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Transient Terminal Cu−Nitrene Intermediates from Discrete Dicopper Nitrenes

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Copper-based catalysts have held prominence in metal-catalyzed aziridination since the discovery that copper promoted the decomposition of benzensufonyl azide to give aziridines in the presence of alkenes.[1] Using PhI═NTs or related sulfonylnitrene precursors in conjunction with a variety of copper complexes with N-donor ligands has resulted in high aziridine yields as well as ee values up to 98% in some cases.[2] While both experimental[3,4] and theoretical[5,6] studies point to Cu−nitrene intermediates, direct evidence for these elusive species is sparse. The use of either PhI═NTs or $N_3Ts/h\nu$ with a C_2-symmetric diimine Cu(I) catalyst gave identical ee values in the aziridination of styrene derivatives, suggesting a common, PhI-free active intermediate.[3] Theoretical studies point to a κ^2-N,O binding mode of the NSO_2R tosylnitrene moiety to a square planar Cu center for which triplet and singlet states are comparable in energy.[5] As cationic[7,8] and neutral[9] catalyst systems also exhibit nitrene insertion into C−H bonds to give sulfonylamines, the synthetic exploration of copper nitrenes offers the potential to understand factors that control these modes of reactivity and to expand the range of nitrene transfer reagents.

We recently reported the use of β-diketiminate ancillary ligands to prepare doubly bridged $[\mathrm{Co}]_2(\mu\text{-NR})_2$, singly bridged $[\mathrm{Ni}]_2(\mu\text{-NR})$, and terminal [M]═NR (M = Co, Ni) imide (or nitrene) complexes.[10] Given our recent isolation of dicopper carbenes $[\mathrm{Cu}]_2(\mu\text{-CPh}_2)$ which dissociate a β-diketiminato Cu(I) fragment in arene solutions (eq 1),[11] we reasoned that the electronic similarities between singlet carbenes and nitrenes might allow similar stabilization of a dicopper nitrene $[\mathrm{Cu}]_2(\mu\text{-NR})$ from organoazides. In fact, Vedernikov and Caulton have reported the generation of a deep purple species identified as $[\{[\mathrm{NNN}]\mathrm{Cu}\}_2(\mu\text{-NTs})]^{2+}$ from NMR and ESI-MS data in the reaction of a cationic Cu(I) catalyst bearing a neutral tridentate ligand with PhI═NTs.[7,12] Moreover, Cui and He have shown that a unique terpyridine-based disilver system serves as an efficient aziridination catalyst.[13]

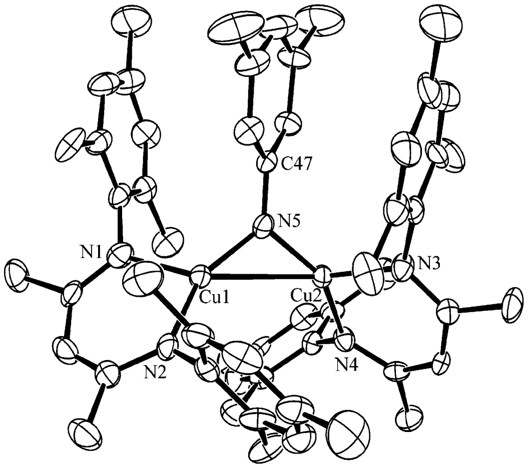
$$2[\mathrm{Cu}](\mathrm{arene}) \xrightarrow[-\mathrm{N_2}]{\mathrm{N_2CPh_2}} [\mathrm{Cu}]_2(\mu\text{-}\mathrm{CPh_2}) \overset{\mathrm{arene}}{\rightleftharpoons} [\mathrm{Cu}]{=}\mathrm{CPh_2} + [\mathrm{Cu}](\mathrm{arene})$$
$$[\mathrm{Cu}] = [\mathrm{Me}_x\mathrm{NN}]\mathrm{Cu}\ (x = 2 \text{ or } 3) \tag{1}$$

