gave principally tetraphenylfuran (20), mp 185–186 °C.[30]

Direct air oxidation of an aliquot of 7a in ether, evaporation of solvent, and direct column chromatography, without intentional hydrolysis, of the residue leads to the isolation of tetraphenylfuran and 3-benzylidene-1,2-diphenylindene.

Nature of the "Pentaphenylborole" Reported by Braye, Hübel, and Caplier. From the foregoing reactions of authentic pentaphenylborole with oxygen and protolyzing agents, it is clear that the boron compound isolated by Braye, Hübel, and Caplier and recrystallized in air from ethanol could not have been the borole. The following repetition of their procedure in our laboratory has clarified the nature of their product.

After conducting the reaction of 5 with dichloro(phenyl)borane in ethyl ether, exactly as published, the dried benzene extract was freed of solvent and chromatographed on silica gel. The sample was introduced onto the column in 4 mL of benzene and eluted with petroleum ether (bp 30–60 °C)–benzene–ethanol gradient. The main fraction, 1.6 g of yellow solid, was recrystallized from a benzene–ethanol pair to give 250 mg of pale yellow crystals, mp 182–184 °C dec, which displayed only one spot on TLC developed with benzene–petroleum ether. A second crop, mp 189–193 °C dec, was completely different by TLC and IR spectroscopy (the latter had an OH band).

The main compound had the following spectral characteristics: IR (mineral oil) no OH or B–O absorptions, but C_6H_5–B bond at 1250 cm⁻¹; ¹H NMR (CDCl₃) br merged peaks at 6.83, 7.0, and 7.33 ppm; UV (95% EtOH) 205, 240, 293, and 366 (sh) nm; mass spectrum *m/e* 814 (M⁺ + 0), 799, 798; mol wt by ¹H NMR vs. (Me₂SiO₃)₃ 880.

(30) Hahn, D. A.; Murray, R. *J. Am. Chem. Soc.* **1914**, *36*, 1484.

Heating a sample of this compound in glacial HOAc for 50 h, dilution with water, collection of the precipitated product, and recrystallization from MeOH gave a colorless solid, mp 147.5–149 °C, that was identified as 1,2,3-triphenylnaphthalene.

On the basis of the foregoing, the boron compound melting at 182–184 °C dec is concluded to be phenylbis(2,3,4-triphenyl-1-naphthyl)borane (22). A sample of Braye, Hübel, and Caplier's compound, kindly provided by Dr. Hübel, was compared with our sample by TLC, NMR, and IR techniques. The two compounds were almost identical by these criteria, except that the BHC sample showed two minor contaminants by TLC. The published elemental analyses (C, 92.16; H, 6.04; B, 2–3) compare reasonably with those calculated for 22 (C, 93.22; H, 5.42; and B, 1.35). The small amount of oxygen contaminants in the BHC sample, as revealed by IR, MS, and TLC techniques, explains the low carbon and hydrogen values.
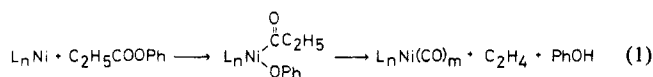
Carbon–Oxygen Bond Cleavage of Esters Promoted by Hydrido and Alkylcobalt(I) Complexes Having Triphenylphosphine Ligands. Isolation of an Insertion Intermediate and Molecular Structure of Phenoxotris(triphenylphosphine)cobalt(I)

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Abstract: Carbon–oxygen bonds in aryl and alkyl carboxylates (R'COOR) are selectively cleaved by CoH(N₂)(PPh₃)₃, and carboxylic esters R'COOCH₂R' are formed by a Tischchenko type dimerization of aldehyde R'CHO, whereas the reaction of CoMe(PPh₃)₃ with the esters yields ketones R'COMe. The reaction products are accounted for by assuming insertion of the ester C=O double bond into the Co–H or Co–Me bond, followed by abstraction of the β-alkoxo group by cobalt. The intermediate (β-(ethoxy)alkoxo)cobalt(I) complex Co(OCH(CF₃)OEt)(PPh₃)₃ has been isolated in the reaction of CoH(N₂)(PPh₃)₃ with ethyl trifluoroacetate as well as by alcoholysis of CoH(N₂)(PPh₃)₃ with CF₃CH(OEt)OH. Treatment of CoH(N₂)(PPh₃)₃ with phenyl acetate affords a tetrahedral phenoxocobalt(I) complex, Co(OPh)(PPh₃)₃. Crystals of the complex are monoclinic, space group $P2_1/c$, with $a = 13.142$ (2) Å, $b = 19.661$ (3) Å, $c = 18.714$ (3) Å, and $\beta = 91.49$ (3)°. Block-diagonal least-squares refinement leads to $R = 0.075$ and $R_w = 0.081$ for 2966 reflections. The molecular structure of the complex consists of a tetrahedron with an O-bonded phenoxo group and three PPh₃ ligands: the average Co–P distance is 2.320 (4) Å and Co–O 1.900 (9) Å, and the average P–Co–P angle is 109.9 (1)°, P–Co–O 109.1 (4)°, and Co–O–C 138.2 (9)°, respectively.

Synthetic methods utilizing selective cleavage of C–O bonds in allyl carboxylates promoted by palladium complexes have been well developed.[1] However, studies on selective cleavage of C–O bonds in carboxylic esters and anhydrides promoted by other transition-metal complexes are limited.[2] Previously we have demonstrated that aryl esters undergo acyl–O bond cleavage and subsequent reactions on interaction with Ni(0) complexes.[3]

$$L_nNi + C_2H_5COOPh \longrightarrow L_nNi\overset{\overset{O}{\underset{\|}{CC_2H_5}}}{\underset{OPh}{}} \longrightarrow L_nNi(CO)_m + C_2H_4 + PhOH \quad (1)$$

In contrast to the reaction of esters with the Ni(O) complexes, transition-metal hydrides are anticipated to behave somewhat

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[§] Hiroshima University.

(1) (a) Heck, R. F. "Organotransition Metal Chemistry"; Academic Press: New York, 1974. (b) Tsuji, J. "Organic Synthesis by Means of Transition Metal Complexes"; Splinger-Verlag: Berlin, 1975. (c) Trost, B. M. *Tetrahedron Lett.* **1977**, *33*, 2615.
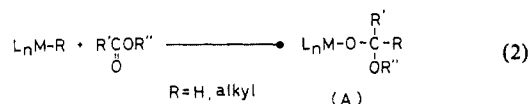
Table I. Products in Reactions of CoH(N₂)(PPh₃)₃ with Phenyl Carboxylates[a]

| phenyl carboxylate (mol/Co)	time, h	gas	liquid	complex[c,d]
CH₃COOPh (12)	48	N₂ (89) H₂ (21) CH₄ (29)	CH₃COOC₂H₅ (40)	Co(OPh)(PPh₃)₃ (43)
C₂H₅COOPh (30)	72	N₂ (85) H₂ (20) C₂H₆ (23)	C₂H₅COO-n-C₃H₇ (33)	Co(OPh)(PPh₃)₃ (62)
n-C₃H₇COOPh (13)	24	N₂ (89) H₂ (22) C₃H₈ (12)	n-C₃H₇COO-n-C₄H₉ (38)	Co(OPh)(PPh₃)₃ (60)
PhCOOPh (8)	24	N₂ (84) H₂ (7)	PhCOOCH₂Ph (28)	Co(OPh)(PPh₃)₃
CH₃COOC₆H₄-p-CH₃ (12)	72	N₂ (57) H₂ (17) CH₄ (7)	nm	CoH(N₂)(PPh₃)₃[c] Co(OC₆H₄-p-CH₃)(PPh₃)₃[c]
CF₃COOPh (2)	1	N₂ (93)	CF₃COOCH₂CF₃ (31)	Co(OPh)(PPh₃)₃ (79)

