Inorg. Chem. **2008**, *47*, 11755−11762

Inorganic Chemistry

Article

Synthesis, Molecular Structures, and Reactivity of Mono- and Binuclear Neutral Copper(I) Carbenes

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Received August 5, 2008

Mononuclear, neutral copper(I) carbenes $[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu{=}CPh_2$ and $[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu{=}C(p\text{-}NO_2C_6H_4)_2$ (**4a,b**) as well as the binuclear μ-carbene copper complex $\{[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu\}_2(\mu\text{-}CPh_2)$ (**5**) have been synthesized. The solid-state structures of **4b** and **5** are reported. Carbene **4b** is active in cyclopropanation of styrene. Reaction of **4b** with $(p\text{-}MeC_6H_4)C{=}N_2$ afforded $[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu{=}C(p\text{-}MeC_6H_4)_2$, the corresponding mixed azine $Ar_2C{=}N{-}N{=}CAr'_2$ and the carbene dimer $Ar_2C{=}CAr'_2$, demonstrating an important pathway for carbene loss in cyclopropanation of olefins via reaction of the copper(I) carbene with nucleophilic diazo compounds. Complex **5** reacted with C_2H_4 or styrene to give 1:1 mixtures of the terminal carbene **4a** and of the corresponding copper(I) olefin complexes, proving unambiguously that binuclear complexes like **5** are not relevant for copper-catalyzed cyclopropanation of olefins with diazo compounds. The electronic structure of **4b** was investigated by means of DFT calculations.

Introduction

Copper-catalyzed cyclopropanation reactions of olefins using diazoalkane derivatives have been of substantial interest and great preparative value for more then 35 years.[1,2] Copper carbenes had been considered to be the active cyclopropanating species in the catalytic cycle,[2,3] although an experimental proof of their existence was only achieved very recently.[4] Introduction of a tailor-made, electron-rich, sterically demanding iminophosphanamide ligand[5] into the organometallic chemistry of copper[6a] and the synthesis of copper(I) olefin complexes like $[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu(\eta^2\text{-}C_2H_4)$[6] have allowed us to synthesize and characterize *in situ* the first neutral α-carbonyl copper(I) carbenes.[4] A report of a unique cationic copper(I) carbene by Barluenga et al. followed soon after.[7] The neutral Cu(I) carbenes were shown to cyclopropanate double bonds[4] but, because of their high reactivity, they could be only formed *in situ* and observed in a steady-state concentration. Also very recently, employment of the β-diketiminate ligand by Warren and Dai[8a] allowed the isolation and X-ray structure determination of the neutral dicopper carbene **1**, and its role in cyclopropanation of olefins was discussed. The authors came to the conclusion that owing to the steric crowding in their dinuclear species **1**, cyclopropanation with **1** likely proceeds through a terminal carbene, structurally analogous to **2**, which was obtained if the more sterically congested β-diketiminate ligand was used.[8a] This interpretation is backed up by the observation that in arene solvent dicopper carbenes dissociate to mononuclear terminal carbene complexes and arene complexes of the (β-diketiminate)Cu-fragment. The reactivity

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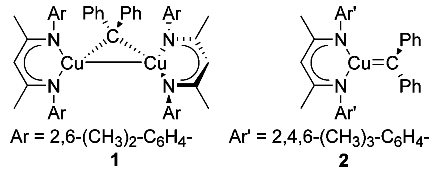


Figure 1

of the dinuclear species **1** but not that of **2** toward diphenyldiazomethane was mentioned to lead to the formation of the azine $Ph_2C{=}NN{=}CPh_2$ (Figure 1). Compound **2** was characterized by X-ray diffraction as a mononuclear copper(I)carbene, but even the bulky ligand was shown not to prevent the formation of a dicopper carbene.[8b] The most recent experimental report supported by DFT calculations about a mononuclear copper(I) diphenyl carbene complex, only detected spectroscopically in solution and unstable even at −30 °C, came from Peters et al.,[8c] who employed the bulky, anionic bis(phosphino)borate ligand $Ph_2B(CH_2P^tBu_2)_2$ as a spectator ligand.

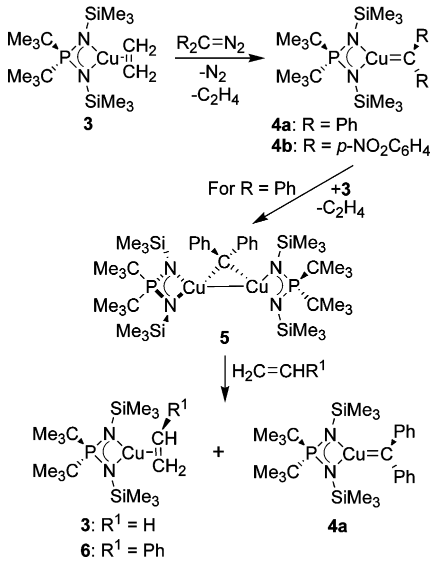
In connection to an extensive density-functional theory (DFT) theoretical study[6b,9] of copper catalyzed cyclopropanation with neutral copper carbenes, their solid state structural data should provide valuable information, that may help to understand the enantiomeric and diastereomeric selectivities that can be achieved if chiral spectator ligands are utilized.[3,10] Isolation of analytically pure copper(I) carbenes was therefore highly desirable since it will allow detailed studies of their properties and reactivity.

Employing the above-mentioned iminophosphanamide ligand, we report here the synthesis, molecular structures, and reactivity of remarkably stable copper(I) carbenes **4a-b** and of the binuclear *μ*-carbene copper complex **5**.

Results and Discussion

Reaction of the copper(I) ethylene complex **3** (Scheme 1) with diphenyldiazomethane at ambient temperature in toluene led to a deep-violet solution of carbene complex **4a** (characterized by NMR spectroscopy). Compound **4a** is significantly more stable in solution than our previously reported α-carbonyl copper carbenes.[4] Its steady-state concentration in, for example, toluene of up to 35%, relative to complex **3**, remains almost constant for several days and allows detailed NMR spectroscopy.

