

Catalytic Formation of Cyclic Carbonates and Carbamates by [Cu(I)](BF₄)₂ (1=2,5,19,22-tetraaza[6,6](1,1')ferrocenophane-1,5-diene)

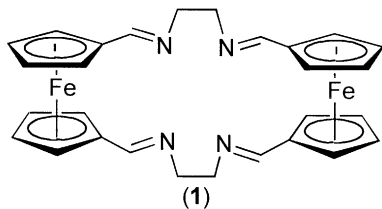
Soon-Chul Kwon, Chan-Sik Cho, Sang-Chul Shim, and Tae-Jeong Kim*

Department of Industrial Chemistry, Kyungpook National University, Taegu 702-701, Korea

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The catalytic incorporation of carbon dioxide into organic substrates leading to the formation of various organic fine chemicals has attracted a considerable attention due to its nontoxicity and low price as compared with carbon monoxide.¹⁻³ Cyclic carbonates and carbamates are among those that are of particular interest due to their usefulness in various areas of organic synthesis and polymer chemistry.⁴⁻⁸

These compounds now known to be obtained catalytically by various transition metal complexes such as CuCl, Cu(acetate)₂, CuCl₂,⁹⁻¹² Ru₃(CO)₁₂,¹³ Pd(PPh₃)₄,¹⁴ CoCp₂,¹⁵ and even simple tertiary phosphines.^{4,5} We have recently demonstrated that some Fe(dppf)(CO)₃, dppf[Fe(CO)₄]₂ (dppf=1,1-bis(diphenylphosphino)ferrocene),¹⁶ and [Cu(I)]PF₆¹⁷ can also be an excellent choice for the same purposes.



These findings coupled with the fact that ferrocene-containing macrocycles may have a potential applications in the fields of molecular ferromagnets,^{18,19} molecular sensors,^{20,21} nonlinear optics,²²⁻²⁶ and small molecule activation²⁷⁻²⁹ have led us to pursue further the coordination chemistry of **1** and catalytic application as ligand to the transformation cited above for comparative purposes. Here we wish to report the preparation of [Cu(I)](BF₄)₂ (**2**) and its application to catalytic activation of propargyl alcohols and phenylacetylene in the presence of CO₂ to form a series of cyclic carbonates and carbamates.

Experimental Section

General Comments. All manipulations were carried out under an argon atmosphere using a double manifold vacuum system and Schlenk techniques. All commercial reagents were used as received unless otherwise stated. Solvents were purified by standard methods and were freshly distilled prior to use. Microanalyses were performed by the Center for Instrumental Analysis, Kyungpook National University. ¹H and ³¹P NMR spectra were recorded on a Varian Unity+ 300 spectrometer operating at 300, 121.5 MHz, respectively. IR spectra were recorded on a Mattson FT-IR Galaxy 6030E spectrophotometer. UV-Vis spectra were measured on a HP

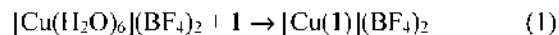
8452A diode-array spectrophotometer. The ligand **1** was prepared according to the literature method.¹⁷

Preparation of 2. To a stirred suspension of [Cu(H₂O)₆](BF₄)₂ (0.26 g, 0.75 mmol) in CH₃CN (50 mL) was added **1** (0.40 g, 0.75 mmol). The reaction mixture was stirred under reflux for 4 h during which reddish brown precipitates deposited. These were collected on a Celite and washed with CH₂Cl₂ (3x5 mL) (0.38 g, 65%). Anal. Calc. for C₂₈H₂₈N₄B₂F₈Fe₂Cu: C, 43.69; H, 3.67; N, 7.28. Found: C, 43.18; H, 3.84; N, 7.36. IR (KBr): ν_{C-N}, 1630, ν_{BF₄}, 1040 cm⁻¹.

Catalysis. Under a stream of nitrogen, acetylenic substrate (5.00 mmol), base (0.50 mmol), and **2** (0.50 mmol) were placed in an autoclave (50 mL). After purging with CO₂ a few times, the reactor was pressurized to the desired pressure (38 atm). The system was heated at 100 °C for 24 h after which the reaction was terminated by rapid cooling, and then the reactor was discharged. After passing the reaction mixture through a short silicagel column to remove the catalyst, the yields were obtained by gas chromatographic analyses, the organic products were characterized and identified according to the literature.

Results and Discussion

Synthesis and Characterization. The Cu(II) complex incorporating the macrocyclic ligand **1** was formed according to the simple substitution reaction represented by equation (1).



