Trans-esterification Reaction Catalyzed by Alkoxo(triphenylphosphine)copper(I) Complexes

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Alkoxocopper and phenoxocopper complexes ROCu $(PPh_3)_n$ (PPh_3=triphenylphosphine; n=1 for R=*n*-C_3H_7 or *i*-C_3H_7; n=2 for R=CH_3, C_2H_5, CH_2=$CHCH_2$, $C_6H_5CH_2$, or C_6H_5) react with esters undergoing exchange of the RO group with carboxylic esters. The alkoxocopper and phenoxocopper complexes are found to be excellent catalysts for the trans-esterification of carboxylic esters, dimethyl carbonate, and trimethyl phosphite with alcohols and phenols. A comparison of the ability of the isopropoxocopper complex as trans-esterification catalyst with that of aluminum isopropoxide and titanium isopropoxide shows the superiority of the isopropoxocopper complex. The rate of trans-esterification between *p*-nitrophenyl acetate and phenol follows the second-order rate law $R=k$[*p*-nitrophenyl acetate][phenol], the activation energy of the reaction being estimated to be 12.4 kcal/mol. A mechanism comprising a nucleophilic attack on the copper-bound carbonyl group of the ester by alcohol is proposed.

Although metal alkoxides and phenoxides are widely utilized as reagents and catalysts for organic syntheses, reports on the utilization of copper alkoxides for organic syntheses are limited.[1] This seems to be due to the availability of only a few stable and well-characterized alkoxocopper and phenoxocopper compounds. In the preceding paper a report was given on the preparation of a series of stable alkoxocopper and phenoxocopper complexes formulated as ROCu-$(PPh_3)_n$ (PPh_3=triphenylphosphine) by the reaction of $CH_3Cu(PPh_3)_2(ether)_{0.5}$ with alcohols and phenol.[2]

In this paper we describe the utilization of the alkoxocopper and phenoxocopper complexes $ROCu(PPh_3)_n$ as the trans-esterification catalyst.

Results and Discussion

Alkoxo and Phenoxo Group Exchange Reactions between $ROCu(PPh_3)_n$ and Esters. Prior to exploration of the catalytic activities of the alkoxocopper and phenoxocopper complexes for trans-esterification, stoichiometric exchange reactions betweeen $ROCu(PPh_3)_n$ and esters were examined in order to find the general trend of the exchange reactions of the RO–Cu complexes against esters. The following exchange reactions were carried out between $ROCu(PPh_3)_n$ and acetic esters:

$$ROCu(PPh_3)_n + CH_3COOR' \xrightarrow{-5\,^\circ C} R'OCu(PPh_3)_n + CH_3COOR \quad (1)$$

R: CH_3(**1a**), C_2H_5(**1b**), *n*-C_3H_7(**1c**), allyl(**1d**), *i*-C_3H_7(**1e**), benzyl(**1f**), C_6H_5(**1g**), n=1 for **1c** and **1e**, n=2 for the others, **1a**, **1c**, and **1f** have diethyl ether as the solvent of crystallization. The results are summarized in Table 1.

Yields of the exchanged esters were determined by means of gas chromatography and those of R'OCu-

Table 1. Alkoxo and phenoxo group exchange reaction between $ROCu(PPh_3)_n$ and CH_3COOR'[a]

$ROCu(PPh_3)_n + CH_3COOR' \longrightarrow R'OCu(PPh_3)_n + CH_3COOR$

$ROCu(PPh_3)_n$	%-Yields[b] of products $R'OCu(PPh_3)_n$ and CH_3COOR				
	R'=C_6H_5	R'=vinyl	R'=benzyl	R'=allyl	R'=C_2H_5
R=CH_3 (**1a**)	92 (89)	96 (75)[c]	82 (75)	76 (61)	46 d)
R=C_2H_5 (**1b**)	78 (70)	93 (22)[c]	78 (69)	74 (56)	— —
R=*n*-C_3H_7 (**1c**)	87 (84)	76 —	75 d)	56 d)	25 d)
R=allyl (**1d**)	96 (91)	32 (15)[c]	48 (50)	— —	20 d)
R=*i*-C_3H_7 (**1e**)	82 (75)	82 —	51 d)	42 d)	18 d)
R=benzyl (**1f**)	95 (92)	84 (69)	— —	33 d)	17 d)
R=C_6H_5 (**1g**)	—	NO[e]	NO[e]	NO[e]	NO[e]