Scheme 1



Slow evaporation at 10^{-3} mbar of a solution in hexane instead of toluene, containing compounds **4a** and **3**, led to the precipitation of brown crystals of the dinuclear copper complex **5**. The compound could not be isolated in analytically pure form as it decomposes rapidly at ambient temperature and the isolated solid is contaminated with traces of **4a**. Its solid-state geometry is shown in Figure 2.

Compound **5** represents a unique *μ*-carbene copper complex with a short Cu(1)−Cu(2) bond [2.4165(3) Å] and Cu−C distances of 1.9225(18) and 1.9222(18) Å. The copper−copper bond in **5** is shorter by 0.047 Å than one reported for binuclear complex **1** [2.4646(7) Å].[8] On the other hand, the copper−carbon separations compared to carbene **1** [1.922(4) and 1.930(4) Å][8] remain almost the same. The solid-state structure of the complex reveals that the two slightly puckered [CuNPN] chelate rings are twisted by 48° and 43° relative to the plane of the three-membered CuCCu ring and twisted by 85° relative to each other. Compound **5** does not exhibit crystallographic C_2-symmetry, presumably because of steric crowding. The copper atoms lie in a tetrahedrally distorted, square planar environment, and the

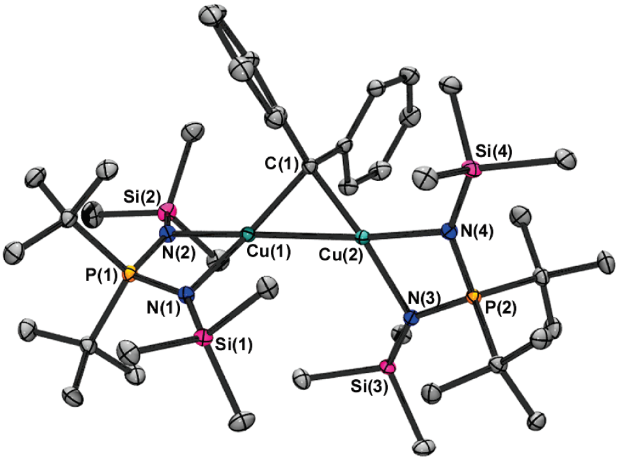


Figure 2. Oak Ridge Thermal Ellipsoid Plot (ORTEP) diagram of the solid-state structure of **5**. 50% ellipsoids, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)−Cu(2) 2.4165(3), Cu(1)−C(1) 1.9225(18), Cu(2)−C(1) 1.9222(18), Cu(1)−N(1) 2.0341(15), Cu(1)−N(2) 2.0470(15), Cu(2)−N(3) 2.0262(15), Cu(2)−N(4) 2.0503(15), P(1)−N(1) 1.6062(15), P(1)−N(2) 1.6123(15), P(2)−N(3) 1.6094(15), P(2)−N(4) 1.6079(15); N(1)−Cu(1)−N(2) 76.33(6), N(3)−Cu(2)−N(4) 76.59(6), Cu(1)−C(1)−Cu(2) 77.88(7).

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carbene carbon atom displays distorted tetrahedral bonding toward the two phenyl rings and the copper centers.

Compound **5** readily reacts with an excess of ethylene already at −30 °C to give a 1:1 mixture of ethylene complex **3** and carbene **4a** (Scheme 1). Reaction of **5** with an excess of styrene, again at −30 °C also led to a 1:1 mixture of the corresponding carbene **4a** and styrene complex **6**.[6b] These data undoubtedly demonstrate that binuclear complex **5** itself is not active in cyclopropanating of olefins, since it reacts with them to form the terminal carbene **4a** and the corresponding olefin complexes. Complex **5** is less stable than Warren's corresponding carbene **1** and decomposes in toluene solution at room temperature within 2 days.

Carbene complex **4b** can be synthesized from copper ethylene complex **3** and di(*p*-nitrophenyl)diazomethane. The stability of **4b** is remarkable: its synthesis was performed at 55 °C over a period of 35 min, and despite these rather drastic conditions, this compound was isolated from the reaction mixture in 55% yield. Lower solubility of carbene **4b** in hexane as compared to **4a** facilitates its purification and crystallization.

No dinuclear species was observed in case of **4b**, presumably because of strengthening of the Cu−C back-bonding as compared to **4a** because of the presence of two strong π-accepting NO_2 groups in the *para* position of the aromatic ring of **4b** that makes it more inert toward the reaction with the olefin complex **3**. This fact can be semiquantitatively understood by comparison of the ^{31}P NMR spectra of compounds **4a-b**. The higher back-bonding in complex **4b** leads to an increased net charge transfer from the nitrogen atoms to copper. In turn, the nitrogen atoms withdraw electron density from the Si and P atoms of the N_2PCu core that leads to the observed deshielding of the phosphorus atom in **4b**. In fact, the phosphorus atom of **4b** resonates at a lower field (66.7 ppm) compared to **4a** (59.6 ppm). Bent's rule[11] predicts that electropositive atoms have the largest s-character in bonds to other electropositive atoms or in lone pairs. Upon increasing the net electronegativity of nitrogen by coordination of an electron-withdrawing ligand (such as a carbene) to copper, both Si and P will decrease the s-character in their bonds to nitrogen. On the other hand, the magnitude of the coupling constants depends on the s-character of the bonds of the coupling atoms.[12] A smaller $^2J_{PSi}$ coupling constant (11.8 Hz) is indeed verified for complex **4b** (**4a**: $^2J_{PSi} = 14.8$ Hz) thus confirming the higher back-bonding in carbene **4b**. The described α-carbonyl copper carbenes $[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu{=}C(Ar)(COOR)$[4] bearing an accepting α-carbonyl group also do not form binuclear species.

