# Reversible Carbon Dioxide Fixation by Organocopper Complexes

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*Summary* Reversible $CO_2$ insertion into the Cu(I) phenylacetylide–phosphine complex, $\mathrm{PhC{\equiv}CCu{\cdot}(PBu^n{}_3)_3}$, is described; the complex behaves as a reversible $CO_2$ carrier under mild conditions.

Interest in transition-metal complexes which reversibly fix $CO_2$ *via* insertion or co-ordination is increasing rapidly, partly because they offer excellent models for investigating the interaction between the transition-metal complexes and $CO_2$, and partly because they may be expected to function as reversible carriers of activated $CO_2$ which can transfer $CO_2$ to other organic substrates. However, there is no precedent for reversible $CO_2$ insertion into the transition metal–carbon bond involved in a variety of transition metal-catalysed reactions. We now report reversible $CO_2$ insertion into the copper–carbon bond of a Cu(I) phenylacetylide complex under mild conditions.

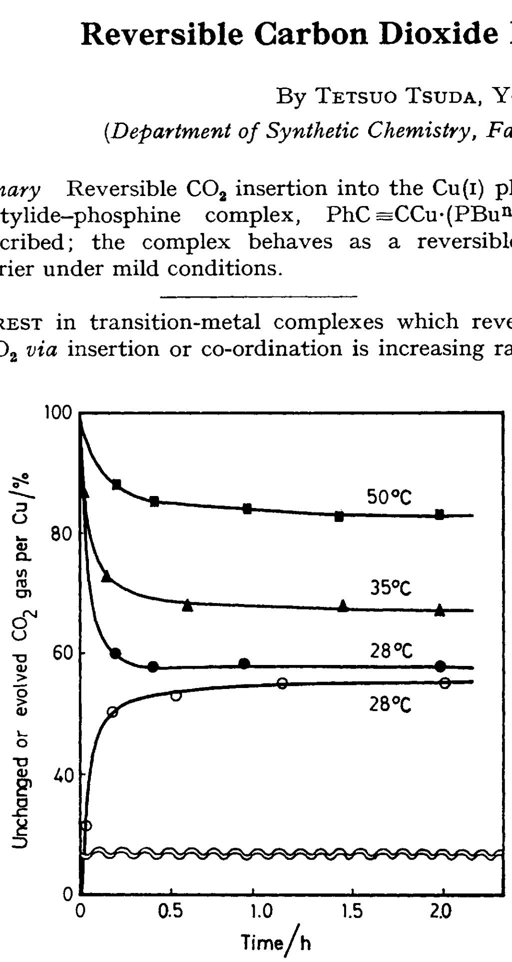

Figure 1 Carboxylation of 0·72 mM (■), 0·57 mM (▲) and 0·46 mM (●) of $\mathrm{PhC{\equiv}CCu{\cdot}(PBu^n{}_3)_3}$ in 5 ml dimethylformamide with an equimolar amount of $CO_2$ gas, and decarboxylation of 1·11 mM (○) of $\mathrm{PhC{\equiv}CCO_2Cu{\cdot}(PBu^n{}_3)_3}$ in 5 ml dimethylformamide.

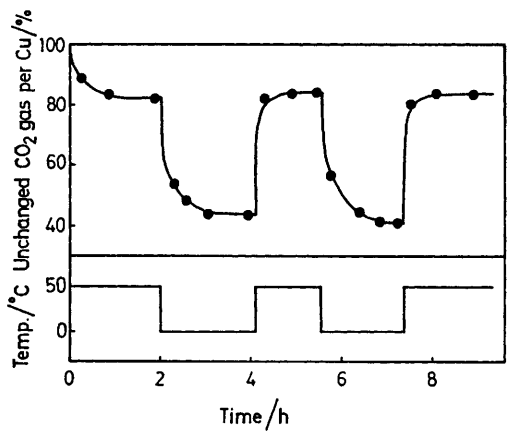

Figure 2. Cycle of $CO_2$ gas absorption-evolution by alternate heating and cooling the system of 0·76 mM $\mathrm{PhC{\equiv}CCu{\cdot}(PBu^n{}_3)_3}$ and 0·76 mM $CO_2$ gas in 5 ml dimethylformamide.

All experiments described below were carried out in a closed vessel of *ca.* 270 ml volume under nitrogen. Cu(I) phenylpropiolate prepared from Cu(I) t-butoxide and phenyl propiolic acid in diethylether at $-10°C$ was found to undergo a quantitative and irreversible decarboxylation in dimethylformamide at 35 °C to produce Cu(I) phenylacetylide. In the presence of three equivalents of $PBu^n_3$, the decarboxylation did not proceed to completion and becomes reversible (equation 1). The reversibility of equation 1

$$PhC{\equiv}CCO_2Cu{\cdot}(PBu^n_3)_3 \rightleftharpoons PhC{\equiv}CCu{\cdot}(PBu^n_3)_3 + CO_2 \quad (1)$$

was demonstrated by the following experimental results; (i) the reaction reached a state of equilibrium (Figure 1); (ii) on treating with methyl iodide, the equilibrated reaction mixture from either the carboxylation of the Cu(I) phenylacetylide–phosphine complex or the decarboxylation of the Cu(I) phenylpropiolate–phosphine complex produced both methyl phenylpropiolate and methylphenylacetylene. Previously we reported $CO_2$ insertion into Cu(I) phenylacetylide in the presence of an equimolar amount of a $\sigma$-donating ligand under the relatively severe conditions of 80 °C and 50 kg $cm^{-2}$ $CO_2$.[1] The present study demonstrated reversible $CO_2$ insertion into the Cu(I) phenylacetylide–phosphine complex at ambient temperature and ordinary $CO_2$ pressure.

Increasing the molar ratio of $PBu^n_3$–$PhC{\equiv}CCu$ from 1 to 2 or 3 increased the rate of carboxylation, but there was no difference in the carboxylation behaviour between the $PhC{\equiv}CCu$–$3PBu^n_3$ and $PhC{\equiv}CCu$–$4PBu^n_3$ systems, which suggests that three $PBu^n_3$ ligands are co-ordinated to the Cu(I) species, forming the co-ordinatively saturated complexes (equation 1). In accord with our previous study,[1] the nature of the ligand played an important role, controlling the equilibrium position in equation 1. A ligand of higher $\sigma$-donating strength promoted carboxylation; the equilibrium values of unchanged $CO_2$ gas were 67% ($PBu^n_3$), 83% ($PPh_3$), and 89% ($P(OMe)_3$).

The reversibility of equation 1 means that the complex acts as a reversible $CO_2$ carrier. This property is illustrated in Figure 2 where alternate heating and cooling of the $PhC{\equiv}CCu{\cdot}(PBu^n_3)_3$–$CO_2$ system causes a cycle of $CO_2$ absorption and evolution. The present carboxylation of the Cu(I) phenylacetylide–phosphine complex is the first example of reversible $CO_2$ insertion into an organotransition metal complex.[2]

(*Received*, 6*th October* 1975; *Com.* 1141.)

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[1] T. Tsuda, K. Ueda, and T. Saegusa, *J.C.S. Chem. Comm.*, 1974, 380.

[2] Cyanomethylcopper(I) (T. Tsuda, T. Nakatsuka, T. Hirayama, and T. Saegusa, *J.C.S. Chem. Comm.*, 1974, 557) has also been found recently to undergo a reversible $CO_2$ insertion into the copper–carbon bond in the presence of phosphine ligand. This work will be reported in a separate paper.