Remarkably Stable Copper(I) α-Carbonyl Carbenes: Synthesis, Structure, and Mechanistic Studies of Alkene Cyclopropanation Reactions[†]

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The reaction of $[tBu_2P(NSiMe_3)_2-\kappa^2N]Cu(\eta^2-C_2H_4)$ (1) with various aryl diazo esters [p-X- C_6H_4 [C(N₂)[C(O)R] allowed us to synthesize the corresponding α -carbonyl copper(I) carbene complexes $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]Cu = C[p-X-C_6H_4][C(O)R]$ (8), where X = OMe, NO₂. The rotation barriers around the Cu–C_{carbene} and C_{carbene}–C_{Ar} bonds or their low limits were determined for some of these compounds by ¹H-VT-NMR spectroscopy. Carbene **8g** with X = OMe and $R = OCH(p-Cl-C_6H_4)_2$ was isolated in analytically pure, crystalline form as the first stable representative of this important class of compounds. Its solid-state molecular structure revealed an orthogonal position of the carbene fragment relative to both the ligand plane and the ester C=O group and a remarkably short $Cu-C_{carbene}$ distance of 1.822(4) Å. Compound 8g reacted with styrene stereoselectively to give the corresponding *trans*-cyclopropane derivative and $[tBu_2P(NSiMe_3)_2-\kappa^2N]Cu(\eta^2-CH_2=CHPh)$. The stoichiometric cyclopropanation of styrene with 8g and the previously described diarylcarbene $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]Cu = C[p-NO_2 - C_6H_4]_2$ (6) in toluene- d_8 revealed that the reactions are first order in both the copper carbenes and the alkene. The activation parameters for 8g ($\Delta H^{\ddagger} = 51.5(9)$ kJ/mol and $\Delta S^{\ddagger} = -127.1(28)$ J/(mol K)] and for 6 (ΔH^{\ddagger} = 53.4(8) kJ/mol and ΔS^{\dagger} = -152.1(23) J/(mol K)) were derived from the kinetics of the cycloproparation processes. Thermal decomposition of carbene 8g in toluene- d_8 displayed first-order kinetics until 20–25% conversion with activation parameters $\Delta H^{\ddagger} = 85.5(24)$ kJ/mol and $\Delta S^{\ddagger} = -49.0(76)$ J/(mol K). Solutions of 6 in toluene-d₈ also decompose in a first-order fashion with $\Delta H^{\dagger} = 66.1(20)$ kJ/mol and $\Delta S^{\dagger} =$ -125.5(56) J/(mol K). A Hammett study employing 8g and para-substituted styrenes afforded $\rho =$ -1.06(19), demonstrating the electrophilic nature of α -carbonyl copper(I) carbene (Fischer-type) complexes. The electronic structure of 8 with X = R = OMe was investigated by DFT methods.

Introduction

Copper catalysis for reactions of diazo compounds with olefins has been known for about a century,¹ but homogeneous catalysts for this process started to appear only 60 years later. In 1966, Nozaki, Noyori, et al. used chiral copper(II) salicylaldimine complexes in cyclopropanation reactions of styrene with ethyl diazoacetate (EDA) as the first application of enantioselective homogeneous transition-metal catalysis.^{2,3} Although the reported enantioselectivities were low, the principle of chiral catalyst development based upon generating and distinguishing between diastereomeric transition states involving transition metals was established. Copper(II) carbenes of the d⁹-ML₅ type were initially proposed to be the active cyclopropanating species. However, the importance of copper(I) in the catalytic cycle was recognized and proven by Aratani and Pfaltz in the 1980s. Copper(II) complexes as such were shown to be inactive and had to be reduced in situ either by addition of hydrazine or by heating with the diazoalkane used.^{4,5} The role of cupracyclobutanes remained unclear. According to Aratani, the results obtained with chiral salicylaldimine ligands were consistent with intermediate cupracyclobutanes formed from copper carbene complexes and olefins.⁴ However, although the predominant cyclopropane configuration was predicted correctly, the hypothesis did not adequately explain the preferred trans selectivity observed in most cases.⁶ An alternative suggestion based on copper(I) carbenes as the active cyclopropanating intermediates was made in 1988 by Pfaltz.⁵ Utilizing C_2 symmetric semicorrin ligands, the expected enantioselectivities of cyclopropanes formed by styrene attack upon the electrophilic carbene center were in agreement with experimental results. The results could be explained nicely in terms of different steric repulsion of the α -acyl substituent of the carbene with bulky groups of the spectator ligand in the diastereomeric transition states.⁵ The proposed Pfaltz model (Figure 1) also explained well the gross influence of the olefin and diazoalkane structures on the cis/trans selectivity, whereas the effect of the semicorrin ligand was predicted to be negligible, since the olefinic substituents were too remote to have any significant interaction

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Figure 1. Pfaltz's model for explaining the observed enantioselectivities in copper-catalyzed cyclopropanation.

with the spectator ligand. Several theoretical^{7–11} and mechanistic^{12–14} studies utilizing neutral and cationic copper complexes as catalytically active species have been performed. Kinetic investigations by Kochi¹² and Perez^{13,14} ascertained the presence of a preequilibrium before the rate-determining N₂ loss of the diazoalkane. Copper(I) alkene complexes were found to be the resting states of the catalytic cycle, and they were the only isolated or detected intermediates until 2000.

Then, however, the synthesis of remarkably stable, neutral iminophosphanamide copper(I) olefin complexes such as 17,15 allowed the isolation of the stable copper diazocarbonyl complex 2^{16} and the detection in solution of the first, quite reactive Fischer-type copper(I) carbene 3, which was active in the cyclopropanation of styrene (Figure 2).¹⁷ Compound 3 is stabilized by the tailor-made anionic ligand and could be completely characterized by spectroscopic methods. The intensely colored copper(I) carbene 3 was observed in a steadystate concentration that precluded its isolation in analytically pure form and thus hampered a detailed study of its properties and reactivity. A report of a second (cationic) copper(I) carbene 4 by Barluenga et al. followed soon after,¹⁸ although its reactivity in cyclopropanation was not reported. Recently, Warren and Dai disclosed the solid-state structure of the diphenylcopper(I) carbene 5 supported by an anionic β -diketiminate ligand.^{19a,b} They have also demonstrated the possibility of formation of binuclear μ -CPh₂ copper(I) carbenes such as 5a. The closely related, also neutral Cu carbene 6 was prepared in our group and used in reaction with diazo compounds to investigate the commonly accepted mechanism of carbene dimer formation.²⁰ Just last year, Peters has reported the spectroscopic characterization in solution of another diphenylcopper(I) carbene, utilizing a bulky bis(phosphino)borate spectator ligand for Cu(I).^{19c}

Despite the great progress toward unraveling the mechanism of copper-catalyzed cyclopropanations achieved over the past decade, the isolation of analytically pure α -carbonyl copper carbenes for mechanistic studies and their structural characterization remained a challenging task.¹⁷ Employing the copper olefin complex 1 and various diazocarbonyl compounds—the most commonly used carbene sources in cyclopropanation

reactions²¹—we report here the synthesis and spectroscopy of a number of α -carbonyl copper(I) carbenes. The isolation of a remarkably stable representative of this new class of Cu(I) organometallic compounds in analytically pure form, its structural characterization, and detailed kinetic studies may help to unravel the true nature of such a species and to deepen the understanding of the observed stereo- and enantioselectivities in cyclopropanation reactions, if instead of our achiral imnophosphanamide a chiral spectator ligand is used.^{5,6,22} Kinetic studies with the diaryl copper carbene **6**²⁰ are also presented in this paper.

Results and Discussion

The reaction of various α -carbonyl diazo compounds with the copper olefin complex 1 (Scheme 1) afforded the corresponding deeply colored carbene complexes 8 in steady-state concentrations significantly higher than that found previously for complex **3** (16%).¹⁷ Although various 2-(*p*-nitrophenyl)-2diazoacetates reacted with 1 at 25 °C to form carbenes 8a,b in a rather low (<20%) steady-state concentrations, performing the reaction at 70 °C for 5-10 min raised the Cu(I) carbene concentrations to 35% and 60% for 8a,b, respectively. Interestingly, ethyl 2-(o-nitrophenyl)-2-diazoacetate, the ortho stereoisomer of 8a, reacted with 1 only slowly to form brown and insoluble, so far unidentified products in most solvents. Amide 7c was more reactive than the esters and gave carbene 8c in a 38.5% steady-state concentration already at room temperature. Subsequent heating of the mixture to 50 °C only led to an increase of the concentration to 46%. Note that replacement of the NMe₂ group of **7c** by the sterically more demanding $NiPr_2$ group of 7d completely suppresses the formation of the corresponding NiPr2-substituted carbene 8d even at elevated temperatures. This clearly demonstrates that large substituents at the carbonyl carbon may completely block carbone formation and, consequently, the following cyclopropanation of an olefin. Carbenes 8b,c reacted with styrene to form exclusively trans cyclopropanes.

The highly nucleophilic *p*-methoxyphenyl diazo esters 7e-g turned out to be very reactive toward complex 1 already at room temperature. In case of compound 7g, the somewhat complicated alcohol HOCH(*p*-ClC₆H₄)₂ has been employed for ester formation. It is responsible for the high crystallization tendency of the corresponding Cu carbene 8g from saturated hydrocarbons. The isolation of 8g is possible in acceptable yield and in analytically pure form.

In ¹H NMR spectra of compounds 8a-g, the two diastereotopic *t*Bu groups at P give rise to two separated doublets





^a Steady-state concentrations in solution indicated in parentheses.

Table 1. Selected ${}^{13}C{}^{1}H$ and ${}^{31}P{}^{1}H$ NMR Spectroscopic Data for Compounds 3 and $8a-g^a$

	Cu=C	<i>C</i> =0	$\delta(^{31}\text{P})$	$^{1}J_{\mathrm{PC}}$	$^{2}J_{\mathrm{PSi}}$
3	229.9	177.9	64.3	63	12.6
8a	219.0	178.3	67.7	61.7	11.2
8b	221.1	177.9	66.7	61.9	11.7
8c	231.7	177.8	67.0	62.4	11.8
8e	232.8	177.9	60.7	63.7	no data
8f	235.8	177.0	59.7	64.4	14.4
8g	230.5	175.9	59.5	64.4	14.3

^a Chemical shifts are given in ppm and coupling constants in Hz.

