Electronic structure and electrophilic reactivity of discrete copper diphenylcarbenes

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Abstract

The β-diketiminato Cu(I) arene adduct {[Me$_3$NN]Cu}$_2$(μ-toluene) (**3**) is prepared in 62% isolated yield by addition of the neutral β-diketimine H[Me$_3$NN] to copper *t*-butoxide in toluene. An X-ray structure of **3** shows that the bridging toluene ligand exhibits η^2-bonding to each Cu center via four contiguous C atoms. Reaction of the dicopper **3** with 1 equiv. N$_2$CPh$_2$ provides {[Me$_3$NN]Cu}$_2$(μ-CPh$_2$) (**4**) as purple crystals in 70% isolated yield. Dicopper carbene **4** possesses a Cu–Cu distance of 2.485(1) Å in the solid state and dissociates a [Me$_3$NN]Cu fragment in arene solvents to provide low concentrations of [Me$_3$NN]Cu=CPh$_2$ (**2**) and [Me$_3$NN]Cu(arene). DFT calculations performed on terminal carbene **2** and dicopper carbene **4** illustrate relationships between these two bonding modes and suggest electrophilic reactivity at the carbene carbon atom bound to Cu. Dicopper carbene **4** undergoes efficient carbene transfer to HC≡CPh and PPh$_3$ resulting in the formation of 1,3,3-triphenylcyclopropene and Ph$_3$P=CPh$_2$ while reaction with the isocyanide CNAr (Ar = 2,6-Me$_2$C$_6$H$_3$) results in loss of the carbene as Ph$_2$C=CPh$_2$. In each case, the [Me$_3$NN]Cu fragment is trapped by the incoming nucleophile as the three-coordinate [Me$_3$NN]Cu(L). Reaction of **4** with O$_2$ rapidly generates benzophenone and {[Me$_3$NN]Cu}$_2$(μ-OH)$_2$.
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1. Introduction

Over the last 40 years, soluble copper(I) and copper(II) complexes have been used in conjunction with α-diazoesters N$_2$CHC(O)OR to cyclopropanate alkenes and have played an important role in the development of this valuable group transfer reaction [1]. The earliest successful example of an enantioselective homogeneous metal catalyst employed chiral copper salicylaldimine complexes which resulted in asymmetric induction in the *cis/trans* cyclopropane mixture formed in the reaction of styrene with N$_2$CHCO$_2$R (R = ethyl, Ph) [2]. This asymmetric induction, as well as systematic changes in the cyclopropane product distribution as a function of steric bulk of the P(OR)$_3$ ligand in a [(RO)$_3$PCuCl] catalyst system [3,4], suggested the intermediacy of a copper–carbene complex.

Several mechanistic [5–8] and theoretical [8–11] studies that implicate Cu(I) carbenes [Cu]=CRR′ as the active species in copper-catalyzed cyclopropanation support these early proposals, though such catalytically active Cu(I) carbenes have proven elusive. A transient copper carbene has been identified via time-resolved FTIR spectroscopy upon addition of N$_2$CHCO$_2$Me to a cationic bis(oxazoline) Cu(I) precatalyst [12]. Employing a neutral Cu(I) complex featuring the strongly donating iminophosphanimide ligand, Hofmann demonstrated that [Bu$^t_2$P(NSiMe$_3$)$_2$-κ^{2}N]Cu(ethylene) reacts with N$_2$C(Ph)(C(O)OMe) to give a mixture in which the carbene [Bu$^t_2$P(NSiMe$_3$)$_2$-κ^{2}N]Cu=C(Ph)(C(O)OMe)

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could be identified by low temperature ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy [13]. Moreover, the presence of two inequivalent Bu^t groups indicated that the carbene is orthogonal to the backbone of the bidentate *N,N*-donor ligand.

Barluenga has used copper salts to catalyze carbene coupling in otherwise thermally stable chromium Fischer carbene complexes of the type (CO)$_5$Cr=C(OR)(R′) to give the alkenes R′(OR)C=C(OR)R′ [14,15]. In one case, a crystallographically copper carbene [Cu{=CR^1(OR^2)}-(MeCN)(OEt$_2$)]$^+$ was isolated from addition of [Cu(NCMe)$_4$][PF$_6$] to (CO)$_5$Cr=CR^1(OR^2) (R^1 = (*E*)-CH=CH-2-furyl; R^2 = menthyl) [14]. While catalytically inactive towards cyclopropanation, dimerization of the carbene in [Cu{=CR^1(OR^2)}(MeCN)(OEt$_2$)]$^+$ is induced upon addition of PBu$_3$. As this Fischer copper carbene com- plex is prepared via transmetallation from (CO)$_5$Cr=CR^1(OR^2), it is reasonable to expect bimetallic [M](μ-CRR′)[Cu] species as intermediates [16]. In fact, spectroscopic data have been reported for two copper-containing bimetallic carbenes Cp(CO)Ru(μ-CPh$_2$)-(CuCl)$_2$ and Cp(CO)Ru(μ-CPh$_2$)CuCp prepared by addition of CuCl to Cp(CO)Rh=CPh$_2$ followed by treatment with NaCp [17].

We recently reported the use of strongly donating β-diketiminato ligands to stabilize the crystallographically characterized copper carbenes {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (**1**) and [Me$_3$NN]Cu=CPh$_2$ (**2**) [18]. Dicopper carbene **1** possesses Cu–C distances of 1.922(4) and 1.930(4) Å as well as a Cu–Cu distance of 2.4635(7) Å found in many polynuclear Cu(I) aryls in which the Cu(I) centers are bridged by sp^2-hybridized C atoms [19]. The considerably shortened Cu–C distance of 1.834(3) Å in the terminal carbene **2** supports significant Cu=C multiple-bond character. The dicopper carbene dissociates a [β-diketiminato]Cu fragment in arene solvents to give an equilibrium mixture of terminal carbene [Cu]=CPh$_2$ and a solvento species [Cu](arene) (Scheme 1). Solutions of these copper carbenes are active in the cyclopropanation of styrene derivatives. Activation parameters for the
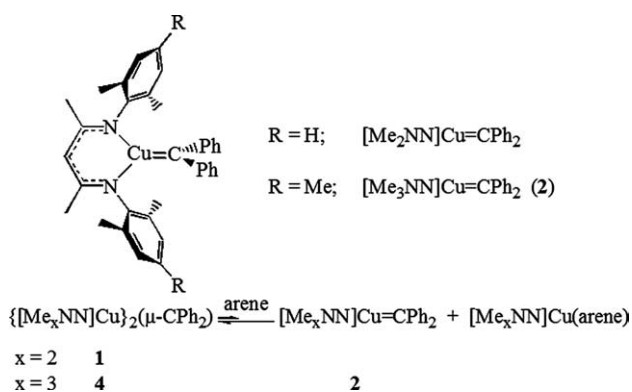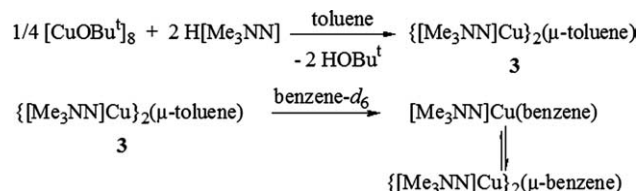
second-order cyclopropanation of styrene by terminal carbene **2** ($\Delta H^{\neq} = 10.4(3)$ kcal/mol and $\Delta S^{\neq} = -32.3(9)$ cal/mol K) were identified employing dioxane as solvent [18].

