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PREPARATION AND PROPERTIES OF HYDRIDE TRIPHENYLPHOSPHINE RUTHENIUM COMPLEXES WITH 3-FORMYL (OR ACYL) PROPIONATE [RuH(OCOCHRCHRCOR')$(PPh_3)_3$] (R = H, CH_3, C_2H_5; R' = H, CH_3, C_6H_5) AND WITH 2-FORMYL (OR ACYL) BENZOATE [RuH(*o*-$OCOC_6H_4COR'$)$(PPh_3)_3$] (R' = H, CH_3)

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Summary

Reactions of five-membered cyclic dicarboxylic anhydrides, such as phthalic anhydride and succinic anhydride, with $RuH_2(PPh_3)_4$ give ruthenium complexes with 2-formyl benzoate [RuH(*o*-$OCOC_6H_4CHO$)$(PPh_3)_3$] and 3-formyl propionate [RuH($OCOCH_2CH_2CHO$)$(PPh_3)_3$], via the C—O bond cleavage of the anhydrides. Similar reactions of methylsuccinic anhydride or ethylsuccinic anhydride with $RuH_2(PPh_3)_4$ afford mixtures of the isomers [RuH($OCOCHRCH_2CHO$)$(PPh_3)_3$] and [RuH($OCOCH_2CHRCHO$)$(PPh_3)_3$] (R = CH_3 or C_2H_5), in ca. 3 to 1 molar ratio in each reaction. Complexes with 2-acyl benzoate or 3-acyl propionate ligands formulated as [RuH(*o*-$OCOC_6H_4COCH_3$)$(PPh_3)_3$] or [RuH($OCOCH_2CH_2COR'$)$(PPh_3)_3$] (R' = CH_3, C_6H_5) are prepared from the reactions of corresponding 2-acyl benzoic or 3-acyl propionic acids with $RuH_2(PPh_3)_4$. Upon contact with hydrogen at elevated pressure, or with hydrogen chloride or carbon monoxide at atmospheric pressure, these complexes release the corresponding γ-lactones, which are formed through the reduction of formyl or acyl groups in the carboxylate ligands followed by intramolecular condensations. Hydrogenation of 3-acyl propionic acids using ruthenium(II) complexes as catalyst gives γ-substituted γ-lactones in high yields.

Introduction

Much interest in organometallic chemistry has been attracted by the transition metal promoted activation reactions of chemical bonds such as C—C, C—O, and C—X (X = Cl, Br) as well as C—C bond formation, since such reactions have potential value in synthetic organic chemistry. The activation of carbon—halogen bonds by transition metal complexes has been well established regard-

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ing both the detailed mechanism and its application to organic synthesis [1,2]. In addition C—C bond activation has been studied in the past several years with particular attention to the chemistry of metallacyclic complexes [3—5]. Recently studies of C—O bond activation have been extensively performed mainly using the C—O bonds in esters and ethers with Fe, Ru, or Ni complexes [6—9]. However, there have also been a few reports concerning the reactions of C—O bonds in acid anhydrides with transition metal complexes such as $[Fe(CO)_4]^-$ or $Co_2(CO)_8$ to give C—O cleaved organic products [10,11] and $IrCl(CO)(PPh_3)_2$ or $Pt(PPh_3)_3$ to give acyl and carboxylate complexes [12].

Previously we have preliminarily reported the reaction of cyclic anhydrides with $RuH_2(PPh_3)_4$ involving C—O bond cleavage to give the ruthenium complexes with 3-formyl propionate and 2-formyl benzoate as ligands [13]. Although some catalytic applications of ruthenium carboxylate complexes have been explored previously [14,15], little attention has been paid to transformation of the carboxylate ligands in these complexes to organic compounds. The complexes obtained from $RuH_2(PPh_3)_4$ and cyclic anhydrides have a formyl group as the functional group in the carboxylate ligands which are subject to reduction followed by condensation by action of hydrogen, hydrogen chloride, or carbon monoxide to give γ-lactones. From these results we have reinvestigated this type of reaction and tried to apply them to synthetic reactions such as catalytic formation of γ-lactones from 3-acylpropionic acids and the asymmetric synthesis of δ-lactones from six-membered cyclic anhydrides using chiral phosphineruthenium complexes as catalyst [16].