 $({}^{3}J_{PH} = \text{ca. 14 Hz})$, indicating a perpendicular position of the carbene unit relative to the spectator ligand plane. The carbene carbon in the ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR spectra appears in the range of 219–235.8 ppm, verifying the presence of an electrophilic carbene center. As is obvious from Table 1, an increase of electron density in the aromatic ring attached to the carbene carbon leads to a deshielding of the carbene signals (except amide **8c**) and a shielding of the phosphorus resonance in the ${}^{31}\text{P}\{{}^{1}\text{H}\}$ NMR spectra. Such a correlation cannot be found for the carbon signals of the carbonyl groups. The higher electron donating capacity of the aryl ring also leads to an increase of the ${}^{1}J_{PC}$ and ${}^{2}J_{PSi}$ coupling constants.

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Figure 3. ¹H-VT-NMR (500.13 MHz, toluene- d_8) spectrum of **8f**, showing coalescence of the ortho and meta aryl protons.

Table 2. Experimental Rotation Barriers ΔG^{\ddagger} of the Aryl Group and the Carbene Unit for Some Copper(I) Carbenes (kJ/mol)

carbene	$C_{carbene}$ - C_{Ar} bond	Cu=C bond
3 ¹⁷	36.8 ± 3.0	>60
8e	not measured	62.2 ± 1.1
8f	49.8 ± 0.9	68.8 ± 1.9
8g	50.1 ± 1.2	>67
8b	fast on NMR time scale	>81

The low-temperature ¹H NMR spectra of compounds 8e-greveal that four protons of the aromatic ring give rise to four doublets, indicating slow rotation on NMR time scale around the C_{carbene}-C_{Ar} bond. Warming the sample in case of **8f** leads to coalescence of the aromatic signals (Figure 3). The activation barriers ΔG^{\ddagger} for **8f.g** derived for this process by means of ¹H-VT-NMR spectroscopy are listed in Table 2. The hindered rotation observed is a consequence of the donation of electron density from the electron-rich π -system of the aromatic ring toward the electrophilic carbene center. In the perpendicular transition state **8f**[‡], the carbene carbon cannot share electron density with the aromatic ring. This is in accordance with the electrophilic character of the carbene carbon centers in **8e**-**g** and clearly requires a qualitative description of these complexes as electrophilic (Fischer-type) carbenes.

From Table 2 it is easily seen that an introduction of the π -donor *p*-OMe into the aromatic ring of **3** dramatically raises the aryl group rotation barrier (by 13 kJ/mol), whereas the π -acceptor NO₂ has the opposite effect. This is exactly to be expected, since the π -system of the aromatic ring in **8f** is more electron-rich than in case of **3**, leading to an improved interaction with the empty p orbital of the carbene carbon and to a strengthening of the C_{carbene}-C_{Ar} bond. In complex **8b**, the presence of the NO₂ group in the aryl ring lowers its electron density and the carbene-aryl interaction becomes less pronounced. For this reason, the rotation of the aromatic ring in compound **8b** was found to be fast on the NMR time scale even at -80 °C.

The relatively high stability of the copper carbene 8f allowed the determination of the rotation barrier of the carbene unit relative to the [PN₂Cu] plane. Coalescence of the signals for

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Figure 4. ¹H-VT-NMR (500.13 MHz, toluene- d_8) spectrum of **8f**, showing the coalescence of the diastereotopic *t*Bu groups.

the two diastereotopic tBu groups of **8f** can be observed by ¹H-VT-NMR spectroscopy upon warming of the carbene solution in toluene- d_8 (Figure 4). A Gibbs free activation enthalpy of $\Delta G^{\ddagger} = 68.8 \pm 1.9$ kJ/mol was found for this process. This value is significantly higher than the olefin rotation barriers of 37-53.7 kJ/mol found in copper(I) olefin complexes [tBu₂P-(NSiMe₃)₂- $\kappa^2 N$]Cu(η^2 -olefin) determined earlier, where olefin = styrene, norbornene, maleic anhydride.^{7,15} This indicates that the carbene moiety is a better π -acceptor than norbornene or even an η^2 -coordinated maleic anhydride. The Cu-carbene rotation barrier in 8e can be determined in a manner similar to that for 8f by means of ¹H-VT-NMR spectroscopy. Here an activation barrier of $\Delta G^{\ddagger} = 62.2 \pm 1.1$ kJ/mol was found for this dynamic process. This value is ca. 6 kJ/mol lower than in the case of 8f, most probably because of the steric demand of the *t*Bu group in the latter.

The magnitude of the carbene fragment rotation barrier should reflect the significance of the copper to carbene back-bonding. This, in turn, should also be a function of the variable electronic properties of the aromatic ring at the carbene carbon. This assumption is very well demonstrated by comparison of the experimental ΔG^{\ddagger} values obtained for the sterically equivalent compounds **8b**,**f**. Replacing the strongly π -donating *p*-OMe group in **8f** by the strongly π -accepting one (*p*-NO₂) results in an increase of the rotation barrier of the carbene moiety by more than 12 kJ/mol (lower limit) because of the strengthened Cu-Cback-bonding. The exact ΔG^{\ddagger} value for compound **8b** cannot be determined, as it decomposes too rapidly above 80 °C. Nevertheless, the low limit of the rotation barrier of the carbene fragment in **8b** was established to be at least 81 kJ/mol.

Compound **8g** turned out to be the first stable Cu(I) α -carbonyl carbene, which was isolated in analytically pure form and as crystalline material. The compound crystallizes with two independent molecules in the unit cell, and Figure 5 shows only one of them. In the solid state, the copper atom is in a trigonal-planar environment as expected, and the atoms Cu, C(1), C(2), and C(31) share the same plane. The angle P–Cu–C(1) is 177.9°, and the carbene unit is nearly orthogonal to the [PN₂Cu] plane, maximizing back-bonding (the angle between planes [PN₂Cu] and [Cu,C(1),C(2),C31] is 97.7°). Notably, the aromatic ring is twisted by only 5.9° relative to the [C(31),C(1),C(2)] plane. This fact could play a significant role in the stabilization of **8g** due to the interaction of the π system of the electron-rich aryl ring with the empty p orbital of the carbene carbon. This interaction is also reflected in a rather short C(1)–C(31) bond

Figure 5. ORTEP plot of 8g. Selected bond lengths (Å) and angles (deg): Cu-C(1) = 1.822(4), Cu-N(1,2) = 2.003(3), 1.993(3), P-N(1,2) = 1.604(3), 1.607(3), C(1)-C(2) = 1.484(6), C(1)-C(31) = 1.434(5), C(2)-O(2) = 1.202(5), C(2)-O(3) = 1.353(5), C(31)-C(32) = 1.418(5), C(32)-C(33) = 1.370(6), C(33)-C(34) = 1.402(6), C(34)-O(1) = 1.353(5); N(2)-Cu-N(1) = 77.8(1), P-Cu-C(1) = 177.9(1), C(1)-Cu-N(2) = 142.2(1), C(1)-Cu-N(1) = 140.0(1), C(31)-C(1)-C(2) = 114.4(3), O(2)-C(2)-C(1) = 125.0(4). Only one hydrogen is shown for clarity. The given geometric data are mean values of two independent molecules.

(1.434(5) Å), which thus has partial double-bond character and leads to the observed slow rotation around the C(1)–C(31) bond (Table 1) on the NMR time scale. The *p*-methoxy group lies in the plane of the aromatic ring, maximizing the conjugation (C(34)–O(1) = 1.353(5) Å).

Interestingly, the carbonyl group of 8g is oriented perpendicular to the carbene moiety (angle between the [Cu(1), C(1), C(1)]C(2),C(31)] and [C(1),C(2),O(2),O(3)] planes: 86.8°). This should be the case for electronic reasons, because the C=O group tries to adopt an orientation with minimized interaction of its acceptor π -system with the "empty" p orbital of the carbene carbon. In fact, such an orientation of the carbonyl function has been predicted in theoretical calculations⁷⁻⁹ and is consistent with a "carbocationic" character of the carbene carbon. However, this effect only persists in the solid-state structure, since in solution there is facile rotation around the C(1)-C(2) bond even at -60 °C on the NMR time scale. The remarkably short Cu=C distance (1.822(4) Å) in 8g is indicative of a double bond and is the shortest copper-carbon distance that has been reported so far. It is slightly shorter than the one reported for Warren's carbene 5 $(1.834(3) \text{ Å})^{19}$ and significantly shorter than found in Barluenga's cationic copper carbene (1.882(3) Å)¹⁸ or for many copper(I) carbenes with Wanzlick-Arduengo carbene ligands^{23,24} with their minimal π -acceptor character. The structural features of carbene 8g are nicely consistent with the mechanistic scenario proposed by Pfaltz⁵ for explaining and predicting product distributions in enantioselective Cu-catalyzed cyclopropanations.

It is remarkable that, according to NMR data and elemental analysis, compound **8g** crystallized together with pentane in a

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1:0.46 ratio, and the cocrystallized solvent could not be removed even at 10^{-3} mbar. The ratio was found to be 1:0.48 in a second synthesis of **8g** under the same reaction conditions.

Although complex 8g is rather stable, its solutions in toluene d_8 slowly decompose at room temperature to give the free iminophosphanamide ligand $tBu_2P(NSiMe_3)(NHSiMe_3) (\delta^{(31}P))$ 30.1), a solvated copper iminophosphanamide fragment $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]Cu(toluene - d_8) (\delta^{(31}P) 63.3, which is very)$ close to that of the corresponding $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]$ -Cu(C₆D₆) with δ (³¹P) 63.2) and several other phosphoruscontaining products, which are difficult to identify. The ¹H NMR spectrum of 8g after thermal decomposition displayed a large number of different products and was not informative. Possibly, the decomposition proceeds via reactive copper ketenes (after a Wolff rearrangement), although such a hypothesis has not been confirmed. Interestingly, our diaryl carbene 6 also decomposed in toluene- d_8 solutions to yield only tetrakis(*p*-nitrophenyl)ethylene, the "carbene dimer" $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]Cu(toluene$ d_8), and some free ligand as the main products. Solutions of 8g are stable at low temperature; in the solid state, compound 8g possesses even greater stability and can be stored without decomposition at -25 °C in a glovebox for several months.

