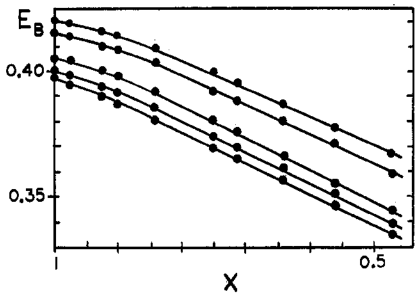

Figure 1.—Cell potential (E_B) in V for 0.0040 *M* solutions of bases in the solvent acetic acid–chlorobenzene. Mole fraction (X) refers to HOAc. Curves in descending order are for LiOAc, NaOAc, KOAc, RbOAc, and CsOAc.

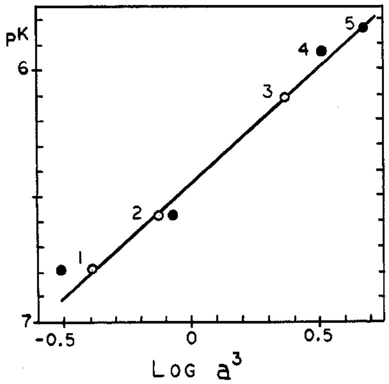

Figure 2.—The relationship of the MOAc ion-pair dissociation constant (pK_B) to the radius (a) of the cation: 1, Li^+; 2, Na^+; 3, K^+; 4, Rb^+; 5, Cs^+. Points ● are Goldschmidt radii and points ○ are radii reported by Waddington (radii in Å).

of the mole fraction of acetic acid in the mixed solvent (for constant C_B) shown in Figure 1 verifies the sequence of increasing degree of dissociation for the group Ia acetates found in acetic acid as the solvent. From a quantitative point of view, the difference between the E_B values of the weakest and strongest bases expressed as $\Delta = (E_B)_{Li} - (E_B)_{Cs}$ gradually increases from 23 mV in pure acetic acid to 32 mV in the mixed solvent having a mole fraction of 0.47 ($D = 5.87$). The comparable values for the differences $\Delta = (E_B)_{Li} - (E_B)_M$ for each metal acetate (MOAc) in the sequence were determined in acetic acid ($X = 1.00$) and in the mixed solvent ($X = 0.47$); and the equivalent E_B change (caused by the addition of chlorobenzene) expressed as a ΔpK_B amounts to no more than 0.11 for NaOAc, 0.34 for KOAc and RbOAc, and 0.41 unit for CsOAc.

It follows from eq 3 that the ion-pair dissociation constant when expressed as pK_B is a linear function of log a^3 with a slope of unity. If the dissociative equilibrium for the acetates involves contact ion pairs in acetic acid media, then one can make the initial assumption justified by Benson and Copeland,[12] namely, that the solution radii are nearly the same as crystal radii for singly charged metallic cations. Various procedures for calculating crystal radii have been reviewed recently by Masterton, Bolocofsky, and Lee;[13] however, for the alkali metal cations, the most important differences among the computed radii are found in the Li^+ and Na^+ values. In constructing Figure 2 the radii obtained by Goldschmidt (as summarized by Pauling[14]) and by Waddington[15] were used, and the empirical slope is 0.96 for the linear plot. When the Stokes radii for the gaseous cations[16] were substituted for crystal radii, the points in the pK_B *vs.* log a^3 graph were more scattered and linearity was uncertain.

In hydrogen-bonding solvents, including water, the order of increasing association of alkali metal salts with increasing cationic radius has been interpreted in terms of a systematic decrease in the extent of solvation of the cation with increasing ionic size.[1] This explanation is supported in part by the fact that the free energies of solvation of these cations[17] and their enthalpies of transfer[18] in both protonic solvents (including HOAc) and polar aprotic solvents follow a decreasing trend with increasing atomic number. By contrast, the reversed association sequence for group Ia acetates in anhydrous acetic acid (*i.e.*, Li > Na > K > Rb > Cs) suggests that the thermodynamic influence from variation in cationic solvation is not the decisive factor determining the order. Here, the dominant structural effect upon the degree of association appears to be the role of variation of cationic radius upon the strength of the coulombic interaction within the ion pair. A comparable condition exists with a change of the anion radius for the rubidium halides in dioxane–water mixtures over a wide dielectric constant interval.[19]

Acknowledgment.—Financial support for this investigation was provided by the National Science Foundation, Grant No. GP 27634.

