

Preparation of Diphenyl(tricyclohexylphosphine)manganese(II) and Its Reactions with Carbon Dioxide and Organic Carbonyl Compounds

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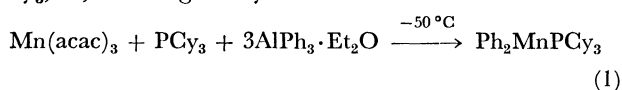
Treatment of $\text{Mn}(\text{acac})_3$ (acac =acetylacetonato ligand) with $\text{AlPh}_3 \cdot \text{Et}_2\text{O}$ in the presence of PCy_3 (Cy =*cyclo*- C_6H_{11}) gave a new diphenylmanganese(II) complex, $\text{Ph}_2\text{MnPCy}_3$ (**1**). Complex **1** reacted with allylic compounds, $\text{CH}_2=\text{CHCH}_2\text{X}$ ($\text{X}=\text{Br}$, OPh , $\text{OCH}_2\text{CH}=\text{CH}_2$, and OCOCH_3), to give allylbenzene. Carbon dioxide was found to be inserted into the phenyl-manganese σ -bond of **1** to give bis(benzoato)manganese complex, $(\text{PhCOO})_2\text{MnPCy}_3$, **2**, which on successive treatment with HCl and diazomethane produced methyl benzoate. Complex **1** reacted with aldehydes, ketones, and esters having no active α -hydrogen atom to give alkoxomanganese species in solution, indicating that the insertion of $\text{C}=\text{O}$ double bond into the phenyl-manganese σ -bond occurred. On the other hand, acetone and acetophenone reacted with $\text{Ph}_2\text{MnPCy}_3$ to give benzene and 2-oxo-alkyl complexes, $(\text{RCOCH}_2)_2\text{Mn}(\text{PCy}_3)_m$ ($\text{R}=\text{Me}$, Ph), **3**. Reaction of alcohols with **1** afforded alkoxomanganese compounds which catalyze the Tishchenko type and Meerwein-Ponndorf type reactions as well as transesterification reactions at room temperature.

Employment of alkylaluminum compounds in combination with transition metal acetylacetonates in the presence of stabilizing ligands has provided useful means in giving alkyl-, hydrido- and low valent transition metal complexes.¹⁾ Extension of the method to the preparation of phenyl-transition metal complexes using triphenylaluminum etherate, $\text{AlPh}_3 \cdot \text{Et}_2\text{O}$, proved successful as well affording new phenyl-nickel,²⁾ chromium,³⁾ cobalt,⁴⁾ and iron⁴⁾ complexes. We now report the preparation of diphenylmanganese(II) complex having tricyclohexylphosphine (PCy_3) from a reaction system composed of $\text{Mn}(\text{acac})_3$, $\text{AlPh}_3 \cdot \text{Et}_2\text{O}$ and PCy_3 . Although there are many reports concerning organomanganese complexes, isolated examples of organomanganese complexes having other ligand than cyclopentadienyl and carbonyl are quite scarce. As a homoleptic phenylmanganese complex without stabilizing ligand, preparation of somewhat impure diphenylmanganese in 1956 presents the sole example,⁵⁾ but characterization of the complex and study of its chemical properties are by no means satisfactory.^{6,7)} We have found that binding of tricyclohexylphosphine ligand confers a considerable stability on the diphenylmanganese. Treatment of the new diphenylmanganese complex with various reagents, particularly organic carbonyl compounds, produced hitherto unknown new types of organic manganese complexes, some of which show catalytic activities for various reactions.

Results and Discussion

Preparation and Characterization of $\text{Ph}_2\text{MnPCy}_3$.

Treatment of $\text{Mn}(\text{acac})_3$ with $\text{AlPh}_3 \cdot \text{Et}_2\text{O}$ in the presence of PCy_3 in a mixture of diethyl ether and toluene at -50°C gave a yellow complex of $\text{Ph}_2\text{MnPCy}_3$, **1**, in a good yield.



