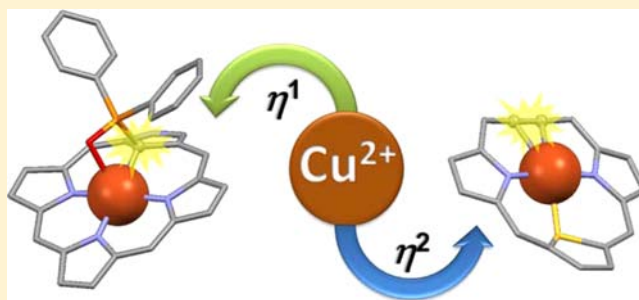# Copper(II) Thiaethyneporphyrin and Copper(II) 21-Phosphoryl N-confused Porphyrin Hybrids. Intramolecular Copper(II)−Carbon Interaction Inside of a Porphyrinoid Surrounding

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Ⓢ *Supporting Information*

ABSTRACT: Stabilization of unusual organocopper(II) species via the very efficient protection of the copper(II)−carbon bond has been achieved encapsulating the copper(II) center in the coordination core of suitably constructed carbaporphyrinoids. Copper(II) was inserted into hybrid N-confused porphyrins which contain 21-diphenylphosphoryl-, 21-diphenylthiophosphoryl-, or 21-phosphinodithioic substituents or into 20-thiaethyneporphyrin, an aromatic porphyrinoid, which combines two structural motifs of 21-thiaporphyrin and ethyne. Two distinctly different types of the copper(II)−carbon bond have been detected. Copper(II) hybrid N-confused porphyrins reveal the η^1-C(21) side-on coordination. The unprecedented equatorial metal(II)$\cdots\eta^2$-CC interaction has been trapped in a copper(II) thiaethyneporphyrin surrounding.

INTRODUCTION

A set of the organometallic derivatives formed by a combination of metal cations and appropriately tuned carbaporphyrinoids may serve as a perfect (chemically and structurally) environment to explore innovative organometallic chemistry in a "vessel" formed by porphyrin-like surrounding.[1−7] The remarkable structural flexibility of carbaporphyrinoids, including N-confused porphyrin, is reflected by formation of various coordination modes inside a macrocyclic frame, with or without formation of a direct metal−carbon bond.[7−22] Atypical oxidation states of metal ions trapped in the organometallic setting including extremely rare organocopper-(II) complexes have been identified.[14,19,23−30]

In fact, the organometallic chemistry of copper is nearly exclusively focused on the metal oxidation state +1.[31−35] Electron-rich organocopper(I) compounds are widely applied as useful reagents in numerous organic syntheses.[33,36] Transient organocopper(III) species were considered in the mechanism of a multiple bond activation via reactive π complexes.[37−41] The several stable organometallic complexes of copper(III) were characterized by X-ray crystallography.[29,42−46] Initially the transient σ-alkyl adducts of copper(II) were postulated to be formed in the reactions of copper(I) complexes with aliphatic radicals obtained by pulse-radiolysis techniques.[47] A detailed study covered the key mechanistic aspects of a mild C−H activation process conducted by a triazamacrocyclic copper(II) complex revealed an aromatic C−H bond in close proximity to the metal center.[48−53] Eventually organocopper(II) compounds were synthesized applying an efficient protection of the copper(II)−carbon bond in the coordination (CNNN) core of N-confused porphyrin,[25,54] N-confused calix[4]phyrin[55] and

subsequently O-confused porphyrin with a pendant pyrrole.[14] As a result of steric constraints imposed by the ligand geometry, the C(21) carbon creates two distinctly different types of the copper(II)−carbon(21) bonds. Specifically the equatorial macrocycle may act as an sp^2 σ-carbanion to coordinate to the copper in the η^1-fashion, but the coordinating C(21) carbon atom preserves trigonal geometry. The copper(II)−carbon(sp^2) bond was also found in the nitrogen-anchored N-heterocyclic carbene complexes.[56] It was also possible to stabilize the copper(II)−carbon(sp^3) bond by coordination of the tripoidal ligand tri(2-pyridylthio)methane (tptmH).[57,58] Recently we have demonstrated that the 21-diphenylphosphoryl-carbaporpholactone hybrid stabilized the organocopper(II) complex, revealing an unprecedented side-on coordination of copper-(II).[17]

Here we have focused on organocopper(II) chemistry of two, recently reported, types of carbaporphyrinoids. Thus the hybrid carbaporphyrins (**1−4**) have been formed in the course of regioselective phosphorylation or thiophosphorylation of N-confused carbaporphyrin (**1−4**). They combine features of N-confused porphyrin and covalently appended diphenylphosphoryl, 21-diphenylthiophosphoryl, or 21-phosphinodithioic units (Chart 1).[59] On the other hand 20-thiaethyneporphyrin **5** is an aromatic porphyrinoid that presents the essential features of [18]triphyrin(4.1.1) combining, however, two structural motifs of 21-thiaporphyrin[60] and ethyne.[15]

As a part of our continuing program aimed to explore organometallic chemistry of paramagnetic carbaporphyri-

Chart 1

Scheme 1. Insertion of Copper(II) to Hybrid N-confused Porphyrins[a]

[a]Conditions: Cu(OAc)$_2$, THF, N$_2$.
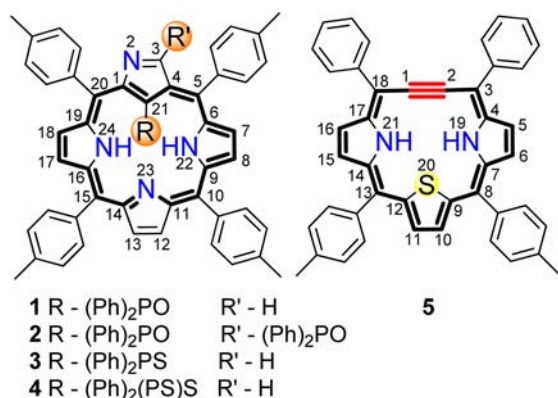
noids,[61] here we report on the synthesis and spectroscopic characterization of copper(II) complexes of these specific **1–5** carbaporphyrinoids. Copper(II) ions are expected to be suitably held via three pyrrolic nitrogens (**1–4**) or two pyrrolic nitrogens and one thiophenic sulfur atoms (**5**) in the T-like fashion. Consequently the inserted copper(II) cation will be conveniently exposed to interact with the C(21) carbon atom (**1–4**) or a conjugated four-carbon linker of porphyrinoid **5**. These studies explore specific macrocyclic factors of importance in the emerging field of copper(II) organometallic chemistry, affording an insight into intramolecular copper(II)-carbaporphyrinoid interactions.

■ RESULTS AND DISCUSSION

Formation and Characterization of Copper(II) Complexes. Copper(II) has been readily inserted into hybrid porphyrinoids **1–4** following the procedure reported previously for analogous derivatives of carbaporpholactone[17] to give copper(II) complexes in which the hybrid porphyrinoids act as dianionic ligands (Scheme 1).

