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Discrete Bridging and Terminal Copper Carbenes in Copper-Catalyzed Cyclopropanation

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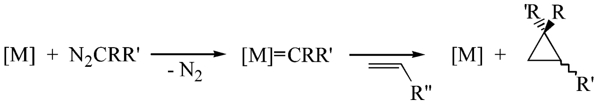
Abstract: The Cu(I) β-diketiminate [Me$_2$NN]Cu(η^2-ethylene) (**2**) catalyzes the cyclopropanation of styrene with N_2CPh_2 to give 1,1,2-triphenylcyclopropane in 67% yield. Addition of N_2CPh_2 to 2 equiv of **2** allows for the isolation of the dicopper carbene $\{[Me_2NN]Cu\}_2(\mu\text{-}CPh_2)$ (**3**) in which the diphenylcarbene moiety is symmetrically bound between two [Me$_2$NN]Cu fragments (Cu−C = 1.922(4) and 1.930(4) Å) with a Cu−Cu separation of 2.4635(7) Å. In toluene-d_8 solution, **3** reversibly dissociates a [Me$_2$NN]Cu fragment to give [Me$_2$NN]Cu(toluene) and the terminal carbene [Me$_2$NN]Cu═CPh$_2$. Dicopper carbene **3** reacts with 3 equiv of styrene to give 1,1,2-triphenylcyclopropane and 2 equiv of [Me$_2$NN]Cu(η^2-styrene) within minutes. DFT studies with simplified ligands indicate a stronger Cu−C π-back-bonding interaction from two Cu(I) centers to the carbene acceptor orbital in a dicopper carbene than that present in a monocopper carbene. Nonetheless, the terminal carbene [Me$_3$NN]Cu═CPh$_2$ (**8**) that possesses a *p*-methyl group on each β-diketiminato *N*-aryl ring may be isolated and exhibits a shortened Cu−C distance of 1.834(3) Å. The stoichiometric cyclopropanation of styrene by **8** in 1,4-dioxane is first-order in both copper carbene **8** and styrene with activation parameters $\Delta H^{\ddagger} = 10.4(3)$ kcal/mol and $\Delta S^{\ddagger} = -32.3(9)$ cal/mol·K. In 1,4-dioxane, **8** decomposes to Ph$_2$C═CPh$_2$ via first-order kinetics with activation parameters $\Delta H^{\ddagger} = 21(1)$ kcal/mol and $\Delta S^{\ddagger} = -8(3)$ cal/mol·K. Arene solutions of thermally sensitive terminal carbene **8** decompose to [Me$_3$NN]-Cu(arene), which reacts with **8** still present in solution to give the more thermally stable $\{[Me_3NN]Cu\}_2$-(μ-CPh$_2$).

Introduction

Copper bronze, copper(II) sulfate, and copper(II) oxide are the longest known catalysts for the decomposition of diazo compounds N_2CR_2.[1] When performed in the presence of alkenes, cyclopropanes are one of several organic products that result from the transient carbene intermediates that are generated.[2] Over the last 40 years, soluble copper(I) and copper(II) complexes have been used to impart greater selectivity for cyclopropanation and have played an important role in the development of this valuable group transfer reaction.[1] In fact, the use of chiral copper salicylaldimine complexes marks the earliest successful use of a chiral, homogeneous metal catalyst to achieve enantioselectivity. Observation of asymmetric induction in the cis/trans cyclopropane mixture formed between the reaction of styrene with N_2CHCO_2R (R = ethyl, Ph) demonstrated participation of the chiral copper complex in the product-determining step.[3]

The successful, catalytic cyclopropanation of alkenes with diazo reagents requires the use of a transition-metal complex to facilitate loss of N_2 from the diazo reagent as well as to stabilize the intermediate carbene species against competing carbene dimerization via weak binding to the metal complex (eq 1).[4−6]



(1)

With the appropriate choice of metal and supporting ligands, carbene transfer to alkenes can proceed with high levels of stereoselectivity.[1,2,7] While complexes of many transition metals may be used in catalytic cyclopropanation, copper is attractive because of its low cost relative to other active metals such as rhodium and ruthenium.

A variety of copper complexes supported by multidentate N-donor ligands catalyze the cyclopropanation of olefins with diazo reagents containing α-carbonyl groups.[1,2] While diastereoselectivities are generally modest and may be improved by increasing the size of the diazo reagent[8] and/or supporting

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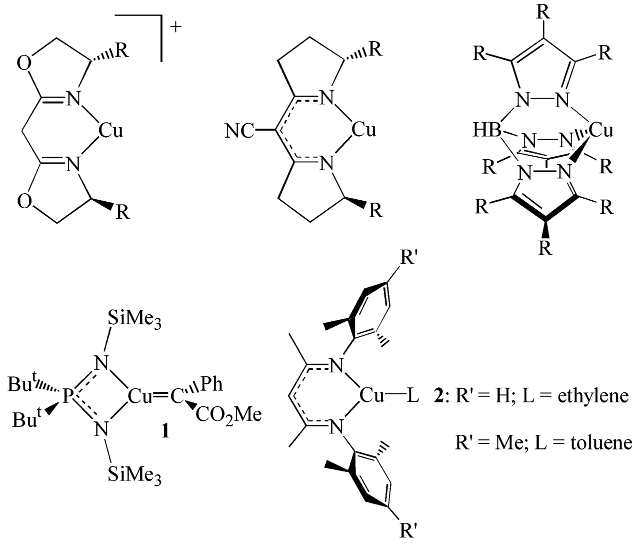


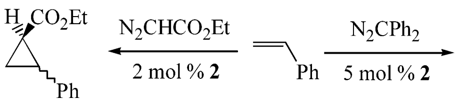
Figure 1. Supporting ligands in copper cyclopropanation catalysts.

ligands,[9] impressive enantioselectivites have been obtained with chiral supporting ligands such as bis(oxazolines) or semicorrins (Figure 1).[7,10] In addition, Pérez and co-workers have shown that electron-deficient tris(pyrazolyl)borates can shift the chemoselectivity of reactions employing N_2CHCO_2Et to give products that derive from carbene insertion into C−H bonds.[11]

Much evidence points to a Cu(I) carbene [Cu]=CRR′ as the key intermediate in copper-catalyzed cyclopropanation. For instance, some structurally characterized [M]=CRR′ complexes of Fe,[12] Ru,[13] and Os[14] isolated from the addition of diazo compounds to cyclopropanation catalysts stoichiometrically cyclopropanate alkenes. Several mechanistic[15−17] and theoretical[17,18] studies implicate Cu(I) complexes as the catalytically active species, though copper(I) carbenes reactive toward cyclopropanation have proven elusive. Hofmann recently described the low-temperature NMR detection of the Cu carbene $[\mathrm{Bu^t_2P(NSiMe_3)_2}\text{-}\kappa^2N]$Cu=C(Ph)C(O)OMe (**1**) in a mixture of 2-phenyl-diazoacetate and $[\mathrm{Bu^t_2P(NSiMe_3)_2}\text{-}\kappa^2N]$Cu(ethylene) in toluene-$d_8$.[19] Addition of styrene resulted in the rapid disappearance of **1** and gave a mixture of cyclopropanation products *cis*- and *trans*-methyl-1,2-diphenylcyclopropanecarboxylate. Time-resolved FT-IR spectroscopy has also been used to identify a transient copper carbene upon addition of N_2CHCO_2Me to a cationic Cu(I) bis(oxazoline) precatalyst.[20] Despite the potential to develop more selective and versatile catalysts based on a detailed understanding of active species involved, experimental progress has lagged considerably behind theoretical studies aimed at characterizing discrete species involved in copper-catalyzed cyclopropanation. Employing electron-rich β-diketiminato supporting ligands,[21−25] we report herein detailed structural, spectroscopic, and kinetic studies that outline the nature of copper carbenes formed in the catalytic cyclopropanation of styrene with N_2CPh_2 using a Cu(I) catalyst.[26]

Results and Discussion

Catalytic Cyclopropanation. Given its similarity to other successful copper complexes employed in the cyclopropanation of alkenes with diazo esters (Figure 1), it is not surprising that the neutral Cu(I) β-diketiminato complex $[\mathrm{Me_2NN}]$Cu(ethylene)[22] (**2**) catalyzes the cyclopropanation of styrene with ethyl diazoacetate (EDA). Addition of EDA in one portion to a toluene solution containing 5 equiv of styrene and 2 mol % **2** gave the corresponding cyclopropane in 77% yield as a 38:62 cis/trans mixture (eq 2). We found, however, that the slow addition of N_2CPh_2 to a toluene solution containing 10 equiv of styrene and 5 mol % **2** results in the formation of 1,1,2-triphenylcyclopropane in 67% yield (eq 2).