The complex is recrystallizable from hot toluene to give yellow-brown crystals which decompose under vacuum at 160 – 165°C . Since the micro-analysis

of $\text{Ph}_2\text{MnPCy}_3$ was not feasible due to its high sensitivity to air, characterization of this paramagnetic complex ($\mu_{\text{eff}}=2.73$ B. M.) was achieved by means of macroscopic analysis of manganese content, infrared spectroscopy and some chemical reactions. The characteristic IR bands of **1** were assigned as follows: 3040 cm^{-1} , $\nu(\text{C}-\text{H})$ of the phenyl group; 2925 and 2850 cm^{-1} , $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ of PCy_3 ; 1445 cm^{-1} , $\delta(\text{C}-\text{H})$ of PCy_3 ; 430 cm^{-1} , $\nu(\text{Mn}-\text{C})$. Treatment of $\text{Ph}_2\text{MnPCy}_3$ with gaseous HCl in diethyl ether gave 1.92 mol of benzene per manganese. Treatment of **1** with an excess amount of methyl iodide gave toluene (0.32 mol per mol of complex) and biphenyl (0.74 mol). A quantitative amount of tricyclohexylphosphine oxide was isolated on decomposition of **1** with aqueous H_2O_2 . Pyrolysis of **1** at 220°C under vacuum gave benzene (0.57 mol per mol of complex) and biphenyl (0.63 mol). The Mn^{2+} content in complex **1** determined by a chelate titration method was 11.4% (Calcd for $\text{C}_{30}\text{H}_{43}\text{PMn}$: Mn , 11.2%).

The reaction of $\text{Mn}(\text{acac})_3$ and $\text{AlPh}_3 \cdot \text{Et}_2\text{O}$ without tertiary phosphine gave Ph_2Mn in a yield of 23% , which was already prepared from MnI_2 and PhLi by Beerman and Clauss.⁵⁾ Addition of PCy_3 in ether to the isolated Ph_2Mn also led to $\text{Ph}_2\text{MnPCy}_3$, **1**. However, less basic tertiary phosphines such as PPh_3 , PPh_2Me and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ did not give isolable adducts of the phosphines with Ph_2Mn . It is noteworthy that the sensitivity of $\text{Ph}_2\text{MnPCy}_3$, **1**, towards air is considerably reduced as compared with that of Ph_2Mn which ignites spontaneously on contact with air.

Reaction of $\text{Ph}_2\text{MnPCy}_3$ with Allylic Compounds.

$\text{Ph}_2\text{MnPCy}_3$, **1**, reacted with allylic compounds, $\text{CH}_2=\text{CHCH}_2\text{X}$ ($\text{X}=\text{Br}$, OPh , $\text{OCH}_2\text{CH}=\text{CH}_2$, and OCOCH_3), to give allylbenzene in fairly high yields (Table 1). Cleavage of $\text{C}-\text{X}$ bond in $\text{CH}_2=\text{CHCH}_2\text{X}$ on reactions with transition metal complexes have been reported in the cases of *e.g.*, $\text{PhNi}(\text{acac})\text{PPh}_3$,⁸⁾ $\text{Ni}(\text{cod})_2$,^{9,10)} ($\text{cod}=1,5\text{-cyclooctadiene}$), and $\text{RuH}_2(\text{PPh}_3)_4$.¹¹⁾ The reaction of $\text{Ph}_2\text{MnPCy}_3$ with $(\text{CH}_2=\text{CHCH}_2)_2\text{O}$ liberated mainly allylbenzene with small amounts of benzene and biphenyl, and gave a pale

TABLE 1. REACTIONS OF $\text{Ph}_2\text{MnPCy}_3$ **1** WITH ALLYL COMPOUNDS

Allyl compound	Reaction condition (Solvent)	Products (mol/mol of 1)		
		Ph-H	Ph-CH ₂ CH=CH ₂	Ph-Ph
CH ₂ =CHCH ₂ Br	r. t., 1 d (Et ₂ O)	trace	2.00	trace
CH ₂ =CHCH ₂ OPh	45 °C, 1 h (Et ₂ O)	0.20	1.60	0.03
(CH ₂ =CHCH ₂) ₂ O	80 °C, 2 h (neat)	0.20	1.34	0.11
CH ₃ COOCH ₂ CH=CH ₂	r. t., 1 d (neat)	0.57	1.17	trace

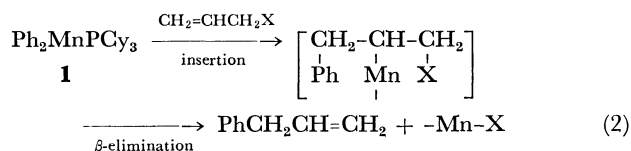
TABLE 2. REACTIONS OF $\text{Ph}_2\text{MnPCy}_3$, **1**, WITH ALDEHYDES AND KETONES^{a)}

