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

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Treatment of Mn(acac)$_3$ (acac=acetylacetonato ligand) with $AlPh_3 \cdot Et_2O$ in the presence of PCy$_3$ (Cy=*cyclo*-C_6H_{11}) gave a new diphenylmanganese(II) complex, Ph$_2$MnPCy$_3$ (**1**). Complex **1** reacted with allylic compounds, $CH_2=CHCH_2X$ (X=Br, OPh, $OCH_2CH=CH_2$, 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, (PhCOO)$_2$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 C=O double bond into the phenyl-manganese σ-bond occurred. On the other hand, acetone and acetophenone reacted with Ph$_2$MnPCy$_3$ to give benzene and 2-oxoalkyl complexes, $(RCOCH_2)_2Mn(PCy_3)_m$ (R=Me, Ph), **3**. Reaction of alcohols with **1** afforded alkoxomanganese compounds which catalyze the Tishchenko type and Meerwein-Pondorf type reactions as well as transesterification reactions at room temperature.

Employment of alkylaluminium 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 triphenylaluminium etherate, $AlPh_3 \cdot Et_2O$, proved successful as well affording new phenyl-nickel,[2] chromium,[3] cobalt,[4] and iron[4] complexes. We now report the preparation of diphenylmanganese(II) complex having tricyclohexylphosphine (PCy$_3$) from a reaction system composed of Mn(acac)$_3$, $AlPh_3 \cdot Et_2O$ 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 Ph$_2$MnPCy$_3$. Treatment of Mn(acac)$_3$ with $AlPh_3 \cdot Et_2O$ in the presence of PCy$_3$ in a mixture of diethyl ether and toluene at −50 °C gave a yellow complex of Ph$_2$MnPCy$_3$, **1**, in a good yield.

$$Mn(acac)_3 + PCy_3 + 3AlPh_3 \cdot Et_2O \xrightarrow{-50\,^{\circ}C} Ph_2MnPCy_3 \tag{1}$$

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 Ph$_2$MnPCy$_3$ was not feasible due to its high sensitivity to air, characterization of this paramagnetic complex (μ_{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}, ν(C–H) of the phenyl group; 2925 and 2850 cm^{-1}, ν_{as}(CH$_2$) and ν_s(CH$_2$) of PCy$_3$; 1445 cm^{-1}, δ(C–H) of PCy$_3$; 430 cm^{-1}, ν(Mn–C). Treatment of Ph$_2$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 $C_{30}H_{43}PMn$: Mn, 11.2%).

The reaction of Mn(acac)$_3$ and $AlPh_3 \cdot Et_2O$ without tertiary phosphine gave Ph$_2$Mn 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$_2$Mn also led to Ph$_2$MnPCy$_3$, **1**. However, less basic tertiary phosphines such as PPh$_3$, PPh$_2$Me and $Ph_2PCH_2CH_2PPh_2$ did not give isolable adducts of the phosphines with Ph$_2$Mn. It is noteworthy that the sensitivity of Ph$_2$MnPCy$_3$, **1**, towards air is considerably reduced as compared with that of Ph$_2$Mn which ignites spontaneously on contact with air.

Reaction of Ph$_2$MnPCy$_3$ with Allylic Compounds. Ph$_2$MnPCy$_3$, **1**, reacted with allylic compounds, $CH_2=CHCH_2X$ (X=Br, OPh, $OCH_2CH=CH_2$, and $OCOCH_3$), to give allylbenzene in fairly high yields (Table 1). Cleavage of C–X bond in $CH_2=CHCH_2X$ on reactions with transition metal complexes have been reported in the cases of *e.g.*, PhNi(acac)PPh$_3$,[8] Ni(cod)$_2$,[9,10] (cod=1,5-cyclooctadiene), and RuH$_2$(PPh$_3$)$_4$.[11] The reaction of Ph$_2$MnPCy$_3$ with $(CH_2=CHCH_2)_2O$ liberated mainly allylbenzene with small amounts of benzene and biphenyl, and gave a pale

TABLE 1. REACTIONS OF Ph_2MnPCy_3 **1** WITH ALLYL COMPOUNDS

Allyl compound	Reaction condition (Solvent)	Products (mol/mol of **1**)		
		Ph-H	$Ph-CH_2CH=CH_2$	Ph-Ph
$CH_2=CHCH_2Br$	r. t., 1 d (Et_2O)	trace	2.00	trace
$CH_2=CHCH_2OPh$	45 °C, 1 h (Et_2O)	0.20	1.60	0.03
$(CH_2=CHCH_2)_2O$	80 °C, 2 h (neat)	0.20	1.34	0.11
$CH_3COOCH_2CH=CH_2$	r. t., 1 d (neat)	0.57	1.17	trace