(2)

Notably, the carbene dimerization byproduct $Ph_2C{=}CPh_2$ was not observed (<1%); the azine $Ph_2C{=}N{-}N{=}CPh_2$ accounted for the remainder of the N_2CPh_2 consumed. Such use of a non-α-carbonyl diazo reagent other than N_2CH_2 for catalytic cyclopropanation is uncommon. Diazo reagents N_2CRR' that do not bear heteroatom-containing α-substituents are much more prone to catalytic dimerization to alkenes $R'RC{=}CRR'$ by metal complexes than the heavily utilized diazo esters.[4,27,28] Examples of selective catalytic group transfer with aryldiazomethanes N_2C-

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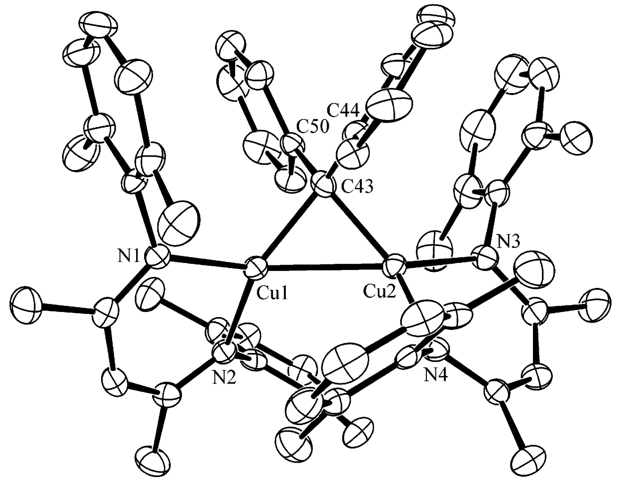
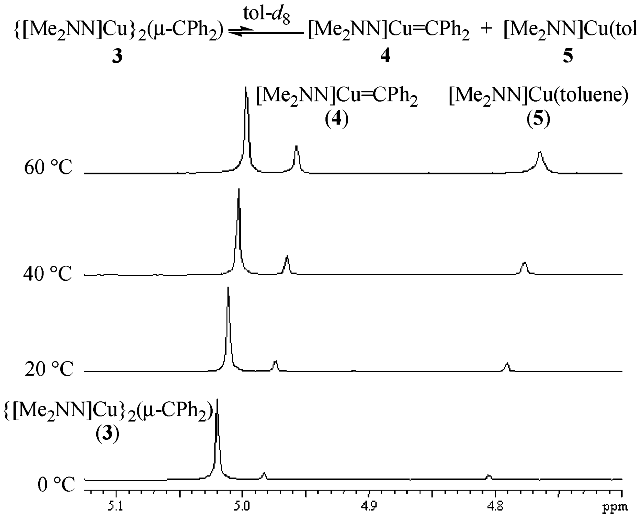


Figure 2. ORTEP diagram of the solid-state structure of $\{[Me_2NN]Cu\}_2(\mu\text{-}CPh_2)$ (**3**) (all H atoms omitted). Selected bond distances (angstroms), angles (deg), and twist angles between planes (deg): Cu1−C43 1.922(4), Cu2−C43 1.930(4), Cu1−Cu2 2.4635(7), Cu1−N1 1.965(3), Cu1−N2 1.955(3), Cu2−N3 1.970(3), Cu2−N4 1.978(3), Cu1−C43−Cu2 79.51(14), N1−Cu1−N2 96.11(13), N3−Cu2−N4 95.85(12), C44−C43−C50 115.0(3), N1−Cu1−N2/C44−C43−C50 89.1, N3−Cu2−N4/C44−C43−C50 83.1.

Scheme 1. Variable Temperature ^1H NMR Spectra (300 MHz) of the β-Diketiminato Backbone C−H Region of **3** in Toluene-d_8



(R)Ar (R = H, Ar) have only recently been reported, employing Fe(II) or Os(II) porphyrin precursors whose active species are the discrete monocarbenes [Fe]=CHAr[12] or the unusual bis(carbene) $[Os](=CPh_2)_2$.[14]

Synthesis and Characterization of Dicopper Carbene $\{[Me_2NN]Cu\}_2(\mu\text{-}CPh_2)$. To investigate the origin of selectivity toward cyclopropanation of styrene by N_2CPh_2 catalyzed by **2**, we slowly added N_2CPh_2 to 2 equiv of $[Me_2NN]Cu(ethylene)$ (**2**) in toluene at −35 °C. Immediate effervescence occurred along with the formation of a purple solution from which the unanticipated dicopper carbene $\{[Me_2NN]Cu\}_2(\mu\text{-}CPh_2)$ (**3**) was isolated in 40% yield as purple crystals from ether (eq 3).

$$\underset{\mathbf{2}}{2\,[Me_2NN]Cu(ethylene)} \xrightarrow[\text{- 2 ethylene}\ \text{- }N_2]{N_2CPh_2} \underset{\mathbf{3}}{\{[Me_2NN]Cu\}_2(\mu\text{-}CPh_2)} \qquad (3)$$

The X-ray structure of **3** • 0.75 hexane shows the diphenylcarbene unit nearly symmetrically bound between two [Me$_2$NN]Cu fragments separated by 2.4635(7) Å with Cu1−C43 and Cu2−C43 distances of 1.922(4) and 1.930(4) Å (Figure 2). The Cu−C distances in **3** are at the low end of the range of 1.911(2)−2.06(2) Å established for bridging sp^2-hybridized aryl groups in multinuclear Cu(I) aryls such as $[CuMes]_x$ (Mes = 2,4,6-trimethylphenyl; x = 4 or 5),[29] which generally exhibit Cu−Cu distances in the range 2.4 to 2.5 Å.[30] The two [Me$_2$NN]Cu fragments are related by a noncrystallographic C_2 axis through C43 that bisects the Cu−Cu vector, and each [Me$_2$NN]Cu fragment is nearly orthogonal to the CPh_2 moiety (83.1 and 89.1° twist angles between the N−Cu−N and C44−C43−C50 planes). While the spectroscopically characterized diphenylcarbene-bridged Rh−Cu complexes $Cp(CO)Rh(\mu\text{-}CPh_2)(CuCl)_2$ and $Cp(CO)Rh(\mu\text{-}CPh_2)CuCp$ have been isolated from the addition of CuCl to $Cp(CO)Rh{=}CPh_2$ followed by subsequent treatment with NaCp,[31] to our knowledge **3** represents the first report of a dicopper carbene.

The ^1H NMR spectrum of **3** in toluene-d_8 at −70 °C (300 MHz) is consistent with its structure in the solid state, giving rise to four separate β-diketiminate Ar−Me resonances, two backbone Me signals, and a solitary backbone C−H singlet at δ 5.010 ppm (Figure S1). Warming this solution results in the coalescence of the backbone Me signals, consistent with the concerted rocking of each [Me$_2$NN]Cu fragment about its respective Cu−CPh$_2$ vector for which an activation barrier $\Delta G^\ddagger$ = 10.1(3) kcal/mol could be established at −32 °C. All four Ar−Me resonances also coalesce above 25 °C as a result of an enantiomerization process. While this could involve rapid dissociation and reassociation of one [Me$_2$NN]Cu fragment from **3**, more likely it is a twisting of the bridging diphenylcarbene ligand about the vector containing C43 that bisects the Cu1−Cu2 axis. Room temperature $^{13}C\{^1H\}$ NMR spectra of **3** reveal the carbene *C*Ph$_2$ signal at δ 189.4 ppm, which is downfield of all other resonances, but typical for bridging carbenes that appear in the range 100−210 ppm if a metal−metal bond is present.[32] For instance, the bridging *C*Ph$_2$ moiety in $Cp(CO)Rh(\mu\text{-}CPh_2)CuCp$ appears at δ 206.3 ppm.[31]

Variable temperature NMR spectra also reveal that **3** is in a reversible equilibrium with two new C_{2v} symmetric copper β-diketiminate species **4** and **5** (Scheme 1). Two backbone C−H signals at δ 4.958 and 4.801 ppm with corresponding Ar−Me resonances at δ 2.03 and 2.40 ppm are observed for **4** and **5**, respectively. These signals increase in intensity from ca. 2 to 30% relative to **3** over the temperature range −70 to 60 °C. Since **5** can be identified as [Me$_2$NN]Cu(toluene) by addition of an authentic sample to the mixture at room temperature (prepared by addition of Tl[Me$_2$NN] to CuBr in toluene), we suggest that **3** reversibly dissociates one [Me$_2$NN]Cu fragment

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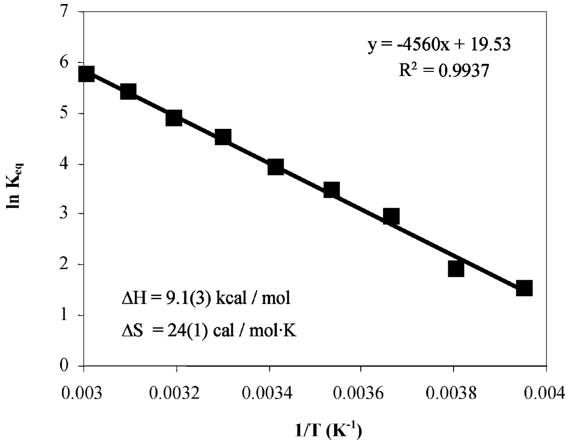
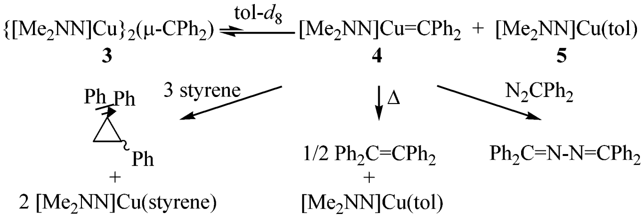


Figure 3. van't Hoff plot for the dissociation of a $[Me_2NN]Cu$ fragment from **3** in toluene-d_8.