Herein we report an improved synthesis for a synthon to the [Me$_3$NN]Cu fragment as well as the isolation of the dicopper carbene {[Me$_3$NN]Cu}$_2$(μ-CPh$_2$) (**4**) previously identified in the decomposition of [Me$_3$NN]-Cu=CPh$_2$ (**2**) in arene solvents. DFT studies on full models of **2** and **4** have been performed to illustrate bonding relationships between these copper carbenes that interconvert in solution. Reactions with selected nucleophiles as well as dioxygen have been carried out to probe the substrate dependence on the ultimate reactivity pathway for the diphenylcarbene functionality.
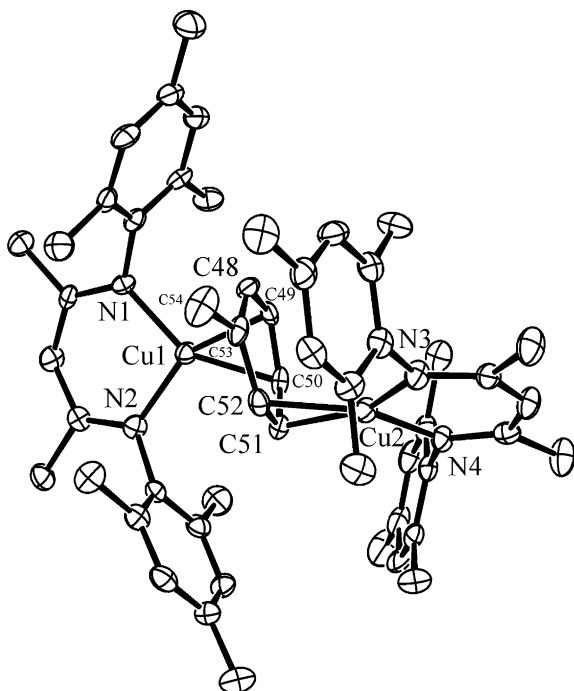
2. Results and Discussion

2.1. Improved synthesis of a synthon to the [Me$_3$NN]Cu fragment

We previously reported that the Cu(I) β-diketiminate [Me$_3$NN]Cu(toluene) could be prepared by addition of the thallium derivative Tl[Me$_3$NN] to CuBr suspended in toluene [18]. We find that the addition of the neutral β-diketimine H[Me$_3$NN] to copper *t*-butoxide in toluene more conveniently provides the colorless {[Me$_3$NN]-Cu}$_2$(μ-toluene) (**3**) in 62% yield (Scheme 2). The X-ray structure of **3** (Fig. 1; Table 1) illustrates the bridging nature of the toluene ligand which coordinates to each [Me$_3$NN]Cu fragment in an η^2-manner through C49–C52 with Cu–C distances of 2.027(5)–2.077(5) Å (Table 2) similar to those found in two other [β-diketiminato]Cu(η^2-benzene) adducts [20,21]. Each coordinated C–C bond is roughly coplanar with the β-diketiminate backbone. Two sets of alternately shorter (1.360(7)–1.403(7) Å) and longer (1.436(7)–1.439(7) Å) C–C distances are found within the bridging toluene ligand, suggesting that coordination to two [Me$_3$NN]Cu fragments somewhat attenuates the aromaticity of this ring. Consistent with the ability of the [β-diketiminato]Cu fragment to bind alkenes [22], two of the three short C–C bonds of toluene coordinate to the [Me$_3$NN]Cu fragments in **3**. It is curious to note that under similar synthetic conditions, the slightly smaller Cu(I) β-diketiminato fragment [Me$_2$NN]Cu crystallizes as the

R = H; [Me$_2$NN]Cu=CPh$_2$

R = Me; [Me$_3$NN]Cu=CPh$_2$ (**2**)

{[Me$_x$NN]Cu}$_2$(μ-CPh$_2$) $\xrightleftharpoons{\text{arene}}$ [Me$_x$NN]Cu=CPh$_2$ + [Me$_x$NN]Cu(arene)

x = 2   **1**
x = 3   **4**   **2**

Scheme 1. Reversible interconversion of β-diketiminato dicopper and terminal carbenes.

1/4 [CuOBu^t]$_8$ + 2 H[Me$_3$NN] $\xrightarrow[\text{- 2 HOBu}^t]{\text{toluene}}$ {[Me$_3$NN]Cu}$_2$(μ-toluene) **3**

{[Me$_3$NN]Cu}$_2$(μ-toluene) **3** $\xrightarrow{\text{benzene-}d_6}$ [Me$_3$NN]Cu(benzene) $\updownarrow$ {[Me$_3$NN]Cu}$_2$(μ-benzene)

Scheme 2. Synthesis and solution behavior of **3**.

Fig. 1. X-ray structure of {[Me₃NN]Cu}₂(μ-toluene) (3).

Table 1
Crystallographic data, collection parameters, and refinement details for **3** and **4**

Compound	**3**	**4**[a]
Formula	$C_{53}H_{66}Cu_2N_4$	$C_{59}H_{68}Cu_2N_4$
Molecular weight	886.18	960.25
Temperature (K)	173(2)	173(2)
Crystal description	Rod	Block
Crystal color	Colorless	Dark purple
Crystal size (mm³)	$0.18 \times 0.16 \times 0.10$	$0.37 \times 0.33 \times 0.18$
System	Monoclinic	Orthorhombic
Space group	$P2(1)/n$	$Pccn$
a (Å)	14.417(2)	26.213(9)
b (Å)	13.915(2)	18.711(7)
c (Å)	23.815(4)	22.001(8)
α (°)	90.00	90.00
β (°)	102.253(3)	90.00
γ (°)	90.00	90.00
Z	4	8
θ Range (°)	1.52–24.75	1.34–25.00
Measured reflections	22 637	42 494
Unique reflections	7897	9224
$R_{(int)}$	0.1000	0.0991
GOF of F^2	0.978	0.979
R_1 ($I > 2\sigma(I)$)	0.0606	0.0704
wR_2 (all data)	0.1466	0.1850
Largest difference peak and hole (e Å⁻³)	0.577 and −0.426	1.053 and −0.799

[a] SQUEEZE subroutine of PLATON[§] employed in refinement of **4** which possesses ca. 0.75 equivalents of disordered pentane per molecule of **4**. [§]A.L. Spek, Acta Crystallogr. A46 (1990), C-34.

{[Me₂NN]Cu}₂ dimer in which each Cu center engages in an η²-arene interaction with an opposing *N*-aryl ring [23].

Table 2
Bond distances (Å) and angles (°) in **3**

Bond distances (Å)	
Cu1–N1	1.942(4)
Cu1–N2	1.922(4)
Cu2–N3	1.930(4)
Cu2–N4	1.933(4)
Cu1–C49	2.027(5)
Cu1–C50	2.077(5)
Cu2–C51	2.044(5)
Cu2–C52	2.072(5)
C48–C49	1.437(7)
C49–C50	1.398(7)
C50–C51	1.436(7)
C51–C52	1.403(7)
C48–C53	1.360(7)
C52–C53	1.439(7)
Bond angles (°)	
N1–Cu1–N2	99.03(17)
N3–Cu2–N4	98.79(17)
C49–Cu1–C50	39.8(2)
C51–Cu2–C52	39.9(2)
N1–Cu1–N2/C49–Cu1–C50	5.5
N3–Cu2–N4/C51–Cu2–C52	4.4
N1–Cu1–N2/N3–Cu2–N4	35.5

Dissolution of {[Me₃NN]Cu}₂(μ-toluene) (**3**) in benzene-d_6 results in ¹H NMR spectra that are nearly C_{2v}-symmetric on the NMR timescale, but indicate the presence of a second species. After standing overnight, the somewhat broad *N*-aryl *m*-H and backbone C–H singlets first observed at δ 6.913 and 4.791 ppm convert to two sets of sharp singlets at δ 6.920 and 6.809 ppm and δ 4.803 and 4.763 ppm. We attribute this to slow, irreversible conversion to two separate Cu(I) benzene complexes (Scheme 2). On the basis of the nearly identical chemical shifts originally observed, we attribute the signals at δ 6.920 and 4.803 ppm to {[Me₃NN]Cu}₂(μ-benzene). A second species in slightly lower abundance is tentatively assigned as the monomeric solvento complex [Me₃NN]Cu(η²-benzene).

