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A New Reversible Carbon Dioxide Carrier. (*tert*-Butyl carbonato)tris(*tert*-butyl isocyanide)copper(I), t-BuOCO$_2$Cu(CN-t-Bu)$_3$

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In the presence of 3 equiv of *tert*-butyl isocyanide, copper(I) *tert*-butoxide absorbed CO$_2$ in benzene at ambient temperature to produce an isolable complex of t-BuOCO$_2$Cu(CNBu-t)$_3$ (**2**): t-BuOCuCNBu-t + 2t-BuNC + CO$_2$ $\rightleftharpoons$ t-BuOCO$_2$Cu(CNBu-t)$_3$. Without the *tert*-butyl isocyanide ligand, no reaction took place. The *tert*-butyl isocyanide ligand is shown to stabilize the t-BuOCO$_2$ group by its σ-donating property. The CO$_2$ molecule of **2** is labile and **2** acts as a reversible CO$_2$ carrier. Refluxing a benzene solution of **2** under nitrogen caused quantitative decarboxylation. The stability of the t-BuOCO$_2$ group toward decarboxylation markedly depended upon the number of *tert*-butyl isocyanide ligands.

Introduction

Considerable current interest exists in the reaction between transition metal complexes and CO$_2$, partly because transition metal complex promoted organic reactions of CO$_2$ circulate carbon resources and partly because the behavior of CO$_2$ as a "small molecule" ligand for transition metals has not been explored until recently in comparison to H$_2$, N$_2$, O$_2$, NO, and CO. Transfer of activated CO$_2$ to an organic substrate in the coordination sphere of a transition metal complex is a promising approach for utilization of CO$_2$ in synthetic organic reactions. In this respect, isolation and characterization of the transition metal complexes which fix CO$_2$ in a reversible way under mild conditions are significant. This type of complex also permits the simultaneous study of carboxylation and decarboxylation and offers an excellent model for investigating the interaction between CO$_2$ and transition metal complexes. Examples of the isolation of this type of transition metal complex, however, are limited.[1]

In our previous study,[2] CO$_2$ was reversibly inserted into copper(II) dimethoxide in pyridine to produce the copper(II) methyl carbonate complex: Cu(OMe)$_2$ + 2CO$_2$ $\rightleftharpoons$ Cu(OCO$_2$Me)$_2$. However, an attempt to isolate this complex by removal of the pyridine solvent resulted in complete decarboxylation. In this paper, isolation and characterization of t-BuOCO$_2$Cu(CN-t-Bu)$_3$ (**2**) which can reversibly fix CO$_2$ via insertion under mild conditions are described (eq 1).

$$\underset{\mathbf{1}}{t\text{-BuOCuCN-}t\text{-Bu}} + 2t\text{-BuNC} + \mathrm{CO_2} \underset{\mathrm{C_6H_6},\ \text{reflux}}{\overset{\mathrm{C_6H_6},\ 10\ ^\circ\mathrm{C}\text{-room temp}}{\rightleftharpoons}} \underset{\mathbf{2}}{t\text{-BuOCO}_2\text{Cu(CN-}t\text{-Bu)}_3} \qquad (1)$$

Results and Discussion

Isolation of 2. A stirred benzene solution of t-BuOCuCN-t-Bu (**1**)[3] containing an additional 2 equiv of *tert*-butyl isocyanide was subjected to contact with a 1.5-fold excess of CO$_2$ gas at 10 °C to absorb 1 equiv of CO$_2$ gas. After the reaction mixture was solidified by cooling to 0 °C, the solvent was removed in vacuo at 0 °C to produce a white solid which was identified as t-BuOCO$_2$Cu(CN-t-Bu)$_3$ (**2**). *tert*-Butyl isocyanide is an indispensable component for the CO$_2$ insertion and copper(I) *tert*-butoxide alone did not react with CO$_2$. The stoichiometry of eq 1 is elucidated in the next section.