[a] All reactions were carried out in toluene at room temperature. [b] Isolated yield. [c] The formation of compounds was confirmed by IR, but yields were not determined owing to difficulties in separating the complexes from the mixture. [d] Cobalt–carbonyl complexes were also formed.[8]

differently, since the transition-metal–hydrogen bond may interact with unsaturated compounds to give an insertion product. The reaction of RuH₂(PPh₃)₄ with alkenyl carboxylates to give alkenes and hydridoruthenium carboxylates has been reported, and the reaction course has been accounted for by insertion of the olefinic double bond into the Ru–H bond followed by elimination of carboxylate entity by ruthenium.[4]
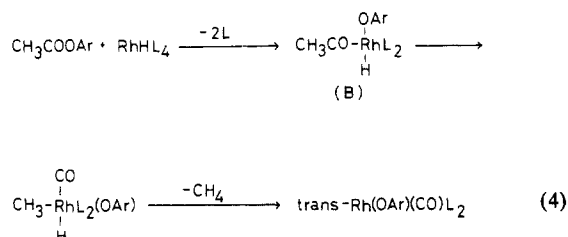
In reactions of metal hydrides or alkyls with carboxylic esters another possible pathway is insertion of the ester carbonyl group into the metal–hydride or metal–alkyl bond to give a metal alkoxide (A).

$$L_nM-R + R'COR'' \longrightarrow L_nM-O-\overset{\overset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle OR''}{|}}{C}}-R \qquad (2)$$

R = H, alkyl   (A)

In our previous study on reactions of aryl esters with RhH(PPh₃)₄ the acyl–O bond cleavage was observed to give a carbonyl-containing aryloxide according to the following stoichiometry.[5]

$$CH_3COOAr + RhHL_4 \xrightarrow{-2L, -CH_4} trans\text{-}Rh(OAr)(CO)L_2 \qquad (3)$$
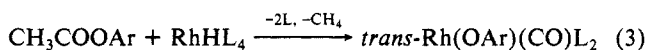
The reaction products were accounted for by assuming a direct oxidative addition of the ester to a coordinatively unsaturated RhHL₃ species to give an intermediate Rh(III) complex (B). The intermediate (B) having the hydrido, acetyl, and aryloxo ligands was thought to undergo subsequent decarbonylation and reductive elimination as follows.

$$CH_3COOAr + RhHL_4 \xrightarrow{-2L} CH_3CO-\overset{\overset{\displaystyle OAr}{|}}{\underset{\underset{\displaystyle H}{|}}{RhL_2}} \longrightarrow$$

(B)

$$CH_3-\overset{\overset{\displaystyle CO}{|}}{\underset{\underset{\displaystyle H}{|}}{RhL_2}}(OAr) \xrightarrow{-CH_4} trans\text{-}Rh(OAr)(CO)L_2 \qquad (4)$$

As an alternative pathway a carbonyl group insertion process such as eq 2 was considered, but the process was disfavored

(2) (a) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7577. (b) Miki, S.; Tatsumi, T.; Kodama, T.; Hidai, M.; Uchida, Y. *Ibid.* **1978**, *100*, 447. (c) Tatsumi, T.; Tominaga, H.; Hidai, M.; Uchida, Y. *Chem. Lett.* **1977**, 37. (d) Komiya, S.; Yamamoto, A.; Yamamoto, T. *Yuki Gosei Kagaku Kyokaishi* **1981**, *38*, 633 and references cited therein.
(3) Yamamoto, T.; Ishizu, J.; Kohara, T.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 3758.
(4) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* **1975**, *87*, 333.
(5) Yamamoto, T.; Miyashita, S.; Naito, Y.; Komiya, S.; Ito, T.; Yamamoto, A. *Organometallics* **1982**, *1*, 808.

Table II. Products in Reactions of CoCH₃(PPh₃)₃ with Phenyl Carboxylates[a]

phenyl carboxylate (mol/Co)	gas	liquid	Co(OPh)-(PPh₃)₃
CH₃COOPh (22)	CH₄ (10)	CH₃COCH₃ (65)	(30)
C₂H₅COOPh (19)	CH₄ (7) C₂H₆ (trace)	C₂H₅COCH₃ (68)	(32)
C₃H₇COOPh (24)	CH₄ (24) C₃H₈ (2)	C₃H₇COCH₃ (62)	(40)
n-C₄H₉COOPh (21)	CH₄ (21) n-C₄H₁₀ (0)	n-C₄H₉COCH₃ (53)	(45)
n-C₉H₁₉COOPh (15)	CH₄ (13) n-C₉H₂₀ (0)	n-C₉H₁₉COCH₃ (87)	(31)
PhCOOPh (18)	CH₄ (3) C₆H₆ (5)	PhCOCH₃ (87)	(35)

[a] Reactions were carried out at 0–20 °C for 2 days in toluene.

because of occurrence of the decarbonylation process, which is amply documented for rhodium complexes.[6] Similar reactions of RuH₂(PPh₃)₄ and aryl carboxylate also caused decarbonylation of the esters and gave RuH₂(CO)(PPh₃)₃ and some RuH(OPh)(PPh₃)₂.[6]

In the present study we have examined the reactions of cobalt hydride and methyl complexes, CoH(N₂)(PPh₃)₃ (1) and CoMe(PPh₃)₃ (2), with esters and observed that the reactions gave products compatible with eq 2. Furthermore, employment of carboxylic esters having electronegative trifluoromethyl groups affords a stable alkoxo complex expected in eq 2. Alkoxides of early transition metals are well-known, but examples of the corresponding alkoxides of late transition metals are limited; examples of alkoxides with β-hydrogen atoms are especially scarce. Thus isolation of the alkoxide having a β-hydrogen atom is significant in its own right and intriguing as well in affording a model complex for reaction 2. Molecular structure of reaction product Co(OPh)(PPh₃)₃ by X-ray crystallographic analysis is also reported.

Results

Reactions of Aryl Carboxylates. Tables I and II summarize products formed in the reactions of CoH(N₂)(PPh₃)₃ (1) and CoMe(PPh₃)₃ (2) with aryl carboxylates. The reactions of 1 with aryl carboxylates (RCOOPh) in toluene proceed smoothly at room temperature with liberation of 1 mol of N₂ per mol of 1 to give

(6) Doughty, D. H.; Pignolet, L. H. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet L. H., Ed.; Plenum Press: New York, 1983.

