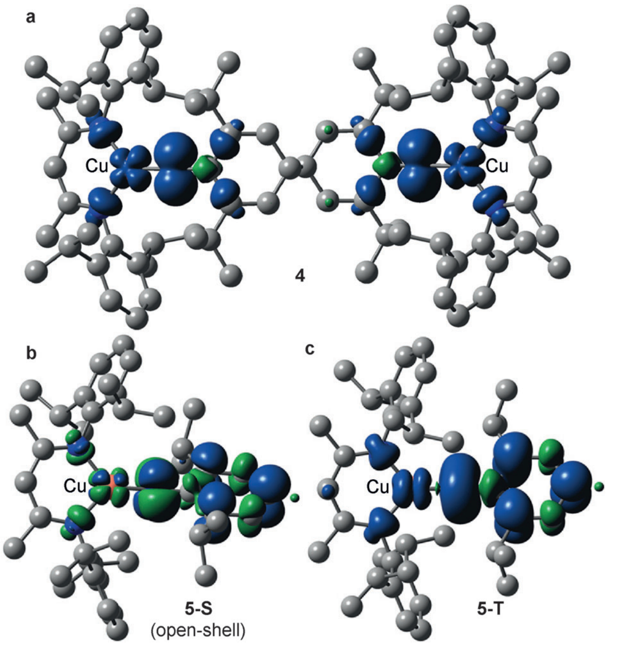
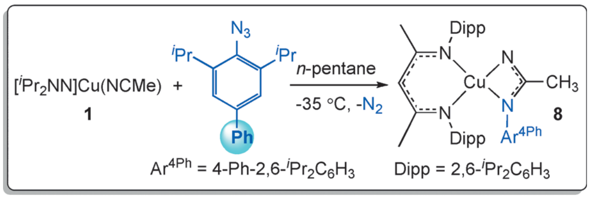


Figure 5. Spin density profiles for a) dicopper diketimide **4** along with terminal nitrene intermediate [^{i}Pr$_2$NN]Cu=NAr^{iPr2} in its b) open-shell singlet state (**5-S**) and c) triplet state (**5-T**). The blue surface indicates excess α-electron density; the green surface indicates excess β-electron density. Isovalue = 0.002.

We also computationally examined the terminal nitrene [^{i}Pr$_2$NN]Cu=NAr^{iPr2} (**5**). Based on earlier studies of related β-diketiminato aryl[12] and alkyl[3c,e] nitrenes, we considered both an open-shell singlet (**5-S**) and triplet (**5-T**). Both spin states give rise to very similar structures with Cu=NAr distances of 1.75 Å for both, each with a nearly linear Cu-N-Ar linkage (Figure S52).[12] The open shell singlet **5-S** is 4.3 kcal mol^{-1} higher in free energy at 298 K than triplet **5-T** using DFT methods. In both spin states, the aryl nitrene substituent possesses alternating spin density (Figures 5 b and c). Most critically, there is substantial spin density on the *p*-position of the nitrene aryl substituent that may facilitate C−C coupling to form the observed dicopper diketimide **4**. Indeed, these DFT methods predict that dimerization of **5-S** to form **4** by C−C bond formation is favorable by 2.8 kcal mol^{-1} in free energy at 298 K.

To sterically block C−C coupling in nitrene intermediates [Cu]=NAr, we examined the reaction of the aryl azide 4-Ph-2,6-^{i}Pr$_2$C$_6$H$_3$N$_3$ (Ar^{4Ph}N$_3$) that possesses a *p*-Ph group with [^{i}Pr$_2$NN]Cu(NCMe) (**1**) (Scheme 4). The deep violet product **8** may be isolated from pentane that retains an equivalent of MeCN, but unfortunately resists X-ray structural characterization. ^{1}H NMR studies of diamagenetic **8** in [D$_6$]benzene reveal a MeCN resonance at δ 0.00 ppm that exchanges