a) Reaction conditions: −5 °C for 12 h for complexes **1a**—**1f**: room temperature for 12 h for complex **1g**. b) Upper figures, %-yield of CH_3COOR; figures in parentheses, % yield of the isolated $R'OCu(PPh_3)_n$. c) C-Bonded acetoxyvinylcopper complex with formation of acetaldehyde. d) A mixture of the starting complex and produced complex was obtained but separation of the mixture was difficult. e) The starting $PhOCu(PPh_3)_2$ was recovered unreacted after 1—2 days.

$(PPh_3)_n$ were calculated from the weights of the isolated complexes. The starting alkoxocopper and phenoxocopper complexes are arranged in the increasing order of stability of the complexes, **1a<1b<1c<1d<1e<1f<1g**,[2] as judged by the decomposition points of the alkoxocopper complexes. Acetic esters are arranged in the decreasing order of the stability of the produced complexes $R'OCu(PPh_3)_n$.

It is seen that, in most cases, the RO group of $ROCu(PPh_3)_n$ can be exchanged with the R'O group of CH_3COOR' even at −5 °C and the yield of the product apparently depends on the relative stability of the complex $R'OCu(PPh_3)_n$ produced. The considerably high yields of products on employment of vinyl acetate seem to be due to high stability of the six-membered C-bonded acetoxyvinylcopper complex formed in the reaction.[2,3] When the starting complex is very stable such as the phenoxocopper complex **1g**, the exchange reaction with alkyl and alkenyl acetates scarcely proceeds. The reaction of **1c** and **1e** with phenyl acetate gave a new phenoxocopper complex containing only one PPh_3 ligand $C_6H_5OCuPPh_3$, whereas $C_6H_5OCu(PPh_3)_2$ has been obtained by the reaction of $CH_3Cu(PPh_3)_2 \cdot 0.5Et_2O$ with phenol.[2] The alkoxo and phenoxo group exchange reaction between $ROCu(PPh_3)_n$ and ester is not restricted to the esters of acetic acid. Employment of other various alkyl and aryl carboxylates also leads to the exchange reaction below room temperature indicating that the RO ligands bonded to copper have high lability toward the attack of esters.

The alkoxo and phenoxo group exchange reaction on copper may proceed through one of the concerted four center mechanisms as shown by Eqs. 2 and 3 or through an oxidative addition of esters to copper (Eq. 4).

$$CH_3COOR' + ROCuL_n \longrightarrow \underset{\mathbf{I}}{\text{R'O-Cu(L}_n\text{)-O-R}} \longrightarrow CH_3COOR + R'OCuL_n \quad (2)$$

$$CH_3COOR' + ROCuL_n \longrightarrow CH_3C(=O)(OR') \rightarrow Cu(OR)L_n \longrightarrow \underset{\mathbf{II}}{CH_3-C(OR')(OR)-O-Cu} \quad (3)$$

$$\longrightarrow \underset{\mathbf{III}}{CH_3-C(OR')(OR)-O-CuL_n} \longrightarrow CH_3COOR + R'OCuL_n$$

$$CH_3COOR' + ROCuL_n \longrightarrow \underset{\mathbf{III}}{CH_3CO(R'O)-O-CuL_n} \longrightarrow CH_3COOR + R'OCuL_n \quad (4)$$

The existence of carboxylic ester-coordinated metal complexes is well known and Lappert showed that the carbonyl group in esters is bonded to metal.[4] Equations 2 and 3 show that the ester coordination to the alkoxocopper complex facilitates the nucleophilic attack on the carbonyl group by the alkoxo group. Since esters can add oxidatively to transition metal compounds such as Ni(0)[5] and Mo(0)[6] complexes with the cleavage of the bond between acyl and alkoxyl groups, the mechanism expressed by Eq. 4 is also conceivable.

Trans-esterification Catalyzed by Alkoxocopper and Phenoxocopper Complexes. Alkoxocopper and phenoxocopper complexes catalyze trans-esterification of carboxylic esters, dialkyl carbonates, and trialkylphosphines under mild conditions. The results are summarized in Table 2.

