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A Fluxional α-Carbonyl Diazoalkane Complex of Copper Relevant to Catalytic Cyclopropanation†

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The neutral copper(I) ethylene complex $[t\mathrm{Bu}_2\mathrm{P}(\mathrm{NSiMe}_3)_2\text{-}\kappa^2N]\mathrm{Cu}(\eta^2\text{-}\mathrm{C}_2\mathrm{H}_4)$ (**1**) reacts with diazophenanthrone (**2**), yielding an equilibrium mixture of **1** and **2** with free ethylene and the novel diazoalkane copper(III) complex **3**, which represents a stabilized analogue of early intermediates in the mechanism of copper-catalyzed cyclopropanation reactions of electron-rich olefins with α-carbonyl diazoalkanes. Its X-ray structure determination displays square-planar coordination of the formally d^8 copper(III) center with a κO:κN-bound diazophenanthrone. The geometry of the coordinated diazoalkane ligand can be directly compared to that of uncomplexed, cocrystallized diazophenanthrone, indicating a formal two-electron ligand reduction upon coordination. LT NMR spectroscopy reveals facile rotation of the diazoalkane ligand in solution even at temperatures below −110 °C. DFT calculations (B3LYP) on the model $[\mathrm{H}_2\mathrm{P}(\mathrm{NH})_2\text{-}\kappa^2N]\mathrm{Cu}(\mathrm{N}_2\mathrm{CHCHO}\text{-}\kappa N\text{:}\kappa\mathrm{O})$ (**4**) help to understand the bonding and fluxionality in **3** and predict a small ligand rotation barrier (through the transition state $\mathbf{4}^{\ddagger}$), in accordance with experimental facts. For model **4**, a low-energy pathway for dinitrogen extrusion and copper(I) carbene formation exists, involving a π-bound carbonyl diazoalkane complex and a carbon-coordinated diazoalkane copper(I) species. This pathway, and thus also cyclopropanation activity, is sterically blocked for **3**, making it an isolable species.

Introduction

Cyclopropanation of olefins with α-carbonyl diazoalkanes mediated by homogeneous copper catalysts has been known for more than 30 years as the first example of enantioselective metal catalysis.[1] Despite its long-standing history, the detailed mechanism of this synthetically important reaction is still unknown. Mechanistic assumptions and stereoselection rules rely upon observed reactivity−selectivity correlations[2] and sparse kinetic data,[3,4] rather than upon a direct observation of species involved in the catalytic cycle. Copper(I) α-carbonyl carbene complexes, generally assumed as reactive intermediates, have remained undetected so far. The role of cupracyclobutane formation versus electrophilic carbene transfer in the cyclopropane-forming step is unclear. The interaction mode of α-carbonyl diazoalkanes with typical copper precatalysts and the pathway of subsequent N_2 extrusion have defied unraveling. Only copper(I) olefin complexes, acting as the catalyst resting state, could be isolated[5] or identified.[6] From kinetic data, a preequilibrium preceding the rate-determining loss of dinitrogen from the diazoalkane has been deduced.[3] It remains unclear, however, whether this equilibrium involves 14-valence-electron copper(I) fragments and olefin complexes[3b] or the latter and copper diazoalkane complexation.[4] In addition, the origin of the specific efficiency of α-carbonyl diazoalkanes as carbene precursors is not yet understood.[2b]

For rhodium catalysis, the detection of a σ-bonded ethyl diazoacetate has been reported.[7] In contrast to copper, coordination chemistry of α-carbonyl diazoalkanes is well established for titanium,[8] vanadium,[8] molybdenum,[9] manganese,[10] iridium,[11] and platinum.[12]

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† Dedicated to Prof. Günter Helmchen on the occasion of his 60th birthday.