The kinetic stabilization by the steric demand and the high basicity of the anionic iminophosphanamide σ - and π -donor ligand, the enforced small N-Cu-N bite angle of 77.8° of the four-membered neutral (chelate)Cu ring system, the strong π -donor substituent OMe of the carbene phenyl ring, and the sterically demanding special ester group are responsible for the unprecedented stability of 8g. The high-lying HOMO of the small-bite-angle d^{10} -ML₂ fragment²⁵ [*t*Bu₂P(NSiMe₃)₂- $\kappa^2 N$]Cu^I results in pronounced π back-bonding from Cu(I) toward the carbene which, together with a strong $Cu(I)-C_{carbene}$ σ -bond resulting from a low-lying LUMO at the copper fragment, leads to a strong and short Cu=C bond. It should be noted here that the characterization of the tailor-made Cu(I) fragment $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]Cu^I$ as a "good" back-bonding fragment is not meant on an absolute but on a relative scale, specific for copper(I) units of the type d¹⁰-L₂Cu. In comparison to many other back-bonding isolobal and isoelectronic metal fragments its π -donor capability toward π -acceptor ligands is weak. Nevertheless, the anionic iminophosphanamide spectator ligand causes the $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]Cu(I)$ building blockisolobal also with a singlet methylene-to function as a strong π -donor relative to other cationic or neutral d¹⁰-L₂Cu fragments. $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]Cu^I$ therefore is particularly well suited for stabilizing metal-ligand coordination in terms of the Dewar-Chatt-Duncanson picture, sufficiently stabilizing the first stable α -carbonyl copper(I) carbenes 8.

Carbene **8g** reacted stereoselectively with an excess of styrene to form the *trans*-cyclopropane derivative (i.e., ester and the phenyl substituents are trans to each other) and the copper styrene complex $[tBu_2P(NSiMe_3)_2-\kappa^2N]Cu(\eta^2-CH_2=CHPh)$ in a nearly 1:1 ratio, indicating almost quantitative conversion of **8g** to cyclopropane. It is reasonable to assume that the large substitutes at the carbene center are responsible for the high trans selectivity observed. In addition, another factor favoring the formation of the trans product could be arene $\pi - \pi$ interactions in the transition state between the *p*-methoxyphenyl substituent of the carbene carbon and the phenyl ring of styrene. The importance of such $\pi - \pi$ interactions was suggested earlier by Woo and co-workers for explaining the high stereoselectivity observed in cyclopropanations of styrene with mesityldiazomethane catalyzed by the iron porphyrin complex Fe(TTP) (TTP = *meso*-tetra-*p*-tolylporphyrin).²⁶ The reaction of pent-1-yne with **8g** yielded, as expected from the acidity of the alkyne, the free iminophosphanamide ligand and yellow copper acetylide. Dimethyl acetylenedicarboxylate was unreactive toward copper carbene **8g**. Complex **8g** is the first stable, isolated, and analytically pure copper(I) α -carbonyl carbene which could be shown to be active in cyclopropanations of olefins.

Kinetic studies with α -carbonyl carbene **8g** and diaryl carbene **6** were performed by means of ¹H NMR spectroscopy.²⁷ For product analysis, we assume here that the decrease of the copper(I) carbene concentration in the presence of an olefin is a result of two independent processes: carbene decomposition and cyclopropanation of the olefin by the copper carbene, i.e.

$$-d[\text{carbene}]/dt = k_{\text{cyclop}}[\text{carbene}][\text{olefin}] + k_{\text{dec}}[\text{carbene}]^n$$

If the decomposition proceeds in a first-order fashion (n = 1) and the olefin concentration is kept constant (pseudo-first-order conditions), one may write

 $-d[carbene]/dt = [carbene]\{k_{pseudo} + k_{dec}\} = [carbene]k_{obs}$

where

$$k_{\rm pseudo} = k_{\rm obs} - k_{\rm dec} = k_{\rm cyclop} [{\rm olefin}]$$

 $(k_{\text{cyclop}} = \text{actual second-order cyclopropanation rate constant}, k_{\text{dec}} = \text{carbene decomposition rate constant}, k_{\text{obs}} = \text{observed}$ first-order cyclopropanation rate constant, $k_{\text{pseudo}} = \text{pseudo-first-order constant}$ corrected with respect to decomposition).

Solutions of carbene 8g in toluene- d_8 decompose in a firstorder manner until 21-25% conversion is reached. Upon further conversion, a strong deviation from first-order kinetics was observed: i.e., the rate of decomposition became considerably faster than that after ca. 3000 s. Presumably, such a deviation may result from a reaction of 8g with its decomposition products. Decomposition of diaryl carbene 6 could be approximated with the first-order kinetics if data points until ca. 1.5 half-lives were collected. The first-order constants for decomposition obtained over a temperature range of 303-333 K (for 8g) or 343-373 K (for 6) allowed the construction of Eyring plots²⁸ which afforded the activation parameters listed in Table 3. These values may be compared to those found for the decomposition of Warren's carbene 5.^{19a,b} Note that ΔH^{\dagger} for the carbene loss in **6** is much lower than ΔH^{\ddagger} in the α -carbonyl carbene case 8g. The large negative entropy of activation in all cases can be attributed to solvent effects. It implies an associative mechanism with a possible coordination of the solvent in the transition state. Indeed, our studies of

(28) See the Supporting Information.

⁽²⁵⁾ Hofmann, P.; Heiss, H.; Müller, G. Z. Naturforsch., B **1987**, 42, 395. The Walsh diagram described in this paper for the frontier orbital energy changes of d^{10} -L₂M metal fragments as a function of their L-M-L angle has been reported multiple times in the literature.

⁽²⁶⁾ Hamaker, C. G.; Mirafzal, G. A.; Woo, K. L. Organometallics 2001, 20, 5171.

⁽²⁷⁾ The concentration of **8g** was monitored by the decrease of the integral intensity of the singlet at δ 3.07 ppm assigned to the methoxy group of **8g**. The kinetic studies with diarylcarbene **6** were performed in a similar manner, except that the integral intensity of the doublet at δ 8.03 ppm assigned to the four aromatic ortho protons was followed to control the carbene concentration. The triplet at δ 1.00 ppm and the quintet at 2.21 ppm were assigned to pentane and C₆D₅CD₂H (toluene), respectively, and were used as convenient internal standards. The target peaks and the reference signals for the kinetic measurements did not overlap with any decomposition or cyclopropanation products. Only in the case of *p*-methoxy-substituted styrene did the reference signal at δ 2.21 (toluene) overlap with the signal of the corresponding cyclopropanation product. In this case a methyl resonance of trace pentane was used to follow the reaction.

 Table 3. Activation Parameters for Thermal Decomposition and

 Cyclopropanation of Styrene with Carbenes 6 and 8g and with

 Warren's Carbene 5

	ΔH^{\ddagger} , kJ/mol	ΔS [*] , J/(mol K)	$\Delta G^{\ddagger}, \mathrm{kJ/mol}^{a}$
dec	85.5(24)	-49.0(76)	100.1(48)
cyclop	51.5(9)	-127.1(28)	89.4(18)
dec	66.1(20)	-125.5(56)	103.5(37)
cyclop	53.4(8)	-152.1(23)	98.7(15)
dec^b	87.8(42)	-33.4(125)	97.8(80)
cyclop ^b	43.5(13)	-135.0(38)	83.7(24)
	dec cyclop dec cyclop dec ^b cyclop ^b	$\begin{tabular}{ c c c c c } \hline \Delta H^{\ddagger}, kJ/mol \\ \hline dec & 85.5(24) \\ cyclop & 51.5(9) \\ dec & 66.1(20) \\ cyclop & 53.4(8) \\ dec^b & 87.8(42) \\ cyclop^b & 43.5(13) \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c } \hline \Delta H^{\ddagger}, \ kJ/mol & \Delta S^{\ddagger}, \ J/(mol \ K) \\ \hline dec & 85.5(24) & -49.0(76) \\ cyclop & 51.5(9) & -127.1(28) \\ dec & 66.1(20) & -125.5(56) \\ cyclop & 53.4(8) & -152.1(23) \\ dec^b & 87.8(42) & -33.4(125) \\ cyclop^b & 43.5(13) & -135.0(38) \\ \hline \end{tabular}$

^a At 298 K. ^b See ref 19a,b.

solvent effects show that the decomposition of **8g** in coordinating solvents such as THF- d_8 proceeds appreciably faster than in toluene- d_8 .

Carbenes **8g** and **6** slowly react with an excess of styrene and exhibit clean pseudo-first-order kinetics in toluene- d_8 . The observed rate constants are doubled upon doubling the concentration of styrene in the reaction mixtures, indicating that the reaction is also first order in styrene and second order overall. The actual rate constants measured at various temperatures allowed the construction of the corresponding Eyring plots, from which the activation parameters of the carbene decomposition and the cyclopropanation were derived (Table 3). These values are in full agreement with an associative mechanism and are somewhat different from those reported for the stoichiometric cyclopropanation of styrene with Warren's terminal carbene **5** and from the cyclopropanation of vinyl acetate with (CO)₅W= CH(*p*-MeOC₆H₄) ($\Delta H^{\ddagger} = 42.0(13)$ kJ/mol and $\Delta S^{\ddagger} = -143.6(29)$ J/(mol K)).²⁹

Comparison of the activation parameters for styrene cyclopropanation and carbene decomposition reveals a significantly larger ΔH^{\ddagger} for carbene loss relative to carbene transfer to styrene. This can be expected, since the breaking of the strong Cu=C bond (calculated D_e of 257.9–312.4 kJ/mol⁷) is not yet compensated by the C–C bond formation in the transition state.

The experimentally derived activation barriers ΔG^{\ddagger} for cyclopropanation of styrene are 40–50 kJ/mol higher than those found in theoretical calculations on small neutral model systems.⁷ However, this difference is understandable, as the large substituents of the spectator ligand as well as at the carbene carbon should definitely destabilize the corresponding associative transition states.

