tomerization to afford naphthol **11**. Further *E*/*Z* isomerization and subsequent lactonization provide product **3a**.

In conclusion, we have demonstrated a novel nickel-catalyzed cyclization of tricyclic alkenes **1** with propiolates **2** to give benzocoumarins or tetrahydrocoumarins in a one-pot reaction. More detailed studies on the scope, mechanism, and utility of this reaction are in progress.

Experimental Section

General procedure for the cyclization of 7-oxabenzonorbornadienes **1** with alkyl propiolates **2**: Freshly distilled CH_3CN (3.0 mL) and **2** (1.2–2.0 mmol) were added to **1** (1.00 mmol), [$NiBr_2$(dppe)] (0.05 mmol), and zinc powder (0.180 g, 2.75 mmol) under nitrogen. The reaction mixture was heated with stirring at 80 °C for 12 h and then cooled and stirred in air for 15 min. The mixture was filtered through Celite and silica gel and washed with dichloromethane. The filtrate was concentrated, and the residue was purified on a silica gel column with hexane/ethyl acetate as eluent to afford the desired cyclization product **3**.

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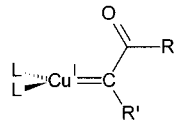
Copper(I) Carbenes: The Synthesis of Active Intermediates in Copper-Catalyzed Cyclopropanation[**]

Bernd F. Straub and Peter Hofmann[*]

The cyclopropanation of olefins with α-carbonyldiazoalkanes mediated by homogeneous copper catalysts has been known for more than 30 years, and was the first reported example of enantioselective transition metal catalysis.[1] Despite this long history, copper(I) α-carbonyl carbene complexes of type **1**, which are generally assumed to be the active intermediates, have remained undetected so far.[2] It is crucial to know their structure in solution to understand the enantiomeric and diastereomeric selectivities that can be achieved if chiral spectator ligands are utilized in cyclopropanation catalysis.[3]



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L = nitrogen or oxygen donor ligand
R = alkyl, aryl, alkoxy, amide
R' = aryl, acyl

Copper carbene complexes in the literature are limited to the linear d^{10}-ML_2 type, with Wanzlick–Arduengo carbene ligands substituted with strong donor groups.[4] These complexes are inactive in cyclopropanation chemistry. Generally, nickel-triad and coinage-metal carbene complexes of the d^{10}-ML_3 type are scarce,[5] probably as a result of the antibonding interaction between the metal d^{10} subshell and the sp^2 lone pair of a singlet carbene fragment.[6]

We have recently introduced an extremely basic, sterically demanding, and highly symmetric iminophosphanamide ligand into organometallic copper chemistry.[7] It stabilizes otherwise elusive or labile copper coordination modes by enhanced metal-to-ligand back donation and by steric shielding of the copper fragment.[7] We used the stable and neutral copper(I) ethylene complex **2**[7a] to isolate the α-carbonyldiazoalkane complex **3**, which is a stabilized model for

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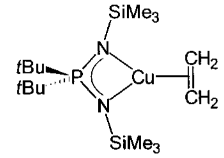

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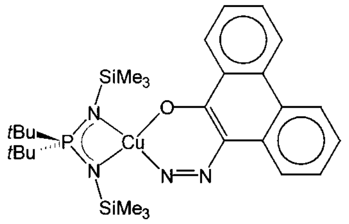
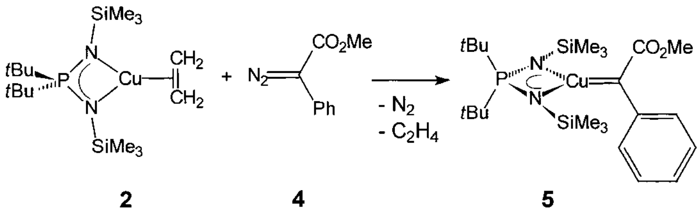


3

intermediates in the catalytic cyclopropanation cycle.[7b] However, **3** does not cyclopropanate olefins.