2.2. Synthesis and characterization of {[Me₃NN]Cu}₂-(μ-CPh₂) (**4**)

Careful addition of 1 equiv. of N₂CPh₂ to {[Me₃NN]-Cu}₂(μ-toluene) (N₂CPh₂:Cu ratio = 1:2) in ether leads to immediate effervescence and formation of a deep purple solution. Crystallization from pentane leads to the isolation of {[Me₃NN]Cu}₂(μ-CPh₂) in 70% yield (Scheme 3). The X-ray structure of {[Me₃NN]Cu}₂(μ-CPh₂) · 0.75 pentane (Fig. 2; Table 1) is very similar to

{[Me₃NN]Cu}₂(μ-toluene) $\xrightarrow[\text{- N}_2,\text{ toluene}]{\text{N}_2\text{CPh}_2\atop\text{ether}}$ {[Me₃NN]Cu}₂(μ-CPh₂)
              3   **4**
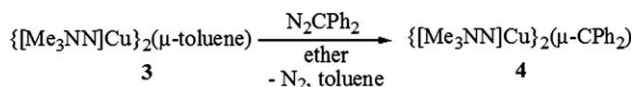
Scheme 3. Synthesis of dicopper carbene **4**.
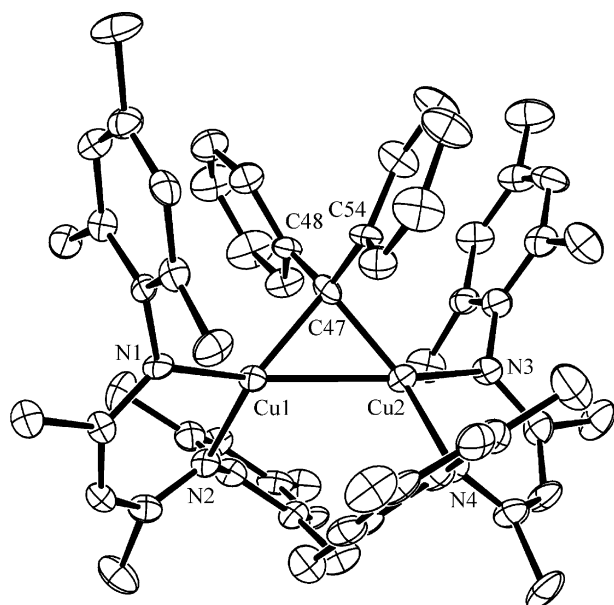
Fig. 2. X-ray structure of $\{[Me_3NN]Cu\}_2(\mu\text{-}CPh_2)$ (**4**).

that of $\{[Me_2NN]Cu\}_2(\mu\text{-}CPh_2)$ (**1**) with Cu–C bond distances of 1.931(5) and 1.933(5) Å (1.922(4) and 1.930(4) Å in **1** [18]) with a Cu–Cu distance of 2.485(1) Å (2.4635(7) Å in **1**) (Table 3). As in **1**, each [β-diketiminato]Cu fragment is roughly orthogonal to the diphenylcarbene functionality as well as orthogonal to each other. Since the initial report of **1**, Gishig and Togni [24] have shown that N-heterocyclic carbenes (NHCs) can also adopt a dicopper binding mode in the coordination of a bis(phosphine)-containaing NHC to copper(I) iodide. The four-coordinate Cu centers in the $[Cu]_2(\mu\text{-}NHC)$ complex exhibit significantly longer Cu–C distances (2.113(5) and 2.174(5) Å) and a shorter Cu–Cu distance (2.3561(13) Å), suggesting a difference in the

Table 3
Bond distances (Å) and angles (°) in **4**

Bond distances (Å)	
Cu1–C47	1.933(5)
Cu2–C47	1.931(5)
Cu1–Cu2	2.485(1)
Cu1–N1	1.971(4)
Cu1–N2	1.963(4)
Cu2–N3	1.981(4)
Cu2–N4	1.967(4)
C47–C48	1.476(7)
C47–C54	1.469(7)
Bond angles (°)	
N1–Cu1–N2	95.68(18)
N3–Cu2–N4	96.06(18)
Cu1–C47–Cu2	80.1(2)
C49–C47–C54	114.9(4)
N1–Cu1–N2/C48–C47–C54	88.2
N3–Cu2–N4/C48–C47–C54	85.7
N1–Cu1–N2/N3–Cu2–N4	85.9

nature of metal–carbene bonding from the dicopper diphenylcarbenes **1** and **4**.

The dicopper carbene $\{[Me_3NN]Cu\}_2(\mu\text{-}CPh_2)$ (**4**) was first observed in solution during the thermal decomposition of the terminal carbene $[Me_3NN]Cu=CPh_2$ (**2**). In benzene-d_6, the bridging carbene of **4** appears at δ 189.0 ppm in the $^{13}C\{^1H\}$ NMR spectrum of **4** (δ 189.4 ppm for **1**). As with **1**, the room temperature ^1H NMR spectrum of **4** in toluene-d_8 indicates a fluxional process assigned as twisting of the bridging CPh_2 ligand about the vector containing the carbene carbon that bisects the Cu–Cu axis. Low temperature (−70 °C) ^1H NMR spectra show the presence of a single backbone C–H resonance at δ 4.99 ppm as well as eight N-aryl and backbone Me resonances from δ 2.86–1.18 ppm, consistent with the approximate C_2 conformation observed in the solid state. As the temperature is raised, both $[Me_3NN]Cu=CPh_2$ (**2**) and $[Me_3NN]Cu(toluene)$ are observed in identical concentrations by their characteristic backbone C–H ^1H NMR signals at δ 4.92 and 4.76 ppm prior to the onset of thermal loss of the CPh_2 functionality as $Ph_2C=CPh_2$. Notably, the relative ratios of $[Cu]_2(\mu\text{-}CPh_2)$, $[Cu]=CPh_2$, and $[Cu](arene)$ species at room temperature do not differ appreciably between the $[Me_2NN]Cu$ and $[Me_3NN]Cu$ systems under comparable concentrations (Scheme 1). Thus the extra steric bulk of the N-aryl p-Me substituents does not overwhelmingly shift the position of equilibrium, despite the initial isolation of the terminal carbene employing the $[Me_3NN]Cu$ fragment.

2.2.1. DFT studies – bonding analysis of $[Me_3NN]Cu=CPh_2$ (2) and $\{[Me_3NN]Cu\}_2(\mu\text{-}CPh_2)$ (4)

DFT calculations (ADF 2002.3–ZORA/TZ2P(+)) were performed on the full systems $[Me_3NN]Cu=CPh_2$ (**2**) and $\{[Me_3NN]Cu\}_2(\mu\text{-}CPh_2)$ (**4**) to illustrate the bonding relationships present between these structurally characterized terminal and dicopper carbenes, emphasizing the nature of the Cu–C π-interactions. Starting with atomic coordinates from the X-ray structures of **2** and **4**, a geometry optimization was carried out in each case. With the exception of the Cu–C distance in terminal carbene **2**, the Cu–ligand distances are marginally longer (0.03–0.04 Å) in the calculated structures (Tables 4 and 5), but otherwise consistent with the X-ray data.

Figs. 3 and 4 illustrate molecular orbitals resulting from σ and π-bonding interactions between the $[Me_3NN]Cu$ and CPh_2 fragments in the terminal carbene $[Me_3NN]Cu=CPh_2$ (**2**). A low-laying filled level (HOMO-15; −7.39 eV) constitutes the Cu–C(carbene) σ-bonding interaction (Fig. 3), comprised of a hybrid Cu orbital ($3d_{z^2}$, $3d_{x^2-y^2}$, and $4p_z$; 21.7% total) and the C(carbene) p_z (9.8%) orbital. A filled level (HOMO-2; −4.83 eV) within the frontier orbitals represents the corresponding σ*-antibonding interaction and is predominantly Cu (48.0%) in character. The Cu–C(carbene)

Table 4
Bond distances (Å) and angles (°) in **2** (DFT)

Bond distances (Å)	
Cu–C24	1.829
Cu–N1	1.940
Cu–N2	1.958
Bond angles (°)	
N1–Cu–N2	94.7
Cu–C24–C25	123.3
Cu–C24–C31	119.1

Cu-C σ-bonding
HOMO-15
(**-7.39 eV**)

Cu-C σ*-antibonding
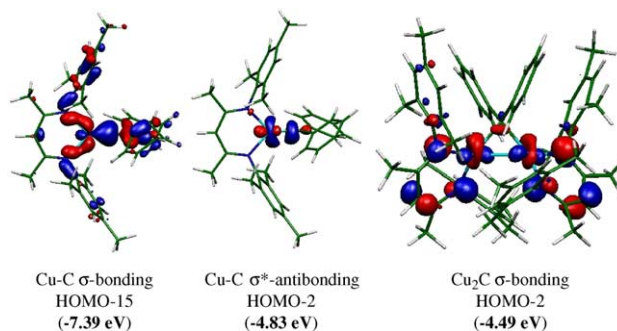HOMO-2
(**-4.83 eV**)

Cu₂C σ-bonding
HOMO-2
(**-4.49 eV**)

Fig. 3. Selected σ-bonding interactions in **2** and **4**.

