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.

CONTRIBUTION FROM THE DEPARTMENT OF
SYNTHETIC CHEMISTRY, FACULTY OF ENGINEERING,
KYOTO UNIVERSITY, KYOTO, JAPAN

Reaction of Cupric Methoxide and Carbon Dioxide

BY TETSUO TSUDA AND TAKEO SAEGUSA*

Received February 16, 1972

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.

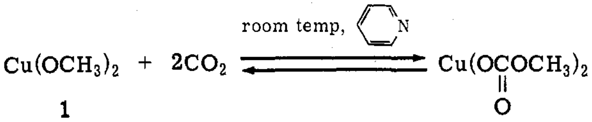
Preparations of $Cu(OCO(O)CH_3)_2$ (2) and (acac)$CuOCO(O)CH_3$ (4) and Their Reactions with Methyl Iodide.—To a suspension of 0.415 g (3.30 mmol) of **1** in 14 ml of pyridine, CO_2 gas was introduced by bubbling at ambient temperature under nitrogen. **1** dissolved within several minutes and CO_2 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.



$$Cu(OCH_3)_2 + 2CO_2 \rightleftharpoons Cu(O\overset{}{\underset{\substack{\| \\ O}}{C}}OCH_3)_2 \quad (1)$$

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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[1] G. Chandra and M. F. Lappert, *Inorg. Nucl. Lett.*, 83 (1965).

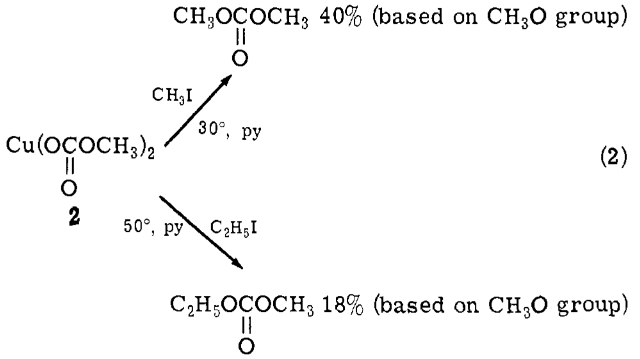
[2] L. S. Pu, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, **90**, 3896 (1968).

[3] C. H. Brubaker, Jr., and M. Wicholas, *J. Inorg. Nucl. Chem.*, **27**, 59 (1965).

[4] J. A. Bertrand and R. I. Kaplan, *Inorg. Chem.*, **4**, 1657 (1965).

regions of 1610–1550 and 1400–1300 cm^{-1}, which arise from antisymmetrical and symmetrical vibrations of COO^- structure,[5] respectively. Thus, it is reasonable to assign two bands of the cupric species of the resultant homogeneous solution at 1665 and 1305 cm^{-1} to methyl carbonate anion. In addition, this assignment is supported by the fact that magnesium methyl carbonate, $Mg(OCO_2CH_3)_2$,[6] has two absorptions at 1655 and 1330 cm^{-1}.

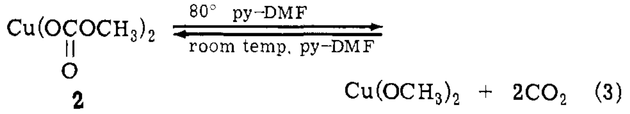
The presence of a methyl carbonate group in **2** was also indicated by the formation of alkyl methyl carbonate when the pyridine solution of **2** was treated with alkyl iodide.



That the stoichiometry of the reaction was two molecules of CO_2 per molecule of **1** was established by the gasometry of the CO_2 absorption.

The uniqueness of pyridine as solvent was shown in the phenomena of dissolution of **1** by introduction of CO_2. In tetrahydrofuran, dimethylformamide (DMF), triethylamine, and tetramethylethylenediamine, no dissolution of **1** was observed. For the reaction of **1** with CO_2, a large amount of pyridine is not always necessary. For example, 0.38 g (3.0 mmol) of **1** reacted with CO_2 in 15 ml of DMF to give a homogeneous blue-green solution when the solvent contained 1 ml (12 mmol) of pyridine. In the absence of pyridine, no change was observed in the suspension of **1** in DMF by introduction of CO_2 at either room temperature or *ca.* 50°.

