Reactions of CO_2 with Cu(I) Alkoxides and Amides to Give Alkylcarbonato-, μ-Carbonato-, Hydrogencarbonato-, and Carbamato-copper Complexes

Takakazu YAMAMOTO, Minoru KUBOTA, and Akio YAMAMOTO*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227

(Received September 13, 1979)

Carbon dioxide reacts with $ROCu(PPh_3)_2$ ($R=C_2H_5$, $C_6H_5CH_2$; PPh_3=triphenylphosphine) to produce $ROCO_2Cu(PPh_3)_2$. Hydrolysis or thermolysis of the alkylcarbonatocopper(I) complexes gives a binuclear carbonatocopper(I) complex $(PPh_3)_2CuOCO_2Cu(PPh_3)_2$, which is further converted into a hydrogencarbonatocopper(I) complex $[HOCO_2Cu(PPh_3)_2]_n$ by the reaction with CO_2 in moist solvents. The IR spectrum of $[HOCO_2Cu(PPh_3)_2]_n$ shows association of the $HOCO_2Cu(PPh_3)_2$ units through hydrogen bonds. The IR spectrum of $[HOCO_2Cu(PPh_3)_2]_n$ also reveals that the mode of the association depends on conditions of the crystallization of the complex. The reaction of $(PPh_3)_2CuOCO_2Cu(PPh_3)_2$ with CH_3I gives $(CH_3O)_2CO$ and the reaction of $[HOCO_2Cu(PPh_3)_2]_n$ with $C_6H_5NH_2$ affords $C_6H_5NHCO_2Cu(PPh_3)_2$ in high yields. Carbon dioxide reacts also with an amidocopper(I) complex $C_6H_5NHCu(PPh_3)_2$ to yield a carbamatocopper(I) complex $C_6H_5NHCO_2Cu(PPh_3)_2$. The reaction of $CH_3Cu(PPh_3)_2$(diethyl ether)$_{0.5}$ with CO_2 in the presence of $HN(C_2H_5)_2$ affords $(C_2H_5)_2NHCO_2Cu(PPh_3)_2$. The isocyanate group of phenyl isocyanate is inserted into the C_2H_5O–Cu bond of $C_2H_5OCu(PPh_3)_2$ to give a (ethyl *N*-phenylcarbamato)copper complex.

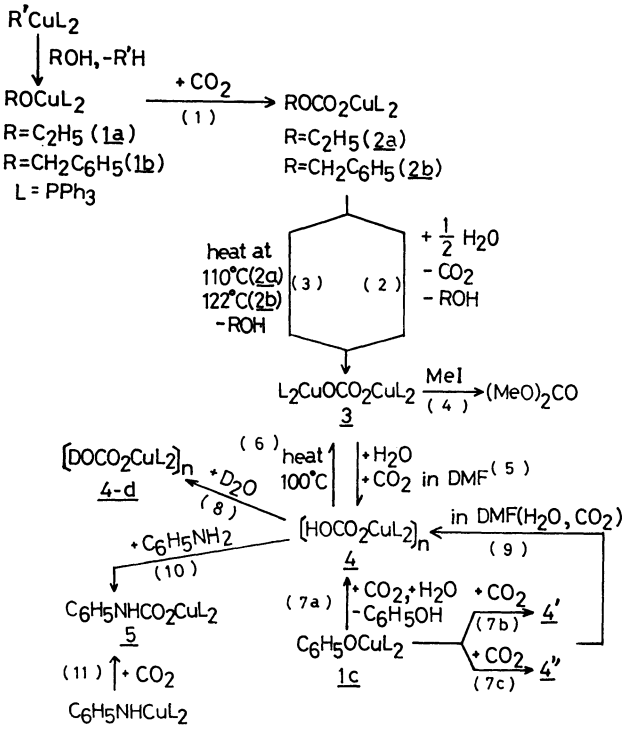
Considerable attention has been focused on the reactions of carbon dioxide with transition metal complexes from the interest of utilizing carbon dioxide for organic syntheses promoted by transition metal complexes.[1-6] Carbon dioxide has been reported to be inserted into metal–carbon,[1d,7-13] –hydride,[1d,14-16] –alkoxide,[17] –hydroxide,[18] and –amide[19] bonds to form carboxylato, alkylcarbonato, hydrogencarbonato, and carbamato complexes.

As a part of our program of studies on the reactivity of copper(I) complexes having Cu–C,[20] Cu–N,[21] Cu–O[22] or Cu–S[11] bonds we have studied[23] also the reaction of CO_2 with $ROCu(PPh_3)_2$ ($R=C_2H_5$, $CH_2C_6H_5$) and expanded the work to investigate the chemical properties of the produced alkylcarbonatocopper(I) complex. The result was compared with the reaction of CO_2 with copper(I) amides and with the reaction of phenyl isocyanate, an isoelectronic compound of CO_2, with a copper ethoxide.

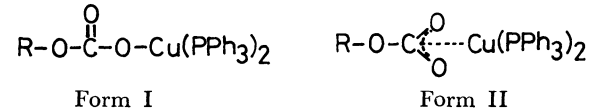
Results and Discussion

Reactions of CO_2 with Alkoxocopper(I) Complexes. Reactions of carbon dioxide with alkoxocopper(I) complexes containing triphenylphosphine are summarized in Scheme 1.