Table 5
Bond distances (Å) and angles (°) in **4** (DFT)

Bond distances (Å)	
Cu1–C47	1.964
Cu2–C47	1.959
Cu1–N1	2.009
Cu1–N2	1.998
Cu2–N3	2.006
Cu2–N4	2.008
Cu1–Cu2	2.521
Bond angles (°)	
N1–Cu1–N2	95.9
N3–Cu2–N4	95.7
Cu1–C47–Cu2	80.0
C49–C47–C54	114.9

π-molecular orbitals are higher in energy (Fig. 4). The filled Cu–C(carbene) π-bonding orbital (HOMO-1; −4.51 eV) is comprised of 19.1% Cu and 6.3% C(carbene) p_y character. The LUMO (−3.20 eV) originates from the π*-interaction between the Cu and carbene fragments consisting of 32.2% C(carbene) and 14.3% Cu d character. Including the participation the two carbene phenyl rings, the LUMO is over 66% localized on the CPh₂ moiety. The relative Cu and C(carbene) contributions to the HOMO and LUMO of [Me₃NN]-Cu=CPh₂ clearly indicate a significant backbonding interaction from the d^{10} Cu(I) center to the carbene acceptor orbital. The substantial energy differences of these π and π* molecular orbitals as compared to the
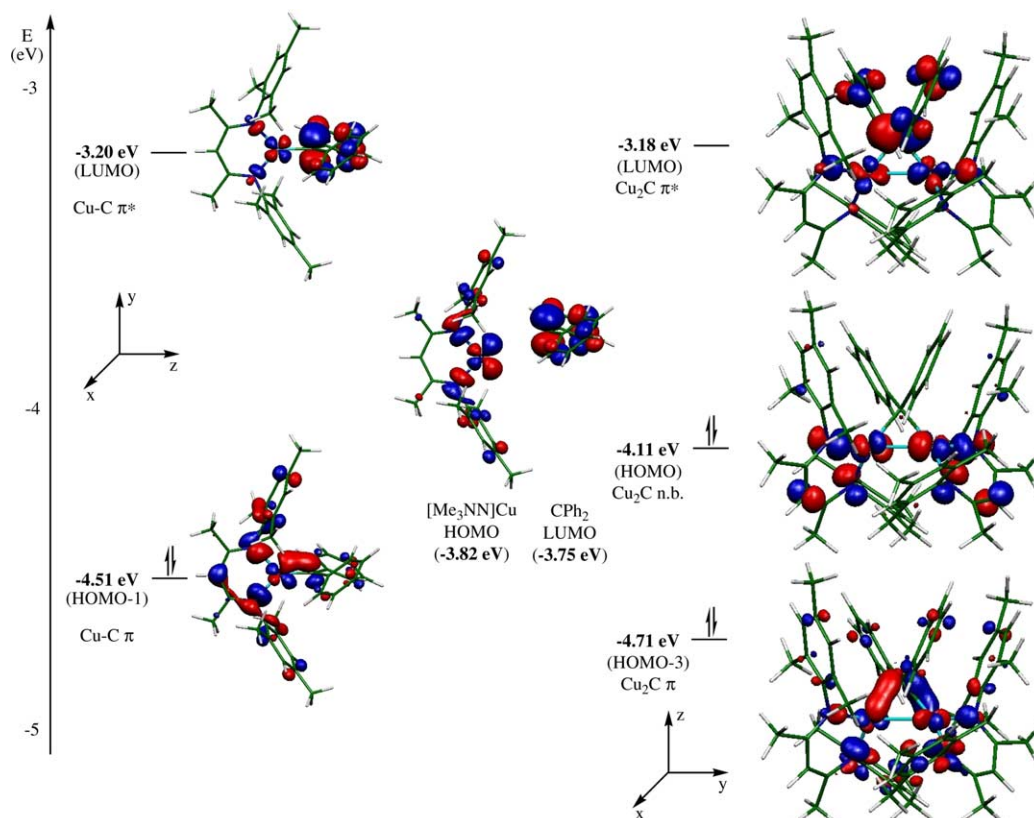

Fig. 4. Cu–C(carbene) π-bonding interactions in **2** (left) and **4** (right).

fragment [Me$_3$NN]Cu HOMO (−3.82 eV) and CPh$_2$ LUMO (−3.75 eV) (employing same coordinates from [Me$_3$NN]Cu=CPh$_2$ calculation) further indicate the importance of π-backbonding in the overall Cu–C(carbene) interaction present in **2**.

In the dicopper carbene {[Me$_3$NN]Cu}$_2$(μ-CPh$_2$) (**4**), two d^{10} Cu centers can interact with the CPh$_2$ π-acceptor orbital. As previously illustrated with the simplified model {[H$_5$C$_3$N$_2$]Cu}$_2$(μ-CH$_2$) [18], a 3-center, 4-electron π-interaction ensues. The HOMO-3 (−4.71 eV) represents the π-bonding interaction involving both Cu centers (17.0% Cu character) and the carbene acceptor orbital (6.7% C(carbene) character). The HOMO (−4.11 eV) is a Cu$_2$C non-bonding (or weakly Cu–Cu π-antibonding) interaction involving the two [Me$_3$NN]-Cu fragments (26.8% Cu d character) in which the C(carbene) atom lies essentially on a nodal plane. The LUMO (−3.18 eV) originates from the Cu$_2$C π*-interaction and is comprised of 26.8% C(carbene) p and 19.2% Cu character. As with [Me$_3$NN]Cu=CPh$_2$, the relative Cu and C(carbene) constituencies of the π and π* molecular orbitals of dicopper carbene **4** are consistent with backbonding from the Cu d^{10} centers to the diphenylcarbene functional group.

Further inspection of the frontier molecular orbitals reveals two additional features. While the availability of a 3-center, 4-electron π-bonding interaction appears to engender enhanced thermal stability to the dicopper carbene as compared to a terminal carbene, σ-interactions within the Cu$_2$C framework (c.f. HOMO-2) certainly contribute Cu–Cu bonding. Secondly, the frontier orbital energy levels of [Me$_3$NN]Cu=CPh$_2$ are significantly higher than in the pared down system [H$_5$C$_3$N$_2$]Cu=CH$_2$ (LUMO = −3.44 eV) [18]. Coupled with the steric bulk of the β-diketiminato and carbene substituents, inductive and resonance effects are also important in allowing the isolation of these reactive species. Moreover, the significant involvement of the diphenylcarbene moiety in the LUMO of both **2** and **4** suggests that these copper carbenes should exhibit marked electrophilic character at the carbene C atom.

2.3. Reactions of {[Me$_3$NN]Cu}$_2$(μ-CPh$_2$) (**4**) with nucleophiles

We chose to survey the reactivity of the dicopper carbene {[Me$_3$NN]Cu}$_2$(μ-CPh$_2$) (**4**) owing to its greater thermal stability as compared to the terminal [Me$_3$NN]-Cu=CPh$_2$ (**2**) which slowly decomposes in arene solvents to generate the carbene coupling product Ph$_2$C=CPh$_2$ as well as **4** and [Me$_3$NN]Cu(arene). In arene solvents, the dicopper carbenes {[Me$_x$NN]-Cu}$_2$(μ-CPh$_2$) are convenient sources of the corresponding terminal carbenes as the former are in equilibrium with [Me$_x$NN]Cu=CPh$_2$ and [Me$_x$NN]Cu(arene) (Scheme 1).

As a basis for comparison, styrene and α-methylstyrene undergo efficient carbene transfer from {[Me$_2$NN]-Cu}$_2$(μ-CPh$_2$) to give the corresponding cyclopropanes. In contrast, reactions with 1,2-disubstituted olefins such as *trans*-β-methylstyrene and cyclooctene are more sluggish and result in predominant Ph$_2$C=CPh$_2$ formation from the thermal decomposition of the copper carbene, even in the presence of 50 equiv. olefin [18]. It should be noted that [Me$_3$NN]Cu=CPh$_2$ cleanly decomposes in dioxane via first-order kinetics to give 1/2 equiv. Ph$_2$C=CPh$_2$ with activation parameters $\Delta H^{\neq} = 21(1)$ kcal/mol and $\Delta S^{\neq} = -8(3)$ cal/mol K [18].