Aldehyde or ketone (mmol)	Amount of 1 (mmol)	Solvent	Product (mol/mol of 1)
Ph ₂ CO ^{b)} (2.26)	0.204	toluene	Ph-H (0.07) ^{c)} , Ph ₃ COH (0.49) ^{c)} , Ph-Ph (0.05) ^{c)}
MeCHO (0.72)	0.290	Et ₂ O	Ph-H (0.79) ^{c)} , PhCH=CH ₂ (0.21) ^{c)} , Ph(Me)C(H)OH (0.40) ^{c)}
EtCHO (0.56)	0.230	Et ₂ O	Ph-H (0.80), PhCOEt (0.09), Ph(Et)C(H)OH (0.45), Ph-Ph (0.05)
PhCHO (neat) (14.7)	0.194	none	Ph-H (0.21), Ph ₂ CO (1.33), PhCH ₂ OH (1.36), PhCOOCH ₂ Ph (67.4) ^{d)}

a) Reactions were carried out at room temperature for 1 d. b) Reaction was carried out at 70 °C for 1 h.
c) Yields after treating the reaction mixture with PhOH or HCl gas. d) Conversion of PhCHO into benzyl benzoate was 89%.

yellow powder, which on treatment with acetyl chloride yielded allyl acetate, suggesting that it contains the allyloxomanganese bond.

Two alternative mechanisms are conceivable in accounting for the products. One involves the insertion of CH₂=CHCH₂X into the Ph-Mn bond followed by β -elimination of X, not of hydrogen as one usually encounters in the decomposition of alkyltransition metal complexes carrying a β -hydrogen:



Similar mechanisms have been proposed in accounting for the reaction products of allylic compounds with $\text{PhNi}(\text{acac})\text{PPh}_3$ and $\text{RuH}_2(\text{PPh}_3)_4$.^{8,11)} The alternative mechanism involves the oxidative addition of CH₂=CHCH₂X to $\text{Ph}_2\text{MnPCy}_3$ with cleavage of the C-X bond followed by reductive elimination to give allylbenzene. Although a similar oxidative addition has been observed in the reactions of bis(cyclooctadiene)nickel(0) with phenyl carboxylate, alkenyl acetate¹⁰⁾ and allylic ethers,^{9,12)} it seems somewhat less likely that the manganese(II) complex attacks these allyl compounds to cause oxidative addition. In fact **1** did not react with benzyl phenyl ether and dibenzyl ether even by heating at 100 °C for 10 h, whereas under similar conditions the C-O bond in these ethers has been reportedly cleaved in the presence of $\text{Ni}(\text{cod})_2$.⁹⁾

Reaction of $\text{Ph}_2\text{MnPCy}_3$ with Carbon Dioxide.

Carbon dioxide reacted with $\text{Ph}_2\text{MnPCy}_3$ at ambient

conditions in toluene or diethyl ether at room temperature to give a dark brown precipitate. This precipitate, after isolation, turned to a white powder on drying *in vacuo*. The infrared spectrum of the complex was identical with that of $(\text{PhCOO})_2\text{MnPCy}_3$, **2**, prepared by the reaction of $\text{Ph}_2\text{MnPCy}_3$ with PhCOOH. The result suggests that insertion of carbon dioxide into the phenyl-manganese σ -bond took place to give benzoatomanganese species. Formation of benzoate derivative of rhodium(I), $(\text{PhCOO})\text{Rh}(\text{PPh}_3)_3$, has been reported by a similar insertion reaction of CO₂ into the Rh-C bond.¹³⁾ The characteristic IR bands of $(\text{PhCOO})_2\text{MnPCy}_3$ were observed at 1550 and 1400 cm⁻¹ which may be assigned to $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$, respectively. Although $(\text{PhCOO})_2\text{MnPCy}_3$, **2**, did not react with methyl iodide at room temperature, treatment of **2** (0.17 g, 0.35 mmol) with gaseous HCl in diethyl ether followed by methylation with diazomethane gave methyl benzoate (0.43 mmol).

$(\text{PhCOO})_2\text{MnPCy}_3$, **2**, is thermally very stable and liberates PCy_3 and only trace amounts of CO and CO₂ on heating at 200 °C *in vacuo* for 40 min. The residue is a dark brown powder, which was judged as $(\text{PhCOO})_2\text{Mn}$ on the basis of its IR spectrum.