Reactions of $C_2H_5OCu(PPh_3)_2$(**1a**)[22a] and $C_6H_5CH_2OCu(PPh_3)_2$(diethyl ether)(**1b**)[22a] with CO_2 at atmospheric pressure and at low temperatures afforded $C_2H_5OCO_2Cu(PPh_3)_2$(**2a**) and $C_6H_5CH_2OCO_2Cu(PPh_3)_2$ (**2b**) (Reaction 1). Very recently a similar reaction of CO_2 with copper(I) *t*-butoxide, *t*-C_4H_9OCu, in the presence of ligands was reported.[17a] Analytical data of **2a** and **2b** (Table 1) agree with the compositions for the alkylcarbonato copper having two PPh_3 ligands. The color and diamagnetism of **2a** and **2b** indicate that the oxidation state of copper is one. Table 2 summarizes the IR absorption bands of the alkylcarbonatocopper(I) and related complexes. Complexes **2a** and **2b** show strong ν(C=O) and ν(C–O) bands at 1660 cm^{-1} and in the region of 1380—1280 cm^{-1}, respectively, and $\pi(CO_3)$ near 800 cm^{-1}.[24] The IR pattern is consistent with the molecular formula and can be compared with those of alkylcarbonatomagnesiums, *t*-butylcarbonatocopper(I),[17a] bis(methylcarbonato)copper(II),[17b] and methyl(methylcarbonato)palladium[25] complexes. The appearance of the ν(C=O) band at a relatively high frequency suggests the coordination of the $ROCO_2$ ligand through one oxygen as represented by Form I.



Scheme 1.



Form I Form II

Table 1. Analytical data of alkylcarbonato, carbonato, hydrogencarbonato, and related copper(I) complexes

Complex	Color	Dp[a] °C	C[b]	H[b]	N[b]	Cu[b]	CO_2/Cu	mol wt[b]
$C_2H_5OCO_2Cu(PPh_3)_2$	White	110[c]	69.2	5.2		9.2	0.41[c]	621
2a		(162)[d]	(69.2)	(5.2)		(9.4)	(0.92)[d]	(677)
$C_6H_5CH_2OCO_2Cu(PPh_3)_2$	White	120—122[c]	70.7	5.3		8.5	0.43[c]	685
2b		(162)[d]	(71.5)	(5.1)		(8.6)	(0.85)[d]	(739)
$(PPh_3)_2CuOCO_2(PPh_3)_2$	White	162	70.9	5.3		10.0	0.48	1140
3			(70.9)	(4.9)		(10.3)		(1240)
$[HOCO_2Cu(PPh_3)_2]_n$	White	*ca.* 100[c]	67.8	4.7		9.5	0.42[c]	
4		(153)[d]	(68.5)	(4.8)		(9.8)	(0.91)	
$[HOCO_2Cu(PPh_3)_2]_n$	White	(150)[d]	68.8	5.0		9.5		821
4′			(68.5)	(4.8)		(9.8)	(0.83)[d]	(650)[e]
$[HOCO_2Cu(PPh_3)_2]_n$	White	(159)[d]	68.1	4.7		9.6		793
4″			(68.5)	(4.8)		(9.8)	(0.77)[d]	(650)[e]
$C_6H_5NHCO_2Cu(PPh_3)_2$	White	205—207	70.5	5.2	2.0			
5			(71.3)	(5.0)	(1.9)			
$(C_2H_5)_2NCO_2Cu(PPh_3)_2\cdot\frac{1}{2}Et_2O$	White	134—135	66.4	5.7	1.7			
6			(67.3)	(5.8)	(1.8)			
$(C_6H_5NCOOC_2H_5)Cu(PPh_3)_2$	White	63—64	72.1	5.4	2.8			668
7			(71.9)	(5.3)	(1.9)			(751)

a) Decomposition point. b) Calculated values in the parentheses. c) Data for the conversion of the complexes into **3** on heating them. d) Data for the complete thermolysis of the complexes. e) Calcd value for $n=1$.