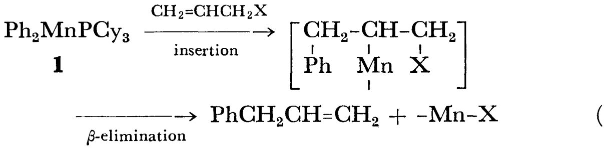
TABLE 2. REACTIONS OF Ph_2MnPCy_3, **1**, WITH ALDEHYDES AND KETONES[a)]

Aldehyde or ketone (mmol)	Amount of **1** (mmol)	Solvent	Product (mol/mol of **1**)
Ph_2CO[b)] (2.26)	0.204	toluene	Ph-H (0.07)[c)], Ph_3COH (0.49)[c)], Ph-Ph (0.05)[c)]
MeCHO (0.72)	0.290	Et_2O	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_2O	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_2CO (1.33), $PhCH_2OH$ (1.36), $PhCOOCH_2Ph$ (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 $CH_2=CHCH_2X$ 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:



$$\underset{\mathbf{1}}{Ph_2MnPCy_3} \xrightarrow[\text{insertion}]{CH_2=CHCH_2X} \left[\begin{array}{ccc} CH_2 & - CH - & CH_2 \\ | & | & | \\ Ph & Mn & X \\ & | & \end{array}\right] \xrightarrow[\beta\text{-elimination}]{} PhCH_2CH=CH_2 + -Mn-X \qquad (2)$$

Similar mechanisms have been proposed in accounting for the reaction products of allylic compounds with $PhNi(acac)PPh_3$ and $RuH_2(PPh_3)_4$.[8,11)] The alternative mechanism involves the oxidative addition of $CH_2=CHCH_2X$ to Ph_2MnPCy_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 acetate[10)] 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 $Ni(cod)_2$.[9)]

Reaction of Ph_2MnPCy_3 with Carbon Dioxide. Carbon dioxide reacted with Ph_2MnPCy_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 $(PhCOO)_2MnPCy_3$, **2**, prepared by the reaction of Ph_2MnPCy_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), $(PhCOO)Rh(PPh_3)_3$, has been reported by a similar insertion reaction of CO_2 into the Rh–C bond.[13)] The characteristic IR bands of $(PhCOO)_2MnPCy_3$ were observed at 1550 and 1400 cm^{-1} which may be assigned to $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$, respectively. Although $(PhCOO)_2MnPCy_3$, **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).

$(PhCOO)_2MnPCy_3$, **2**, is thermally very stable and liberates PCy_3 and only trace amounts of CO and CO_2 on heating at 200 °C *in vacuo* for 40 min. The residue is a dark brown powder, which was judged as $(PhCOO)_2Mn$ 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 CO_2 insertion reaction.

Reactions of Ph_2MnPCy_3 with Aldehydes and Ketones. Anionic nature of the phenyl ligand in Ph_2MnPCy_3, **1**, was demonstrated through its reactions with organic carbonyl compounds such as aldehydes, ketones and esters, where secondary alcohols from the first compound

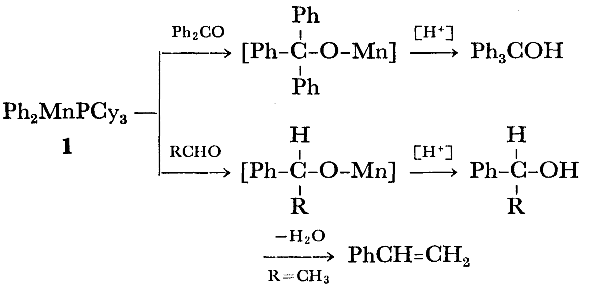
Table 3. Reactions of Ph_2MnPCy_3 **1** with esters[a)]

Ester ($PhCOOCH_2R$)	Products (mol/mol of **1**)						
	PhH	RCH_2OH	Ph-Ph	PhCOPh	Ph_3COH	Others	
$PhCOOCH_2$-H	b)	b)	0.11	0.26	0.35		c)
	b)	b)	0.11	0.20	0.74		d)
$PhCOOCH_2Me$	0.35	0.18	0.06	0.07	0.75		c)
	0.35	0.52	0.05	0.10	0.70		d)
$PhCOOCH_2Ph$	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 phenylmanganese 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.