Although the insertion of carbon dioxide into the carbon-manganese σ -bond has been briefly reported for Me_2Mn ,⁷⁾ the present result exhibits the first example of the isolation of the carboxylato manganese complex as a result of the CO₂ insertion reaction.

Reactions of $\text{Ph}_2\text{MnPCy}_3$ with Aldehydes and Ketones. Anionic nature of the phenyl ligand in $\text{Ph}_2\text{MnPCy}_3$, **1**, was demonstrated through its reactions with organic carbonyl compounds such as aldehydes, ketones and esters, where secondary alcohols from the first compound

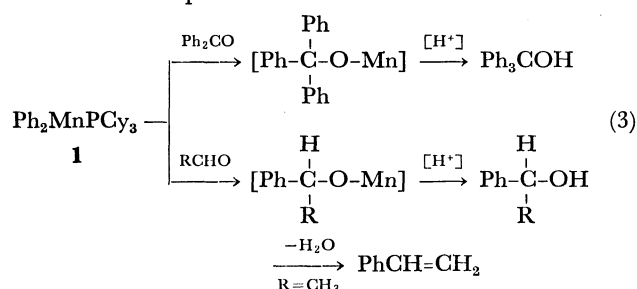
TABLE 3. REACTIONS OF $\text{Ph}_2\text{MnPCy}_3$ **1** WITH ESTERS^{a)}

Ester ($\text{PhCOOCH}_2\text{R}$)	Products (mol/mol of 1)						
	PhH	RCH_2OH	Ph-Ph	PhCOPh	Ph_3COH	Others	
$\text{PhCOOCH}_2\text{-H}$	b)	b)	0.11	0.26	0.35	c)	
	b)	b)	0.11	0.20	0.74	d)	
$\text{PhCOOCH}_2\text{Me}$	0.35	0.18	0.06	0.07	0.75	c)	
	0.35	0.52	0.05	0.10	0.70	d)	
$\text{PhCOOCH}_2\text{Ph}$	0.23	0.11	0.07	0.11	0.36	PhCHO , 0.17 c)	
	0.28	0.51	0.04	0.09	0.56	PhCHO , 0.07 d)	
	PhH	EtOH	Ph-Ph	PhCOPh	Ph_3COH	Ph_2CHOH	PhCOOEt
HCOOEt	0.34	0.54	0.00	0.08	trace	0.46	trace d)

a) Reactions were carried out at 70 °C for 10 minutes in toluene solution. b) Not measured. c) Yield before treating the reaction system with PhOH. d) Yield after treating the reaction system with PhOH.

and tertiary alcohols from the last two compounds were detected as the main products (*vide infra*). The results indicate that the chemical property of phenyl-manganese complex **1** resembles considerably to that of a phenyl Grignard reagent especially in respect of the stoichiometric reactions with carbonyl compounds.

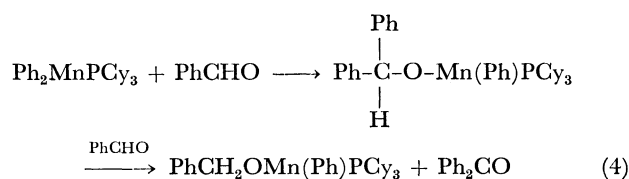
Complex **1** reacted with benzophenone, acetaldehyde and propionaldehyde to give, after treatment with gaseous HCl or phenol, triphenylmethanol, 1-phenylethanol and 1-phenyl-1-propanol, respectively (Table 2). These results suggest the existence of alkoxomanganese intermediates in the reaction mixtures as shown in Eq. 3.



The formation of styrene after treatment of the reaction mixture of **1** and acetaldehyde with phenol is considered to be the result of dehydration of 1-phenylethylalcohol catalyzed by phenol which is a weak acid (Eq. 3). The acid-catalyzed dehydration reaction of alcohol is well known.¹⁴⁾

The reaction of **1** with a large excess of acetaldehyde without solvent at -50 °C to room temperature afforded polyether of the type $-\text{[CH(CH}_3\text{)}-\text{O]}_n-$ probably as a result of consecutive insertion of acetaldehyde into Mn-O bond.¹⁵⁾