From density functional theory studies of less-congested model systems, a low-energy pathway for N_2 extrusion has been calculated, which leads to copper(I) carbenes.[7b, 8] The neutral precursor compound **2**, which allows convenient associative ligand substitution at the metal fragment, seemed ideal to provide access to copper(I) carbenes by reaction with α-carbonyldiazo compounds in solution.

Ethylene complex **2** reacts with methyl 2-phenyl-2-diazoacetate (**4**) in $[D_8]$toluene, C_6D_6, or pentane at ambient temperature to yield an intensely violet solution, after evolution of N_2 (Scheme 1). A single new copper complex is formed in a steady-state concentration of 15 to 25% of the ethylene complex concentration. This species was unambiguously identified as copper(I) carbene **5** by ^{1}H, $^{13}C\{^{1}H\}$, $^{29}Si\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectroscopy.



Scheme 1. Formation of copper(I) carbene **5**.

All of diazoalkane **4** had been consumed within an hour at ambient temperature, to give 2,3-diphenyl maleate and fumarate derivatives as the main decomposition products. Complex **5** started to disappear as soon as **4** was completely consumed. Within a few minutes, all of **5** had decomposed, and the violet color had faded. Upon cooling a reaction mixture of **2**, **4**, and **5** to −33 °C, the steady-state concentration of carbene complex **5** was maintained for several hours without significant evolution of nitrogen.

The main evidence for the structure of carbene complex **5** was derived from the $^{13}C\{^{1}H\}$ NMR signal of the carbene carbon atom at $\delta = 229.9$ (Figure 1). The downfield ^{13}C NMR signal for the carbonyl carbon atom of complex **5** at $\delta = 177.9$ also indicates the presence of an electrophilic carbene center. Both ^{13}C NMR signals disappear as the thermal decomposition of **5** goes to completion, or as **5** is consumed by the addition of styrene (see below). Low-temperature fast-atom bombardment (LT-FAB) mass spectra of solutions containing **5** confirm the presence of the molecular ion (*m/z* 531.2).

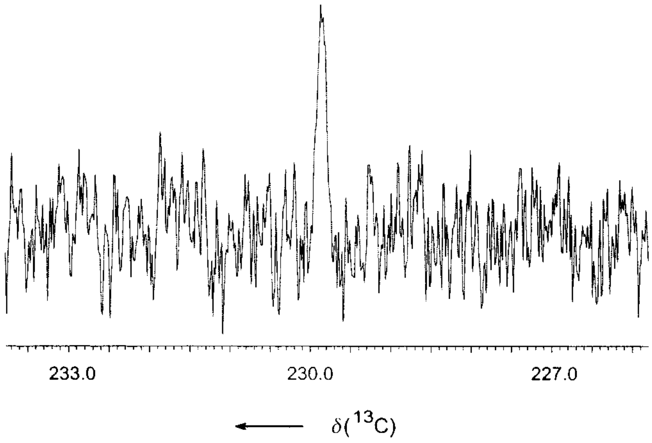


Figure 1. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $[D_8]$toluene (−33 °C, 75.47 MHz), showing the signal for the carbene carbon atom.

The *tert*-butyl groups of the iminophosphanamide ligand of **5** remain diastereotopic on the NMR time scale even at 28 °C (Figure 2), which proves that the the PN_2Cu chelate ring and the carbene plane are mutually orthogonal. The rotational barrier of the carbene fragment around the Cu–C double bond must amount to at least 60 kJ mol^{-1}.