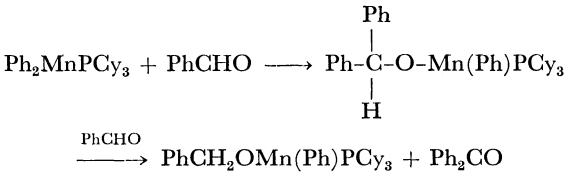
$$\underset{\mathbf{1}}{Ph_2MnPCy_3} \xrightarrow{Ph_2CO} [Ph\text{-}\overset{Ph}{\underset{Ph}{C}}\text{-}O\text{-}Mn] \xrightarrow{[H^+]} Ph_3COH$$

$$\underset{\mathbf{1}}{Ph_2MnPCy_3} \xrightarrow{RCHO} [Ph\text{-}\overset{H}{\underset{R}{C}}\text{-}O\text{-}Mn] \xrightarrow{[H^+]} Ph\text{-}\overset{H}{\underset{R}{C}}\text{-}OH \xrightarrow[R=CH_3]{-H_2O} PhCH{=}CH_2 \qquad (3)$$

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 $\text{-}[CH(CH_3)\text{-}O]_n\text{-}$ probably as a result of consecutive insertion of acetaldehyde into Mn–O bond.[15)]

Ph_2MnPCy_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 chrolide. 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.



$$Ph_2MnPCy_3 + PhCHO \longrightarrow Ph\text{-}\overset{Ph}{\underset{H}{C}}\text{-}O\text{-}Mn(Ph)PCy_3 \xrightarrow{PhCHO} PhCH_2OMn(Ph)PCy_3 + Ph_2CO \qquad (4)$$

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 organotransition 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 ν(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.

$$2CH_3COCH_3 + \underset{\mathbf{1}}{Ph_2MnPCy_3} \longrightarrow 2PhH + \underset{\mathbf{3}}{(CH_3COCH_2)_2Mn(PCy_3)_m}$$

$$\big\downarrow MeI$$

$$CH_3CH_2COCH_3 + CH_3COCH_2CH_2COCH_3 \qquad (5)$$

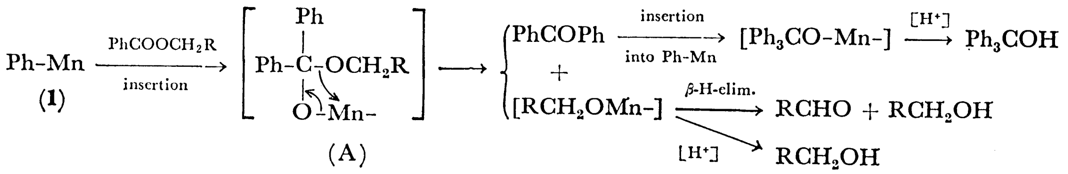
TABLE 4. REACTION OF SECONDARY ALCOHOLS WITH BENZALDEHYDE AND ACETOPHENONE IN THE PRESENCE OF ALKOXOMANGANESE COMPOUND[a)]

Reactant (mmol)	Product (mol/mol of complex **1**)			
$\mathrm{Ph_2CHOH}$ (2.16) PhCHO (4.95)	$\mathrm{PhCH_2OH}$ (8.6)	$\mathrm{Ph_2CO}$ (9.3)	PhH (1.9)	$\mathrm{PhCOOCH_2Ph}$ (6.2)
$\mathrm{Me_2CHOH}$ (12.8) PhCHO (9.90)	$\mathrm{PhCH_2OH}$ (8.2)[b)]	$\mathrm{Me_2CO}$ (3.5)[b)]	PhH (1.7)[b)]	PhCOO*i*Pr (0.9)[b)]
Ph(Me)CHOH (2.91) PhCHO (4.95)	$\mathrm{PhCH_2OH}$ (4.9)	Ph(Me)CO (2.0)	PhH (1.5)	
$\mathrm{Ph_2CHOH}$ (5.76) MeCOPh (8.60)	Ph(Me)CHOH (trace)	$\mathrm{Ph_2CO}$ (trace)		
$\mathrm{Me_2CHOH}$ (7.85) MeCOPh (5.16)	Ph(Me)CHOH (0.4→0.7[b)])	$\mathrm{Me_2CO}$ (0.4)	PhH (1.6)	

a) Reactions were carried out at room temperature for 1 d. The amount of $\mathrm{Ph_2MnPCy_3}$ **1** used for each reaction was about 0.1 g (0.22 mmol). b) The yield after heating the system at 70 °C for 9 h.