We now wish to report full details of C—O bond activation in cyclic anhydrides promoted by $RuH_2(PPh_3)_4$ to give 3-formyl propionate-ruthenium complexes, and the reactions of these complexes with some reducing agents to form γ-lactones. In this connection the catalytic hydrogenation of 3-acyl propionic acids using ruthenium complexes to give γ-lactones will be also described.

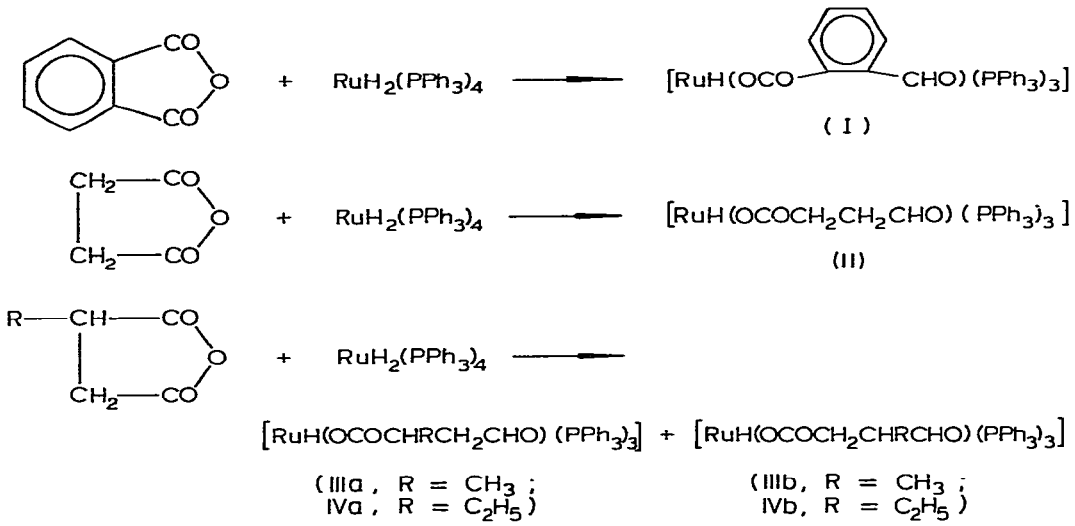
Results and discussion

Reaction of five-membered cyclic anhydrides with $RuH_2(PPh_3)_4$

Reactions of five-membered cyclic anhydrides with $RuH_2(PPh_3)_4$ in toluene solution afford ruthenium hydride complexes with 2-formyl-benzoate or 3-formyl propionate as ligands.

The reactions proceed smoothly under mild conditions. In reactions of cyclic anhydrides with unsymmetrical structure such as methyl or ethyl succinic anhydride two possible isomers (IIIa and IIIb, or IVa and IVb) are obtained as mixtures in the molar ratio of about 3/1. These complexes are thermally stable in the solid state under nitrogen and decompose above 150°C. In solution, however, they are not stable even under nitrogen. Owing to this instability in solution, II and IVab were isolated as crystals in relatively poor yields. (IVab stands for a mixture of IVa and IVb.) The complexes were characterized on the basis of IR, ^1H NMR, and ^{31}P NMR spectra and elemental analyses. Tables 1 and 2 summarize these data.

The IR spectra of the complexes I, II, IIIab, and IVab show a single Ru—H stretching band at 1960—1980 cm^{-1} and a strong band due to C=O stretching



frequency of the aldehyde group at 1690—1725 cm^{-1} in addition to the bands due to the triphenylphosphine coordinated to ruthenium. The symmetric and asymmetric stretching frequencies of the carboxylate group appear at 1520—1530 and 1430—1435 cm^{-1}, respectively. The peak positions and the differences between the two peaks, $\Delta\nu[\nu_{as}(COO) - \nu_{s}(COO)]$, indicate that the carboxylate groups coordinate to ruthenium as symmetrical bidentate ligands [17,18]. In the ^1H NMR spectra of I, II, IIIab, and IVab a characteristic pseudo quartet appears at δ —17.8 to —18.3 ppm due to the hydride bonded to ruthenium [18]. The $^{31}P\{^1H\}$ NMR spectrum of I shows a triplet and a doublet in a 1 to 2