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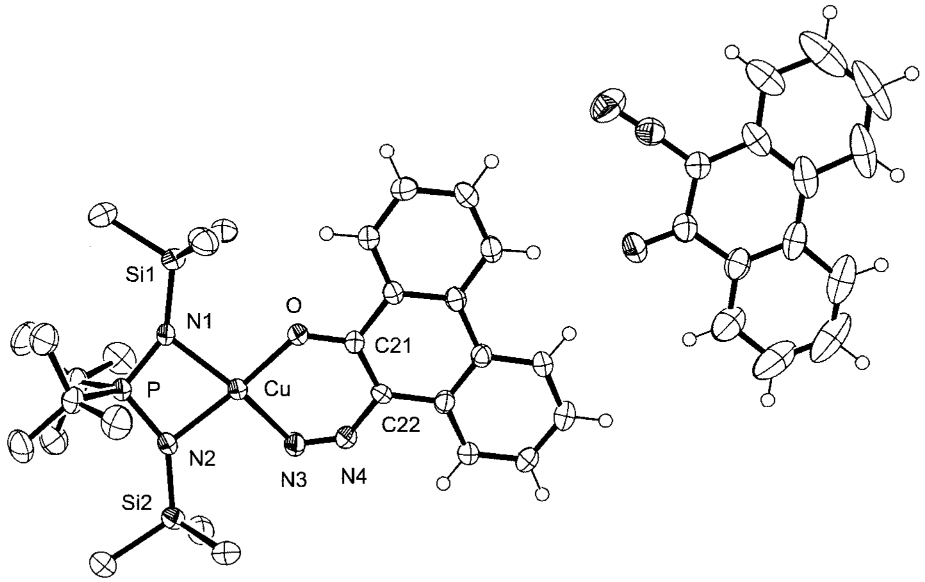
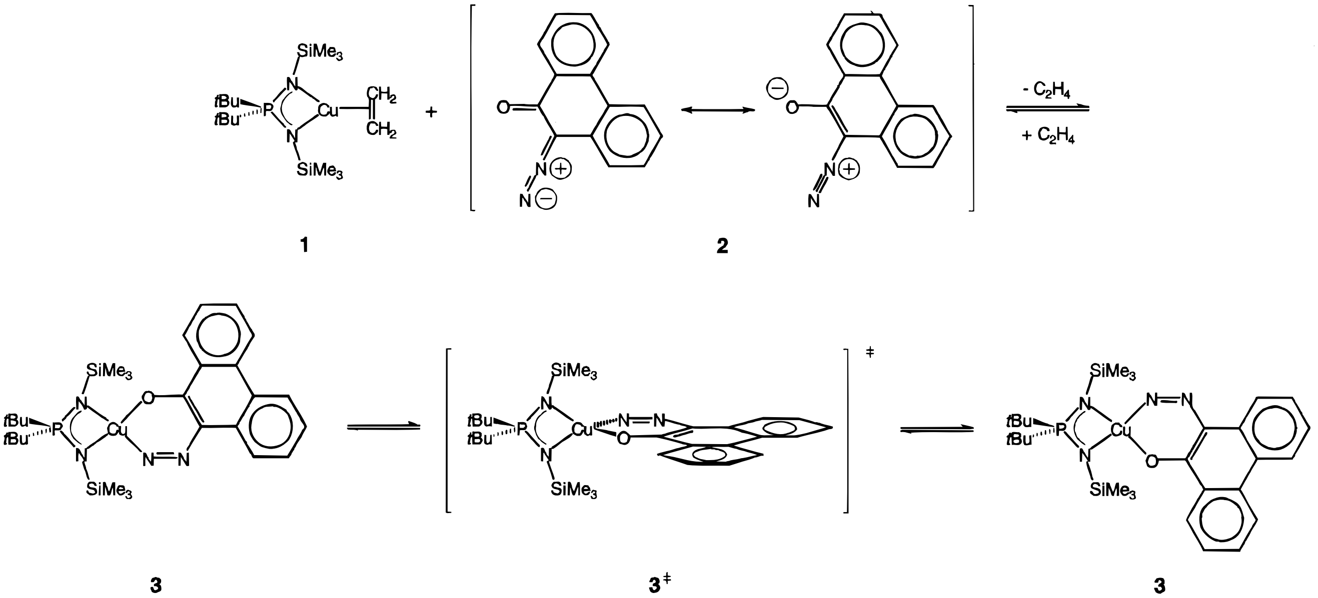


Figure 1. Molecular structure of **3·2** in the solid state. Hydrogens of the iminophosphanamide ligand are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 1. Synthesis of Complex 3 and Degenerate Rearrangement through Transition State $3^{\ddagger}$



Here we report the synthesis, structure, and bonding properties of a remarkably stable, fluxional copper α-carbonyl diazoalkane complex, accessible from the tailor-made copper(I) ethylene iminophosphanamide complex $[t\mathrm{Bu}_2\mathrm{P(NSiMe}_3)_2\text{-}\kappa^2 N]\mathrm{Cu}(\eta^2\text{-}\mathrm{C_2H_4})$ (**1**).[13]

Results and Discussion

Synthesis of 3. Reacting **1** with diazophenanthrone (**2**) in toluene yields an equilibrium mixture of **1** and **2** with ethylene and the brown copper α-carbonyl diazoalkane complex **3** (Scheme 1). Compound **3** is stable in solution at ambient temperature and can be isolated by removing ethylene and toluene in vacuo.