Table 2. IR and NMR spectral data of the complexes

Complex	Frequencies in cm^{-1}				NMR(δ, ppm)[a]
	ν(C=O)	ν(C-O)	$\pi(CO_3)$	ν(O-H)	
2a	1660 s	1380 m	800 m		1.12(3H, t, CH_3), 4.12(2H, q, CH_2),
		1285 m			7.0(18H, *o*-, *p*-phenyl), 7.6(12H, *m*-phenyl)
2b	1660 s	1380 m	805 m		5.20(2H, s, CH_2), 7.0(23H, *o*-, *p*-phenyl(PPh_3) +
		1280 s			$CH_2C_6\underline{H}_5$), 7.6(12H, *m*-phenyl(PPh_3))
2a′	1600 s	1390 m	810 m		
		1300 s			
3		1475 s	830 m		*ca.* 7.2(phenyl)
		1340 s			
4	1610 s	1400 m	820 m	2670 sh	
		1320 s		2600 m	
4′	1610 s	1400 m	820 m	2610 w	
	1640 s	1300 s			
	1595 s				
4″	1595 s	1445 sh	820 m	2600 w, br	
		1350 w			
5	1600 s	1420 s	815 sh		6.7—7.2(5H, N-$C_6\underline{H}_5$, *ca.* 7.3(phenyl(PPh_3)),
	1580 s	1350 s	795 m		8.1(1H, s, N$\underline{H}$)
6	1550 s	1400 s	795 m		1.08(9H, N-$CH_2C\underline{H}_3$ and O-$CH_2C\underline{H}_3$),
		1290 s			3.22(2H, O-CH_2), 3.56(4H, N-CH_2),
					7.0(18H, m, *p*-phenyl), 7.6(12H, *o*-phenyl)
7	1590 m				1.04(3H, t, CH_3), 4.48(2H, q, CH_2),
					7.0(23H, m, *p*-H of PPh_3 and N-$C_6\underline{H}_5$),
					7.6(12H, *o*-H of PPh_3)

a) Solvent: C_6D_6 for **2a**, **2b**, and **7**; CD_2Cl_2 for **3** and **5**; toluene-d_8 for **6**.

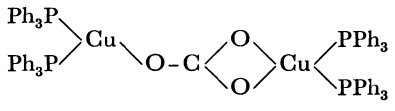
However, the coordinating mode of the alkylcarbonato ligand to Cu changes depending on delicate conditions of crystallization. For example, addition of hexane to a diethyl ether–ethyl alcohol (1:1) solution of **2a** gives complex **2a'** with the same composition as **2a** but with the different IR spectrum of **2a'** showing the ν(C=O) bands at considerably lower frequency, 1600 cm^{-1}. The lowering of ν(C=O) band suggests that the $C_2H_5OCO_2$ ligand in **2a'** coordinates to Cu through two oxygens as represented by Form II or the C–O oxygen has intermolecular interaction with Cu to form a polymeric compound in the solid state. Complex **2a'** can be reverted to **2a** by crystallization of **2a'** from toluene–ether. Cryoscopic molecular weight determination of **2a** and **2b** in dioxane (Table 2) reveals that they exist as monomers in the solutions. The somewhat lower observed values than the calculated molecular weights suggest partial dissociation of PPh_3 from the complexes. The reaction of ethyl bromide with **2a** affords diethyl carbonate in 10% yield. Although the formation of the alkylcarbonato complexes can be formally explained as insertion of CO_2 into the RO–Cu bond, the possibility of an indirect route as shown below promoted by intervention of a small amount of water cannot be ruled out.

$$ROCuL_2 + H_2O \rightarrow HOCuL_2 + ROH \quad (12)$$

$$ROH + CO_2 \rightleftharpoons ROCO_2H \quad (13)$$

$$ROCO_2H + HOCuL_2 \rightarrow ROCO_2CuL_2 + H_2O \quad (14)$$

Hydrolysis of **2a** or **2b** yields a μ-carbonatocopper(I) complex formulated as $(PPh_3)_2CuOCO_2Cu(PPh_3)_2$ (Reaction 2). Heating of **2a** and **2b** at 110 °C and 122 °C respectively also gives the carbonato complex, CO_2, and ROH (Reaction 3), but the source of hydrogen for ROH and stoichiometry of Reaction 3 have not been clarified. Recently similar dinuclear complexes having μ-carbonato ligand coordinated through one and two oxygens to two transition metals have been reported.[26,27] Similarlity of the IR spectrum of **3**, showing carbonato bands at 1480, 1370, and at 835 cm^{-1}, with those of $Pd_2Me_2(CO_3)(PPh_3)_3$[26] and $Rh_2(CO_3)(PPh_3)_5$,[27] for which the singly and doubly O-bonded structures have been established, suggests an unsymmetric structure as shown below.



3

The IR spectrum of a symmetrical singly O-bonded μ-carbonatorhodium complex $Rh_2(CO)_2(CO_3)L_4$,[28] showing the carbonato bands at 1533, 1300, 1275, and 829 cm^{-1}, is somewhat different from those of the unsymmetrical carbonato complexes. The presence of two PPh_3 per Cu in **3** has been confirmed not only by elemental analysis but also by an NMR technique using acetone as a reference. Cryoscopic molecular weight determination in dioxane demonstrates that **3** remains binuclear in the solvent, although the somewhat low observed value for **3** suggests a partial dissociation of PPh_3 from **3** in the solution. The carbonato complex **3** has a higher thermal stability than **2a**, **2b**, and a hydrogencarbonatocopper(I) complex $HOCO_2Cu(PPh_3)_2$ **4** (*vide infra*) and thermolysis at 162 °C liberates *ca.* 1 mol of CO_2 per **3**.