When an equimolar amount of an ester and an alcohol is used and the free energy change in the trans-esterification is small, as in the ester interchange between methyl carboxylates and ethanol (Table 2, Nos. 1 and 4,), about half of the starting ester is interchanged with alcohol. The extent of ester interchange increases with increase in the amount of alcohol (Nos. 4, 5, and 19). An ester with a bulky alkyl group such as *t*-butyl acetate did not undergo the interchange reaction smoothly (No. 3).

The trans-esterification of alkenyl carboxylates presents a special case. Vinyl acetate and isopropenyl acetate were converted into alkyl acetate in high yields by the exchange reaction with alcohols. In these cases, however, alkenols which may be produced as intermediates are considered to have been converted into their stabler tautomers, acetaldehyde and acetone.

$$CH_2=CH(OCOCH_3)(R') + R''OH \xrightarrow{CuOR(PPh_3)_n} CH_2=CH(OH)(R') + CH_3COOR'' \quad (5)$$

$$CH_2=CH(OH)(R') \rightarrow CH_3-C(=O)-R'$$

Since the amount of acetaldehyde was much smaller than that of methyl acetate in No. 5, the major part of acetaldehyde seems to be further converted into polyaldols by copper complex.[7] When the starting ester has more than two alkoxyl groups as in dimethyl fumarate, dimethyl carbonate, and trimethyl phosphite, a mixture of partially and fully interchanged prodcuts was obtained, the ratio between the products depending upon the relative amount of alcohol to ester.

A comparison of the catalytic activity of i-$C_3H_7OCuPPh_3$ with that of typical trans-esterification catalysts at 0 °C is given in Table 3. We see that i-$C_3H_7OCuPPh_3$ has much higher activity than the corresponding aluminum and titanium alkoxides and an activity comparable to that of i-C_3H_7ONa which is a much stronger base than i-$C_3H_7OCuPPh_3$. Thus the present system is expected to provide synthetic utility specially when applied to systems which are susceptible to attack of strong base.

TABLE 2. TRANS-ESTERIFICATION OF CARBOXYLIC ESTERS

No.	Ester (mmol)	Alcohol	Molar ratio (alcohol/ester)	Catalyst[a]	Temp (°C)	Time (h)	Products (%-yield/starting ester)
1	CH_3COOCH_3 (20)	C_2H_5OH	1.0	**1b** (0.16)	−5	12	$CH_3COOC_2H_5$ (41)
2	$C_6H_5COOCH_3$ (10)	C_2H_5OH	2.0	**1b** (0.32)	0	12	$C_6H_5COOC_2H_5$ (59)
3	CH_3COO-t-C_4H_9 (10)	C_2H_5OH	6.0	**1b** (0.32)	0	12	$CH_3COOC_2H_5$ (6)
4	CH_2=$C(CH_3)COOCH_3$ (10)	C_2H_5OH	1.0	**1b** (0.32)	0	12	CH_2=$C(CH_3)COOC_2H_5$ (48)
5	CH_2=$C(CH_3)COOCH_3$ (6.8)	C_2H_5OH	9.0	**1b** (0.32)	0	24	CH_2=$C(CH_3)COOC_2H_5$ (73)
6	CH_3COOCH=CH_2 (60)	CH_3OH	1.0	**1a** (0.32)	−5	12	CH_3COOCH_3 (91), CH_3CHO (20)
7	$CH_3COOC(CH_3)$=CH_2 (30)	C_2H_5OH	2.0	**1b** (0.32)	0	12	$CH_3COOC_2H_5$ (100), CH_3COCH_3 (100)
8	CH_3OCOCH=$CHCOOCH_3$ (10)	C_2H_5OH	2.0	**1b** (0.32)	0	12	$CHCOOC_2H_5$(49), C_2H_5OCOCH=$CHCOOC_2H_5$ (42)
9	CH_3OCOCH=$CHCOOCH_3$ (10)	C_2H_5OH	10.0	**1b** (0.32)	0	12	$CHCOOC_2H_5$(73), C_2H_5OCOCH=$CHCOOC_2H_5$ (10)
10	$(CH_3O)_2CO$ (20)	C_2H_5OH	2.0	**1b** (0.32)	0	12	$(C_2H_5O)_2CO$ (7), $C_2H_5O(CH_3O)CO$ (48)
11	$(CH_3O)_2CO$ (20)	C_2H_5OH	10.0	**1b** (0.32)	0	12	$(C_2H_5O)_2CO$ (63), $C_2H_5O(CH_3O)CO$ (34)
12	$P(OCH_3)_3$ (10)	C_2H_5OH	4.0	**1b** (0.32)	0	12	$P(OEt)_3$ (18), $P(OEt)_2OMe$ (37), $P(OMe)_2OEt$ (41)
13	$P(OCH_3)_3$ (20)	C_2H_5OH	10.0	**1b** (0.32)	0	12	$P(OEt)_3$ (60), $P(OEt)_2OMe$ (37), $P(OMe)_2OEt$ (2)
14	$CH_3COOCH_2C_6H_5$ (20)	i-C_3H_7OH	3.0	**1e** (0.32)	0	12	$CH_3COOCH(CH_3)_2$ (70)
15	CH_3COO-p-$C_6H_5NO_2$ (20)	C_6H_5OH	2.0	**1g** (0.30)	r.t.[b]	12	$CH_3COOC_6H_5$ (57)
16	CH_3COO-p-$C_6H_5OCH_3$ (20)	C_6H_5OH	2.0	**1g** (0.30)	r.t.[c]	12	$CH_3COOC_6H_5$ (17)
17	$CH_3COOC_2H_5$ (20)	C_6H_5OH	1.0	**1g** (0.30)	50[d]	10	no reaction proceeds
18	CH_3COOCH_3 (20)	C_2H_5OH	1.0	**1g** (0.30)	r.t.	12	$CH_3COOC_2H_5$ (55)
19	CH_2=$C(CH_3)COOCH_3$	C_2H_5OH	20.0	**1g** (0.30)	55[e]	1	CH_2=$C(CH_3)COOC_2H_5$ (94)

