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Organocopper(II) Complex of 21-Diphenylphosphoryl-Carbaporpholactone Hybrid: A Side-On Coordination Mode of Copper(II)

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Organocopper(II) complexes are extremely rare,[1,2] which remains in contrast to the rich organometallic chemistry of copper(I) and copper(III).[1f,2a−d] Originally such organometallic compounds were synthesized applying an efficient macrocyclic protection of the copper(II)−carbon bond in the dianionic (CNNN) coordination core of N-confused porphyrin and analogues,[1] where the equatorial macrocycle contains an sp^2 σ-carbanion unit. The copper(II)−carbon(sp^2) bond was also found in the nitrogen-anchored N-heterocyclic carbene complexes.[2] It was also possible to stabilize the copper(II)−carbon(sp^3) bond by coordination of a tripoidal ligand tri(2-pyridylthio)methane (tptmH).[3]

Here we report on the synthesis and structural characterization of the 21-diphenylphosphoryl-carbaporpholactone **1** and its copper(II) complex. This represents the first thorough structural characterization of such a hybrid system. The structure of the copper(II) complex is of particular interest because of the limited ability of copper(II) to form organometallic compounds, the geometric constraints imposed by the macrocycle and the variety of modes (C-bound; O-bound; C,O-bound) available for copper(II)/21-diphenylphosphoryl-furanone coordination.

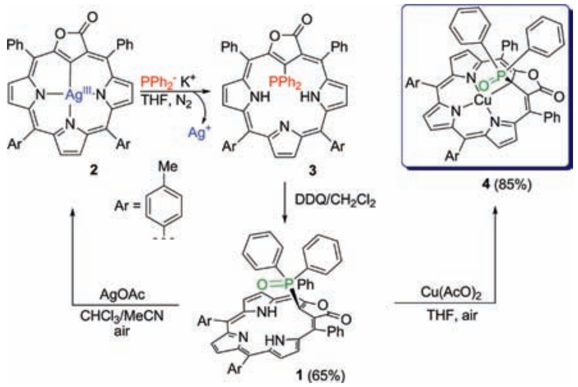
2 was treated with potassium diphenylphosphide. The solution color changed from red to green reflecting a formation of two carbaporpholactone derivatives with diphenylphosphanyl (**3**) or diphenylphosphoryl (**1**) moieties attached at the C(21) position (Scheme 1). The oxidation of the reaction mixture with DDQ followed by chromatography on basic alumina gave exclusively **1**.

A regioselective mechanism of phosphanylation can be suggested where the silver(III) species undergoes reversible axial coordination of diphenylphosphide followed by a reductive elimination of two anionic ligands (diphenylphosphanide and deprotonated furanone) already in the required *cis* orientation, to yield **3** with silver(I) removal. The presence of oxidizing agents in the reaction mixture forces the subsequent partial transformation of **3** into **1**. An insertion of silver(I) into **1** produces silver(III) carbaporpholactone **2** (a reverse process).

1 adopts a saddle conformation in the solid state (Figure 1). The C(21)−P bond lies near the furanone plane with the angles between this plane and the corresponding bonds of 27°. The tilted position of furanone and some bending of the C−P bond from its plane allow locating the 21-diphenylphosphoryl unit above the macrocylic plane and accommodating the ruffled geometry presented in Figure 1.

The reaction of copper(II) acetate and **1** under mild conditions resulted in the formation of copper(II) 21-diphenylphosphorylcarbaporpholactone **4**. The EPR spectrum recorded for **4** reveals typical features diagnostic for the copper(II) electronic structure ($g_{\|} = 2.158$, $g_{\perp} = 2.041$, $g_o = 2.082$, $-A_{\|}^{Cu} = 164$, $-A_{\perp}^{Cu} = 25$, $-A_o^{Cu} = 65.9$, $-A_o^{N} = 13.7$) resembling copper(II) N-confused porphyrin derivatives.[1a,f] The superhyperfine coupling pattern indicates a presence of three pyrrolic nitrogen donors in the first coordination sphere.

Scheme 1. Synthesis of 21-Diphenylphosphorylcarbaporpholactone



The cyclic voltammetry experiment demonstrated the half-wave potentials for four one-electron processes of **4**: two reductions (1) −943 and (2) −1997 and two oxidations (3) 155 and (4) 900 (in mV vs Fc/Fc$^+$). Consequently, the first reduction and the first oxidation absent in the cyclic voltammogram of **1** correspond to Cu^{II}/Cu^{I} and Cu^{II}/Cu^{III} metal-centered processes.

The coordinating environment of copper(II) forms a square-pyramid (X-ray analysis, Figure 3) with the equatorial positions occupied by the cavity donors (C(21), N(22), N(23), N(24)) and apically located oxygen atom. Actually, the appended diphenylphosphoryl arm allows forming a peculiar four-membered ring due to coordination of carbon and oxygen atoms. The Cu−C(21) bond length equals 2.232(2) Å and is evidently longer than that reported for copper(II) N-confused calix[4]phyrin (2.007(4) Å),[1b] copper(II) O-confused porphyrin with a pendant pyrrole ring (1.939(4) Å),[1f] and copper(II) coordinated by tripoidal ligand (2.001(8) Å)[2] but shorter than the distance between copper(II) and the inner carbon C(22) (2.698(5) Å) of copper(II) 22-chloro-*m*-benziporphyrin.[5] Importantly the C(21) atom of **4** 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.[4]