Compound **2** showed its ir ν(OCO$_2$-t-Bu) absorption at 1650, 1310, and 1013 cm^{-1}. Acidolysis by 18 N sulfuric acid released CO$_2$ gas in 99% yield. Compound **2** reacted with allyl bromide in benzene at 50 °C to give allyl *tert*-butyl carbonate in 95% yield. Based on the fact that the most common coordination number of cuprous state is 4, **2** is reasonably assumed to be a coordinatively saturated and monomeric complex in which the t-BuOCO$_2$ group is coordinated toward copper as a monodentate ligand. Actually, **2** was found to have a degree of association of 0.90 by cryoscopic measurement in benzene.

Compound **2** is air sensitive but is stable under nitrogen below ca. 10 °C. Slight decarboxylation occurs slowly under nitrogen at ca. 30 °C. Compound **2** is soluble in common organic solvents and is the first example of the isolation of a copper alkyl carbonate complex. As is described in the introductory section, an attempt to isolate the Cu(OCO$_2$Me)$_2$ complex which can reversibly fix CO$_2$ in pyridine has been unsuccessful due to the facile decarboxylation.[2]

Role of the *tert*-Butyl Isocyanide Ligand in the CO$_2$ Insertion into the Copper(I) *tert*-Butoxide–*tert*-Butyl Isocyanide Complex. The CO$_2$ insertion into transition metal complexes is not a general reaction in comparison with the reaction of CO$_2$ with organometallics of the main group. Exploration of the factors influencing the CO$_2$ insertion into transition metal complexes is important. In the present study, a reasonable elucidation of the role of the *tert*-butyl isocyanide ligand as an indispensable component in the formation of **2** can be derived from the marked difference of the ir ν(N$\equiv$C) of the ligand between the starting complex **1** and the resulting complex **2**.

An isocyanide ligand is known to function as either a σ donor or a π acceptor depending upon the nature of metal.[4] A convenient criterion for distinguishing these two types of coordination is the ir ν(N$\equiv$C) frequency of an isocyanide ligand. The *tert*-butyl isocyanide ligand acting as a σ donor exhibits an increase of its ν(N$\equiv$C) in comparison with that

Table I. Effect of the Kind of Ligand upon CO_2 Insertion[a]

t-BuOCu + 3L + CO_2 → t-BuOCO$_2$CuL$_3$

	L				
	P(n-Bu)$_3$	PPh$_3$	t-Bu-NC	P(O-Me)$_3$	None
CO_2 absorbed, % based on t-BuOCu	~100	94[b]	88	7	0

[a] Carboxylations were carried out at 21 °C for 1 h in a ~100-ml flask using 0.849–1.16 mmol of t-BuOCu, 1.30 equiv of CO_2 per t-BuOCu, and 3.0–4.1 ml of benzene. [b] t-BuOCO$_2$Cu(PPh$_3$)$_3$ was isolated and characterized.

of the free *tert*-butyl isocyanide (ν(N≡C) 2138 cm^{-1}) by the contribution of the :C$^-$≡N$^+$R structure. The *tert*-butyl isocyanide ligands coordinated to ordinary Cu(I) salts including t-BuNCCuCl (ν(N≡C) 2189 cm^{-1}) and t-BuNCCuOAc (ν(N≡C) 2169 cm^{-1})[5] show this type of behavior. On the contrary, a considerable decrease of the ν(N≡C) is observed when the *tert*-butyl isocyanide ligand acts as a π acceptor. Compound **1**, which has been recently isolated by us,[3] shows a considerable decrease for ν(N≡C) of the ligand (ν(N≡C) 2102 cm^{-1}). This finding indicates that *tert*-butyl isocyanide of **1** functions as a π-accepting ligand due to the increased π-back-donating ability of Cu(I) atom caused by σ donation from the t-BuO group.

Another interesting observation is that **1** was obtained by evaporation of a benzene solution of copper(I) *tert*-butoxide containing 3 equiv of *tert*-butyl isocyanide whose ν(N≡C) appeared at 2132 and 2107 cm^{-1} as a doublet. This finding suggests that only one *tert*-butyl isocyanide among the three added *tert*-butyl isocyanides is coordinated toward copper(I) *tert*-butoxide as the π acceptor and the two remaining *tert*-butyl isocyanide molecules exist in a free state. The stoichiometry of eq 1 is based on this result.