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Hydride and Carbonyl Complexes of Rhodium-Containing Di(tertiary phosphines and arsines)[1]

BY JOEL T. MAGUE

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Previously we have reported briefly on oxidative addition to $[Rh(cis\text{-}(C_6H_5)_2AsCH{=}CHAs(C_6H_5)_2)_2]Cl$.[2] We now report the details of a more convenient synthesis of this and related complexes and present complete spectroscopic data on a number of hydrido and carbonyl complexes derived from them.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen or Matheson CP grade carbon monoxide, and all solvents were appropriately dried and distilled before use. Hydrated rhodium(III) chloride was obtained from A. D. MacKay, Inc., and the published procedures were used to prepare *cis*-1,2-bis-

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(1) Supported by the National Science Foundation (Grants GP-8066 and GP-16380) and by the Gulf Research and Development Co.

(2) J. T. Mague and J. P. Mitchener, *Chem. Commun.*, 911 (1968).

(diphenylphosphino)ethylene,[3] *cis*-1,2-bis(diphenylarsino)ethylene,[4] 1,2-bis(dimethylarsino)benzene,[5] and dichlorobis(cycloocta-1,5-diene)dirhodium(I).[6] Abbreviations for the specific ligands which will be used in the remainder of the paper are given in Table I while L_2 will be used as a general abbreviation for them.

Microanalyses were by Galbraith Microanalytical Laboratory, Knoxville, Tenn., and Meade Microanalytical Laboratory, Amherst, Mass. Infrared spectra were obtained on Beckman IR-5A, IR-18A, and IR-11 instruments using Nujol mulls and dichloromethane solutions. High-field ^1H nmr spectra were obtained on a Jeolco C-60HL spectrometer in dichloromethane solutions using tetramethylsilane as an internal standard.

Preparation of $(C_6H_5)(CH_3)PCH_2CH_2P(CH_3)(C_6H_5)$.—As an alternative to the published procedure,[7] we have employed the reaction of $(C_6H_5)(CH_3)PLi$ with 1,2-dichloroethane. In a typical preparation, 40.69 g (0.33 mol) of methylphenylphosphine in 300 ml of dry tetrahydrofuran was treated with an equimolar amount of *n*-butyllithium in hexane at 0° followed by 15.71 g (0.17 mol) of 1,2-dichloroethane in 100 ml of tetrahydrofuran. Following the addition, the mixture was refluxed for 20 min, the solvent was stripped, and the resulting oil was poured into dilute aqueous base. The oil was extracted into dichloromethane, the extract was dried over anhydrous sodium sulfate, and the volume reduced to about 20 ml. Addition of ethanol precipitated a white solid which was collected and recrystallized from ethanol to yield 12.34 g (27%) of the white, crystalline diphosphine, mp 87–89°.

$[Rh(L_2)_2]Cl$ Complexes.—A suspension of $[Rh(C_8H_{12})Cl]_2$ (0.2 g, 0.41 mmol) in 20 ml of dry acetonitrile was treated with 1.64 mmol of the appropriate ligand either in the neat form or in benzene solution. The reaction mixture turned a dark red-orange and all the solid dissolved. Addition of diethyl ether precipitated the product as yellow to orange crystals which were filtered under nitrogen and dried in a nitrogen stream. Metathetical reactions with $NaB(C_6H_5)_4$, $NaBF_4$, or $LiPF_6$ in acetonitrile or absolute methanol readily produce salts of these anions.