Insertion of copper(II) cation was accompanied by a color change of the reaction mixture from green to red in case of **1-(Cu)**, **3-(Cu)**, **4-(Cu)** and from orange to green for **2-(Cu)**. Solutions of the copper(II) complexes are not reactive toward dioxygen for several hours. The UV–vis absorption spectra of copper(II) porphyrinoids demonstrate the similar patterns consisting of Soret band (slightly broadened for **3-(Cu)**) and two Q bands (Figure 1). The presence of copper(II) paramagnetic species was confirmed each time by electron paramagnetic resonance (EPR) spectroscopy (vide infra).

Analogously copper(II) has been inserted into thiaethyneporphyrin **5** to give the four coordinated complex of copper(II) thiaethyneporphyrin **5-(Cu)** (Scheme 2).

20-Thiaethyneporphyrin **5** acts as a dianionic ligand coordinating through the two nitrogen and one sulfur donor atoms. To complete the coordination sphere of the metal, interaction with the ethyne moiety is readily implied (vide infra). **5-(Cu)** is reactive toward dioxygen in solution. The process results eventually in the complete degradation of carbaporphyrinoid. Thus all manipulations including chromatography have been carried in anaerobic conditions. The identity of **5-(Cu)** was confirmed by high-resolution mass spectrometry.

The UV–vis absorption spectrum of **5-(Cu)** is presented in Figure 2. This complex has spectral characteristics that resemble that reported for **5-(Ni)**.[15] The small hypsochromic
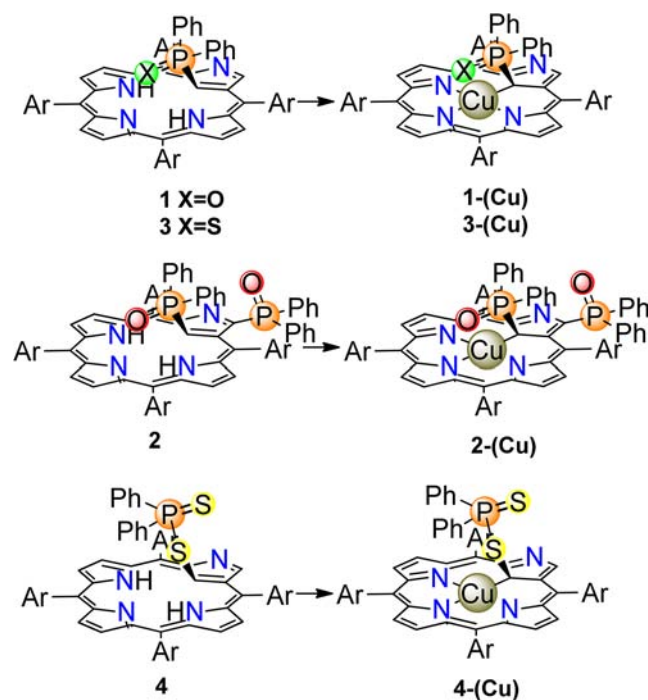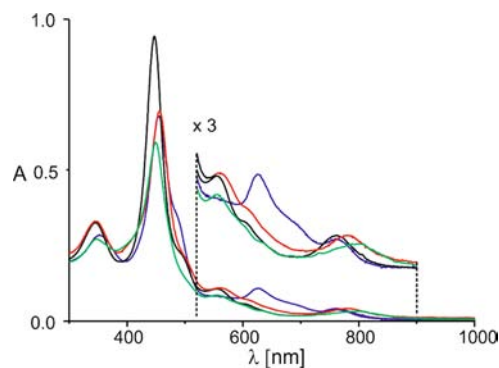

Figure 1. UV–vis absorption spectra (dichloromethane), **1-(Cu)** (black), **2-(Cu)** (blue), **3-(Cu)** (red), and **4-(Cu)** (green).

Scheme 2. Insertion of Copper(II) to Thiaethyneporphyrin 5[a]
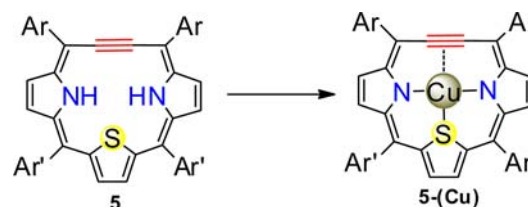
[a]Conditions: Cu(AcO)$_2$, THF, N$_2$.

shift of the Soret-like band has been determined for **5-(Cu)** with respect to free base **5**.

Molecular Structure of 1-(Cu). The coordinating about the copper(II) ion is square pyramidal (X-ray analysis), with the C(21), N(22), N(23), and N(24) atoms occupying the equatorial positions and the phosphine oxide oxygen atom in

Figure 2. UV−vis absorption spectra (dichloromethane) of **5** (black) and **5**-(**Cu**) (red).

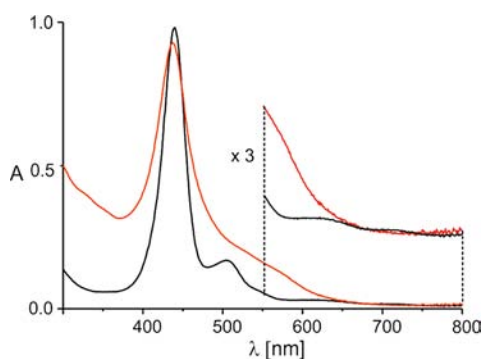the apical position. Actually, the appended diphenylphosphoryl arm creates a peculiar four-membered ring due to simultaneous coordination of C(21) and oxygen(PO) atoms. The Cu−C(21) bond length equals 2.154(3) Å which is significantly (0.078 Å) shorter than one observed for analogous copper(II) 21-carbaporpholactone (2.232(2) Å)[17] but longer once compared to copper(II) seen in N-confused calix[4]phyrin (2.007(4) Å),[55] copper(II) O-confused porphyrin with a pendant pyrrole ring (1.939(4) Å),[14] and copper(II) coordinated by the tripoidal ligand (2.001(8) Å).[57,58] The markedly longer distance has been determined for copper(II) and the inner carbon C(22) (2.698(5) Å) of copper(II) 22-chloro-*m*-benziporphyrin.[19] Importantly the C(21) atom of **1**-(**Cu**) approaches the copper(II) ion at a distance much shorter than the sum of van der Waals radii (3.1 Å) reflecting the formation of a weak bond.[62]

While the three pyrrole rings reside close to a $(C_{meso})_4$ plane, the N-confused pyrrole is sharply tipped out and the C(21)−P bond is almost perpendicular to the same plane. The P−C(21)−Cu bond angle equals 88.5(2)°. Such an architecture allows coordination to the copper(II) ion in an η^1-fashion through the C(21) carbon atom. The similar side-on coordination has been considered, based on spectroscopic evidence only, for copper(II) 2-aza-2-methyl-21-methyl-21-carbaporphyrin.[25] Thus the copper(II) lies significantly out of the plane of the N-confused pyrrole, with the angle between the N-confused pyrrole plane and the Cu^{II}−C(21) bond being 41.8° (Figure 3). To get a quantitative measure of the distortion from the idealized geometry around the C(21) coordination center, the sums of the bond angles have been analyzed (Σ = C(1)−C(21)−C(4) + C(1)−C(21)−C(P) + C(4)−C(21)−P). The comparison of experimental (Σ = 335.9°) and idealized tetrahedral (Σ = 328.5°) or trigonal (Σ = 360°) parameters reveals the marked degree of pyramidal distortion from the trigonal geometry expected for the ultimate side-on coordination. Insertion of copper(II) into **1** adjusted the geometry to accommodate the copper(II) as the trigonal geometry around C(21) is expected for the free macrocycle.