A similar β-oxo-alkyl type compound of gold has been reported.[18)]

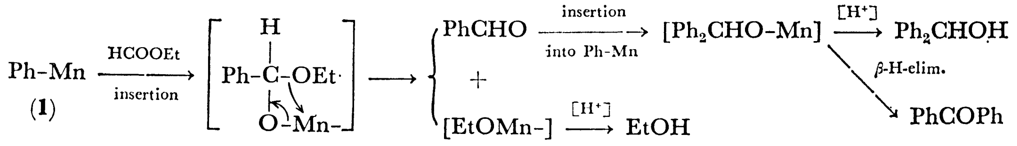
Reactions of Ph_2MnPCy_3 with Esters. The insertion reaction of the C=O double bond into Ph–Mn σ-bond was similarly observed when alkyl and benzyl benzoates, $\mathrm{PhCOOCH_2R}$ (R=H, $\mathrm{CH_3}$, Ph) were allowed to react with **1**. In these cases, benzophenone, triphenylmethanol, benzene, biphenyl, primary alcohols ($\mathrm{RCH_2OH}$) and benzaldehyde (when R=Ph) were yielded as organic products (Table 3). Treatment of the reaction mixture with phenol caused the significant increase in the yields of alcohols indicating the existence of an alkoxomanganese intermediate ($\mathrm{Ph_3COMn}$– and $\mathrm{RCH_2OMn}$–) in the reaction mixtures as is assumed in the preceding section. Thus, the reaction between $\mathrm{Ph_2MnPCy_3}$ and alkyl benzoate seems to proceed through an alkoxomanganese intermediate produced by the insertion of C=O double bond of the ester into the Ph–Mn σ-bond followed by β-alkoxy-elimination as shown in eq. 6.



(6)

The acetal type intermediate (A) in Eq. 6 may decompose to alkoxomanganese and benzophenone, the latter of which may react further with Ph–Mn species to give triphenylmethyloxomanganese compound, $\mathrm{Ph_3C}$–O–Mn– (*vide supra*). These alkoxomanganese species may liberate the corresponding alcohols on treatment with phenol. Provided the reaction proceeds according to Eq. 6, the ratio of the products ($\mathrm{PhCOPh+Ph_3COH}$)/($\mathrm{RCH_2OH+RCHO}$) ($=\gamma$), whould be 1.0. In fact experimental values of $\gamma=1.5$ for R=Me and $\gamma=1.1$ for R=Ph have been obtained supporting the validity of the proposed reaction scheme.

The reaction of ethyl formate with complex **1** proceeded similarly to those of alkyl benzoates.



(7)

In this case, also, the observed value of the ratio, $\gamma=$ ($\mathrm{PhCOPh+Ph_2CHOH}$)/(EtOH) was 1.0 in accordance with the expected value of 1.0 for the assumed mechanism.

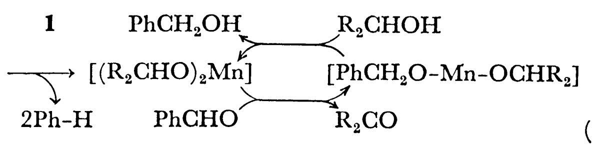
Reactions of Secondary Alcohols and Benzaldehyde or Acetophenone in the Presence of Alkoxomanganese. The above results of conversion of benzaldehyde with $\mathrm{Ph_2MnPCy_3}$, **1**, into benzophenone and benzyloxomanganese (Eq. 4) prompted us to investigate the possibility of catalytic Meerwein-Pondorf type reaction in the presence of alcohol promoted by the manganese complex.

As Table 4 shows, the catalytic Meerwein-Pondorf type reaction did take place when the mixtures of benzaldehyde and diphenylmethanol and of benzaldehyde and 2-propanol were allowed to react in the presence of **1**.

$$\mathrm{PhCHO + Ph_2CHOH \xrightarrow{1} PhCH_2OH + Ph_2CO} \tag{8}$$

$$\mathrm{PhCHO + Me_2CHOH \xrightarrow{1} PhCH_2OH + Me_2CO} \tag{9}$$

In each case about two moles of benzene was produced per mol of **1** indicating the conversion of the diphenylmanganese into the alkoxomanganese species. The reaction path might be similar to that proposed for the Meerwein-Pondorf reaction using isopropoxoaluminium[19)] as shown below :



(10)

TABLE 5. TRANSESTERIFICATION REACTIONS USING ALKOXOMANGANESE COMPOUND[a]