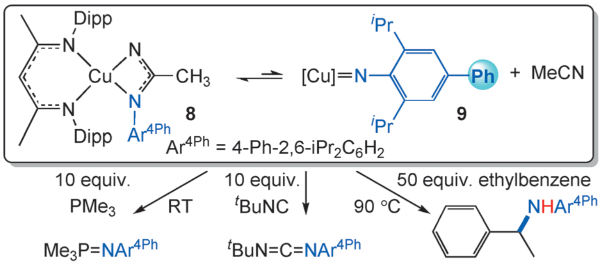


Scheme 4. Synthesis of [^{i}Pr$_2$NN]Cu(κ^2-*N*,*N*-NC(Me)Ar^{4Ph}) (**8**).

rapidly with added MeCN. Unlike the κ^1-N bound MeCN ligand in [^{i}Pr$_2$NN]Cu(NCMe) that exhibits a $\nu_{C\equiv N}$ stretch at 2221 cm^{-1}, **8** possesses no high energy stretch. Rather, we note a band in the IR spectrum of solid **8** at 1533 cm^{-1} that shifts to 1519 cm^{-1} when prepared from [^{i}Pr$_2$NN]Cu(N^{13}CMe). These data are consistent with insertion of MeCN into [Cu]=NAr to give the κ^2-diazametallocyclobutene **8**. Such nitrile insertion into [M]=NR functionalities is quite uncommon, though previously observed in the reaction of nucleophilic metal-imides [Ti]=NR, [U]=NR with organonitriles R′C≡N.[13a–d] Amidine products RNHC(=NTs)Me have been observed in C−H amidation of substrates R-H with PhI=NTs carried out in MeCN with Mn, Fe, and Cu-based catalysts,[13e,f] suggested to proceed via [M](κ^2-*N*,*N*-NC(Me)NTs) intermediates.[13e]

DFT studies indicate that the κ^2-*N*,*N* insertion product **8** is 2.7 kcal mol^{-1} lower in free energy than separated MeCN and terminal arylnitrene [^{i}Pr$_2$NN]Cu=NAr^{4Ph} (**9**), the only bound state identified by DFT. MCSCF calculations on terminal [^{i}Pr$_2$NN]Cu=NAr^{4Ph} (**9**) indicate that the open-shell singlet state is highly multi-configurational and lies 10 kcal mol^{-1} below the triplet (see the Supporting Information for additional details), as discussed previously for both [^{i}Pr$_2$NN]Cu=NAr^{iPr2} (**5**) and simpler copper nitrene models.[3e, 12]

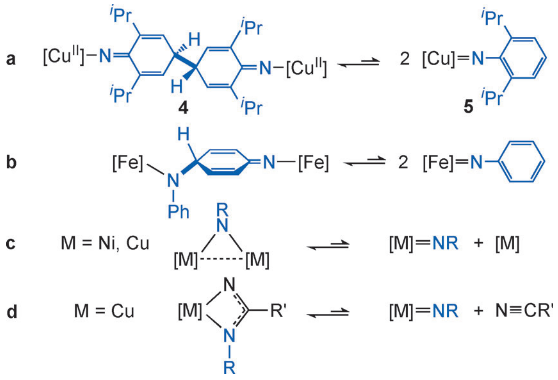
Curiously, the UV-vis spectra of dicopper diketimide **4** and nitrene–MeCN adduct **8** in dilute pentane are similar in form with strong bands at $\lambda = 560$ and 639 nm (**4**) or 533 and 630 nm (**8**) (Figures S1 and S4). This observation suggests that both may exist as the closely related terminal nitrenes [^{i}Pr$_2$NN]Cu=NAr^{iPr2} (**5**) and [^{i}Pr$_2$NN]Cu=NAr^{4Ph} (**9**) in dilute solution. Indeed, freezing point depression measurements in cyclohexane suggest that both diketimide **4** and MeCN adduct **8** are ca. 35 % and 80 % dissociated to the corresponding terminal nitrenes **5** and **9** (Scheme 3 a and Scheme 5). Accordingly, reactivity studies of nitrene-MeCN adduct **8** demonstrate quantitative nitrene group transfer to nucleophiles such as PMe$_3$ as well as ^{t}BuNC. Heating isolated **8** with 50 equiv ethylbenzene at 90 °C allows for isolation of the C−H amination product in 71 % yield (Scheme 5).