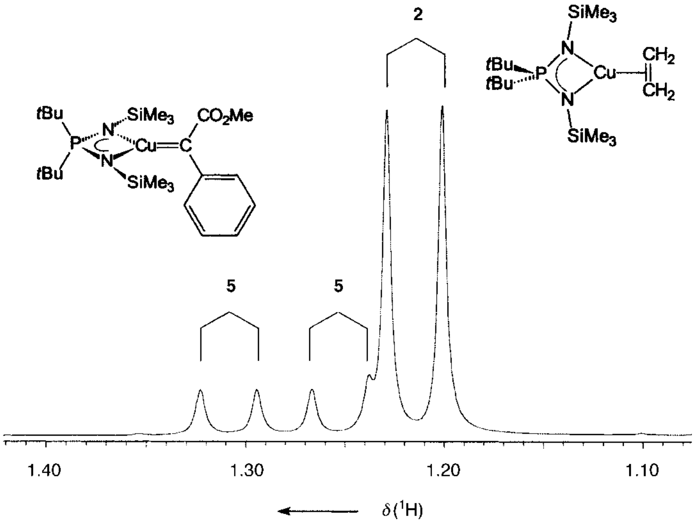


Figure 2. ^{1}H NMR spectrum (C_6D_6, 500.13 MHz, 28 °C) of the *tert*-butyl region of carbene complex **5** ($^{3}J_{PH} = 14$ Hz) and of ethylene complex **2** ($^{3}J_{PH} = 14$ Hz).

Variable temperature (VT) ^{1}H NMR spectroscopy shows a coalescence of the signals for the diastereotopic *ortho*-phenyl protons of carbene complex **5** at -70 ± 4 °C and 300.13 MHz (Figure 3). The upfield signal for the *ortho* protons overlaps with those of diazoalkane **4** and of the fumarate and maleate derivatives present in solution, and thus cannot be observed. However, an activation barrier of $\Delta G^{\neq} = (36.8 \pm 3.0)$ kJ mol^{-1} for the rotation of the phenyl group can be derived from the coalescence temperature and the observed chemical shift data for the *ortho* protons.

In the transition state $\mathbf{5}^{\neq}$, the carbene center cannot withdraw electron density from the π system of the phenyl ring. The observed rotational barrier of the phenyl substituent is in accordance with the electrophilic character of the carbene carbon atom in **5** and a qualitative description of

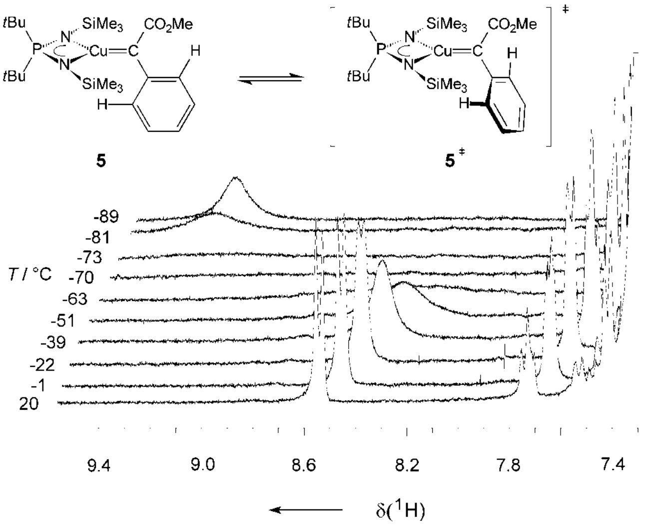


Figure 3. VT ^{1}H NMR spectra showing coalescence of the signals for the *ortho* phenyl protons ($^3J_{HH} = 8$ Hz) of carbene complex **5** in [D$_8$]toluene at 300.13 MHz. At low temperatures, the upfield signal overlaps with other signals.

the complex as a Fischer-type carbene. The ^{31}P and ^{29}Si chemical shifts of **5** indicate that the carbene ligand is a better π acceptor than ethylene, but a weaker one than, for example, an η^2-coordinated maleic anhydride.[8a]

The intense violet color ($\lambda_{max} = 496$ nm in pentane) can be rationalized by either a $\pi \rightarrow \pi^*$ transition of the copper–carbon double bond with predominant metal-to-ligand charge-transfer character, or by an excitation from a former sp^2 carbene lone pair localized in the copper–carbon σ bond to the π* lowest unoccupied molecular orbital (LUMO) with primarily carbene p-orbital character.

