The Oxidative Addition of Dibenzoyl Peroxide to Copper(I) Chloride. The Crystal and Molecular Structure of [CuCl(PhCO₂)₂(py)₂] (py = pyridine)

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Dibenzoyl peroxide readily undergoes oxidative addition to copper(I) chloride in pyridine affording a stable copper(III) complex with tetragonal pyramidal geometry.

Copper(I) and copper(II) compounds have proved to be of considerable interest for their ability to catalyse peroxide decompositions in their reactions with alkenes[1] and aromatic compounds,[1] and the oxidative carbonylation of alcohols.[2] The reaction of peroxides with Cu^I species and rate enhancements over uncatalysed thermal reactions have been ascribed to an induced radical mechanism[3,4] [reaction (1)].

$$(RO)_2 + Cu^I \rightarrow Cu^{II}(OR) + RO^{\bullet} \qquad (1)$$

Dibenzoyl peroxide readily undergoes oxidative addition to Cu^0 in pyridine (py) to yield $[Cu_2(PhCO_2)_4(py)_2]$.[5] The aim of the present project was to determine whether dibenzoyl peroxide is able to undergo oxidative addition to Cu^I species, such as CuCl and CuBr. A pyridine solution (5 ml) of copper(I) chloride (1 mmol) treated with dibenzoyl peroxide (1 mol equiv.) under an inert atmosphere at room temperature gave a homogeneous blue solution. The solution was kept overnight, and blue microcrystals of $[CuCl_2(py)_2]$ slowly deposited. This complex was filtered off and ether (10 ml) was layered on the filtrate. After slow mixing of the solvents, large, blue needles of $[CuCl(PhCO_2)_2(py)_2]$ crystallized from the solution along with fine deposits of $[CuCl_2(py)_2]$. After filtration the needles could easily be separated. $[CuCl(PhCO_2)_2(py)_2]$ is stable in air for weeks but decomposes in solution. It is sensitive towards acids, bases, and water and oxidizes alcohols. Studies are in progress to evaluate its use as oxidant for organic compounds. The same reaction with CuBr gave only $[CuBr_2(py)_2]$.

$[CuCl(PhCO_2)_2(py)_2]$ shows strong IR absorptions: $\nu(CO_2)_{as}$ at 1600 and $\nu(CO_2)_s$ at 1380 cm^{-1}. Its electronic reflectance spectrum shows bands at 263, 282, 614, and 662
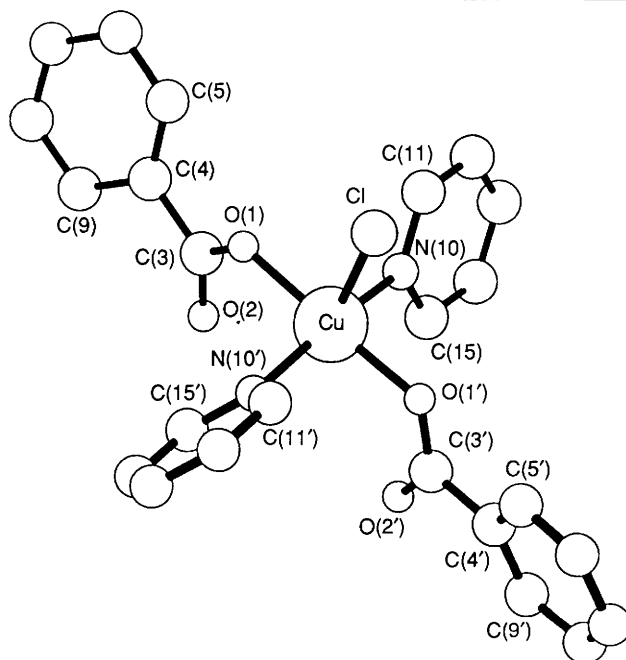
**Figure 1.** Structure of $[CuCl(PhCO_2)_2(py)_2]$. Relevant bond lengths (Å) and angles (°): Cu(1)–Cl(1) 2.274(3), Cu(1)–O(1) 1.933(3), Cu(1)–N(10) 2.035(4), Cu(1)–O(1') 1.928(3), Cu(1)–N(10') 2.045(4), Cl(1)–Cu(1)–O(1) 89.8(2), Cl(1)–Cu(1)–N(10) 94.7(3), Cl(1)–Cu(1)–O(1') 88.3(2), Cl(1)–Cu(1)–N(10) 96.8(3), O(1)–Cu(1)–N(10) 88.2(3), O(1)–Cu(1)–O(1') 178.1(2), O(1)–Cu(1)–N(10') 91.8(3), N(10)–Cu(1)–O(1') 92.0(3), N(10)–Cu(1)–N(10') 168.6(3), O(1')–Cu(1)–N(10), 88.4(3).

nm. The compound is diamagnetic as found for most of the other copper(III) compounds so far characterized.[6] Crystals of [CuCl(PhCO$_2$)$_2$(py)$_2$] grown from the reaction mixture by adding diethyl ether were used for the crystallographic investigation.† In the complex molecule, shown in Figure 1, the five ligands have a square-based pyramidal arrangement about the Cu^{III} atom. The basal sites of the square pyramid are occupied by two benzoate and two py ligands in a *trans*-configuration, while the chlorine atom is situated axially. The benzoate ligands are monodentate, the nonco-ordinated oxygen atoms pointing away from the chlorine. The Cu–O bond lengths of 1.933(3) Å for Cu(1)–O(1) and 1.928(3) Å for the Cu(1)–O(1′) differ only slightly from the values of 1.96 Å for Cu–O found for [Cu(H$_2$O)$_3$(PhOCH$_2$CO$_2$)$_2$].[7] The Cu(1)–Cl(1) bond length of 2.274(3) Å does not differ significantly from that found in [CuCl(diphos)$_2$(ClO$_4$)$_2$][8] [diphos =

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o-phenylenebis(dimethylphosphine)]. The Cu(1)–O(2) and Cu(1)–O(2′) distances are 3.080(4) and 3.139(4) Å respectively.

Presently we cannot distinguish between a concerted and an induced radical reaction mechanism, in which the radical is captured successively by Cu^I and then by Cu^{II} in the formation of [CuCl(PhCO$_2$)$_2$(py)$_2$] [reaction (2)]. However, [{CuCl(Ph-CO$_2$)(py)}$_2$] reacts with dibenzoyl peroxide in py to give [CuCl(PhCO$_2$)$_2$(py)$_2$].

$$\begin{matrix} (PhCO_2)_2 + CuCl \\ [CuCl(PhCO_2)] + PhCO_2^\cdot \end{matrix} \longrightarrow [CuCl(PhCO_2)_2(py)_2] \quad (2)$$
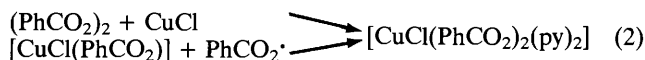
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