The molecular structure of **4b** was determined by single crystal X-ray analysis (Figure 3). The copper atom is in a trigonal planar environment; the [NPNCu] ring and the carbene carbon share the same plane (torsion angle N(1)−N(2)−Cu−C(1): −178.8°), and the connecting line P−Cu−C(1) is almost linear. The carbene unit is nearly orthogonal relative to the [N_2Cu] plane (angle between [N_2Cu] plane and line C(31)−C(41): 11°). The carbene carbon is slightly pyramidalized by 6° (vector C(1)−Cu(1) vs plane [C(31)−C(1)−C(41)]). The NO_2 groups are essentially coplanar with the phenyl rings, maximizing conjugation. The Cu=C distance (1.8321(18) Å) represents a double bond, has a very similar value to the one reported for terminal carbene **2** (1.834(3) Å),[8] and is significantly shorter than found for Barluenga's cationic copper carbene (1.882(3) Å),[7] and for copper carbenes with Wanzlick−Arduengo carbene ligands[13a,b] with their minimal acceptor character, or for (NHC) copper alkyls.[13c]

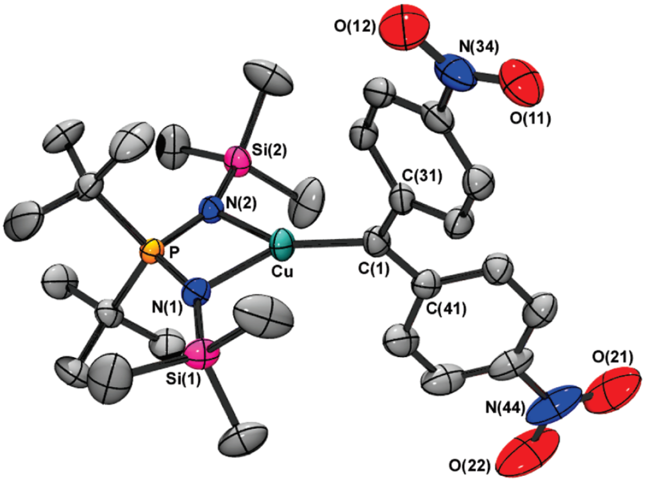

Figure 3. ORTEP diagram of the solid state structure of **4b**. 50% ellipsoids, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu−C(1) 1.8321(18), Cu−N(1) 1.9711(16), Cu−N(2) 1.9658(14), P−N(1) 1.6031(15); N(1)−P-N(2) 101.84(8), N(1)−Cu−N(2) 78.49(6), P−Cu−C(1) 175.68(6), N(2)−Cu−C(1)−C(31) 103.3(2), N(2)−Cu-C(1)−C(41) −83.8(2).

^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} spectra of **4b** are in agreement with its solid-state structure. The two Bu-groups in **4b** in the ^{1}H NMR spectrum give rise to only one doublet at δ 1.36 ppm indicating a C_{2v}-symmetrical molecule in solution. The carbene carbon resonates at 239.7 ppm (**4a**, 264.5 ppm) in accordance with an electrophilic carbene center.[14] In the dinuclear species **5** the bridging carbon gives rise to a ^{13}C signal at 184.7 ppm (189.41 in Warren's compound **1**), clearly indicative of the different bonding situation in both cases. Interestingly, the orthogonality of the carbene fragment in copper(I) diarylcarbenes in solution may be indirectly confirmed by spectroscopic detection of the complex with an unsymmetrical carbene unit, $[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu{=}C(p\text{-}NO_2C_6H_4)(Ph)$, where the two Bu groups are diastereotopic and therefore appear in the ^{1}H NMR spectrum as two doublets at 1.42 and 1.38 ppm ($^3J_{HP} = 14.7$ Hz). The phosphorus signal in $[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu{=}C(p\text{-}NO_2\text{-}C_6H_4)(Ph)$ at δ 63.1 ppm was found approximately in between the chemical shifts found for compounds **4a** (δ 59.6) and **4b** (δ 66.7). Unfortunately, the unsymmetrical carbene complex $[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu{=}C(p\text{-}NO_2C_6H_4)(Ph)$ was formed in a very low (9%) steady-state concentration that prevented further examination of its properties.

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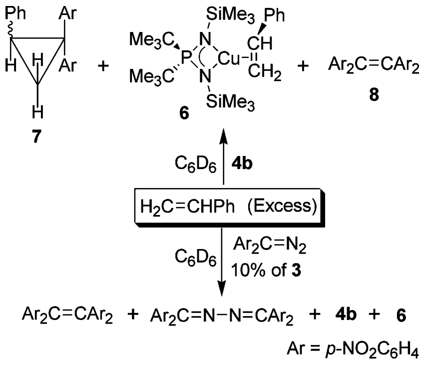
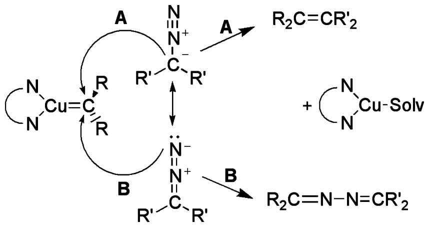
Scheme 2



Scheme 3

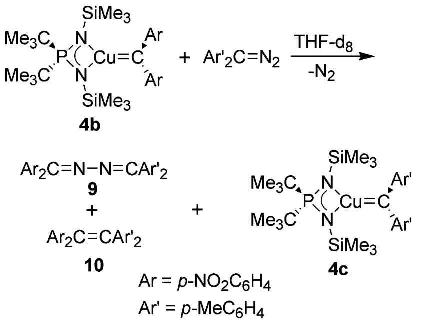


The steric shielding by and the high basicity of the anionic iminophosphanamide σ- and π-donor ligand, the enforced small N−Cu−N bite angle of 78.5° of the four-membered neutral chelate ring system, and the strong π-acceptor substituents NO_2 of the carbene phenyl rings are responsible for the unprecedented stability of **4b**. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the d^{10}-ML_2 fragment[15] lead to increased π-backbonding from Cu(I) toward the carbene and a strong σ-bond, thus strengthening of the Cu=C interaction.