TABLE 1

ANALYTICAL DATA OF THE RUTHENIUM COMPLEXES I—VII

Complex		Yield (%)	M.p. (°C) (dec.)	Analysis (Found (calc.) (%))		
				C	H	Cl
$[RuH(OCOC_6H_4CHO)(PPh_3)_3]\cdot CH_2Cl_2$	(I)	66	176—178	68.4) (67.8)	4.5 (4.7)	6.3 (6.3)
$[RuH(OCOCH_2CH_2CHO)(PPh_3)_3]$	(II)	18	188—191	70.7 (70.3)	5.4 (5.2)	
$[RuH(OCOCH(CH_3)CH_2CHO)(PPh_3)_3]$ $[RuH(OCOCH_2CH(CH_3)CHO)(PPh_3)_3]$	(IIIa) (IIIb)	71	177—182	70.7 (70.6)	5.4 (5.3)	
$[RuH(OCOCH(C_2H_5)CH_2CHO)(PPh_3)_3]$ $[RuH(OCOCH_2CH(C_2H_5)CHO)(PPh_3)_3]$	(IVa) (IVb)	27	155—160			[a]
$[RuH(OCOCH_2CH_2COCH_3)(PPh_3)_3]\cdot THF$	(V)	70	210—212	69.4 (70.3)	5.2 (5.6)	
$[RuH(OCOC_6H_4COCH_3)(PPh_3)_3]\cdot THF$	(VI)	74	200—202	70.9 (71.5)	5.2 (5.4)	
$[RuH(OCOCH_2CH_2COC_6H_5)(PPh_3)_3]\cdot THF$	(VII)	62	199—202	72.0 (71.8)	5.8 (5.6)	

[a] Microanalysis of IVab were not feasible due to their instabilities.

TABLE 2

IR AND ^{1}H NMR DATA OF THE RUTHENIUM COMPLEXES I–VII

Complex	IR (cm^{-1})				^1H NMR [a]		
	ν(Ru–H)	ν(C=O)	ν_{as}(COO)	ν_s(COO)	Ru–*H* [b]	*CH*O	others [c]
I	1960	1700	1520	1435	−17.8(q)	10.68(s)	7.75(m, C_6H_4, 2 H)
II	1980	1720	1530	1430	−18.0(q)	9.22(s)	1.80(bs, CH_2–CH_2)
IIIa	2000	1720	1520	1420	−18.2(q)	9.43(s)	0.75(d, CH_3)
IIIb						9.25(s)	0.65(d, CH_3)
IVa	1920	1720	1520	1435	−18.2(q)	9.40(s)	0.43(t, CH_3)
IVb					−18.3(q)	9.23(s)	0.56(t, CH_3)
V	1975	1710	1525	1430	−19.7(q)		1.63(s, CH_3) 1.85(m, CH_2, 2 H) 2.00(m, CH_2, 2 H)
VI	1995	1700	1530	1405	−18.2(q)		2.30(s, CH_3)
VII	1975	1685	1530	1405	−18.0(q)		2.23(t, CH_2) 2.50(t, CH_2) 7.80(m, C_6H_5, 2 H)

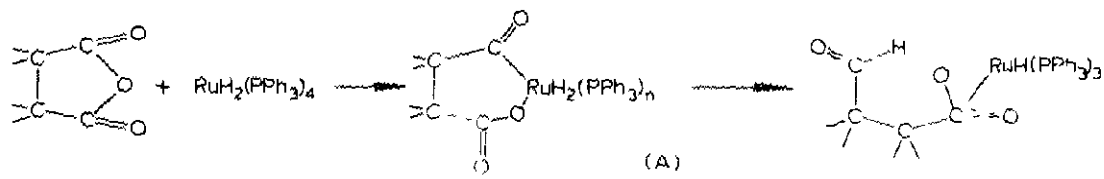
[a] δ-Values (ppm) are shown measured in C_6D_6. Abbreviations: s singlet, d doublet, t triplet, q quartet, bs broad singlet, m multiplet. [b] J(P–H) 26–27 Hz. [c] Peak of phenyl protons of PPh_3 appears at 6.6–7.6 ppm.

