Synthesis, Reactions and Catalytic Properties of Stable Alkoxocopper, Phenoxocopper and Related Copper Complexes Containing Triphenylphosphine Ligands

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A variety of new alkoxocopper and phenoxocopper(I) complexes containing triphenylphosphine ligands have been prepared by the reactions of methylbis(triphenylphosphine)copper(I) etherate (I) with the corresponding alcohols and phenols. The isolated complexes were characterized by elemental analysis, IR and NMR spectroscopy and chemical reactions. The reactions of the alkoxocopper and phenoxocopper complexes with alkyl halides and acyl halides or carboxylic anhydrides yield ethers and carboxylic esters, respectively. The stoichiometric exchange reactions of the alkoxo group in the alkoxocopper complexes with carboxylic esters proceed smoothly and the alkoxocopper complexes were found to act as excellent catalysts for the transesterifications between carboxylic esters and alcohols. The exchange reactions take place also between the alkoxocopper complexes and phenols or thiols producing phenoxocopper or alkylthiocopper complexes with the liberation of alcohols. Amides and nitromethane react with the alkoxocopper complexes releasing alcohols to give *N*-bonded amidocopper and *O*-bonded acinitrocopper complexes, respectively. The thermolysis of the alkoxocopper complexes in various solvents were studied and the mechanism and the factors influencing the course of thermolysis discussed.

The versatility of alkyl- and arylcopper(I) reagents in organic syntheses has been well established[1] but the utility of alkoxo- and phenoxocopper(I) complexes has been less explored.[2] There are only a few reported examples of well characterized alkoxocopper compounds. Poorly characterized copper methoxide has been reported to be thermally unstable and explosive.[3] *t*-Butoxocopper provides the most stable example amongst the known alkoxocopper compounds without ligands and the reactions of copper *t*-butoxide have been studied.[5–7] Other primary and secondary alkoxides are less stable and they have been prepared by heterogeneous reactions *in situ* and characterized only through indirect means.[8] Copper phenoxide is more stable than the alkoxide and substituted and unsubstituted phenoxocopper compounds have been prepared and utilized for ether and ester syntheses.[9] Copper(II) alkoxides, copper(II) methoxides[3a,10] and copper(II) acetylacetonate methoxide[11] are known.

The remarkable stabilizing effect of tertiary phosphines on the thermal stability of alkylcopper compounds has been reported before.[12,13] The reactions of alcohols with the alkylcopper(I) complexes having tertiary phosphine ligands led to the preparation of a variety of stable alkoxocopper(I) complexes having tertiary phosphine ligands. The stabilizing effect of the tertiary phosphine ligands was also evident in the alkoxocopper complexes which provide convenient materials for studying the properties of the synthetically useful alkoxocopper complexes and allow examination of the mechanism of thermolysis of the alkoxocopper complexes and to compare the results with the thermolysis behavior of the alkylcopper complexes. This paper describes the synthesis and properties of the alkoxocopper complexes containing triphenylphosphine.

Results and Discussion

Synthesis of Alkoxocopper(I) Complexes with Triphenylphosphine Ligands. Methylbis(triphenylphosphine)copper etherate, $CH_3Cu(PPh_3)_2\cdot 0.5Et_2O$ (I)[12] reacts with alcohols and phenols to give alkoxo- and phenoxocopper complexes (II—XI) containing triphenylphosphine ligands. Some complexes include diethyl ether as the solvent of crystallization.

$$CH_3Cu(PPh_3)_2\cdot 0.5Et_2O + ROH \xrightarrow{Et_2O} ROCu(PPh_3)_m(Et_2O)_n + CH_4 \quad (1)$$

$R = $ Me (II), Et (III), Pr^n (IV), $CH_2{=}CH{-}CH_2{-}$ (V), Pr^i (VI), $PhCH_2{-}$ (VII)

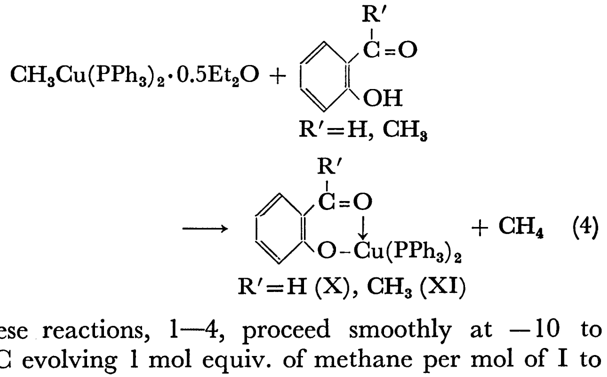
Ethylene glycol reacts at one of the hydroxyl groups producing hydroxyethoxocopper complex (VIII):

$$CH_3Cu(PPh_3)_2\cdot 0.5Et_2O + HOCH_2CH_2OH \xrightarrow{Et_2O} \underset{\text{(VIII)}}{HOCH_2CH_2OCu(PPh_3)_2} + CH_4 \quad (2)$$

