

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

By TETSUO TSUDA, HIROSHI WASHITA, KATSUHIKO WATANABE, MASAHIRO MIWA, and TAKEO SAEGUSA*
(Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan)

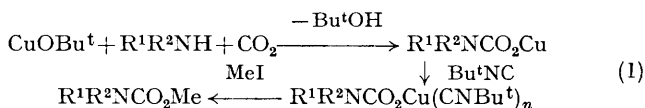
Summary Efficient copper-promoted urethane formation from carbon dioxide, amines, and alkyl halides is described; an intermediate copper(I) carbamato-complex has been isolated and characterized.

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).

RECENTLY, CO₂ 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)].

TABLE. Preparation of the methyl carbamates R¹R²NCO₂Me from the amines R¹R²NH.

R ¹	Amine R ¹ R ² NH	R ²	Ligand	% Yield of carbamate R ¹ R ² NCO ₂ Me
H		H	Bu ^t NC	56
Bu ^t		H	"	39
Bu ^t		H	"	99
Et		Et	"	94
"		"	PBu ⁿ ₃	58
"		"	P(OMe) ₃	3
"		"	None	0
Bu ⁿ		Bu ⁿ	Bu ^t NC	95
			"	83
			"	79
Ph		H	"	76



The following operation is typical (all stages carried out under nitrogen). To a stirred benzene (3.0 ml) solution containing copper(I) *t*-butoxide² (0.50 mmol), *t*-butyl isocyanide (1.50 mmol), and diethylamine (0.55 mmol), CO₂ gas (1.50 mmol) was introduced under atmospheric pressure. The mixture was stirred for 3 h at ambient

The factors influencing the formation of urethanes were examined using diethylamine as substrate. A σ -donating ligand such as Bu^tNC or PBuⁿ₃ 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 $\text{Et}_2\text{NCO}_2\text{Cu}\cdot(\text{CN}\text{-Bu}^\dagger)_n$ (**1**).[†] Similarly, $\text{Et}_2\text{NCO}_2\text{Cu}$ (**2**)[†] was isolated by evaporation of the benzene solution of copper(I) t-butoxide, diethylamine, and CO_2 in the absence of $\text{Bu}^\dagger\text{NC}$. 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 $\text{Bu}^\dagger\text{NC}$ 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 $\text{Bu}^\dagger\text{NC}$ to produce an isolable $\text{PhNHCO}_2\text{Cu}\cdot(\text{CN}\text{Bu}^\dagger)_n$ 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.

(Received, 5th May 1978; Com. 483.)

[†] 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.