Preparation of Urethanes from Carbon Dioxide *via* a Copper(I) Carbamato-complex

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Summary Efficient copper-promoted urethane formation from carbon dioxide, amines, and alkyl halides is described; an intermediate copper(I) carbamato-complex has been isolated and characterized.

Recently, CO_2 uptake by transition metal amide complexes to produce transition metal carbamato-complexes has been studied from the mechanistic and structural viewpoints.[1] Little is known, however, about the reaction and stability of the carbamato ligand. Here we report the efficient, copper-promoted formation of urethanes from carbon dioxide, amines, and alkyl halides involving an isolable copper(I) carbamato-complex as the key intermediate [reaction (1)].

$$\begin{tikzcd}
\mathrm{CuOBu^t}+\mathrm{R^1R^2NH}+\mathrm{CO_2} \arrow[r, "-\mathrm{Bu^tOH}"] & \mathrm{R^1R^2NCO_2Cu} \arrow[d, "\mathrm{Bu^tNC}"] \\
\mathrm{R^1R^2NCO_2Me} & \mathrm{R^1R^2NCO_2Cu(CNBu^t)}_n \arrow[l, "\mathrm{MeI}"']
\end{tikzcd} \qquad (1)$$

The following operation is typical (all stages carried out under nitrogen). To a stirred benzene (3·0 ml) solution containing copper(I) t-butoxide[2] (0·50 mmol), t-butyl isocyanide (1·50 mmol), and diethylamine (0·55 mmol), CO_2 gas (1·50 mmol) was introduced under atmospheric pressure. The mixture was stirred for 3 h at ambient temperature and then treated with methyl iodide (0·75 mmol) to produce methyl *NN*-diethylcarbamate in 94% yield based on copper(I) t-butoxide. Other amines under similar conditions also gave the corresponding methyl carbamates in good yields (Table).

Table. Preparation of the methyl carbamates $R^1R^2NCO_2Me$ from the amines R^1R^2NH.

Amine R^1R^2NH		Ligand	% Yield of carbamate $R^1R^2NCO_2Me$
R^1	R^2		
H	H	Bu^tNC	56
Bu^n	H	"	39
Bu^t	H	"	99
Et	Et	"	94
"	"	PBu^n_3	58
"	"	$P(OMe)_3$	3
"	"	None	0
Bu^n	Bu^n	Bu^tNC	95
$-[CH_2]_5-$		"	83
$-CH_2CH_2OCH_2CH_2-$		"	79
Ph	H	"	76

The factors influencing the formation of urethanes were examined using diethylamine as substrate. A σ-donating ligand such as Bu^tNC or PBu^n_3 is necessary for the reaction to occur. Copper(I) t-butoxide was the most effective among the copper(I) salts examined; copper(I) acetate produced the carbamate in 16% yield, and copper(I) chloride and n-butylthiolate were ineffective.

Evaporation of the reaction mixture before the addition of MeI under reduced pressure produced $Et_2NCO_2Cu\cdot(CNBu^t)_n$ (**1**).† Similarly, Et_2NCO_2Cu (**2**)† was isolated by evaporation of the benzene solution of copper(I) t-butoxide, diethylamine, and CO_2 in the absence of Bu^tNC. The complex (**1**) reacted with MeI in benzene at ambient temperature to give methyl *NN*-diethylcarbamate in 86% yield, but (**2**) produced the carbamate only in the presence of added Bu^tNC ligand. These findings suggest that (**1**) is the key intermediate for the methyl carbamate formation reaction.

Another function of the σ-donating ligand is the stabilization of the carbamato-ligand. The complex (**2**) was decarboxylated reversibly at ambient temperature in a polar solvent such as hexamethylphosphoric triamide (HMPA); equilibrium amounts of CO_2 gas evolved were 35% at 25 °C and 45% at 60 °C. Complex (**1**), however, is stable toward decarboxylation at ambient temperature in HMPA. Similarly, the σ-donating ligand played a crucial role in the preparation of the copper(I) carbamato-complex derived from less basic amines. A benzene solution of copper(I) t-butoxide and aniline alone did not absorb CO_2, but did so in the presence of Bu^tNC to produce an isolable $PhNHCO_2Cu\cdot(CNBu^t)_n$ complex (**3**).†

Transition metal carbamato-complexes are usually prepared by the reaction of transition metal amides and CO_2.[1] The present study provides a new method for preparation of transition metal carbamato-complexes from transition metal alkoxides.

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† Identified by its Cu content, CO_2 evolution on acidolysis, and i.r. spectra. n was calculated to be 1·4 for (**1**) and 1·6 for (**3**) on the basis of the Cu content of the complex.

[1] M. H. Chisholm and M. W. Extine, *J. Amer. Chem. Soc.*, 1977, **99**, 782 and references therein. See also T. V. Ashworth, M. Nolte, and E. Singleton, *J. Organometallic Chem.*, 1976, **121**, C57.

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