Although the postulated structure for **3** indicates the presence of two different $Cu(PPh_3)_2$ moieties, ^{31}P-NMR shows only one sharp peak at 1.62 ppm (half width=7 Hz) downfield from external PPh_3 even at −83 °C in toluene. Rapid intramolecular exchange of the CO_3 group between two CuL_2 moieties or rapid exchange of the coordinated PPh_3 with free PPh_3 partly liberated from **3** accounts for the ^{31}P-NMR data. The rapid exchange between the coordinated PPh_3 and free PPh_3 certainly takes place in the presence of PPh_3 added as the ^{31}P-NMR spectrum of a mixture of **3** and PPh_3 (1:4 molar ratio) shows only one relatively broad signal at 1.16 ppm (half width=38 Hz) downfield from external PPh_3 at −63 °C. The reaction of **3** with CH_3I affords dimethyl carbonate in 82% yield (Reaction 4).

The reaction of **3** with H_2O in the presence of CO_2 in *N,N*-dimethylformamide (DMF) yields a hydrogencarbonatocopper(I) complex **4** (Reaction 5). Since **2a** and **2b** are converted into **3** (Eq. 2) by the hydrolysis and **3** is converted into **4** (Eq. 5) on standing them in solutions containing H_2O and CO_2, prolonged reaction of the alkoxocopper(I) complexes, **1a** and **1b**, with CO_2 in moist solvents is expected to yield directly the final product **4** through the serial Reactions 1, 2, and 5. This actually occurs in the reaction of **1a** with CO_2.

Similar reactions of a phenoxocopper(I) complex $PhOCu(PPh_3)_2$ **1c** with CO_2 in moist solvents also affords the hydrogencarbonatocopper(I) complex directly (Reaction 7a), but the IR spectrum of the complex varies depending on the preparative conditions and it was revealed that there are three types of complexes **4**, **4'**, and **4''** with the same composition $HOCO_2Cu(PPh_3)_2$.

$C_6H_5OCu(PPh_3)_2 + CO_2$ in moist THF

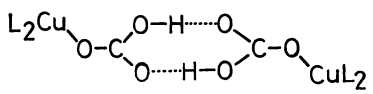
1c → **4** (7a) [−10—0 °C]

→ **4'** (7b)

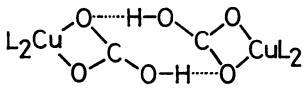
→ **4''** (7c) [−10—0 °C, $+10C_6H_5OH$; −30 °C]

In the case of the reaction of **1c** attempts for the isolation of the complexes of type **2** and **3** were not successful even by using solvents dried over Na, presumably due to the high reactivities of **2** and **3** with water under the preparative conditions by using **1c** as the starting material and to the difficulty to remove a trace of water from the solvents and CO_2 gas employed.

The IR absorption bands in the region of 2600 cm^{-1} ascribable to the bridging ν(O–H···O) band observed in the three hydrogencarbonato complexes **4**, **4'**, and **4''** suggest the presence of associated species for these complexes. There are at least two ways of association as depicted below, which have been established by X-ray crystallography for $[PdR(OCO_2H)L_2]_2$[29,30] and $[RhH_2(OCO_2H)L_2]_2$.[28]

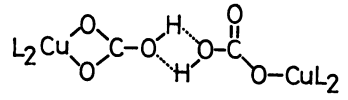


Form A[29]



Form B[28]

Other modes of association as illustrated below may be also possible.



Form C

Assignment of the hydrogencarbonato complexes **4**, **4'**, and **4''** to the respective associated forms is not possible solely on the basis of the IR spectra, but the complex **4'** showing the high ν(C=O) band at 1640 cm^{-1} may be related to a species having non-interacting C=O group such as that represented by Form C. On deuteriation of **4** by treating with D_2O (Reaction 8), the ν(O–H···O) bands at 2670 and 2600 cm^{-1} are shifted to 2100 and 2040 cm^{-1}, while a δ(OHO) band hidden under absorption bands of PPh_3 in a region of 1400—1500 cm^{-1} appears at 1060 cm^{-1} and a coupled vibration ν(C–O)+ν(C=O)+δ-(OHO) at 1325 cm^{-1} is shifted up to 1365 cm^{-1}. These trends are consistent with those observed for $[Rh(CO)(O_2COH)L_2]_2$[28] and hydrogencarbonato dimer anion.[31]

Formation of the hydrogencarbonato complexes **4**, **4'**, and **4''** depends on slight differences in experimental conditions. Complex **4'** or **4''** in a moist DMF solution can be converted into **4** by addition of a 1:1 mixture of hexane and diethyl ether to crystallize out **4** (Reaction 9). The existence of the hydrogencarbonatocopper(I) complexes **4'** and **4''** predominantly as a monomer in solution is demonstrated by the cryoscopic molecular weight determination of **4'** and **4''** as well as by the IR spectrum of **4''** in $CHCl_3$. The ν(O–H···O) band of **4''** at 2600 cm^{-1} disappears whereas new bands at 3300 cm^{-1} (ν(O–H)) and 1660 cm^{-1} (ν(C=O)) emerge on dissolving in $CHCl_3$, indicating that the hydrogen bond is cleaved in the solution.

$$[HOCO_2Cu(PPh_3)_2]_n \xrightarrow{\text{organic solvent}} n\,H\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}Cu(PPh_3)_2 \quad (15)$$