Phenoxotris(triphenylphosphine)cobalt(I)

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Table III. Products in Reactions of $CoH(N_2)(PPh_3)_3$ and $CoCH_3(PPh_3)_3$ with Alkyl Carboxylates[a]

| complex	ester (mol/Co)	time, h	temp, °C	products (%/Co)		
				gas	liquid	complex
$CoH(N_2)(PPh_3)_3$	$CH_3COOC_2H_5$ (26)	24	20	no reaction		
	$C_2H_5COOC_2H_5$ (82)	72	20	N_2 (22) H_2 (trace) C_2H_6 (trace)	$C_2H_5COOC_3H_7$ (12)	$CoH(N_2)(PPh_3)_3$ (73)
	$C_2H_5COOC_2H_5$ (152)	4	40	N_2 (85) H_2 (3)	$C_2H_5COOC_2H_5$ (32)	Co metal
	$CH_3COOCH_2CF_3$ (2)	48	20	N_2 (98) H_2 (23) CH_4 (1)	$CH_3COOC_2H_5$ (30)	$Co(OCH_2CF_3)(PPh_3)_3$ (40)
	$PhCOOCH_2CF_3$ (2)	48	20	N_2 (100) H_2 (17) C_6H_6 (32)	$PhCOOCH_2Ph$ (28)	$Co(OCH_2CF_3)(PPh_3)_3$[b] $CoH(CO)(PPh_3)_3$[b]
$CoCH_3(PPh_3)_3$	$CH_3COOCH_2CF_3$ (2)	48	0	CH_4 (32)	CH_3COCH_3 (67)	$Co(OCH_2CF_3)(PPh_3)_3$ (60)
	$PhCOOCH_2CF_3$ (2)	48	0	CH_4 (43) C_6H_6 (20)	$PhCOCH_3$ (33)	$Co(OCH_2CF_3)(PPh_3)_3$ (33)

[a] In toluene. [b] Yield not measured.

phenoxotris(triphenylphosphine)cobalt(I) (**3**) and carboxylic esters, $RCOOCH_2R$. Complex **2** also reacts with phenyl carboxylates

$$CoH(N_2)(PPh_3)_3 + RCOOPh \rightarrow$$
$$\mathbf{1}$$

$$Co(OPh)(PPh_3)_3 + RCOOCH_2R + N_2 \quad (5)$$
$$\mathbf{3}$$
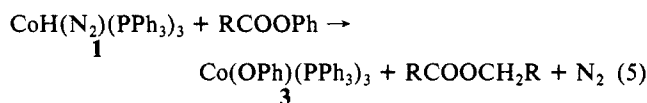
to afford **3** and corresponding alkyl methyl ketone in good yields.

$$CoMe(PPh_3)_3 + RCOOPh \rightarrow Co(OPh)(PPh_3)_3 + RCOMe$$
$$\mathbf{2} \qquad\qquad\qquad\qquad \mathbf{3}$$
$$(6)$$
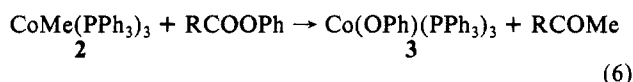
In both reactions small amounts of alkane, RH, and Co-carbonyl complexes[8] were also obtained (ca. 10%/Co). Hydrogen gas also was evolved in the reactions of **1** with esters.[9] In the case of the reaction of complex **2**, 10–30% of methane was evolved by the partial thermal decomposition of **2** under these conditions.[10] Complex **3** is moderately air-sensitive but thermally very stable. It has been fully characterized by elemental analysis, IR spectroscopy, magnetic susceptibility, and X-ray structural analysis as well as by chemical reactions. Complex **3** has also been prepared independently by the reaction of **1** with phenol. The reaction was accompanied by evolution of nitrogen and hydrogen gases (eq 7).
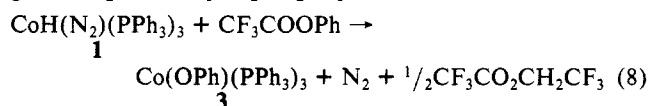
$$CoH(N_2)(PPh_3)_3 + PhOH \rightarrow Co(OPh)(PPh_3)_3 + N_2 + H_2$$
$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{3}$$
$$(7)$$
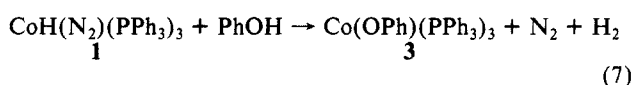
The magnetic susceptibility of **3** (3.3 μ_B) suggests its high spin d^8 tetrahedral configuration. The IR spectrum of **3** shows a strong $\nu(C-O)$ band at 1280 cm^{-1}, characteristic of transition-metal phenoxides.[11] The structure of **3** was unequivocally determined by single-crystal X-ray diffraction studies (vide infra).

p-Tolyl acetate, having an electron-releasing methyl substituent, was found to react more slowly than the unsubstituted phenyl

(7) (a) Bennett, M. A.; Robertson, G. B.; Whimp, P. O.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3028. (b) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993. (c) Bradley, D. C.; Merhotra, R. C.; Gaur, D. P. "Metal Alkoxides"; Academic Press: London, 1978 and references cited therein. (d) Arther, T.; Robertson, D. R.; Tocher, D. A.; Stephenson, T. A. *J. Organomet. Chem.* **1981**, *208*, 389.

(8) Formation of $CoH(CO)(PPh_3)_3$ ($\nu(C=O)$ 1920 cm^{-1})[10] and an uncharacterized carbonyl complex ($\nu(C=O)$ 1900, 1870 cm^{-1}) was inferred by IR spectroscopy (KBr).

(9) At present, the mechanism for the hydrogen gas evolution is not clear. However, proton abstraction from esters by cobalt hydride as well as reductive coupling of hydridic hydrogens produced by orthometalation of the triphenylphosphine ligand might be responsible for the results.

(10) Yamamoto, A.; Kitazume, S.; Pu, L. S.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 371.

(11) (a) Keim, W. *J. Organomet. Chem.* **1968**, *14*, 179. (b) Cole-Hamilton, D. J.; Young, R. S.; Wilkinson, G. *J. Chem. Soc. Dalton Trans.* **1976**, 1995.

acetate, giving products only in low yields after 3 days. Similar retardation effects of electron-releasing substituents on the C–O bond-cleavage reactions of para-substituted phenyl acetate with $RhH(PPh_3)_4$ have been previously noted.[5]
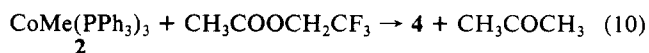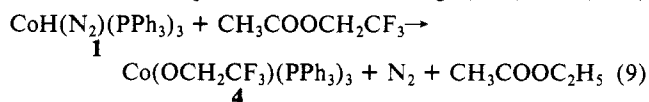
On the other hand, the reaction of **1** with phenyl trifluoroacetate having an electron-withdrawing CF_3 group proceeded rapidly to give **3**, N_2, and $CF_3CO_2CH_2CF_3$.

$$CoH(N_2)(PPh_3)_3 + CF_3COOPh \rightarrow$$
$$\mathbf{1}$$

$$Co(OPh)(PPh_3)_3 + N_2 + {}^1/_2CF_3CO_2CH_2CF_3 \quad (8)$$
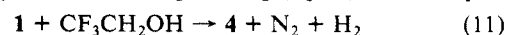$$\mathbf{3}$$

Carboxylic esters $RCOOCH_2R$ formed in the reaction of **1** with $RCOOPh$ are regarded to be produced by Tischchenko type dimerization of aldehydes that are derived by combination of the hydrido ligand in **1** with the acyl entity in $RCOOPh$. The result is in contrast with formation of alkanes and a carbonyl rhodium complex $Rh(CO)(OPh)(PPh_3)_2$ in the reaction of $RhH(PPh_3)_4$ with phenyl carboxylates.