a) **1a**=$CH_3OCu(PPh_3)_2 \cdot 0.5Et_2O$, **1b**=$C_2H_5OCu(PPh_3)_2$, **1e**=$i$-$C_3H_7OCuPPh_3$, **1g**=$C_6H_5OCu(PPh)_2$. b) In 15 ml of toluene. c) In 10 ml of toluene. d) In 5 ml of toluene. e) In 10 ml of THF.

TABLE 3. COMPARISON OF CATALYTIC ACTIVITIES OF i-$C_3H_7OCuPPh_3$ **1e** WITH THOSE OF $Al(O$-i-$C_3H_7)_3$, $Ti(O$-i-$C_3H_7)_4$, AND i-C_3H_7ONa FOR THE TRANS-ESTERIFICATION OF $CH_3COOCH_2C_6H_5$ WITH i-C_3H_7OH[a]

Catalyst	Yield of CH_3COO-i-C_3H_7 (%)
i-$C_3H_7OCuPPh_3$	70
$Ti(O$-i-$C_3H_7)_4$	20
$Al(O$-i-$C_3H_7)_3$	negligible
i-C_3H_7ONa	76

a) The reactions were carried out at 0 °C for 12 h using 0.32 mmol of the catalyst, 20 mmol of benzyl acetate and 60 mmol of isopropyl alcohol.

Figure 1 shows the time course of the trans-esterification of p-nitrophenyl acetate with phenol catalyzed by $C_6H_5OCu(PPh_3)_2$ under the conditions where the ratio of p-nitrophenyl acetate to phenol or that of phenol to p-nitrophenyl acetate was kept at 100. The data obtained under the two different situations fit the same curve. The first-order plot (log Co/C *vs.* t) of the data in Fig. 1 gives a straight line indicating that the rate of trans-esterification is proportional to both the concentration of p-nitrophenyl acetate and that of phenol:

$$R = k[p\text{-nitrophenyl acetate}][\text{phenol}] \quad (6)$$

When the molar ratio of p-nitrophenyl acetate to phenol is unity, the time course of conversion follows the second-order rate law supporting the validity of Eq. 6. From the temperature dependence of the second-order rate constant k (Table 4) the activation energy for trans-esterification was calculated to be E_a=12.4 kcal/mol. The rate of trans-esterification increases linearly with increase in the catalyst concentration.