Complexes **4**, **4'**, and **4''** can be also obtained in the reactions of CO_2 with various organocopper(I) complexes such as cyanoethyl-,[32] nitroalkyl-,[32] and methylcopper(I)[20] complexes. Although it was previously reported that the reaction of the methylcopper-(I) complex $CH_3Cu(PPh_3)_2$(diethyl ether)$_{0.5}$ with CO_2 afforded $CH_3COOCu(CO_2)(PPh_3)_2$, whose characterization was based on the liberation of CH_3COOH and CO_2 upon acidolysis,[11] it has been later found that the product of the reaction was a mixture of $CH_3COOCu(PPh_3)_2$, **4'**, and **4''**. Heating of **4** at *ca.* 100 °C for 1.5 h yields the carbonato complex **3** (Reaction 6). The reaction of **4** with aniline affords a phenylcarbamatocopper(I) complex **5** in 79% yield (Reaction 10). The analytical data of **5** (Table 1) roughly agree with the formulation and the appearance of the ν(C=O) band at a relatively low frequency (Table 2) suggests the coordination of the carbamato ligand to copper through two oxygens. It is reported that the ν(C=O) absorption appears in a region of 1636—1680 cm^{-1} when a carbamato ligand coordinates to transition metal through one oxygen whereas the carbamato ligand coordinated through two oxygen gives rise to the ν(C=O) at lower frequencies.[19a]

Complex **5** may be formed through the condensation reaction between $C_6H_5NH_2$ and $HOCO_2$ ligand of **4** (Eq. 16) or through the formation of a phenylcarbamic acid by the reaction of $C_6H_5NH_2$ and CO_2 partly liberated from **4** (Eqs. 17a—17c).

$$C_6H_5\overset{H}{N}(H+HO)CO_2CuL_2 \longrightarrow C_6H_5NHCO_2CuL_2 + H_2O \quad (16)$$

(**4** → **5**)

$$\mathbf{4} \rightleftharpoons \underset{A}{HOCu(PPh_3)_2} + CO_2 \quad (17a)$$

$$\left.\begin{array}{l} C_6H_5NH_2 + CO_2 \rightleftharpoons C_6H_5NHCOOH, \\ \text{or} \\ 2C_6H_5NH_2 + CO_2 \rightleftharpoons C_6H_5NH_3{}^+C_6H_5NHCO_2{}^- \end{array}\right\} \quad (17b)$$

$$\left.\begin{array}{l} C_6H_5NHCOOH + A \rightleftharpoons \mathbf{5} + H_2O \\ \text{or} \\ C_6H_5NH_3{}^+C_6H_5NHCO_2{}^- + A \\ \qquad \rightarrow \mathbf{5} + C_6H_5NH_2 + H_2O \end{array}\right\} \quad (17c)$$

Equilibria of type 17b are known[33] and formation of carbamic acid has been proposed as the key step in an amine catalyzed exchange reaction between CO_2 and transition metal carbamates.[19b] Complex **5** affords a small amount (5 mol % per **5**) of ethyl phenylcarbamate by the reaction with C_2H_5I.

Reactions of Amidocopper(I) Complexes with CO_2. The reaction of phenylamidocopper(I) complex C_6H_5-$NHCu(PPh_3)_2$[21] with CO_2 gives the phenylcarbamatocopper(I) complex **5**. (Reaction 11). Reaction 11 may proceed through direct insertion of CO_2 into the Cu–N bond or an indirect route involving partial liberation of $C_6H_5NH_2$ from $C_6H_5NHCu(PPh_3)_2$ by the reaction with a trace of H_2O (Eq. 18) and formation of the carbamic acid (Eq. 17b).

$$C_6H_5NHCu(PPh_3)_2 + H_2O \rightleftharpoons HOCu(PPh_3)_2 + C_6H_5NH \quad (18)$$

$$C_6H_5NH_2 + CO_2 \rightleftharpoons C_6H_5NHCOOH \quad (17b)$$

$$HOCu(PPh_3)_2 + C_6H_5NHCOOH \rightarrow \mathbf{5} + H_2O \quad (19)$$

The formation of a carbamatocopper complex through the equilibrium of type 17b seems to occur in the reaction of $CH_3Cu(PPh_3)_2$(diethyl ether)$_{0.5}$ with diethylamine and CO_2.

$$CH_3Cu(PPh_3)_2(\text{diethyl ether})_{0.5} + (C_2H_5)_2NH + CO_2 \rightarrow \underset{\mathbf{6}}{(C_2H_5)_2NCOOCu(PPh_3)_2} \quad (20)$$

Although the interaction of the methylcopper complexes with N–H compounds generally affords amidocopper(I) complexes such as $C_6H_5NHCu(PPh_3)_2$ with

liberation of CH_4, the interaction of the methylcopper complex with diethylamine does not lead to the corresponding amidocopper(I) complex due to the too weak acidity of the hydrogen in $(C_2H_5)_2NH$.[21] Therefore the formation of **6** by Reaction 20 is considered to proceed most probably through the formation of diethylcarbamic acid which has acidic hydrogen. Similar behavior of methylpalladium complexes has been observed in the reactions with amines and CO_2.[26] The analytical data and IR and NMR spectral data of **6** agree with the formulation for **6**. Formation of methyl diethylcarbamate by the reaction of **6** with CH_3I in 58% yield also supports the formation of the carbamatocopper(I) complex.