Ester ($PhCOOR$)	Alcohol ($R'OH$)	Products, mol/mol of compound		
		$PhCOOR'$	ROH	PhH
$PhCOOCH_2Ph$ (5.3 mmol)	$EtOH$ (34.7 mmol)	18.7 (0.63)[c]	17.1	1.7
$PhCOOCH_2Ph$ (5.9 mmol)[d]	$EtOH$ (34.7 mmol)[d]	8.7 (0.98)[c]	8.3	—[d]
$PhCOOCH_2Ph$ (5.3 mmol)	Me_2CHOH (13.1 mmol)	1.2	0.4	1.6
$PhCOOCH_2Ph$ (5.3 mmol)	Me_3COH (5.2 mmol)[e]	0.0	0.0	1.4
$PhCOOPh$ (1.1 mmol)	$MeOH$ (71.4 mmol)	6.7 (1.0)[c]	5.8	1.7
$PhCOOPh$ (2.6 mmol)	Me_2CHOH (22.7 mmol)	3.2→7.4[b] (0.73)[c]	0.9→5.4[b] (0.53)[c]	1.6
$PhCOOPh$ (2.0 mmol)	Me_3COH (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 Ph_2MnPCy_3, **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)			
		$PhCOOR$	$PhCH_2OH$	$PhCOOCH_2Ph$	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 $PhCH_2OH$ was added together with EtOH.

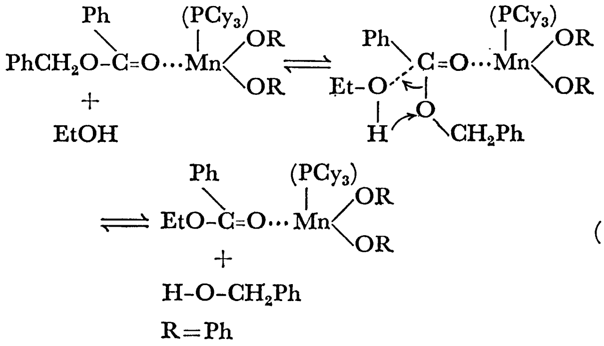
By-products of the present reaction system such as benzyl benzoate and isopropyl benzoate might be produced by Tishchenko type reaction (*vide supra*) and that followed by transesterification (alcoholysis) (*vide infra*), respectively.

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 alkoxomanganese, only 0.7 mol of 1-phenylethanol per mol of Ph_2MnPCy_3 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 isopropoxoaluminium.

Transesterification Reactions Using Alkoxomanganese Compounds. The transesterification reactions between alkyl benzoate and various alcohols were examined using dialkoxomanganese compounds prepared *in situ* from Ph_2MnPCy_3, **1**, and alcohols.

$$PhCOOR + R'OH \xrightarrow{(R'O)_2Mn} PhCOOR' + ROH \qquad (11)$$

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 Ph_2MnPCy_3 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 alkoxyl group as shown below.



(12)

The transesterification reaction using transition metal compounds such as described here and that with alkoxocopper compounds[21] 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.

$$2PhCHO \xrightarrow{(RO)_2Mn} PhCOOCH_2Ph \xrightarrow[ROH]{(RO)_2Mn} PhCOOR + PhCH_2OH \qquad (13)$$

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 $(MeO)_2Mn$,[22] $(EtO)_2Mn$[23] and $(i\text{-}PrO)_2Mn$,[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. $AlPh_3 \cdot Et_2O$ 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 Ph_2MnPCy_3, ***1***. To the mixture of $Mn(acac)_3$ (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, $AlPh_3 \cdot Et_2O$ (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 $Mn(acac)_3$ used). The crude product (2.0 g) was recrystallized from hot toluene (95 °C) to give yellow brown crystals of Ph_2MnPCy_3 (1.3 g, recrystallization yield, 65%). Analytical data and physical properties of **1** are mentioned in the text.

Reaction of Ph_2MnPCy_3, ***1***, *with Allylic Compounds.* To a flask containing Ph_2MnPCy_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 chrolide at room temperature to give allyl acetate. The other reactions of Ph_2MnPCy_3 with allylic compounds were carried out in a similar fashion.

Reaction of Ph_2MnPCy_3 with Carbon Dioxide. On bubbling carbon dioxide into the toluene suspension of Ph_2MnPCy_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 $(PhCOO)_2MnPCy_3$ **2**. Characterization of this compound was achieved as mentioned in the text.

Reactions of Ph_2MnPCy_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 Ph_2MnPCy_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 Ph_2MnPCy_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 Ph_2MnPCy_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 $(CH_3COCH_2)_2MnPCy_3$) isolated from this reaction system, reacted with methyl iodide to give ethyl methyl ketone (0.7 μl, 0.008 mmol) and acetonyl 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 Ph_2MnPCy_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 Ph_2MnPCy_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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