Phenol reacts similarly with I to give the known phenoxocopper complex prepared by different route.[9]

$$CH_3Cu(PPh_3)_2\cdot 0.5Et_2O + PhOH \xrightarrow{Et_2O} \underset{\text{(IX)}}{PhOCu(PPh_3)_2} + CH_4 \quad (3)$$

o-Formyl- and *o*-acetyl-substituted phenols afford six-membered chelates:



These reactions, 1—4, proceed smoothly at −10 to 0 °C evolving 1 mol equiv. of methane per mol of I to give white or yellow precipitate of II—XI in high yields.

Table 1 summarizes the yields, melting points, analytical results and molecular weights of the isolated copper complexes and Table 2 shows the relevant NMR and IR data. The alkoxocopper complexes are sensitive to oxygen and water but their thermal stabilities are substantially enhanced in comparison with the alkoxocopper compounds without triphenylphosphine as exemplified by the high melting point (dec) 65 °C of $CH_3OCu(PPh_3)_2\cdot 0.5Et_2O$ compared with CH_3OCu which explodes on heating. The decomposition temperature of the series of alkoxocopper complexes rises with increasing alkyl chain length, a similar trend being observed in the thermal stabilities of alkylcopper complexes.[12] Albeit the alkoxocopper complexes have high decomposition temperatures in the solid state, they are less stable in solution and decompose in benzene at about 0 °C preventing the cryoscopic determination of the molecular weight in benzene. The reaction of I with ethylene glycol was expected to yield a bridged ethylene glycol derivative of copper. The molecular weight and analytical data of VIII together with the presence of the free ν(OH) band at 3300 cm^{-1} in the IR spectrum indicated that one of the two OH groups of ethylene glycol remains intact after reaction with I.

The phenoxocopper complexes showed much higher decomposition temperatures than the alkoxocopper complexes. The formation of the six-membered chelates in X and XI was deduced on the basis of the shifts of the ν(C=O) bands to lower frequencies (35 and 40 cm^{-1}) from those of the free salicylaldehyde and *o*-hydroxyacetophenone. These alkoxocopper complexes containing triphenylphosphine may also be obtained by the reaction of lithium or sodium alkoxide with bromobis(triphenylphosphine)copper, but the yield was poor and the purification of the product was more difficult than that of the complexes prepared by Eq. 1.

The phenoxocopper complex was prepared by the reaction of cuprous oxide with phenol in the presence of triphenylphosphine giving a yield of 59% based on copper.

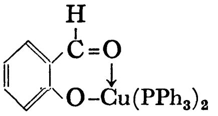
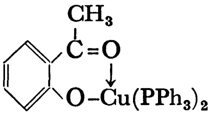
$$Cu_2O + 2PhOH + 4PPh_3 \xrightarrow{75\ ^\circ\text{C in toluene}} \underset{\text{IX}}{2PhOCu(PPh_3)_2} + H_2O$$

The reaction required a higher temperature and a longer reaction period than the preparation starting from I.

The preparation of alkoxocopper complexes higher than butoxocopper was also attempted using I but the reaction was too slow to give the corresponding alkoxocopper complexes without the decomposition of the alkoxocopper complexes formed.

Reactions of Alkoxocopper Complexes. One of the features of the alkoxocopper complexes is the ability to exchange the alkoxo group. The alkoxo group bound to copper can be readily displaced by other components to give new organic copper complexes. The reactions appear to proceed smoothly, particularly when the product is more stable than the starting alkoxocopper complex. Thus, ethoxocopper complex III reacts with 1.5 equivalents of phenol in diethyl ether at 0 °C to

Table 1. Analytical data of alkoxocopper complexes

Complex		Yield (%)	Mp[a)] (°C)	Analysis Found (Calcd) (%) C	H	*M.W.*[b)] (Calcd)
$CH_3OCu(PPh_3)_2\cdot 0.5Et_2O$	(II)	59	65 (dec)	71.2 (71.4	5.16 5.79)	
$CH_3CH_2OCu(PPh_3)_2$	(III)	72	88 (dec)	71.5 (72.1	5.51 5.53)	
$CH_3CH_2CH_2OCuPPh_3\cdot 0.5Et_2O$	(IV)	77	89 (dec)	65.2 (65.5	6.26 6.41)	
$CH_2{=}CHCH_2OCu(PPh_3)_2$	(V)	66	98 (dec)	72.9 (72.6	5.47 5.43)	
$(CH_3)_2CHOCuPPh_3$	(VI)	79	118 (dec)	65.3 (65.5	5.45 5.72)	
$PhCH_2OCu(PPh_3)_2\cdot Et_2O$	(VII)	72	145 (dec)	73.3 (73.4	5.68 6.18)	712±10 (768.5)
$HOCH_2CH_2OCu(PPh_3)_2$	(VIII)	76	123 (dec)	70.5 (70.3	5.20 5.40)	601±10 (648.5)
$PhOCu(PPh_3)_2$	(IX)	48	218	73.5 (74.0	5.04 5.14)	635±10 (680.5)
	(X)	86	207—208 (dec)	73.2 (72.8	5.29 4.94)	659±10 (708.5)
	(XI)	76	179—180 (dec)	72.8 (73.1	5.19 5.12)	674±10 (722.5)