Scheme 2. Reactivity of Dicopper Carbene **3**



to give an equilibrium concentration of the monomeric carbene $[Me_2NN]Cu{=}CPh_2$ (**4**). A related Cu(I) benzene adduct supported by a fluorinated *β*-diketiminate ligand has been structurally characterized by Sadighi.[24] The temperature dependence of the equilibrium constant over the temperature range −20 to 60 °C allows the determination of the thermodynamic parameters $\Delta H = 9.1(3)$ kcal/mol and $\Delta S = 24(1)$ cal/mol•K for this process (Figure 3). Notably, no significant broadening of the closely spaced backbone C−H ^{1}H NMR resonances of **3** and **4** occurs until the temperature is raised above 60 °C, indicating that **3** and **4** do not interconvert quickly on the NMR time scale over this temperature range.

Reactivity of Dicopper Carbene $\{[Me_2NN]Cu\}_2(\mu\text{-}CPh_2)$. Dicopper carbene **3** is reactive toward cyclopropanation. As monitored by ^{1}H NMR spectroscopy, a benzene-d_6 solution of **3** in the presence of 3 equiv of styrene quantitatively gives 1,1,2-triphenylcyclopropane and 2 equiv of Cu−styrene complex $[Me_2NN]Cu(styrene)$[22] within minutes (Scheme 2). In light of the sterically crowded nature of dicopper carbene **3**, we assume that the reactive species is the terminal carbene **4** formed by the reversible dissociation of one $[Me_2NN]Cu$ fragment from **3**. Scouting experiments indicate that the facility of carbene transfer is sensitive to the degree and pattern of alkene substitution. While reaction of **3** with a 50-fold excess of α-methylstyrene in toluene at room temperature gives clean conversion to the corresponding cyclopropane, the 1,2-disubstituted trans-*β*-methylstyrene requires heating at 45 °C for 2 h under similar conditions to completely consume the copper carbene **3**. In the latter case, carbene dimerization competes with cyclopropanation to give a 73:27 ratio of $Ph_2C{=}CPh_2$ to cyclopropane. The aliphatic olefins cyclooctene and 1-hexene (50 equiv) also sluggishly react with **3** at 45 °C to predominately give $Ph_2C{=}CPh_2$ with a low (ca. 20%) conversion to the corresponding cyclopropanes.

Table 1. Calculated Bond Distances (angstroms) and Angles (deg) for Models **6**, **7-C$_{2v}$**, and **7-C$_2$**

parameter	6	7-C_{2v}	7-C_2
Cu−C	1.785	1.885	1.892
Cu−N	1.917	1.932	1.904 (Cu−N1) 1.924 (Cu−N2)
Cu−Cu	n/a	2.530	2.321[a]
N−Cu−N	92.5	95.5	95.3
Cu−C−Cu	n/a	84.5	75.7
N−Cu−N/H−C−H	90	90	89.2

[a] In sterically unencumbered **7-C$_2$**, the Cu centers can approach each other much closer than possible in **3** (Cu−Cu = 2.4635(7) Å). Constraining the Cu−Cu distance to 2.46 Å did not result in calculated energies or metrical parameters markedly different from those of unconstrained **7-C$_2$**.

Direct reaction of N_2CPh_2 with dicopper carbene **3** gives the azine $Ph_2C{=}N{-}N{=}CPh_2$ isolated in 37% yield as colorless crystals from pentane (Scheme 2). Benzophenone azine forms quantitatively upon addition of N_2CPh_2 to the discrete rhodium carbene $Cp(Sb^iPr_3)Rh{=}CPh_2$.[31] This azine is also the primary product when N_2CPh_2 is added to $Rh_2(OAc)_4$,[28] the prototypical member of an efficient family of dirhodium(II) carboxylate and carboxamide catalysts for alkene cyclopropanation with α-carbonyl diazo reagents.[5,7,33] This byproduct identified in the cyclopropanation of styrene with N_2CPh_2 catalyzed by **2** thus results from competition between styrene and the diazo reagent for the copper carbene, underscoring the requirement for slow addition of the diazo reagent to minimize the concentration of N_2CPh_2 during the course of catalytic cyclopropanation.

Given the ready reactivity of **3** toward styrene, its thermal stability in arene solutions is surprising. Fifty-seven percent of **3** in an initially 20 mM benzene-d_6 solution is still present after 56 h at room temperature. This paradoxical behavior may be explained by the equilibrium between the dicopper carbene **3** and the presumably less thermally stable terminal carbene $[Me_2NN]Cu{=}CPh_2$ (**4**) along with a $[Me_2NN]Cu(arene)$ species (Scheme 2). As **3** decomposes, $Ph_2C{=}CPh_2$ and additional $[Me_2NN]Cu(arene)$ are formed, thereby shifting the equilibrium toward more thermally stable **3**. We see no evidence of $[Me_2NN]Cu(Ph_2C{=}CPh_2)$ formation; presumably, the tetrasubstituted alkene is too sterically encumbered to bind to the $[Me_2NN]Cu$ fragment.

DFT Calculations Employing Simplified Models. DFT calculations employing simplified models of the mono- and dicopper carbenes (Table 1) were carried out to identify electronic factors that could account for the stability of the bridged carbene **3** relative to the terminal carbene **4**. In accord with previous theoretical studies on Cu(I) carbenes supported by bidentate N-donor ligands,[17,18] the hypothetical monomeric carbene $[H_5C_3N_2]Cu{=}CH_2$ (**6**) favors an orientation in which the methylene moiety is orthogonal to the backbone. This disposition maximizes back-bonding to the empty carbene p orbital from the filled d orbital of the d^{10} Cu(I) center that is most destabilized by the *β*-diketiminate supporting ligand (Figures 4 and 5). Bearing this geometric relationship in mind, inspection of the X-ray structure of **3** shows that the CPh_2 moiety is essentially orthogonal to the backbone of each unique $[Me_2NN]Cu$ fragment (83.1 and 89.1° twist angles). Thus, the diphenylcarbene moiety in **3** adopts an orientation that would appear to allow back-bonding from each $[Me_2NN]Cu$ fragment the carbene is bound to.

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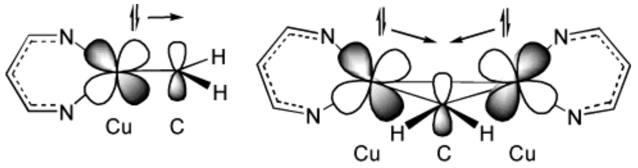


$[H_5C_3N_2]Cu{=}CH_2$ (**6**) $\{[H_5C_3N_2]Cu\}_2(\mu\text{-}CH_2)$ (**7-C$_{2v}$**)

Figure 4. π-Back-bonding interactions in C_{2v} symmetric copper carbenes.

To qualitatively assess differences in back-bonding interactions between mono- and dicopper carbenes, a dicopper carbene was modeled with the C_{2v}-species $\{[H_5C_3N_2]Cu\}_2(\mu\text{-}CH_2)$ (**7-C$_{2v}$**) (Table 1, Figure 5). In **7-C$_{2v}$**, the difference in energy between the orbitals ascribed to Cu−C π-bonding and π^*-antibonding (2.92 eV) is greater than the corresponding difference in **6** (2.39 eV), consistent with a stronger π-back-bonding interaction in the dicopper carbene. Modeling the C_2 symmetric structure that **3** possesses in solution, we further reduced the symmetry of the simplified dicopper carbene to C_2 (**7-C$_2$**) (Table 1). The mutual "twisting" of each [β-diketiminato]Cu fragment along the Cu−C vectors allows more direct overlap between the corresponding orbitals of predominately d heritage on Cu and the carbene acceptor orbital in **7-C$_2$** (Figure 6) as compared to those in **7-C$_{2v}$**. This results in an even larger energy separation between the Cu−C π and π^* orbitals (3.54 eV), suggesting a further enhanced interaction. These calculations on simple models indicate stronger π-back-bonding in dicopper carbenes via a three-center, four-electron interaction in comparison to the simple π-back-bonding present in monocopper carbenes. Considering the weak back-bonding ability typically associated with Cu(I) complexes, two Cu(I) centers can be more effective than one at stabilizing a strongly π-accepting carbene.