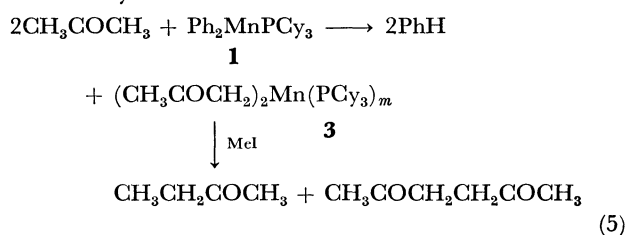
$\text{Ph}_2\text{MnPCy}_3$, **1**, was found to convert benzaldehyde catalytically into benzyl benzoate at room temperature. The reaction was accompanied by formation of 0.21 equiv. of benzene, 1.33 equiv. of benzophenone and 1.36 equiv. of benzyl alcohol as Table 2 shows. The pale brown powder, isolated from this reaction system, liberated benzyl acetate on the reaction with acetyl chloride. The result suggests that the powder contains benzyloxo group bonded to manganese. The reaction of **1** with benzaldehyde may be, again, explained by the insertion of the C=O double bond into the Ph-Mn σ -bond as shown in Eq. 4.



The benzyloxomanganese thus produced is considered to be responsible for the catalytic Tischchenko type reaction converting benzaldehyde into benzyl benzoate. A Tischchenko type reaction catalyzed by ruthenium complexes has been recently reported.¹⁶⁾

The insertion of aldehydes and ketones into the metal-carbon σ -bond, a quite common reaction observed in the reactions of non-transition metal alkyls and aryls such as Grignard reagents, has some precedents also among the reactions involving organo-transition metal compounds.^{3,17)}

Formation of benzene in the reactions of **1** with benzaldehyde, acetaldehyde, and propionaldehyde may be accounted for by assuming a β -hydrogen elimination from the presumed intermediate, alkoxomanganese complex bearing a β -hydrogen, followed by reductive elimination with the remaining phenyl group bonded to manganese. The alternative to the above mechanism is the abstraction of protonic α -hydrogen at the α -carbon of aliphatic aldehydes. This type of reaction may be predominantly taking place in the reactions of **1** with acetone and acetophenone which carry active α -hydrogens. In these cases about two moles of benzene were liberated to leave white complexes. The IR spectrum of the complex derived from acetone showed the $\nu(\text{C=O})$ band at 1690 cm^{-1} with a shift of 30 cm^{-1} from that of free acetone. Although insolubility of the complex in common organic solvents hindered its purification, this complex is considered to be (2-oxopropyl)manganese, since treatment of the complex with methyl iodide gave methyl ethyl ketone and acetonylacetone.



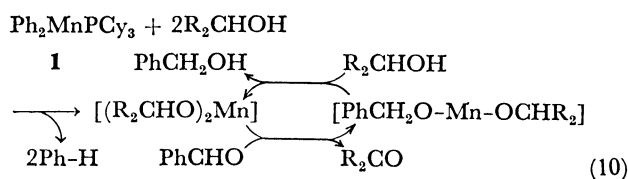


TABLE 5. TRANSESTERIFICATION REACTIONS USING ALKOXOMANGANESE COMPOUND^{a)}

Ester (PhCOOR)	Alcohol (R'OH)	Products, mol/mol of compound		
		PhCOOR'	ROH	PhH
PhCOOCH ₂ Ph (5.3 mmol)	EtOH (34.7 mmol)	18.7 (0.63) ^{e)}	17.1	1.7
PhCOOCH ₂ Ph (5.9 mmol) ^{d)}	EtOH (34.7 mmol) ^{d)}	8.7 (0.98) ^{e)}	8.3	— ^{d)}
PhCOOCH ₂ Ph (5.3 mmol)	Me ₂ CHOH (13.1 mmol)	1.2	0.4	1.6
PhCOOCH ₂ Ph (5.3 mmol)	Me ₃ COH (5.2 mmol) ^{e)}	0.0	0.0	1.4
PhCOOPh (1.1 mmol)	MeOH (71.4 mmol)	6.7 (1.0) ^{e)}	5.8	1.7
PhCOOPh (2.6 mmol)	Me ₂ CHOH (22.7 mmol)	3.2→7.4 ^{b)} (0.73) ^{e)}	0.9→5.4 ^{b)} (0.53) ^{e)}	1.6
PhCOOPh (2.0 mmol)	Me ₃ COH (5.0 mmol) ^{e)}	0.3	0.0	1.8
PhCOOMe (4.0 mmol)	PhOH (4.1 mmol) ^{e)}	0.0	0.0	1.8
PhCOOCHMe ₂ (3.1 mmol)	PhOH (5.3 mmol) ^{e)}	0.0	0.0	1.6
PhCOOCMe ₃ (2.8 mmol)	PhOH (3.6 mmol) ^{e)}	0.2	0.0	1.8