a) Measured in vacuum-sealed capillaries. b) Cryoscopic in benzene.

TABLE 2. ^{1}H-NMR AND IR DATA OF ALKOXOCOPPER COMPLEXES

Complex	^{1}H-NMR (solvents)		IR[a] (KBr disk) (cm^{-1})
II	δ 1.1 (t, 3H in Et_2O) δ 3.2(q, 2H in Et_2O) δ 3.4 (s, 3H in OCH_3) δ 7.0 (m, 18H in PPh_3)	δ 7.6 (m, 12H in PPh_3) (toluene-d_8, -20 °C)	ν (C–O) 1050 (m) and 985 (m)
III	δ 1.2 (t, 3H) δ 3.9 (q, 2H) δ 7.0 (m, 18H) δ 7.5 (m, 12H)	(toluene-d_8, -20 °C)	ν (C–O) 1105 (s) and 1045 (m)
IV	δ 0.85 (t, 3H) δ 1.1 (t, 3H in Et_2O) δ 1.6 (m, 2H) δ 3.2 (q, 2H in Et_2O)	δ 4.2 (q, 2H) δ 7.0 (m, 9H in PPh_3) δ 7.6 (m, 6H in PPh_3) (toluene-d_8, -32 °C)	ν (C–O) 1060 and 1020
V	δ 3.8 (m, 2H) δ 5.0 (m, 1H) δ 5.3 (m, 1H) δ 5.8 (m, 1H)	δ 7.0 (m, 18H in PPh_3) δ 7.4 (m, 12H in PPh_3) (toluene-d_8, -20 °C)	ν (C–O) 1140 (w), 1120 (w) or 1010 (w)
VI	δ 1.3 (d, 6H) δ 4.5 (m, 1H) δ 7.0 (m, 9H in PPh_3) δ 7.7 (m, 6H in PPh_3)	(toluene-d_8, -30 °C)	ν (C–O) 1125 (s)
VII	δ 1.1 (t, 6H in Et_2O) δ 3.2 (q, 4H in Et_2O) δ 5.0 (s, 2H) δ 7.0 (m, 18H in PPh_3 and 5H in Ph)	δ 7.4 (m, 12H in PPh_3) (toluene-d_8, -32 °C)	ν (C–O) 1100 (m)
VIII	δ 4.1 (m, 4H) δ 5.7 (s, 1H broad) δ 7.1 (m, 18H in PPh_3) δ 7.5 (m, 12H in PPh_3)	(benzene-d_6, r.t.)	ν (O–H) 3300 (s, broad) ν (C–O) 1070 (vs)
IX	δ 6.5—6.9 (m, 4H in PhO group) δ 7.0 (m, 18H in PPh_3 and 1H in PhO group) δ 7.6 (m, 12H in PPh_3)	(benzene-d_6, r.t.)	ν (C=C) 1580 (s) ν (C–O) 1270 (s), 1150 (m)
X	δ 7.0 (m, 18H in PPh_3 and 2H in phenoxo group) δ 7.6 (m, 12H in PPh_3 and 2H in phenoxo group) δ 9.26 (s, 1H)	(benzene-d_6, r.t.)	ν (C=O) 1630 (vs) ν (C–O) 1230 (w), 1140 (s) or 1015 (m)
XI	δ 2.12 (s, 3H) δ 7.0 (m, 18H in PPh_3 and 2H in phenoxo group) δ 7.6 (m, 12H in PPh_3 and 2H in phenoxo group)	(benzene-d_6, r.t.)	ν (C=O) 1603 (vs) ν (C–O) 1245 (m), 1205 (s) or 1025 (w)

a) vs=very strong, s=strong, m=medium, w=weak.

produce the more thermally stable phenoxocopper complex IX in high yield:

$$\underset{\text{III}}{EtOCu(PPh_3)_2} + PhOH \longrightarrow \underset{\text{IX (78\%)}}{PhOCu(PPh_3)_2} + \underset{(85\%)}{EtOH}$$