Synthesis and Characterization of Terminal Carbene [Me$_3$NN]Cu═CPh$_2$. Nonetheless, steric factors undoubtedly play a role in the relative stability of mono- and dicopper carbenes. Given the small enthalpy of dissociation from **3** to generate the terminal carbene [Me$_2$NN]Cu═CPh$_2$ (**4**), we felt that a slight modification to the β-diketiminate ligand might sufficiently destabilize this singly bridged dicopper species to isolate a terminal carbene.[34] Low-temperature addition of N$_2$-CPh$_2$ to an ether solution of [Me$_3$NN]Cu(toluene) that possesses an additional methyl group in the 4-position of each β-diketiminato *N*-aryl ring results in the isolation of the terminal carbene [Me$_3$NN]Cu═CPh$_2$ (**8**) as purple crystals in 20% recrystallized yield (eq 4). ^{1}H NMR analysis of an aliquot of the reaction mixture indicates >90% conversion to the terminal carbene **8**, its isolation in pure form hampered by its high solubility and thermal sensitivity.

$$[Me_3NN]Cu(toluene) \xrightarrow[-\ N_2]{N_2CPh_2} \underset{\mathbf{8}}{[Me_3NN]Cu{=}CPh_2} \qquad (4)$$

The X-ray structure of **8** reveals a contracted Cu−C bond distance of 1.834(3) Å relative to that of the dicopper carbene **3** (Figure 7). This Cu−C distance is consistent with multiple-bond character, and **8** exhibits structural parameters similar to those of the related d^{10} Ni(0) carbene (^{t}Bu$_2$PCH$_2$CH$_2$PBu$^t{}_2$)-Ni═CPh$_2$, which has a Ni−C distance of 1.836(2) Å.[35] The Cu−C bond in **8** is shorter than that (1.882(3) Å) found in a structurally characterized three-coordinate cationic copper(I)

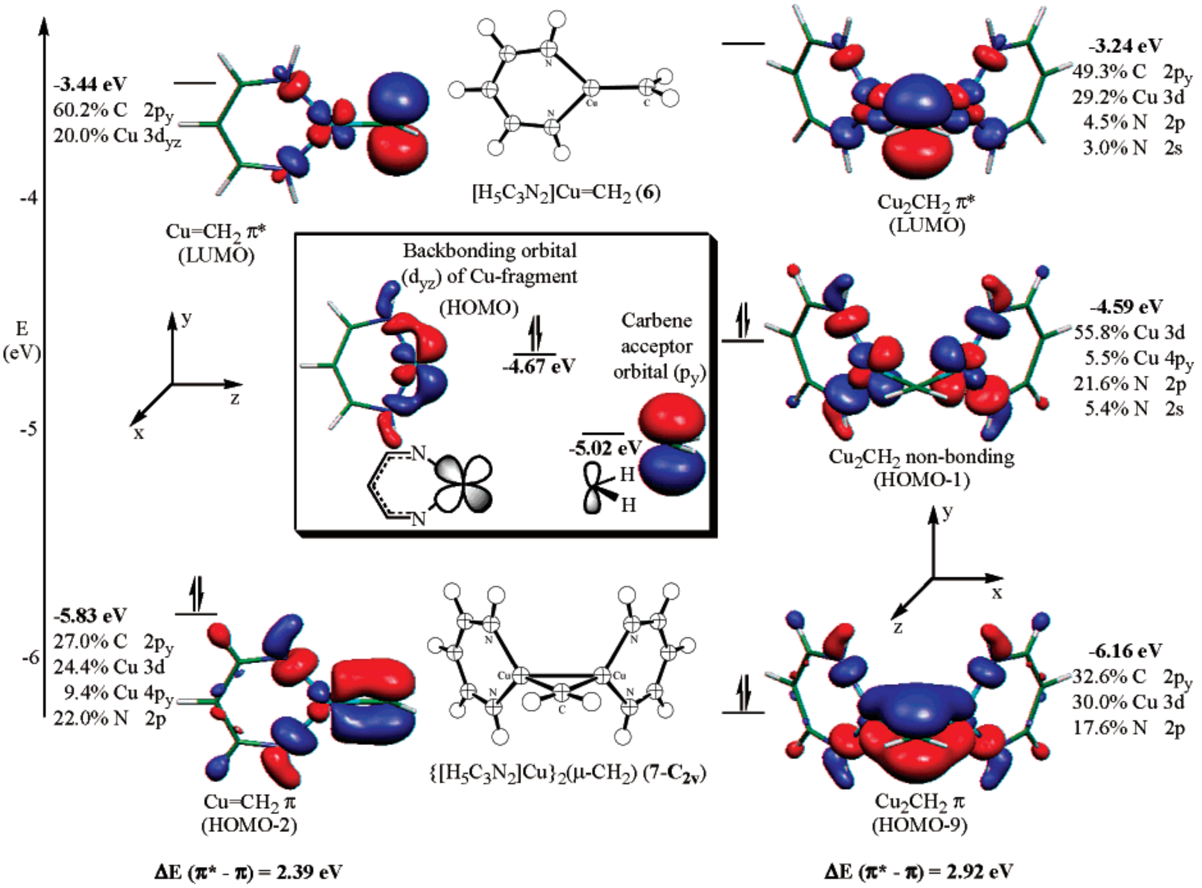


Figure 5. Correlation diagram illustrating Cu−C π-interactions in C_{2v} symmetric monocarbene **6** (left) and dicopper carbene **7-C$_{2v}$** (right).

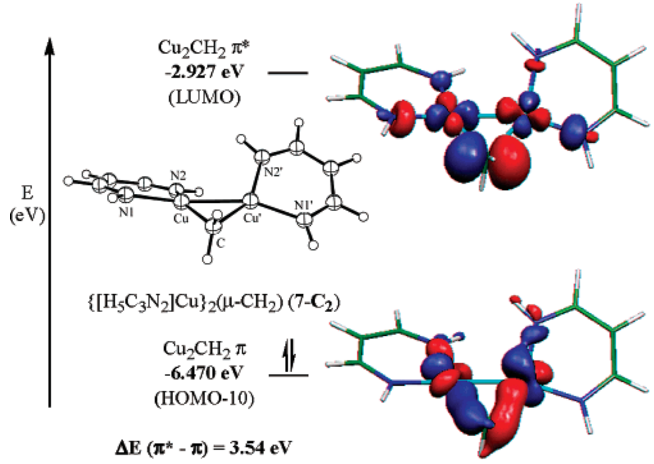


Figure 6. Cu−carbene orbital interactions in C_2 symmetric $\{[H_5C_3N_2]Cu\}_2$-(μ-CH_2) (**7-C_2**).

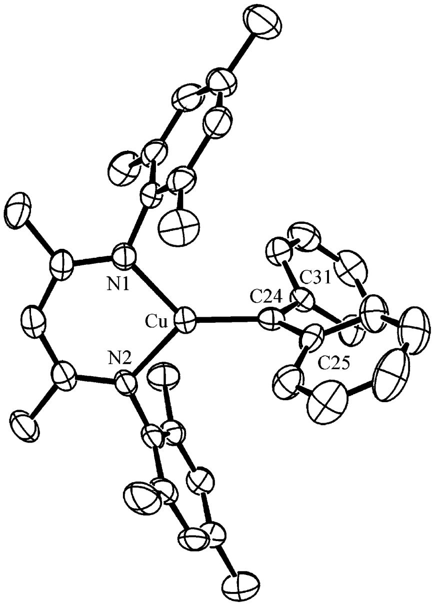


Figure 7. ORTEP diagram of the solid-state structure of $[Me_3NN]Cu{=}CPh_2$ (**8**) (all H atoms omitted). Selected bond distances (angstroms), angles (deg), and twist angles between planes (deg): Cu−C24 1.834(3), Cu−N1 1.906(3), Cu−N2 1.922(3), N1−Cu−N2 96.10(12), C25−C24−C31 117.3(3), N1−Cu−N2/C25−C24−C31 89.0.

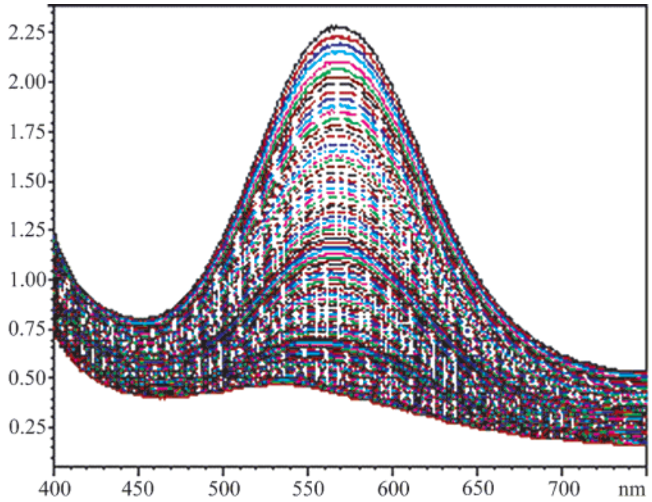
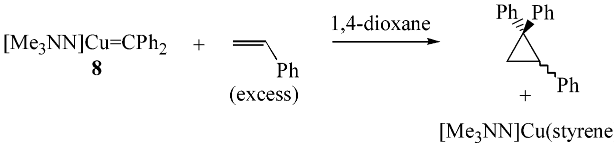


Figure 8. Representative UV−vis spectrum for the cyclopropanation of styrene (100 equiv) by $[Me_2NN]Cu{=}CPh_2$ (**8**) (dioxane, 30.2 °C).