In **2**, the coordinated *tert*-butyl isocyanide ligands showed their ν(N≡C) at 2160 cm^{-1}, acting as the σ donor. The shift of the ν(N≡C) to higher frequency caused by the CO_2 insertion may be rationalized by the decrease of the π-back-donating ability of Cu(I) atom due to the change of the strongly σ-donating t-BuO ligand to the weakly σ-donating t-BuOCO$_2$ group. In conclusion, the role of the *tert*-butyl isocyanide in the formation of **2** may be understood on the basis of the stabilization of the t-BuOCO$_2$ group by its σ-donating property. This conclusion means that the CO_2 insertion into copper(I) *tert*-butoxide is promoted by the presence of a σ-donating ligand. Table I shows the effect of the kind of ligand upon the CO_2 insertion into copper(I) *tert*-butoxide. The order of effectiveness of various ligands is parallel with that of the σ-donating strength of the ligand.[6]

A σ-donating ligand has been found to be an indispensable component in a variety of copper-promoted reactions.[7] Its role has been explained in terms of the increase of the nucleophilic reactivity of the reacting group due to its electron donation to copper and its ability to dissociate the aggregation of a copper complex. The relation between the effect of the *tert*-butyl isocyanide ligand on the aggregation of the copper(I) *tert*-butyl carbonate complex and the stability of the t-BuOCO$_2$ group is discussed in the following sections.

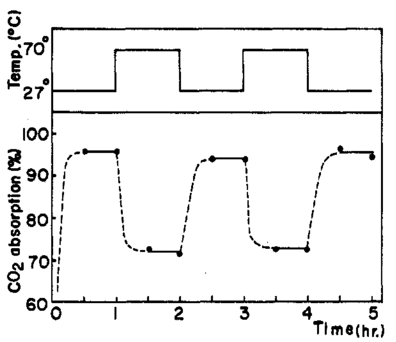


Figure 1. Cycle of reversible carboxylation and decarboxylation. CO_2 gas absorption (percent based on copper) by alternate heating and cooling of the system t-BuOCu (0.248 mmol)–t-BuNC (0.744 mmol)–CO_2 (0.609 mmol) in 5 ml of toluene.

Function of 2 as a Reversible CO_2 Carrier. The most interesting property of **2** is its facile decarboxylation under mild conditions which means reversibility of the formation of **2** (eq 1). The decarboxylation of **2** was examined by means of ir spectroscopy. Refluxing a benzene solution of **2** under a stream of nitrogen for 1.5 h caused a complete decarboxylation, which was evidenced by disappearance of the ν(OCO$_2$-t-Bu) absorption (1650, 1307, 1008 cm^{-1}) with simultaneous appearance of the bands due to **1** (2109, 938 cm^{-1}) and the free *tert*-butyl isocyanide (2132 cm^{-1}) (eq 1). Introduction of CO_2 to the decarboxylated reaction mixture at ambient temperature regenerated the original ir spectrum of **2**. These results demonstrate the reversible CO_2 insertion into the system of **1** + 2t-BuNC. Table II summarizes the principal ir data of the reversible CO_2 fixation by **2** together with those by the unisolable complexes t-BuOCO$_2$Cu(CN-t-Bu)$_2$ and t-BuOCO$_2$CuCN-t-Bu which are described in the next section. In other words, **2** functions as a reversible CO_2 carrier. Figure 1 illustrates this interesting behavior obtained by means of gasometry. An alternate process of heating and cooling a toluene solution of **2** under nitrogen in a closed vessel effected a cycle of CO_2 evolution and absorption.