The actual second-order rate constants determined for the cyclopropanation of styrene with **8g** over the temperature range of 303-333 K exceed the decomposition rates obtained at these temperatures by a factor of 17-62 (Table 4). This rate difference rationalizes the efficient conversion of the carbene to the corresponding cyclopropane. On the other hand, the second-order rate constants determined for cyclopropanation of styrene with **6** over a temperature range of 323-373 K (Table 5) exceed the decomposition rates obtained at the same temperatures by only a factor of 2-5. This is consistent with the appearance of significant amounts of the carbene dimer tetrakis(*p*-nitrophenyl)ethylene in the reaction of **6** with styrene²⁰ and underscores the need to use an excess of an alkene under typical catalytic cyclopropanation conditions with a low concentration of the copper catalyst.

Complexes **8g** and **6** were also utilized in cyclopropanation reactions of para-substituted styrenes p-R-C₆H₄CH=CH₂ (R = OCH₃, CH₃, H, CF₃) in order to test the electronic influence of olefin substrate structures via potential LFE correlations of the Hammett-type. The results presented in Tables 6 and 7 clearly demonstrate the electrophilic nature of the copper(I) carbenes. Styrenes with electron-donating para substituents accelerate the cyclopropanation rate, whereas the electron-deficient p-(trifluoromethyl)styrene has the opposite effect. This is in accordance with theoretical model calculations which predicted a substantially higher activation barrier for cyclopropanation of ethylene compared to the more electron-rich vinyl alcohol.⁷ The reaction of the diarylcarbene 6 with p-CF₃-C₆H₄CH=CH₂ proceeded so slowly that only small amounts of the corresponding cyclopropane were detected by ¹H NMR spectroscopy, and the decomposition products dominated in the reaction mixture. For that reason, it was not possible to obtain reliable first-order cyclopropanation constants for this olefin. Nevertheless, the data indicate qualitatively that electron-poor olefins are also less reactive in cyclopropanation with diarylcarbenes such as 6. Interestingly, Warren and Dai have reported that p-(trifluoromethyl)styrene had little influence on the reaction rate compared to styrene in cyclopropanations employing diphenyl copper carbene 5.^{19a} We cannot rationalize this observation at this point.

A reasonable linear correlation in a $\log(k_x/k_H)$ vs standard σ^+ substituent constants Hammett plot (Figure 6) was found with $\rho = -1.06(19)$. This value may be compared to that reported for cyclopropanation of para-substituted styrenes with EDA and neutral copper(I) complexes such as $Tp^{Me}CuC_2H_4$ ($\rho = -0.85(7)$, Tp^{Me} = hydrotris(3,5-dimethyl-1-pyrazolyl)borate)³⁰ and with -1.23 to -0.99 (with an average of -1.11) for a BpCuL series [Bp = dihydrobis(1-pyrazolyl)borate].¹³ The Hammett reaction constant ρ determined for **8g** is substantially larger (more negative) than the one derived for the cyclopropanation with a cationic bis-oxazoline copper(I) complex ($\rho = -0.51$),⁸ and for the stoichiometric reaction of para-substituted styrenes with the isolated highly electrophilic carbene {Fe(TPFPP)[C(Ph)(CO_2Et)]} ($\rho = -0.41(5)$, TPFPP = *meso*-tetrakis(pentafluorophenyl)porphyrin).³¹

For both carbenes **6** and **8g**, the data points fit better to σ^+ than to σ . This is to be expected, since reactions which proceed along with the concomitant development of an electron deficiency are better correlated with substituent constants based upon e.g. an S_N1 bond breaking reaction than the ionization of benzoic acids.³² In conjunction with a relatively small negative ρ value of -1.06 obtained for carbene **8g**, these data suggest an early associative transition state with only a moderate positive charge being developed at the benzylic carbon (Figure 7). Therefore, the picture of the transition state derived for copper carbenes from our experimental results is also in good agreement with the Pfaltz model⁵ and with the results obtained from previous theoretical calculations.^{7–9}

DFT calculations²⁸ were employed for copper carbene **8e**. This system is very similar to the X-ray characterized carbene **8g**, where only the larger ester group $-\text{COOCH}(p\text{-}\text{ClC}_6\text{H}_4)_2$ replaces $-\text{COOCH}_3$. BP86/SV(P) geometry optimization of **8e** yielded a minimum energy structure with an orthogonal position of the carbene moiety relative to the PN₂Cu planes, as was found earlier for high-level DFT calculations utilizing smaller iminophosphanamide model systems.⁷

The geometrical features of the optimized copper carbene **8e** are in reasonable agreement with the solid-state structure of **8g**,

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⁽³²⁾ Connors, K. A. Chemical Kinetics; VCH: Weinheim, Germany, 1990.

Table 4. Observed First-Order and Actual Second-Order Rate Constants for Styrene Cyclopropanation with 8g over a Temperature Range of303-333 K at a 20:1 Olefin/Carbene Ratio under Pseudo-First-Order Conditions ([styrene] = [2.75(1) × 10⁻¹ M)

		·- •	
$k_{\rm obs},~{\rm s}^{-1}$	$k_{\rm dec}, \ {\rm s}^{-1}$	$k_{\rm pseudo}, {\rm s}^{-1}$	$k_{\text{cyclop}}, \text{L/(mol s)}$
$[5.94(6)] \times 10^{-4}$	$[3.27(9)] \times 10^{-5}$	$[5.61(6)] \times 10^{-4}$	$[2.04(2)] \times 10^{-3}$
$[1.160(4)] \times 10^{-3}$	$[9.71(21)] \times 10^{-5}$	$[1.063(5)] \times 10^{-3}$	$[3.87(2)] \times 10^{-3}$
$[1.89(1)] \times 10^{-3}$	$[2.02(6)] \times 10^{-4}$	$[1.69(1)] \times 10^{-3}$	$[6.14(5)] \times 10^{-3}$
$[3.09(4)] \times 10^{-3}$	$[3.83(24)] \times 10^{-4}$	$[2.71(5)] \times 10^{-3}$	$[9.85(17)] \times 10^{-3}$
$[4.64(4)] \times 10^{-3}$	$[8.09(29)] \times 10^{-4}$	$[3.83(5)] \times 10^{-3}$	$[1.39(2)] \times 10^{-2}$
	$\frac{k_{\rm obs}, {\rm s}^{-1}}{[5.94(6)] \times 10^{-4}} \\ [1.160(4)] \times 10^{-3} \\ [1.89(1)] \times 10^{-3} \\ [3.09(4)] \times 10^{-3} \\ [4.64(4)] \times 10^{-3} \\ \end{array}$	$\begin{array}{c c} k_{\rm obs}, {\rm s}^{-1} & k_{\rm dec}, {\rm s}^{-1} \\ \hline [5.94(6)] \times 10^{-4} & [3.27(9)] \times 10^{-5} \\ [1.160(4)] \times 10^{-3} & [9.71(21)] \times 10^{-5} \\ [1.89(1)] \times 10^{-3} & [2.02(6)] \times 10^{-4} \\ [3.09(4)] \times 10^{-3} & [3.83(24)] \times 10^{-4} \\ [4.64(4)] \times 10^{-3} & [8.09(29)] \times 10^{-4} \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table 5. Observed First-Order and Actual Second-Order Rate Constants for Styrene Cyclopropanation with 6 over a Temperature Range of303-333 K at a 40:1 Olefin/Carbene Ratio under Pseudo-First-Order Conditions ([styrene] = [6.26(2)] × 10⁻¹ M)

<i>T</i> , K	$k_{\rm obs}, \ {\rm s}^{-1}$	$k_{\rm dec}, \ { m s}^{-1}$	$k_{\rm pseudo}, {\rm s}^{-1}$	$k_{\rm cyclop}, {\rm mol}^{-1} {\rm s}^{-1}$
323 ^a	$[1.51(6)] \times 10^{-4}$	$[3.93(16)] \times 10^{-5}$	$[1.11(6)] \times 10^{-4}$	$[1.78(10)] \times 10^{-4}$
343	$[5.37(8)] \times 10^{-4}$	$[1.80(7)] \times 10^{-4}$	$[3.57(11)] \times 10^{-4}$	$[5.71(17)] \times 10^{-4}$
353	$[9.995(75)] \times 10^{-4}$	$[3.40(10)] \times 10^{-4}$	$[6.60(12)] \times 10^{-4}$	$[1.06(2)] \times 10^{-3}$
363	$[1.78(4)] \times 10^{-3}$	$[6.44(26)] \times 10^{-4}$	$[1.13(5)] \times 10^{-3}$	$[1.81(8)] \times 10^{-3}$
373	$[3.08(5)] \times 10^{-3}$	$[1.27(5)] \times 10^{-3}$	$[1.81(8)] \times 10^{-3}$	$[2.89(12)] \times 10^{-3}$

^{*a*} k_{dec} at 323 K was obtained by extrapolation of the Eyring plot for decomposition of **6**.

Table 6. Rate Constants for Cyclopropanation of Para-Substituted Styrenes *p*-R-C₆H₄CH=CH₂ by Copper Carbene 8g at 303 K and a 1:20 Carbene/Olefin Ratio

R	$k_{\rm obs}, \ {\rm s}^{-1}$	$k_{\rm dec}, \ {\rm s}^{-1}$	$k_{\rm pseudo}, \ {\rm s}^{-1}$	$k_{\rm X}/k_{\rm H}$
Н	$[6.63(9)] \times 10^{-4}$	$[3.27(9)] \times 10^{-5}$	$[6.30(9)] \times 10^{-4}$	1.000
CF ₃	$[3.20(3)] \times 10^{-4}$	$[3.27(9)] \times 10^{-5}$	$[2.87(3)] \times 10^{-4}$	0.4559
CH ₃	$[1.75(2)] \times 10^{-3}$	$[3.27(9)] \times 10^{-5}$	$[1.72(2)] \times 10^{-3}$	2.725
OCH_3	$[8.64(56)] \times 10^{-3}$	$[3.27(9)] \times 10^{-5}$	$[8.61(56)] \times 10^{-3}$	13.661

Table 7. Rate Constants for Cyclopropanation of Para-Substituted Styrenes *p*-R-C₆H₄CH=CH₂ by Copper Carbene 6 at 343 K and a 1:40 Carbene/Olefin Ratio

R	$k_{\rm obs},~{\rm s}^{-1}$	$k_{\rm dec}, \ {\rm s}^{-1}$	$k_{\rm pseudo}, \ {\rm s}^{-1}$	$k_{\rm X}/k_{\rm H}$
Н	$[5.37(8)] \times 10^{-4}$	$[1.80(7)] \times 10^{-4}$	$[3.57(11)] \times 10^{-4}$	1.00
CH ₃	$[1.18(1)] \times 10^{-3}$	$[1.80(7)] \times 10^{-4}$	$[1.00(2)] \times 10^{-3}$	2.808
OCH_3	$[4.47(14)] \times 10^{-3}$	$[1.80(7)] \times 10^{-4}$	$[4.29(14)] \times 10^{-3}$	12.02



Figure 6. Superimposed Hammett plots from cyclopropanation reactions of *p*-R-substituted styrenes using compounds 6 and 8g.



