$[(\eta^5\text{-}C_5HR_4)CuCO]$ (R = $CHMe_2$) – A Remarkably Stable Copper Carbonyl Complex and its Reaction with P_4

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Abstract. Carbonyl(tetraisopropylcyclopentadienyl)copper has been synthesized and isolated and can be stored at room temperature for several days. $[(C_5HR_4)Cu(CO)]$ (R = $CHMe_2$) has been characterized by ^1H and ^{13}C NMR, C,H analysis, mass spectrometry, and IR spectroscopy. Its reaction with white phosphorus yields a mixture of $[(C_5HR_4)Cu(\eta^2\text{-}P_4)]$ with edge-opened P_4 coordinated to a Cu^{III} atom and $[(C_5HR_4)Cu(\mu,\eta^{2:1}\text{-}P_4)Cu(C_5HR_4)]$ with an additional $Cu(C_5HR_4)$ fragment coordinated to one atom of the P_4 ligand (R = $CHMe_2$).

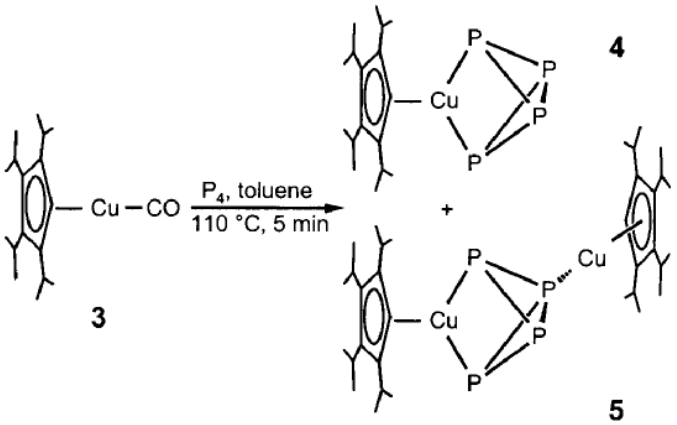
The cyclopentadienylcopper carbonyl parent compound $[(C_5H_5)CuCO]$ (**1**) [1] and its pentamethyl derivative $[(C_5Me_5)CuCO]$ (**2**) [2] can be generated in solution and decompose quickly at room temperature. Both complexes could not be isolated and have been characterized by IR and ^1H NMR spectroscopy.

Since the tetraisopropylcyclopentadienyl ligand has been used successfully to stabilize unusual half sandwich complexes of the 3d transition metals [3], we were interested in the possible stabilization of the copper(I) carbonyl fragment by this extremely bulky ring system. In this paper we wish to report on the stabilization of the copper(I) carbonyl fragment with the tetraisopropyl cyclopentadienyl ligand and the generation of novel copper complexes with P_4 ligands.

In THF at –78 °C copper(I) chloride reacts with sodium tetraisopropylcyclopentadienide to form a dark green solution, which upon subsequent exposure to an atmosphere of carbon monoxide slowly turns brown upon thawing to room temperature. Removal of the solvent in vacuo gives a dark brown oil containing small amounts of impurities, but only one tetraisopropylcyclopentadienyl complex, which could be demonstrated to be the title compound $[(C_5HR_4)CuCO]$ (R = $CHMe_2$) (**3**). This compound is well soluble in all common aprotic solvents and has been stored in the refrigerator at 5 °C for three weeks without noticeable decomposition. ^1H NMR spectra of **3** exhibit the typical set of signals for the tetraisopropylcyclopentadienyl ligand and the IR absorption of the carbonyl ligand occurs at 2062 cm^{-1} in toluene solution. The carbonyl bands for **1** and **2** have been found at 2093 and 2075 cm^{-1}, respectively. **3** is the first cyclopentadienylcopper carbonyl, which could be characterized by elemental analysis and by ^{13}C NMR spectroscopy. Besides the expected signals for the tetraisopropylcyclopentadienyl ring a broad singlet at 188 ppm could be observed at –60 °C, which was not detectable at room temperature. EI mass spectra of **3** showed the molecular ion with 50% intensity.

The decomposition of **3** has been monitored in toluene solution at room temperature. After three days the carbonyl absorption of **3** started to decrease and could no longer be detected after seven days.

In toluene solution under reflux **3** reacted with white phosphorus to form a mixture of two tetraisopropylcyclopentadienyl copper complexes with P_4 ligands, $[(\eta^5\text{-}C_5HR_4)CuCO]$ (R = $CHMe_2$). By two dimensional ^{31}P NMR spectroscopy the two sets of signals could be assigned. The more symmetric compound corresponds to the formula $[(\eta^5\text{-}C_5HR_4)Cu(\eta^2\text{-}P_4)]$ (R = $CHMe_2$) (**4**) (scheme 1).



Scheme 1

^{31}P NMR spectra of **4** show a triplet at –134 ppm ($J_{P,P}$ = 178 Hz) and another triplet at –348 ppm ($J_{P,P}$ = 178 Hz). The second component (**5**) is less symmetric, but should have a similar structure. The spectral features are a pseudo triplet at –141 ppm ($J_{P,P}$ = 178 Hz) and two pseudo quartets at –311

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