Reactions of $CH_3Cu(PPh_3)_2$(diethyl ether)$_{0.5}$ with NH_3 and $C_6H_5NHNH_2$ under the bubbling of CO_2 also afford white copper complexes whose IR spectra show the formation of similar carbamatocopper(I) complexes. However, full characterization of the complexes were not successful due to the instability of complexes. The reaction of C_2H_5Br with the product of the reaction with NH_3 gives ethyl carbamate (20% based on copper).

$$CH_3Cu(PPh_3)_2(\text{diethyl ether})_{0.5} + NH_3 + CO_2 \rightarrow [NH_2COOCu(PPh_3)_2] \xrightarrow{C_2H_5Br} NH_2COOC_2H_5 \ (20\%) \quad (21)$$

It is reported that the reaction of $CuN(Si(CH_3)_3)_2$ with CO_2 affords copper(I) isocyanate.[34] However, no indication for the formation of copper(I) isocyanate complex was obtained in the reactions described above.

Insertion of Phenyl Isocyanate into the Cu–O Bond of ***1a***. Since phenyl isocyanate can be regarded as an isoelectronic compound of CO_2 and some examples of insertion of isocyanate into a metal–oxygen bond are known,[35] a reaction of phenyl isocyanate with the ethoxocopper(I) complex **1a** was examined to find out that **1a** undergoes a ready insertion of the isocyanate into the Cu–O at −10 to 0 °C to afford (ethyl phenylcarbamato-*N*-)copper(I) complex **7**.

$$\mathbf{1a} + C_6H_5\text{-}N{=}C{=}O \rightarrow C_6H_5\text{-}N(Cu(PPh_3)_2)\text{-}COOC_2H_5 \quad (22)$$

7

As for the direction of the insertion of the isocyanate group into the C–O bond, a reverse type of insertion to afford $C_6H_5N(OC_2H_5)COCu(PPh_3)_2$ is possible, although it is less likely in view of the probable polarization of the Cu–O bond as $Cu^{\delta+}$–$O^{\delta-}$.

Experimental

General Procedure and Material. Preparation and recrystallization of copper complexes were carried out under deoxygenated nitrogen or argon or under vacuum. Solvents were dried by usual methods, distilled, and stored under argon or nitrogen. IR spectra were recorded on a Hitachi Model 295 spectrometer. ^{1}H-NMR spectra were recorded on a Japan Electron Optics Lab. JNM-PS-100 spectrometer. TMS was used as the internal standard. ^{31}P-NMR spectra were obtained in the pulsed Fourier transform mode at 40.50 MHz. Identification of the evolved gas was made with a Hitachi RMU 5B mass-spectrometer and a Shimadzu GC-5B gas chromatograph, and the amount of gas was measured with a Toepler pump. The microanalysis of carbon, hydrogen, and nitrogen was performed by Mr. T. Saito in our laboratory with a Yanagimoto CHN Autocorder Type MT-2. The alkoxo and phenoxo copper complexes **1a**, **1b**, and **1c** were prepared as previously reported.[22a] Carbon dioxide was dried by passing through a cold trap cooled to −78 °C.

*Preparation of Ethylcarbonatobis(triphenylphosphine)copper(I) (**2a** and **2a′**).* The ethoxocopper(I) complex **1a** (630 mg, 1.0 mmol) was dissolved in a mixture of diethyl ether (5 ml) and ethyl alcohol (5 ml). The atmosphere in the reaction vessel was replaced with CO_2 (50 ml) at −40 °C. The mixture was stirred at −40——30 °C for 1 h to yield a transparent colorless solution. Concentration of the solution to about 5 ml by evaporation and addition of excess hexane gave a white precipitate. Recrystallization from toluene–diethyl ether yielded white crystals of **2a** (550 mg, 81%). Drying the white precipitate obtained from diethyl ether–ethyl alcohol–hexane in vacuum gave **2a′**.

*Preparation of Benzylcarbonatobis(triphenylphosphine)copper(I) (**2b**).* The benzyloxocopper(I) complex **1b** (1.3 g, 2.0 mmol) was dissolved in a mixture of diethyl ether (3 ml) and benzyl alcohol (2 ml). The gas in the reaction vessel was evacuated and then CO_2 (50 ml) was introduced at −30 °C. Stirring the mixture for 1 h at −30——20 °C afforded a transparent solution. Condensing the solution and addition of hexane (15 ml) gave a white precipitate. Recrystallization from diethyl ether–toluene containing a small amount of PPh_3 yielded 530 mg (yield=36%) of **2b**.

*Preparation of Tetrakis(triphenylphosphine)(μ-carbonato)dicopper-(I) (**3**).* The ethylcarbonatocopper(I) complex **2a** (250 mg, 0.37 mmol) was dissolved in 20 ml of THF. Water (14 mg, 0.75 mmol) was added to the solution and the solution was stirred for 0.5 h at room temperature to yield a white precipitate with liberation of C_2H_5OH (0.34 mmol) and CO_2 (0.17 mmol). Recrystallization from CH_2Cl_2–hexane gave **3** (150 mg, yield=88%).