A solution of pure carbene **4b** in C_6D_6 slowly reacts with styrene to form correspondingly substituted cyclopropane, styrene complex **6**, and some carbene dimer (Scheme 2). The latter compound could appear because of carbene thermal decomposition, a possibility already demonstrated by Warren.[8] However, reaction of styrene with $(p\text{-}NO_2C_6H_4)_2C{=}N_2$ in the presence of *catalytic* amounts of copper ethylene complex **3** did not afford the desired cyclopropane **7**. Instead, the carbene dimer and the azine were observed as the main products. The formation of some carbene **4b** and copper styrene complex **6** was also detected by ^1H NMR and ^{31}P NMR spectroscopy.

From the first point of view, these results look surprising since carbene **4b** was unambiguously shown to be the active cyclopropanating species. However, the coupling products may arise from a reaction of the electrophilic copper(I) carbene with the nucleophilic diazo compound, which, in principle, may attack the carbene carbon of **4b** either by the diazo carbon or the terminal nitrogen atom. The former interaction will lead, after nitrogen loss, to the carbene dimer, whereas the latter will yield the corresponding azine (Scheme 3). The solvated iminophosphanamide fragment formed will immediately react further with another molecule of the diazo compound to produce the respective copper carbene, thus continuing the cycle. Stabilization of the upper resonance form (case A) by delocalization of the negative charge through an R′ group (like in case of diazo esters) and small substituents at the diazo carbon should favor formation of carbene dimers. The upper resonance form must also be the main contribution to the structure of $(p\text{-}NO_2C_6H_4)_2C{=}N_2$, but the large *para*-nitrophenyl substitutents may disfavor dimer formation. Although the appearance of the azine byproduct in accordance with the proposed mechanism is obvious, the appearance of the carbene dimer can be alternatively ascribed to the carbene decomposition, and the possibility of path A in Scheme 3 will therefore require an additional verification.

Scheme 4



Upon addition of a solution of carbene complex **4b** to a solution of $(p\text{-}CH_3C_6H_4)_2C{=}N_2$ in THF-d_8, gas evolution was observed, and carbene dimer **10** and azine **9** were quickly formed in 1:6 ratio, respectively (Scheme 4). These compounds were characterized *in situ* by ^1H NMR spectroscopy and mass-spectrometry. The starting carbene **4b** was consumed in several minutes, and another copper carbene complex **4c** appeared in the reaction mixture. The carbene **4c** could be formed by a reaction of the solvated copper iminophosphanamide fragment (liberated upon reaction of **4b** with the diazoalkane) with another molecule of $(p\text{-}CH_3C_6H_4)_2C{=}N_2$. Compound **4c** further reacted with the diazo compound to produce the azine and dimer products. The formation of carbene **4c** was confirmed by comparison of its ^1H and ^{31}P NMR data (δ ^{31}P 56.5 in THF-d_8) with the spectra of a sample prepared independently from the copper olefin complex **3** and $(p\text{-}CH_3C_6H_4)_2C{=}N_2$ (δ ^{31}P 57.9 in toluene-d_8). Hence, the experimental data strongly suggest the mechanism depicted in Scheme 3 and support the mechanism proposed by Pérez et al.[16,17] for maleic and fumaric ester formation in copper-catalyzed cyclopropanations with EDA.

Very similarly, carbene **4b** reacted with α-carbonyl diazo ester $[p\text{-}MeOC_6H_4]C(N_2)[COOtBu]$ (**11**) to yield the dimer $(p\text{-}NO_2C_6H_4)_2C{=}C(p\text{-}MeOC_6H_4)(COOtBu)$ (**12**) and α-carbonyl carbene $[Bu^t{}_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu{=}C(p\text{-}MeOC_6H_4)(COOtBu)$ (**13**) (δ ^{31}P in CD_2Cl_2: 60.7). In this case,

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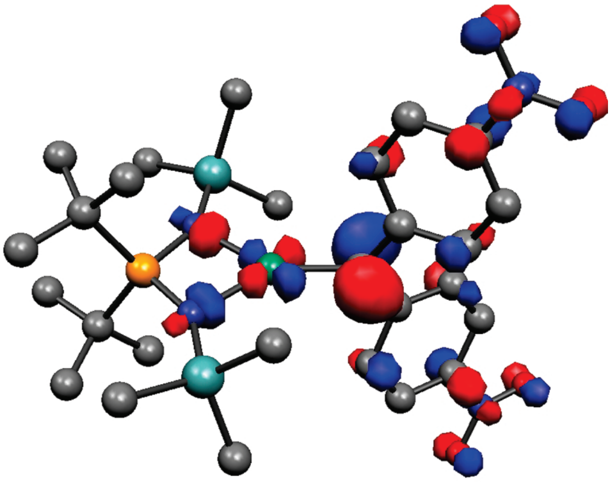


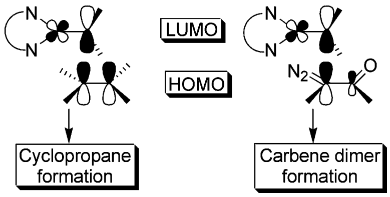
Figure 4. BP86/SV(P)-optimized structure of **4b** in the gas phase together with a graphical representation of its LUMO. Selected bond lengths (Å) and angles (deg): Cu−C(1) 1.863, Cu−N(1) 2.024, Cu−N(2) 2.024; N(1)−P−N(2) 100.6, N(1)−Cu−N(2) 77.2, P−Cu−C(1) 179.9, N(2)−Cu−C(1)−C(31) 94.5, N(2)−Cu−C(1)−(41) −85.4. The atom numbering is the same as in the solid-state structure of **4b** in Figure 2.

however, the formation of the mixed dimer proceeds rather slowly, presumably, because of the low reactivity of the α-carbonyl diazo compound. After 30 min at room temperature, the ratio of **4b** to **13** was only 5:1 and did not change significantly after subsequent heating of the reaction mixture for 5 min at 60 °C. This suggests that after some time, the diazo ester is being decomposed by the more reactive α-carbonyl carbene slowly formed in the course of the reaction. We failed to detect any azine product in this reaction.