Fischer carbene $[Cu\{{=}CR^1(OR^2)\}(MeCN)(OEt_2)]^+$ (R^1 = (E)-CH═CH-2-furyl; R^2 = menthyl) isolated by carbene transfer from a Cr complex.[36] In addition, the Cu−C distance in **8** is shorter than that found in three-coordinate (1.914(4)−1.9938(14) Å)[37] and two-coordinate (1.850(4)−1.9124(16) Å)[38,39] N-heterocyclic copper(I) carbenes for which copper carbene π-back-bonding is expected to be less important.[39] Maximizing π-back-bonding with the $[Me_3NN]Cu$ fragment, the carbene ligand in **8** is essentially orthogonal to the β-diketiminate backbone (89.0° twist angle). The ^1H NMR spectrum of **8** in benzene-d_6 exhibits C_{2v} symmetry, and the backbone C−H resonance at δ 4.989 ppm has a similar chemical shift as that ascribed to $[Me_2NN]Cu{=}CPh_2$ (**4**) at δ 4.958 ppm. The carbene carbon resonates at δ 253.1 ppm in the $^{13}C\{H\}$ NMR spectrum of **8**, downfield of the carbene resonance in the bridged species **3** as well as Hofmann's terminal $Bu^t{}_2P(NSiMe_3)_2$-κ^2N]-Cu═C(Ph)C(O)Me (**1**) observed at δ 229.9 ppm,[19] but within the approximate range 200−400 ppm established for terminal carbenes.[32]

Kinetic Studies for Cyclopropanation of Styrene Derivatives by $[Me_3NN]Cu{=}CPh_2$. Terminal carbene **8** quickly reacts with styrene at room temperature to give 1,1,2-triphenylcyclopropane and exhibits clean pseudo-first-order kinetics in 1,4-dioxane in the presence of excess styrene (eq 5).



(5)

Monitoring the decrease of the UV−vis signal of **8** at λ = 566 nm (Figure 8), the observed first-order rate constant at 40 °C doubles from 1.5(1) × 10^{-4} s^{-1} to 2.8(1) × 10^{-4} s^{-1} upon increasing the equivalents of styrene present from 50 to 100, indicating that the reaction is also first-order in styrene. Rate constants obtained over the temperature range 17.5−60.2 °C (Table 2) under pseudo-first-order conditions employing 100 equiv of styrene allow the construction of an Eyring plot that affords the activation parameters $\Delta H^\ddagger$ = 10.4(3) kcal/mol and $\Delta S^\ddagger$ = −32.3(9) cal/mol·K (Figure 9). These values are clearly consistent with a facile associative mechanism and may be compared to those reported for the stoichiometric cyclopropanation of vinyl acetate with $(CO)_5W{=}CH(p\text{-}OMeC_6H_4)$ ($\Delta H^\ddagger$ = 10.0(3) kcal/mol and $\Delta S^\ddagger$ = −34.2(7) cal/mol·K).[40] A Hammett plot employing p-substituted styrenes $CH_2{=}CHAr$

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(34) While the two [β-diketiminato]Ni fragments in $\{[Me_2NN]Ni\}_2(\mu\text{-}NAd)$ are bridged by a single adamantylimido ligand, the corresponding terminal Ni-imide $[Me_3NN]Ni{=}NAd$ may be isolated provided that additional Me groups in the p-positions of each β-diketiminato N-aryl ring are present: Kogut, E.; Wiencko, H. L.; Zhang, L.; Warren, T. H., submitted for publication to *J. Am. Chem. Soc.*

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Table 2. Observed First-Order and Actual Second-Order Rate Constants for Styrene Cyclopropanation by **8** under Pseudo-First-Order Conditions with [Styrene] = 0.0839(2) M

T (°C)	k_{obs} (s^{-1})	*k* ($M^{-1}\,s^{-1}$)
17.5	$7.79(5) \times 10^{-5}$	$9.29(6) \times 10^{-4}$
30.2	$1.69(5) \times 10^{-4}$	$2.02(6) \times 10^{-3}$
40.5	$2.83(5) \times 10^{-4}$	$3.42(6) \times 10^{-3}$
50.0	$5.31(5) \times 10^{-4}$	$6.38(6) \times 10^{-3}$
60.2	$9.0(1) \times 10^{-3}$	$1.08(2) \times 10^{-2}$

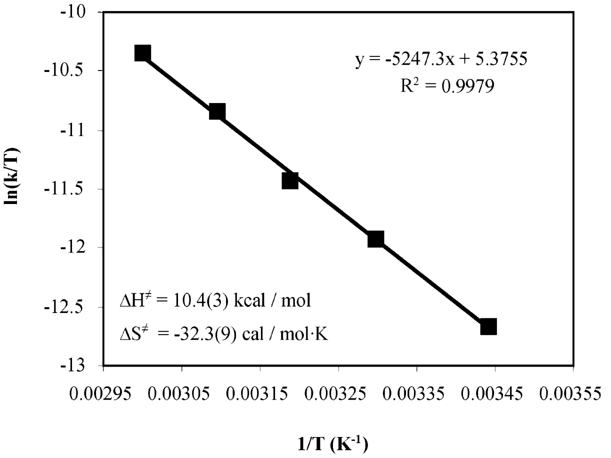

Figure 9. Eyring plot for the cyclopropanation of styrene by **8** in dioxane over the temperature range 17.5−60.2 °C.

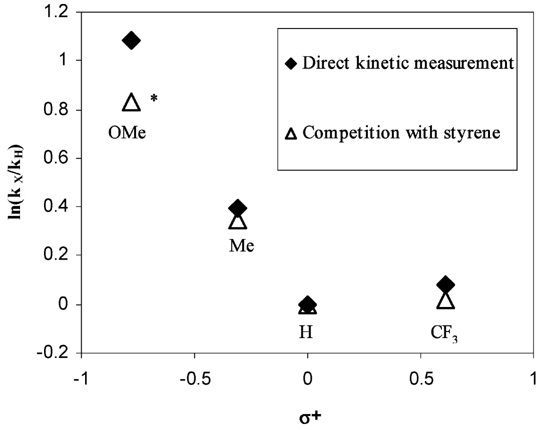

Figure 10. Hammett plot of cyclopropanation of *p*-substituted styrenes. (* denotes estimated value due to overlapping GC peaks in competition experiment.)

(Ar = *p*-XC_6H_5; X = OMe, Me, H, CF_3) indicates the electrophilic nature of copper carbene **8** as electron-rich substituentents (X = OMe, Me) accelerate cyclopropanation,[16,17] though the electron-poor styrene derivative (X = CF_3) has little influence on the rate compared to styrene measured directly by kinetics or via competition experiments (Figure 10).

Decomposition of [Me_3NN]Cu═CPh_2. Dilute (ca. 0.8 mM) solutions of the terminal carbene **8** in 1,4-dioxane cleanly decompose in a first-order fashion to the carbene coupling product $Ph_2C═CPh_2$ and the solvated [Me_3NN]Cu fragment (eq 6).

$$\underset{\mathbf{8}}{[Me_3NN]Cu{=}CPh_2} \xrightarrow{\text{1,4-diox}} 1/2\ Ph_2C{=}CPh_2 + [Me_3NN]Cu(solv) \quad (6)$$

The first-order rate constants for decomposition obtained over a temperature range 30−60 °C measured by UV−vis spectroscopy (Table 3) are only 30−100 times lower than the actual second-order rate constants determined in the cyclopropanation of styrene at these temperatures. This comparison underscores the importance of excess alkene present under typical catalytic conditions dilute in copper catalyst to achieve clean cyclopropanation. Activation parameters $\Delta H^‡ = 21(1)$ kcal/mol and $\Delta S^‡ = -8(3)$ cal/mol·K reveal a significantly larger $\Delta H^‡$ for carbene loss relative to transfer to styrene. This is to be expected as the breaking Cu−carbene bond is not compensated by C−C bond formation in the transition state and suggests a lower limit to the Cu−carbene bond strength.

Table 3. Observed First-Order Rate Constants for Thermal Decomposition of **8**

T (°C)	*k* (s^{-1})
32.2	$1.92(5) \times 10^{-5}$
40.0	$4.0(1) \times 10^{-5}$
49.0	$1.26(5) \times 10^{-4}$
60.0	$3.4(1) \times 10^{-4}$

Scheme 3. Formation of Dicopper Carbene **9** via Decomposition of **8** in Arene Solvents

$$\underset{\mathbf{8}}{[Me_3NN]Cu{=}CPh_2} \xrightarrow{\text{arene}} 1/2\ Ph_2C{=}CPh_2 + [Me_3NN]Cu(arene)$$

$$\underset{\mathbf{8}}{[Me_3NN]Cu{=}CPh_2} + [Me_3NN]Cu(arene) \xrightleftharpoons{\text{arene}} \underset{\mathbf{9}}{\{[Me_2NN]Cu\}_2(\mu\text{-}CPh_2)}$$

In more concentrated arene solutions (40 mM), [Me_3NN]-Cu═CPh_2 (**8**) decomposes to [Me_3NN]Cu(arene), which combines with **8** still present to form an equilibrium concentration of the dicopper carbene {[Me_3NN]Cu}$_2$(μ-CPh_2) (**9**) (Scheme 3). In benzene-d_6, this new species exhibits a backbone C−H ^{1}H NMR resonance at δ 5.018 ppm, and its $^{13}C\{^1H\}$ NMR spectrum reveals a carbene signal at δ 189.0 ppm, chemical shifts nearly identical to those observed for **3**. Arene solutions of **8** still retain cyclopropanation activity after 2 days at room temperature as the more thermally stable dicopper carbene **9** becomes the predominant Cu-containing species after a few hours in solution.