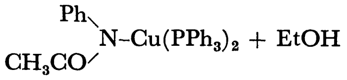
Such alcohol exchange reactions have been extensively utilized in the preparation of new alkoxides of Al, Ge, Sn, Ti, Zr, Hf, Nb, Ta, Fe, La, Th, U, and Pu.[14]

Similarly thiols react smoothly with the ethoxocopper complex with the liberation of ethanol:

$$EtOCu(PPh_3)_2 + EtSH \longrightarrow \underset{\text{XII (82\%)}}{EtSCu(PPh_3)_2} + \underset{(89\%)}{EtOH}$$

An amide also is exchanged with the alkoxocopper complex quite readily. Complex III reacts with an equivalent amount of acetanilide in diethyl ether at 0 °C to produce the thermally stable (acetanilido-*N*)-bis(triphenylphosphine)copper (XIII) and ethanol:

$$EtOCu(PPh_3)_2 + PhNHCOCH_3 \longrightarrow$$



$$\begin{matrix} Ph \diagdown \\ \quad N\text{–}Cu(PPh_3)_2 + EtOH \\ CH_3CO \diagup \end{matrix}$$

XIII (65%) (72%)

The ν(C=O) band in XIII was observed at 1685 cm^{-1}

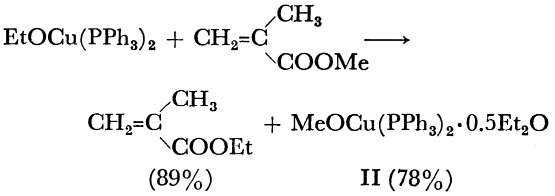
with scarcely any shift from that of the free acetanilide suggesting the *N*-bonded structure.

Furthermore, the alkoxocopper complex reacts with active methylene compounds such as nitromethane and acetylacetone to afford the known complexes XIV and XV:[15,16)]

$$\underset{\text{III}}{\text{EtOCu(PPh}_3)_2} + \text{CH}_3\text{NO}_2 \longrightarrow \underset{\text{XIV (82\%)}}{(\text{CH}_2\text{NO}_2)\text{Cu(PPh}_3)_2} + \underset{(87\%)}{\text{EtOH}}$$

$$\text{EtOCu(PPh}_3)_2 + \text{Hacac} \longrightarrow \underset{\text{XV (74\%)}}{(\text{acac})\text{Cu(PPh}_3)_2} + \underset{(80\%)}{\text{EtOH}}$$

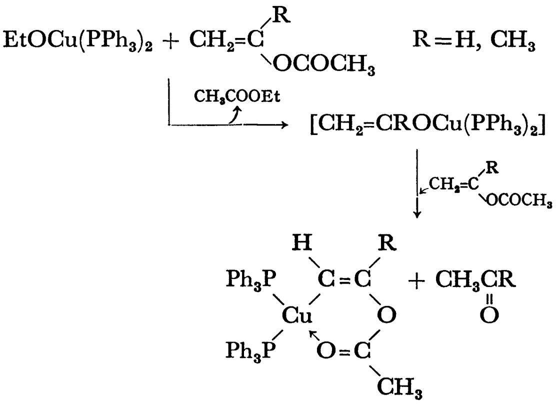
The reactive alkoxocopper complexes function as a transesterification reagent for various carboxylic esters. The reaction of the ethoxocopper complex III with methyl methacrylate, for example proceeds smoothly below room temperature to yield ethyl methacrylate and the methoxocopper complex II in high yields:



$$\text{EtOCu(PPh}_3)_2 + \text{CH}_2{=}\text{C}(\text{CH}_3)\text{COOMe} \longrightarrow \underset{(89\%)}{\text{CH}_2{=}\text{C}(\text{CH}_3)\text{COOEt}} + \underset{\text{II (78\%)}}{\text{MeOCu(PPh}_3)_2\cdot 0.5\text{Et}_2\text{O}}$$

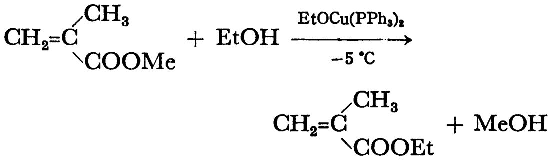
Related transesterification reactions between carboxylic esters and metal alkoxides such as tin,[17)] aluminium,[18)] zirconium, hafnium,[19)] and titanium[19,20)] are known.