Figure 7. Qualitative transition state representation for styrene cyclopropanations with copper carbenes 8.

although the Cu=C, Cu-N, and P-N bonds are slightly too long on the BP86/SV(P) level. The calculated copper-carbene bond in **8e** (1.850 Å) is 0.02-0.04 Å shorter than in some copper(I) N-heterocyclic carbene complexes (1.868(6) and 1.888(6) Å)^{23,24,33} and falls within the lower range for the Cu–C bonds calculated for Wanzlick–Arduengo carbene copper complexes in MP2³⁴ or BP86³⁵ calculations (1.84–1.89 Å). However, the Cu=C separation calculated for **8e** is significantly larger compared to the values computed for a small iminophosphanamide model system such as $[H_2P(NH)_2-\kappa^2N]Cu=$ CH(HC=O) (1.794 Å)⁷ and for a cationic copper carbene model complex (1.782 Å).⁹ Such a discrepancy can be first of all attributed to steric reasons.

The calculated HOMO-1 of **8e** (Figure 8) shows π -backbonding from the copper atom to the carbone carbon. A population analysis reveals that the copper-carbon π -bond is localized predominantly on copper (76.9%) mainly as a d-orbital contribution (85.1%). Mixing with symmetry-equivalent s and p orbitals was found to be <1% and 14.2%, respectively. The carbon part of this bond (23.1%) is represented by a pure p orbital (100%). A population analysis for 8e gave a Mulliken charge of the carbon of -0.0163. This bonding pattern clearly identifies 8e as an electrophilic Fischer-type carbene. The LUMO of 8e has its major coefficient at the carbene fragment's carbon atom as an "empty" p orbital. These results are in agreement with earlier calculations on neutral β -diketiminate-supported diphenylcarbene copper complexes.^{19b} The intense color of the d¹⁰ complexes 8 can also be explained on the basis of these features.¹⁷



Figure 8. Graphical representation of HOMO-1 (left) and LUMO (right) of copper carbene 8e.

Conclusions

Employment of a tailor-made, sterically demanding, electronrich iminophosphanamide ligand leads to a sufficient stabilization of a number of α -carbonyl copper(I) carbenes **8** to allow

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their characterization in solution and in two cases even their isolation in analytically pure form. Their relative stability enabled us to determine the carbene fragment vs Cu(I) metal fragment rotation barriers, which indicated a significant backbonding character of the Cu=C bond. The electron-rich aryl ring at the carbon decreases the metal to carbone backbonding but stabilizes the carbene center by means of a donor interaction of the aryl ring π -system with the carbene's empty p orbital. The solid-state structure of carbene 8g is in agreement with the Pfaltz model of cyclopropanation stereochemistry and with predictions from quantum chemistry. To our knowledge, compound 8g is the first stable structurally characterized α -carbonyl copper carbene. Reaction of this carbene with styrene proceeds stereoselectively and affords trans-cyclopropane and a copper styrene complex in ca. 1:1 ratio. Kinetic experiments with pure 8g and previously characterized diaryl carbene 6 are fully consistent with an associative mechanism. The relative small negative ρ values derived from the Hammett plot for 8g suggest an early transition state where only a partial positive charge is building up at the benzylic carbon in the rather early transition state. DFT calculations performed on the full system 8e are consistent with the description of this compound as an electrophilic Fischer-type d¹⁰-ML₂(carbene) complex.

Finally we note that copper ethylene complex 1 also catalyzes the aziridination of styrene with PhI=NTs as a nitrene source, and synthetic as well as mechanistic and theoretical studies devoted to the characterization of the presumably highly electrophilic nitrenes bound to the copper-iminophosphanamide fragment will be a subject of further studies in our laboratory.

Experimental Section

Unless otherwise stated, all experiments were performed under an Ar atmosphere using a Braun glovebox or by Schlenk techniques. Tetrahydrofuran, pentane, hexane, toluene, and diethyl ether were distilled over benzophenone sodium-ketyl and kept under Ar. Toluene- d_8 was stirred over CaH₂ and then degassed three times prior to use. Tetrahydrofuran-d₈ was distilled over sodium and degassed three times. Pyridine, piperidine, iPr₂NH, and NEt₃ were distilled under Ar over KOH. DBU was purified by vacuum distillation. Commercially available EDA was distilled under vacuum prior to use and kept under Ar. Styrene and p-methylstyrene were distilled under vacuum prior to use and degassed three times. p-Methoxystyrene and p-(trifluoromethyl)styrene were passed through a short neutral Al₂O₃ column and degassed three times. All other commercially available reagents, including ABSA (p-acetamidobenzenesulfonyl azide), were used as received. Solutions of LDA were freshly prepared from iPr2NH and nBuLi and used immediately. Ethyl diazo(4-nitrophenyl)acetate,³⁶ TsN₃ (tosyl azide),³⁷ TryN₃ (2,4,6-triisopropylbenzenesulfonyl azide),³⁸ and complex 1¹⁵ were prepared according to known procedures.

The NMR spectra were recorded on Bruker 500, 300, and 250 MHz spectrometers at temperatures specified below. ¹H and ¹³C NMR chemical shifts are reported in parts per million and are referenced to the deuterated solvent used. ³¹P NMR spectra are calibrated either with external 85% H₃PO₄ or, where possible, by traces of free iminophosphanamide ligand (δ 30.1). Mass spectra were recorded on a JMS 700 instrument (JEOL). Elemental analyses were performed in the "Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg".

The solutions of copper carbenes 6 and 8g and olefins for kinetic measurements were prepared using a volumetric flask, divided in

equivalent portions, and kept at -78 °C. All kinetic studies were performed by ¹H NMR spectroscopy on the Bruker 500 MHz NMR spectrometer equipped with an internal thermocouple sensor. The sample was allowed to reach thermal equilibrium for ca. 4 min prior to measurements. The errors of the rate constants and the activation parameters were calculated as described in ref 32.

Ethyl Diazo(2-nitrophenyl)acetate.³⁹ To a well-stirred solution of ethyl (2-nitrophenyl)acetate (300 mg, 1.434 mmol), Bu₄NBr (0.28 eq., 130 mg, 0.403 mmol), 18-crown-6 (13 mg), and TsN₃ (230 mg) in 15 mL of C₆H₆ was added dropwise a 20% aqueous solution of KOH (15 mL). The reaction mixture was stirred at 38 °C for 1 h, and the benzene phase slowly acquired a yellow color. The temperature was maintained at 40 °C for 1.5 h, and the organic layer changed its color to red. TLC control showed almost complete conversion of the starting material. An additional 40 mg of TsN₃ was added, and stirring was continued at 38 °C for 40 min. Et₂O was added, and the organic phase was separated. The water phase was diluted with more H2O (20 mL) and extracted with Et2O (15 mL). The combined organic extracts were washed with H₂O (20 mL) and brine (10 mL), dried over Na₂SO₄, and evaporated to give a yellow oil which was purified by column chromatography (SiO₂, EtOAc-hexane 1:5) to yield 0.26 g (77%) of a yellow-orange oil. Crystallization from EtOH gave an analytically pure sample. Mp: 48 °C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ 7.82–7.85 (m, 1H, arom), 7.42-7.49 (m, 1H arom), 7.24-7.36 (m, 2H, arom), 4.08 (q, ${}^{3}J_{\text{HH}} = 7.1$ Hz, OCH₂), 1.09 (t, ${}^{3}J_{\text{HH}} = 7.1$ Hz, CH₃).

tert-Butyl (4-Nitrophenyl)acetate.40 A 100 mL flask equipped with a calcium chloride drying tube and a magnetic stirring bar was charged with (4-nitrophenyl)acetic acid (5 g, 27.6 mmol), dry CH₂Cl₂ (50 mL), tBuOH (8 mL, 82.20 mmol), and DMAP (2.70 g, 22.08 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, and then the cooling bath was removed and stirring was continued at room temperature for 34 h. During this time, a white precipitate was formed. The reaction mixture was filtered through a layer of Celite. The Celite was washed with CH_2Cl_2 , and the combined organic fractions were washed with cold concentrated citric acid $(2 \times 30 \text{ mL})$, cold saturated NaHCO₃ $(2 \times 30 \text{ mL})$, and brine (30 mL), dried over Na₂SO₄, and evaporated. The product was purified by column chromatography (SiO₂, EtOAc-hexane 1:7) to yield 6.05 g (75%) of a colorless liquid, which crystallized on storage in the refrigerator. An analytical sample was obtained by recrystallization of the product from hexane. Yield: 4.24 g (65%). Mp: 55 °C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ 8.17 (d, ³J_{HH} = 8.75 Hz, 2H, arom), 7.43 (d, ${}^{3}J_{HH} = 8.75$ Hz, 2H, arom), 3.63 (s, 2H, ArCH₂), 1.43 (s, 9H, C(CH₃)₃). Anal. Calcd for C₁₂H₁₅NO₄: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.72; H, 6.38; N, 5.90.

tert-Butyl Diazo(4-nitrophenyl)acetate (7b). To a mixture of *tert*-butyl (4-nitrophenyl)acetate (1.5 g, 6.325 mmol) and ABSA (1.5 equiv, 2.28 g, 9.488 mmol) in dry THF (10 mL) was added Et₃N (1.5 equiv, 1.32 mL, 9.488 mmol). The reaction mixture became yellow-brown. After 10 min of stirring at room temperature TLC showed the reaction to be not yet complete. DBU (1.5 equiv, 1.42 mL, 9.488 mmol) was added slowly (exothermic reaction), and the reaction mixture was stirred at room temperature for another 10 min, until TLC showed the reaction to have gone to completion. H₂O was added, and the product was extracted two times with Et₂O. The combined ether fractions were washed with concentrated citric acid (2 × 30 mL) solution, water (2 × 30 mL), and brine, dried (Na₂SO₄), filtered, and evaporated to give a yellow oil. Column chromatography (EtOAc—hexane 1:7) afforded a yellow solid (1.62 g, 97.6%) which can be recrystallized from EtOAc—hexane 1:7

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⁽³⁹⁾ Prepared by the method of: Lombardo, L.; Mander, L. N. *Synthesis* **1980**, 368, which has been slightly modified.