Few reports which describe the CO_2 insertion into a transition metal–oxygen bond affording isolable complexes have been published. Bicarbonato complexes of [M(OCO$_2$H)(CO)(PPh$_3$)$_2$] (M = Ir(I), Rh(I)) are thermally stable, producing no change on pumping for months.[8] Compound **2** is distinguished from these precedents by its interesting feature of the instability of the inserted CO_2 molecule.

In the biological biotin-dependent carboxylations, the carboxybiotinyl–enzyme reversibly formed by carboxylation of the biotinyl–enzyme in the presence of ATP is known to function as a carrier of activated CO_2 (eq 2).[9] Very recently,

Table II. Ir Data (cm^{-1}) of Reversible CO_2 Fixation by t-BuOCO$_2$Cu(CN-t-Bu)$_n$ in Benzene[a]

Complexes	Reaction conditions	ν(N≡C)	ν(OCO$_2$-t-Bu)	ν(CuO-t-Bu)
t-BuOCO$_2$Cu(CN-t-Bu)$_3$[b]	Before decarboxylation	2160	1650, 1307, 1008	
	After decarboxylation (1.5-h reflux)	2132, 2109		938
	After carboxylation	2162	1656, 1309, 1010	
t-BuOCO$_2$Cu(CN-t-Bu)$_2$[c]	Before decarboxylation	2153	1656, 1302, 1005	
	After decarboxylation (65-min reflux)	2129, 2104		937
	After carboxylation	2156	1658, 1306, 1015	
t-BuOCO$_2$CuCN-t-Bu[c]	Before decarboxylation	2160, 2104[d]	1666, 1300, 1050	935[d]
	After decarboxylation (10-min reflux)	2107		937
	After carboxylation	2160, 2104[d]	1670, 1300, 1040	937[d]

[a] Ir spectra were taken at ambient temperature. [b] Isolated complex was used. [c] Prepared in benzene by carboxylating the reaction mixtures of t-BuOCu + 2t-BuNC and t-BuOCu + t-BuNC, respectively. [d] These absorptions mean incomplete carboxylation.

$$CO_2 + \text{biotinyl-enzyme} \rightleftharpoons \text{carboxybiotinyl-enzyme}$$

$$\text{carboxybiotinyl-enzyme} + \text{substrate} \rightarrow \text{biotinyl-enzyme} + \text{carboxy-substrate} \qquad (2)$$

2 has been found to act as a carrier of activated CO_2 (eq 3[10] and eq 4[11]). Exploration of the CO_2 transfer to various

$$t\text{-BuOCO}_2\text{Cu(CN-}t\text{-Bu)}_3 \xrightarrow[\text{tetralin, } N_2]{120\text{–}130\ ^\circ C} CO + t\text{-BuNCO} + t\text{-BuOCuCN-}t\text{-Bu} + t\text{-BuNC} \qquad (3)$$

$$t\text{-BuOCO}_2\text{Cu(CN-}t\text{-Bu)}_3 \xrightarrow[\text{toluene, room temp}]{HN(SiMe_3)_2} (t\text{-BuNC})_3\text{CuNCO} + O(SiMe_3)_2 + t\text{-BuOH} \qquad (4)$$

organic substrates using the reversibly CO_2-fixing transition metal complexes is an attractive research subject in which isolation and characterization of this type of transition metal complexes are important.

Effect of the Number of *tert*-Butyl Isocyanide Ligands upon Stability of the Inserted CO_2 Molecule in the *t*-BuOCO₂ group. To investigate the effect of the number of *tert*-butyl isocyanide ligands upon the CO_2 insertion into copper(I) *tert*-butoxide, preparations of t-BuOCO$_2$CuCN-t-Bu (**3**) and t-BuOCO$_2$Cu(CN-t-Bu)$_2$ (**4**) by carboxylating the **1** and **1** + t-BuNC systems were attempted.