In the transesterification reaction of carboxylic esters with alkoxocopper and phenoxocopper complexes it has been noted that reactive alkoxocopper complexes such as methoxo- and ethoxocopper complexes undergo transesterification with a variety of carboxylic esters but the more stable complexes are less reactive. Thus, the phenoxocopper complex failed to react with ethyl acetate, benzyl acetate, allyl acetate, and vinyl acetate, whereas the ethoxocopper complex III underwent the transesterification with all of these esters to give excellent to moderate yields. The reactions of III with vinyl and isopropenyl acetates proceed beyond the simple transesterification and give the known C-bonded 1-acetoxyvinyl and 1-acetoxy-1-methylvinylcopper complexes[21)] together with by-product acetatocopper complex in high yields:



R=H (XVI), CH$_3$ (XVII)

Furthermore, the alkoxocopper complexes serve as excellent catalysts for transesterification between various esters and alcohols. The transesterification reactions of alkyl methacrylates, alkenyl acetates, alkyl acetates, alkyl benzoates, aryl acetates, alkyl carbonates, and alkyl phosphites with alcohols are catalyzed by small amounts of the alkoxocopper complexes under very mild conditions.



$$\text{CH}_2{=}\text{C}(\text{CH}_3)\text{COOMe} + \text{EtOH} \xrightarrow[-5\,^\circ\text{C}]{\text{EtOCu(PPh}_3)_2} \text{CH}_2{=}\text{C}(\text{CH}_3)\text{COOEt} + \text{MeOH}$$

conversion = 73%

Since the catalytic reactions proceed cleanly under mild and neutral conditions, the alkoxocopper complexes provide some synthetic utility.

Reactions of organic halides with copper alkoxides without the tertiary phosphine ligands have been examined by Whitesides[8)] and Hashimoto,[9)] and the formation of various ethers has been reported. The alkoxo- and phenoxocopper complexes prepared in the present study react readily with organic halides producing ethers.

$$\underset{\text{III}}{\text{EtOCu(PPh}_3)_2} + \text{Bu}^n\text{Cl} \xrightarrow{-5\,^\circ\text{C, Et}_2\text{O}} \underset{(36\%)}{\text{CH}_3\text{OBu}^n}$$

$$\underset{\text{VIII}}{\text{HOCH}_2\text{CH}_2\text{OCu(PPh}_3)_2} + \text{MeI} \xrightarrow{-30\text{--}-10\,^\circ\text{C}} \underset{(76\%)}{\text{HOCH}_2\text{CH}_2\text{OMe}}$$

$$\underset{\text{IX}}{\text{PhOCu(PPh}_3)_2} + \text{MeI} \xrightarrow{\text{room temp}} \underset{(99\%)}{\text{PhOMe}}$$

The reactions of the alkoxocopper complexes with acyl chloride have been further examined. Complex III reacts readily with propionyl chloride to produce ethyl propionate in good yield:

$$\text{EtOCu(PPh}_3)_2 + \text{CH}_3\text{CH}_2\text{COCl} \longrightarrow \underset{(82\%)}{\text{CH}_3\text{CH}_2\text{COOEt}}$$

Reaction of the ethoxocopper complex III with acetic anhydride also produces ethyl acetate and the known acetatocopper complex XVI in good yields.

$$\text{EtOCu(PPh}_3)_2 + (\text{CH}_3\text{CO})_2\text{O} \longrightarrow \underset{76\%}{\text{CH}_3\text{COOEt}} + \underset{\text{XVIII (72\%)}}{\text{CH}_3\text{COOCu(PPh}_3)_2}$$

Similar reactions of metal alkoxides with acyl halides and acid anhydrides have been reported.[22,23)]

Thermal Decomposition of Alkoxocopper Complexes. In contrast to the copper alkoxides without tertiary phosphine the thermal stabilities of the present alkoxocopper complexes with triphenylphosphine ligands are considerably enhanced. For a comparison of the thermolysis behavior of simple copper alkoxides with that of phosphine-stabilized alkoxocopper complexes the thermolysis products in various media were examined and compared with those reported by Whitesides (Table 3).

Table 3. Thermal decomposition of alkoxocopper complexes[a)]

Complex	Solvent (H donor ability)[b)]	Alcohol/[c)] Carbonyl	Product balance, %
$CH_3CH_2OCu(PPh_3)_2$ (III)	benzene (0.0004)	9.4	92
	toluene (1.0)	16.8	89
	THF (23)	22.3	95
$CH_3CH_2CH_2OCuPPh_3 \cdot 0.5Et_2O$ (IV)	benzene (0.0004)	11.7	89
	THF (23)	18.2	92
$CH_2{=}CHCH_2OCu(PPh_3)_2$ (V)	benzene (0.0004)	5.2	95
	THF (23)	13.2	99
$(CH_3)_2CHOCuPPh_3$ (VI)	benzene (0.0004)	4.7	86
	toluene (1.0)	4.3	90
	THF (23)	20.5	93
$PhCH_2OCu(PPh_3)_2 \cdot Et_2O$ (VII)	benzene (0.0004)	1.0	96
	toluene (1.0)	1.2	85
	THF (23)	3.0	93
	toluene and styrene[d)] (1: 1)	3.2	87
$PhOCu(PPh_3)_2$ (IX)	in the solid state[e)]	only PhOH	89