The geometry parameters of the BP86/SV(P) optimized structure of **4b** (Figure 4) in the gas phase are in reasonable agreement with its solid-state structure. A population analysis for **4b** reveals that the copper−carbon π-bond is localized predominantly at the copper fragment (74.7%) with mainly d-orbital contributions (82.3%). Mixing with s and p orbitals was found to be 14.6% and 3.1%, respectively. This bonding pattern clearly identifies **4b** as an electrophilic Fischer-type metal carbene complex, in agreement with calculations published earlier by us,[6b] by Warren et al.[8a,b] and by Peters.[8c]

The chelate ligand enforced distortion of d^{10}-ML_3 complexes $[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu{=}CR_2$ from trigonal ground-state geometries of normal d^{10}-ML_3 systems with monodentate ligands toward Y-shape structures with abnormally small L−M−L (N−Cu−N) angles leads to more a pronounced sd-mixing at the metal center, strengthening the σ-component of the Cu to carbene bond. The mixing of copper p-orbitals and d-orbitals (i.e., intrafragment polarization of the small bite angle $[Bu^t_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu$ unit), on the other hand decreases the antibonding orbital interaction between the copper atom and the nitrogen atoms of the iminophosphanamide ligand and rehybridizes the copper d-orbitals, especially the one within the chelate ligand plane pointing with p-symmetry toward the carbene, thus leading to the observed orientational preferences of, for example, carbenes and olefins at the Cu-fragment. This dp-mixing, however, does not mean a strong participation of the copper p-orbitals in the metal-carbene bond since the copper d-orbitals are much lower in energy, far apart from the Cu 4p energies. The Cu 4p orbitals rather play the role of polarization functions.

Scheme 5



The LUMO of the model complex **4b** (π*) has the major coefficient at the carbene atom and is located predominantly on the carbene carbon as an empty p-orbital (Figure 4). Interaction of this π*-orbital with the π-orbital (HOMO) of an olefin will lead to the desired reaction, cyclopropane formation (Scheme 5), whereas the interaction with the HOMO of a diazoalkane may yield the corresponding carbene dimer (side reaction), thus rationalizing the experimental data presented above.

Conclusions

Copper ethylene complex **3** reacts with diphenyldiazomethane causing formation of the mononuclear terminal copper(I) carbene **4a**. Upon removal of ethylene, this compound can react further with **3** to yield the binuclear copper(I) carbene **5**, which itself is shown not to be active in the cyclopropanation of olefins. Introduction of two strong π-accepting p-NO_2 groups into both aromatic rings of the carbene **4a** allowed isolation of the terminal carbene **4b** active in cyclopropanation of olefins. Complex **4b** is stable toward a reaction with copper complex **3** and does not form the corresponding binuclear species. The molecular geometries of **4b** and **5** have been determined in the solid state. The structural and electronic structure features of carbene **4b** are consistent with the mechanistic scenario proposed by Pfaltz[3] for explaining and predicting product distributions in enantioselective Cu-catalyzed cyclopropanations and with theoretical results from quantum chemistry. The electronic structure of **4b** was investigated by means of quantum-chemical calculations, the results of which are consistent with the description of this complex as a Fischer-type d^{10}-ML_3 carbene. The data presented in this paper have also demonstrated that it is the reaction of mononuclear copper carbenes with diazo compounds that may lead to carbene dimers or azines, the typical side products in the cyclopropanation of olefins with diazoalkanes, thus revealing another, in addition to carbene decomposition,[8] pathway for carbene loss. This also rationalizes once more the well-known need to maintain the low concentration of diazo compounds under typical catalytic conditions to minimize the formation of carbene dimers according to the mechanism shown in Scheme 3. Further mechanistic and reactivity studies utilizing complex **4b** and its congeners are now in progress and will be reported separately.

Experimental Section

All experiments were performed under an Ar atmosphere using a Braun glovebox or by Schlenk techniques. Hexane and toluene were distilled over Na and kept under Ar. Benzene-d_6 and toluene-d_8, dichloromethane-d_2 were stirred over CaH_2 and degassed trice prior to use. THF-d_8 was refluxed over Na and degassed trice. Styrene was distilled in vacuum, degassed trice and kept under Ar in the glovebox at −15 °C.

Diphenyldiazomethane,[18] di(*p*-tolyl)diazomethane,[18] di(*p*-nitrophenyl)diazomethane,[19] were synthesized according to known procedures. NMR spectra were recorded on a Bruker 250 or 500 MHz spectrometer at temperatures specified below. ^{1}H,^{13}C NMR chemical shifts are reported in parts per million and are referenced to the deuterated solvent used.

Calculations were carried out on a 56 CPU cluster with Intel Xeon processors (2.66 GHz) using Turbomole (version 5.7)[20] software package. For the DFT calculations, the BP86 functional (Becke's exchange[21] and Perdew's gradient corrected[22] correlation functional) was utilized. The implemented split-valence SV(P) basis set was employed for geometry optimization of **4b**, whereas a triple-ξ quality basis TZVP was used for the single-point energy calculation on the SV(P)-optimized structure of **4b**.