2.4. Reaction of {[Me$_3$NN]Cu}$_2$(μ-CPh$_2$) (**4**) with phenylacetylene

Reaction of {[Me$_3$NN]Cu}$_2$(μ-CPh$_2$) with 10 equiv. phenylacetylene in benzene-d_6 results in a change in color from intense purple to light green over 15 min. GC/MS analysis indicates that efficient carbene transfer to phenylacetylene occurs as the major Ph$_2$C-containing species exhibits an m/z of 268 assigned as 1,3,3-triphenylcyclopropene [25]; little Ph$_2$C=CPh$_2$ was present (Scheme 4). ^{1}H NMR analysis shows that the resulting [Me$_3$NN]Cu fragment was trapped as the phenylacetylene adduct [Me$_3$NN]Cu(η^2-HC≡CPh) (**5**) by characteristic signals at δ 4.871 and 3.997 ppm attributed to new backbone C–H and coordinated H–C≡CPh resonances. The alkyne adduct **5** can be isolated as colorless crystals from pentane by addition of 2 equiv. phenylacetylene to {[Me$_3$NN]Cu}$_2$(μ-toluene) (Scheme 5).

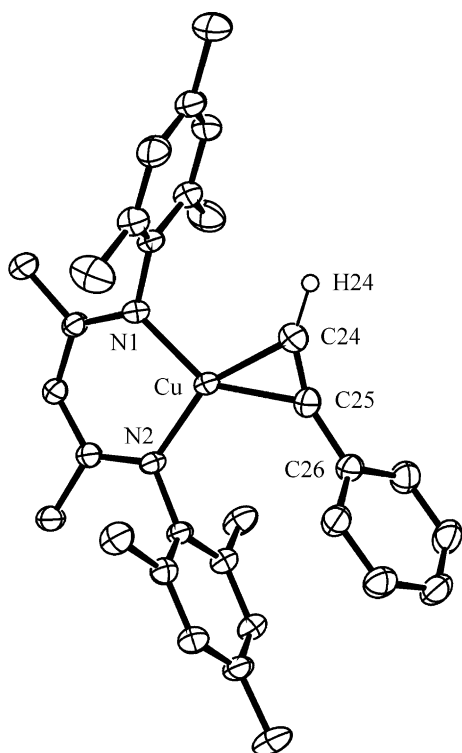The X-ray structure of [Me$_3$NN]Cu(η^2-HC≡CPh) · 0.5 pentane (Fig. 5; Table 6) shows that the phenylacetylene ligand is coplanar with the β-diketiminato backbone, reminiscent of the structures of [Me$_2$NN]-Cu(η^2-ethylene) [22] and [Me$_2$NN]Cu(η^2-styrene) [22] as well as other cationic Cu(I) alkene and alkyne complexes supported by chelating diimines such as bipy [26] and 1,10-phenanthroline [27]. This orientation
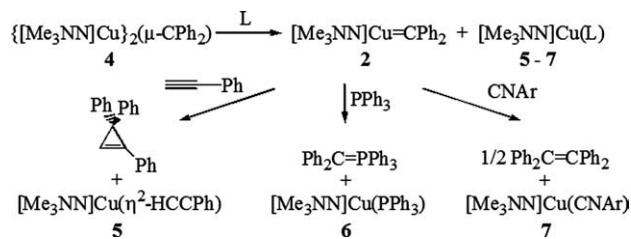
Scheme 4. Reactivity of dicopper carbene **4** with nucleophiles.
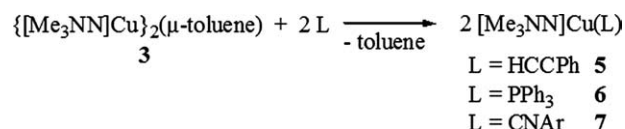
Scheme 5. Syntheses of [Me$_3$NN]Cu(L) (**5–7**) from **3**.

Fig. 5. X-ray structure of [Me$_3$NN]Cu(η^2-HC≡CPh) (**5**).

(1.183–1.193 Å) [28] (Table 7). In addition, the C–C bond in **5** is also longer than that reported in the cationic [(phen)Cu(η^2-HCCPh)]$^+$ (1.218(13) Å) [27] as well a neutral Cu(I) phenylacetylene complex supported by a monoanionic, tripodal Kläui ligand (1.208(7) Å) [29]. Further evidence for an enhanced backbonding interaction is provided by variable temperature ^{1}H NMR spectra which reveal inequivalent sets of Ar-H, *p*-Me, *o*-Me, and backbone Me resonances at low temperature. The value $\Delta G^{\neq} = 13.4(3)$ kcal/mol at −10 °C was calculated from the coalescence of the backbone-Me signals, notably higher than the $\Delta G^{\neq} = 10.7(3)$ kcal/mol at −58 °C reported for rotation of the styrene ligand in [Me$_2$NN]-Cu(η^2-H$_2$C=CHPh) [22]. The coordinated alkyne exhibits a characteristic C≡C stretch at 1984 cm^{-1}.

allows for efficient overlap of the HOMO of the [Me$_3$NN]Cu fragment (Fig. 4) with an alkyne C–C π^* orbital. The alkyne C24–C25 distance of 1.236(3) Å in **5** is longer than that reported for free phenylacetylene

Table 7
Bond distances (Å) and angles (°) in **5**

Bond distances (Å)	
Cu–N1	1.924(2)
Cu–N2	1.914(2)
Cu–C24	1.919(2)
Cu–C25	1.983(2)
C24–C25	1.236(3)
C25–C26	1.458(3)
Bond angles (°)	
N1–Cu–N2	98.68(7)
C24–Cu–C25	36.88(9)
C24–C25–C26	158.5(2)
C25–C24–H24	147.5
N1–Cu–N2/C24–Cu–C25	2.5

Table 6
Crystallographic data, collection parameters, and refinement details for **5–7**

Compound	**5**	**6**	**7**
Formula	C$_{33.5}$H$_{36}$CuN$_2$[a]	C$_{41}$H$_{44}$CuN$_2$P	C$_{32}$H$_{38}$CuN$_2$
Molecular weight	530.18	659.29	528.19
Temperature (K)	173(2)	173(2)	173(2)
Crystal description	Block	Chunk	Block
Crystal color	Colorless	Colorless	Yellow
Crystal size (mm^3)	$0.39 \times 0.34 \times 0.18$	$0.34 \times 0.29 \times 0.26$	$0.45 \times 0.41 \times 0.36$
System	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/n$	$P2/n$
a (Å)	8.2895(6)	10.9249(19)	17.565(7)
b (Å)	13.5421(11)	16.301(3)	7.758(3)
c (Å)	15.1011(12)	20.081(4)	22.375(9)
α (°)	113.864(1)	90.00	90.00
β (°)	103.487(1)	101.108(3)	107.762(6)
γ (°)	95.267(1)	90.00	90.00
Z	2	4	4
θ Range (°)	1.54–28.29	1.62–28.32	1.30–28.26
Measured reflections	16 104	32 022	24 490
Unique reflections	6886	8509	6838
$R_{(int)}$	0.0269	0.0688	0.0256
GOF of F^2	1.111	1.074	1.067
R_1 ($I > 2(I)$)	0.0400	0.0646	0.0343
wR_2 (all data)	0.1230	0.1585	0.1028
Largest difference peak and hole (e Å^{-3})	0.721 and −0.585	0.592 and −1.066	0.362 and −0.332

[a] Some H atoms on the disordered pentane of solvation not included in refinement.

2.4.1. Reaction of {[Me₃NN]Cu}₂(μ-CPh₂) (4) with triphenylphosphine

Reaction of dicopper carbene 4 with excess PPh₃ (ca. 8 equiv.) in benzene-d_6 results in a similar color change over 5 min as described above, indicating consumption of the dicopper carbene. Two sharp ³¹P NMR resonances at δ 7.36 and −4.79 ppm signal the presence of the carbene transfer product Ph₃P=CPh₂ [30–32] as well as free PPh₃, respectively. In addition, a broad resonance at δ 5.20 ppm indicates the formation of [Me₃NN]Cu(PPh₃) (6) (Scheme 4) which can be prepared in 92% yield as colorless crystals by addition of 2 equiv. PPh₃ to a solution of {[Me₃NN]Cu}₂(μ-toluene) (Scheme 5). Integration of the Ph₃P=CPh₂ ³¹P NMR resonance vs. that of [Me₃NN]Cu(PPh₃) indicates that the ylide was formed in 76% yield. GC/MS analysis suggests that Ph₂C=CPh₂ accounts for the remainder of the CPh₂ fragment lost from dicopper carbene 4.