a) Reactions were carried out at room temperature for 1 d. The amount of Ph₂MnPCy₃, **1** used for each reaction was about 0.1 g (0.22 mmol). b) The yields were measured after heating the system at 70 °C for 15 h. c) Yields calculated on the basis of mol of PhCOOR used. d) This reaction was carried out using isolated (PhO)₂Mn (0.16 g, 0.66 mmol) as catalyst at room temperature for 2 d. e) Diethyl ether was used as solvent.

TABLE 6. REACTIONS OF BENZALDEHYDE AND PRIMARY ALCOHOLS IN THE PRESENCE OF ALKOXOMANGANESE COMPOUND^{a)}

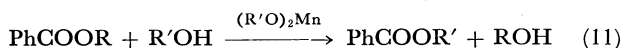
PhCHO (ml)	ROH (ml)	Products (mol/mol of complex)			
		PhCOOR	PhCH ₂ OH	PhCOOCH ₂ Ph	PhH
(2.1)	MeOH (0.8) ^{b)}	1.6	1.2	0	1.7
(0.2)	EtOH (0.2) ^{b)}	1.4	1.2	0	1.7
(1.5)	EtOH (0.6) ^{c)}	14.3	—	14.2	1.8

a) Reactions were carried out at room temperature for 1 d. The amount of complex **1** used for each reaction was about 0.1 g (0.22 mmol). b) Diethyl ether was used as solvent. c) 0.5 ml of PhCH₂OH was added together with EtOH.

By-products of the present reaction system such as benzyl benzoate and isopropyl benzoate might be produced by Tishchenko type reaction (*vide supra*) and that followed by transesterification (alcoholysis) (*vide infra*), respectively.

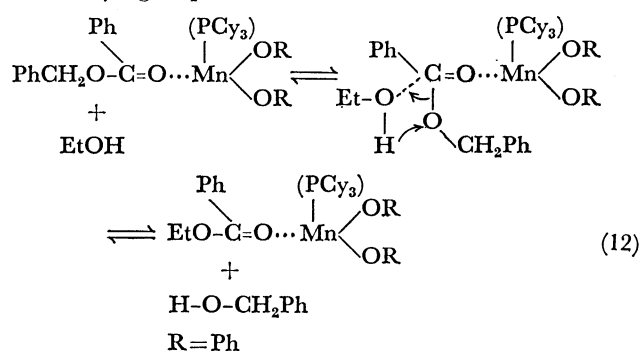
When acetophenone was used in place of benzaldehyde, on the other hand, only minimal amounts of Meerwein-Pondorf type reaction products were obtained (Table 4). Even when the system which contains acetophenone and isopropyl alcohol was heated at 70 °C for 9 h in the presence of alkoxmanganese, only 0.7 mol of 1-phenylethanol per mol of Ph₂MnPCy₃ was produced. A steric hindrance in the transition state may affect the reactivity of the present system as was proposed for the Meerwein-Pondorf reaction using isopropoxoaluminum.

Transesterification Reactions Using Alkoxmanganese Compounds. The transesterification reactions between alkyl benzoate and various alcohols were examined using dialkoxmanganese compounds prepared *in situ* from Ph₂MnPCy₃, **1**, and alcohols.



As Table 5 shows, the catalytic reactions of the transesterification reactions proceed at room temperature when primary alcohols were used. The ease of transesterification reactions of alcohols decreased in the order of prim. alcohol ≫ sec. alcohol ≫ tert. alcohol ≈ phenol. This tendency corresponds to the order of the ester yields in the acid catalyzed ester formation

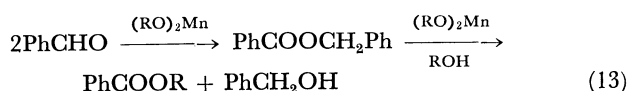
reaction from carboxylic acid and alcohols.²⁰⁾ The isolated (PhO)₂Mn, which was prepared by the reaction of Ph₂MnPCy₃ with phenol, was found also to catalyze the transesterification reaction between benzyl benzoate and ethanol (Table 5, line 2). Catalyst (PhO)₂Mn used in this reaction was recovered without suffering from alcoholysis with ethyl alcohol. This suggests that the reaction mechanism for the present transesterification reaction may be manganese-assisted replacement of alkoxy group as shown below.