In addition to the bands due to the unreacted complex of **1** (ν(CuO-t-Bu) 935 cm^{-1}, ν(N≡C) 2104 cm^{-1}), the ir spectrum obtained by carboxylation of **1** in benzene showed the ν(OCO$_2$-t-Bu) band at 1666, 1300, and 1050 cm^{-1} which is slightly different from those of **2** and **4** (Table II). This finding suggests that carboxylation of **1** in benzene without an additional *tert*-butyl isocyanide was incomplete under usual conditions to give an equilibrium mixture of **1** and **3** (see eq 5). The CO_2 molecule in **3** was readily removed in a reversible

$$\underset{1}{t\text{-BuOCuCN-}t\text{-Bu}} + CO_2 \overset{C_6H_6\text{, room temp}}{\rightleftharpoons} \underset{3}{t\text{-BuOCO}_2\text{CuCN-}t\text{-Bu}} \quad (5)$$

way be refluxing a benzene solution of **3** under nitrogen only for 10 min. Evaporation of the benzene solution containing **1** and **3** at 0 °C in vacuo resulted in a complete decarboxylation to regenerate the starting complex of **1**, while **2** and **4** did not undergo complete decarboxylation under similar conditions (vide infra).

In contrast, carboxylation of **1** with one additional *tert*-butyl isocyanide proceeded to completion in benzene (Table II) to yield **4**. The possibility of intervention of **2** in this reaction by disproportionation, $2t$-BuOCO$_2$Cu(CN-t-Bu)$_2$ ⇌ t-BuOCO$_2$Cu(CN-t-Bu)$_3$ + t-BuOCO$_2$CuCN-t-Bu, may be excluded on the basis of the absence of the characteristic ir absorption of **1** which must concomitantly be formed in equilibrium with **3**. Although **4** is stable in benzene solution at ambient temperature, removal of the solvent caused partial decarboxylation and disproportionation of the *tert*-butyl isocyanide ligand to produce a white solid consisting of an equimolar mixture of **1** and **2** (Scheme I). The experimental evidence supporting Scheme I is as follows. (i) The resulting white solid was identified: Cu content by iodometry 19.5% (calcd 19.6%); CO_2 content by acidolysis 103%; ir (Nujol) 2160, 2102 cm^{-1} (ν(N≡C)), 938 cm^{-1} (ν(CuO-t-Bu)), 1650, 1310, 1015 cm^{-1} (ν(OCO$_2$-t-Bu)); NMR (C_6H_6) τ 8.20 (singlet, broad, 18 H, t-BuO), 9.05 (singlet, 36 H, t-BuNC). (ii) The equimolar mixture of **1** and **2** obtained by evaporation of a benzene solution of **4** was carboxylated in benzene to regenerate the original ir spectrum of **4**. (iii) In the presence of an equimolar amount of **2**, **1** underwent a quantitative carboxylation in benzene. A reasonable explanation for Scheme I is that, on removing benzene in vacuo at 0 °C, **4** releases CO_2 to produce **1** and one free *tert*-butyl isocyanide which subsequently is coordinated to another molecule of **4** to form the stable, coordinatively saturated complex **2**.

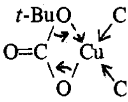
Scheme I

$$\underset{1}{t\text{-BuOCuCN-}t\text{-Bu}} + t\text{-BuNC} + CO_2 \xrightarrow{C_6H_6} \underset{4}{t\text{-BuOCO}_2\text{Cu(CN-}t\text{-Bu)}_2}$$

$$\underset{C_6H_6,\ ^1/_2CO_2}{\overset{-C_6H_6,\ -^1/_2CO_2}{\rightleftharpoons}} \ ^1/_2\underset{2}{t\text{-BuOCO}_2\text{Cu(CN-}t\text{-Bu)}_3} + \ ^1/_2\underset{1}{t\text{-BuOCuCN-}t\text{-Bu}}$$

On the basis of the results obtained, it may be concluded that the stability of the CO_2 molecule in the t-BuOCO$_2$ group estimated by the extent of carboxylation and the ease of decarboxylation is diminished by decreasing the number of the *tert*-butyl isocyanide ligands from 3 to 1. This conclusion may be understood by the σ-donating effect of the ligand as described previously. In addition, the stability of the t-BuOCO$_2$ group may be discussed in terms of aggregation of the copper complexes.