a) Alkoxocopper complexes (0.20 g) in 2 ml of various solvents were heated at the boiling points or at 100 °C for 30 min in a closed system. b) The method used to estimate these numbers is described in Ref. 8. c) "Alcohol/carbonyl" in the ratio of the alcohol- and carbonyl-containing products derived from the alkoxo moiety of the alkoxocopper complexes. d) Ethyl benzene (10% per Cu) was detected. e) The phenoxocopper complex was heated above decomposition point in a closed system for 30 min.

The alkoxocopper complexes liberate alcohols, aldehydes or ketones on thermolysis, the former being produced in higher yields relative to those of the carbonyl-containing products. Two principal pathways are possible in the thermolysis of the secondary and primary alkoxocopper complexes. One involves the β-elimination mechanism forming aldehyde and copper hydride which may further react with another alkoxocopper complex to produce an alcohol. The other involves the homolytic splitting of the Cu–O bond producing alkoxy radicals which either disproportionate to the alcohol and aldehyde or abstract hydrogen from the solvent to generate the alcohol. Table 3 indicates the effects of solvents with different hydrogen atom donating abilities on the alcohol/carbonyl ratio. It can be seen that an effective hydrogen donor such as tetrahydrofuran significantly increased the ratio. The result as a whole agrees with the result of Whitesides who used copper alkoxide without the tertiary phosphine ligands and is compatible with the homolytic cleavage of the RO–Cu bond, although the formation of a "free radical" in the homolysis remains to be established. In the benzyloxocopper complex VII the decomposition behavior seems to be somewhat different from that of the rest of the complexes. Furthermore, when the thermolysis was carried out in the presence of styrene, a significant amount of ethylbenzene was produced. The result may be taken as an indication of the presence of β-hydrogen elimination in thermolysis of VII.

Experimental

All preparations, recrystallizations and reactions of copper complexes were carried out under deoxygenated nitrogen, argon, or in a vacuum. Solvents were dried by the usual procedures, distilled and stored under argon or nitrogen. IR spectra were recorded on a Hitachi Model 295 spectrometer using KBr discs under nitrogen. ^1H-NMR spectra were recorded with a Japan Electron Optics Lab. JNM-PS 100 spectrometer (TMS as internal standard). Evolved gas was analyzed with a Hitachi RMU 5B mass-spectrometer and a Shimadzu GC-5B gas chromatograph, and the volume measured with a Toepler pump. The microanalysis of carbon, hydrogen and nitrogen was performed by Mr. T. Saito in this laboratory with a Yanagimoto CHN Autocorder Type MT-2.

Preparation of Methoxobis(triphenylphosphine)copper(I) Etherate (II) and Related Alkoxocopper Complexes III, IV, V, VI, and VII. Methanol (109 μl, 3.2 mmol) was added to the methylcopper complex, $CH_3Cu(PPh_3)_2 \cdot 0.5Et_2O$ (I) (1.732 g, 2.706 mmol) suspended in diethyl ether (5 ml). After stirring the yellow suspension at −10 to 0 °C for a day a white precipitate was produced with the evolution of methane (0.92 mol per mol of Cu). The white precipitate was recrystallized from a mixture of diethyl ether and methanol to give II (1.047 g).

Other alkoxocopper complexes: III, IV, V, VI, and VII were prepared by the reaction of I with the corresponding alcohols in a similar way to that for II.

Preparation of (2-Hydroxyethoxo)bis(triphenylphosphine)copper (VIII). Ethylene glycol (16 mmol) was added to I(1.682 g, 2.63 mmol) suspended in diethyl ether (5 ml). After stirring the yellow suspension at −10 °C for 0.5 h a white precipitate was produced with the evolution of methane (0.92 mol per mol of Cu). The white precipitate was recrystallized from a mixture of toluene and ethylene glycol to give VIII (1.279 g).

Preparation of Phenoxobis(triphenylphosphine)copper (IX). Phenol (0.188 g, 2 mmol) was added to I (1.280 g, 2 mmol) suspended in diethyl ether (10 ml). The yellow suspension was stirred at 0 °C for 20 min to produce a white precipitate with the evolution of 1.0 mol of methane per Cu. Recrystallization of the precipitate from toluene afforded white crystals of IX (0.653 g).