Conclusions

The unprecedented dicopper carbene bonding motif in {[β-diketiminato]Cu}$_2$(μ-CPh_2) (**3** and **9**) results in an extraordinary solution lifetime for metal carbene species that readily cyclopropanate alkenes at room temperature. DFT calculations indicate that the additional Cu(I) fragment present in dicopper carbenes enhances π-back-donation via a three-center, four-electron interaction with the carbene acceptor orbital as compared to the simple back-bonding present in a monocopper carbene. The active intermediate in cyclopropanation is the terminal carbene [Me_2NN]Cu═CPh_2 (**4**) formed by reversible dissociation of one [Me_2NN]Cu fragment from **3** or the structurally characterized [Me_3NN]Cu═CPh_2 (**8**), which exhibits clean, pseudo-first-order kinetics in the cyclopropanation of styrene derivatives. To our knowledge, the X-ray structures of {[Me_2NN]Cu}$_2$(μ-CPh_2) (**3**) and [Me_3NN]Cu═CPh_2 (**8**) are the first of copper carbenes reactive toward cyclopropanation. Comparison of the activation parameters for styrene cyclopropanation and thermal loss of diphenylcarbene from **8** indicates only a small difference in $\Delta G^‡$ at room temperature that narrowly favors cyclopropanation. As the rate of styrene cyclopropanation is also first-order in styrene, the use of excess styrene minimizes thermal decomposition of the intermediate metal carbene, an important consideration in most catalytic cyclopropanation protocols.

Future reports will explore the ability of this Cu(I) system to stabilize carbenes derived from a wider range of diazo reagents and examine their group transfer reactivity to other unsaturated substrates. Furthermore, the unique bonding mode observed in the dicopper carbenes **3** and **9** suggests the use of two [β-diketiminato]Cu fragments in concert to stabilize other highly electrophilic functional groups such as nitrenes (NR) for related copper-catalyzed group transfer processes.[41]

Experimental Section

General Considerations. All experiments were carried out in a dry nitrogen atmosphere using glovebox and standard Schlenk line techniques when required. 4A molecular sieves were activated at 180 °C in vacuo for 24 h. Anhydrous toluene was purchased from Aldrich and was stored over 4A molecular sieves prior to use. Diethyl ether, pentane, and hexane were distilled before use from sodium/benzophenone. All deuterated solvents were sparged with nitrogen, dried over 4A molecular sieves, and stored under nitrogen. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Mercury Varian 300 MHz spectrometer at 300 and 75.4 MHz, respectively, at 25 °C unless otherwise noted. The spectra were indirectly referenced to TMS using residual solvent signals as internal standards. GC−MS spectra were recorded on a Fisions Instruments MD800, UV−vis spectra were taken with an Agilent 8453 diode array spectrometer, and elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratory.

Anhydrous CuBr was obtained from Strem and used as received. Styrene and para-substituted styrenes were obtained from Aldrich and passed through activated Al_2O_3 before use. Ethyl diazoacetate containing up to 10% dichloromethane was obtained from Aldrich and used as received. Tetraphenylethylene and naphthalene for GC−MS standards were obtained from Aldrich and Acros, respectively, and used as received. Tl[Me$_2$NN],[22] Tl[Me$_3$NN],[34] [Me$_2$NN]Cu(ethylene),[22] diphenyldiazomethane,[42] and *para*-trifluoromethylstyrene[43] were synthesized according to literature procedures.

Computational Details. The DFT calculations employed the Becke−Perdew exchange correlation functional[44] using the Amsterdam Density Functional suite of programs (ADF 2002.03).[45] Slater-type orbital (STO) basis sets employed for H, C, and N atoms were of triple-ζ quality augmented with two polarization functions (ZORA/TZP2−ADF basis V), while an improved triple-ζ basis set with two polarization functions (ZORA/TZP2+) was employed for the Cu atom. Scalar relativistic effects were included by virtue of the zero order regular approximation (ZORA).[46] The 1s electrons of C and N as well as the 1s−2p electrons of Cu were treated as frozen core. The Vosko, Wilk, and Nusair (VWN) functional was used for local density approximation (LDA).[47] The contour plots in Figures 5 and 6 were rendered with the MOLEKEL molecular graphics package.[48]

Employing typical bond distances and angles for the β-diketiminate ligand, coordinates for the simplified molecules [$C_3H_2N_2$]Cu═CH$_2$ (**6**) and {[$C_3H_2N_2$]Cu}$_2$(μ-CH$_2$) in C_{2v} symmetry (**7-C$_{2v}$**) as well as C_2 symmetry (**7-C$_2$**) (z-axis unique) were developed, optimized, and converged. In the absence of symmetry constraints, optimization of [$C_3H_2N_2$]Cu═CH$_2$ starting with a twist angle of 45° between the β-diketiminate backbone and carbene planes gave a converged structure nearly identical to the C_{2v} model **6**, indicating an electronic preference for the carbene to be perpendicular to the β-diketiminate backbone. An alternative C_{2v} structure for **6** in which the β-diketiminate backbone and carbene moieties are coplanar was significantly higher in electronic energy. Despite the dramatic simplification of models **6** and **7** relative to {[Me$_2$NN]Cu}$_2$(μ-CPh)$_2$ (**3**) and [Me$_3$NN]Cu═CPh$_2$ (**8**), bond distances in the models were in reasonable agreement to those found in the X-ray structures of **3** and **8**, but tended toward shorter Cu−ligand bond distances because of the absence of steric effects present in the full systems **3** and **8**.

Catalytic Cyclopropanation of Styrene and EDA by [Me$_2$NN]Cu(ethylene) (2). EDA (0.28 mg, 2.211 mmol) (commercial sample contained ca. 10% CH_2Cl_2) was added to a solution of [Me$_2$NN]Cu(ethylene) (0.017 g, 0.044 mmol) and styrene (1.150 g, 11.06 mmol) in 5 mL of toluene. The mixture was stirred for 2h, naphthalene (0.195 g) was added as an internal standard, and an aliquot of the resulting solution was diluted and analyzed by GC−MS to give a 76.9% yield of 1-ethoxycarbonyl-2-phenyl-cyclopropane with diastereoselectivity of cis/trans ≈ 38/62. The trans isomer was isolated and characterized by ^{1}H NMR, which was consistent with literature data.[49]

Catalytic Cyclopropanation of Styrene and N$_2$CPh$_2$ by [Me$_2$NN]Cu(ethylene) (2). To a solution of [Me$_2$NN]Cu(ethylene) (0.015 g, 0.038 mmol) and styrene (0.780 g, 7.50 mmol) in 10 mL of toluene, a solution of N$_2$CPh$_2$ (0.165 g, 0.757 mmol) in 9 mL of toluene was added by syringe pump at room temperature over a period of 20 h. After stirring at RT for another 6 h, we added naphthalene (0.112 g) as an internal standard, and an aliquot of the resulting solution was passed through silica gel and analyzed by GC−MS to give a 68% yield of 1,1,2-triphenylcyclopropane[14] along with the azine Ph$_2$C═N−N═CPh$_2$[50] in ca. 30% yield.

Preparation of {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (3). A cooled (−35 °C) solution of N$_2$CPh$_2$ (0.074 g, 0.34 mmol) in 3 mL of toluene was added with stirring to a cooled (−35 °C) solution of [Me$_2$NN]Cu(ethylene) (0.268 g, 0.675 mmol) in 5 mL of toluene. The color of solution turned dark purple immediately, and effervescence was observed. After being stirred at room temperature for 3 min, the reaction mixture was placed into the freezer and allowed to stand overnight. The volatiles were removed in vacuo, and the residue was extracted with ether (10 mL) and filtered through Celite. The filtrate was concentrated and allowed to stand at −35 °C. Dark purple crystals which had formed were collected on a frit, washed with cold ether, and dried in vacuo to afford 0.122 g (40.3%) of product as a 1:1 ether solvate. Recrystallization from hexane afforded crystals of **3** • 0.75 hexane suitable for X-ray diffraction. ^{1}H NMR (toluene-d_8, −70 °C): δ 7.3−6.4 (m, 20, Ar), 6.16 (d, 2, *o*-CPh$_2$), 5.010 (s, 2, backbone-C*H*), 2.951 (s, 6, Ar−C*H*$_3$), 1.953 (s, 6, Ar−C*H*$_3$), 1.920 (s, 6, Ar−C*H*$_3$), 1.639 (s, 6, backbone-C*H*$_3$), 1.565 (s, 6, backbone-C*H*$_3$), 1.213 (s, 6, Ar−C*H*$_3$). ^{13}C{^{1}H} NMR (toluene-d_8, −70 °C): δ 189.41 (*C*Ph$_2$), 162.75 (imine), 161.18 (imine), 152.98, 148.46, 147,50, 138.14, 137.04, 133.12, 132.91, 129.36, 128.84, 128.21, 127.32, 125.13, 124.82, 124.49 (four aromatic resonances obscured or coincident), 96.81 (backbone-*C*H), 21.46, 21.21, 20.95, 20.70, 20.45. 20.19 (one backbone *Me* obscured or coincident). Anal. Calcd for $C_{55}H_{60}N_4Cu_2$: C, 73.06; H, 6.69; N, 6.20. Found: C, 73.19; H, 6.65; N, 6.09.