The addition of styrene to solutions containing **5** leads to the disappearance of the violet color of the reaction mixture within several seconds at room temperature, even in the presence of excess **4**. This observation is consistent with the assignment of **5** as a copper(I) carbene species. Only traces of **5** remain detectable by ^{31}P{^{1}H} NMR spectroscopy, and the styrene was cyclopropanated to give a mixture of *cis*- and *trans*-methyl-1,2-diphenylcyclopropanecarboxylate (ratio greater than 8:1).[9] This result is strong evidence that the active species in copper-catalyzed cyclopropanation reactions are indeed copper(I) carbene complexes, as proposed in the literature.[2, 3, 10]

When the steric shielding is increased by replacing the CO$_2$Me group of **4** with a bis(4-chlorophenyl)methyl ester group, or by introducing a 9-phenanthryl substituent and an isopropyl ester moiety, the resulting carbene complexes are slightly more stable and have very similar spectroscopic properties. However, the isolation of any analytically pure copper(I) carbene complexes and of single crystals suitable for X-ray diffraction studies has so far been hampered by the high solubility of our systems with iminophosphanamide ligands, and remains a challenging task.

In summary, the first copper(I) carbenes have been synthesized and characterized spectroscopically in solution. Their structural features and their concomitant reactivity patterns are fully consistent with the mechanistic scenario put forward by Pfaltz and co-workers for explaining and predicting product distributions in enantioselective copper-catalyzed cyclopropanations.[3] Mechanistic studies utilizing **5** and its congeners, as well as quantum-chemical investigations, are presently being pursued in our laboratory and will be reported separately.

Experimental Section

Diazoalkane **4** was prepared according to a literature procedure[11] and was purified by short-path distillation at 10^{-3} mbar. [D$_8$]Toluene and C$_6$D$_6$ were dried over CaH$_2$ and saturated with argon. Ethylene complex **1** was prepared according to ref. [7a].

5: Methyl 2-phenyl-2-diazoacetate (**4**) (98 mg) was dissolved in [D$_8$]toluene (0.5 mL) in an NMR tube, and ethylene complex **1** (58 mg) was added. The solution instantly became intensely violet, and gas evolution was observed.

Spectroscopic data of **5**: ^{1}H NMR (500.13 MHz, C$_6$D$_6$, 28 °C): $\delta = 8.68$ (d, $^3J_{HH} = 8$ Hz, 2H; *ortho*-C$_6$H$_5$), 3.61 (s, 3H; OCH$_3$), 1.31 (d, $^3J_{PH} = 14$ Hz, 9H; C(CH_3)$_3$), 1.25 (d, $^3J_{PH} = 14$ Hz, 9H; C(CH_3)$_3$), 0.24 (s, 18H; SiMe$_3$), the signals for *meta* and *para* phenyl protons overlap with signals of diazoalkane **4**, and of diphenyl fumarate and maleate derivatives; ^{13}C{^{1}H} NMR (125.76 MHz, [D$_8$]toluene, −33 °C): $\delta = 229.9$ (s; Cu=C), 177.9 (s; CO), 27.3 (brs; C(CH$_3$)$_3$), 27.2 (brs; C(CH$_3$)$_3$), 4.9 (s; Si(CH$_3$)$_3$), phenyl, methoxy, and quaternary *tert*-butyl carbon signals cannot be assigned unambigously; ^{29}Si{^{1}H} NMR (59.63 MHz, C$_6$D$_6$, 25 °C): $\delta = -10.2$ (d, $^2J_{SiP} = 12.2$ Hz); ^{31}P{^{1}H} NMR (121.49 MHz, [D$_8$]toluene, 25 °C): $\delta = 64.3$ (s + satellites, $^2J_{SiP} = 12.6$ Hz, $^1J_{CP} = 63$ Hz); UV/Vis (pentane) $\lambda_{max} = 496$ nm ($\varepsilon \approx 10^3$ M^{-1}cm^{-1}); LT-FAB:[12] m/z (%): 531.2 (1.8; [M^+]); VT ^{1}H NMR ([D$_8$]toluene, 300.13 MHz): *ortho*-C$_6$H$_5$, $T_c = -70 \pm 4$ °C, $k_c = (700 \pm 100)$ Hz; external temperature calibration by using MeOH.

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