The transesterification reaction using transition metal compounds such as described here and that with alkoxy-copper compounds²¹⁾ have some advantages in that they act under neutral and mild conditions.

The reaction between benzaldehyde and primary alcohols to give alkyl benzoate directly through the combination of the catalytic Tishchenko type reaction and transesterification reaction was attempted and the

results are summarized in Table 6.



Although the yield of methyl benzoate or ethyl benzoate was not high when methanol or ethanol alone was used, a high yield of ethyl benzoate was obtained when ethanol was allowed to react in the presence of benzyl alcohol. The result suggests that the (benzyloxo)manganese species have higher activity towards Tishchenko type reaction than methoxo- or ethoxomanganese species.

Some alkoxomanganese compounds which are analogous to those prepared *in situ* in the present work have been isolated, for example $(\text{MeO})_2\text{Mn}$,²²⁾ $(\text{EtO})_2\text{Mn}$ ²³⁾ and $(i\text{-PrO})_2\text{Mn}$,²³⁾ although none of their reactions has been examined.

Experimental

All reactions and manipulations were carried out under dry, oxygen-free nitrogen or *in vacuo* using Schlenk-type flasks.

Solvents were dried and purified in the usual manner and stored under an atmosphere of nitrogen. Carbon dioxide was dried by passing the gas through columns containing CaCl_2 and P_2O_5 . Allylic compounds and esters were distilled over calcium hydride *in vacuo* and stored under nitrogen atmosphere. Aldehydes and ketones were purified by distillation under reduced pressure. Methanol and ethanol were purified by distilling over magnesium turnings. Other liquid alcohols were dried by Drierite and degassed under vacuum. $\text{AlPh}_3 \cdot \text{Et}_2\text{O}$ was prepared from PhMgBr and AlCl_3 according to the reported method.²⁴⁾ Tris(acetylacetonato)manganese(III) (Tokyo Kasei Industrial Co.) was used as purchased without further purification. Tricyclohexylphosphine was prepared according to the literature method.²⁵⁾

Infrared spectra were recorded on a Hitachi model 295 spectrometer using KBr disks prepared under inert atmosphere. The magnetic susceptibility was measured by Gouy method using Shimadzu MB-100 apparatus at 23 °C and the diamagnetic corrections for the coordinated ligands were made on the basis of the Pascal's constants. The organic products formed in the various reactions were quantitatively analyzed by GLC using internal standard. GLC was recorded on a Shimadzu GC-3BT or GC-6A gas chromatography using SDC-550, SDC-410 and/or PEG-20M columns and helium as a carrier gas.

Preparation of $\text{Ph}_2\text{MnPCy}_3$, **1.** To the mixture of $\text{Mn}(\text{acac})_3$ (2.1 g, 6.0 mmol), PCy_3 (2.0 g, 7.1 mmol), diethyl ether (20 ml) and toluene (5 ml) cooled at -50 °C, $\text{AlPh}_3 \cdot \text{Et}_2\text{O}$ (6.1 g, 18.3 mmol) was added. On stirring the mixture, the initial black suspension turned to a yellow suspension. After raising the temperature of the system to room temperature, the precipitate was filtered, washed with diethyl ether and dried *in vacuo*. The yellow powder thus obtained weighed 2.8 g (93% of the theoretical amount based on $\text{Mn}(\text{acac})_3$ used). The crude product (2.0 g) was recrystallized from hot toluene (95 °C) to give yellow brown crystals of $\text{Ph}_2\text{MnPCy}_3$ (1.3 g, recrystallization yield, 65%). Analytical data and physical properties of **1** are mentioned in the text.

Reaction of $\text{Ph}_2\text{MnPCy}_3$, **1, with Allylic Compounds.** To a flask containing $\text{Ph}_2\text{MnPCy}_3$ (0.246 g, 0.502 mmol), dialkyl ether (2 ml) was added and heated at 70–80 °C for 2 h.