Several copper alkoxides are known to be present in highly polymerized forms by the copper–oxygen–copper bridge.[12] Copper(I) *tert*-butoxide also is supposed to be associated on the basis of its relatively low solubility and sublimability (ca. 170 °C (1 mm)).[13] Although **1** is soluble in common organic solvents and sublimable under relatively mild conditions (ca. 90 °C (1 mm)), it has a degree of association of about 4–5 in cyclohexane. This finding suggests that the t-BuOCu moiety has the tendency to aggregate. As is described previously, **2** is coordinatively saturated and monomeric. On the other hand, **4** is coordinatively unsaturated and polymerizable. It may be assumed that an intramolecular (for example, eq 6) or intermolecular coordination of the t-BuO moiety of the t-BuOCO$_2$ group to the vacant site on copper promotes the decarboxylation to form the stable aggregate of **1**. Compound **4** is stabilized toward decarboxylation in benzene which may be considered to prevent the coordination of the t-BuO group onto copper by solvation of the t-BuOCO$_2$ group. According to this explanation, more facile decarboxylation of **3** is understandable. Formation of the stable aggregate of **1** also may be a driving force of the decarboxylation of **2**. In conclusion, it is interesting that the stability of the CO_2 molecule fixed in the transition metal complex can be controlled by the number of other ligands coordinated.



$$\rightarrow t\text{-BuOCuCN-}t\text{-Bu} + CO_2 + t\text{-BuNC} \qquad (6)$$

Experimental Section

Infrared spectra were recorded with a Hitachi EPI-G3 grating spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Hitachi R-20B spectrometer. Analytical GLC analyses were performed on Shimadzu 4APT and GC-2C instruments with a thermal conductivity detector. Carbon dioxide analysis was carried out by GLC using an activated charcoal column, hydrogen carrier gas, and methane as an internal standard. Iodometry and cryoscopy were carried out using conventional methods. *tert*-Butyl isocyanide was prepared according to Ugi's procedure.[14] Benzene and toluene were distilled from calcium hydride under nitrogen. Carbon dioxide was a commercial gas reagent (assay: minimum 99.99 vol %) which was supplied from Seitetsu Kagaku Co. and was used without further purification. Allyl bromide was treated with molecular sieves and deoxygenated using a stream of nitrogen. Tri-*n*-butylphosphine, triethylphosphine, triphenylphosphine, and trimethyl phosphite were commercial reagents and used after deoxygenation by a stream of nitrogen.

Preparation of Copper(I) *tert*-Butoxide.[13] In a sublimation apparatus, commercial anhydrous cuprous chloride (2.18 g, 22.0 mmol), lithium *tert*-butoxide (1.60 g, 20.0 mmol), and 25 ml of anhydrous tetrahydrofuran were stirred overnight at ambient temperature under nitrogen atmosphere. The solvent was removed under reduced pressure and a resulting yellow solid was subjected to sublimation at 170 °C (0.8 mm) to give pale yellow crystals of copper(I) *tert*-butoxide (2.32 g, 17 mmol).