$[Rh(CO)(o\text{-}C_6H_4(As(CH_3)_2)_2)_2]PF_6$.—To a benzene solution of $[Rh(CO)_2Cl]_2$ (0.1 g, 0.26 mmol) in ethanol (10 ml) was added 0.29 g (1.04 mmol) of 1,2-bis(dimethylarsino)benzene. The solution turned orange as carbon monoxide was evolved. Addition of 0.15 g of NH_4PF_6 in ethanol produced an immediate precipitate of golden crystals which were collected, washed with diethyl ether, and dried *in vacuo*. The same complex results from the treatment of a dichloromethane solution of $[Rh(o\text{-}C_6H_4(As(CH_3)_2)_2)_2]PF_6$ with carbon monoxide.

$[RhHCl(o\text{-}C_6H_4(As(CH_3)_2)_2)_2]PF_6$.—A solution of $[Rh(o\text{-}C_6H_4(As(CH_3)_2)_2)_2]Cl$ in methanol or ethanol was treated with an equimolar amount of NH_4PF_6 to produce a precipitate of pale yellow microcrystals which were collected, washed with diethyl ether, and dried *in vacuo*. The same complex can be prepared by treating the Rh(I) complex with NH_4Cl in ethanol followed by $LiPF_6$ or by the reaction of $[Rh(o\text{-}C_6H_4(As(CH_3)_2)_2)_2]PF_6$ with anhydrous HCl in dichloromethane solution.

$[RhH_2(o\text{-}C_6H_4(As(CH_3)_2)_2)_2]B(C_6H_5)_4$.—Molecular hydrogen was bubbled through a solution of $[Rh(o\text{-}C_6H_4(As(CH_3)_2)_2)_2]B(C_6H_5)_4$ in dry, deoxygenated tetrahydrofuran whereupon the bright yellow solution lightened and took on a greenish cast. Addition of diethyl ether precipitated the product as pale greenish yellow crystals which were collected, washed with diethyl ether, and dried *in vacuo*. Attempts at recrystallization even in a hydrogen atmosphere were unsuccessful.

$[RhHCl(L_2)_2][Rh(CO)_2Cl_2]$ Complexes.—A solution of 0.2 g (0.76 mmol) of hydrated rhodium(III) chloride in 25 ml of absolute ethanol was refluxed for 5 hr while carbon monoxide was passed through it. To the cooled, pale yellow solution was added 0.76 mmol of the ligand in benzene. After carbon monoxide evolution had ceased, the product was induced to crystallize by the addition of diethyl ether. The crystals were collected, washed with diethyl ether, and dried *in vacuo*. Bromo analogs were prepared analogously from hydrated rhodium(III) bromide while a deuterido analog could be obtained using absolute C_2H_5OD as the solvent.

Results and Discussion

Analytical and spectroscopic data on the complexes are presented in Tables I and II, respectively. In addition to previously mentioned abbreviations, X will be used to designate a halogen.

In a previous paper, the preparation of $[Rh(vdiphos)_2][Rh(CO)_2X_2]$ and $[Rh(CO)(vdiars)_2][Rh(CO)_2X_2]$ complexes from either $[Rh(CO)_2Cl]_2$ or $[(n\text{-}C_4H_9)_4N][Rh(CO)_2Br_2]$ was described.[8] In an attempt to prepare these complexes by the more convenient method of Chatt and Shaw[9] involving the reduction of hydrated rhodium(III) halides in refluxing ethanol in the presence of carbon monoxide we obtained instead the $[Rh(CO)_2X_2]^-$ salts of the hydridohalo oxidative adducts to the desired cations. Subsequently, James, *et al.*,[10a] reported a study of the kinetics of the reduction of $RhCl_3 \cdot 3H_2O$ in *N,N*-dimethylacetamide in which it was postulated that the elements of HCl are liberated. Presumably the reaction takes substantially the same course in ethanol as the reduced rhodium solution is definitely acid. Similar results have been observed in analogous iridium systems.[10b] The proton nmr spectrum of this solution does not show the presence of any detectable concentration of a hydrido species. However, upon addition of ligand, a high-field signal immediately appears. In the preparation of **4** and **5**, the solution resulting after the initial evolution of carbon monoxide is deep orange and a further slow evolution of CO occurs over a period of several minutes with the solution becoming more yellow. The addition of ether to initiate precipitation causes a further lightening to the final pale yellow of the product. We suggest that some $[Rh(CO)(vdiars)_2]^+$ [8] is initially formed which is subsequently converted into the hydrido species. The analytical data obtained for **2** indicate probable contamination by some $[Rh(vdiphos)_2][Rh(CO)_2Br_2]$ but attempts at recrystallization led only to decomposition. The spectroscopic data (*vide infra*) leave little doubt, however, that the hydrido complex was the major species obtained.