EPR Spectral analysis. The EPR spectra recorded for **1**-(**Cu**), **2**-(**Cu**), **3**-(**Cu**), **4**-(**Cu**), and **5**-(**Cu**) provided the conclusive evidence for the copper(II) oxidation state in all investigated complexes (Figure 4, Table 1). The values of **g** and **A** tensor components reveal the typical features diagnostic for the copper(II) electronic structure d^9: $(d_{xz})^2$, $(d_{yz})^2$, $(d_{xy})^2$, $(d_{z^2})^2$, $(d_{x^2-y^2})^1$ (Table 1). The observed values nicely correspond to those determined for already reported copper-(II) complexes of carbaporphyrinoids (Table 1) confirming the
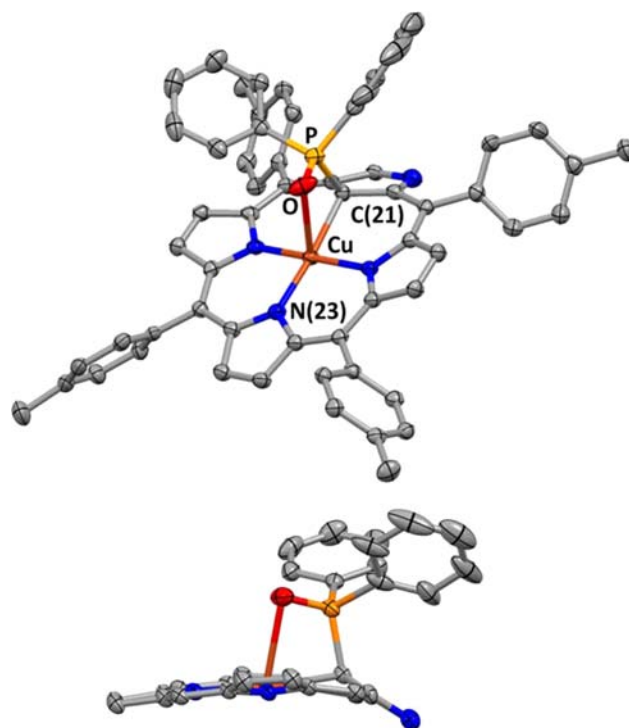

Figure 3. Molecular structure of **1**-(**Cu**) (top: perspective view, bottom: side view with aryl groups omitted for clarity). The thermal ellipsoids represent 50% probability.

square planar surrounding of the copper(II) ion with three nitrogen and one carbon donor atoms.[14,25] The isotropic ^{14}N EPR superhyperfine coupling patterns of **1**-(**Cu**), **2**-(**Cu**), **3**-(**Cu**), and **4**-(**Cu**) indicate a presence of three pyrrolic nitrogen donor atoms in the first coordination sphere, showing well resolved splitting into seven lines associated with the interaction of the electron with three nearly equivalent nitrogen atoms (Figure 4).

The distinct spectroscopic signature has been determined for copper(II) thiaethyneporphyrin **5**-(**Cu**). In particular the multiplicity of superhyperfine splitting (quintet) reflects the presence of two nitrogen donor atoms (Figure 4 E, F). In fact the smaller $A_{\parallel}^{Cu}$ as compared for instance to copper(II) N-confused porphyrins can be related to the number of nitrogen donor atoms in the first coordination sphere. Actually, similar values have been reported for derivatives of copper(II) dipyrromethenes where the coordination of two nitrogen donor atoms was firmly determined.[63] The axial coordination of tetrahydrofuran (THF) to **5**-(**Cu**) yielding **5**-(**Cu**)-**THF** (Scheme 3) is clearly detected by the significant modification of the EPR parameters.

DFT Studies. The principal geometries of copper(II) N-confused porphyrin hybrids (**1**-(**Cu**), **2**-(**Cu**), **3**-(**Cu**), **4**-(**Cu**)) and copper(II) thiaethyneporphyrin **5**-(**Cu**) were subjected to DFT optimizations at the B3LYP level of theory using the 6-31G** basis set. The final geometries are shown in Figures 5 and 6. In each case a genuine energy minimum was obtained. Significantly the DFT optimized structural parameters of **1**-(**Cu**) are essentially similar to those determined by X-ray crystallography (Table 2). In the previous report we have determined that the DFT optimization reproduced satisfactorily the X-ray molecular structure of nickel(II) and palladium(II) thiaethyneporphyrin.[15] These comparisons add credibility to
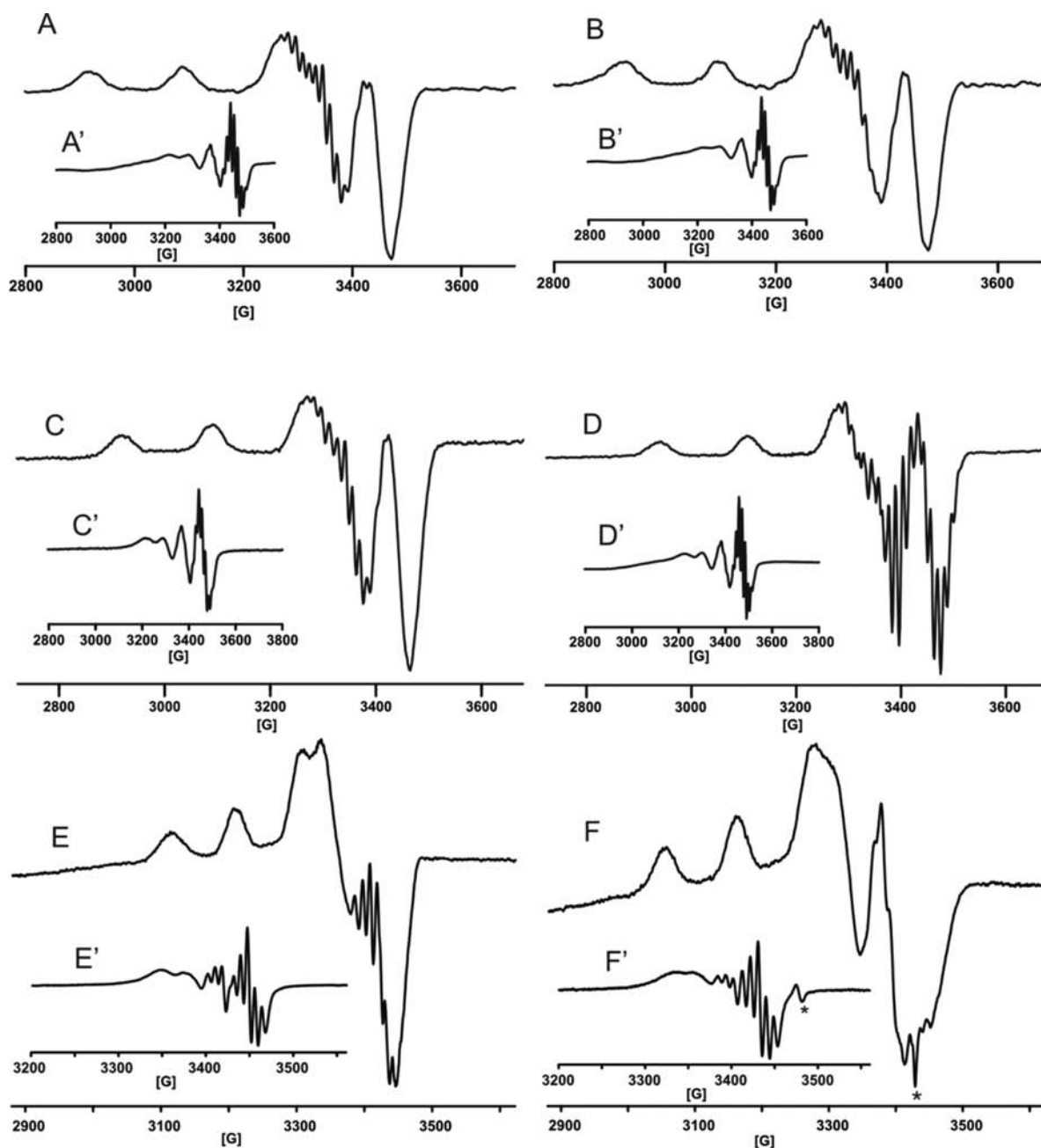
Figure 4. EPR spectra of **1-(Cu)** (A), **2-(Cu)** (B), **3-(Cu)** (C), **4-(Cu)** (D) (all at toluene/dichloromethane mixture 2/8 v/v, 77 K) and **5-(Cu)** (E) (toluene, 77 K), **5-(Cu)-THF** (F) (toluene/THF, 77 K). Insets A′, B′, C′, D′, E′, and F′ present the corresponding isotropic spectra collected at 298 K. Asterisks denote the signal of the quartz radical. Conditions: microwave frequency ν = 9.5749 GHz; microwave power 31.7 mW, modulation amplitude, 5.19 G; modulation frequency 100 kHz.