Bonding and Fluxionality. Diamagnetic **3** could be completely characterized by spectroscopy and by single-crystal X-ray diffraction (Figure 1). In the solid state, **3** possesses a nearly square-planar coordination environment around copper, indicating a formal d^8-ML_4 copper(III) species. Accumulation of negative charge on the diazoalkane moiety is corroborated by DFT calculations (NBO analysis; see Computational Procedure in the Experimental Section) for the model complex $[\mathrm{H_2P(NH)_2}\text{-}\kappa^2 N]\mathrm{Cu}(\mathrm{N_2CHCHO}\text{-}\kappa N{:}\kappa \mathrm{O})$ (**4**) (Figure 2 and Table 1). The computationally derived charge transfer of −0.54 is substantiated experimentally from a structure comparison of the diazophenanthrone ligand in complex **3** with fortuitously cocrystallized free diazoalkane **2** (Figure 1 and Table 1) in the unit cell. Elongated C−O, C−N, and N−N bonds and a shorter C−C bond of the diazoalkane ligand reflect its formal two-electron reduction (Table 1). Accordingly, the N−N bond stretching frequency in **4** is computed at 1759 cm^{-1}, in reasonable agreement with the experimental value of the intense IR absorption of 1700 cm^{-1} in **3**.

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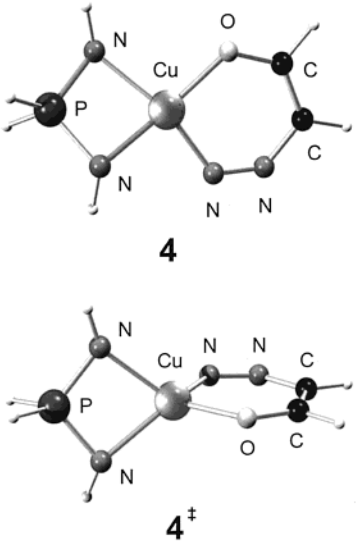

4

4‡

Figure 2. B3LYP ground-state structure **4** and transition state geometry **4**‡ for the model $[H_2P(NH)_2\text{-}\kappa^2N]Cu(N_2\text{-}CHCHO\text{-}\kappa N{:}\kappa O)$.

Table 1. Bond Distances (Å) and Bond Angles (deg) for 2 and 3 (X-ray) and for *s-cis*-N_2CHCHO, 4, and 4‡ (DFT)[a]

	2[b]	*s-cis*-N_2CHCHO[c]	**3**[b]	**4**[c]	**4**‡ [c]
Cu−N1			2.047(3)	2.0505	2.0749
Cu−N2			2.006(2)	1.9604	2.0512
Cu−N3			1.914(3)	1.8660	1.8325
Cu−O			1.878(2)	1.8560	1.8881
C21−O	1.223(4)	1.2192	1.291(4)	1.2746	1.2657
C21−C22	1.442(5)	1.4551	1.394(4)	1.3862	1.3963
C22−N4	1.332(5)	1.3127	1.374(4)	1.3685	1.3620
N3−N4	1.120(4)	1.1350	1.190(3)	1.1998	1.1850
O−C21−C22	122.9(3)	125.59	124.2(3)	126.17	125.91
C21−C22−N4	114.3(3)	118.63	117.2(3)	118.63	116.46
C22−N4−N3	176.2(4)	176.52	134.3(3)	132.48	134.39
N4−N3−Cu			123.8(2)	122.76	124.34
N3−Cu−O			90.8(1)	94.79	92.96
Cu−O−C21			128.8(2)	125.03	125.93
N1−Cu−N2			76.1(1)	76.00	74.15

[a] Atom labeling is according to Figure 1. [b] Data from X-ray diffraction. [c] Data from DFT model.