integrated intensity ratio at 84.9 and 51.9 ppm downfield from the signal of free triphenylphosphine as the external standard, which is characteristic of an AB_2 spin system. These spectral features indicate that the obtained ruthenium complexes (I—IVab) each have octahedral configuration and that the hydride is bonded to ruthenium *cis* to three phosphorus atoms meridionally oriented around ruthenium and that the carboxylate group occupies the remaining two sites as a bidentate ligand [18].

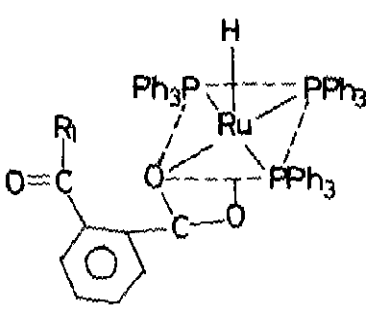
The ^1H NMR spectrum of IIIab shows two singlets due to the aldehyde protons at 9.43 and 9.25 ppm in the integrated intensity ratio of 73/27 and two doublets of methyl protons at 0.75 and 0.65 ppm in the same ratio, indicating that in this reaction two possible isomers IIIa and IIIb are actually obtained in about 3/1 molecular ratio. By comparison of the chemical shift of the aldehydic proton in the complex to those of simple aldehydes, the major peak at 9.43 ppm can be assigned to that of complex IIIa and the minor peak at 9.25 ppm to that of complex IIIb [19]. Complexes IVa and IVb obtained from the reaction of ethylsuccinic anhydride with $RuH_2(PPh_3)_4$ are similarly assigned and their ratio is determined as 3/1.

A possible mechanism for the formation of ruthenium complexes I—IVab is shown in Scheme 1, taking the postulated mechanisms for the reactions of anhydrides with some other transition metal complexes into consideration [12].

SCHEME 1

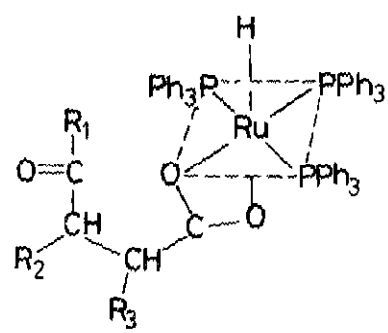


One of the C—O bonds of the cyclic anhydride is attacked by the ruthenium complex, followed by the oxidative addition to ruthenium to form an inter-



(I, VI)

(I, $R^1 = H$
VI, $R^1 = CH_3$)



(II, III, IIIa, IIIb, IVa, IVb, V, VII)

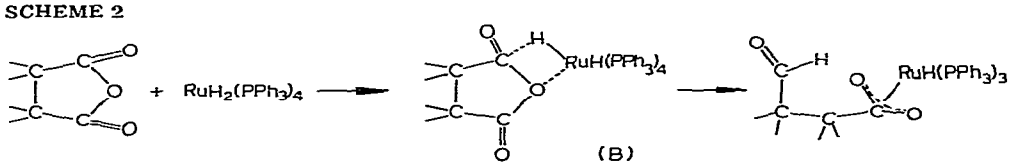
(II, $R^1 = R^2 = R^3 = H$,
IIIa, $R^1 = R^2 = H$, $R^3 = CH_3$,
IIIb, $R^1 = R^3 = H$, $R^2 = CH_3$,
IVa, $R^1 = R^2 = H$, $R^3 = C_2H_5$,
IVb, $R^1 = R^3 = H$, $R^2 = C_2H_5$,
V, $R^1 = CH_3$, $R^2 = R^3 = H$,
VII, $R^1 = C_6H_5$, $R^2 = R^3 = H$)

Fig. 1. The structure of the ruthenium complexes I—VII.

mediary ruthenium(IV) complex (A) having a metallacyclic structure. The aldehyde group is subsequently formed by reductive elimination of an acyl group and a hydride ligand of A to give a 3-formyl propionate ligand. On this mechanism the regioselectivity of the reaction of methyl- (or ethyl-) succinic anhydride with $RuH_2(PPh_3)_4$ can be explained as follows. The C—O bond adjacent to the methyl or ethyl group should be less reactive because of the more severe steric repulsion between triphenylphosphine ligands and a methyl or ethyl group.