Preparation of IX from Cu_2O, PhOH, and PPh_3. A mixture of Cu_2O (0.143 g, 1 mmol), PhOH (0.190 g, 2 mmol), and PPh_3 (1.05 g, 4 mmol) in toluene (10 ml) was heated at 75 °C for 10 h. The gray precipitate produced was recrystallized from toluene to give $PhOCu(PPh_3)_2$ (IX) (0.803 g, yield 59% based on Cu_2O).

Preparation of (o-Formylphenoxo)bis(triphenylphosphine)copper (X) and (o-Acetylphenoxo)bis(triphenylphosphine)copper (XI). Salicylaldehyde (1.5 mmol) was added to I (0.944 g, 1.475 mmol) suspended in diethyl ether (10 ml). On stirring the yellow emulsion at −10—0 °C for 1 h an orange precipitate was produced with the evolution of methane (0.86 mol per mol of Cu). The precipitate was recrystallized from toluene to give orange crystals of X (0.899 g).

Complex XI (0.549 g) was prepared by the reaction of I (0.64 g, 1 mmol) with *o*-hydroxyacetophenone (1 mmol) in a similar way to the preparation of complex X.

Reaction of III with Phenol. Phenol (0.48 mmol) was added to III (0.20 g, 0.32 mmol) suspended in diethyl ether (2 ml). After stirring the white suspension at −5 to 0 °C for 10 h a clear supernatant and precipitate were produced. The formation of ethanol (yield 85% per Cu) was confirmed in the supernatant by GLC analysis. The precipitate was recrystallized from toluene to give white crystals of IX (0.168 g, yield 78%) which was identified on the basis of its IR spectrum.

Reaction of III with Ethanethiol. The reaction of III (0.20 g, 0.32 mmol) with ethanethiol (0.48 mmol) in diethyl ether (2 ml) at −5 to 0 °C for 10 h produced a white precipitate and released ethanol (yield 89% based on Cu). The precipitate was crystallized from toluene to give white crystals of XII (0.168 g, yield 82%); mp 139 °C (dec). Found: C, 70.4; H, 5.3; S, 5.1%. Calcd for $C_{38}H_{35}P_2SCu$: C, 70.4; H, 5.4; S, 4.9%. IR(KBr): 2950 w, 2900 w, 2850 w, 1235 m cm^{-1} and other absorptions due to PPh_3 ligands. ^1H-NMR (C_6D_6, r.t.): δ 1.2 (t, 3H), 2.8 (q, 2H), 7.1 (m, 18H, *m,p*-phenyl), 7.5 (m, 12H, *o*-phenyl).

Reaction of III with Acetanilide. The reaction of III (0.100 g, 0.158 mmol) with acetanilide (0.158 mmol) in diethyl ether (2 ml) at 0 °C for 24 h liberated ethanol (yield 72% based on Cu) to give a precipitate which on recrystallization from a mixture of diethyl ether and toluene afforded white crystals of XIII (0.074 g, yield 65%). Complex XIII, mp 151 °C (dec). Found: C, 72.7; H, 5.5; N, 2.4%. $C_{34}H_{38}ONP_2Cu$ calcd for: C, 73.2; H, 5.3; N, 1.9%. IR(KBr): 1680 m, 1585 m, 1510 s, 1490 s, 1450 w, 1240 m, 940 m, 800 m, 580 w, cm^{-1} and other absorptions to PPh_3. ^1H-NMR (C_6D_6, r. t.): δ 2.16 (s, 3H), 7.0 (m, 23H, 18H of *m,p*-phenyl of PPh_3 and 5H of phenyl), 7.6 (m, 12H, *o*-phenyl of PPh_3).

Reaction of III with Nitromethane and Acetylacetone. Nitromethane (1 ml) was introduced into a Schlenk type flask containing III (0.100 g, 0.158 mmol) in diethyl ether (1 ml) by a trap-to-trap distillation in a vacuum. After stirring the white emulsion at −20 to 0 °C for 24 h a white precipitate was produced with liberation of ethanol (yield 87% per Cu). The precipitate was repeatedly washed with THF and dried in a vacuum to give the white complex XIV (0.084 g, yield 82%) which was characterized as nitromethanidobis(triphenylphosphine)copper(I) on the basis of its IR and ^1H-NMR spectra. $(CH_2NO_2)Cu(PPh_3)_2$ (XIV), IR(KBr): ν(C=N), 1562 s, 1550 m; $\nu(NO_2$, asym), 1250 s; $\nu(NO_2$, sym), 952 s cm^{-1}. ^1H-NMR (CD_2Cl_2): δ 5.76 (s, 2H, CH_2), 7.1 (m, 30H, $2PPh_3$).