Remarkably, the copper iminophosphanamide fragment of complex **3** displays C_{2v} symmetry on the NMR time scale even at temperatures below −110 °C, indicating an extremely facile fluxional process, which we assign to a diazoalkane ligand rotation, interconverting degenerate square-planar structures (Scheme 1). The rotational barrier $\Delta G^{\ddagger}$ must lie distinctly below 35 kJ mol^{-1}. B3LYP DFT calculations on model **4** predict an activation barrier of $\Delta E = 19.6$ kJ mol^{-1}.[14] The distorted tetrahedral model transition state **4**‡ possesses more copper(I) character than ground-state structure **4**. This is apparent from shorter C−O and N−N bonds, from an elongated C−C bond (Table 1), and from a diminished charge transfer of −0.39 to the diazoalkane subunit compared to **4**. Nevertheless, copper 3d orbitals still interact with the diazoalkane ligand in **4**‡, reflecting that there is only a very formal dividing line between copper oxidation states I (d^{10}) and III (d^8 low spin).[15]

The electronic differences between **4** and **4**‡ are too minute to seriously discuss a redox process upon rotation of the ligand in ground state **3** and transition state **3**‡.

Stability of 3. The nearly thermoneutral equilibrium between **3** and ethylene versus ethylene complex **1** and diazoalkane **2** in solution can be assigned to the enhanced capto-dative stabilization of copper(III) by the $\kappa O{:}\kappa N$-bound diazophenanthrone ligand. Diazo and carbonyl vibration frequencies of diazophenanthrone (**2**) clearly demonstrate the importance of the 10-diazonio-9-phenanthrenolate resonance structure with a Lewis-basic phenolate and a Lewis-acidic diazonio group. The chelating,[16] electron-rich, anionic, and hard spectator ligand $[tBu_2P(NSiMe_3)_2]^-$ is tailored to additionally stabilize high copper oxidation states.[13] The reliability of the level of theory chosen for the DFT calculations for models **4** and **4**‡ above is underlined by the calculated gas-phase energy difference of 13.0 kJ mol^{-1} for the model reaction of $[H_2P(NH)_2\text{-}\kappa^2N]Cu(\eta^2\text{-}C_2H_4)$ and N_2-CHCHO to give **4** and C_2H_4. This number is in reasonable accord with the observed equilibrium of **1**−**3** and ethylene in solution.

The equilibrium concentration of the α-carbonyl diazoalkane complex should be distinctly lower than the olefin complex concentration, if diazo ester derivatives and less donating ligands are employed. The same applies for cationic copper(I) catalysts.

Thus, the kinetic stability of **3** toward loss of dinitrogen can be attributed to the intrinsic stability and the rigid skeleton of diazophenanthrone (**2**), to the steric demand of both ligands, and to the reduced basicity of the diazo carbon compared to diazo ester derivatives commonly used in cyclopropane synthesis.

Relevance to Copper-Catalyzed Cyclopropanation. The results presented here bear some relevant mechanistic implications for copper-catalyzed cyclopropanation. For the first time, a stable α-carbonyl diazoalkane complex of copper (**3**) has been synthesized. An equilibrium between a copper olefin complex and a copper diazoalkane complex via mutual associative ligand displacement has been directly observed (Scheme 1). The formation of structurally similar, but kinetically less stable, α-carbonyl diazoalkane complexes from diazo ester derivatives and other Cu(I) precatalysts via Cu(I) olefin complexes as catalyst resting states thus seems plausible. That such a preequilibrium exists[3,4] with cyclopropanation catalysts is reflected in retarded decomposition rates of diazo ester derivatives upon addition of, e.g., styrene (this is also observed with ethylene complex **1**). We do not expect a dissociative equilibrium of copper(I) olefin complexes with coordinatively unsaturated copper(I) species and free olefin to be essential for cyclopropanation reactions,[3] as we have observed only associative ligand exchange in $[tBu_2P(NSiMe_3)_2\text{-}\kappa^2N]Cu$ olefin complex chemistry.[13]

It is reasonable to assume that $\kappa O{:}\kappa N$-bound α-carbonyl diazoalkane copper complexes such as **3,** resulting

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[14] For model calculations on related degenerate rearrangements of d^8-ML_4 complexes with a P_2PtSn_2 core see: Obora, Y.; Tsuji, Y.; Nishiyama, K.; Ebihara, M.; Kawamura, T. *J. Am. Chem. Soc.* **1996**, *118*, 10922.