[Bu$^t_2$P(NSiMe$_3$)$_2$-κ^2*N*]Cu=CPh$_2$ (4a). To a solution of **3** (60 mg, 0.146 mmol) in toluene-d_8 (0.3 mL) in an NMR tube was added a solution of diphenyldiazomethane (31 mg, 0.16 mmol)) in toluene-d_8 (0.3 mL). The reaction mixture instantly became intensively violet and gas evolution was observed. Spectral data of **4a**: ^{1}H NMR (248 K, toluene-d_8; 500.13 MHz): δ 8.28 (d, $^3J_{HH}$ 7.3 Hz, *o*-arom. H; 4H), 7.39 (t, $^3J_{HH}$ 7.6 Hz, *p*-arom. H; 2H), 1.46 (d, $^3J_{PH}$ 14 Hz, $C(CH_3)_3$; 18H), 0.31 (s, $Si(CH_3)_3$; 18H); ^{13}C{^{1}H} NMR (248 K, toluene-d_8, 125.77 MHz): δ 264.5 (s, Cu=*C*), 37.2 (d, $^1J_{CP}$ 64.4 Hz, $\mathit{C}(CH_3)_3$), 27.7 (d, $^2J_{CP}$ 2.4 Hz, $C(\mathit{C}H_3)_3$), 5.3 (s, $Si(\mathit{C}H_3)_3$); ^{31}P{^{1}H} NMR (248 K, toluene-d_8, 202.47 MHz): δ 59.6 (s+sat, $^1J_{PC}$ 63.9 Hz, $^2J_{PSi}$ 14.8 Hz); the signals for *m*-arom. protons overlap with signals of the diazoalkane. Compound **4a** cannot be isolated completely free of starting material **3**.

[Bu$^t_2$P(NSiMe$_3$)$_2$-κ^2*N*]Cu=C(*p*-NO$_2$C$_6$H$_4$)$_2$ (4b). A mixture of **3** (200 mg, 0.487 mmol) and di(*p*-nitrophenyl)diazomethane (131 mg, 0.462 mmol) was stirred in absolute toluene (14 mL) at 55 °C for 35 min. The dark-violet solution was evaporated at 0 °C and 10^{-3} mbar. The residue was treated with absolute hexane (12 mL), vigorously stirred at r.t. for 5 min, and the solution obtained was filtered under Ar via cannula into a Schlenk vessel cooled to 0 °C. The violet solution was slowly cooled to −80 °C and kept at this temperature overnight. A dark crystalline solid deposited. The solvent was removed from the crystals via cannula, and the product was washed with cold (−78 °C) hexane (2 × 2 mL). The reaction vessel was then evacuated to 10^{-3} mbar, and the temperature was slowly increased to −10 °C. Finally, the product was dried in vacuo (10^{-3} mbar) for 4 min at 20 °C to completely remove the solvent. Yield based on diazo compound 55%. The product slowly decomposes in solution and in the solid state at room temperature, but at lower temperatures it can be kept under Ar even in solution without significant decomposition. ^{1}H NMR (248K, toluene-d_8; 500.13 MHz): δ 7.91 (d, $^3J_{HH}$ 8.5 Hz, *o*-arom. H; 4H), 7.71 (d, $^3J_{HH}$ 8.5 Hz, *m*-arom. H; 4H), 1.36 (d+sat, $^1J_{CH}$ 124.8 Hz, $^3J_{PH}$ 14.3 Hz, $C(CH_3)_3$; 18H), 0.19 (s+sat, $^1J_{CH}$ 117.5 Hz, $Si(CH_3)_3$; 18H); ^{13}C{^{1}H} NMR (248 K, toluene-d_8, 125.77 MHz): δ 239.7 (s, Cu=*C*), 160.0, 147.3, 128.5, 125.2 (all s, arom. C), 37.3 (d, $^1J_{CP}$ 63.2 Hz, $\mathit{C}(CH_3)_3$), 27.2 (d, $^2J_{CP}$ 2.4 Hz, $C(\mathit{C}H_3)_3$), 5.2 (s, $Si(\mathit{C}H_3)_3$); ^{31}P{^{1}H} NMR (248K, toluene-d_8, 202.47 MHz): δ 66.7 (s+sat, $^1J_{PC}$ 62.6 Hz, $^2J_{PSi}$ 11.8 Hz). Anal. Calc. for $C_{27}H_{44}CuN_4O_4PSi_2$ (%): C 50.72; H 6.94; N 8.76; P 4.84. Found: C 50.97, H 7.01, N 8.75, P 4.60. FAB (NPOE): *m*/*z* = 639.3 (2.2%) [MH$^+$], 581.1 (6.5%) [(M$^+$) − *t*Bu)], correct isotopic pattern. A sample of **4b** suitable for X-ray analysis was obtained by slow crystallization from a diluted hexane solution at −35 °C over a period of 1 month.

[Bu$^t_2$P(NSiMe$_3$)$_2$-κ^2*N*]Cu=C(*p*-MeC$_6$H$_4$)$_2$ (4c). A solution of di(*p*-tolyl)diazomethane (24.3 mg, 0.109 mmol) in toluene-d_8 (0.3 mL) was added to a solution of the copper complex **3** (50 mg, 0.122 mmol) in toluene-d_8 (0.3 mL), and a deep-violet solution was formed. The reaction mixture was agitated at r. t. for 4 min and placed in an NMR tube. The copper carbene **4c** in a 27% steady-state concentration was detected by ^{1}H, ^{31}P and ^{13}C NMR spectroscopy. ^{1}H NMR (253K, toluene-d_8; 500.13 MHz): δ 8.26 (d, $^3J_{HH}$ = 8.3 Hz, 4 arom. H), 6.94 (d, $^3J_{HH}$ = 8.3 Hz, 4 arom. H), 1.88 (s, 6H, CH_3), 1.51 (d, $^3J_{HP}$ = 13.7 Hz, 18H, $C(CH_3)_3$), 0.35 (s, 18H, $Si(CH_3)_3$). ^{31}P{^{1}H} NMR (253K, toluene-d_8, 202.47 MHz): δ 57.9 (s+sat, $^1J_{PC}$ = 64.5 Hz, $^2J_{PSi}$ = 16.1 Hz). ^{13}C{^{1}H} NMR (253K, toluene-d_8, 125.77 MHz): δ 266.4 (s, Cu=*C*), 37.2 (d, $^1J_{PC}$ = 64.3 Hz, $\mathit{C}(CH_3)_3$), 27.8 (s, $C(\mathit{C}H_3)_3$), 22.1 (s, CH_3), 5.39 (s, $Si(\mathit{C}H_3)_3$).