Scheme 5. Reactivity of nitrene–MeCN adduct **8** via terminal nitrene **9**.

We specifically targeted arylnitrene intermediates [Cu]=NAr since we anticipated that they would be less reactive towards H-atom transfer (HAT) than corresponding alkylnitrenes. For instance, [Cu]=NR (*R* = 1-Ad[3e] or ^{t}Bu[3c]) intermediates undergo facile intra- and intermolecular HAT reactions with C−H bonds, driven by the strong N−H bond in the HAT product (e.g 98.4 kcal mol^{-1} for [Cl$_2$NN]Cu-NHAd).[3c] Accordingly, addition of AdN$_3$ to [^{i}Pr$_2$NN]Cu-(NCMe) (**1**) at room temperature led to intramolecular C−H amination[3e] of a β-diketiminato tertiary benzylic *o*-^{i}Pr C−H bond (Scheme S15, Figure S17). This difference in HAT reactivity between alkyl- and arylnitrene intermediates may be related to the higher N−H BDEs of alkylamines H$_2$NR (95–100 kcal mol^{-1})[9] vs. anilines H$_2$NAr (86–95 kcal mol^{-1}),[9] though we cannot discount steric differences between specific [Cu]=NAr and [Cu]=NAd intermediates.

The dicopper diketimide **4** and MeCN insertion adduct **8** join two other structural motifs identified in iron, nickel, and copper chemistry that are proposed to dissociate into reactive terminal nitrenes/ imides [M]=NR (Scheme 6). Complementing the reversible C−C coupling pathway of copper arylnitrene [Cu]=NAr (**5**) (Scheme 3 a and Scheme 6 a), Betley et al. showed that sterically unencumbered high spin [Fe^{III}]=NAr species could asymmetrically dimerize via N−C coupling (Scheme 6 b).[14] Heating this N−C coupled product in toluene at 80 °C led to C−H amination consistent with a terminal [Fe]=NPh intermediate.[14] Dinickel[15a–c] and dicopper[3c,e,f] nitrenes [M]$_2$(μ-NR) may dissociate into terminal species [M]=NR, which participate in nitrene group transfer including sp^3 C−H amination (Scheme 6 c). This study also suggests reversible insertion of nitriles (Scheme 5 and Scheme 6 d) as an additional method to stabilize highly reactive [M]=NR species. This family of masked terminal nitrene/imide motifs reveals important design considerations in the development of new catalytic nitrene transfer systems.



Scheme 6. Masked forms of terminal Fe, Ni and Cu imides/nitrenes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C–H amination · copper · group transfer · ketimide · nitrenes · triazenide

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[16] Section 26 in the Supporting Information and CCDC 1502970, 1502971, 1502972, 1502973, 1502974, 1502975 and 1502976 for complexes **2**–**4**, **6**, **7**, **10**, and **11** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Communications

C–H Amination

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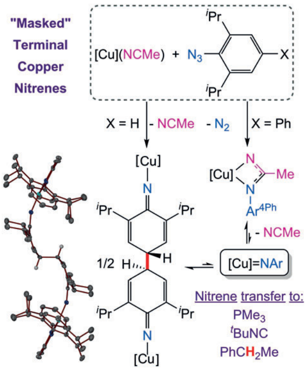
Elusive Terminal Copper Arylnitrene Intermediates



Attempts at isolating terminal arylnitrenes [Cu]=NAr result in a dicopper diketimide (see scheme, left) formed through reversible C–C coupling at the *para* position of the NAr group or acetonitrile insertion to give a diazametallacyclobutene (right). Experimental and theoretical studies reveal that both intermediates serve as "masked" sources of the corresponding terminal nitrene [Cu]=NAr that undergoes nitrene transfer to PMe$_3$, CN^{t}Bu, and benzylic C–H bonds.