The reaction of III (0.20 g, 0.32 mmol) with acetylacetone (1 ml) was carried out in a similar way to give a white precipitate with the liberation of ethanol (80% per Cu). Recrystallization from diethyl ether gave acetylacetonatobis(triphenylphosphine)copper(I) (0.163 g, yield 74%).[16] (acac) Cu-$(PPh_3)_2$ (XV), IR(KBr): ν(C=O), 1598 vs cm^{-1}. ^1H-NMR (C_6D_6): δ 2.04 (s, 6H, $2CH_3$), 5.56 (s, 1H), 7.1 (m, 18H, *m,p*-phenyl), 7.7 (m, 12H, *o*-phenyl).

Exchange Reaction of III with Methyl Methacrylate. A suspension of III (0.20 g, 0.32 mmol) in diethyl ether (2 ml) was treated with methyl methacrylate (0.32 mmol) at −5 °C for 12 h. Formation of ethyl methacrylate (yield 89% based on Cu) was confirmed by gas chromatographic analysis. The precipitate formed after the reaction was characterized as II (yield 78%) on the basis of its IR spectrum.

Reaction of III with Vinyl Acetate and Isopropenyl Acetate. Vinyl acetate (2 ml) was introduced into a Schlenk type flask containing III (0.20 g, 0.32 mmol) by a trap-to-trap distillation in a vacuum. After stirring the white emulsion at −5 to 0 °C for 12 h, ethyl acetate (yield 97% based on Cu), acetaldehyde (yield 15% based on Cu) and a small amount of polyvinyl acetate were produced besides a white precipitate. The precipitate was recrystallized from THF to give white crystals (174 mg, yield 81% based on Cu) of 1-acetoxyvinylbis(triphenylphosphine)copper[21](XVI) which was identified by IR and ^1H-NMR spectroscopy. Complex XVI, IR(KBr): ν(C=O) 1605 cm^{-1}. ^1H-NMR (C_6D_6): δ 1.92 (s, 3H, CH_3); 5.23 (d, 1H, $J=7$ Hz, =CH); δ 7.0 (m, 18H, *m,p*-phenyl); 7.6 (m, 12H, *o*-phenyl); 8.62 (d, 1H, $J=7$ Hz, =CH).

The reaction of III (0.20 g, 0.32 mmol) with isopropenyl acetate (2 ml) was carried out in a similar way to that of vinyl acetate to produce ethyl acetate, acetone and a precipitate (180 mg) containing 1-acetoxy-1-methylvinylbis(triphenylphosphine)copper[21](XVII) and acetatobis(triphenylphosphine)copper[21] (XVIII) which were identified by IR and ^1H-NMR spectroscopy. Complex XVII, IR(KBr): ν(C=O) 1595 cm^{-1}. ^1H-NMR (C_6D_6): δ 2.0 (s, 6H, $OCOCH_3$ and CH_3); 5.42 (s, 1H); 7.0 (m, 18H, *m,p*-phenyl); 7.6 (m, 12H, *o*-phenyl). Complex XVIII, IR(KBr): ν(OCO, asym), 1550; ν(OCO, sym), 1413; δ(OCO, sym), 667 cm^{-1}. ^1H-NMR (C_6D_6): δ 2.36 (s, 3H, CH_3); 7.0 (m, 18H, *m,p*-phenyl); 7.6 (m, 12H, *o*-phenyl).

Catalytic Transesterification Reaction Using III. Complex III (0.100 g, 1.06 mmol) was dissolved in a mixture of methyl methacrylate (0.73 ml, 6.77 mmol) and ethanol (5 ml) and the solution stirred at −5 °C for 24 h. Ethyl methacrylate was identified by gas chromatographic analysis of the reaction mixture (yield 73%).

Reaction of Alkoxocopper Complexes with Alkyl Halides. A measured amount of an alkyl halide was introduced into a Schlenk type flask containing the alkoxocopper complex by a trap-to-trap distillation in a vacuum or by means of a syringe at −30 °C. The reaction mixture was stirred for 12 to 24 h below 0 °C. The amount of ether formed in the reaction was determined by means of gas chromatography.

Reaction of III with Propionyl Chloride. Propionyl chloride (0.458 mmol) was added to III (0.20 g, 0.32 mmol) suspended in diethyl ether (2 ml). After stirring the white suspension at −5 °C for 2 h ethyl propionate (yield 82% per Cu) was produced.

Reaction of III with Acetic Anhydride. Acetic anhydride (0.458 mmol) was added to III (0.20 g, 0.32 mmol) suspended in diethyl ether (2 ml). After stirring the white suspension at −5 °C to r.t. for 24 h a white precipitate and ethyl acetate (yield 76% per Cu) were produced. The precipitate was crystallized from THF to give white crystals which were characterized as $CH_3COOCu(PPh_3)_2$ (XVIII) (yield 72%) on the basis of its IR and ^1H-NMR spectra.

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