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Preliminary communication

HYDROCONDENSATION OF CO_2

II *. REACTION OF CARBON DIOXIDE AND CARBON MONOXIDE WITH $[HCuPPh_3]_6$

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Summary

The products formed in the reactions of CO_2 and CO with the hexameric copper hydride $[HCuPPh_3]_6$ have been isolated and identified. Reactions of the formate $(Ph_3P)_2CuOCOH$, the product of CO_2 insertion into the H—Cu bond, have also been studied.

The successful exploitation of carbon dioxide as a source of chemical carbon requires a knowledge of the different modes of reaction of CO_2 with organotransition metal compounds. This has been an area of intensive research and amongst the many results recorded (for reviews see references 2 to 4) it has been reported that CO_2 reacts with transition metal hydrides to give both "normal" products (formates MOCOH) and "abnormal" products (metal carboxyllates) [2]. Such compounds could thus be key intermediates in the catalytic transformations of carbon dioxide. In parallel with our studies on the Cu [1] and Pd-catalysed transformations of CO_2 and CO, we have therefore also studied certain stoechiometric reactions of CO_2 and CO. We report below some observations on the reactions of CO_2 and CO with the hexameric copper hydride $[HCuPPh_3]_6$ [5].

We observed that CO_2 reacts with the hexamer in benzene solution at room temperature to give a complex mixture of products containing metallic copper, the formate $(Ph_3P)_2CuOCOH$ (isolated and characterized by analysis and IR) and a non-crystalline material (ν_{max} 2960, 1265, 1100, 800 cm^{-1}). Carbon monoxide and traces of methane were also observed. In the presence of one equivalent of phosphine, again at room temperature (48 h), the reaction pro-

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* For part I see ref. 1.

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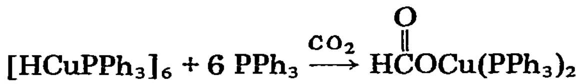
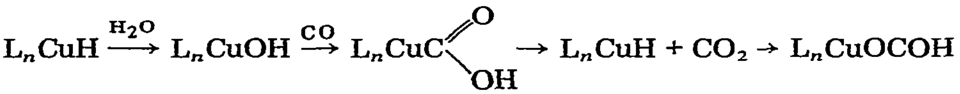
ceeded according to following stoechiometry:



$$[\mathrm{HCuPPh_3}]_6 + 6\ \mathrm{PPh_3} \xrightarrow{\mathrm{CO_2}} \mathrm{HC(=O)OCu(PPh_3)_2}$$

The formation of this formate, which is identical with that prepared from the Cu/formic acid reduction of copper(II) formate in the presence of PPh_3, is additional confirmation of the stoechiometry of the starting hydride.

Reaction of the hydride with CO is much slower. It is inhibited by hydrogen and promoted by the presence of traces of water. The main organometallic product is again the formate ($HCOOCu(PPh_3)_2$), but appreciable quantities of carbon dioxide are also formed. The formate could be formed from the hydride and CO_2, though the origin of such carbon dioxide is not clear. Metallocarboxylates have been proposed as intermediates in several examples of homogeneous metal-catalyzed water gas shift reactions [3,4]. We suggest that in the present case the CO_2 may be formed from a metallocarboxylate:



$$\mathrm{L}_n\mathrm{CuH} \xrightarrow{\mathrm{H_2O}} \mathrm{L}_n\mathrm{CuOH} \xrightarrow{\mathrm{CO}} \mathrm{L}_n\mathrm{CuC(=O)OH} \rightarrow \mathrm{L}_n\mathrm{CuH} + \mathrm{CO_2} \rightarrow \mathrm{L}_n\mathrm{CuOCOH}$$

The formate $L_2CuOCOH$ would thus seem to be an intermediate common to the reactions of CO_2 and CO with the hydride. The hydride itself is not active as a catalyst in the transformation of CO_2/H_2 mixtures since it is not stable under the reaction conditions. However, it is known that $(Ph_3P)_3CuCl$ [6] and other copper(I) complexes (e.g. $[(CuCl)_2dpm]_2$ and $[Cu_3Cl_2dpm_3]Cl$) [7] will catalyse the formation of HCOOEt from CO_2/H_2 in $EtOH/NEt_3$, albeit with low turnover numbers. In order to ascertain the role of formato- or alkoxycarbonylcopper compounds as intermediates in this transformation of CO_2 we studied some reactions of the formate $(Ph_3P)_2CuOCOH$.

The results summarized in Fig. 1 indicate that in the presence of H_2, protic solvents, or hydride donors or acceptors, the formato group is neither reduced nor transformed into organic formate (formamide). Instead extensive decomposition, to CO_2, or ligand metathesis was observed. The borohydride obtained by ligand exchange (which is identical to an authentic specimen) reacts with

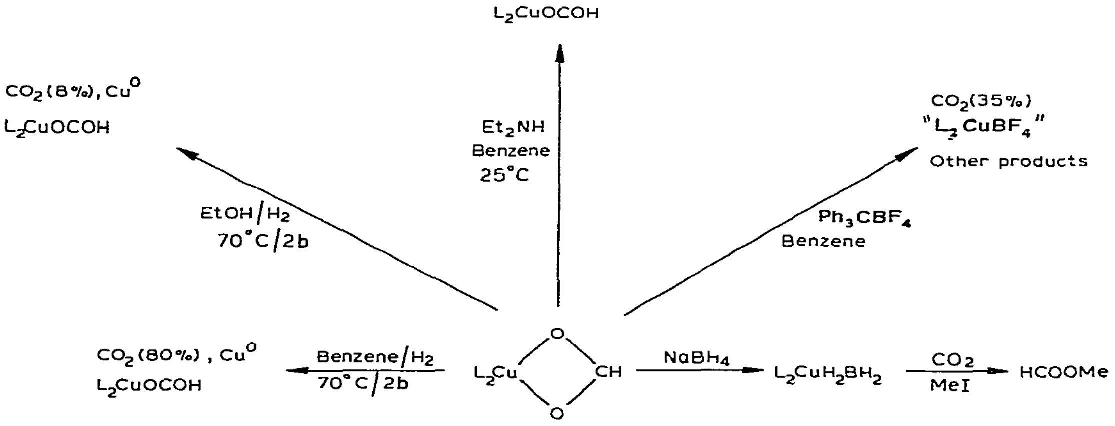


Fig. 1. Transformation of the formatocopper(I) complex, $L = PPh_3$.

CO_2 to give a formate, identified by IR spectroscopy (1560, 1340 cm^{-1}) and by reaction with CH_3I (to give $HCOOCH_3$). The inertness of the copper(I) borohydride towards methyl iodide permits the following stoechiometric transformation of CO_2

$$CO_2 + L_2CuH_2BH_2 + CH_3I \xrightarrow[25^\circ\ C/b]{C_6H_5Cl} HCOOCH_3$$

It must be concluded that formatocopper complexes are unlikely intermediates in the formation of organic formate (formamide) from CO_2/H_2 and constitute instead "stable end products".

We are currently studying the synthesis and reactions of the corresponding alkoxycarbonyl complexes, since our preliminary results indicate that methyl formate is obtained by the action of H_2/CH_3OH on the palladium analogue $L_2PdClCOOCH_3$.

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