Reactions of Alkyl Carboxylates. Table III summarizes products of the reactions of complexes **1** and **2** with alkyl and trifluoroethyl carboxylates. Complex **1** showed no reactivity toward alkylcarboxylates such as methyl acetate at room temperature, but upon heating the reaction mixture at 40 °C, cobalt metal deposited was accompanied by formation of aldehyde dimer. Supposed methoxo–cobalt complex formed analogously to the above reaction (5) could not be isolated, probably because of its thermal instability.

However, 2,2,2-trifluoroethyl acetate, carrying an electron-withdrawing CF_3 group in the alkoxy unit, reacted smoothly in toluene with **1** at room temperature, giving 30% of ethyl acetate and (trifluoroethoxo)tris(triphenylphosphine)cobalt(I), **4**, with evolution of dinitrogen. Complex **2** also reacted with 2,2,2-trifluoroethyl acetate at 0 °C to give **4** with liberation of 67% of acetone. The IR spectrum of **4** shows strong $\nu(C-F)$ and $\nu(C-O)$

$$CoH(N_2)(PPh_3)_3 + CH_3COOCH_2CF_3 \rightarrow$$
$$\mathbf{1}$$

$$Co(OCH_2CF_3)(PPh_3)_3 + N_2 + CH_3COOC_2H_5 \quad (9)$$
$$\mathbf{4}$$

$$CoMe(PPh_3)_3 + CH_3COOCH_2CF_3 \rightarrow \mathbf{4} + CH_3COCH_3 \quad (10)$$
$$\mathbf{2}$$

bands at 1140 and 1190 cm^{-1}, respectively. The magnetic susceptibility of **4** (3.0 μ_B) suggests its tetrahedral structure similar to complex **3**. Acidolysis of **4** with dry HCl gave a quantitative yield of trifluoroethanol. The alkoxo complex **4** was also obtained by alcoholysis of **1** with trifluoroethanol, the reaction being accompanied by evolution of H_2 and N_2 (eq 11). A complex

$$\mathbf{1} + CF_3CH_2OH \rightarrow \mathbf{4} + N_2 + H_2 \quad (11)$$

corresponding to A in eq 2 was, in fact, isolated when ethyl trifluoroacetate was treated with the cobalt hydride complex **1**.

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Table IV. Products in Reactions of $CoH(N_2)(PPh_3)_3$ and $CoCH_3(PPh_3)_3$ with Carboxylic Anhydrides

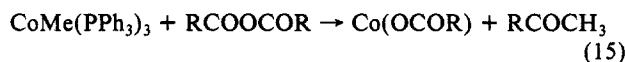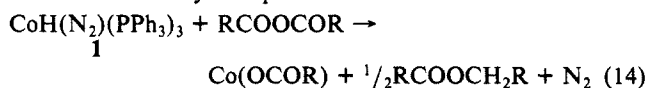| complex	acid anhydride (mol/Co)	products (%/Co)		
		gas	liquid	complex
$CoH(N_2)(PPh_3)_3{}^a$	$(CH_3CO)_2O$ (1.0)	N_2 (89) H_2 (4) CH_4 (38)	$CH_3COOC_2H_5$ (23)	$Co(OCOCH_3){}^c$
	$(C_2H_5CO)_2O$ (2.0)	N_2 (84) H_2 (15) C_2H_6 (26)	C_2H_5COO-n-C_3H_7 (28)	$Co(OCOC_2H_5)$
	$(n$-$C_3H_7CO)_2O$ (1.9)	N_2 (81) N_2 (13) C_3H_8 (16)	n-C_3H_7COO-n-C_4H_9 (30)	$Co(OCO$-n-$C_3H_7)$
$CoCH_3(PPh_3)_3{}^b$	$(CH_3CO)_2O$ (1.5)	CH_4 (21)	CH_3COCH_3 (68)	$Co(OCOCH_3){}^c$ $Co(CO)_n(PPh_3)_m$
	$(C_2H_5CO)_2O$ (1.1)	CH_4 (10) C_2H_4 (7) C_2H_6 (11)	$C_2H_5COCH_3$ (74)	$Co(OCOC_2H_5)$ $Co(CO)_n(PPh_3)_m$
	$(n$-$C_3H_7CO)_2O$ (1.3)	CH_4 (6) C_3H_6 (7) C_3H_8 (2)	n-$C_3H_7COCH_3$ (76)	$Co(OCO$-n-$C_3H_7)$ $Co(CO)_n(PPh_3)_m$

^{a} In toluene at room temperature for 1 day. ^{b} In THF at –40–20 °C. ^{c} The compound can be purified by recrystallization from pyridine (see ref 4).

The same complex was also obtained by treatment of **1** with hemiacetal, $CF_3CH(OEt)OH$ (eq 12 and 13). Complex **5** proved

$$1 + CF_3COOC_2H_5 \rightarrow \underset{\textbf{5}}{Co(OCH(OEt)CF_3)(PPh_3)_3} + N_2$$
(12)

$$1 + CF_3CH(OEt)OH \rightarrow 5 + H_2 + N_2$$ (13)
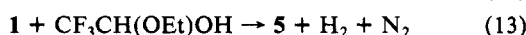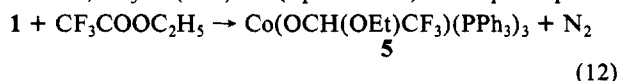
to be thermally quite stable despite that it has a β-hydrogen atom. It was recrystallized from a mixture of toluene and hexane. The IR spectrum of **5** shows characteristic ν(C–F) and ν(C–O) bands at 1140 and 1200 cm^{-1}, respectively. The observed magnetic susceptibility of 2.6 μ_B for **5** suggests a tetrahedral structure similar to **3** and **4**. Acidolysis of **5** with dry HCl readily liberated trifluoroacetaldehyde ethyl hemiacetal quantitatively. Unfortunately actual β-OEt elimination reaction from **5** could not be confirmed, since thermolysis of **5** in toluene at 150 °C for 5 h have no characterizable materials.

Reaction of Carboxylic Anhydrides. Complexes **1** and **2** react also with acid anhydrides to cause C–O bond cleavage reactions. Table IV summarizes the products in the reactions of **1** and **2** with carboxylic anhydrides. Complex **1** react with acid anhydrides to afford cobalt carboxylates, esters, and dinitrogen. The similar reaction of **2** proceeds smoothly to give cobalt carboxylates and alkyl methyl ketones. In these reactions small amounts of RH and cobalt carbonyl complex were also formed.

$$CoH(N_2)(PPh_3)_3 + RCOOCOR \rightarrow$$
$$\textbf{1}$$

$$Co(OCOR) + {}^1/_2RCOOCH_2R + N_2 \quad (14)$$

$$CoMe(PPh_3)_3 + RCOOCOR \rightarrow Co(OCOR) + RCOCH_3$$
(15)

Description of the Molecular Structure of 3. Crystallographic data are summarized in Table V with those of the structure refinements. The final atomic parameters are given in Table VI. The structure of the complex molecule with the numbering scheme is shown in Figure 1. The unit cell packing features viewed down the b-axis are illustrated in Figure 2 (supplementary material). Selected bond distances and bond angles are listed in Table VII, and selected interatomic distances and the least-squares planes are listed in Tables VIII and IX (supplementary material).