We initially explored the reactivity of organoazides with $[\mathrm{Me_2NN}]\mathrm{Cu}(2,4\text{-lutidine})$, a competent catalyst for the aziridination of olefins such as styrene and cyclooctene with PhI═NTs.[14] No interaction of the organoazides with the $[\mathrm{Me_2NN}]\mathrm{Cu}$ center could be inferred by ^{1}H NMR spectroscopy in benzene-d_6. Presumably, the weak σ-donor ability of the azide does not allow it to successfully compete with 2,4-lutidine. Instead, the reaction between $\{[\mathrm{Me_3NN}]\mathrm{Cu}\}_2(\mathrm{toluene})$[11b] (**1**) and 1 equiv N═N═NAr (Ar = 3,5-$\mathrm{Me_2C_6H_3}$) in toluene results in immediate effervescence and dramatic coloration of the solution to dark violet from which crystals of $\{[\mathrm{Me_3NN}]\mathrm{Cu}\}_2(\mu\text{-NAr})$ (**2**) may be isolated from pentane at −35 °C in 77% yield. X-ray analysis shows that the nitrene moiety is nearly symmetrically bound between two $[\mathrm{Me_3NN}]\mathrm{Cu}$ fragments separated by 2.911(1) Å with Cu−N distances of 1.794(5) and 1.808(5) Å. The Cu−μ_2−NAr distances in **2** are shorter than the range of Cu−N distances (1.842(5)−1.893(6) Å) reported for μ_3-NPh groups in Fenske's $[\mathrm{Cu_{24}(NPh)_{14}}]^{4-}$ and $[\mathrm{Cu_{12}(NPh)_8}]^{4-}$ clusters prepared from copper(I) salts and $\mathrm{Li_2NPh}$.[15] The structure of dicopper nitrene **2** is conceptually similar to $\{[\mathrm{Me_2NN}]\mathrm{Cu}\}_2(\mu\text{-CPh}_2)$ in which the two copper centers are separated by 2.4635(7) Å.[11a] The longer Cu···Cu separation in **2** is attributed to the ability of an sp^2-hybridized nitrene to σ-donate to the two copper centers via two lone pairs; in contrast, the diphenylcarbene moiety can donate only one lone pair shared between two copper fragments. This difference in bonding is also reflected in the wider Cu1−N5−Cu2 angle (107.8(2)°) in **2** than for the corresponding Cu−C−Cu angle (79.51(14)°) in $\{[\mathrm{Me_2NN}]\mathrm{Cu}\}_2(\mu\text{-CPh}_2)$.[11a]

Scheme 1. Synthesis and Structure of **2**

$$\{[\mathrm{Me_3NN}]\mathrm{Cu}\}_2(\mathrm{toluene}) \xrightarrow[-\,\mathrm{N_2}]{\mathrm{N{=}N{=}NAr}} \{[\mathrm{Me_3NN}]\mathrm{Cu}\}_2(\mu\text{-NAr})$$

1 **2**



Variable temperature ^{1}H NMR (500 MHz) spectra of diamagnetic **2** in toluene-d_8 reveal two separate fluxional processes. At −85 °C, four β-diketiminato Ar−H, six Ar−Me, and one broadened backbone Me resonance are observed consistent with the approximate C_2 symmetry observed in the solid-state that relates each $[\mathrm{Me_3NN}]\mathrm{Cu}$ fragment. Upon warming to 0 °C, only two β-diketiminato Ar−H and o-Ar−Me resonances are observed owing to a low-energy rocking motion about the Cu···Cu vector with an activation barrier $\Delta G^{\neq} = 9.4(2)$ kcal/mol at −72 °C. Further warming to 45 °C gives C_{2v}-symmetric ^{1}H NMR spectra due to pairwise coalescence of these Ar-*H* and *o*-Ar-*Me* resonances with an activation barrier $\Delta G^{\neq} = 14.7(2)$ kcal/mol at 29−34 °C. While the higher energy process is consistent with rapid dissociation/reassociation of a $[\mathrm{Me_3NN}]\mathrm{Cu}$ fragment from **2**, we instead favor complete rotation of the $[\mathrm{Me_3NN}]\mathrm{Cu}$ fragments along the individual Cu−N bonds at the expense of the Cu···Cu interaction. We see no evidence for rapid exchange between $[\mathrm{Me_3NN}]\mathrm{Cu}(\mathrm{solvent})$ and **2** upon addition of **1** to solutions of **2** at room temperature. Moreover, only one backbone C−H signal is observed for the dicopper nitrene from −85 to +50 °C. This stands in contrast to arene solutions of

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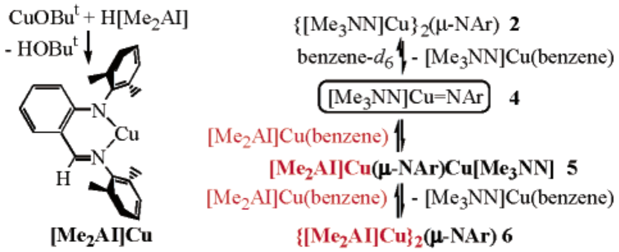
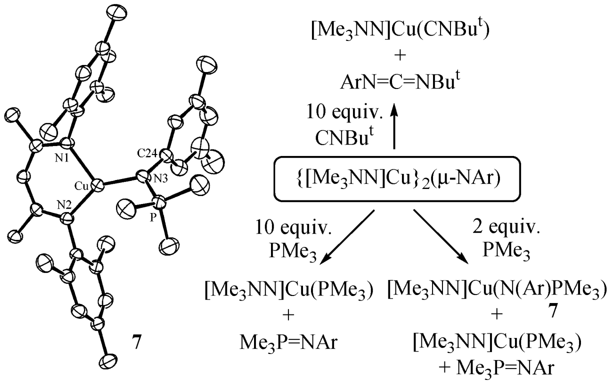
Scheme 2. Synthesis of **3** and Chemical Exchange with **2**



Scheme 3. Electrophilic Reactivity of **2** and X-ray Structure of **7**



$\{[Me_xNN]Cu\}_2(\mu\text{-}CPh_2)$ which display signals for both the dicopper carbene as well as $[Me_xNN]Cu{=}CPh_2$ and $[Me_xNN]Cu(solvent)$ above 0 °C (eq 1).