⁽⁴⁰⁾ Prepared by the method of: Neises, B.; Steglich, W. *Organic Syntheses*; Wiley: New York, 1992; Collect. Vol. 70, p 93, which was slightly modified.

with addition of small portions of CHCl₃. Yield after recrystallization: 1.46 g (88%), light-yellow solid. Mp: 118–119 °C. ¹H NMR (500.13 MHz, CDCl₃, 298 K): δ 8.19 (d, ³*J*_{HH} = 8.95 Hz, 2H, arom), 7.63 (d, ³*J*_{HH} = 8.95 Hz, 2H, arom), 1.55 (s, 9H, C(CH₃)₃). ¹³C{¹H} NMR (125.77 MHz, CDCl₃, 298 K): δ 162.9 (*C*=O), 144.8, 134.6, 124.2, 123.1 (all arom H), 83.2 (*C*(CH₃)₃), 28.3 (C(*C*H₃)₃). Anal. Calcd for C₁₂H₁₃N₃O₄: C, 54.75; H, 4.98; N, 15.96. Found: C, 54.72; H, 4.91; N, 16.00.

N,*N*-**Diisopropyl-2-(4-nitrophenyl)acetamide.** This compound was prepared from iPr₂NH and (4-nitrophenyl)acetic acid chloride followed by purification of the product by column chromatography (EtOAc-petroleum ether 1:2.5) and recrystallization from EtOAc-hexane 1:5. The crude product (mp 70–71 °C) was used further without additional purification. ¹H NMR (250 MHz, CD₂Cl₂, 298 K): δ 8.14 (d, ³*J*_{HH} = 8.8 Hz, 2H, arom), 7.39 (d, ³*J*_{HH} = 8.9 Hz, 2H, arom), 3.91 (sep, ³*J*_{HH} = 6.6 Hz, 1H, NC*H*(CH₃)₂), 3.75 (s, 2H, CH₂), 3.43 (br. s, 1H, NC*H*(CH₃)₃), 1.37 (d, ³*J*_{HH} = 6.6 Hz, 6H, NCH(CH₃)₃).

2-Diazo-N,N-diisopropyl-2-(4-nitrophenyl)acetamide (7d). To a stirred solution of N,N-diisopropyl-2-(4-nitrophenyl)acetamide (0.5 g, 1.89 mmol) and ABSA (0.5 g, 2.083 mmol) in absolute THF (8 mL) was added dropwise DBU (0.31 mL, 2.083 mmol) at 0 °C. The cooling bath was removed, and the reaction mixture was stirred at room temperature for ca. 1.5 h (TLC control). An additional 80 mg of AzN₃ and 0.07 mL of DBU were added, and the dark solution was stirred for a further 30 min. The solvent was removed on a rotary evaporator, and the residue was purified by column chromatography on deactivated SiO₂ (EtOAc-hexane 1:2.5) to give an orange oil which quickly crystallized on standing. The product was recrystallized from warm EtOAc-hexane 1:5. The mother liquor after crystallization was concentrated by evaporation followed by crystallization of more product from light petroleum. Yield: 50%. $R_f = 0.95$ (EtOAc-hexane 1:2.5). Mp: 87–88 °C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ 8.18 (d, ${}^{3}J_{HH} = 9.2$ Hz, 2H, arom), 7.28 (d, ${}^{3}J_{HH} = 9.2$ Hz, 2H, arom), 3.74 (sep, ${}^{3}J_{HH} = 6.7$ Hz, 2H, NCH(CH₃)₂), 1.35 (d, ${}^{3}J_{HH} = 6.7$ Hz, 12H, NCH(CH₃)₃). Anal. Calcd for C₁₄H₁₈N₄O₃: C, 57.92; H, 6.25; N, 19.30. Found: C, 57.77; H, 6.20; N, 19.18.

N,N-Dimethyl-2-(4-nitrophenyl)acetamide. (4-Nitrophenyl)acetic acid chloride (3 g, 15.04 mmol) was dissolved in dry C₆H₆ (100 mL), and the solution was cooled to 0 °C. Me₂NH gas was bubbled through the solution, and a precipitate was formed. The reaction mixture was poured on water, and the organic layer was separated, washed with water, dried (Na₂SO₄), and evaporated to give a solid which was recrystallized from EtOAc-hexane 1:5. Yield: 2.58 g (82.4%). Mp: 89–90 °C. ¹H NMR (250 MHz, CDCl₃, 298 K): δ 8.15 (d, ³J_{HH} = 8.8 Hz, 2H, arom), 7.40 (d, ³J_{HH} = 8.8 Hz, 2H, arom), 3.78 (s, 2H, CH₂), 3.03 (s, 3H, NCH₃), 2.96 (s, 3H, NCH₃). Anal. Calcd for C₁₀H₁₂N₂O₃: C, 57.69; H, 5.81; N, 13.45. Found: C, 57.59; H, 5.78, 13.40.

2-Diazo-*N*,*N***-dimethyl-2-(4-nitrophenyl)acetamide (7c).** This compound was prepared in a manner similar to that described for **7d**, from *N*,*N*-dimethyl-2-(4-nitrophenyl)acetamide and ABSA in THF. Extractive workup followed by column chromatography (SiO₂, EtOAc-hexane 2:1) gave a yellow-orange product. Crystalization from EtOAc-hexane 1:5 afforded red-orange plates. Yield: 45%. Mp: 118–119 °C. ¹H NMR (500 MHz, toluene-*d*₈, 298 K): δ 7.91 (d, ³*J*_{HH} = 8.9 Hz, 2H, arom), 6.98 (d, ³*J*_{HH} = 8.9 Hz, 2H, arom), 2.48 (s, 6H, N(CH₃)₂). ¹³C NMR (125.77 MHz, toluene-*d*₈, 298 K): δ 162.9 (s, *C*=O), 145.2, 135.7, 124.2, 123.4 (all s, arom C), 62.6 (s, *C* = N₂), 36.8 (s, N(CH₃)₂). Anal. Calcd for C₁₀H₁₀N₄O₃: C, 51.28; H, 4.30; N, 23.92. Found: C, 51.26; H, 4.29; N, 23.92.

Methyl Diazo(4-methoxyphenyl)acetate (7e). Method A. To a stirred solution of LDA (1.1 equiv, 2.05 mmol) in dry THF (7 mL) was added dropwise methyl(4-methoxyphenyl)acetate (0.3 mL, 0.335 g, 1.86 mmol) via a syringe at -75 °C. The reaction mixture was stirred at -75 °C for 1 h followed by dropwise addition of a solution of TsN₃ (1.15 equiv, 420 mg, 2.14 mmol) in THF (2 mL). The reaction mixture was stirred at -75 °C for 10 min, the cooling bath was removed, and the mixture was warmed to ambient temperature. Upon warming, a white precipitate was formed, and the viscosity increased. The reaction mixture was stirred at room temperature for 3 h. After the reaction had been completed (TLC), THF was removed in vacuo below 40 °C, the residue was quenched with Et₂O (40 mL) and H₂O (30 mL), and the layers were separated. The water phase was washed with ether (20 mL), and the combined organic extracts were washed with water (30 mL) and brine (20 mL), dried (Na₂SO₄), and evaporated to give an orange oil which was purified by column chromatography (50 mL SiO₂, EtOAc-hexane 1:7). Yield: 0.34 g (88.7%), orange solid. An analytical sample and a sample for carbene synthesis were prepared by crystallization of the product from EtOAc-hexane 1:7 (mp 50 °C). ¹H NMR (500.13 MHz, CDCl₃, 298 K): δ 7.37 (d, ³*J*_{HH} = 8.55 Hz, 2H, arom), 6.93 (d, ${}^{3}J_{\text{HH}} = 8.55$ Hz, 2H, arom), 3.84 (s, 3H, OCH₃), 3.80 (s, 3H, OCH₃). Anal. Calcd for C₁₀H₁₀N₂O₃: C, 58.25; H, 4.89; N, 13.59. Found: C, 58.17; H, 4.84; N, 13.63.

Method B.³⁹ To a well-stirred mixture of methyl (4-methoxyphenyl)acetate (0.5 g, 2.78 mmol), Bu₄NBr (250 mg, 0.778 mmol), TryN₃ (1.03 g, 3.336 mmol), 18-crown-6 (30 mg), and C₆H₆ (10 mL) was added dropwise a 66% aqueous solution of KOH (15 mL). The reaction mixture was stirred at 39 °C for 25 min, an additional 100 mg (0.4 equiv) of TryN₃ was added, and the mixture was stirred at 38 °C for another 15 min. Ether was added, and the layers were separated. The organic phase was washed with water and brine, dried (Na₂SO₄), and evaporated. Yield of the product after chromatography (EtOAc—hexane 1:7): 86 mg (15%). Spectroscopic data were identical with those of a sample prepared by method A.

Bis(4-chlorophenyl)methyl (4-Methoxyphenyl)acetate. This compound was prepared from bis(4-chlorophenyl)methanol (3.06 g, 12.10 mmol), pyridine (2.57 mL, 31.85 mmol), and (4-methoxyphenyl)acetyl chloride (2 mL, 12.74 mmol) in toluene (150 mL). Extractive workup followed by recrystallization from EtOAc-petroleum ether 1:5, column chromatography (SiO₂, EtOAc-petroleum ether 1:5), and one more recrystallization from the same solvent mixture afforded 2.68 g (54.5%) of analytically pure material. Mp: 95–96 °C. ¹H NMR (250 MHz, CDCl₃, 293 K): δ 7.31 (d, ³J_{HH} = 8.6 Hz, 4H, arom), 7.21 (d, ³J_{HH} = 8.8 Hz, 2H arom), 7.19 (d, ³J_{HH} = 8.6 Hz, 4H, arom), 6.89 (d, ³J_{HH} = 8.8 Hz, 2H, arom), 6.80 (s, 1H, OCH), 3.84 (s, 3H, OCH₃), 3.69 (s, 2H, ArCH₂). Anal. Calcd for C₂₂H₁₈Cl₂O₃: C, 65.85; H, 4.52; Cl, 17.67. Found: C, 65.64; H, 4.54; Cl, 17.53.