An alternative mechanism involving a four center intermediate (B) between Ru—H and C—O bonds of the anhydride may also be possible (Scheme 2).

SCHEME 2

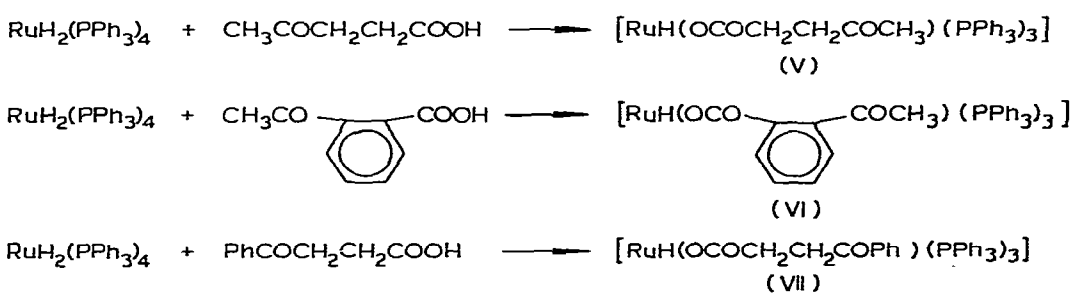


There is no experimental evidence for either mechanism. However, C—O bond activation by transition metal complexes has been considered to involve the oxidative addition process to a metal center in most cases and, eventually, the isolation of acyl and carboxylate complexes of iridium or platinum via oxidative addition of the C—O bond of the anhydride has been performed [12]. These facts suggest that the former mechanism (Scheme 1) is more reasonable than the latter (Scheme 2).

Reaction of aldehydic or keto acids with $RuH_2(PPh_3)_4$

The triphenylphosphineruthenium hydride complexes with simple carboxylates as ligands, formulated as $[RuH(OCOR)(PPh_3)_3]$ (R = CH_3, C_2H_5, C_6H_5, CF_3, C_2F_5), have been previously prepared from the reaction of sodium salts of the corresponding carboxylic acids with $RuCl_2(PPh_3)_3$ in the presence of hydrogen [18] and from the reaction of carboxylic acids with $RuH_2(PPh_3)_4$ [20,21]. Complex I, prepared from the reaction of phthalic anhydride with $RuH_2(PPh_3)_4$, was also independently obtained from the reaction of *o*-phthalaldehydic acid with $RuH_2(PPh_3)_4$ in high yield. During this conversion, reactions of the aldehyde group with $RuH_2(PPh_3)_4$ such as further reduction of the carbonyl group to alcohol [22] or C—H activation to form esters [23] were not observed.

Similarly, the keto acids, such as levulinic acid, *o*-acetyl benzoic acid, and 3-benzoyl propionic acid react with $RuH_2(PPh_3)_4$ to afford triphenylphosphineruthenium hydride complexes with 3-acyl propionate or 2-acyl benzoate ligands (V, VI, and VII, respectively).



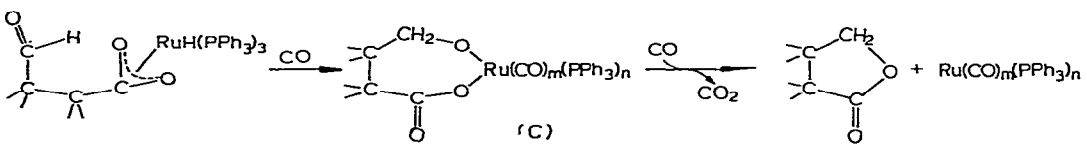
These complexes are rather stable in solution compared to I—IVab and can be isolated as crystals in high yields. The IR and ^{1}H NMR spectral and analytical data of these complexes show that they have similar structures as I—IVab (Tables 1 and 2).