Mechanism of Trans-esterification. A simple extension of the observation on stoichiometric exchange reactions between esters and the alkoxocopper complexes to catalytic trans-esterification promoted by the alkoxocopper complexes leads to the following mechanism comprising two steps, (1) the exchange between the ester and the alkoxocopper, and (2) the exchange between the alcohol used and the newly formed alkoxo-

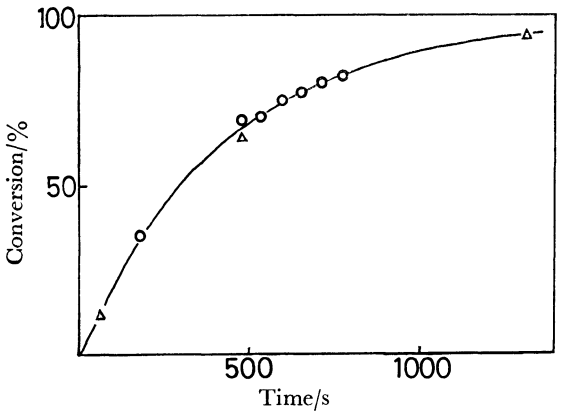


Fig. 1. Trans-esterification of *p*-nitrophenyl acetate with phenol catalyzed by $C_6H_5OCu(PPh_3)_2$. (a) ○, CH_3COO-*p*-$C_6H_4NO_2$=0.5 mmol (90 mg), C_6H_5OH=50 mmol (4.70 g), catalyst=85 mg, in this case the conversion is based on CH_3COO-*p*-$C_6H_4NO_2$. (b) △, CH_3COO-*p*-$C_6H_4NO_2$=50 mmol (9.00 g), C_6H_5OH=0.5 mmol (47 mg), catalyst=85 mg, in this case the conversion is based on C_6H_5OH. Solvent=toluene (10 ml) Temp=50 °C.

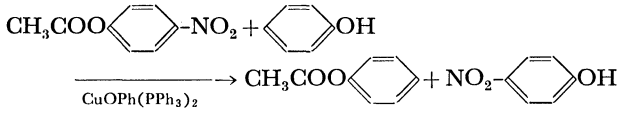


Table 4. Temperature dependence of the second-order rate constant k in the trans-esterification of CH_3COO-*p*-$C_6H_4NO_2$ with C_6H_5OH[a]

Temp (K)	$1/T$	k(l·mol^{-1}·s^{-1})
323	3.10×10^{-3}	0.8×10^{-4}
353	2.84×10^{-3}	4.0×10^{-4}
383	2.61×10^{-3}	17.0×10^{-4}
	E_a=12.4 kcal/mol	

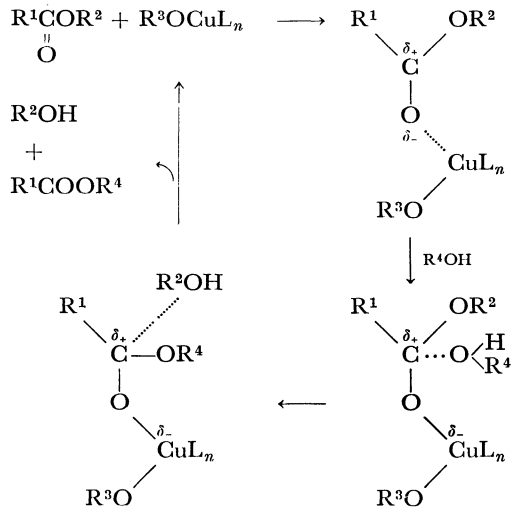
a) Catalyst=$C_6H_5OCu(PPh_3)_2$ (0.13 mmol). [CH_3COO-*p*-$C_6H_5NO_2$]=[C_6H_5OH]=1.0 mol/l. Solvent=toluene.

copper complex.:

$$R^1COOR^2 + R^3OCuL_n \longrightarrow R^2OCuL_n + R^1COOR^3$$
$$R^2OCuL_n + R^3OH \longrightarrow R^3OCuL_n + R^2OH$$
$$R^1COOR^2 + R^3OH \xrightarrow[ROCuL_n]{} R^1COOR^3 + R^2OH \quad (7)$$

Such a trans-esterification reaction does not seem to constitute the main mechanistic pathway for the following reasons. (a) The phenoxocopper complex **1g**, which undergoes exchange reaction with neither aliphatic esters nor alcohols, catalyzes the trans-esterification between methyl acetate and ethanol. (b) The exchange reaction between *p*-NO_2-$C_6H_4OCu(PPh_3)_2$ and phenol is extremely slow as compared to the relatively fast trans-esterification between *p*-nitrophenyl acetate and phenol catalyzed by **1g**. (c) The kinetic results expressed by Eq. 6 are not compatible with the stepwise mechanism shown by Eq. 7.