The crystal structure is composed of discrete $Co(OPh)(PPh_3)_3$ molecules. The Co atom is surrounded by an O-bonded OPh group and three P atoms of the PPh_3 ligands in a tetrahedral arrangement. The Co–P distances of 2.307 (4) Å, 2.329 (4) Å, and 2.324 (4) Å for P1, P2, and P3 atoms (average 2.320 Å) are slightly longer than the average values of 2.240 (6) Å and 2.227 (2) Å for Co–P distances in tetrahedral $CoCl(PMe_3)_3{}^{12}$ and [Co-

Table V. Crystal Data and Refinements Conditions for $Co(OPh)(PPh_3)_3$

formula	$C_{60}H_{50}OP_3Co$
mol wt	938.9
cryst system	monoclinic
space group	$P2_1/c$
z	4
a	13.142 (2) Å
b	19.661 (3) Å
c	18.714 (3) Å
β	91.49 (3)
vol	4833 (2) Å^3
density (calcd)	1.29 g/cm^3
cryst dimensn	0.5 × 0.5 × 0.4 mm^3
radiatn	Mo Kα (λ = 0.7107 Å)
no. of unique reflectns	4655 ($2\theta < 50°$)
no. of reflectns with $F_o > 3\sigma(F_o)$	2966 ($2\theta < 50°$)
final $R_1{}^a$	7.5%
final $R_2{}^b$	8.1%

$^a R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^b R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.
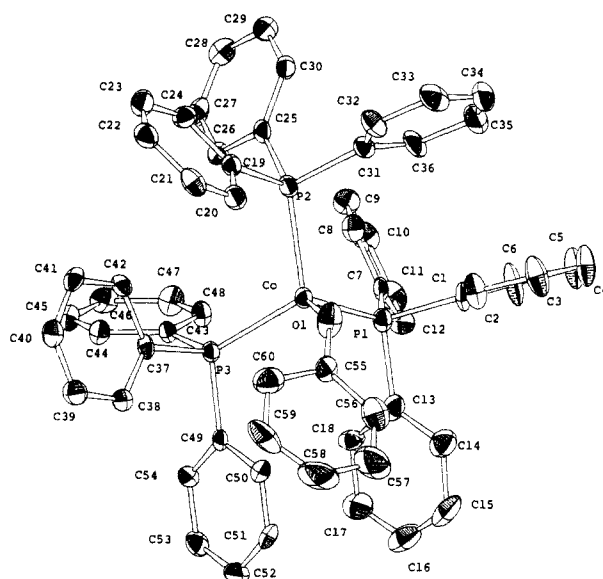
Figure 1. An ORTEP drawing of the $Co(OPh)(PPh_3)_3$ molecule with the numbering scheme. All atoms are drawn with the 25% probability ellipsoid.

$(PMe_3)_4]BPh_4$,^{13} suggesting the presence of significant interligand steric repulsion.^{14} The Co–O distance 1.900 (9) Å is comparable

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Phenoxotris(triphenylphosphine)cobalt(I)

J. Am. Chem. Soc., Vol. 108, No. 3, 1986 389

Table VI. Atomic Parameters ($\times 10^4$) and Thermal Parameters[a]

atom	x	y	z	beqv
C0	2689 (1)	774 (1)	2419 (1)	3.4
P1	2122 (3)	293 (2)	3460 (2)	3.9
P2	4407 (3)	531 (2)	2278 (2)	3.8
P3	1662 (2)	342 (2)	1497 (2)	3.3
O1	2713 (9)	1740 (5)	2450 (5)	7.0
C1	2665 (11)	731 (7)	4250 (6)	4.9
C2	3010 (13)	1380 (7)	4204 (7)	6.2
C3	3385 (15)	1742 (8)	4799 (8)	7.9
C4	3421 (15)	1413 (9)	5442 (8)	7.9
C5	3115 (15)	753 (9)	5498 (7)	8.0
C6	2718 (14)	400 (8)	4913 (7)	7.8
C7	2254 (9)	-622 (6)	3691 (6)	3.7
C8	3117 (11)	-943 (7)	3449 (7)	5.1
C9	3269 (11)	-1632 (7)	3555 (8)	5.5
C10	2551 (12)	-2016 (7)	3885 (8)	6.2
C11	1702 (12)	-1694 (7)	4135 (7)	5.7
C12	1554 (10)	-1014 (7)	4048 (7)	4.7
C13	751 (11)	421 (7)	3580 (7)	5.1
C14	379 (12)	964 (9)	4001 (8)	6.8
C15	-685 (14)	1047 (9)	4040 (9)	8.1
C16	-1306 (13)	596 (10)	3699 (9)	8.6
C17	-972 (12)	99 (9)	3295 (8)	7.1
C18	64 (10)	2 (8)	3229 (7)	5.4
C19	4935 (9)	971 (6)	1498 (6)	3.6
C20	4678 (10)	1632 (7)	1362 (7)	4.9
C21	5076 (11)	1975 (7)	784 (7)	5.3
C22	5698 (10)	1650 (8)	324 (7)	5.5
C23	5961 (11)	995 (9)	452 (7)	6.1
C24	5587 (10)	642 (7)	1038 (7)	4.7
C25	4950 (9)	-324 (7)	2201 (6)	3.8
C26	4403 (9)	-818 (7)	1842 (6)	4.1
C27	4797 (12)	-1478 (8)	1788 (8)	5.8
C28	5697 (11)	-1662 (7)	2099 (7)	5.3
C29	6267 (11)	-1160 (8)	2443 (7)	5.8
C30	5898 (10)	-513 (7)	2503 (6)	4.4
C31	5169 (9)	908 (6)	3024 (7)	4.0
C32	5772 (11)	1466 (8)	2971 (8)	5.6
C33	6291 (12)	1735 (8)	3573 (9)	7.2
C34	6173 (13)	1422 (9)	4221 (8)	7.3
C35	5598 (12)	888 (10)	4293 (8)	7.4
C36	5086 (10)	590 (8)	3691 (7)	5.8
C37	1924 (9)	759 (7)	635 (5)	3.5
C38	1222 (10)	1158 (7)	273 (6)	4.3
C39	1487 (11)	1485 (8)	-361 (7)	5.4
C40	2427 (11)	1427 (8)	-620 (7)	5.3
C41	3135 (10)	1029 (7)	-283 (7)	4.5
C42	2886 (9)	682 (7)	360 (6)	4.0
C43	1627 (9)	-552 (7)	1248 (6)	3.8
C44	1546 (10)	-777 (7)	533 (6)	4.3
C45	1506 (11)	-1459 (8)	383 (7)	5.3
C46	1582 (11)	-1952 (7)	909 (8)	5.7
C47	1656 (12)	-1721 (8)	1612 (8)	6.0
C48	1707 (10)	-1054 (7)	1773 (6)	4.4
C49	299 (9)	526 (7)	1580 (6)	3.5
C50	33 (10)	1147 (7)	1878 (7)	4.6
C51	-953 (10)	1343 (7)	1934 (7)	4.6
C52	-1717 (10)	914 (9)	1699 (7)	5.6
C53	-1483 (10)	298 (8)	1415 (7)	5.6
C54	-462 (10)	106 (7)	1349 (7)	4.4
C55	2125 (11)	2232 (7)	2290 (7)	4.7
C56	1517 (13)	2560 (9)	2770 (9)	7.5
C57	909 (17)	3025 (12)	2623 (12)	12.5
C58	783 (15)	3205 (11)	1961 (12)	11.7
C59	1322 (15)	2943 (11)	1405 (10)	10.3
C60	2033 (12)	2444 (9)	1576 (9)	7.4

[a] Thermal parameters are given by the equivalent temperature factors ($\mathring{A}^2$).

with those found in peroxy(*p*-quinolato)(Shiff base)cobalt(III), 1.854–1.929(11) $\mathring{A}$,[14] and in (salicylato)tetraamminecobalt(III), 1.89 (1) $\mathring{A}$.[16]

(14) The intermolecular close contacts around the phenoxo ligand are summarized in Table XIII. All values are in normal range and no noticeable intermolecular interactions with the surrounded molecules is present.