the geometry of the DFT optimized structure of **2-(Cu)**, **3-(Cu)**, **4-(Cu)** and in particular **5-(Cu)**.

In each copper(II) hybrid N-confused porphyrin case, the three pyrrole rings reside close to a $(C_{meso})_4$ plane, the N-confused pyrrole is sharply tipped out, and the C(21)−P bonds (**1-(Cu)**, **2-(Cu)**, **3-(Cu)**) or C(21)−S (**4-(Cu)**) are almost perpendicular to the same plane (Figure 5). Such an architecture allows coordination to the copper(II) ion in an η^1-fashion through the C(21) carbon atom.

The bond indices calculated for the Cu⋯C contact according to the Wiberg method[66] are comparable to Cu−N bond orders (Table 3). The significant increase of indices has been noted once 21-diphenylphosphoryl-carbaporpholactone **9-(Cu)** was

replaced by 21-diphenylphosphoryl-N-confused porphyrin **1-(Cu)**.

DFT optimized geometry of **5-(Cu)** (Figure 6) reflects the balance among constraints of the macrocycle ligand, the size of the copper(II) ion, and the predisposition of the copper(II) for square planar geometry. The bond length pattern of aromatic **5** is preserved in **5-(Cu)**. The most notable feature of **5-(Cu)** is the nature of the Cu(II)⋯C(1), Cu(II)⋯C(2), and Cu(II)−S(20) interactions. In fact the coordination mode detected for copper(II) thiaethyneporphyrin **5-(Cu)** does not have a precedent in the literature. In particular, the acetylene unit approaches copper(II) at distances much shorter (Cu⋯C(1) 2.346 Å, Cu⋯C(2) 2.346 Å) than the expected van der Waals

Table 1. Spin-Hamiltonian Parameters of Copper(II) Complexes of Carbaporphyrinoids

complex	$g_{\parallel}$	$g_{\perp}$	g_o	$A_{\parallel}{}^{Cu}$	$A_{\perp}{}^{Cu}$	$A_o{}^{Cu}$	$A_o{}^{N}$
1-(Cu)[a]	2.159	2.034	2.075	172.0	26.0	40.0	13.0
2-(Cu)[a]	2.153	2.033	2.073	172.0	27.5	39.0	12.0
3-(Cu)[a]	2.157	2.035	2.076	170.0	29.5	37.0	13.0
4-(Cu)[a]	2.144	2.032	2.069	169.0	28.0	75.0	12.0
5-(Cu)[b]	2.101	2.039	2.057	94.4	8	29	10
5-(Cu)-THF[c]	2.129	2.059	2.063	107.4	12	28.4	9
6-(Cu)[64]	2.190	2.045		211			
7-(Cu)[60,65]	2.212	2.051	2.141	159.5		70.0	
8-(Cu)[63]	2.272	2.062	2.130	108		56.2	9.8
9-(Cu)[17]	2.158	2.041	2.082	164.0	25.0	38.3	13.7
10-(Cu)[14]	2.134	2.029	2.073	154.0	29.0	30.0	21.6
11-(Cu)[25]	2.190	2.050	2.110	154	13	60	13
12-(Cu)[25]	2.139	2.057	2.070	143	37	23	18.3

[a]Frozen solution spectra taken at 77 K, isotropic recorded at 298 K. The solvent used: toluene/dichloromethane mixture (8/2 v/v). [b]Toluene. [c]Toluene/THF. Hyperfine constants are in 10^{-4} cm^{-1}; 6 porphyrin, 7 21-thiaporphyrin, 8 substituted dipyrromethenes, 9 21-diphenylphosphoryl-carbaporpholactone, 10 O-confused oxaporphyrin, 12 N-confused porphyrin, 12 C(21) deprotonated N-confused porphyrin.

Scheme 3. Coordination of THF to 5-(Cu)[a]
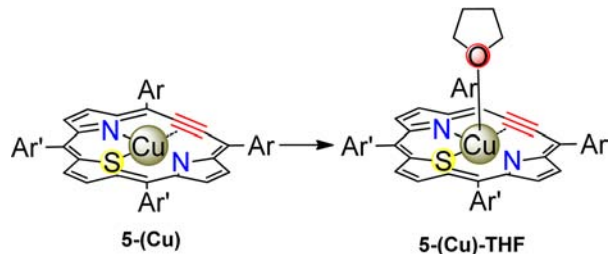
[a]Conditions: THF, N$_2$.

contact (Cu···C 3.1 Å).[62] Thus the copper(II) ion interacts with thiaethyneporphyrin in an η^2-fashion engaging the C(1) and C(2) carbon atoms. The C(18)−C(1)−C(2)−C(3) butyne moiety is slightly bent toward copper(II) as clearly reflected by the appropriate bond angles ($\angle$C(18)C(1)C(2) = $\angle$C(1)C(2)C(3) = 177.6°). The bond lengths C(1)−C(2) (1.254 Å) and C(2)−C(3)/C(18)−C(1) (1.372 Å) approach those detected in the free base 5.[15] While the thiophene ring is planar, it is sharply bent out of the plane of the porphyrin. The shape of the porphyrin resembles that seen in metal(II) complexes of 21-thiaporphyrins.[3,60,67,68] The dihedral angle between the thiophene plane and the CuN(19)N(21)C(1)-C(2) plane is 26.2°. This bending opens up the center of the porphyrin to accommodate the copper(II) and allows the copper(II) to interact with the thiophene sulfur in a side-on fashion. The angle between the center of thiophene and the Cu−S(20) bond is 126.5°. Similar angles are found in copper(II) 21-thiaporphyrin.[69] The Cu−S(20) distance, 2.177(1) Å, is clearly a bonding distance. Thus the thiophene is σ-bonded to copper(II) through sulfur which has pyramidal geometry.