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from α-carbonyl diazoalkanes and typical copper(I) precatalysts, generally represent the initial intermediates of catalytic cyclopropanation and that N_2 extrusion occurs from these species. An intramolecular rate-determining dinitrogen loss from α-carbonyl diazoalkane copper complexes is also consistent with the rate law of dinitrogen evolution in copper-catalyzed cyclopropanation reactions.[3,4]

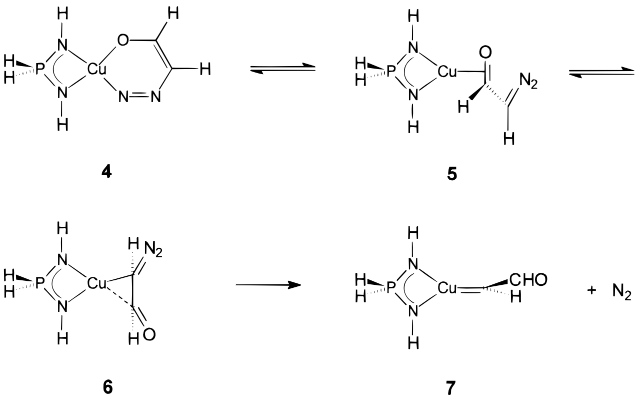
Not surprisingly, α-carbonyl diazoalkane complex **3** does not yield cyclopropanes upon treatment with e.g. the standard test olefin styrene, but an equilibrium analogous to that with ethylene (Scheme 1) is established between **3** and this olefin as well. If ethylene complex **1** and diazo esters instead of diazophenanthrone (**2**) are reacted with styrene, catalytic formation of cyclopropanes is observed. This indicates that the consecutive formation of another type of reactive intermediate, presumably copper(I) carbenes, generated by N_2 extrusion from initially formed κO:κN-bound α-carbonyl diazoalkane copper complexes, is a prerequisite for catalytic cyclopropanation activity—prevented in the case of **3** by appropriate ligand design and substrate choice.

Apart from copper(I) triflate,[4] chelating, strongly electron-donating nitrogen ligands are mandatory for highly active copper(I) catalysts.[2a,6,13,18] This type of ligand is suited for strengthening the back-bonding capabilities of copper(I), leading to stable olefin complexes,[13,19] which function as catalyst resting states.[6] Simultaneously, high oxidation states of copper as in **3** are stabilized by such ligands.

As to the pathway for N_2 elimination and copper carbene formation from κO:κN-bound α-diazo carbonyl complexes, we have performed DFT calculations for model complex **4** on the same level of theory as for the ligand rotation process and for the olefin displacement equilibrium, where the computed energies compare well with experiment. There is a low-energy rearrangement pathway from **4** to the less stable complex **5** (33.2 kJ mol^{-1} higher in energy) with a η^2-carbonyl-bound diazoalkane, which is a minimum on the energy surface. This structure is easily transformed into another intermediate **6** (59.1 kJ mol^{-1} above **4**), in which the copper fragment binds to the two carbons of the diazocarbonyl moiety. Dinitrogen extrusion from this species finally leads to the copper formyl carbene complex **7** (Scheme 2). The formation of structures analogous to model **6** by associative ligand exchange of the olefin complex resting state thus seems disfavored compared to the intramolecular rearrangement pathway via analogues of **4** and **5**. For synthetically more realistic α-carbonyl diazoalkane substrates and copper catalysts instead of model **6**, the direct associative formation of this penultimate precursor of N_2 extrusion will additionally suffer from steric hindrance, and structures such as **6** may even disappear as local minima.

As none of the local minima and transition states were found to exceed the energy of **4** by more than 82.0 kJ mol^{-1},[17] the computed overall activation barrier is in good agreement with the observed fast decomposition of sterically unhindered α-carbonyl diazoalkanes by ethylene complex **1**. The ability of carbonyl groups to coordinate to the copper center accounts at least in part for the particular efficiency of α-carbonyl diazoalkanes in copper-catalyzed cyclopropanation reactions of olefins.[2b] For strongly Lewis-acidic, cationic copper catalysts such as copper(I) triflate, a κ^1O-diazoalkane complex might well be an additional intermediate.

Scheme 2. Dinitrogen Extrusion Pathway[a] from Model Complex 4 to Carbene Complex 7



[a] The "nonclassical" structure **6** describes a η^2(C,C) coordination with a dominant diazo carbon copper interaction.