(15) Nishinaga, A.; Tomita, H.; Nishizawa, K.; Matsuura, T. *J. Chem. Soc., Dalton Trans.* **1981**, 1504.

Table VII. Selected Bond Distances and Angles for Co(OPh)(PPh₃)₃

Bond Distances, $\mathring{A}$			
Co–P1	2.307 (4)	P2–C19	1.848 (12)
Co–P2	2.329 (4)	P2–C25	1.833 (14)
Co–P3	2.324 (4)	P2–C31	1.852 (13)
Co–O1	1.900 (9)	P3–C37	1.850 (11)
P1–C1	1.839 (13)	P3–C43	1.818 (14)
P1–C7	1.856 (13)	P3–C49	1.839 (12)
P1–C13	1.839 (15)	O1–C55	1.270 (17)

Bond Angles, deg			
P1–Co–P2	110.3 (1)	Co–P1–C13	112.7 (4)
P1–Co–P3	106.5 (1)	Co–P2–C19	112.2 (4)
P2–Co–P2	112.8 (1)	Co–P2–C25	125.2 (4)
P1–Co–O1	112.9 (3)	Co–P2–C31	109.8 (4)
P2–Co–O1	101.1 (4)	Co–P3–C37	111.6 (4)
P3–Co–O1	113.4 (3)	Co–P3–C43	123.6 (4)
Co–P1–C1	111.1 (5)	Co–P3–C49	114.4 (4)
Co–P1–C7	124.4 (4)	Co–O1–C55	138.2 (10)

Scheme I

$Y = -Ar, -COR$
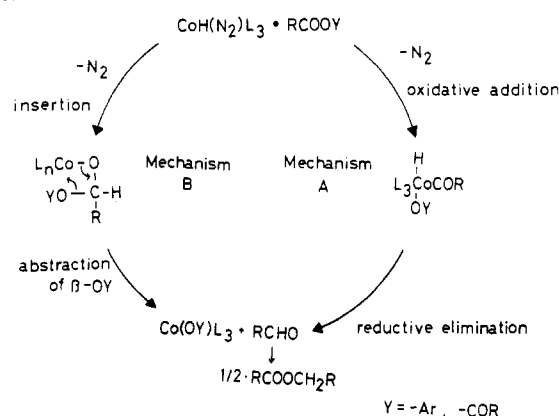
Both the P–Co–P angles of 110.3 (2)°, 106.5 (2)°, and 112.8 (2)° (average 109.9°) and the P–Co–O angles of 112.9 (3), 101.1 (4), and 113.4(3)° (average 109.1°) strongly support that the present complex has a tetrahedral coordination around the central cobalt atom.

The significant results about the coordination geometry of the phenoxo ligand are as follows: (1) The unidentate nature of the phenoxo ligand (Co–O 1.900 (9) $\mathring{A}$ and Co–O–C angle 138.2 (9)°). (2) Though the average P–Co–O angle is 109.1 (4)°, the C–O bond apparently tilts toward one of the P atom. (For P2, the P–Co–O angle is 101.1 (4)°. (3) There is considerable intramolecular close contact between the carbon atoms of the phenoxo ligand and Co atom (Co–C55 = 2.970 (13), Co–C56 = 3.899 (17), and Co–C60 = 3.735 (18) $\mathring{A}$). (4) The C–O bond distance 1.270 (17) $\mathring{A}$ is fairly short compared with 1.359 (10) $\mathring{A}$ for the phenoxo ligand in dichloro(diphenoxo)titanium(IV),[17] suggesting the partial double bond character. From these results, it is inferred that a slight contribution of side-on type coordination of the phenoxo ligand is involved in the Co–OPh bond. However, the structure determined here is definitely different from that of RuH(OPh)(PPh₃)₂ for which η^5-coordination of the phenoxo ligand through the phenyl ring was proposed.[18]

Discussion

Mechanism for C–O Bond Cleavage. Two mechanisms are compatible with the reaction products in Tables I, II, and III produced in the reactions of **1** and **2** with esters and acid anhydrides (mechanisms A and B in Scheme I).

Mechanism A involves the direct oxidative addition of an ester to the Co(I) complex involving the acyl–O bond cleavage to yield a hydrido(acyl)cobalt(III) intermediate and subsequent reductive

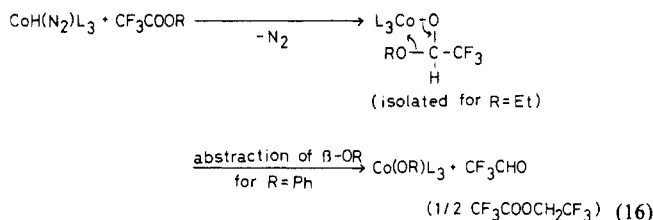(16) Kushi, Y.; Hosoo, T.; Kuroya, H. *J. Chem. Soc. D* **1970**, 20.
(17) Watenpaugh, K.; Caughlan, C. N. *Inorg. Chem.* **1966**, *5*, 1782.
(18) The unusual η^5-coordination of phenoxo ligand is found in RuH(OPh)(PPh₃)₂.[11b]

elimination of the acyl and hydrido ligands from the Co(III) intermediate. Aldehyde that is assumed to be generated is spontaneously converted into ester by Tischchenko type dimerization. Such a dimerization of aldehydes to esters is known to be catalyzed by group 8–10 transition-metal hydrides.[19] The resultant complex is phenoxo- or alkoxocobalt(I) complex, **3** or **4**.

Mechanism B constitutes insertion of the carbonyl group in the ester into the Co–H bond to form a (β-phenoxyalkoxo)cobalt(I) intermediate, the process being reminiscent of the reactions of Grignard reagents with esters. Abstraction of the alkoxy group at the β-position by cobalt gives **3** and aldehyde which dimerizes into ester as discussed as above. Similar alkoxy elimination from such an intermediate has been previously proposed in the reaction of Ph_2MnPCy_3 with ester.[20]

Although both mechanisms are consistent with the reaction products, isolation of the ((β-ethoxy)alkoxo)cobalt complex **5** on treatment of **1** with CF_3COOEt clearly indicates that the insertion of the carbonyl group in ester into the Co–H bond occurs at least for this type of ester having an electronegative group (eq 16).

$$CoH(N_2)L_3 + CF_3COOR \xrightarrow[-N_2]{} L_3Co\begin{smallmatrix}O\\|\\RO-C-CF_3\\|\\H\end{smallmatrix}$$

(isolated for R=Et)

$$\xrightarrow[\text{for R=Ph}]{\text{abstraction of } \beta\text{-OR}} Co(OR)L_3 + CF_3CHO$$

(1/2 $CF_3COOCH_2CF_3$)   (16)

Formation of $Co(OPh)(PPh_3)_3$ in the reaction of **1** with CF_3COOPh further suggests that abstraction of the OPh group from a putative intermediate product of the insertion process occurs in preference to the usually observed β-hydrogen elimination.