Table II presents complete spectroscopic data for the oxidative adducts of HCl and HBr with **10** whose preparation has been previously reported.[2] The analogous HCl adduct of $[Rh(vdiphos)_2]Cl$ (**6**) is reported here for the first time. Spectroscopic evidence has been obtained for the existence of $[RhHBr(vdiphos)_2]B(C_6H_5)_4$ in solution (τ_{Rh-H} 24.9; $J_{Rh-H} = 18$, $J_{P-H} = 11.5$ Hz), but we have been unable to obtain satisfactory analytical data for the solid complex. Possibly contamination with $[RhBr_2(vdiphos)_2]B(C_6H_5)_4$, produced by further reaction of HBr with the hydrido complex,[11] has occurred. The trans stereochemistry for the two phosphine complexes is demonstrated by the appearance of the hydride resonance as a doublet of quintets and by the shift to lower fields in changing from the chloride to the bromide.[12] An analogous shift for the arsine complexes indicates that these are also trans adducts. Comparison of these results with those

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(11) The conversion of hydride complexes into halide complexes by reaction with hydrogen halides is well known. See, *e.g.*, A. P. Ginsburg, *Transition Metal Chem.*, **1**, 112 (1965), and references therein.

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TABLE I

ANALYTICAL DATA ON COMPLEXES

Compd no.	Complex[a]	% calcd C	H	X	% found C	H	X
1	$[RhHCl(vdiphos)_2][Rh(CO)_2Cl_2]$	55.81	3.91	9.15	55.90	4.20	8.84
2	$[RhHBr(vdiphos)_2][Rh(CO)_2Br_2]$	50.10	3.51	18.46	53.84	3.77	16.67
3	$[RhDCl(vdiphos)_2][Rh(CO)_2Cl_2]$	55.81	3.90	9.15	56.20	3.97	8.81
4	$[RhHCl(vdiars)_2][Rh(CO)_2Cl_2]$	48.55	3.40	7.96	48.43	3.68	8.10
5	$[RhHBr(vdiars)_2][Rh(CO)_2Br_2]$	44.08	3.09	16.29	46.38	3.35	16.14
6	$[RhHCl(vdiphos)_2]Cl$	64.54	4.69	7.33	64.25	4.50	7.86
7	$[RhHCl(diars)_2]PF_6$[b]	28.05	3.77	4.14	27.56	3.81	4.71
8	$[RhH_2(diars)_2]B(C_6H_5)_4$	53.04	5.47		51.21	5.17	
9	$[Rh(diars)_2]Cl$	33.80	4.55	4.99	33.15	5.26	4.36
10	$[Rh(vdiars)_2]Cl$	56.42	4.04	3.20	58.99	4.36	3.49
11	$[Rh(MPPE)_2]Cl$	55.94	5.88	5.16	56.20	6.01	4.98
12	$[Rh(CO)(diars)_2]PF_6$	29.74	3.81	13.44	29.49	3.93	14.16

[a] Abbreviations used for ligands here and elsewhere are the following: vdiphos = *cis*-1,2-bis(diphenylphosphino)ethylene; vdiars = *cis*-1,2-bis(diphenylarsino)ethylene; diars = *o*-phenylenebis(dimethylarsine); MPPE = 1,2-bis(methylphenylphosphino)ethane. [b] Fluorine analysis: calcd, 13.31; found, 12.26.