Use of a chemically distinct Cu(I) β-diketiminato analogue[16a,b] $\{[Me_2AI]Cu\}_2$ (**3**) prepared from the corresponding free iminoaniline[16c] and CuO^{t}Bu in 77% yield provides evidence for the terminal nitrene intermediate $[Me_3NN]Cu{=}NAr$ (**4**) generated by slow, reversible loss of a $[Me_3NN]Cu$ fragment from $\{[Me_3NN]Cu\}_2(\mu\text{-}NAr)$ (**2**) (Scheme 2). Addition of 1 equiv **3** to room temperature benzene-d_6 solutions of the dicopper nitrene **2** results in the formation of new species within 15 min. After 3 h, new anilidoimine iminyl C−H ^{1}H NMR resonances for the unsymmetric $[Me_2AI]Cu(\mu\text{-}NAr)Cu[Me_3NN]$ (**5**) and to a lesser extent, the symmetric $\{[Me_2AI]Cu\}_2(\mu\text{-}NAr)$ (**6**) at δ 7.649 and 7.740 ppm are clearly evident along with corresponding β-diketiminato C−H resonances for **5** and $[Me_3NN]Cu(arene)$ at δ 4.874 and 4.808 ppm. The new symmetric dicopper nitrene **6** may be isolated in 49% yield from the reaction between $\{[Me_2AI]Cu\}_2$ and N_3Ar, while **5** is formed as the predominant species when a 1:1 mixture of $\{[Me_3NN]Cu\}_2(toluene)$ and $\{[Me_2AI]Cu\}_2$ reacts with N_3Ar. In the exchange reactions shown in Scheme 2, the crowded nature of dicopper nitrenes **2** and **5** strongly implicates the transient generation of the terminal copper nitrenes $[Me_3NN]Cu{=}NAr$ (**4**) and $[Me_2AI]Cu{=}NAr$ by loss of a $[Me_3NN]Cu$ fragment from **2** or **5** to afford the new unsymmetric and symmetric dicopper nitrenes **5** and **6**.

Preliminary reactivity studies demonstrate group transfer of the nitrene moiety in **2** and **6** to strong nucleophiles. Reaction of **2** with 10 equiv PMe_3 or CN^{t}Bu in benzene-d_6 leads to rapid formation of $Me_3P{=}NAr$ or ArN═C═N^{t}Bu in 94% and 92% yields by ^{1}H NMR (Scheme 3). $[Me_3NN]Cu(PMe_3)$ and $[Me_3NN]Cu(CN^t\text{-}Bu)$ form concomitantly, verified via their independent syntheses from **1** and PMe_3 or CN^{t}Bu. Similar group transfer reactivity takes place with the anilidoimine-based dicopper nitrene **6**. Reaction of **2** with only 2 equiv PMe_3 leads to the formation of a third P-containing substance **7** exhibiting a ^{31}P NMR signal at δ 21.7 ppm in benzene-d_6. This new species is $[Me_3NN]Cu(N(Ar)PMe_3)$ confirmed by its independent synthesis from **1** and $Me_3P{=}NAr$. The X-ray structure of **7** shows trigonal coordination at N with Cu−N3 and N3−P distances of 2.010(3) and 1.586(3) Å, respectively.[17] Reaction of **2** with 10 equiv styrene in benzene over ca. 3 h results in ArN═NAr as the predominate nitrene-containing product; no aziridination is observed. In the absence of styrene, other nitrene-based decomposition products are also present which include H_2NAr and ArNHNHAr.

In summary, reaction of N_3Ar with $\{[Me_3NN]Cu\}_2(toluene)$ leads to the dicopper nitrene $\{[Me_3NN]Cu\}_2(\mu\text{-}NAr)$ (**2**). Crossover experiments with the Cu(I) anilidoimine **3** suggest slow dissociation of a $[Me_3NN]Cu$ fragment from dicopper nitrenes **2** and **5** to give terminal Cu-nitrene intermediates. While reaction of **2** with CN^t-Bu and PMe_3 results in smooth group transfer, weaker nucleophiles such as styrene result in the nitrene coupling product ArN═NAr. Factors that govern this selectivity will be explored by the use of electronically diverse nitrene substituents, especially since β-diketiminato Cu(I) complexes catalyze the aziridination of styrene with PhI═NTs, a source of the particularly electron-poor tosylnitrene.

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Supporting Information Available: Experimental procedures with characterization data as well as crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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