{[Bu$^t_2$P(NSiMe$_3$)$_2$-κ^2*N*]Cu}$_2$(μ-CPh$_2$) (5). To a stirred solution of **3** (100 mg, 0.243 mmol) in hexane (2.5 mL) was added a solution of diphenyldiazomethane (35 mg, 0.182 mmol) in hexane (2.5 mL). The resulting, intensely violet solution was stirred for 50 min at ambient temperature and then slowly concentrated at 10^{-3} mbar to give a dark crystalline residue. Hexane (8 mL) was added, and the reaction mixture was stirred for 15 min at room temperature, then filtered under Ar via a cannula into a cooled to 0 °C Schlenk vessel. The brown solution was slowly cooled to −80 °C and kept at this temperature overnight. The solvent above the precipitated dark crystals (some of which were suitable for X-ray analysis) was removed via cannula, and the product was washed two times with cold (−78 °C) hexane and dried in high vacuum (10^{-3} mbar) to yield complex **5** (53 mg). The compound decomposes in solution at room temperature, and the isolated solid is contaminated with carbene **4a**. Spectral data of **5**: ^{1}H NMR (263 K, toluene-d_8; 500.13 MHz): δ 1.41(br. s, $C(CH_3)_3$; 9H), 1.05 (br. s, $C(CH_3)_3$; 9H), 0.88 (br. s, $Si(CH_3)_3$; 9H); 0.26 (br. s, $Si(CH_3)_3$; 9H); ^{13}C{^{1}H} NMR (263 K, toluene-d_8, 125.77 MHz): δ 184.7 (Cu-μ-*C*Ph$_2$), 38.0−39.0 (br. m, $2\mathit{C}(CH_3)_3$), 29.4 (br. s, $C(\mathit{C}H_3)_3$), 28.5 (br. s, $C(\mathit{C}H_3)_3$); 9.1 (br. s, $Si(\mathit{C}H_3)_3$); 7.1 (br. s, $Si(\mathit{C}H_3)_3$); ^{31}P{^{1}H} NMR (263K, toluene-d_8, 202.47 MHz): δ 65.4 (s+sat, $^1J_{PC}$ 60.9 Hz, $^2J_{PSi}$ 11.7 Hz).

Reaction of 4b with (p-CH$_3$C$_6$H$_4$)$_2$C=N$_2$. A solution of carbene **4b** (10 mg, 0.0157 mmol) in THF-d_8 (0.3 mL) at r. t. was added to a solution of an excess of $(p\text{-}CH_3C_6H_4)_2C{=}N_2$ (14 mg, 0.0631 mmol) in THF-d_8 (0.3 mL), and gas evolution was observed. All **4b** was consumed within several minutes. Spectroscopic data for the mixed azine **9**: ^{1}H NMR (500 MHz, THF-d_8): δ 8.34 (d, $^3J_{HH}$ = 8.35 Hz, 4H arom.), 8.17 (d, $^3J_{HH}$ = 8.65 Hz, 4H arom.), 7.70 (d, $^3J_{HH}$ = 8.65 Hz, 4H arom.), 7.61 (d, $^3J_{HH}$ = 8.35 Hz, 4H arom.), 2.39 (s, 3H, $2CH_3$). MS-EI$^+$: *m*/*z* = 478.1 (40%) (M$^+$). Spectroscopic data for the mixed dimer **10**: δ ^{1}H NMR (500 MHz, THF-d_8): 8.39 (d, $^3J_{HH}$ = 8.35 Hz, 4H arom.), 8.03 (d, $^3J_{HH}$ = 8.05 Hz, 4H arom.), 7.66 (d, $^3J_{HH}$ = 8.0 Hz, 4H arom.), 7.29 (d, $^3J_{HH}$ = 8.35 Hz, 4H arom.), 2.41 (s, 6H, $2CH_3$). MS-EI$^+$: *m*/*z* = 450.1 (20%) (M$^+$).

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Table 1. Crystal Data and Structure Refinement for **4b** and **5**

	4b	**5**
empirical formula	$C_{27}H_{44}CuN_4O_4PSi_2$	$C_{41}H_{82}Cu_2N_4P_2Si_4$
formula weight	639.35	932.49
temp (K)	200(2)	100(2) K
wavelength (Å)	0.71073	0.71073 Å
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
Z	4	4
a (Å)	8.9181(1)	11.5457(6)
b (Å)	19.8468(3)	26.9652(14)
c (Å)	19.2042(2)	15.9658(8)
α (deg)	90	90
β (deg)	102.726(1)	94.153(1)
γ (deg)	90	90
V (Å^3)	3315.56(7)	4957.6(4)
D_{calc} (g/cm^3)	1.28	1.25
abs. coeff. (mm^{-1})	0.81	1.05
crystal shape	polyhedron	polyhedron
crystal size (mm^3)	0.48 × 0.36 × 0.2	0.38 × 0.24 × 0.04
θ range for data coll. (deg)	1.5 to 27.5	1.5 to 28.3
collec. rflns.	34170	50764
independent rflns	7608	12282
observed rflns	6034	10544
goodness of fit on F^2	1.02	1.12
final R indices ($I > 2\sigma(I)$)	R1 = 0.033; wR2 = 0.083	R1 = 0.032; wR2 = 0.079
largest diff. peak and hole (e Å^{-3})	0.36 and −0.38	0.51 and −0.34

Reaction of 4b with diazo ester 11. The experiment was performed as described above. Spectroscopic data for the mixed dimer **12**: ^{1}H NMR (500.13 MHz, CD_2Cl_2): δ 7.74 (d, $^3J_{HH} = 8.7$ Hz, 4H arom.), 7.31 (d, $^3J_{HH} = 8.7$ Hz, 2H arom.), 7.17 (d, $^3J_{HH} = 8.7$ Hz, 2H arom.), 3.82 (s, 3H, OCH_3), 1.42 (s, 9H, $O(CH_3)_3$). The signal of four other aromatic protons of the p-$NO_2C_6H_4$-rings cannot be assigned exactly. MS-EI$^+$: m/z 476.1 (11%) (M$^+$).