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At −70 °C, [Me$_2$NN]Cu═CPh$_2$ (**4**) and [Me$_2$NN]Cu(toluene) (**5**) were also present in ca. 2% of the concentration {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (**3**) as determined by ^{1}H NMR. Selected ^{1}H NMR resonances for [Me$_2$NN]Cu═CPh$_2$ (**4**): δ 7.400 (d, 2, *o*-Ph), 4.958 (s, 1, backbone-C*H*), 2.026 (s, 6, Ar−C*H*$_3$). Selected ^{1}H NMR resonances for [Me$_2$NN]Cu(toluene) (**5**): δ 4.801 (s, 1, backbone-C*H*), 2.384 (s, 6, Ar−C*H*$_3$). With increasing temperature, **4** and **5** increased in intensity at the expense of **3**.

The thermal decomposition of compound **2** in benzene-*d*$_6$ (ca. 20 mM) was monitored by ^{1}H NMR spectroscopy. After 56 h at room temperature, 57% of the initial concentration of **2** was still present. The other β-diketiminate containing product observed was the solvento species [Me$_2$NN]Cu(benzene-*d*$_6$).

Preparation of [Me$_2$NN]Cu(toluene) (5). A solution of [Me$_2$NN]Tl (0.450 g, 0.883 mmol) in 5 mL of toluene was stirred with powdered CuBr (0.325 g, 2.262 mmol) for 1 day. The volatiles were removed in vacuo, the residue was extracted with 10 mL of pentane, and the mixture was filtered through Celite. The filtrate was concentrated, a few drops of toluene were added, and the solution was allowed to stand at −35 °C to give 0.118 g (28.9%) dark brown crystals. ^{1}H NMR (benzene-*d*$_6$): δ 6.9−7.1 (m, 11, Ar-*H*), 4.769 (s, 1, backbone-C*H*), 2.128 (s, 3, toluene-C*H*$_3$), 2.011 (s, 12, Ar−C*H*$_3$), 1.625 (s, 6, backbone-C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-*d*$_6$, partial data): 162.42, 150.55, 132.33, 130.63, 129.28, 94.42 (backbone-*C*H), 23.28, 19.03, 18.69. Anal. Calcd for $C_{28}H_{33}N_2Cu$: C, 72.93; H, 7.21; N, 6.07. Found: C, 72.66; H, 7.09; N, 5.94.

Determination of Thermodynamic Parameters ΔH and ΔS for the Dissociation of One [Me$_2$NN]Cu Fragment from {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (3) in Toluene. A sample of {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (0.020 g, 0.024 mmol) was dissolved in 1 mL of toluene-*d*$_8$ in a volumetric flask and transferred to an NMR tube. ^{1}H NMR spectra were acquired every 10° over the range of temperatures −20 to 60 °C. The use of relative integrals for the β-diketiminato backbone C−H resonances corresponding to {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (**3**) (δ 5.010 ppm), [Me$_2$NN]Cu═CPh$_2$ (**4**) (δ 4.958 ppm), and [Me$_2$NN]Cu(toluene) (**5**) (δ 4.801 ppm) against an internal standard allowed the calculation of the equilibrium constants at different temperatures using the following dependence with an initial {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$)} (**3**) concentration of 0.024 M:

$$K_{\mathrm{eq}} = \frac{[\text{initial concn (M) of } \mathbf{3}] \times \{([\mathrm{Me_2NN}]\mathrm{Cu{=}CPh_2}) \times ([\mathrm{Me_2NN}]\mathrm{Cu(toluene)})\}}{\{[\mathrm{Me_2NN}]\mathrm{Cu}\}_2(\mu\text{-}\mathrm{CPh_2})}$$

A van’t Hoff plot of ln K_{eq} vs 1/*T* allowed in calculation of $\Delta H = 9.1$ (3) kcal/mol (from slope) and $\Delta S = 24(1)$ cal/mol·K (from intercept) (Figure 3).

Reaction of {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (3) with Styrene. Styrene (0.010 g, 0.009 mmol) and {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (0.026 g, 0.003 mmol) were dissolved in 0.75 mL of benzene-*d*$_6$ and stirred until the purple color of **2** completely disappeared (ca. 45 min). ^{1}H NMR analysis showed that [Me$_2$NN]Cu(styrene)[22] at δ 4.858 ppm (1H, s, backbone C−H), 2.215 ppm (6H, br. s, Ar−C*H*$_3$), 1.724 ppm (6H, br. s, Ar−C*H*$_3$), 1.585 ppm (6H, s, backbone-C*H*$_3$), and 1,1,2-triphenylcyclopropane at δ 2.870 ppm (1H, m, C*H*Ph) were formed in a 2:1 ratio. 1,1,2-Triphenylcyclopropane[14] was also identified by GC−MS.

Reaction of {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (3) with N$_2$CPh$_2$. A solution of N$_2$CPh$_2$ (0.028 g, 0.128 mmol) in 2 mL of toluene was added with stirring to a solution of {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (0.114 g, 0.126 mmol) in 5 mL of ether. After being stirred at room temperature for 15 min, the reaction mixture was placed into the freezer and allowed to stand overnight. Colorless crystals were isolated by decantation of the solution, rinsed with chilled pentane, and dried in vacuo to give 0.019 g (37%) of the azine Ph$_2$C═N−N═CPh$_2$,[50] whose identity was confirmed by GC−MS.

Table 4. Cyclopropanation of Alkenes by {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (**3**)

olefin	yield of cyclopropane[a]	tetraphenylethylene[a]	reaction time[b]
styrene	100	0	1/2
α-methylstyrene	100	0	2
trans-β-methylstyrene	26.8 (32.0[c])	73.2	2 (45 °C)[d]
cyclooctene	19.7	80.3	2 (45 °C)[d]
1-hexene	21.0	79.0	2 (45 °C)[d]
No. olefin	0	100	2 (45 °C)[d]

[a] In percent. [b] In hours. [c] This yield was determined directly from the cyclopropane peak area using the same response factor determined for 1,1,2-triphenylcyclopropane. [d] No change after stirring for 2 h at room temperature and then heating to 45 °C for 2 h.

Survey of Reactivity of {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (3) with Different Olefins. A 10.0-mL solution of {[Me$_2$NN]Cu}$_2$(μ-CPh$_2$) (0.101 g, 0.112 mmol, 0.012 mM) in toluene was divided into five 2.0-mL portions. Fifty equivalents of each olefin (1.117 mmol) were added individually to separate 2.0-mL portions of dicopper carbene. In the case of styrene and α-methylstyrene, the corresponding solutions turned yellow within 2 h at room temperature. For the other alkenes, the resulting solutions were heated at 45 °C for 2 h to completely discharge the intense purple color of the copper carbene species. A solution of naphthalene (0.052 g) in 10.0 mL of toluene was divided to five 2-mL portions and added individually as an internal standard to each of the five solutions above. The resulting solutions were analyzed by GC−MS (Table 4). In all cases the yield of Ph$_2$C═CPh$_2$ was determined directly against the internal naphthalene standard. The yield of cyclopropane was obtained by mass balance since no other Ph$_2$C-containing products were observed. In the case of styrene, the quantitative conversion to 1,1,2-triphenylcyclopropane was verified by using an authentic standard. A blank solution without olefin was decomposed under the same conditions to give a quantitative yield of Ph$_2$C═CPh$_2$.

Preparation of [Me$_3$NN]Cu(toluene). An analogous procedure as that for [Me$_2$NN]Cu(toluene) was followed employing [Me$_3$NN]Tl (0.491 g, 0.913 mmol) and CuBr (0.386 g, 2.690 mmol) to give 0.148 g (33.2%) dark brown crystals. ^{1}H NMR (benzene-*d*$_6$): δ 6.8−7.1 (m, 11, Ar-*H*), 4.797 (s, 1, backbone-C*H*), 2.269 (s, 6, Ar−C*H*3), 2.106 (s, 3, toluene-C*H*$_3$), 2.032 (s, 12, Ar−C*H*$_3$), 1.672 (s, 6, backbone-C*H*$_3$). ^{13}C{^{1}H} NMR (benzene- *d*$_6$, partial data): 162.72, 160.96, 148.19, 141.80, 137.80, 131.97, 130.30, 129.26, 94.46 (backbone-*C*H), 23.27, 21.15, 18.98, 18.65. Anal. Calcd for $C_{30}H_{37}N_2Cu$: C, 73.66; H, 7.62; N, 5.73. Found: C, 73.34; H, 7.31; N, 5.31.

Preparation of [Me$_3$NN]Cu═CPh$_2$ (8). A cooled (−35 °C) solution of N$_2$CPh$_2$ (0.061 g, 0.280 mmol) in 3 mL of ether was added with stirring to a cooled (−35 °C) solution of [Me$_3$NN]Cu(toluene) (0.135 g, 0.276 mmol) in 5 mL of ether. The color of solution turned metallic purple immediately. After being stirred at room temperature for 3 min, the reaction mixture was filtered through Celite, and the filtrate was concentrated and allowed to stand at −35 °C to give dark purple crystals. The product was isolated and recrystallized from pentane at −35 °C to afford 0.031 g (20%) of product. ^{1}H NMR (benzene-*d*$_6$): δ 7.376 (dd, 4, *m*-CPh), 7.138 (m, 2, *p*-CPh), 6.866 (t, 4, *o*-CPh), 6.643 (s, 4, Ar-*H*), 4.941 (s, 1, backbone-C*H*), 2.331 (s, 12, Ar-*o*-C*H*$_3$), 1.996 (s, 6, Ar-*p*-C*H*$_3$), 1.593 (s, 6, backbone-C*H*$_3$). ^{13}C{^{1}H} NMR (benzene-*d*$_6$): δ 253.10 (*C*Ph$_2$), 162.23, 155.86, 148.83, 132.54, 130.89, 129.23, 128.92, 128.88, 128.82, 96.44 (backbone-*C*H), 23.18 (Ar-*o*-*C*H$_3$), 21.27 (Ar-*p*-*C*H$_3$), 19.31 (backbone-*C*H$_3$). Anal. Calcd for $C_{36}H_{39}N_2Cu$: C, 76.77; H, 6.98; N, 4.97. Found: C, 76.89; H, 6.73; N, 4.63.