TABLE II

SPECTRAL DATA ON COMPLEXES

Complex	$\nu_{C\equiv O}$, cm^{-1} Nujol mull	CH$_2$Cl$_2$ soln	ν_{Rh-H} Nujol mull	CH$_2$Cl$_2$ soln	ν_{Rh-X} (X=Cl, Br), cm^{-1}	τ_{Rh-H}, ppm
1	2060, 1974	2070, 1996	2079	*a*	317, 287	26.0 (J_{Rh-H} = 16.2, J_{P-H} = 12.5 Hz)
2	2058, 1984	2060, 1993	*a*	*a*	225, 201	24.9 (J_{Rh-H} = 18, J_{P-H} = 11.5 Hz)
3	2058, 1976	2070, 1995	1502ν_{Rh-D}	*c*	317, 287	
4	2058, 1980	2066, 1992	*a*	*a*	322, 296	29.3 (J_{Rh-H} = 11.3 Hz)
5	2058, 1980	2064, 1992	*a*	*a*	234, 215 sh, 210	27.9 (J_{Rh-H} = 11.9 Hz)
6			2078	2075	286	25.9 (J_{Rh-H} = 16.1, J_{P-H} = 12.6 Hz)
7			2000	*b*	*c*	*b*
8			1966 sh, 1948	1950 sh, 1940		21.9 (broad)
$[RhH_2(vdiars)_2]Cl$[d]			1982, 1969	1988 sh, 1975		21.2 (broad)
$[RhHCl(vdiars)_2]Cl$[d]			2052	2049	277	29.1 (J_{Rh-H} = 11.2 Hz)
$[RhHBr(vdiars)_2]Cl$[d]			2045	2042	*c*	27.9 (J_{Rh-H} = 11.9 Hz)
12	1953	1966				
$[Rh(CO)(vdiars)_2]B(C_6H_5)_4$[d]	1956	1979				

[a] Obscured by $\nu_{C\equiv O}$. [b] Insufficiently soluble. [c] Obscured by ligand absorption. [d] Reference 2.

obtained for **1**, **2**, **4**, and **5** clearly demonstrate the presence of the *trans*-$[RhHX(L_2)_2]^+$ ions in these latter complexes. The infrared spectra of **1**–**5** in the carbonyl and metal–halogen regions show that $[Rh(CO)_2X_2]^-$ ions are present,[8] with the lower energy metal–halogen band generally obscuring ν_{Rh-X} for the cation.

If the reduction is carried out in C_2H_5OD as the solvent, the deuterido complex, **3**, is obtained as would be expected on the basis of the mechanism proposed by James, *et al.* [10]

Two very common starting points for the preparation of Rh(I) complexes are $[Rh(CO)_2Cl_2]^-$, prepared as described by Chatt,[9] or $[Rh(CO_2)_2Cl]_2$. Preparation of the latter species, though not difficult, is rather time consuming while the former can be gotten in as little as 3 hr. It has the disadvantage, however, as pointed out here, that the elements of HCl are present in the reduced solution and can be expected to add oxidatively to any derivative of $[Rh(CO)_2Cl_2]^-$ prepared by this route which is readily susceptible to oxidative addition (*e.g.*, the relatively basic $[Rh(L_2)_2]^+$ complexes described below). This point has apparently not been emphasized previously presumably since the phosphine, arsine,[9] and trichlorotin[13] derivatives prepared by this method were not basic enough to add HCl. This difficulty can be avoided by treating the reduced solution with a suitable base (*e.g.*, $NaHCO_3$) prior to adding the ligand. In this way we have, for example, been able readily to obtain the previously reported complex $[Rh(CO)(vdiars)_2][Rh(CO)_2Cl_2]$[8] from the reduced solution.

While a variety of Rh(I) complexes of di(tertiary phosphines and arsines) can be prepared by the method just described, the more basic ligands initially produce five-coordinate carbonyl adducts like **12**. Although it is sometimes possible to effect decarbonylation by refluxing in a nitrogen stream,[4] decomposition often occurs. A considerably more convenient synthesis of the coordinatively unsaturated $[Rh(L_2)_2]Cl$ complexes which were desired for studies of oxidative addition reactions involves the reaction of $[Rh(C_8H_{12})Cl]_2$[6] with a stoichiometric quantity of the appropriate di(tertiary phosphine or arsine) ligand.[14] While **10** seems relatively stable to air and moisture, **11** and particularly **9** are slowly decomposed.