Reactions of I—VII with hydrogen chloride and with carbon monoxide

The ruthenium complexes obtained are expected to be reactive to some reducing agents or reagents with hydrogen sources since they have a carbonyl group as the functional group to be easily reduced. In this connection reactions of the complexes with hydrogen chloride and carbon monoxide were investigated. Actually the reaction of I, II, and IIIab with hydrogen chloride was found to give phthalide, γ-butyrolactone, and a mixture of 2-methyl-γ-lactone and 3-methyl-γ-lactone, respectively. It is assumed that in this reaction the carbonyl group of aldehyde is reduced to alcohol or alkoxide by the hydride originally present in the complex or hydrogen generated via the oxidative addition of hydrogen chloride to ruthenium, and the following acid promoted intramolecular condensation occurs to form a lactone ring.

Contact of benzene solutions of complexes I—VII with carbon monoxide at normal pressure also gives the corresponding γ-lactones through reduction of the carbonyl groups followed by condensation. It is of interest to note that carbon dioxide is evolved from the reaction mixtures. This indicates that the 3-formyl (or acyl) propionate ligand, upon conversion to lactone, liberates an oxygen atom which is transferred to carbon monoxide to produce carbon dioxide. The mechanism shown in Scheme 3 of this lactone formation by the action of carbon monoxide on complexes I—VII can be assumed.

SCHEME 3



Coordination of carbon monoxide to ruthenium causes the hydride transfer to the aldehyde or keto group to form an alkoxy and carboxylate complex (C) which undergoes deoxygenation of one of the oxygen atoms in the ligand [24—26]. This is followed by the spontaneous formation of a lactone ring via reductive elimination. A carbonyl ligand accepts the oxygen atom to yield carbon dioxide which is subsequently released from ruthenium.

It is also possible that either solvent molecules or hydrogen generated by the well known water-gas shift reaction [27] catalyzed by ruthenium, acts as hydrogen sources in this reaction. In order to test these possibilities further studies were made. The recovered lactones from a reaction using C_6D_6 as the solvent contained no deuterium atoms. The addition of a small amount of water (5—10% for Ru) to the reaction mixture produced neither γ-lactones nor carbon dioxide probably because decomposition of the complexes by water preferentially took place. These results suggest that the hydrogen source in this reaction is the hydride originally present in the ruthenium complex and is not the hydrogen derived from the water-gas shift reaction catalyzed by ruthenium

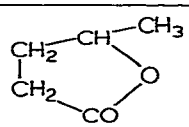
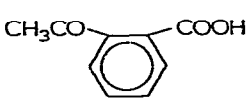
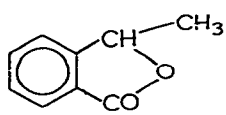
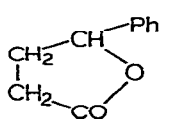
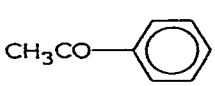
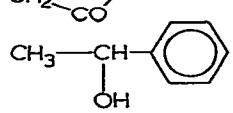
and that the carbon dioxide is formed from the reaction of carbon monoxide coordinated to ruthenium with carboxylate ligands. It may be said that in this reaction deoxygenation of organic compounds was accomplished by carbon monoxide in the presence of a ruthenium complex. Similar reactions have been reported in a few cases [25,26] and in this sense our present observations are of considerable interest.

Reaction of I—VII with hydrogen and catalytic hydrogenation of aldehydic or keto acids using ruthenium complexes

The reactions of complexes I—VII with hydrogen at elevated pressure gave the corresponding γ-lactones similarly to the reaction with hydrogen chloride or with carbon monoxide. However the yields were relatively high (54—78%). The observations mentioned above indicate that five-membered cyclic anhydrides are converted to γ-lactones through the formation of complexes I—IVab, followed by their reaction with hydrogen. Catalytic hydrogenation of cyclic anhydrides to obtain lactones using $RuCl_2(PPh_3)_3$ as catalyst has been reported previously [28,29]. On the basis of these observations it can be expected that 3-acyl propionic acids are hydrogenated catalytically to form γ-substituted γ-lactones using ruthenium complexes as catalyst, since these keto acids are also converted to γ-lactones through the formation of complexes V, VI, and VII and their reactions with hydrogen. The ruthenium-catalyzed hydrogenation of 3-acyl propionic acids or 2-formyl benzoic acid was examined with expectation of lactone formation. It was revealed that both $RuH_2(PPh_3)_4$ and $RuCl_2(PPh_3)_3$ catalyzed hydrogenation of the keto acids such as levulinic acid, *o*-acetylbenzoic acid, and 3-benzoyl propionic acid to give γ-lactones. The