The present results are in contrast with the previously observed formation of $Rh(CO)(OAr)(PPh_3)_2$ in the reaction of $RhH(PPh_3)_4$ with CH_3COOAr.[6] It is known that Rh(I) complexes are active for decarbonylation of aldehydes and acyl halides in processes involving oxidative addition of these substrates.[20] Therefore, it is possible that the reaction of the rhodium hydride with esters proceeds through a different mechanism involving the direct oxidative addition of esters to the rhodium(I) hydride complex. The previously observed trend that $CoH(N_2)(PPh_3)_3$ is more reactive than $RhH(PPh_3)_4$ in insertions of the C=O double bond of ketones into the metal–hydride bond[21] is also in line with the higher reactivity of $CoH(N_2)(PPh_3)_3$ than $RhH(PPh_3)_4$ in insertion of the carbonyl group in esters.

The reactions of acid anhydrides with **1** and **2** also are accountable in a mechanism similar to B.

In conclusion, the present results indicate that reactions of esters with transition-metal hydrides can proceed by the insertion–elimination mechanism, particularly when the complex has a hydridic hydrogen and reacts with carbonyl compounds having an electrophilic carbonyl group. However, the results found here do not exclude the possible route of the direct oxidative addition of esters involving the acyl–O bond cleavage of other transition-metal hydrides.

Experimental Section

General Procedure and Materials. All the reactions were carried out under deoxygenated nitrogen or argon or in vacuo. $CoH(N_2)(PPh_3)_3$ and $CoCH_3(PPh_3)_3$ were prepared by the method previously reported.[10] $CH_3COOCH_2CF_3$, $C_6H_5COOCH_2CF_3$, and $CH_3COOC_6H_4$-p-CH_3 were synthesized according to methods given in the literature.[22] Phenyl acetate, other esters, and acid anhydrides were purchased from Tokyo Kasei Co., Ltd., and purified by recrystallization or distillation. Im-

purities in phenyl carboxylates such as phenol and carboxylic acids were carefully removed by reacting them with acid chloride in the presence of pyridine until no phenol was detected by GC and washing with 5% $NaHCO_3$ solution. Solvents were dried by usual procedure, distilled, and stored under argon or nitrogen.

Spectroscopic Measurement and Analysis. IR spectra and magnetic susceptibilities were recorded on a Hitachi 295 spectrometer and Shimadzu Magnetic Balance type MB-100, respectively. The microanalysis of C, H, and N was performed by Mr. Saito at Research Laboratory of Resources Utilization with a Yanagimoto CHN Autocorder type MT-3. Cobalt analysis was carried out with an ammonium thiocyanate method.[23] Phosphorus analysis was carried out by the spectroscopic analysis of triphenylphosphine oxide obtained after oxidation of the compound with 35% hydrogen peroxide. Gases were analyzed by gas chromatography after collecting the evolved gases by a Toepler pump, by which the gas volumes were measured. Amounts of the organic products were determined quantitatively by gas chromatography with suitable internal standards.

Reactions of 1 and 2 with Esters and Acid Anhydrides. Typical experimental procedures are described below. Details of reaction conditions and results of other reactions are summarized in Tables I–IV.

Reaction of 1 with Phenyl Acetate. Phenyl acetate (5.0 mmol) was added to a Schlenk-type flask containing $CoH(N_2)(PPh_3)_3$ (365 mg, 0.42 mmol) in toluene (2 mL) in vacuo. After 2 days, the evolution of N_2 (0.37 mmol), CH_4 (0.12 mmol), and H_2 (0.088 mmol) was observed. Analysis of the liquid phase by GLC showed formation of $CH_3COOC_2H_5$ (0.168 mmol). Hexane (20 mL) was added to the mixture to give a yellow precipitate, which was separated by filtration, washed with hexane, and dried in vacuo; yield 169 mg (43%/Co). Recrystallization from a benzene–hexane mixture afforded brown crystals of $Co(OPh)(PPh_3)_3$ (**3**): mp 178 °C dec; IR: ν(C–O) 1280 cm^{-1}, μ_{eff} = 3.3 μ_B. Anal. Calcd for $C_{60}H_{50}OP_3Co$: C, 76.8; H, 5.4; P, 9.9; Co, 6.3. Found: C, 76.5; H, 5.4; P, 9.8; Co, 6.4. The IR spectrum of the recovered solid from hexane solution showed ν(C=O) bands at 1920, 1900, and 1870 cm^{-1}, which are characteristic of cobalt carbonyl complexes.[8]

Reaction of 1 with Phenol. Toluene (5 mL) was added to a mixture of **1** (4.10 g, 4.7 mmol) and phenol (0.52 g, 5.5 mmol) by trap-to-trap distillation. After 1 h at room temperature, a dark red solution containing a yellow precipitate was obtained. Both nitrogen (4.6 mmol) and hydrogen (4.6 mmol) gases were detected in the gas phase. The precipitate was separated by filtration, washed with hexane, and dried in vacuo; yield 3.90 g (88%/Co).

Reaction of 1 with 2,2,2-Trifluoroethyl Acetate. Trifluoroethyl acetate (9.78 mmol) was added to a toluene (4 mL) solution of **1** (458 mg, 0.53 mmol). After evacuation of gas in the flask, the solution was stirred at room temperature for 2 days to give N_2 (0.51 mmol), $CH_3COOC_2H_5$ (0.16 mmol), and a brown solution. Addition of hexane (30 mL) afforded a yellow solid of **4** (200 mg, 40%). Recrystallization of **4** from toluene–hexane gave brown prisms. **4**: mp 158 °C dec; μ_{eff} = 3.0 μ_B. Anal. Calcd for $C_{56}H_{43}OF_3P_3Co$: Co, 6.2; P, 9.8. Found: Co, 5.9; P, 9.7.

Reaction of 1 with Trifluoroethanol. Trifluoroethanol (0.28 mmol) was added to a toluene solution (2 mL) of **1** (200 mg, 0.23 mmol). After evacuation of gas in the flask, the solution was stirred at room temperature for 1 day to give a brown solution liberating H_2 (0.22 mmol) and N_2 (0.22 mmol). Addition of hexane (40 mL) to the brown solution afforded a yellow solid of **4** (117 mg, 60%).

Reaction of 4 with HCl. Dry HCl (0.3 mmol) was introduced to the ether solution of **4** (94.0 mg, 0.10 mmol) to give H_2 (0.030 mmol, 50%/Co) and CF_3CH_2OH (0.097 mmol, 98%/Co).