The X-ray structure of [Me₃NN]Cu(PPh₃) (Fig. 6; Table 6) shows trigonal coordination at Cu with a Cu–P distance of 2.161(1) Å (Table 8), similar to Cu–P distances (2.134(1) and 2.1877(7) Å) found in two other neutral, three-coordinate Cu(I) complexes supported by chelating anionic *N,N*-donors [33,34]. The Cu–N distances in 6 (1.940(2) and 1.955(2) Å) are longer than in the phenylacetylene adduct 5 (1.914(2) and 1.924(2) Å) suggestive of a more electron-rich Cu(I) center. At typical NMR concentrations in benzene-d_6 (ca. 0.1 mM), the ³¹P NMR resonance for the coordinated PPh₃ ligand is always broad, suggesting that the arene solvent is somewhat competitive with PPh₃ for binding to the [Me₃NN]Cu fragment.
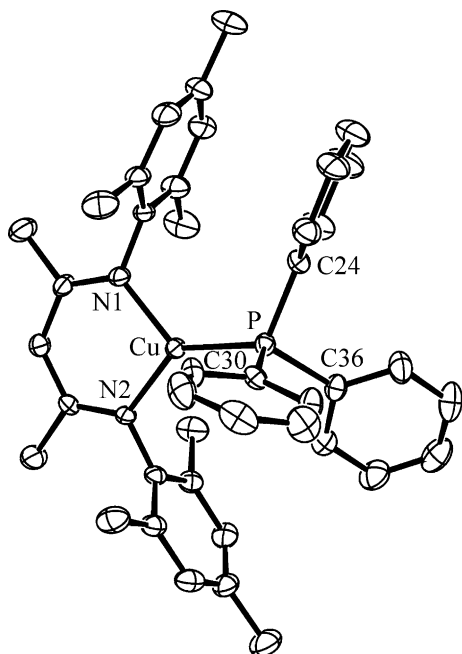
Table 8
Bond distances (Å) and angles (°) in 6

Bond distances (Å)	
Cu–N1	1.955(2)
Cu–N2	1.940(2)
Cu–P	2.161(1)
P–C24	1.830(3)
P–C30	1.829(3)
P–C36	1.892(3)

Bond angles (°)	
N1–Cu–N2	97.77(10)
N1–Cu–P	126.79(8)
N2–Cu–P	135.32(8)

2.4.2. Reaction of {[Me₃NN]Cu}₂(μ-CPh₂) (4) with 2,6-dimethylphenyl isocyanide

Reaction of dicopper carbene 4 with 2,6-dimethylphenyl isocyanide also induces diphenylcarbene loss from {[Me₃NN]Cu}₂(μ-CPh₂), but GC/MS analysis indicates that Ph₂C=CPh₂ is the predominant CPh₂-containing product (Scheme 4). The [Me₃NN]Cu fragment is trapped as [Me₃NN]Cu(CNAr) (7) (Ar = 2,6-Me₂C₆H₃) which can be isolated in 91% yield as yellow crystals yield by addition of 2 equiv. CNAr to {[Me₃NN]Cu}₂(μ-toluene) (3) (Scheme 5). The X-ray structure of 7 (Fig. 7; Tables 6 and 9) shows trigonal coordination at Cu, and is very similar to two β-diketiminato Cu(I) adducts reported by Tolman [35,36]. The isocyanide adduct 7 possesses C_{2v}-symmetry in solution with a backbone ¹H NMR resonance at δ 5.037 ppm and a CN stretch in its IR spectrum at 2121 cm⁻¹.

This linear σ-donor, π-acid ligand very efficiently induces loss of diphenylcarbene from 4 as Ph₂C=CPh₂. Upon addition of 2 equiv. of CNAr to 4 in benzene-

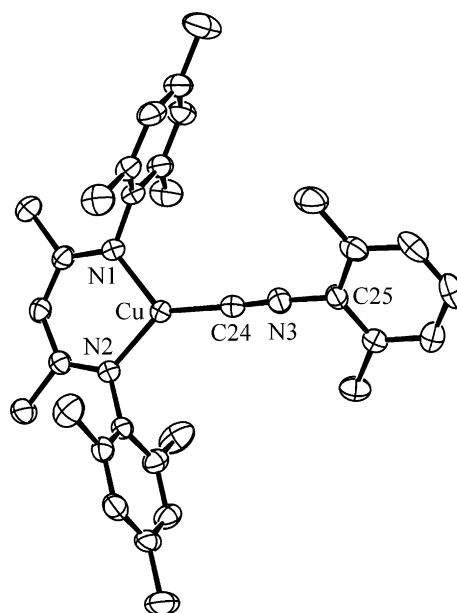Fig. 6. X-ray structure of [Me₃NN]Cu(PPh₃) (6).

Fig. 7. X-ray structure of [Me₃NN]Cu(CNAr) (7).

Table 9
Bond distances (Å) and angles (°) in **7**

Bond distances (Å)	
Cu–N1	1.945(1)
Cu–N2	1.926(2)
Cu–C24	1.814(2)
C24–N3	1.159(2)
N3–C25	1.396(2)
Bond angles (°)	
N1–Cu–N2	97.85(6)
N1–Cu–C24	126.63(7)
N2–Cu–C24	135.51(6)
Cu–C24–N3	177.41(15)
C24–N3–C25	177.01(16)

d_6, the predominant Cu-containing species after 10 min is [Me$_3$NN]Cu(CNAr) – less than 5% each of copper carbenes **2** and **4** could be observed by ^{1}H NMR analysis. This is to be contrasted with the significant thermal stability of these mono and dicopper carbenes in arene solvents which exhibit cyclopropanation activity after standing two days at room temperature. In contrast to HC≡CPh and PPh$_3$ which may attack the carbene carbon atom leading to group transfer of the carbene moiety, perhaps the linear isonitrile attacks the Cu-center of [Me$_3$NN]Cu=CPh$_2$ (generated by dissociation of {[Me$_3$NN]Cu}$_2$(μ-CPh$_2$)) with concomitant loss of carbene (Scheme 4).

2.4.3. Reaction of {[Me$_3$NN]Cu}$_2$(μ-CPh$_2$) (**4**) with dioxygen

Reaction of dicopper carbene **4** in ether solvent with dioxygen results in the instantaneous decoloration of the intense purple color of **4** to give a brown solution containing a brown precipitate. GC/MS analysis shows the formation of Ph$_2$C=O as the major Ph$_2$C-containing product (Scheme 6). In accordance with the dioxygen reactivity of [Me$_2$NN]Cu(η^2-ethylene) which forms brown {[Me$_2$NN]Cu}$_2$(μ-OH)$_2$ (v_{OH} = 3646 cm^{-1}) [22] via the intermediacy of a Cu$_2^{III}$(μ-O)$_2$ species [22,36,37], the brown precipitate observed in the reaction of **4** with O$_2$ is likely {[Me$_3$NN]Cu}$_2$(μ-OH)$_2$. This is supported by observation of a sharp IR v(OH) stretch at 3648 cm^{-1} in the precipitate, identical to that observed upon oxygenation of a solution of {[Me$_3$NN]Cu}$_2$(μ-toluene). Such [M]=CPh$_2$ reactivity with dioxygen has been previously observed in the reaction of the aza-macrocycle supported Fe(II) carbene (tmtaa)Fe=CPh$_2$ with O$_2$ to give Ph$_2$C=O and (tmtaa)Fe-O-Fe(tmtaa) [38].
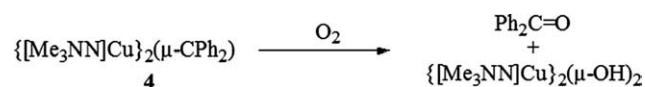
Scheme 6. Reactivity of dicopper carbene **4** with dioxygen.