Complexes **9**–**11** undergo a wide variety of oxidative addition reactions although in many cases we have experienced considerable difficulty in obtaining analytically pure products. Results of these studies will be reported at a later date. For the purposes of minimizing the occurrence of mixtures of products in these sorts of reactions it is best to use the hexafluorophosphate or tetraphenylborate salts of the Rh(I) complexes as substrates rather than the halides since the halide counterions seem to be readily taken into the coordination sphere. Whether this is the result of the oxidative addition reactions proceeding *via* a two-step displacement process[15] with exchange after the first step or from exchange with the oxidative adduct after

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(13) J. V. Kingston and G. R. Scollary, *J. Chem. Soc. A*, 3399 (1971).

(14) A variant of this procedure which can be used to prepared hexafluorophosphate salts of the $[Rh(L_2)_2]^+$ ions has recently been reported: R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, **93**, 3089 (1971).

(15) A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, **9**, 2658 (1970).

it is completely formed is not yet clear although we would favor the former interpretation. This problem is particularly prevalent when the addend molecule produces a species which is a poorer ligand than chloride. Thus the reaction of **10** with HF in tetrahydrofuran produces $[RhHCl(vdiars)_2]^+$ while if $[Rh(vdiars)_2]PF_6$ is used, no reaction appears to occur. The considerable basicity of **9** is apparent when one attempts to prepare the hexafluorophosphate salt by metathesis with NH_4PF_6. The production of **7** rather than a Rh(I) species and the evolution of ammonia in the process shows that the bound hydrogen arises *via* deprotonation of the ammonium ion. The same complex can be prepared by reaction of **9** with NH_4Cl followed by $LiPF_6$, from the reaction of **9** with HPF_6, or from the reaction of HCl with $[Rh(diars)_2]PF_6$. This appears to be the first example of this process in systems of this sort.

Like **10**, **9** readily activates molecular hydrogen. The appearance of a broad featureless band in the high-field ^1H nmr spectrum indicates that exchange of free and bound hydrogen is occurring but no evidence for catalytic activity under mild conditions has been obtained.

Carbon monoxide readily reacts with **9** to produce the five-coordinate complex **12** isolated as the hexafluorophosphate salt. The same species also can be gotten by reaction of diars with $[Rh(CO)_2Cl]_2$ followed by precipitation with NH_4PF_6 as mentioned above.

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Reaction of Cupric Methoxide and Carbon Dioxide

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Much attention has been paid to the reactions between transition metal compounds and simple molecules such as nitrogen and oxygen. However, the reactions of CO_2 have been little studied in the transition metal chemistry. Concerning the insertion reaction of CO_2 which is the extensively studied reaction in the main group metal compounds, few examples have been known in the transition metal compounds such as $Ti[N(CH_3)_2]_4$[1] and $H(N_2)Co[P(C_6H_5)_3]_3$.[2] Herein, we report the insertion reaction of CO_2 into the copper–oxygen bond of cupric methoxide.

Experimental Section

All procedures were carried out under nitrogen.

Materials.—$Cu(OCH_3)_2$ (**1**)[3] and $(acac)CuOCH_3$ (**3**)[4] were prepared according to the methods reported in the literature. CO_2 was a commercial gas reagent (assay: minimum 99.99 vol %), which was used without further purification. Pyridine was refluxed and distilled over KOH after drying by calcium hydride at room temperature. Methyl and ethyl iodides were distilled over calcium chloride.

Instrumentation.—The ir spectra were obtained on a Hitachi Model EPI-G3 grating spectrophotometer. Visible spectra were recorded with a Hitachi Model EPS-3T spectrometer using a Pyrex cell of 10-mm path length. Esr spectra were obtained with a Nippon Denshi Model JES-3BS-X spectrometer.