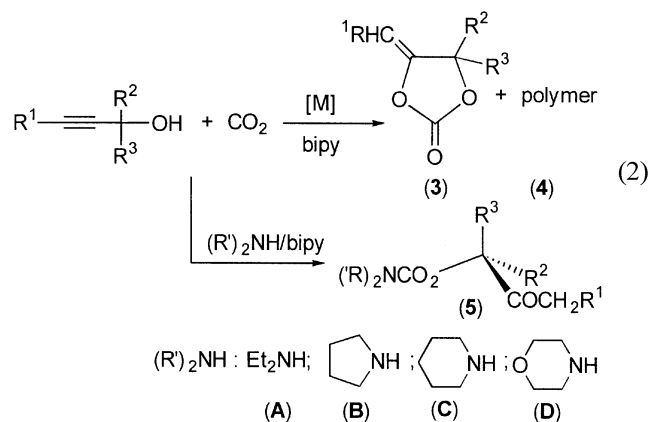
Elemental analysis and other spectroscopic data are consistent with the formulation. Both **1** and **2** show the characteristic imine stretching bands (ν_{C-N}) in the region of 1609-1639 cm⁻¹ which move to lower frequency upon complexation.

Catalysis. In spite of numerous examples for copper macrocycle³⁰⁻³³ and their reaction chemistry with small molecules such as carbon monoxide,^{34,35} olefins,³⁵ and carbon dioxide,³⁶ their use as homogeneous catalyst in organic synthesis via the activation of these small molecules are rare. Such example include catalytic oxidation with dinuclear Cu(II) macrocyclic dioxygen complexes,³⁷⁻⁴⁰ epoxydation of styrene by Cu(II) macrocycles.⁴¹

The present work is the continuation and the extension of our previous work on the catalytic formation of cyclic carbonates and carbamates by cationic Cu(I) complex incorpo-

rating the ferrocene-containing tetraazamacrocyclic [Cu(I)]-PF₆,¹⁷ for the incorporation of carbon dioxide. As mentioned above, this type of transformation represented by equation (2) is well established.^{4,5} Here [M] represents various types of catalysts such as those mentioned above.

In the present work, the same reactions were carried out



employing **2** as catalyst. Tables 1 and 2 present the yields of various cyclic carbonates (**3**) and carbamates (**5**), respectively, under a standard set of conditions. Both tables show that our new copper(II) complex **2** is an excellent catalyst giving almost quantitative product yields in most cases. These results along with our previous ones are among the highest yields reported in the literature.^{4,5,17}

Once again the presence of substituents (R² & R³) other than hydrogen at the α -carbon of the propargyl alcohol has proven to be essential to maintain high product yields as seen from entry 1 of Table 1 and entries 13-16 of Table 2. A dramatic example for these observations is the exclusive formation of a polycarbonate (**4**) instead of the desired cyclic carbonate (entry 1 of Table 1). The polymer formation from this reaction was confirmed by comparing the infrared pattern of the product with that of related polycarbonates obtained under different catalytic conditions.^{42,43} Comparison of molecular weights and other spectroscopic data such as NMR, however, could not be made due to the insolubility of our product in any organic solvent.

The yields drop also when the terminal acetylenic hydrogen is replaced by other bulkier substituents, which may be

Table 1. Yields of cyclic carbonates (**3**) catalyzed by **2**^a

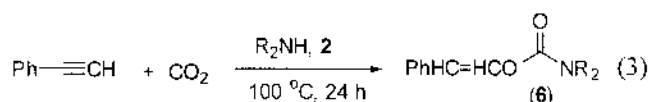
Entry	Substrate			Yield(%) ^b	
	R ¹	R ²	R ³	3	4
1	H	H	H	-	>95 ^c
2	H	Me	Me	96	-
3	H	Me	Et	97	-
4	H	Me	Ph	92	-
5	Ph	Me	Me	0	-

^aReaction conditions: [substrate]=5 mmol (neat); [catalyst]=0.05 mmol; [bipy]=0.5 mmol; P(CO₂)=38 atm; temperature=100 °C; reaction time=24 h. ^bGC yield based on the substrate. ^cBased on the weight of isolated product.

Table 2. Yields of carbamates (**5**) catalyzed by **2**^a

Entry	Substrate			Amine	Yield (%) ^b
	R ¹	R ²	R ³		
1	H	Me	Me	A	97
2				B	96
3				C	96
4				D	94
5	H	Me	Et	A	94
6				B	92
7				C	90
8				D	84
9	H	Me	Ph	A	92
10				B	90
11				C	90
12				D	84
13	H	H	H	A	44
14				B	40
15				C	40
16				D	30
17	Ph	Me	Me	A	42
18				B	45
19				C	40
20				D	35

^aReaction conditions: [substrate]=5 mmol; [catalyst]=0.05 mmol; [base]=0.5 mmol; P(CO₂)=38 atm; temperature=100 °C; reaction time=24 h. ^bGC yield based on the substrate.



explained in terms of steric hindrance (entry 5 of Table 1 & entries 17-20 of Table 2).

The same observations are made with the reaction of simple unfuntioalized alkyne such as phenyl acetylene (equation 3) as can be seen from Table 3. The mechanisms that can be cited for equations 2 and 3 may be the same proposed by us in our previous report.¹⁷

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Table 3. Yields of **6** catalyzed by **2**^a

Entry	Substrate	Amine	Yield(%) ^b
1	Phenyl acetylene	A	67
2		B	64
3		C	67
4		D	64

^aReaction conditions are the same as those described in the footnote of Table 2. ^bGC yields.

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