3. Conclusion

The dicopper carbene {[Me$_3$NN]Cu}$_2$(μ-CPh$_2$) (**4**) has been isolated and crystallographically characterized from the reaction of {[Me$_3$NN]Cu}$_2$(μ-toluene) (**3**) with 1 equiv. N$_2$CPh$_2$. The structural characterization of dicopper carbene **4** allows direct comparisons with the structurally characterized [Me$_3$NN]Cu=CPh$_2$ (**2**). DFT calculations performed on full models of **2** and **4** indicate significant Cu–C(carbene) π-bonding in each which occurs in the dicopper carbene via a 3-center, 4-electron interaction. In both cases, the phenyl substituents of the carbene participate in the complex's LUMO which is predominately diphenylcarbene in character, suggesting electrophilic reactivity at the carbene carbon. Such reactivity is observed with HC≡CPh and PPh$_3$ resulting in carbene group transfer to give 1,3,3-triphenylcyclopropene and Ph$_2$C=PPh$_3$, while the isonitrile CNAr simply induces diphenylcarbene loss as Ph$_2$C=CPh$_2$. Further reactivity studies are required to better understand factors that control carbene group transfer vs. simple carbene loss as Ph$_2$C=CPh$_2$. The ability of a nucleophile to coordinate to the sterically protected Cu center in three-coordinate [β-diketiminato]Cu=CPh$_2$ species may favor carbene dimerization as observed during the addition of PBu$_3$ to the Fischer alkoxycarbene [Cu{=CR^1(OR^2)}(MeCN)(OEt$_2$)]$^+$ [14]. Nonetheless, the observed electrophilic reactivity of the copper diphenylcarbenes contrasts sharply with that of the isoelectronic (^{t}Bu$_2$PCH$_2$CH$_2$P^{t}Bu$_2$)Ni=CPh$_2$ which behaves as a *C*-centered nucleophile [39]. Dioxygen also rapidly reacts with the copper carbenes to give benzophenone, opening the possibility of metathesis reactions between [Me$_3$NN]=CPh$_2$ and other double bonds E=E'.

4. Experimental

4.1. General experimental details

All experiments were carried out in a dry nitrogen atmosphere using an MBraun glovebox and/or standard Schlenk techniques. 4A molecular sieves were activated in vacuo at 180 °C for 24 h. Dry toluene was purchased from Aldrich and was stored over activated 4A molecular sieves. Benzene, diethyl ether, tetrahydrofuran (THF) and pentane were distilled before use from sodium/benzophenone and dichloromethane was distilled from calcium hydride. All deuterated solvents were sparged with nitrogen, dried over activated 4A molecular sieves and stored under nitrogen. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Mercury Varian 300 MHz spectrometer (300, 121.5, and 75.4 MHz, respectively) at 25 °C unless otherwise noted. ^{1}H and ^{13}C NMR spectra were indirectly referenced to TMS using residual solvent signals as internal standards, while [31]P

NMR spectra were referenced against external 85% H_3PO_4. GC/MS spectra were recorded on a Fisions Instruments MD800. Phenylacetylene was passed through activated alumina prior to use. Copper *t*-butoxide [40] was prepared by addition of 1 equiv. *t*-butanol to mesitylcopper [41–43] in toluene. Triphenylphosphine and 2,6-diphenyl isocyanide were obtained from Aldrich and used as received. 2,4-bis(2,4,6-dimethylphenyllimido)pentane, (H[Me$_3$NN]) [44] and diphenyldiazomethane [45] was synthesized according to literature procedures.

4.2. DFT calculation details

The DFT calculations employed the Becke–Perdew exchange correlation functional [46–48] using the Amsterdam Density Functional suite of programs (ADF 2002.03) [49,50]. Slater-type orbital (STO) basis sets employed for H, C, and N atoms were of triple-ζ quality augmented with two polarization functions (ZORA/ TZ2P – ADF basis V) while an improved triple-ζ basis set with two polarization functions (ZORA/TZ2P+) was employed for the Cu atom. Scalar relativistic effects were included by virtue of the zero order regular approximation (ZORA) [51–53]. The 1s electrons of C and N as well as the 1s–2p electrons of Cu were treated as frozen core. The VWN (Vosko, Wilk, and Nusair) functional was used for LDA (local density approximation) [54]. The contour plots in Figs. 3 and 4 were rendered with the MOLEKEL molecular graphics package [55,56].

4.2.1. Preparation of {[Me$_3$NN]Cu}$_2$(μ-toluene) (3)

A solution of H[Me$_3$NN] (1.70 g, 5.35 mmol) in 10 ml of toluene was stirred for 1 h with a solution of copper (I) *t*-butoxide. The reaction mixture was filtered through Celite, and the volatiles were removed in vacuo to give a brown oil. Addition of pentane (ca. 10 mL) to the brown residue induced crystallization. After standing at −35 °C, 1.60 g (62%) of colorless crystals were isolated. ^{1}H NMR (benzene-d_6): δ 7.131–7.022 (m, 5, toluene-Ar), 6.913 (br s, 8, Ar-*H*), 4.791 (s, 2, backbone-C*H*), 2.264 (br s, 12, Ar-*p*-C*H$_3$*), 2.103 (s, 3, toluene-C*H$_3$*), 2.023 (br s, 24, Ar-*p*-C*H$_3$*) (shoulder at 1.922), 1.660 (br s, 12, backbone-C*H$_3$*). ^{13}C{^{1}H} NMR (benzene d_6): δ 162.74, 148.27, 131.81, 130.32, 129.29 (tol), 128.91, 128.50 (tol), 125.65 (tol), 94.54 (backbone-*C*H), 23.16, 21.06, 18.81, 18.71. After standing overnight in benzene-d_6, 2 species are observed by ^{1}H NMR in nearly identical ratios. Species 1 (nearly identical to initial spectrum): δ 6.920 (s, 4, Ar-H), 4.803 (s, 1, backbone C–H), 2.275 (s, 6, Ar-*p*-CH$_3$), 2.029 (s, 12, Ar-*o*-CH$_3$), 1.669 (s, 6, backbone-C*H$_3$*); Species 2 (becomes more distinct with time): δ 6.809 (s, 4, Ar-*H*), 4.763 (s, 1, backbone C–H), 2.239 (s, 6, Ar-*p*-CH$_3$), 1.901 (s, 12, Ar-*o*-CH$_3$), 1.585 (s, 6, backbone-C*H$_3$*). Unable to obtain satisfactory elemental analysis due to extreme air sensitivity.

4.2.2. Preparation of {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (4)

A chilled (−35 °C) solution of N$_2$CPh$_2$ (0.015 g, 0.073 mmol) in ether was added in one portion to a chilled solution of {[Me$_3$NN]Cu}$_2$(μ-toluene) (0.068 g, 0.077 mmol) in 5 mL of ether. Evolution of N$_2$ gas was observed with the formation of a dark purple solution. After stirring for 10 min, the solution was filtered through Celite and the volatiles were removed in vacuo. The residue was extracted with pentane, concentrated and was allowed to stand overnight at −35 °C. The product was isolated and recrystallized from pentane to afford 0.050 g (70%) of dark purple crystals suitable for X-ray diffraction. ^{1}H NMR (toluene-d_8, −70 °C): δ 7.3–6.4 (br m, 6, *m* and *p*-CPh$_2$), 7.07 (s, 2, Ar-*H*), 6.81 (s, 2, Ar-*H*), 6.61 (br, 2, *o*-C*Ph$_2$*), 6.33 (br s, 2, Ar-*H*), 6.28 (br s, Ar-*H*), 6.18 (d, 2, *o*-C*Ph$_2$*), 4.99 (s, 2, backbone-C*H*), 2.86 (s, 6, Ar-C*H$_3$*), 2.36 (s, 6, Ar-C*H$_3$*), 2.01 (s, 6, Ar-C*H$_3$*), 1.87 (s, 6, Ar-C*H$_3$*), 1.86 (s, 6, backbone-C*H$_3$*), 1.63 (s, 6, backbone-C*H$_3$*), 1.54 (s, 6, backbone-C*H$_3$*) 1.18 (s, 6, Ar-C*H$_3$*); ^{13}C{^{1}H} NMR (benzene-d_6, 25 °C – partial data): δ 189.0 (*C*Ph$_2$), 162.95 (imine), 148.69, 144.22, 131.79, 129.36, 128.84, 128.21, 126.78, 96.93 (backbone-*C*H), 23.45, 23.06, 21.05, 20.81, 19.46, 18.85; Anal. Calc. for C$_{59}$H$_{68}$N$_4$Cu$_2$: C, 73.79; H, 7.14; N, 5.83. Found: C, 73.85; H, 7.66; N, 5.81%.