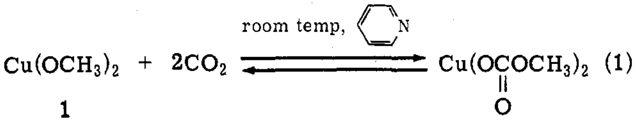
Preparations of $Cu(OCO(O)CH_3)_2$ (2) and $(acac)CuOCO(O)CH_3$ (4) and Their Reactions with Methyl Iodide.—To a suspension of 0.415 g (3.30 mmol) of **1** in 14 ml of pyridine, CO_2 gas was introduced by bubbling at ambient temperature under nitrogen. **1** dissolved within several minutes and CO_2 bubbling was continued for 30 min. By the addition of a small amount of pyridine, the total volume of the solution was adjusted exactly to 15 ml. A 3-ml aliquot of this solution (0.66 mmol **2**) was taken by a hypodermic syringe and cooled to *ca.* −40°, to which 0.084 ml (1.33 mmol) of methyl iodide was added. When the mixture was allowed to warm to an ambient temperature, an exothermic reaction took place to give a brown solution which was heated further at *ca.* 80°. The volatile material obtained from distillation of the resulting viscous solution was analyzed by glpc (Silicone DC-550 on Celite), and dimethyl carbonate was detected in a yield of 40% based on methoxy group of **1**. The reaction of **3** with CO_2 was carried out similarly to produce a pyridine solution of **4**. The reaction of **4** with methyl iodide was performed also by a procedure similar to that in the case of **2**.

Decarboxylation of 2 in Pyridine–DMF.—In a pyridine (3 ml)–DMF (45 ml) mixture, 1.10 g (8.74 mmol) of **1** was dissolved by introduction of CO_2 to form **2**. The volume of the resulting homogeneous blue-green solution was adjusted to 50 ml by the addition of DMF. A 5-ml aliquot of this solution (0.87 mmol of **2**) was heated gradually to 80° under nitrogen. At 70–75°, a blue solid of **1** precipitated slightly and at 80° this precipitate appeared extensively. By introduction of CO_2 at ambient temperature, this blue precipitate was redissolved and gave the original homogeneous blue-green solution. When this solution was treated with 0.22 ml (3.45 mmol) of methyl iodide, dimethyl carbonate was formed in a yield of 21%.

Gasometry.—A flask containing 0.201 g (1.60 mmol) of **1** in 4 ml of pyridine was connected to an ordinary gas buret filled with CO_2 gas over ligroin saturated with CO_2. After the pyridine suspension of **1** was solidified by chilling to *ca.* −70° with a Dry Ice–methanol bath, the flask was evacuated. Then, CO_2 gas was introduced and the reaction mixture was warmed to ambient temperature under magnetical stirring. The CO_2 absorption by **1** was followed with time at 19.6°, *i.e.*, the amount of CO_2 absorbed was 75.0 ml (3.12 mmol) at 20 min after introduction of CO_2 gas, 77.5 ml (3.22 mmol) at 30 min and 77.0 ml (3.20 mmol) at 60 min. The amount of CO_2 gas absorbed was calibrated by the reference experiment in the absence of **1**.

Results and Discussion

In this study, we have found a facile CO_2 insertion into the copper–oxygen bond of cupric dimethoxide (**1**) in a specific solvent of pyridine to form a cupric methyl carbonate (**2**), in which the CO_2 moiety is labile.



$$\underset{\mathbf{1}}{Cu(OCH_3)_2} + 2CO_2 \xrightleftharpoons{\text{room temp, pyridine}} Cu(O\underset{\underset{O}{\|}}{C}OCH_3)_2 \quad (1)$$

2

1 is insoluble in common organic solvents due to its polymeric structure.[3] In the present study, it was found that bubbling CO_2 gas into a suspension of **1** in pyridine at ambient temperature caused rapid dissolution of **1** to produce a homogeneous blue-green solution. The formation of **2** was confirmed by the following chemical and spectroscopic examinations.

The ir spectrum of the resulting solution showed strong absorptions at 1665 and 1305 cm^{-1}. It has been accepted that metal carboxylate has two bands in the

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