*Preparation of Hydrogencarbonatobis(triphenylphosphine)copper(I) (**4**).* Complex **3** (310 mg, 0.25 mmol) was dissolved in 15 ml of DMF containing 0.5 ml of H_2O. The gas in the reaction vessel was evacuated and CO_2 (50 ml) was introduced at −30 °C. After stirring the solution for 2 h at −30 °C, an excess amount of diethyl ether was added and the solution was cooled to −70 °C to obtain a white precipitate, which was washed with diethyl ether repeatedly and dried in vacuum to yield 160 mg (yield=49%) of **4**. Deuteriation of **4** was performed by stirring a suspension of **4** in excess D_2O at room temperature.

*Preparation of Complex **4′**.* Immediately after addition of 0.5 ml of water into a THF solution (5 ml) containing $C_6H_5OCu(PPh_3)_2$ **1c** (0.34 g, 0.5 mmol) and C_6H_5OH (5 mmol), CO_2 gas was bubbled into the solution at −10 to 0 °C for 5 min to produce a white precipitate. The precipitate was washed repeatedly with diethyl ether and dried under vacuum to give a white complex of **4′** (272 mg, yield 84%).

*Preparation of Complex **4″**.* CO_2 gas was bubbled into a THF solution (5 ml) of a mixture of **1c** (340 mg, 0.5 mmol) and 0.5 ml of water at −30 °C for 5 min to produce a white precipitate, which was washed repeatedly with diethyl ether and dried in vacuum to yield 280 mg (yield=91%) of **4″**. Complexes **4**—**4″** were also prepared through the pathways described in the text.

*Preparation of Phenylcarbamatobis(triphenylphosphine)copper(I) (**5**).* The hydrogencarbonato complex **4** was dissolved in 10 ml of DMF containing 0.5 ml (5.5 mmol) of aniline. The mixture was stirred at −30 °C in an atmosphere of

CO_2. After 10 h diethyl ether and hexane were added to the solution and the mixture was cooled to −78 °C to produce a white solid, which was collected by filtration and dried in vacuum to yield 190 mg (yield=79%) of **5**.

Preparation of Diethylcarbamatobis(triphenylphosphine)copper(I) (6). Diethylamine (71 μl, 0.69 mmol) was added to $CH_3Cu(PPh_3)_2$ (diethyl ether)$_{0.5}$[20] suspended in 10 ml of diethyl ether. After evacuation of the gas in the reaction vessel, 100 ml of CO_2 was introduced at −20 °C and the mixture was stirred for 30 min at the temperature. The color of the solution turned from light yellow to white. Addition of hexane to the solution yielded 420 mg (yield=89%) of **6**.

Preparation of (Ethyl Phenylcarbamato-N-)bis(triphenylphosphine)-copper(I) (7). Phenyl isocyanate (2 mmol) was added into a flask containing **1a** (630 mg, 1 mmol) and the white emulsion was stirred at −10—0 °C for 5 h to produce a white precipitate. Recrystallization from diethyl ether–toluene gave white crystals of **7** (600 mg, yield=80%).

Thermolysis of the Complexes. A Schlenk type tube containing 260 mg (0.39 mmol) of **2a** was immersed in an oil bath and the temperature was raised gradually. The color of the complex was slightly changed from white to brown at 110 °C and evolution of CO_2 started at the temperature. Heating of the complex at 110 °C afforded 0.16 mmol of CO_2 (41 mol%/**2a**), 0.36 mmol of C_2H_5OH (92 mol%/**2a**), and 210 mg of a brownish solid, whose IR spectrum essentially coincided with that of **3** prepared by the acidolysis of **2a**. Heating of **2a** at higher temperature, 162 °C, caused further liberation of CO_2 (0.92 mol%/**2a**) coordinated to Cu. The other thermolyses of the complexes were carried out in similar manners and the amount of CO_2 evolved is given in Table 1.

Reactions of the Complexes with Alkyl Halides. Methyl iodide (5 ml) was added to a flask containing 640 mg (0.52 mmol) of **3** and the mixture was stirred overnight at room temperature. Gas chromatographic analysis of the reaction mixture showed the formation of 0.43 mmol (82 mol%/**3**) of dimethyl carbonate. The other reaction of the complexes with alkyl halides were carried out in similar manners.

References

1) (a) M. E. Vol'pin, *Pure Appl. Chem.*, **30**, 607 (1972); (b) M. E. Vol'pin, *Z. Chem.*, **12**, 361 (1972); (c) M. E. Vol'pin and I. S. Kolomnikov, *Pure Appl. Chem.*, **33**, 567 (1972); *Organomet. React.*, **5**, 313 (1975).

2) Y. Iwashita, *Kagaku Kogyo*, **23**, 1596 (1972).

3) (a) M. Kobayashi and S. Inoue, *Kagaku*, **28**, 942 (1973); (b) S. Inoue, *Sekiyu Gakkai Shi*, **17**, 199 (1974); (c) S. Inoue, "Miriyo-Shigen to Gosei-Kagaku, Kagaku-Zokan 63," Kagaku-Dojin (1974), p. 29.