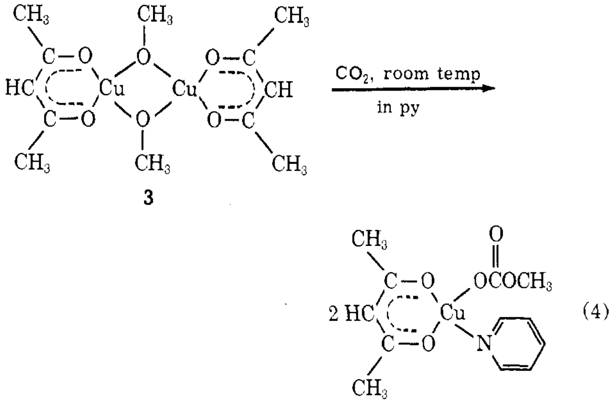
The CO_2 moiety in **2** is labile. When a solution of **2** in a pyridine–DMF mixture was heated at 80° under nitrogen, a blue precipitate of **1** was formed. This blue solid was redissolved by CO_2 to a blue-green solution which gave dimethyl carbonate in a yield of 21% by treatment with methyl iodide. This observation indicates the reversibility of the CO_2 insertion.



$$\underset{\mathbf{2}}{Cu(O\underset{\underset{O}{\|}}{C}OCH_3)_2} \xrightleftharpoons[\text{room temp, py–DMF}]{80^\circ\ \text{py–DMF}} Cu(OCH_3)_2 + 2CO_2 \quad (3)$$

Removal of pyridine solvent also caused the liberation of CO_2 from **2**. Thus, both the precipitate obtained by the addition of a large amount of benzene to the pyridine solution of **2** and the residue obtained by evaporation of pyridine from pyridine solution of **2** at a reduced pressure showed no carbonyl ir absorption and did not produce dimethyl carbonate when they were treated with methyl iodide. In comparison with other metal methyl carbonates, for instance, Mg $(OCO(O)CH_3)_2$,[6] in which the CO_2 moiety is stable, the lability of CO_2 moiety in **2** is very interesting and constitutes another characteristic of the present study in addition to the specific action of pyridine solvent.

To obtain more detailed information on the resulting cupric methyl carbonate complex, a well-defined complex of cupric acetylacetonate methoxide, $(acac)CuOCH_3$[4] (**3**), was investigated, for which a square-planar dimeric structure has been proposed. **3** underwent a facile CO_2 insertion to produce $(acac)CuOCO(O)CH_3$ (**4**).



3

4

A suspension of violet **3** in pyridine rapidly became a homogeneous blue-green solution by the introduction of CO_2 at room temperature. Absorptions at 1670 and 1310 cm^{-1} appeared in ir spectrum, and dimethyl carbonate was formed when the resulting solution was treated with methyl iodide. Evaporation of pyridine solvent, however, caused the loss of the CO_2 molecule.

The visible spectrum of **4** in pyridine consisted of a broad and asymmetric band centered around 675 nm. A similar spectrum with λ_{max} 680 nm was observed in the pyridine solution of **2**. These absorptions are similar in wavelength to that of a square-planar complex of **3**[4] and may be interpreted as a composite band arising from d–d transitions in a square-planar Cu(II) complex.[4,7]

The pyridine solutions of **2** and **4** showed strong typical esr signals of cupric species at room temperature. Each esr spectrum consisted of four lines whose intensity increased with increasing magnetic field. In the case of **4**, the values of $g_{av} = 2.142$ and $A_{iso} = 62$ G were obtained. This fact makes a sharp contrast to the absence of esr signals of $Cu(OCH_3)_2$ and $(acac)CuOCH_3$ in solid state, and also to the reported low magnetic moment of $Cu(OCH_3)_2$ ($\mu = 1.07$ BM)[3] and $(acac)CuOCH_3$ ($\mu = 0.75$ BM)[4] which are less than the calculated, spin-only value of 1.73 BM for divalent copper. This reduced magnetic moment of **3** and **1** has been explained on the basis of the dimeric and polymeric structure of the complexes which permit spin coupling by the copper–copper interaction. Combining the results of visible and esr spectra, it is reasonable to assume a monomeric square-planar structure for **2** and **4** in which pyridine molecule may coordinate as a ligand to copper atom.

[5] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p 174.

[6] E. Szarvasy, *Ber.*, **30**, 1836 (1897).

[7] L. F. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand-Field Theory," Methuen, London, 1966, p 95.

When CO_2 was introduced into the suspension of $Co(OCH_3)_2$ or $Ni(OCH_3)_2$ in pyridine, neither the dissolution nor the color change was observed.

The facile insertion of CO_2 to cupric methoxide, **1** and **3**, and the liberation of CO_2 from copper methyl carbonate, **2** and **4**, may be regarded as a reversible CO_2 fixation by cupric methoxide, and these observations may be utilized for synthetic organic reactions using CO_2.

Acknowledgment.—We are grateful to Mr. S. Kumai for his experimental contributions to this study.

CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY, UNIVERSITY OF MELBOURNE, PARKVILLE, 3052, AUSTRALIA

A Carbonyl Fluoride of Rhenium

BY T. A. O'DONNELL* AND K. A. PHILLIPS

Received February 28, 1972

There are many molecular carbonyl halides of transition metals in which the halogen is chlorine, bromine, or iodine,[1] but only two carbonyl fluorides of transition metals have been reported: tetrafluorodicarbonylmolybdenum(IV) which probably has a dimeric structure[2] and difluorotricarbonylruthenium(II) which has been shown to have a tetrameric structure.[3]

The only known carbonyl chlorides, bromides, and iodides of rhenium are the monomeric pentacarbonyls and the dimeric tetracarbonyls of rhenium(I).[1]

We have isolated trifluorotricarbonylrhenium(III), $Re(CO)_3F_3$, from the reaction of a limited amount of rhenium hexafluoride with decacarbonyldirhenium(0) in Kel-F apparatus. Anhydrous hydrogen fluoride is used as a solvent for the rhenium hexafluoride during the preparation, and tungsten hexafluoride is used as a solvent to purify the product by removing rhenium pentafluoride which is also formed. This solvent would also remove any oxide fluorides of rhenium which are possible impurities in the rhenium hexafluoride. A porous disk of sintered PTFE is used for separation of solids from liquids. The general procedure is similar to that which we have previously described.[2]

Anhydrous hydrogen fluoride and some rhenium hexafluoride are condensed onto the decacarbonyldirhenium(0) at −196° and the frozen solid mixture is allowed to melt. The mixture becomes dark brown and carbon monoxide gas is evolved. The gas can be removed after the reaction mixture is again solidified. Additions of rhenium hexafluoride are repeated until the mixture separates to a dark brown solid and a pale green solution. The solid is trifluorotricarbonylrhenium(III) and the green color in the liquid hydrogen fluoride is due to rhenium pentafluoride.[4] If more rhenium hexafluoride is added, there is rapid evolution of carbon monoxide, the brown solid is rapidly decomposed, and only the green solution remains.

When the mixture separates, no more rhenium hexafluoride is added, instead, the solution is poured off through the porous disk and the hydrogen fluoride is distilled from the apparatus. Tungsten hexafluoride is condensed onto the brown solid, allowed to melt, and then the resulting solution, green due to rhenium pentafluoride, is separated from the solid by pouring through the filter. This process of washing the solid with tungsten hexafluoride is repeated several times to remove all traces of the rhenium pentafluoride. The final product is a finely divided, free flowing, dark brown solid.

Results

Analyses for both rhenium and fluoride in aqueous solution can be obtained if the rhenium is present as perrhenate. There is no chemical interference between the two anionic species, the perrhenate can be determined from its uv absorbance,[5] and the fluoride can be determined using an ion-selective electrode. However, it was found to be difficult to oxidize the rhenium in this compound to oxidation state VII. After the compound was heated with sodium peroxide, an insoluble yellow-brown gelatinous material formed in water instead of the expected colorless perrhenate. A similar result followed fusion with a mixture of potassium nitrate and potassium hydroxide. The original compound dissolves slowly in water but addition of hydrogen peroxide forms the insoluble gelatinous material. It is known that some yellow-brown compounds of rhenium(IV) containing hydroxo and/or oxo groups are oxidized only very slowly.[6] Apparently the rhenium in the compound is oxidized from oxidation state III to IV but further oxidation is slow because of formation of intractable polymeric materials of indefinite composition. Repeated additions of hydrogen peroxide to the compound in aqueous alkali and prolonged boiling for several hours eventually gives a colorless solution containing perrhenate and fluoride, and this was analyzed.

Analysis for coordinated carbon monoxide in most transition metal carbonyl complexes can be accomplished by displacing the ligands with a bromine carrier,[7] but this method does not displace any carbon monoxide from trifluorotricarbonylrhenium(III). However, it was found that the carbonyl ligands are displaced when a mixture of the compound with solid iodine is heated strongly. This mixture was placed in an evacuated glass apparatus and heated with a flame to liberate gaseous carbon monoxide, which was then determined by pressure–volume measurements. The solid residue in the apparatus had no ir absorptions near 2000 cm^{-1} which indicates that all of the carbonyl ligands had been displaced. *Anal.* Calcd for $Re(CO)_3F_3$: Re, 56.9; CO, 25.7; F, 17.4. Found: Re, 55; CO, 25; F, 16.7.

Nujol mulls of trifluorotricarbonylrhenium(III) and decacarbonyldirhenium(0) were prepared in an atmosphere of dry argon to avoid contamination by hydrolysis or oxidation.[8] The ir absorptions in the carbonyl stretching region[9] for the spectrum of the carbonyl fluoride are at higher wave numbers than those

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(1) F. Calderazzo in "Halogen Chemistry," Vol. 3, V. Gutmann, Ed., Academic Press, London, 1967, p 383 ff.

(2) T. A. O'Donnell and K. A. Phillips, *Inorg. Chem.*, **9**, 2611 (1970).

(3) C. J. Marshall, R. D. Peacock, D. R. Russell, and I. L. Wilson, *Chem. Commun.*, 1643 (1970).

(4) G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1099 (1960).

(5) J. B. Headridge, *Analyst (London)*, **83**, 690 (1958).

(6) E. K. Maun and N. Davidson, *J. Amer. Chem. Soc.*, **72**, 2254 (1950).

(7) A. D. Campbell and P. E. Nelson, *Talanta*, **16**, 875 (1969).

(8) N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **3**, 1123 (1964).