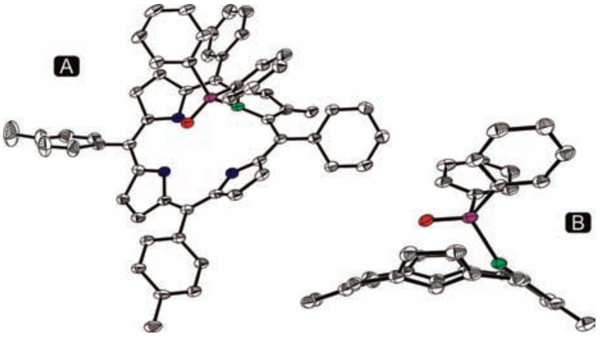


Figure 1. Crystal structure of **1** (30% thermal ellipsoids). A perspective (A) and a side (B, aryl groups omitted for clarity) view.

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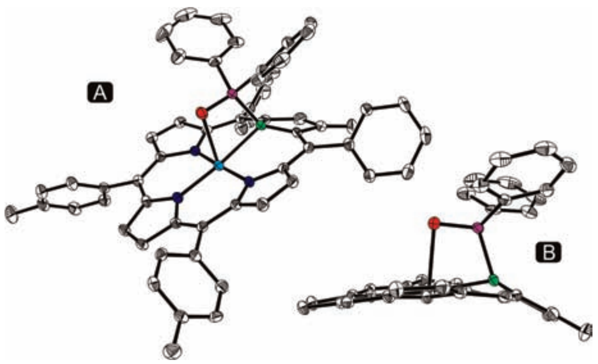

Figure 2. Crystal structure of **4** (50% thermal ellipsoids). A perspective (A) and a side (B, aryl groups omitted for clarity) view.

Coordination of copper(II) modifies slightly the conformation of carbaporpholactone preserving a saddle-like arrangement of five-membered rings. While the three pyrrole rings reside close to a $(C_{meso})_4$ plane, the furanone is sharply tipped out and C(21)−P is almost perpendicular to the same plane. 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.[1a]

Thus the copper(II) lays out of the furanone, with the angle between the furanone plane and the $Cu^{II}-C(21)$ bond being 28.5° (Figure 2). To get a quantitative measure of the distortion from the idealized geometry around C(21) coordination center, the sums of the bond angles have been analyzed ($\Sigma = C(1)-C(21)-C(4) + C(1)-C(21)-C(P) + C(4)-C(21)-P$). The comparison of experimental ($\Sigma = 342.2°$) and idealized tetrahedral ($\Sigma = 328.5°$) or trigonal ($\Sigma = 360°$) parameters reveals the marked degree of pyramidal distortion from the trigonal geometry expected for the pure side-on coordination. Insertion of copper(II) into **1** adjusted the geometry to accommodate the copper(II), as the trigonal geometry around C(21) has been determined for the free macrocycle ($\Sigma = 356.5°$). The situation bears some distant resemblance, as far as bond lengths and coordination geometry around a specific donor are concerned, to five-coordinate N-methylated porphyrin complexes of the metals of the first transition row. There, the N-methylated nitrogen−metal bonds fall in the range 2.257(5)−2.530(7) Å when the other regular M−N distances are markedly shorter.[7]

The DFT-optimized structure (UB3LYP/6-31G**) of **4** is very similar to the X-ray geometry. Significantly, the calculated bond lengths of the copper(II) closely resemble those determined by the X-ray studies. Application of the atoms in molecules (AIM)[8a,b] theory allows deriving chemically relevant information from the topology of the electron density in **4**. Figure 3 shows the bond (BCPs) and ring (RCPs) critical points in the central part of the structure. The observed bond critical point indicates the bonding pathway for Cu(II)···C(21). The values characterizing the parameters for the critical points (see SI, Table S3) agree with the presence of the coordination bond.[8a,b] The bond index calculated for the Cu···C contact (0.1930) according to the Wiberg method[9] is comparable to Cu−N (0.2110, 0.1921, 0.2070) bond orders.

In conclusion the 21-diphenylphosphoryl-carbaporpholactone hybrid is an aromatic porphyrinoid, which preserves the essential features of the carbaporpholactone frame. The created coordination center provides a suitable environment allowing stabilization of the organocopper(II) complex revealing an unprecedented side-on coordination of copper(II). In terms of characterization of intermediates involved in selective C−H(X) bond activation by copper under mild conditions,[1,4c,d,5,10] the molecular structure of **4** provides a structural model of the copper(II)−C−H(X) transient species.

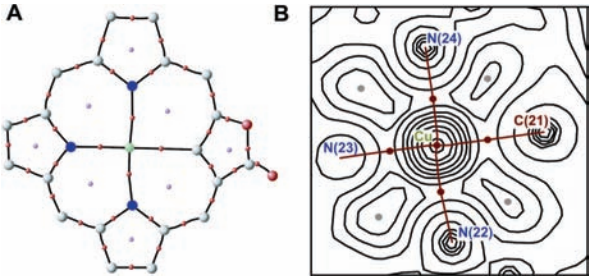

Figure 3. Molecular graph of the central part of **4** illustrating the existence of a Cu−C(21) bond (AIM formalism). Part A shows position of Bond Critical Points (BCPs) and Ring Critical Points (RCPs). Part B shows the electron density distribution of **4**. Red curves show bond paths.

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Supporting Information Available: Synthetic procedures, and additional spectroscopic and crystallographic data together with computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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