4.2.3. Preparation of [Me$_3$NN]Cu(η^2-HC≡CPh) (5)

Phenylacetylene (0.069, 0.67 mmol) was added to a solution of {[Me$_3$NN]Cu}$_2$(μ-toluene) (0.300 g, 0.339 mmol) in 1 mL toluene. The volatiles were removed in vacuo immediately and the resulting solid residue was extracted with pentane, concentrated and was allowed to stand for two days at −35 °C to give 0.275g (81%) of the product as colorless crystals. ^{1}H NMR (toluene-d_8, −70 °C): δ 6.730 (m, 2, Ar-*H*), 6.719 (t, 1, *p*-Ph), 6.583 (t, 2, *m*-Ph), 6.435 (d, 2, *o*-Ph), 6.288 (s, 2, Ar-*H*), 4.871 (s, 1, backbone-C*H*), 3.997 (s, 1, C≡C–*H*), 2.194 (s, 6, Ar-*o*-CH$_3$), 2.157 (s, 6, Ar-*p*−*H*), 2.039 (s, 6, Ar-*o*-CH$_3$), 2.025 (s, 3, Ar-p-*H*), 1.656 (s, 3, backbone –CH$_3$), 1.591 (s, 3, backbone –C*H$_3$*); ^{13}C{^{1}H} NMR (benzene d_6, 25 °C): δ 163.14, 148.86, 132.10, 130.26, 129.28, 129.05, 126.66, 124.12, 103.99 (H*C*CPh), 94.68 (backbone-*C*H), 86.87 (HC*C*Ph), 22.68, 20.92, 18.74. IR (cm^{-1}): 3169 (ν_{CH}), 1894 ($\nu_{HC≡CPh}$). Anal. Calc. for C$_{31}$H$_{35}$N$_2$Cu: C, 74.59; H, 7.07; N, 5.61. Found: C, 74.41; H, 7.01; N, 5.65%.

4.2.4. Preparation [Me$_3$NN]Cu(PPh$_3$) (6)

A solution of triphenylphosphine (0.059 g, 0.226 mmol) in 1 mL toluene was added to a solution of {[Me$_3$NN]Cu}$_2$(μ-toluene) (0.100 g, 0.113 mmol) in 1 mL toluene. The volatiles were removed in vacuo immediately to give an oil which crystallized upon addition of pentane (2 mL). After standing at −35 °C, 0.129 g (92%) colorless crystals were isolated. ^{1}H NMR (benzene-d_6): δ

6.98–6.88 (m, 15, Ar-*H*), 6.690 (s, 4, Ar-H), 5.086 (s, 1, backbone-C*H*), 2.198 (s, 6, Ar-*p*-C*H*₃), 2.154 (s, 12, Ar-*o*-C*H*₃), 1.795 (s, 6, backbone-C*H*₃). ^{13}C{^{1}H} NMR (benzene−d_6, partial data): δ 162.81, 150.52, 133.57 (J_{PC} = 15.6 Hz), 131.06, 130.21, 129.28, 129.10, 128.72 (J_{PC} = 9 Hz), 128.47 (J_{PC} = 9.6 Hz), 22.84, 21.00, 18.99; ^{31}P NMR (benzene-d_6): δ 5.20. Anal. Calc. for C₄₁H₄₄N₂CuP: C, 74.69; H, 6.73; N, 4.25. Found: C, 74.54; H, 7.04; N, 4.35%.

4.2.5. Preparation of [Me₃NN]Cu(CNAr) (7)

A solution of 2,6-dimethylphenyl isocyanide (0.030 g, 0.226 mmol) in 1 mL toluene was added to a solution of {[Me₃NN]Cu}₂(μ-toluene) (0.100 g, 0.113 mmol) in 1 mL toluene. The volatiles were removed in vacuo immediately to give an oil. Addition of pentane (2 mL) followed by standing at −35 °C allowed for the isolation of 0.100g (91%) yellow crystals. ^{1}H NMR (benzene-d_6): δ 6.884 (s, 4, Ar-*H*), 6.594 (t, 1, Ar-p-*H*), 6.394 (d, 2, Ar-m-*H*), 5.037 (s, 1, backbone-C*H*), 2.405 (s, 12, Ar-*o*-C*H*3), 2.213 (s, 6, Ar-*H*), 1.810 (s, 6, Ar-*H*), 1.628 (s, 6, backbone-C*H*₃). ^{13}C{^{1}H} NMR (benzene-d_6): δ 163.18, 153.95, 150.94, 135.15, 131.59, 130.23, 129.36, 127.85, (one aromatic resonance missing or obscured), 94.77, 22.76, 21.32, 19.58, 18.39. IR (cm^{-1}): 2121 (v_{CN}). Anal. Calc. for C₃₂H₃₈N₃Cu: C, 72.76; H, 7.25; N, 7.96. Found: C, 73.13; H, 7.05; N, 8.05%.

4.2.6. Reaction of {[Me₃NN]Cu}₂(μ-CPh₂) with HC≡CPh

10 equiv. phenylacetylene (57 μL, 0.52 mmol) was added to a solution of {[Me₂NN]Cu}₂(μ-CPh₂) (0.050 g, 0.052 mmol) in ca. 1 mL benzene-d_6. The intense purple color of **4** was discharged over 15 min to result in a greenish solution which revealed [Me₃NN]Cu(η^2-HC≡CPh) as the only Cu(I) β-diketiminato product. After standing for 1 h, the solution was pale yellow and analysis by GC/MS indicated a peak with *m/z* = 268 (1,3,3-triphenylcyclopropene) as the major Ph₂C-containing species.

4.2.7. Reaction of {[Me₃NN]Cu}₂(μ-CPh₂) with PPh₃

8 equiv. triphenylphosphine (0.057 g, 0.219) was added to a solution of {[Me₂NN]Cu}₂(μ-CPh₂) (0.026 g, 0.027 mmol) in ca. 1 mL benzene-d_6. The intense purple color of **4** was discharged over 10 min to result in a greenish solution. Analysis by ^{31}P NMR spectroscopy indicates the presence of Ph₃P=CPh₂ (δ 7.36 ppm), [Me₃NN]-Cu(PPh₃) (δ 5.20 ppm), and free PPh₃ (δ −4.79 ppm). Integration of the Ph₃P=CPh₂ resonance against the [Me₃NN]Cu(PPh₃) formed indicates a 76% yield of ylide formation. An authentic sample of Ph₃P=CPh₂ was prepared by the method of Staudinger from PPh₃ and N₂CPh₂ to first give colorless Ph₃P=N–N=CPh₂ which affords red Ph₃P=CPh₂ upon extrusion of N₂ with heating of Ph₃P=N–N=CPh₂ in the melt [30,31].

4.2.8. Reaction of {[Me₃NN]Cu}₂(μ-CPh₂) with CNAr

Approx. 2 equiv. 2,6-dimethylphenyl isocyanide (0.003 g, 0.02 mmol) was added to a solution of {[Me₂NN]Cu}₂(μ-CPh₂) (0.012 g, 0.011 mmol) in ca. 1 mL benzene-d_6. The intense purple color of **4** was discharged to give a much less intense indigo solution. Analysis by ^{1}H NMR spectroscopy indicates [Me₃NN]-Cu(CNAr) as the major [Me₃NN]Cu product with {[Me₃NN]Cu}₂(μ-CPh₂) and [Me₃NN]Cu=CPh₂ present in less than 5 mol%. Ph₂C=CPh₂ was observed by ^{1}H NMR spectroscopy (multiplets between δ 7.16–7.11 and 6.96–6.85 ppm), corroborated by GC/MS analysis as the sole Ph₂C-containing species.

4.2.9. Reaction of {[Me₃NN]Cu}₂(μ-CPh₂) with O₂

Bubbling O₂ gas through a ca. 0.1 mM ether solution of {[Me₃NN]Cu}₂(μ-CPh₂) resulted in the immediate discharge of the deep purple solution to give a brown precipitate. Analysis by GC/MS indicates Ph₂C=O as the predominant Ph₂C-containing species. IR analysis of the brown precipitate gives a sharp stretch at 3648 cm^{-1}, identical to that produced by oxygenation of {[Me₃NN]Cu}₂(μ-toluene) under similar conditions, consistent with the formation of {[Me₃NN]Cu}₂(μ-OH)₂. (v_{OH} = 3646 cm^{-1} for {[Me₂NN]Cu}₂(μ-OH)₂).

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 279253–279257 for compounds **3–7**.

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