From the available experimental evidence we propose that the trans-esterification reaction proceeds through the copper-assisted nucleophilic replacement mechanism as shown below:



In view of the loosening of the carbonyl group in esters on their coordination to metal compounds as shown by infrared work by Lappert,[4c] the nucleophilic attack of the carbonyl carbon whose electron density decreases by coordination of the carbonyl group to metal is plausible. The mechanism is in line with the second-order rate equation, provided that the attack of alcohol on the metal-coordinated ester is the rate-determining step. According to the reaction mechanism the activation energy for the trans-esterification consists of the energy for the coordination of R^1COOR^2 to $R^3OCu(PPh_3)_n$ and that for the nucleophilic attack of R^4OH to the reaction intermediate.

Experimental

General. Preparation and the reaction of copper complexes were carried out in Schlenk type flasks under deoxygenated nitrogen or argon, or in a vacuum. Solvents were dried by the usual procedure, distilled, and stored in argon or nitrogen. IR spectra were recorded on a Hitachi Model 295 spectrophotometer. Microanalysis of carbon, hydrogen and nitrogen was carried out by Mr. T. Saito in our laboratory with a Yanagimoto CHN Autocorder Type MT-2.

Materials. Esters used in the reaction were sufficiently pure as checked by gas chromatography. Alkoxocopper and phenoxocopper complexes **1a**—**1g** were prepared as reported in the preceding paper.[2] *p*-Nitrophenoxocopper complex *p*-$O_2NC_6H_4OCu(PPh_3)_2$ was prepared similarly; yield=90%. Found: C, 69.7; H, 4.69; N, 2.10%. Calcd for $C_{42}H_{34}CuNO_3P_2$: C, 69.5; H, 4.68; N, 1.93%. IR (KBr): 1580, 1505, 1307, 1280 cm^{-1}. NMR (C_6D_6): δ 6.48 (d, 2H), 7.0 (m, 18H), 7.4 (m, 12H), 8.04 (d, 2H).

Stoichiometric Exchange Reactions between $ROCu(PPh_3)_n$ and Carboxylic Esters. Phenyl acetate (64 mg, 0.47 mmol) was added to **1c** (200 mg, 0.47 mmol) suspended in 2 ml of diethyl ether at −5 °C. Stirring of the mixture at −5 °C for 12 h gave 0.41 mmol (87% per **1c**) of propyl acetate and a white precipitate. The white precipitate was recrystallized from toluene and dried in a vacuum to give a new phenoxocopper complex having one PPh_3 ligand, $C_6H_5OCuPPh_3$ (172 mg, 84% per **1c**). Found: C, 68.3; H, 4.50%. Calcd for $C_{24}H_{20}CuOP$: 68.8; H, 4.78%. IR(KBr): 1580, 1270 cm^{-1}. Other stoichiometric exchange reactions

of alkoxocopper and phenoxocopper complexes with carboxylic esters were carried out in a similar manner.

Catalytic Trans-esterification. Methyl acetate (1.48 g, 20 mmol) was added to an ethyl alcohol (0.92 g, 20 mmol) solution of **1c** (68 mg, 0.16 mmol) at −5 °C. Stirring of the solution at the temperature for 12 h afforded 8.2 mmol of ethyl acetate as determined by gas chromatography. Trans-esterification of carboxylic esters and trimethyl phosphite was carried out in a similar manner.

Kinetic Study. Kinetic study on the trans-esterification of CH_3COO-*p*-$C_6H_4NO_2$ by C_6H_5OH was carried out in a Schlenk type flask immersed in a thermostatted oil bath. The solvent, reactants, and catalyst were transferred in an atmosphere of nitrogen. The time-dependent conversion was measured by pipetting out each fraction of the solution at a set time and analyzing it by gas chromatography.

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