Preparation and Identification of 2. In a glovebox filled with nitrogen, copper(I) *tert*-butoxide (0.732 g, 5.36 mmol) was placed in a 200-ml flask equipped with a three-way stopcock. Benzene (20 ml) and *tert*-butyl isocyanide (1.34 g, 16.1 mmol) were added using a hypodermic syringe through the three-way stopcock under a countercurrent stream of nitrogen. The flask was kept at 10 °C and the benzene solution was magnetically stirred. CO_2 (187 ml, 8.04 mmol) was introduced through the serum-stoppered three-way stopcock using a hypodermic syringe. After the reaction mixture was stirred at 10 °C for 3 h, it was solidified by cooling to 0 °C and was evaporated in vacuo at 0 °C to remove benzene. A white solid of **2** was obtained: Cu (iodometry) 15.1% (calcd. for **2** 14.8%); ir (Nujol) 2160 cm^{-1} (ν(N≡C), 1650, 1310, 1013 cm^{-1} ($\nu(OCO_2\text{-}t\text{-Bu})$); NMR ($C_6D_6$) τ 9.05 (singlet, 27 H, *t*-BuNC), 8.25 (singlet, 9 H, *t*-BuO); CO_2 content (CO_2 gas evolution by acidolysis with 60% sulfuric acid) 99%. Compound **2** (0.190 g, 0.441 mmol) was reacted with allyl bromide (0.15 ml, 1.76 mmol) in 5 ml of benzene at 50 °C for 1 h to produce allyl *tert*-butyl carbonate in 95% yield: NMR (C_6D_6) τ 5.60 (methylene protons of allylic group, 2 H), 4.00–5.30 (vinyl protons of allylic group, 3 H), 8.70 (*t*-Bu group, 9 H); ir (liquid film) 3080 cm^{-1}, 1645 cm^{-1} (terminal vinyl group), 1740 cm^{-1} (ν(C=O)).

Formation of 1 by the Reaction of Copper(I) *tert*-Butoxide and an Excess of *tert*-Butyl Isocyanide. Under nitrogen, copper(I) *tert*-butoxide (0.089 g, 0.65 mmol), *tert*-butyl isocyanide (0.22 ml, 1.95 mmol), and 5 ml of benzene were stirred under nitrogen at ambient temperature for 30 min. Evaporation of benzene under reduced pressure produced a pale yellow solid, whose ir and NMR spectra agreed with those of the authentic sample of **1**: NMR (C_6D_6) τ 8.11 (singlet, 9 H, *t*-BuO), 9.02 (singlet, 9 H, *t*-BuNC); ir (Nujol) 2102 cm^{-1} (ν(N≡C)) 1220, 1195 cm^{-1} (ν(*t*-Bu)), 945 cm^{-1} (ν(*t*-BuO)).

Effect of Ligand upon CO_2 Insertion. As a typical procedure, the reaction of copper(I) *tert*-butoxide and CO_2 using tri-*n*-butylphosphine as a ligand is illustrated here. In a 100-ml, two-necked flask equipped with a three-way stopcock and a serum stopper, copper(I) *tert*-butoxide (0.158 g, 1.16 mmol), tri-*n*-butylphosphine (0.87 ml, 3.48 mmol), and 3 ml of benzene were stirred under nitrogen at ambient temperature. CO_2 (36.3 ml, 1.51 mmol) and methane (36.3 ml, 1.51 mmol) as the GLC internal standard were added using a hypodermic syringe. After 1 h, the gaseous phase of the reaction mixture was analyzed by GLC. CO_2 gas (28.0 ml, 1.16 mmol) was absorbed by the copper(I) *tert*-butoxide–tri-*n*-butylphosphine complex. In the case of triphenylphosphine, $t\text{-BuOCO}_2\text{Cu(PPh}_3)_3$ complex was isolated. It quantitatively evolved CO_2 on acidolysis and showed ir absorptions due to the $t\text{-BuOCO}_2$ group at 1646, 1305, and 1017 cm^{-1}.

Reversible CO_2 Uptake by Copper(I) *tert*-Butoxide–*tert*-Butyl Isocyanide Complex. (a) Gasometric Method. In a 100-ml, serum-stoppered flask, copper(I) *tert*-butoxide (0.0339 g, 0.248 mmol), *tert*-butyl isocyanide (0.083 ml, 0.744 mmol), and 5 ml of toluene were stirred under nitrogen at ambient temperature. CO_2 (15 ml, 0.609 mmol) and methane (5.0 ml, 0.203 mmol) as internal standard were added with hypodermic syringes. The gaseous phase was analyzed for CO_2 absorption by GLC after 30 min and 1 h, respectively. Then, the flask was placed in a water bath of 70 °C and the gaseous phase was analyzed after 30 min and 1 h, respectively. The flask was removed from the water bath and was cooled with a stream of water. The reaction mixture was stirred at ambient temperature for GLC gas analysis. These procedures were repeated.