***tert*-Butyl (4-methoxyphenyl)acetate.** A 100-ml flask equipped with a calcium chloride drying tube and magnetic stirring bar was charged with acid (6 g, 36.14 mmol) of dry CH_2Cl_2 (50 mL), t-BuOH (10.4 mL, 108.4 mmol), and dimethylaminopyridine (DMAP) (3.53 g, 28. 91 mmol). The solution was stirred and cooled in an ice bath to 0 °C while carboxydiimide (8.20 g, 39.75 mmol) was added in three portions. The reaction mixture was stirred at 0 °C for 15 min, then the cool bath was removed and stirring was continued at r. t. for 34 h, and during this time, a white precipitate was formed. The reaction mixture was filtered through celite; the celite was washed with CH_2Cl_2, the combined organic phases were washed with cold 0.5 N HCl (2 × 30 mL), cold saturated $NaHCO_3$ (2 × 30 mL), brine (30 mL), dried over Na_2SO_4 and evaporated. The product was purified by column chromatography on SiO_2 (EtOAc-Hexane 1:7) to yield 6.05 g (75%) of a colourless liquid. The product may be additionally purified by vacuum distillation, bp 129−131 °C/7 mbar (lit.[23] 117−121 °C/0.3 Torr). ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ 7.18 (d, $^3J_{HH} = 8.60$ Hz, 2H arom.); 6.84 (d, $^3J_{HH} = 8.60$ Hz, 2H arom.); 3.77 (s, 3H, OCH_3); 3.45 (s, 2H, $ArCH_2$); 1.43 (s, 9H, $C(CH_3)_3$).

***tert*-Butyl diazo(4-methoxyphenyl)acetate (11). Method A.** To a solution of LDA (3.72 mmol) in dry THF (15 mL) at −75 °C was added dropwise via a syringe *tert*-butyl (4-methoxyphenyl)acetate (0.751 g, 3.38 mmol). The reaction mixture was stirred at −30 °C for 2 h, followed by dropwise addition at −75 °C of a solution of TsN_3 (1.15 equiv, 770 mg, 3.887 mmol) in THF (5 mL). The reaction mixture was stirred at this temperature for 10 min. The cooling bath was removed and the mixture was stirred at r. t. for further 3 h until the reaction was complete (TLC-control). THF was removed in vacuo at a bath temperature <40 °C. Extractive workup followed by column chromatography (EtOAc-hexane 1:10) afforded 180 mg (21.5%) of pure diazo ester, mp 58 °C. If necessary, **11** can be recrystallized from pentane or hexane. Compound **11** is thermo- and light-sensitive and must be stored in a dark, cold place. ^{1}H NMR (500.13 MHz, $CDCl_3$, 298 K): δ 7.36 (d, $^3J_{HH} = 8.8$ Hz, 2H arom.), 6.91 (d, $^3J_{HH} = 8.8$ Hz, 2H arom.), 3.79 (s, 3H, MeO), 1.53 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$, 298 K): δ 165.1 ($C=O$); 157.8; 125.9; 117.6; 114.5; (all arom. C); 81.8 ($OC(CH_3)_3$); 55.3 (H_3CO); 28.4 ($C(CH_3)_3$). Anal. Calc. for $C_{13}H_{16}N_2O_3$ (%): C 62.89, H 6.50, N 11.28; Found: C 63.06, H 6.55, N 10.89.

Method B. To a stirred solution of *tert*-butyl diazo(4-methoxyphenyl)acetate (2.18 g, 10.58 mmol) and p-acetamidobenzenesulfonyl azide (5.1 g, 21.2 mmol) in absolute THF (18 mL) was added DBU (3.2 mL, 21.1 mmol). The reaction mixture was stirred at r. t. for 3 h and then allowed to stand at room temperature for 7 days with occasional shaking. The red-orange solution was carefully decanted from an oily residue and evaporated. Column chromatography (EtOAc-hexane 1:7) afforded a red oil that crystallized. Recrystallization from pentane gave an analytically pure sample (40%). The spectroscopic data are analogous to the sample obtained according to method A.

Crystal Structure Analysis. Data were collected on Bruker SMART (for **4b**) and APEX (for **5**) CCD diffractometers, and the structure solutions were performed using the SHELXTL-PLUS (2008/4) software package.[24] Intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[24] based on the Laue symmetry of the reciprocal space. Crystal data and structure refinement for **4b** and **5** are summarized in Table 1. A complete list of bond lengths and angles, atom coordinates, and thermal parameters for **4b**, **5**, and **11** are summarized and given in the Supporting Information. Crystals of **4b** and **5** suitable for X-ray analysis were obtained as described above. In both cases, a sample of crystals was placed in a pool of cold paraffin oil in an atmosphere of cold CO_2. An appropriate crystal was selected and removed from the oil with a glass fiber. With the oil-covered crystal adhering to the end of the glass fiber, the sample was very quickly transferred to an N_2 cold stream on the diffractometer.

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Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft (SFB 623 "Molecular Catalysts") is gratefully acknowledged.

Supporting Information Available: A detailed listing of crystal data and structure refinement, atomic coordinates, thermal parameters, bond distances and bond angles for **4b**, **5** and **11**; ^{1}H NMR spectrum of the reaction of complex **4b** with styrene; ^{31}P NMR spectra of compounds **4a-c** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 237519 (**4b**) and CCDC 237520 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

IC801443Y