Bis(4-chlorophenyl)methyl Diazo(4-methoxyphenyl)acetate (7g). Bis(4-chlorophenyl)methyl (4-methoxyphenyl)acetate (1 g, 2.46 mmol) and ABSA (0.89 g, 3.69 mmol) were suspended in absolute THF, and then DBU (0.55 mL, 0.56 g, 3.69 mmol) was added in one portion. The reaction mixture was stirred for 1 h at room temperatue and then allowed to stand at ambient temperature in a dark place for 7 days. TLC (EtOAc-hexane 1:7) showed complete conversion of the starting material. The solvent was removed in vacuo, and the residue was purified by column chromatography (SiO₂, EtOAc-hexane 1:5) to give a red-orange oil that was dried at 10⁻³ mbar. Yield: 1.05 g of an orange oil, purity >90%. The product is light sensitive and slowly decomposes at room temperature; therefore, it must be stored under Ar in a dark, cold (-35 °C) place. ¹H NMR (250 MHz, CDCl₃, 298 K): δ 7.27–7.41 (m, 10H, arom), 7.00 (s, OCH), 6.97 (d, ${}^{3}J_{HH} = 8.9$ Hz, 2H, arom), 3.84 (s, 3H, OCH₃). MS-EI: m/z 398.0 (2%) [(M - $N_2)^+$].

 $[tBu_2P(NSiMe_3)_2-\kappa^2N]Cu=C[(p-NO_2-C_6H_4)(COOEt)]$ (8a). Copper complex 1 (40 mg, 0.097 mmol) and diazo compound 7a (0.85 eq, 20 mg, 0.083 mmol) were mixed in 0.5 mL of toluene-d₈ and placed in an NMR tube after complete dissolution. The solution in the NMR tube was heated to 70 °C for 5 min, and the steady-state concentration of carbene complex 8a reached 35%. ¹H NMR

(500.13 MHz, toluene- d_8 , 235 K): δ 8.62 (d, ${}^{3}J_{HH} = 8.5$ Hz, 2 arom H), 7.32 (d, ${}^{3}J_{HH} = 8.5$ Hz, 2 arom H), 4.20 (q, ${}^{3}J_{HH} = 7.2$ Hz, 2H, CH₂), 1.37 (d, ${}^{3}J_{HP} = 14.3$ Hz, 9H, C(CH₃)₃), 1.30 (d, ${}^{3}J_{HP} = 14.6$ Hz, 9H, C(CH₃)₃), 0.33 (s, 18H, Si(CH₃)₃). The signal of the CH₃ group overlaps with *t*Bu group signals of the carbene complex and of the starting ethylene complex. ${}^{31}P{}^{1}H{}$ NMR (202.47 MHz, toluene- d_8 , 235 K): δ 67.7 (s + sat., ${}^{2}J_{PSi} = 11.2$ Hz, ${}^{1}J_{PC} = 60.8$ Hz). ${}^{13}C{}^{1}H{}$ NMR (125.77 MHz, toluene- d_8 , 235 K): δ 219.0 (Cu=*C*), 178.3 (*C*=O), 37.7 (d, ${}^{1}J_{PC} = 61.7$ Hz, *C*(CH₃)₃), 37.6 (d, ${}^{1}J_{PC} = 61.7$ Hz, *C*(CH₃)₃), 27.6 (s, C(CH₃)₃), 5.5 (s, Si(CH₃)₃); aromatic signals omitted.

 $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]Cu = C[(p-NO_2 - C_6H_4)(COOtBu)] (8b).$ The copper complex 1 (40 mg, 0.097 mmol) and the diazo compound 7b (0.9 equiv, 23 mg, 0.0876 mmol) were mixed in 0.5 mL of toluene- d_8 , and when dissolution was complete, the solution was transferred to an NMR tube. The color slowly changed to dark violet, but even after 40 min at room temperature the carbene concentration remained very low. The solution in the NMR tube was heated to 70 °C for 10 min, and the steady-state concentration of the carbene complex 8b reached 60.2%. ¹H NMR (500.13 MHz, toluene- d_8 , 235 K): δ 8.59 (d, ${}^{3}J_{\text{HH}} = 8.7$ Hz, 2 arom H), 7.25 (d, ${}^{3}J_{\text{HH}} = 8.7 \text{ Hz}, 2 \text{ arom H}), 1.74 (s, 9H, OC(CH_3)_3), 1.36 (d, {}^{3}J_{\text{HP}} =$ 14.1 Hz, 9H, C(CH₃)₃), 1.34 (d, ${}^{3}J_{HP} = 13.9$ Hz, 9H, C(CH₃)₃), 0.33 (s, 18H, Si(CH₃)₃). ³¹P{¹H} NMR (202.47 MHz, toluene-d₈, 235 K): δ 66.7 (s + sat., ²J_{PSi} = 11.7 Hz, ¹J_{PC} = 62.1 Hz). ¹³C{¹H} NMR (125.77 MHz, toluene-d₈, 235 K): δ 221.1 (Cu=C), 177.9 (C=O), 81.7 (s, OC(CH₃)₃), 37.62 (d, $J_{PC} = 61.9$ Hz, $C(CH_3)_3$), 37.59 (d, $J_{PC} = 61.9$ Hz, $C(CH_3)_3$), 28.4 (s, $OC(CH_3)_3$), 27.7 (s, C(CH₃)₃), 27.6 (s, C(CH₃)₃), 5.53 (s, Si(CH₃)₃); signals corresponding to the aromatic ring omitted.

 $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]Cu = C[(p-NO_2 - C_6H_4)(CONMe_2)] (8c).$ To a mixture of copper complex 1 (40 mg, 0.0973 mmol) and diazo compound 7c (20.5 mg, 0.0876 mmol) was added toluene- d_8 , and after the reaction mixture was shaken at ambient temperature for 5 min, an intense violet solution was obtained. This solution was placed in an NMR tube. ¹H NMR (500.13 MHz, toluene-d₈, 263 K): δ 8.85 (d, ${}^{3}J_{\text{HH}} = 8.8$ Hz, 2 arom H), 7.45 (d, ${}^{3}J_{\text{HH}} = 8.8$ Hz, 2 arom H), 2.78 (s, 3H, $N(CH_3)_2$), 2.40 (s, 3H, $N(CH_3)_2$), 1.44 (d, ${}^{3}J_{\rm HP} = 14.4$ Hz, 9H, C(CH₃)₃), 1.43 (d, ${}^{3}J_{\rm HP} = 14.4$ Hz, 9H, C(CH₃)₃), 0.29 (s, 18H, Si(CH₃)₃). ³¹P{¹H} NMR (202.47 MHz, toluene- d_8 , 263 K): δ 67.0 (s + sat, ${}^1J_{PC} = 62$ Hz, ${}^2J_{PSi} = 11.8$ Hz). ¹³C{¹H} NMR (125.77 MHz, toluene- d_8 , 263 K): δ 231.7 (s, Cu=C), 177.8 (s, C=O), 155.1, 147.7, 132.4, 126.1 (all s, arom C), 37.4 (d, ${}^{1}J_{PC} = 62.4$ Hz, $C(CH_3)_3$), 37.2 (d, ${}^{1}J_{PC} = 62.4$ Hz, $C(CH_3)_3$, 35.1 (s, NCH₃), 33.0 (s, NCH₃), 27.7 (d, ${}^2J_{CP} = 2.2$ Hz, $C(CH_3)_3$, 27.3 (d, ${}^2J_{CP} = 2.2$ Hz, $C(CH_3)_3$), 5.26 (d, ${}^3J_{CP} = 2.2$ Hz, Si(CH₃)₃).

 $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]Cu = C[(p-MeO - C_6H_4)(COOMe)] (8e).$ Copper complex 1 (40 mg, 0.097 mmol) and diazo compound 7e (18 mg, 0.087 mmol) were dissolved in toluene- d_8 (0.5 mL). Gas evolution was observed, and the reaction mixture became intensively violet. The reaction mixture was agitated at room temperature for 1 min, transferred to an NMR tube, and kept at room temperature for a further 4 min. ¹H NMR (500.13 MHz, toluene- d_8 , 237 K): δ 9.61 (br s, 1H arom (ortho)), 6.79 (d, ${}^{3}J_{HH} = 7.35$ Hz, 2H, arom), 6.52 (br s., 1H arom (ortho)), 3.73 (s, 3H, OCH₃), 2.96 (s, 3H, OCH₃), 1.48 (d, ${}^{3}J_{HP} = 13.9$ Hz, 9H, C(CH₃)₃), 1.39 (d, ${}^{3}J_{HP} =$ 14.3 Hz, 9H, C(CH₃)₃), 0.47 (s, 18H, Si(CH₃)₃). ${}^{31}P{}^{1}H{}$ NMR (202.48 MHz, toluene- d_8 , 237 K): δ 60.74 (s). ¹³C{¹H} NMR (125.77 MHz, toluene- d_8 , 237 K): δ 232.8 (s, Cu=C), 177.9 (s, C=O), 37.5 (d, ${}^{2}J_{CP} = 63.7$ Hz, C(CH₃)₃), 37.4 (d, ${}^{2}J_{CP} = 63.7$ Hz, *C*(CH₃)₃), 28.2 (s, C(*C*H₃)₃), 28.0 (s, C(*C*H₃)₃), 5.65 (s, Si(*C*H₃)₃). ¹H-VT-NMR (500 MHz, toluene- d_8): tBu, $T_c = 301 \pm 4$ K, $k_c =$ 101.4 Hz.