TABLE 3

CATALYTIC HYDROGENATION OF KETO ACIDS [a]

Substrate	Product [b]	Catalyst	Yield (%) [c]
$CH_3COCH_2CH_2COOH$		$RuCl_2(PPh_3)_3$	99 (86)
		$RuH_2(PPh_3)_4$	58 (40)
		$RhCl(PPh_3)_3$	4
		$RuCl_2(PPh_3)_3$	64 (51)
$PhCOCH_2CH_2COOH$		$RuCl_2(PPh_3)_3$	56 (39)
		$RuCl_2(PPh_3)_3$	29

[a] 0.5 mol% of catalyst was used for 45—50 mmol substrate. Initial H_2 12 kg/cm^2, 180°C, 24 h. [b] All products were identified by IR, ^{1}H NMR, and mass spectra. [c] Yields by gas chromatography. Isolated yields are shown in parentheses.

results obtained under the several conditions are summarized in Table 3. $RhCl(PPh_3)_3$ was found to exhibit much lower catalytic activity for this hydrogenation than the ruthenium complexes. The hydrogenation of *o*-acetyl benzoic acid to form 3-methyl phthalide proceeds much more smoothly than hydrogenation of acetophenone to 1-phenylethanol under similar conditions. These facts suggest that coordination of a carboxylate group to ruthenium promotes the hydrogenation of a carbonyl group to induce ring closure giving the corresponding lactone.

Experimental

Materials and general procedures

Phthalic anhydride, succinic anhydride, levulinic acid, and *o*-phthalaldehydic acid were purchased and purified by recrystallization or distillation. Methylsuccinic anhydride [30], ethylsuccinic anhydride [31], *o*-acetyl benzoic acid [32], and 3-benzoyl propionic acid [33] were prepared according to literature methods. Preparation and recrystallization of ruthenium and rhodium complexes were carried out under nitrogen or argon. Solvents were dried in the usual manner, distilled, and stored under nitrogen. $RuH_2(PPh_3)_4$ [34], $RuCl_2(PPh_3)_3$ [35], and $RhCl(PPh_3)_3$ [36] were prepared according to literature methods from $RuCl_3 \cdot 3H_2O$ and $RhCl_3 \cdot 3H_2O$, respectively.

Measurements

Infrared spectra were recorded on a Shimadzu IR-400 spectrophotometer using samples as neat liquids or KBr disks. ^1H NMR spectra were measured with a Hitachi R-40 spectrometer using tetramethylsilane as the internal standard. Gas chromatographic analyses were carried out on a 2 m column of 20% PEG 20 M on Chromosorb-W with a Shimadzu Gas Chromatograph Model 6-AM. GC-MS spectra were recorded on a Hitachi R-80 spectrometer. Microanalysis of ruthenium compounds were performed by Mr. Toyoji Saito in Tokyo Institute of Technology.

Reaction of cyclic anhydrides with $RuH_2(PPh_3)_4$

A toluene (10 ml) solution of $RuH_2(PPh_3)_4$ (0.49 g, 0.43 mmol) and phthalic anhydride (0.070 g, 0.47 mmol) was stirred at 40°C for 5 h. The resulting red solution was cooled overnight below 0°C to give a yellow crystalline powder, which was filtered off, washed with Et_2O and then hexane, and dried in vacuo. Recrystallization from a mixture of CH_2Cl_2 and Et_2O gave orange crystals of $[RuH(o\text{-}OCOC_6H_4CHO)(PPh_3)_3] \cdot CH_2Cl_2$ (I) (0.33 g, 66%).