Reaction of 1 with Acetic Anhydride. Acetic anhydride (0.36 mmol) was added to a toluene (2 mL) solution of **1** (307 mg, 0.35 mmol). After evacuation of gas in the flask, stirring the solution at room temperature for 1 day gave N_2 (0.31 mmol), CH_4 (0.13 mmol), $CH_3COOC_2H_5$ (0.080 mmol), and a brown solution to which 20 mL of hexane was added to give a white violet precipitate of $Co(OCOCH_3)$ (16 mg, 39%): IR spectrum, ν(OCO)$_{asym}$ 1540, ν(OCO)$_{sym}$ 1420 cm^{-1}.

Reaction of 1 with Ethyl 1,1,1-Trifluoroacetate. Ethyl 1,1,1-trifluoroacetate (2.0 mL) was added to a toluene solution (10 mL) of **1** (1.55 g, 1.77 mmol) and PPh$_3$ (1.5 g, 5.3 mmol). After evacuation of gas in the flask, stirring the solution at room temperature liberated N_2 (1.6 mmol). Hexane (40 mL) was added to a brown solution. After filtration, it was kept at −20 °C giving brown crystals of **5**. The resulted crystals were filtered, washed with hexane, and dried in vacuo (500 mg, 30%). **5**: mp 136 °C dec; μ_{eff} = 2.6 μ_B. Anal. Calcd for $C_{58}H_{51}O_2F_3P_3Co$: C, 70.4; H, 5.2; P, 9.4; Co, 6.0. Found: C, 71.0; H, 5.3; P, 9.3; Co, 6.0.

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Reaction of 1 with Trifluoroacetaldehyde Ethyl Hemiacetal. Trifluoroacetaldehyde ethyl hemiacetal (1.8 mL) was added to a toluene solution (10 mL) of **1** (1.63 g, 1.8 mmol) and PPh$_3$ (1.10 g, 4.0 mmol) by a trap-to-trap distillation. After 1 day at 0 °C, H$_2$ (1.5 mmol) and N$_2$ (1.5 mmol) were detected in the gas phase. Then hexane (40 mL) was added to the brown solution. Similar workup in the reaction of **1** with ethyl trifluoroacetate gave brown crystals (350 mg, 20%). **5**: mp = 135 °C dec; μ_{eff} = 2.6 μ_B. Anal. Calcd: see above. Found: C, 70.5; H, 5.3; P, 9.2; Co, 5.9.

Reaction of 5 with Dry HCl. Dry HCl (0.8 mmol) was introduced to the ether solution of **5** (243 mg, 0.246 mmol) to give trifluoroacetaldehyde ethyl hemiacetal (0.22 mmol, 90%).

Reaction of 2 with Phenyl Propionate. Phenyl propionate (3.5 mmol) was added to **2** (164 mg, 0.19 mmol) in a Schlenk flask. After evacuation of gas in the flask, the mixture was stirred at 0 °C for 5 h and gradually warmed to room temperature. After 1 day, CH$_4$ (0.013 mmol) and C$_2$H$_5$COCH$_3$ (0.13 mmol) were liberated, and a brown solution containing a yellow precipitate was obtained. Hexane (40 mL) was added to the mixture, and the precipitate was separated by filtration, washed with hexane, and dried in vacuo (52 mg, 32%). **3**: IR ν(C–O) 1280 cm^{-1}. The reactions of 2,2,2-trifluoroethyl carboxylates and carboxylic anhydrides were carried out analogously.

X-ray Measurement. The cell dimensions and space-group symmetries were preliminarily checked by Weissenberg photographs by using Ni Kα radiation. The systematic absences suggested the space group *P*2$_1$/*c*. Determination of cell constants and collection of intensity data were carried out on a Riganku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Unit cell constants were determined by least squares refinement of 25 reflections. Intensity data were collected by an ω-2θ scan mode up to 2θ = 50° with the scan rate of 16°/min at 50/KV, 170 mA. The scan range was (1.0 + 0.45 tan θ)°. Standard *LP* corrections were applied, but corrections for the absorption effect were neglected (μ(Mo Kα) = 4.9 cm^{-1}). The number of independent reflections used for the structure refinement $F_o > 3\sigma F_o$ is 2966.

Determination and Refinement of the Structure. The structure of the compound was solved by the heavy-atom method. All the non-hydrogen atoms were refined anisotropically. Subsequent difference Fourier maps did not reveal the positions of hydrogen atoms because the thermal vibration of the molecule was fairly large. The largest peak in a final difference map was ca. 1.0 eA^{-3} around the Co atom. The final anisotropic thermal parameters and the listing of observed and calculated structure factors are available as supplementary materials. All the atomic scattering factors were taken from Cromer and Waber.[23] The anomalous dispersidon coefficients of Cromer and Liberman were used for Co atom.[24] Block-diagonal least-squares refinement to minimized function $w(F_o - kF_c)^2$ was employed. The weight w was taken as (σ + $aF_o + bF_o^2$)$^{-1}$, where σ is the standard deviation for each reflection, and the values of a and b used were 0.2 and 0.009, respectively. All the computations were carried out on a HITAC computer at the Hiroshima University Information Processing Center. The computer programs used were UNICS program with a slight modification.[25] An ORTEP drawing was carried out by the XTL system on a Syntex diffractometer.[26]

Supplementary Material Available: Selected intermolecular short contacts (Table XIII), selected least-squares planes and dihedral angles (Table IX), F_o and F_c tables (Table X), anisotropic temperature factors (Table XI), mean-square displacement tensor of atoms (Table XII), atomic parameters for the hydrogen atoms (Table XIII), and the unit cell packing diagram in **3** (28 pages). Ordering information is given on any current masthead page.

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Fixation and Activation of Carbon Dioxide on Aluminum Porphyrin. Catalytic Formation of Carbamic Ester from Carbon Dioxide, Amine, and Epoxide

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Abstract: Carbon dioxide is trapped by (5,10,15,20-tetraphenylporphinato)aluminum acetate in the presence of a secondary amine in the form of an aluminum carbamate on the opposite side to the acetate group with respect to the porphyrin plane. Carbon dioxide thus trapped by aluminum porphyrin is activated enough to undergo a catalytic reaction involving secondary amine and epoxide to afford dialkylcarbamic ester under atmospheric pressure at room temperature.

Carbon dioxide is one of the most ubiquitous carbon resources, but its activation is essential for chemical fixation and utilization because of the inertness under ordinary conditions. Although there are a number of studies as to the activation of carbon dioxide, the examples of the catalytic fixation so far reported are rather limited.[1]

We have investigated the fixation of carbon dioxide catalyzed by metalloporphyrins and reported previously that aluminum porphyrin having an axial aluminum alkoxide group (**1**, X = OR) in the presence of 1-methylimidazole catalyzes the reaction between carbon dioxide and epoxide to form cyclic carbonate, in-

Al(TPP)X **1**
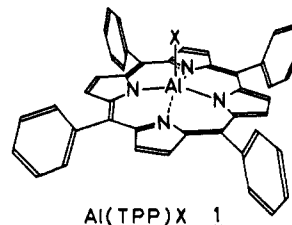
volving the insertion of carbon dioxide into the aluminum alkoxide bond.[2] Our related studies revealed that (*N*-methyl-5,10,15,20-tetraphenylporphinato)zinc ethyl (Zn(NMTPP)Et (**2**)) reacts with a mixture of carbon dioxide and secondary amine to

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