 $[tBu_2P(NSiMe_3)_2-\kappa^2N]Cu=C[(p-MeO-C_6H_4)(COOtBu)]$ (8f). Copper complex 1(40 mg, 0.097 mmol) and diazo compound 7f (0.9 equiv, 22 mg, 0.088 mmol) were dissolved in 0.5 mL of toluene- d_8 , and the resulting dark violet solution was placed in an NMR tube. After 10 min of shaking at room temperature, the NMR measurement was performed at 235 K. Carbene 8f was formed in a steady-state concentration of 59.2%. ¹H NMR (500.13 MHz, 235 K, toluene-d₈): δ 9.47 (br s, 1H, o-C₆H₄), 7.85 (br s, 1H, o-C₆H₄), 6.46 (br s, 1H, m-C₆H₄), 6.17 (br s, 1H, m-C₆H₄), 2.98 (s, 3H, OCH₃), 1.81 (s, 9H, OC(CH₃)₃), 1.47 (d, ${}^{3}J_{HP} = 13.8, 9H, C(CH_{3})_{3})$, 1.45 (d, ${}^{3}J_{\text{HP}} = 14.0$ Hz, 9H, C(CH₃)₃), 0.48 (s, 18H, Si(CH₃)₃). ³¹P{¹H} NMR (202.47 MHz, 235 K, toluene- d_8): δ 59.7 (s + sat, ${}^{2}J_{PSi} = 14.4 \text{ Hz}, {}^{1}J_{PC} = 64.1 \text{ Hz}$). ${}^{13}C{}^{1}H} \text{ NMR} (125.77 \text{ MHz},$ 235 K, toluene-d₈): δ 235.8 (Cu=C), 177.0 (C =O), 55.6 (s, $OC(CH_3)_3$), 37.5 (d, ${}^1J_{PC} = 64.4$ Hz, $C(CH_3)_3$), 37.4 (d, ${}^1J_{PC} =$ 64.4 Hz, C(CH₃)₃), 29.1 (s, OC(CH₃)₃), 28.1 (s, C(CH₃)₃), 28.0 (s, C(CH₃)₃), 5.75 (s, Si(CH₃)₃). ¹H-VT-NMR (500.13 MHz, toluened₈,): *o*-H, $T_c = 270 \pm 6$ K, $k_c = 1807$ Hz; *m*-H, $T_c = 254 \pm 4$ K, $k_{\rm c} = 305$ Hz, tBu, $T_{\rm c} = 314.1 \pm 4$ K, $k_{\rm c} = 23.5$ Hz.

 $[tBu_2P(NSiMe_3)_2 - \kappa^2 N]Cu = C\{(p-MeO - C_6H_4)[COOCH(p-K_2)]Cu = C\}$ ClC₆H₄)₂]} (8g). Copper complex 1 (100 mg, 0.243 mmol) and diazo compound 7g (100 mg, 0.231 mmol) were stirred for 20 min in absolute hexane (14 mL) under a slight dynamic vacuum at 36-37 °C. The solvent was carefully removed at -3 °C and 10^{-3} mbar, and the dark residue was treated with absolute hexane (8 mL), vigorously stirred at room temperature for 2 min, and filtered via a filter cannula into another Schlenk vessel cooled to -3 °C. The clear, deep violet solution was *slowly* cooled to -60 °C and kept at this temperature for 2 days. Dark crystals precipitated, and the supernatant solvent was removed via cannula. The remaining solid was washed with cold (-78 °C) absolute pentane (8 mL) and dried under high vacuum (10^{-3} mbar) at -20 °C and finally for 2 min at room temperature to yield 126 mg of dark crystalline material. According to elemental analysis, it was contaminated with the starting diazo compound 7g and cocrystallized hexane (both ca. 17 mol %). Recrystallization from absolute pentane gave a sample completely free of the starting diazo ester ($8g \cdot 0.46C_5H_{12}$), 100 mg, 53%). According to the ¹H NMR and elemental analysis, the product crystallized with 0.46 equiv of pentane. ¹H NMR (500.13 MHz, THF- d_8 , 238 K): δ 9.30 (d, ${}^{3}J_{\text{HH}} = 8.2$ Hz, 1 arom H), 7.50 (d, ${}^{3}J_{\text{HH}} = 8.5$ Hz, 4 arom H), 7.47 (d, ${}^{3}J_{\text{HH}} = 8.2$ Hz, 1 arom H), 7.39 (d, ${}^{3}J_{HH} = 8.5$ Hz, 4 arom H), 7.21 (s, CH), 7.16 (d, ${}^{3}J_{\rm HH} = 7.0$ Hz, 1 arom H), 6.81 (d, ${}^{3}J_{\rm HH} = 7.60$ Hz, 1 arom H), 3.88 (s, OCH₃), 1.36 (d, ${}^{3}J_{HP} = 14.2$ Hz, 9H, C(CH₃)₃), 1.28 (d, ${}^{3}J_{\text{HP}} = 14.5 \text{ Hz}, 9\text{H}, \text{C(CH}_{3})_{3}), -0.05 \text{ (s, Si(CH}_{3})_{3}). {}^{31}\text{P}\{{}^{1}\text{H}\} \text{ NMR}$ (202.47 MHz, THF- d_8 , 238 K): δ 59.5 (s + sat, ${}^1J_{PC} = 63.9$ Hz, ${}^{2}J_{\text{PSi}} = 14.3 \text{ Hz}$). ${}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR (125.77 MHz, THF- d_{8} , 238 K): δ 230.5 (s, Cu=C), 175.9 (s, C=O), 166.9, 143.9, 143.7, 140.3, 134.1, 134.0, 129.7, 129.3, 117.9, 117.1 (all arom H), 75.0 (s, CH), 56.6 (s, OCH₃), 37.43 (d, ${}^{2}J_{CP} = 64.4$ Hz, C(CH₃)₃), 37.39 (d, ${}^{2}J_{CP} =$ 64.4 Hz, C(CH₃)₃), 27.8 (s, C(CH₃)₃), 27.7 (s, C(CH₃)₃), 5.1 (s, Si(CH₃)₃). ¹H-VT-NMR (500.13 MHz, THF-d₈): o-H, $T_c = 277$ \pm 5 K, $k_c = 917.5$ Hz; m-H, $T_c = 257 \pm 4$ K, $k_c = 174$ Hz. MS-FAB (NPOE): 782.5 (20%), $[MH^+]$, 725.4 (14%), $[MH^+ - tBu]$, correct isotopic pattern. Anal. Calcd for C36H52Cl2CuN2O3PSi2. 0.46C5H12: C, 56.35; H, 7.05; N, 3.43; Cl, 8.71; P, 3.80. Found: C, 56.47; H, 6.89; N, 3.72; Cl, 8.73; P, 3.81. UV–vis (in THF): λ_{max} 527 nm ($\epsilon = (1.1 - 1.7) \times 10^4$).

[*t*Bu₂P(NSiMe₃)₂- $\kappa^2 N$]Cu(C₆D₆). The free iminophosphanamide ligand (0.32 g, 1 mmol) was dissolved in hexane (5 mL), treated with 1.6 M of *n*-BuLi (0.75 mL, 1.2 mmol), and then added to a cooled (-70 °C) suspension of CuBr · Me₂S (0.246 g, 1.2 mmol) in hexane (6 mL). After it was stirred at room temperature for 3 h, the reaction mixture was allowed to stand for 2 days, and the liquid above the black solid precipitate was decanted with a filter cannula. The clear solution obtained was evaporated at 10⁻³ mbar to give ca. 0.20 g of an oil, which was analyzed by NMR. ¹H NMR (C₆D₆, 500.13 MHz): 1.43 (d + sat, ³J_{HP} = 14 Hz, ¹J_{CH} = 126.5 Hz, 18H, *t*Bu), 0.65 (s + sat, ¹J_{CH} = 117.8 Hz, 18H, SiMe₃). ³¹P{¹H} NMR (C₆D₆, 202.47 MHz): δ 63.2 (s).

empirical formula	C27H44CuN4O4PSi2
formula wt	782.39
temp (K)	200(2)
wavelength (Å)	0.710 73
cryst syst	triclinic
space group	$P\overline{1}$
Z	4
a (Å)	12.5036(2)
b (Å)	18.8771(3)
<i>c</i> (Å)	20.9013(3)
α (deg)	91.8980(10)
β (deg)	94.7360(10)
γ (deg)	92.4700(10)
V (Å ³)	4908.62(13)
D_{calcd} (g/cm ³)	1.059
abs coeff (mm ⁻¹)	0.66
cryst shape	polyhedron
cryst size (mm ³)	$0.38 \times 0.20 \times 0.14$
θ range for data collecn (deg)	1.0-24.7
no. of collected rflns	41 715
no. of indep rflns	16 670
no. of obsd rflns	10 070
goodness of fit on F^2	1.00
final R indices $(I > 2\sigma(I))$	R1 = 0.053, wR2 = 0.138
largest diff peak and hole (e $Å^{-3}$)	0.65 and -0.37

Crystal Structure Analysis of 8g. Crystals of **8g** suitable for X-ray analysis were obtained by crystallization from a concentrated solution of crude **8g** in pentane at 0 °C. Data were collected on a Bruker SMART diffractometer, and the structure solution was performed using the SHELXTL-PLUS (5.10) software package.⁴¹ Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS⁴²

based on the Laue symmetry of the reciprocal space. The structure was solved by direct methods and refined against F^2 with a fullmatrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package. A total of 924 parameters were refined, hydrogen atoms were treated using appropriate riding models, and disordered solvent electron density was assigned using several carbon atoms with different occupancies. Crystal data and structure refinement details for **8g** are summarized in Table 8.

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Supporting Information Available: An ORTEP diagram of **8g** with a complete list of bond lengths and angles, ORTEP plots of diazo compounds **7b,d,f** and ethyl diazo(2-nitrophenyl)acetate, computational details and Cartesian coordinates of the optimized structure of **8e**, ¹H, ³¹P, and ¹³C NMR spectra of compound **8g**, ³¹P NMR spectra of **6** and **8g** after complete decomposition, and time vs concentration and Eyring plots for carbenes **6** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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⁽⁴¹⁾ Sheldrick, G. M. SHELXTL-PLUS, Bruker Analytical X-ray Division, Madison, WI, 1997.

⁽⁴²⁾ Sheldrick, G. M. SADABS, Bruker Analytical X-ray Division, Madison, WI, 2001.