Conclusions

The existence of copper(III) α-carbonyl diazoalkane complexes, formed in an associative equilibrium from copper(I) olefin complexes and α-carbonyl diazoalkanes, has been established for the stabilized system **3**, resulting from diazophenanthrone (**2**) and the ethylene complex $[t\mathrm{Bu}_2\mathrm{P}(\mathrm{NSiMe}_3)_2\text{-}\kappa^2N]\mathrm{Cu}(\eta^2\text{-}\mathrm{C}_2\mathrm{H}_4)$ (**1**). The highly fluxional complex **3** can serve as a plausible model for primary intermediates in the copper-catalyzed cyclopropanation of electron-rich olefins. The high reactivity of α-carbonyl-substituted diazoalkanes in copper-catalyzed cyclopropanation is related to the ease of intramolecular dinitrogen extrusion from the diazoalkane complex with the σ- or π-coordinated carbonyl group playing a crucial role. Copper α-carbonyl carbenes have to be viewed as the active intermediates of the cyclopropanation step. Due to its ability to stabilize elusive copper coordination compounds, the $[t\mathrm{Bu}_2\mathrm{P}(\mathrm{NSiMe}_3)_2\text{-}\kappa^2N]\mathrm{Cu}$ fragment seems to be suited well to gain more insight into the chemistry of these species.[17]

Experimental Section

Computational Procedure. For the DFT calculations, the empirically parametrized B3LYP method[20a−c] within the Gaussian 98 package (revision A.5) was used.[20d] All geometry optimizations and frequency analyses were performed using the 6-31G(d) basis set (NIMAG = 0 for ground states and NIMAG = 1 for transition states). E[6-31G(d)]: **4**, −2 355.665 586 au; $\mathbf{4}^{\ddagger}$, −2 355.653 384 au. Single-point energies and NBO[20e] analyses were determined with the 6-311+G(2d,p) basis set. E[6-311+G(2d,p)]: **4**, −2 356.029 340 au; $\mathbf{4}^{\ddagger}$, −2 356.020 344 au. Zero-point corrections are included, based on the unscaled 6-31G(d) frequency analyses. Zero-point energy: **4**, 254.06 kJ mol^{-1}; $\mathbf{4}^{\ddagger}$, 250.08 kJ mol^{-1}.

Starting Materials. Synthesis and characterization of the ethylene complex **1** have been described in ref 13. Diazophenanthrone (**2**; mp 111 °C, IR (KBr, cm^{-1}) 2127 (s), 2087

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[17] Straub, B. F.; Hofmann, P. Manuscript in preparation.

[18] For example, the synthetically important bis(oxazoline)copper(I) triflates: Evans, D. A.; Woerpel, K. A.; Scott, M. J. *Angew. Chem.* **1992**, *104*, 439; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 430.

[19] Thompson, J. S.; Harlow, R. L.; Whitney, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3522.

(m), 1615 (m), 1602 (s) cm^{-1}) was prepared in analogy to ref 21 from phenanthroquinone and tosyl hydrazide. Solvents were dried with Na/$(C_6H_5)_2CO$ and freshly distilled prior to use.

Synthesis of [tBu$_2$P(NSiMe$_3$)$_2$-κ^2N]Cu[O(N$_2$)C$_2$(C$_{12}$H$_8$)-κO:κN] (3). Diazophenanthrone (**2**; 237 mg, 1.08 mmol) in 30 mL of toluene was added to 477 mg (1.16 mmol) of ethylene complex **1** in 20 mL of toluene under an atmosphere of argon. Toluene and ethylene were completely removed from the intensely brown solution at 10^{-3} mbar. The residue was recrystallized from 100 mL of pentane at −80 °C. Diazoalkane complex **3** (491 mg, 98% purity, 0.80 mmol, 74% yield) was isolated as a microcrystalline dark brown solid.