Kinetic Studies for the Cyclopropanation of Styrene with [Me$_3$NN]Cu═CPh$_2$ (8) in 1,4-Dioxane. A 25.0-mL stock solution of [Me$_3$NN]Cu═CPh$_2$ (11.8 mg, 0.021 mmol) and styrene (218 mg, 2.10 mmol) in 1,4-dioxane was prepared using a volumetric flask. This stock solution was divided to five 5.0-mL portions, and each was frozen in dry ice until used. In separate experiments, the decreasing concentration

Table 5. Relative Rates of Cyclopropanation of Styrene Derivatives by $[Me_3NN]Cu{=}CPh_2$ (**8**)

styrene derivative (p-X–C_6H_4–CH=CH_2)	rate constant for cyclopropanation (UV–vis, k_{obs} (s^{-1}))	yield of (X=H) cyclopropane (%)	k_X/k_H (competition)	k_X/k_H (UV–vis)
X = OMe	$7.27(9) \times 10^{-4}$	30.3[a]	2.3[a]	2.95
X = Me	$3.65(5) \times 10^{-4}$	41.5	1.41	1.48
X = H	$2.47(5) \times 10^{-4}$	100	1.00	1.00
X = CF_3	$1.35(5) \times 10^{-4}$ $(1.05(5) \times 10^{-4})$[b]	49.5	1.02	1.28

[a] The yield of 1,1,2-triphenylcyclopropane could not be accurately obtained because of the overlapping of *p*-methoxystyrene and the naphthalene standard in the gas chromatogram. The ratio of k_X/k_H comes from the ration of peak area in GC−MS. [b] The relative rate for cyclopropanation of *para*-trifluoromethylstyrene vs styrene was determined in a separate run; the number in parentheses is the corresponding rate constant for styrene cyclopropanation under the slightly different conditions.

of $[Me_3NN]Cu{=}CPh_2$ over time was quantified by UV−vis spectroscopy by monitoring the decrease in intensity of the band due to **8** at $\lambda_{max} = 566$ nm at the temperatures 17.5, 30.2, 40.5, 50.0, and 60.2 °C. Data were generally taken for ca. 3 half-lives. Temperatures can be deemed accurate ±0.5 °C. Plots of $\ln[A_t - A_\infty]$ versus time gave straight lines with observed rate constants that appear in Table 2. Uncertainties in reported rate constants were estimated on the basis of inspection of the sensitivity of the fits of the $\ln[A_t - A_\infty]$ versus time plots. The concentration of styrene was 0.08385 M in each case, leading to $k_{act} = k_{obs}/0.0839$ M.

Relative Rates for Cyclopropanation of para-Substituted Styrenes (p-X−C_6H_4−CH=CH_2) with $[Me_3NN]Cu{=}CPh_2$ (8). Two separate methods were used to determine the relative rates of cyclopropanation k_X/k_H for para-substituted styrenes (X = OMe, M, H, CF_3) compared to that of styrene (X = H) collected in Table 5 used to prepare the Hammet plot in Figure 10.

(a) Competition Experiments. A solution of $[Me_3NN]Cu{=}CPh_2$ (10.9 mg, 0.019 mmol) with an internal standard of naphthalene in 1,4-dioxane was diluted to 10.0 mL using a volumetric flask. The solution was divided to five 2-mL portions to which styrene and a substituted styrene were added. The solutions were stirred for 1 h and analyzed by GC−MS. The yield of 1,1,2-triphenylcyclopropane (Y_H) was determined against the naphthalene standard. As <1% $Ph_2C{=}CPh_2$ was observed in each of these competition experiments, the yield of the *p*-substituted 1,1,2-triphenylcyclopropane (Y_X) was determined by mass balance. The relative rate k_X/k_H was thus determined by the relationship: $k_X/k_H = Y_X/Y_H = (100 - Y_H)/Y_H$ (Table 5).

(b) Direct Kinetic Measurements. For comparison, kinetic studies were carried out with para-substituted styrenes (X = OMe, Me, H, CF_3) by the method described for the cyclopropanation of styrene by **8** using 100 equiv of the substituted styrene. The temperature of the UV−vis cell was thermostated at 40.0 °C during the kinetic measurements for each member of the series. The rate constants k_X and k_H thus were independently measured under identical conditions, allowing for the tabulation of k_X/k_H for each styrene derivative (Table 5).

Kinetic Studies for Decomposition of $[Me_3NN]Cu{=}CPh_2$ (8) in 1,4-Dioxane at Various Temperatures. A 25.0-mL stock solution of $[Me_3NN]Cu{=}CPh_2$ (11.8 mg, 0.021 mmol) in 1,4-dioxane was prepared using a volumetric flask. This stock solution was divided to five 5.0-mL portions and frozen in dry ice until used. In separate experiments, the decreasing concentration of $[Me_3NN]Cu{=}CPh_2$ over time was quantified by UV−vis spectroscopy by monitoring the decrease in intensity of the band due to **8** at $\lambda_{max} = 566$ nm at the temperatures 32.2, 40.0, 49.0, and 60.0 °C. Data were generally taken for ca. 3 half-lives. Temperatures can be deemed accurate ±0.5 °C. Plots of $\ln[A_t - A_\infty]$ versus time gave straight lines with observed rate constants that appear in Table 3. Uncertainties in reported rate constants were estimated on the basis of inspection of the sensitivity of the fits of the $\ln[A_t - A_\infty]$ versus time plots.

Thermal Decomposition of $[Me_3NN]Cu{=}CPh_2$ (8) in Benzene-d_6. An approximate 40 mM solution of $[Me_3NN]Cu{=}CPh_2$ (0.015 g) in benzene-d_6 (0.7 mL) was prepared and monitored by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy at room temperature. Within 2.5 h, the ^{13}C NMR signal of CPh_2 at δ 253.10 ppm decayed, and a new resonance at δ 189.0 ppm grew in. After 12 h, there was a 1.55:1.00:0.19 molar ratio of $\{[Me_3NN]Cu\}_2(\mu\text{-}CPh_2)$/$[Me_3NN]Cu{=}CPh_2$/$[Me_3NN]Cu$(benzene-$d_6$) in the solution. Partial NMR data for $\{[Me_3NN]Cu\}_2(\mu\text{-}CPh_2)$ (**9**): ^1H NMR (benzene-d_6): δ 5.018 (s, backbone-C*H*), 1.624 (s, backbone-CH_3), 1.8−2.3 (br, Ar−CH_3). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 189.0 (*C*Ph_2), 97.11 (backbone-*C*H), 23.92 (Ar-*o*-*C*H_3), 21.28 (Ar-*p*-*C*H_3), 19.99 (backbone-*C*H_3). Partial data for $[Me_3NN]Cu$(benzene-d_6): ^1H NMR (benzene-d_6): δ 4.810 (s, backbone-C*H*), 2.033 (s, 12, Ar−CH_3).

X-ray Structure Refinement Details. Single crystals of each compound were mounted under mineral oil on glass fibers and immediately placed in a cold nitrogen stream at −90(2) °C on a Bruker SMART CCD system. Hemispheres of data were collected (0.3° ω-scans; $2\theta_{max} = 56°$; monochromatic Mo Kα radiation, $\lambda = 0.7107$ Å) and integrated with the Bruker SAINT program. Structure solutions were performed using the SHELXTL/PC suite[51] and XSEED.[52] Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using Blessing's method as incorporated into the program SADABS.[53] Non-hydrogen atoms were refined with aniostropic thermal parameters, and hydrogen atoms were included in idealized positions. Because disordered hexane molecules of solvation were found in the initial refinement of $\{[Me_2NN]Cu\}_2(\mu\text{-}CPh_2)$ (**3**) that could not be satisfactorily modeled, the SQUEEZE subroutine of PLATON[54] was used. A total of 314 solvent electrons were identified corresponding to ca. 0.75 molecules of hexane per $\{[Me_2NN]Cu\}_2(\mu\text{-}CPh_2)$ (six hexanes per unit cell), and the reflection data were refined excluding the solvent to give refinement details collected in Tables S1−S5.

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Supporting Information Available: VT ^1H NMR spectra for **3**, additional calculational details for calculated structures **6**, **7-C2v**, and **7-C$_2$**, plots of $\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ versus time for cyclopropanation of styrene by **8** from 17.5 to 60.2 °C, representative UV−vis plot for thermal decomposition of **8**, plots of $\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ versus time for thermal decomposition of **8** from 30.2 to 60.0 °C, tables of X-ray refinement data, bond distances, and bond angles along with fully labeled ORTEP plots for **3** and **8** (also provided in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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