(b) Infrared Spectroscopic Method. In a 100-ml, two-necked flask equipped with a reflux condenser, the isolated complex of **2** (1.80 g, 4.18 mmol) was dissolved in 13 ml of benzene under nitrogen. An aliquot of the benzene solution was removed and subjected to ir measurement. Then, the benzene solution was refluxed for 1.5 h under a stream of nitrogen which was passed through a three-way stopcock on the top of the reflux condenser. After the reaction mixture was cooled to ambient temperature, the ir spectrum of an aliquot of the resulting solution was measured. After CO_2 (120 ml, 5.16 mmol) was introduced to the flask through the serum-capped three-way stopcock, the benzene solution was magnetically stirred for 1 h at ambient temperature. Then, the ir spectrum of the resulting reaction mixture was taken. The results of ir measurements are listed in Table II. The reversible CO_2 fixations by the systems *t*-BuOCu (0.223 g, 1.64 mmol)–2*t*-BuNC and *t*-BuOCu (0.136 g, 0.993 mmol)–*t*-BuNC were similarly carried out.

Carboxylation of 1. According to the described procedure, copper(I) *tert*-butoxide (0.136 g, 0.993 mmol), *tert*-butyl isocyanide (0.111 ml, 0.993 mmol), and 3.6 ml of benzene in a 100-ml flask were reacted with CO_2 (90 ml, 3.87 mmol) at 10 °C for 3 h. Removal of benzene in vacuo at 0 °C produced a pale yellow solid whose ir spectrum was the same as that of the authentic sample of **1**.

Carboxylation of the System of *t*-BuOCu–2*t*-BuNC. A mixture of copper(I) *tert*-butoxide (0.300 g, 2.19 mmol), *tert*-butyl isocyanide (0.491 ml, 4.38 mmol), and 8 ml of benzene in a 200 ml-flask was reacted with CO_2 (209 ml, 8.76 mmol) at 10 °C for 1 h. Evaporation of benzene under reduced pressure at 0 °C produced a white solid of an equimolar mixture of **1** and **2**: Cu (iodometry) 19.5% (calcd. for **1** + **2** 19.6%); CO_2 content (CO_2 gas evolution by acidolysis with 60% sulfuric acid) 103%; ir (Nujol) 2160, 2102 cm^{-1} (ν(N≡C)), 938 cm^{-1} (ν(O-*t*-Bu)), 1650, 1310, 1015 cm^{-1} ($\nu(OCO_2\text{-}t\text{-Bu})$); NMR ($C_6D_6$) τ 8.20 (singlet, broad, 18 H, *t*-BuO), 9.05 (singlet, 36 H, *t*-BuNC).

Carboxylation of an Equimolar Mixture of 1 and 2. In a 200-ml, two-necked flask, equipped with a three-way stopcock and a serum stopper, 4 ml of benzene solution containing **2** (0.172 g, 0.400 mmol) and 1 ml of a benzene solution of **1** (0.088 g, 0.400 mmol) were mixed under nitrogen. CO_2 gas (90 ml, 3.65 mmol) was added. The reaction mixture was stirred for 1.5 h at ambient temperature. An aliquot of the resulting benzene solution showed the same ir spectrum as that obtained in the carboxylation of the system *t*-BuOCu–2*t*-BuNC.

Registry No. 1, 53513-39-6; **2**, 59922-80-4; $t\text{-BuOCO}_2\text{Cu(CN-}t\text{-Bu)}_2$, 59922-81-5; $t\text{-BuOCO}_2\text{CuCN-}t\text{-Bu}$, 59922-82-6; $t\text{-BuOCO}_2\text{Cu(P(}n\text{-Bu)}_3)_3$, 59922-83-7; $t\text{-BuOCO}_2\text{Cu(PPh}_3)_3$, 59922-84-8; $t\text{-BuOCO}_2\text{Cu(P(OMe)}_3)_3$, 59922-85-9; CO_2, 124-38-9.

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