The interaction involving the metal(II) and the ethyne fragment in 5-(Cu) is of special interest. Comparison of the Wiberg bond indices is helpful in discussing the copper(II)···η^2-C(1)C(2) interaction. The data gathered in Table 4 provide
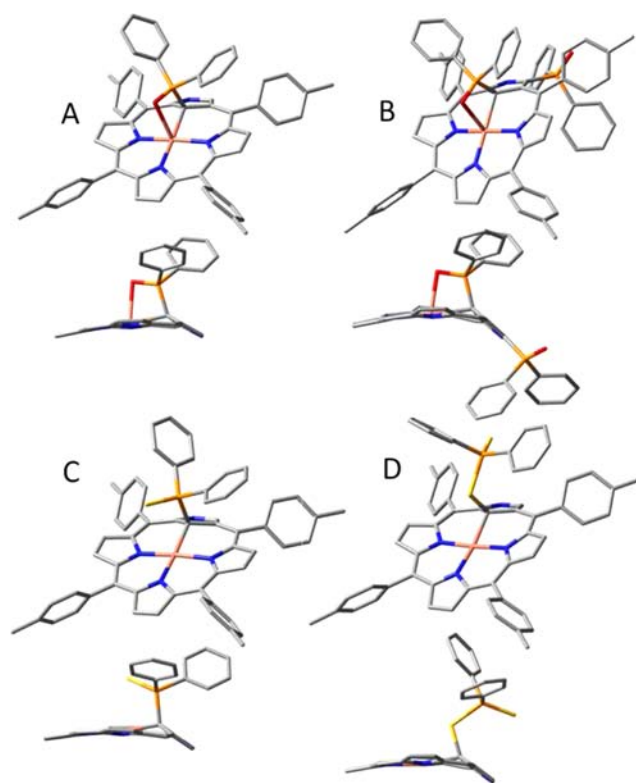

Figure 5. DFT (B3LYP/6-31G**) optimized geometries of (A) 1-(Cu), (B) 2-(Cu), (C) 3-(Cu), and (D) 4-(Cu). Side projections emphasize the conformations of the macrocycles. Outer hydrogen atoms and *meso*-substituents (bottom views) are omitted for clarity.
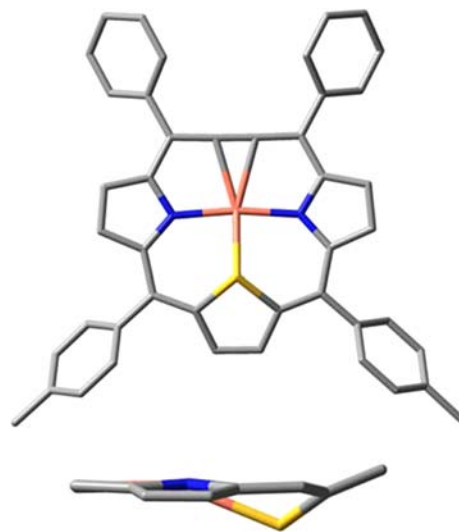
Figure 6. DFT (B3LYP/6-31G**) optimized geometry of 5-(Cu). Projections emphasize the conformations of the macrocycles. Outer hydrogen atoms and *meso*-substituents (bottom view) are omitted for clarity.

examples of typical coordination bonds Cu−N, M−S, and the metal(II)···η^2-C(1)C(2) itself. Evidently, the copper(II)···C(1) and copper(II)···C(2) interactions have significant bonding character albeit smaller than simultaneously coordinating nitrogen atoms and noticeably reduced in comparison with relevant previously studied 5-(Ni) and 5-(Pd).[15]

Conclusion. The present work offers the spectroscopic evidence for stabilization of unusual organocopper(II) species

Table 2. Structural Parameters Obtained from DFT Calculations

	bond length (Å)		bond angle (deg)		
compound	Cu−C(21)	Cu−X	Cu−C(21)−P	Cu−C(21)−P−X[a]	Σ
1-(Cu)	2.181	2.451[a]	86.2	17.5[a]	339.2[d]
1-(Cu)[c]	2.154(3)	2.547(2)	88.5	−22.9	335.9[d]
2-(Cu)	2.278	2.329[a]	84.0	−8.2[a]	345.9[d]
3-(Cu)	2.133	3.138[b]	95.1	−33.2[b]	332.3[d]
4-(Cu)	2.145	2.697[b]	85.2	166.6	332.7[e]

[a]X = O. [b]X = S. [c]X-ray data.,[17] [d]Σ = C(1)−C(21)−C(4) + C(1)−C(21)−P + C(4)−C(21)−P. [e]Σ = C(1)−C(21)−C(4) + C(1)−C(21)−S + C(4)−C(21)−S.

Table 3. Wiberg Bond Indices for Copper(II) Hybrid N-confused Porphyrin

compound	Cu−C(21)	Cu−N(22)	Cu−N(23)	Cu−N(24)	Cu−P	Cu−O	Cu−S
1-(Cu)	0.2548	0.3064	0.2941	0.3035	0.0553	0.1294	
2-(Cu)	0.2074	0.3152	0.2964	0.3069	0.0503	0.1513	
3-(Cu)	0.2721	0.2924	0.2786	0.2911	0.0527		
4-(Cu)	0.2668	0.3229	0.3172	0.3235			0.1293
9-(Cu)[17a]	0.1930	0.2110	0.1921	0.2070			

[a]**9-(Cu)** copper(II) 21-diphenylphosphoryl-carbaporpholactone.

Table 4. Wiberg Bond Indices for 20-Thiaethyneporphyrin Complexes

	complex			
bond	**5-(Cu)**	**5-(Ni)**[15]	**5-(Pd)**[15]	**5**[15]
M−C1	0.1036	0.1589	0.1649	
M−C2	0.1036	0.1589	0.1650	
M−N19	0.2973	0.3888	0.4700	
M−N21	0.2973	0.3888	0.4700	
M−S20	0.3490	0.5514	0.6329	
C18−C1	1.3809	1.3681	1.4201	1.4475
C1−C2	2.2005	2.1604	2.0097	2.2621
C2−C3	1.3809	1.3681	1.4201	1.4475

encapsulated in the coordination core of suitably constructed carbaporphyrinoids. As a result of steric constraints imposed by the ligand geometry, two distinctly different types of the copper(II)−carbon bond have been explored. Thus hybrid N-confused porphyrin containing diphenylphosphoryl, 21-diphenylthiophosphoryl, or 21-phosphinodithioic substituents reveal η^1-C(21) side-on coordination. In terms of characterization of intermediates involved in selective C−H(X) bond activation by copper under mild conditions, the molecular structure of **4** provides a structural model of the copper(II)-C-H(X) transient species.[19,50,51,53,70] Thiaethyneporphyrin-aromatic porphyrinoid, which combines two structural motifs of 21-thiaporphyrin and ethyne, affords a unique opportunity to detect unprecedented copper(II)$\cdots\eta^2$-CC interactions. In contrast alkene and alkyne coordinations to copper(I) center in an η^2-fashion have been well documented in the literature.[71−74] Significantly the CC unit is located in the plane defined by the remaining three donor atoms. Evidently carbaporphyrinoids provide a stimulating environment to explore specific issues of organometallic chemistry applying the macrocyclic platform concept as the suitable approach.

