Cyanomethylcopper(I). A Stable Alkylcopper *via* Decarboxylation

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Summary The preparation and characterization of the stable alkylcopper(I), cyanomethylcopper(I), *via* ready decarboxylation of Cu^{I} and Cu^{II} cyanoacetates are reported.

Alkylcopper(I) compounds are generally unstable, except for the perfluorinated compounds.[1] Recently, the preparation of the stable trimethylsilylmethylcopper(I) has been reported.[2] We now describe the preparation of the relatively stable cyanomethylcopper(I), NCCH$_2$Cu, (I), by the ready decarboxylation[3] of copper(I) and copper(II) cyanoacetates.

The following operations were carried out under nitrogen. Reaction of equimolar quantities of cyanoacetic acid and copper(I) t-butoxide[4] in tetrahydrofuran (THF) followed by evaporation under reduced pressure gave the white copper(I) cyanoacetate, a suspension of which, when heated to *ca.* 50° in dimethylformamide (DMF), turned yellow with evolution of CO$_2$. After filtration, washing with THF, and drying *in vacuo*, a dark yellow solid was obtained (95%), which was identified as compound (I) by its Cu content (60·7% by iodometry), acetolysis at room temperature to give MeCN (82%) and CuOAc, and its i.r. absorption at 2206 cm^{-1} [ν(C$\equiv$N)].

The insolubility of (I) in common organic solvents suggests a high degree of association. However, it is soluble in DMF in the presence of an equimolar amount of Bu^{t}OLi, with the formation of a complex. Compound (I) is air-sensitive, but is stable under nitrogen up to *ca.* 100°. The increased thermal stability of (I), in comparison with the unstable methylcopper which has been reported to decompose at $-25°$,[5] shows that the cyano-group has a stabilizing effect on the organocopper probably owing to its electron-withdrawing properties and co-ordinating ability towards copper. The stabilization of organocopper compounds by fluorinated groups is known.[1,6] The preparation of (I) suggests that decarboxylation is an effective method for the synthesis of organocopper compounds bearing electron-withdrawing functional groups.

Recently, the cyanomethylcopper complex has been produced *in situ* at $-25°$, without isolation and characterization, by metathesis between CuI and cyanomethyllithium (from MeCN and Bu^{n}Li at $-78°$), and has been used for the conversion of allylic halides into $\gamma\delta$-unsaturated nitriles.[7] The decarboxylation of copper(I) cyanoacetate can be used for the preparation of cyanomethylcopper(I) free of co-ordinating ligands. This is significant, because of the restrictions on the preparation of organocopper compounds possessing a functional group by the metathesis of copper salts with an organolithium or a Grignard reagent caused by the low reaction temperature and the concomitant formation of lithium or magnesium halide.

Compound (I) is a cyanomethylating agent: reaction with CH$_2$=CHCH$_2$Br,[7] PhCH$_2$Br, or PhI gave CH$_2$=CHCH$_2$CH$_2$CN, PhCH$_2$CH$_2$CN, or PhCH$_2$CN, respectively.

Interestingly, copper(II) cyanoacetate is decarboxylated smoothly under mild conditions to give (I) and succinonitrile. To our knowledge, this is the first example of the isolation of an organocopper(I) species and the effective formation of a symmetrical coupling product in copper(II) decarboxylation.

$$\mathrm{Cu(OMe)_2 + 2NCCH_2CO_2H} \xrightarrow[\text{THF, room temp.}]{-2\mathrm{MeOH}} \mathrm{(NCCH_2CO_2)_2Cu}$$

$$\xrightarrow[\text{DMF}]{50^\circ} \underset{(77\%)}{\mathrm{NCCH_2Cu}} + \underset{(96\%)}{\tfrac{1}{2}\mathrm{NCCH_2CH_2CN}} + 2\mathrm{CO_2}$$

The mildness of the present decarboxylation contrasts sharply with ordinary decarboxylations of aromatic copper carboxylates, requiring severe conditions which frequently destroy the organocopper intermediates and cause reduction of the copper(II) carboxylate.[8]

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[1] J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, *Chem. Comm.*, 1967, 1259.

[2] M. F. Lappert and R. Pearce, *J.C.S. Chem. Comm.*, **1973**, **24**,

[3] There is one precedent for the isolation of an arylcopper(I) *via* decarboxylation, *i.e.*, pentafluorophenylcopper; see A. Cairncross, J. R. Roland, R. M. Henderson, and W. A. Sheppard, *J. Amer. Chem. Soc.*, 1970, **92**, 3187.

[4] T. Tsuda, T. Hashimoto, and T. Saegusa, *J. Amer. Chem. Soc.*, 1972, **94**, 658.

[5] K. H. Thiele and J. Köhler, *J. Organometallic Chem.*, 1968, **12**, 225.

[6] A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, 1968, **90**, 2186.

[7] E. J. Corey and I. Kuwajima, *Tetrahedron Letters*, 1972, 487, stated that the metathesis between cyanomethyl-lithium and copper(I) iodide at $-25°$ in pentane–THF gave a red solution of cyanomethylcopper. On the basis of the insolubility of (I) isolated *via* decarboxylation, the reported cyanomethylcopper appears to be co-ordinated to, *e.g.*, LiI.

[8] T. Cohen and R. A. Schambach, *J. Amer. Chem. Soc.*, 1970, **92**, 3189, and references therein.