Complexes II, IIIab, and IVab were obtained in a similar way to I in yields of 18, 71, and 27%, respectively. The ratio of obtained isomers IIIa/IIIb, and IVa/IVb were determined by ^1H NMR spectra of freshly prepared complexes as 3/1 in each case. Attempts to separate these isomeric complexes by fractional crystallization or column chromatography on degassed silica gel or alumina failed because these complexes were not stable enough to handle in solution over a period of several hours even under nitrogen.

Reaction of aldehydic or keto acids with $RuH_2(PPh_3)_4$

A toluene solution (10 ml) of $RuH_2(PPh_3)_4$ (0.84 g, 0.79 mmol) and levulinic acid (0.090 g, 0.78 mmol) was stirred for 0.5 h at room temperature. After complete evaporation of the solvent, 10 ml of Et_2O were added to the red oily product to give a yellow solid which was filtered off and washed with Et_2O repeatedly. The yellow product was recrystallized from a THF/Et_2O mixture to give orange yellow crystals of V (0.59 g, 70%).

Complexes VI and VII were also prepared by similar reactions of $RuH_2(PPh_3)_4$ with *o*-acetyl benzoic acid and 3-benzoyl propionic acid in 74 and 62% yields.

Similar reaction of $RuH_2(PPh_3)_4$ with *o*-phthalaldehydic acid gave complex I in 75% yield.

Reaction of I—IIIab with hydrogen chloride

Contact of dried hydrogen chloride at atmospheric pressure with complex I (0.31 g, 0.28 mmol) dispersed in 5 ml of Et_2O gave a pink white reaction mixture. The precipitate was filtered off and washed repeatedly with Et_2O. Organic product in the combined filtrate and washings was identified as phthalide using GC-MS measurements and its yield was determined by gas chromatography as 33% for complex I. Similar reactions of II with hydrogen chloride gave γ-butyrolactone in 41% yield. A mixture of IIIa and IIIb gave 2-methyl-γ-lactone and 3-methyl-γ-lactone in the same proportion as that of starting IIIa and IIIb (28%).

Reaction of I—VII with carbon monoxide

A benzene solution (5 ml) of I (0.29 g, 0.25 mmol) was evacuated and brought in contact with carbon monoxide at atmospheric pressure at —78°C in a closed system. Stirring for 10 h at room temperature resulted in change of color of the mixture from orange to pale yellow. Gaseous product, carbon dioxide (13% for I), evolved during the reaction and was analyzed by mass spectrometry after collecting with a Topler pump. In solution phthalide (21% for I) was detected by gas chromatography. Similarly, the reaction of II with carbon monoxide gave γ-butyrolactone (34%) and carbon dioxide (23%). A mixture of IIIa and IIIb also gave 2-methyl-γ-lactone and 3-methyl-γ-lactone (18%).

Complexes V, VI, and VII afforded corresponding γ-lactones in relatively low yields (8—13% for Ru), respectively.

Reaction of I—VII with hydrogen

To a preevacuated 50 ml stainless steel autoclave containing a toluene solution of complex I (0.48 g, 0.42 mmol), hydrogen was introduced at 5 kg/cm^2. The mixture was stirred at 150°C overnight. After the usual work-up, phthalide (69% for I) was detected by gas chromatographic analysis. Similar reactions of the complexes with hydrogen gave the corresponding γ-lactones in high yields (54—78%).

Catalytic hydrogenation of aldehydic or keto acids

$RuCl_2(PPh_3)_3$ (0.26 g, 0.27 mmol) and levulinic acid (5.7 g, 49 mmol) were

dissolved in toluene (35 ml). The resulting brown solution was transferred to a stainless steel autoclave (100 ml) containing anhydrous $MgSO_4$. After evacuation of the system hydrogen was charged at 10 kg/cm^2. The reaction mixture was heated to 180°C with stirring for 24 h. After work-up the organic product was isolated by fractional distillation. The yield of the product was determined by gas chromatography using propiophenone as an internal standard. In this reaction γ-valerolactone was obtained as the sole hydrogenation product. Hydrogenation using other substrates such as *o*-phthalaldehydic acid, *o*-acetylbenzoic acid, and 3-benzoylpropionic acid were carried out in a similar manner.

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