■ **EXPERIMENTAL SECTION**

Solvents and Reagents. Ethyl acetate and hexane were used without purification. CH_2Cl_2 was distilled over CaH_2. THF was distilled over sodium with benzophenone as oxygen presence indicator in argon atmosphere. $(AcO)_2Cu$ was used as received. Carbaporphyr-

inoids: 5,10,15,20-tetratolyl-2-aza-21-diphenylphosphoryl-21-carbaporphyrin[59] **1**; 5,10,15,20-tetratolyl-2-aza-3,21-bis(diphenylphosphoryl)-21-carbaporphyrin[59] **2**; 5,10,15,20-tetratolyl-2-aza-21-diphenylthiophosphoryl-21-carbaporphyrin[59] **3**; 5,10,15,20-tetratolyl-2-aza-21-carbaporphyrino-21-diphenylphosphinodithioate[59] **4**; and 3,18-diphenyl-8,13-di-*p*-tolyl-20-thiaethyneporphyrin[15] **5** were prepared by previously reported methods.

Copper(II) 5,10,15,20-Tetratolyl-2-aza-21-diphenylphosphoryl-21-carbaporphyrin 1-(Cu). A 11.4 mg portion (0.013 mmol) of **1** was dissolved in 25 mL of freshly distilled THF, and 12 mg (0.065 mmol) of $(AcO)_2Cu$ was added. The green reaction mixture immediately turned to brown-red. The mixture was stirred at 293 K for 1 h. Subsequently the solvent was removed, and the dry crude residue was dissolved in CH_2Cl_2 and filtered to remove copper(II) salts. Next, the solvent was removed, and the residue was chromatographed on basic alumina G(IV) column. The strong red fraction eluted with dichloromethane was collected and recrystallized from dichloromethane/*n*-hexane to give **1-(Cu)** (9 mg of red amorphous solid). Yield: 75%. **UV−vis** (CH_2Cl_2, λ_{max} [nm], log ε): 346 (4.51), 447 (4.97), 554 (4.03), 761 (3.62). **HR-MS** (ESI+, FT-MS): m/z [M+H]$^+$ 932.2727, calcd for $C_{60}H_{46}CuN_4OP^+$ 932.2700.

Copper(II) 5,10,15,20-Tetratolyl-2-aza-3,21-bis-(diphenylphosphoryl)-21-carbaporphyrin 2-(Cu). A 8.2 mg portion (0.008 mmol) of **2** was dissolved in 25 mL of freshly distilled THF, and 10 mg (0.04 mmol) of $(AcO)_2Cu$ was added. The red-orange reaction mixture turned slowly green. The mixture was stirred at 293 K for 1 h. Subsequently the solvent was removed, and the dry crude residue was dissolved in dichloromethane and filtered to remove copper(II) salts. Next the solvent was removed, and the residue was chromatographed on a basic alumina G(IV) column. The strong green fraction eluted with ethyl acetate was collected and recrystallized from dichloromethane/*n*-hexane to give **2-(Cu)** (7.5 mg of red amorphous solid). **Yield**: 85%. **UV−vis** (CH_2Cl_2, λ_{max} [nm], log ε): 352 (4.46), 454 (4.83), 628 (4.03), 762 (3.59). **HR-MS** (ESI+, FT-MS): m/z [M+H]$^+$ 1132.3060, calcd for $C_{72}H_{55}CuN_4O_2P_2^+$ 1132.3091.

Copper(II) 5,10,15,20-Tetratolyl-2-aza-21-diphenylthiophosphoryl-21-carbaporphyrin 3-(Cu). Nine milligrams (0.010 mmol) of **3** was dissolved in 25 mL of freshly distilled THF, and 10 mg (0.05 mmol) of $(AcO)_2Cu$ was added. The green reaction mixture turned slowly brown-red. The mixture was stirred at 293 K for 1 h. Subsequently the solvent was removed, and the dry crude residue was dissolved in dichloromethane and filtered to remove copper(II) salts. Next the solvent was removed, and the residue was chromatographed on basic alumina G(IV) column. The strong red fraction eluted with dichloromethane/ethyl acetate (v/v 9/1) was collected and recrystallized from dichloromethane/*n*-hexane to give **3-(Cu)** (8 mg of red

amorphous solid). **Yield**: 85%. **UV−vis** (CH$_2$Cl$_2$, λ_{max} [nm], log ε): 344 (4.52), 456 (4.84), 560 (4.04), 780 (3.62). **HR-MS** (ESI+, FT-MS): m/z [M+H]$^+$ 948.2463, calcd for C$_{60}$H$_{46}$CuN$_4$PS$^+$ 948.2471.

Copper(II) 5,10,15,20-Tetratolyl-2-aza-21-carbaporphyrino-21-diphenylphosphino-dithioate 4-(Cu). Seven milligrams (0.008 mmol) of **4** was dissolved in 25 mL of freshly distilled THF, and 8 mg (0.04 mmol) of (AcO)$_2$Cu was added. The green reaction mixture turned slowly brown-red. The mixture was stirred at 293 K for 1 h. Subsequently the solvent was removed, and the dry crude residue was dissolved in dichloromethane and filtered to remove copper(II) salts. Next the solvent was removed, and the residue was chromatographed on basic alumina G(IV) column. The strong brown fraction (red in solution) eluted with dichloromethane was collected and recrystallized from dichloromethane/n-hexane to give **4-(Cu)** (8 mg of red amorphous solid). **Yield**: 95%. **UV−vis** (CH$_2$Cl$_2$, λ_{max} [nm], log ε): 347 (4.43), 449 (4.77), 555 (3.94), 805 (3.51). **HR-MS** (ESI+, FT-MS): m/z [M+H]$^+$ 980.2162, calcd for C$_{60}$H$_{46}$CuN$_4$PS$_2$$^+$ 980.2192.