The initial yellow suspension turned to a deep yellow solution. Allylbenzene (0.675 mmol), benzene (0.097 mmol) and biphenyl (0.057 mmol) were formed, as judged by GLC analysis. Hexane (5 ml) was added to the solution to give a pale yellow precipitate which was filtered and dried *in vacuo*. The pale yellow powder thus obtained was allowed to react with acetyl chloride at room temperature to give allyl acetate. The other reactions of $\text{Ph}_2\text{MnPCy}_3$ with allylic compounds were carried out in a similar fashion.

Reaction of $\text{Ph}_2\text{MnPCy}_3$ with Carbon Dioxide. On bubbling carbon dioxide into the toluene suspension of $\text{Ph}_2\text{MnPCy}_3$ for one day at room temperature, the initial yellow suspension turned to a dark brown suspension. The precipitate was filtered and dried *in vacuo* to give a white powder of $(\text{PhCOO})_2\text{MnPCy}_3$ **2**. Characterization of this compound was achieved as mentioned in the text.

Reactions of $\text{Ph}_2\text{MnPCy}_3$ with Esters, Aldehydes, and Ketones. Since the method is general, some typical reactions are described here, the organic reaction products are being listed in Tables 2 and 3.

a) Reaction with Benzyl Benzoate: To a flask containing $\text{Ph}_2\text{MnPCy}_3$ (0.094 g, 0.191 mmol), toluene (1 ml) and benzyl benzoate (1 ml) were added. On heating the system at 70 °C for ten minutes, the initial yellow suspension turned to a yellow solution. Formation of benzene (0.021 mmol), benzaldehyde (0.032 mmol), benzyl alcohol (0.021 mmol), biphenyl (0.013 mmol), benzophenone (0.020 mmol) and triphenylmethanol (0.068 mmol) were observed by GLC analysis. The amounts of these reaction products changed on treatment with phenol as follows: benzene (0.053 mmol), benzaldehyde (0.013 mmol), benzyl alcohol (0.098 mmol), benzophenone (0.018 mmol) and triphenylmethanol (0.107 mmol).

b) Reaction with Benzaldehyde: To a flask containing $\text{Ph}_2\text{MnPCy}_3$ (0.095 g, 0.194 mmol), benzaldehyde (1.5 ml, 15 mmol) was added and stirred at room temperature for one day. A dark brown solution thus formed contained benzene (0.04 mmol), benzyl alcohol (0.264 mmol), benzophenone (0.258 mmol) and benzyl benzoate (13.1 mmol) as analyzed by GLC.

c) Reaction with Acetone: To a flask containing $\text{Ph}_2\text{MnPCy}_3$ (0.137 g, 0.279 mmol) and diethyl ether (2 ml), acetone (75 μl , 1.02 mmol) was added and stirred for one day. A pale yellow suspension thus obtained was analyzed by GLC and found to contain benzene (0.447 mmol) and unreacted acetone (0.38 mmol). White powder (0.027 g, 0.060 mmol calculated as $(\text{CH}_3\text{COCH}_2)_2\text{MnPCy}_3$) isolated from this reaction system, reacted with methyl iodide to give ethyl methyl ketone (0.7 μl , 0.008 mmol) and acetyl acetone (0.6 μl , 0.005 mmol).

Reactions between Alcohols and Aldehydes or Ketones in the Presence of Alkoxomanganese Compound Prepared *in situ*.

To a flask containing $\text{Ph}_2\text{MnPCy}_3$ (0.099 g, 0.202 mmol) and diphenylmethanol (0.40 g, 2.16 mmol), was added diethyl ether (2 ml) to give a white suspension. Benzaldehyde (0.5 ml) was added to this system which was stirred for one day at room temperature. Benzene (0.39 mmol), benzyl alcohol (1.74 mmol), benzophenone (1.88 mmol) and benzyl benzoate (1.26 mmol) were formed, as analyzed by GLC.

The reactions listed in Tables 4 and 6 carried out similarly.

Transesterification Reactions Using Alkoxomanganese Compound Prepared *in situ*.

To a flask containing $\text{Ph}_2\text{MnPCy}_3$ (0.087 g, 0.178 mmol) ethanol (1.0 ml) was added to give a pale brown suspension. Benzyl benzoate (1.0 ml, 5.3 mmol) was added to this system and the mixture was stirred for one day at room temperature. The GLC analysis of the reaction mixture revealed the formation of benzene

(0.30 mmol), benzaldehyde (0.047 mmol), benzyl alcohol (3.05 mmol) and ethyl benzoate (3.05 mmol).

The other transesterification reactions listed in Table 5 were carried out in a similar fashion.

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