4) M. Hidai, T. Hikida, and Y. Uchida, *Sekiyu Gakkai Shi*, **17**, 193 (1974).

5) T. Saegusa and T. Tsuda, *Kagaku Kogyo*, **26**, 562 (1975).

6) (a) T. Ito and A. Yamamoto, *Yuki Gosei Kagaku Kyokai Shi*, **34**, 308 (1976); (b) T. Ito and A. Yamamoto, "Organic and Bio-organic Chemistry of Carbon Dioxide," ed by S. Inoue and N. Yamazaki, Kodansha Ltd. Tokyo, in press.

7) V. Zucchini, E. Albizzati, and V. Giannini, *J. Organomet. Chem.*, **26**, 357 (1971).

8) H. H. Karsch, *Chem. Ber.*, **110**, 2213 (1977).

9) G. N. Schrauzer and J. W. Sibert, *J. Am. Chem. Soc.*, **92**, 3509 (1970).

10) I. S. Kolomnikov, H. Stepovskaya, S. Tyrlik, and M. E. Vol'pin, *Zh. Obshch. Khim.*, **42**, 1652 (1972).

11) A. Miyashita and A. Yamamoto, *J. Organomet. Chem.*, **113**, 187 (1976).

12) (a) T. Tsuda, K. Ueda, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, **1974**, 380; (b) T. Tsuda, H. Habu, and T. Saegusa, *ibid.*, **1974**, 620; (c) T. Tsuda, Y. Chujo, and T. Saegusa, *ibid.*, **1975**, 963.

13) T. Yamamoto and A. Yamamoto, *Chem. Lett.*, **1978**, 615.

14) (a) L. S. Pu, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **90**, 3896 (1968); (b) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *ibid.*, **93**, 317 (1971); (c) S. Komiya and A. Yamamoto, *J. Organomet. Chem.*, **46**, C58 (1972).

15) A. Misono, Y. Uchida, M. Hidai, and T. Kuse, *J. Chem. Soc., Chem. Commun.*, **1968**, 981.

16) I. S. Kolomnikov, A. I. Gusev, G. G. Aleksandrov, T. S. Lobeeva, Yu. I. Struchkov, and M. E. Vol'pin, *J. Organomet. Chem.*, **59**, 349 (1973).

17) (a) T. Tsuda, Y. Chujo, and T. Saegusa, 38th National Meeting of the Chemical Society of Japan, Nagoya, October 1978, 4G09; (b) T. Tsuda and T. Saegusa, *Inorg. Chem.*, **11**, 2561 (1972).

18) B. R. Flynn and L. Vaska, *J. Am. Chem. Soc.*, **95**, 5081 (1973).

19) (a) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **99**, 782 (1977); (b) M. H. Chisholm and M. W. Extine, *ibid.*, **99**, 792 (1977); (c) T. Tsuda, M. Miwa, and T. Saegusa, 37th National Meeting of the Chemical Society of Japan, Yokohama, April 1978, 4L41.

20) (a) A. Yamamoto, A. Miyashita, T. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **45**, 1583 (1972); (b) T. Ikariya and A. Yamamoto, *J. Organomet. Chem.*, **72**, 145 (1975); (c) A. Miyashita and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **50**, 1102 (1977).

21) T. Yamamoto, Y. Ehara, M. Kubota, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, in press.

22) (a) M. Kubota and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2909 (1978); (b) M. Kubota, T. Yamamoto, and A. Yamamoto, *ibid.*, **52**, 146 (1979).

23) A part of results described in this paper was reported in "3rd Symposium on the Utilization of Carbon Dioxide in Chemistry," Tokyo (1977), No. 19.

24) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York (1970), p. 169.

25) F. Ozawa, T. Ito, and A. Yamamoto, "4th Symposium on the Utilization of CO_2 in Chemistry," Kyoto (1978), No. 10.

26) F. Ozawa, T. Ito, and A. Yamamoto, *Chem. Lett.*, **1979**, 735.

27) S. Krogsrud, S. Komiya, T. Ito, J. A. Ibers, and A. Yamamoto, *Inorg. Chem.*, **15**, 2798 (1976).

28) T. Yoshida, D. L. Thorn, T. Okano, J. A. Ibers, and S. Otsuka, *J. Am. Chem. Soc.*, **101**, 4212 (1979).

29) R. J. Crutchley and J. Powell, *Inorg. Chim. Acta*, **24**, L15 (1977).

30) T. Ito, H. Tsuchiya, and A. Yamamoto, *Chem. Lett.*, **1976**, 851.

31) K. Nakamoto, Y. A. Sarma, and H. Ogoshi, *J. Chem. Phys.*, **43**, 1177 (1965).

32) T. Yamamoto, M. Kubota, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 1835 (1978).

33) (a) A. Jensen, M. B. Jensen, and C. Faurhold, *Acta Chem. Scand.*, **8**, 1129 (1954); (b) F. Calderazzo, G. Dell'Amico, R. Netli, and M. Pasquali, *Inorg. Chem.*, **17**, 471 (1978).

34) T. Tsuda, H. Washita, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, **1977**, 468.

35) A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, **1965**, 5238.