Copper(II) 3,18-Diphenyl-8,13-di-p-tolyl-20-thiaethyneporphyrin 5-(Cu). Copper(II) insertion and chromatography were carried in the inert atmosphere of the MBraun glovebox using degassed solvents. Ten milligrams (0.016 mmol) of **5** was dissolved in 10 mL of THF, and 32 mg (0.16 mmol) of (AcO)$_2$Cu was added. Reaction mixture slowly turned from orange to brown-red. The mixture was stirred at 229 K for 3 h. Subsequently the solvent was removed under vacuum, and the dry crude residue was chromatographed on silica gel. The first light-brown fraction eluted with dichloromethane contained **5-(Cu)**. The second fraction eluted with dichloromethane/THF (9:1, v/v) yielded the mixture of **5-(Cu)** and its THF adduct as confirmed by EPR. Yield of **5-(Cu)**: 20%. **UV−vis** (CH$_2$Cl$_2$, λ_{max} [nm]): 437. **HR-MS** (ESI+, TOF-MS): m/z M$^{\bullet+}$ 681.1424, calcd for [C$_{44}$H$_{30}$N$_2$SCu]$^{\bullet+}$ 681.1420.

Instrumentation. EPR spectra were recorded on the Brüker ESP 300 spectrometer operating with an X-band equipped with an ER 035 Gmeter and a HP 53550B microwave frequency counter. The X-band EPR spectra were analyzed using the SimFonia software (Brüker). Absorption spectra were recorded on a Varian Carry-50 Bio spectrophotometer. Mass spectra (High Resolution and Accurate Mass) were recorded using the electrospray technique.

Crystallography. X-ray quality crystals of **1-(Cu)** were prepared by diffusion of hexane into a dichloromethane solution contained in a tube stored in a room temperature. Data were collected at 100 K on an PX-k geometry diffractometer, with Mo Kα radiation (λ = 0.71073). Data were corrected for Lorentz and polarization effects. Crystal data are compiled in Supporting Information, Table S1. The structure was solved by a heavy metal method with the Dirdif software[75] and refined by full-matrix least-squares method by using SHELXL-97 with anisotropic thermal parameters for the non-H atoms. Scattering factors were those incorporated in SHELXS-97.[76,77] Hydrogen atoms were introduced with HFIX command. The SQUEEZE procedure was used with PLATON to remove disordered hexane molecules. Additional details are included in the Supporting Information, CIF files.

DFT Calculations. Geometry optimizations were carried out within unconstrained C_1 symmetry, with starting coordinates derived from molecular mechanics calculations.[78] Becke's three-parameter exchange functional with the gradient-corrected correlation formula of Lee, Yang, and Parr (DFT-B3LYP) was used with the 6-31G** basis set.[79,80] Harmonic vibrational frequencies were calculated using analytical second derivatives. The structure was found to have converged to a minimum on the potential energy surface. The resulting zero-point vibrational energies were included in the calculation of relative energies. The analysis of Wiberg's bond indices was performed for the final geometry using NBO.3.0 software.[81]

ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of computational results (Cartesian coordinates); table of crystal data (cif file), mass spectrometry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Pawlicki, M.; Latos-Grażyński, L. Carbaporphyrinoids - Synthesis and Coordination Properties. In *Handbook of Porphyrin Science: with Applications to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; World Scientific Publishing: Singapore, 2010; pp 104−192.

(2) Chmielewski, P. J.; Latos-Grażyński, L. *Coord. Chem. Rev.* **2005**, *249*, 2510−2533.

(3) Latos-Grażyński, L. Core Modified Heteroanalogues of Porphyrins and Metalloporphyrins. In *The Porphyrin Handbook*, Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; pp 361−416.

(4) Toganoh, M.; Furuta, H. Synthesis and Metal Coordinationof N-Fused and N-confused Porphyrinoids. In *Handbook of Porphyrin Science: with Applications to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine*, Kadish, K. M., Smith, K. M., Guilard, R., Eds.; World Scientific Publishing: Singapore, 2010; pp 295−367.

(5) Toganoh, M.; Furuta, H. *Chem. Commun.* **2011**, *48*, 937−954.

(6) Harvey, J. D.; Ziegler, C. J. *Coord. Chem. Rev.* **2003**, *247*, 1−19.

(7) Stępień, M.; Latos-Grażyński, L. *Acc. Chem. Res.* **2005**, *38*, 88−98.

(8) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Głowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779−781.

(9) Chmielewski, P. J.; Latos-Grażyński, L.; Głowiak, T. *J. Am. Chem. Soc.* **1996**, *118*, 5690−5701.

(10) Stępień, M.; Latos-Grażyński, L. *Chem.—Eur. J.* **2001**, *7*, 5113−5117.

(11) Stępień, M.; Latos-Grażyński, L.; Szterenberg, L.; Panek, J.; Latajka, Z. *J. Am. Chem. Soc.* **2004**, *126*, 4566−4580.

(12) Pawlicki, M.; Latos-Grażyński, L. *J. Org. Chem.* **2005**, *70*, 9123−9130.

(13) Pawlicki, M.; Latos-Grażyński, L.; Szterenberg, L. *Inorg. Chem.* **2005**, *44*, 9779−9786.

(14) Pawlicki, M.; Kańska, I.; Latos-Grażyński, L. *Inorg. Chem.* **2007**, *46*, 6575−6584.

(15) Nojman, E.; Berlicka, A.; Szterenberg, L.; Latos-Grażyński, L. *Inorg. Chem.* **2012**, *51*, 3247−3260.

(16) Szyszko, B.; Latos-Grażyński, L.; Szterenberg, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 6587−6591.

(17) Grzegorzek, N.; Pawlicki, M.; Szterenberg, L.; Latos-Grażyński, L. *J. Am. Chem. Soc.* **2009**, *131*, 7224−7225.

(18) Pacholska-Dudziak, E.; Skonieczny, J.; Pawlicki, M.; Szterenberg, L.; Ciunik, Z.; Latos-Grażyński, L. *J. Am. Chem. Soc.* **2008**, *130*, 6182−6195.

(19) Hung, C. H.; Chang, F. C.; Lin, C. Y.; Rachlewicz, K.; Stępień, M.; Latos-Grażyński, L.; Lee, G. H.; Peng, S. M. *Inorg. Chem.* **2004**, *43*, 4118−4120.

(20) Furuta, H.; Morimoto, T.; Osuka, A. *Inorg. Chem.* **2004**, *43*, 1618−1624.

(21) Lash, T. D.; Colby, D. A.; Graham, S. R.; Ferrence, G. M.; Szczepura, L. F. *Inorg. Chem.* **2003**, *42*, 7326−7338.

(22) Lash, T. D.; Rasmussen, J. M.; Bergman, K. M.; Colby, D. A. *Org. Lett.* **2004**, *6*, 549−552.

(23) Chmielewski, P. J.; Latos-Grażyński, L. *Inorg. Chem.* **1997**, *36*, 840−845.

(24) Chmielewski, P. J.; Latos-Grażyński, L. *Inorg. Chem.* **2000**, *39*, 5639−5647.

(25) Chmielewski, P. J.; Latos-Grażyński, L.; Schmidt, I. *Inorg. Chem.* **2000**, *39*, 5475−5482.

(26) Rachlewicz, K.; Wang, S. L.; Ko, J. L.; Hung, C. H.; Latos-Grażyński, L. *J. Am. Chem. Soc.* **2004**, *126*, 4420−4431.

(27) Bohle, D. S.; Chen, W. C.; Hung, C. H. *Inorg. Chem.* **2002**, *41*, 3334−3336.