Mp: 146 °C dec (gas evolution). IR (KBr, cm^{-1}): ν 1700 (s, CN_2) cm^{-1}. Anal. Calcd for $C_{28}H_{44}N_4CuOPSi_2$: C, 55.74; H, 7.35; N, 9.29; P, 5.13. Found: C, 56.10; H, 7.42; N, 9.36; P, 4.94. ^1H NMR (300.13 MHz, [D$_8$]toluene, 25 °C): δ 8.78 (dd, ^3J(H,H) = 9 Hz, ^4J(H,H) = 1.5 Hz, 1H; CH-8), 8.09 (d, ^3J(H,H) = 7 Hz, 1H; CH-5), 8.07 (d, ^3J(H,H) = 7 Hz, 1H; CH-4), 7.83 (d, ^3J(H,H) = 8 Hz, 1H; CH-1), 7.35 (d pseudo-t, ^4J(H,H) = 1.5 Hz, H; CH-6), 7.31 (pseudo-t, H; CH-7), 7.26 (pseudo-t, 1H; CH-2), 7.17 (pseudo-t, 1H; CH-3), 1.36 (d, ^1J(C,H) = 125.2 Hz, ^3J(P,H) = 14.2 Hz, 18H; tBu), 0.43 (s, ^1J(C,H) = 116.4 Hz, 18H; SiMe$_3$). $^{13}C\{^1H\}$ NMR (125.76 MHz, [D$_8$]toluene, 25 °C): δ 146.25 (CO-9), 134.61, 130.80 (CH-6), 129.38, 129.02 (CH-8), 128.29 (CH-2), 126.80 (CH-7), 126.01, 125.86, 124.26 (CH-3), 123.72 (CH-1), 123.02 (CH-4), 122.93 (CH-5), 100.33 (CN_2-10), 37.50 (d, ^1J(C,P) = 63 Hz, ^1J(C,C) = 33.3 Hz; PCCH$_3$), 28.24 (d, ^2J(C,P) = 2 Hz, ^1J(C,C) = 33.3 Hz; PCCH$_3$), 5.90 (d+sat, ^1J(Si,C) = 57.5 Hz, ^3J(C,P) = 2 Hz; SiMe$_3$). $^{29}Si\{^1H\}$ NMR (99.36 MHz, [D$_8$]toluene, 25 °C): δ −10.7 (d+sat, ^1J(Si,C) = 57.5 Hz, ^2J(Si,P) = 10.6 Hz). $^{31}P\{^1H\}$ NMR (121.49 MHz, [D$_8$]toluene, 25 °C): δ 66.3 (s, ^2J(Si,P) = 10.6 Hz, ^1J(C,P) = 63 Hz). UV (pentane, nm): additional λ_{max} compared to **2**: ∼280, 413. LT-FAB:[22] m/z (%) 602.2 (16.3) [M$^+$], 325.1 (11.5) [LCu − SiMe$_2$ + H$^+$], 321.2 (32.3) [LH$_2^+$], 263.2 (100) [LH$_2^+$ − SiMe$_2$], 249.2 (10.7) [LH$_2^+$ − SiMe$_3$ + H].

Table 2. Crystallographic Data for [tBu$_2$P(NSiMe$_3$)$_2$-κ^2N]Cu[O(N$_2$)C$_2$(C$_{12}$H$_8$)-κO:κN]·O(N$_2$)C$_2$(C$_{12}$H$_8$) (3·2)

chem formula	$C_{42}H_{52}CuN_6O_2PSi_2$
fw	823.59
space group	$C2/c$
a, Å	56.4064(10)
b, Å	10.5976(1)
c, Å	14.0372(2)
β, deg	91.514(1)
V, Å^3	8388.1(2)
Z	8
T, K	200(2)
2θ range, deg	$4.0 < 2\theta < 55$
ρ_{calcd}, g cm^{-3}	1.304
μ(Mo Kα), cm^{-1}	6.59
no. of rflns collcd	42266
no. of unique rflns ($I > 2\sigma(I)$)	9633
no. of params	499
R1^a ($I > 2\sigma(I)$)	0.054
wR2^b ($I > 2\sigma(I)$)	0.095

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

X-ray Diffraction Analysis. Crystals of **3**, cocrystallized with **2** in a 1:1 ratio, suitable for X-ray diffraction analysis were obtained by slowly concentrating a saturated solution of diazophenanthrone (**2**) and diazoalkane copper complex **3** in pentane at 20 °C. The solution was directly obtained from a mixture of Li[tBu$_2$P(NSiMe$_3$)$_2$], CuBr·SMe$_2$, and excess diazoalkane **2** in pentane by filtration through Celite, complete removal of solvent, and redissolution in pentane. An empirical absorption correction was applied using SADABS[23] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL-PLUS (5.03) software package.[24] Crystallographic data are given in Table 2.

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Supporting Information Available: Tables of atomic coordinates, equivalent isotropic displacement parameters, anisotropic displacement parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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