(28) Furuta, H.; Ogawa, T.; Uwatoko, Y.; Araki, K. *Inorg. Chem.* **1999**, *38*, 2676−2682.

(29) Maeda, H.; Ishikawa, Y.; Matsuda, T.; Osuka, A.; Furuta, H. *J. Am. Chem. Soc.* **2003**, *125*, 11822−11823.

(30) Lash, T. D.; Colby, D. A.; Lisa, F. S. *Inorg. Chem.* **2004**, *43*, 5258−5267.

(31) Casitas, A.; King, A. E.; Parella, T.; Costas, M.; Stahl, S. S.; Ribas, X. *Chem. Sci.* **2010**, *1*, 326−330.

(32) van Koten, G. *Organometallics* 2012, **2012**, *31*, 7634−7646.

(33) The Chemistry of Organocopper Compounds . In *The Chemistry of Functional Groups*, Rappaport, Z., Ilan, M., Eds.; Wiley: Chichester, U.K., 2009.

(34) *Modern Organocopper Chemistry*; Krause, N., Ed.; Wiley-VCH: New York, 2002.

(35) Sperotto, E.; van Klink, G. P.; van Koten, G.; de Vries, J. G. *Dalton Trans.* **2010**, *39*, 10338−10351.

(36) *Organocopper reagents*; Taylor, R. J. K., Ed.; Oxford University Press: New York, 1994.

(37) Chounan, Y.; Ibuka, T.; Yamamoto, Y. *Chem. Commun.* **1994**, 2003−2004.

(38) Fernández de la Pradilla, R.; Rubio, M. B.; Marino, J. P.; Viso, A. *Tetrahedron Lett.* **1992**, *33*, 4985−4988.

(39) Nakamura, E.; Mori, S.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 4900−4910.

(40) Krause, N.; Gerold, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 186−204.

(41) Nakamura, E.; Mori, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3750−3771.

(42) Furuta, H.; Maeda, H.; Osuka, A. *J. Am. Chem. Soc.* **2000**, *122*, 803−807.

(43) Maeda, H.; Osuka, A.; Furuta, H. *J. Am. Chem. Soc.* **2003**, *125*, 15690−15691.

(44) Willert-Porada, M. A.; Burton, D. J.; Baenzinger, N. C. *Chem. Commun.* **1989**, 1633−1634.

(45) Neumann, D.; Roy, T.; Tebbe, K.-F.; Crump, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1482−1483.

(46) Eujen, H.; Hoge, B.; Brauer, D. J. *J. Organomet. Chem.* **1996**, *519*, 7−20.

(47) Navon, N.; Golub, G.; Cohen, H.; Meyerstein, D. *Organometallics* **1995**, *14*, 5670−5676.

(48) Casitas, A.; Canta, M.; Sola, M.; Costas, M.; Ribas, X. *J. Am. Chem. Soc.* **2011**, *133*, 19386−19392.

(49) King, A. E.; Huffman, L. M.; Casitas, A.; Costas, M.; Ribas, X.; Stahl, S. S. *J. Am. Chem. Soc.* **2010**, *132*, 12068−12073.

(50) Ribas, X.; Jackson, D. A.; Donnadieu, B.; Mahia, J.; Parella, T.; Xifra, R.; Hedman, B.; Hodgson, K. O.; Llobet, A.; Stack, T. D. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2991−2994.

(51) Ribas, X.; Calle, C.; Poater, A.; Casitas, A.; Gomez, L.; Xifra, R.; Parella, T.; Benet-Buchholz, J.; Schweiger, A.; Mitrikas, G.; Sola, M.; Llobet, A.; Stack, T. *J. Am. Chem. Soc.* **2010**, *132*, 12299−12306.

(52) Xifra, R.; Ribas, X.; Llobet, A.; Poater, A.; Duran, M.; Sola, M.; Stack, T. D. P.; Benet-Buchholz, J.; Donnadieu, B.; Mahia, J.; Parella, T. *Chem.—Eur. J.* **2005**, *11*, 5146−5156.

(53) Campbell, A. N.; Stahl, S. S. *Acc. Chem. Res.* **2012**, *45*, 851−863.

(54) Furuta, H.; Maeda, H.; Osuka, A. *Org. Lett.* **2002**, *4*, 181−184.

(55) Furuta, H.; Ishizuka, T.; Osuka, A.; Uwatoko, Y.; Ishikawa, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 2323−2325.

(56) Hu, X. L.; Castro-Rodriguez, I.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 12237−12245.

(57) Santo, R.; Miyamoto, R.; Tanaka, R.; Nishioka, T.; Sato, K.; Toyota, K.; Obata, M.; Yano, S.; Kinoshita, I.; Ichimura, A.; Takui, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 7611−7614.

(58) Kinoshita, I.; Wright, L. J.; Kubo, S.; Kimura, K.; Sakata, A.; Yano, T.; Miyamoto, R.; Nishioka, T.; Isobe, K. *Dalton Trans.* **2003**, *2003*, 1993−2003.

(59) Grzegorzek, N.; Latos-Grażyński, L.; Szterenberg, L. *Org. Biomol. Chem.* **2012**, *10*, 8064−8075.

(60) Latos-Grażyński, L.; Lisowski, J.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 4428−4429.

(61) Pacholska-Dudziak, E.; Latos-Grażyński, L. *Eur. J. Inorg. Chem.* **2007**, 2594−2608.

(62) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(63) Murakami, Y.; Matsuda, Y.; Sakata, K. *Inorg. Chem.* **1971**, *10*, 1734−1738.

(64) Manaboran, P. T.; Roger, M. T. *Electron Spin Resonance of Metal Complexes*; Ye, T. W., Ed.; Plenum: New York, 1969.

(65) Lisowski, J.; Grzeszczuk, M.; Latos-Grażyński, L. *Inorg. Chim. Acta* **1989**, *161*, 153−163.

(66) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083−1096.

(67) Latos-Grażyński, L.; Lisowski, J.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1989**, *28*, 1183−1188.

(68) Latos-Grażyński, L.; Lisowski, J.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1989**, *28*, 3328−3331.

(69) Latos-Grażyński, L.; Lisowski, J.; Chmielewski, P. J.; Grzeszczuk, M.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1994**, *33*, 192−197.

(70) Ribas, X.; Xifra, R.; Parella, T.; Poater, A.; Sola, M.; Llobet, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 2941−2944.

(71) Chen, T. Y.; Vaissermann, J.; Doppelt, P. *Inorg. Chem.* **2001**, *40*, 6167−6171.

(72) Dias, H. R.; Richey, S. A.; Diyabalanage, H. V. K.; Thankamani, J. J. *Organomet. Chem.* **2005**, *690*, 1913−1922.

(73) Bellott, B. J.; Girolami, G. S. *Organometallics* **2009**, *28*, 2046−2052.

(74) Allen, J. J.; Barron, A. R. *Dalton Trans.* **2011**, *40*, 1189−1194.

(75) *The DIRDIF-99 program system, C*; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands.: 1999.

(76) *SHELXL97 - Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(77) *SHELXS97 - Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

(78) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

(79) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(80) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(81) *The NBO3.0 program*; University of Winsconsin: Madison, WI, 1996.