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CARBON—OXYGEN BOND CLEAVAGE OF ALKENYL CARBOXYLATE PROMOTED BY TRANSITION METAL HYDRIDES

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Summary

Group VIII transition metal hydrides promote the smooth cleavage of the C—O bond of alkenyl carboxylates to afford metal-carboxylato complexes which release alkenes at ambient conditions. Coordination of the olefinic double bond of the alkenyl carboxylate to the coordinatively unsaturated hydrido complex, produced by the partial dissociation of ligands from the hydrido complex, is considered to be necessary for the reaction to proceed.

Cleavage of carbon—carbon and carbon—halogen bonds promoted by transition metal complexes is well known and has found some synthetic applications [1], but the C—O bond cleavage has received less attention [2]. We have found that some transition metal hydrides promote the facile cleavage of the C—O bond in alkenyl carboxylates and reported the results in a preliminary form [3]. This paper is concerned with the detailed study of the reactions of alkenyl carboxylates with a variety of transition metal hydrides.

Results and discussion

Vinyl carboxylates and allyl acetate react with various transition metal hydrides at room temperature liberating olefins and affording carboxylato complexes. Table 1 summarizes the reactions and the reaction products. The reaction of vinyl acetate with $RuH_2(PPh_3)_4$ (I) [4] serves as a typical example. The reaction proceeds slowly at room temperature liberating 1 mol equivalent of ethylene accompanied by a small amount of ethane and giving a known complex $RuH(OOCCH_3)(PPh_3)_3$ [5] as characterized by elemental analysis, IR, ^1H and ^{31}P NMR, melting point and chemical reactions. No hydrogenation product of vinyl acetate was detected in the reaction product and no hydrogen evolution was observed.

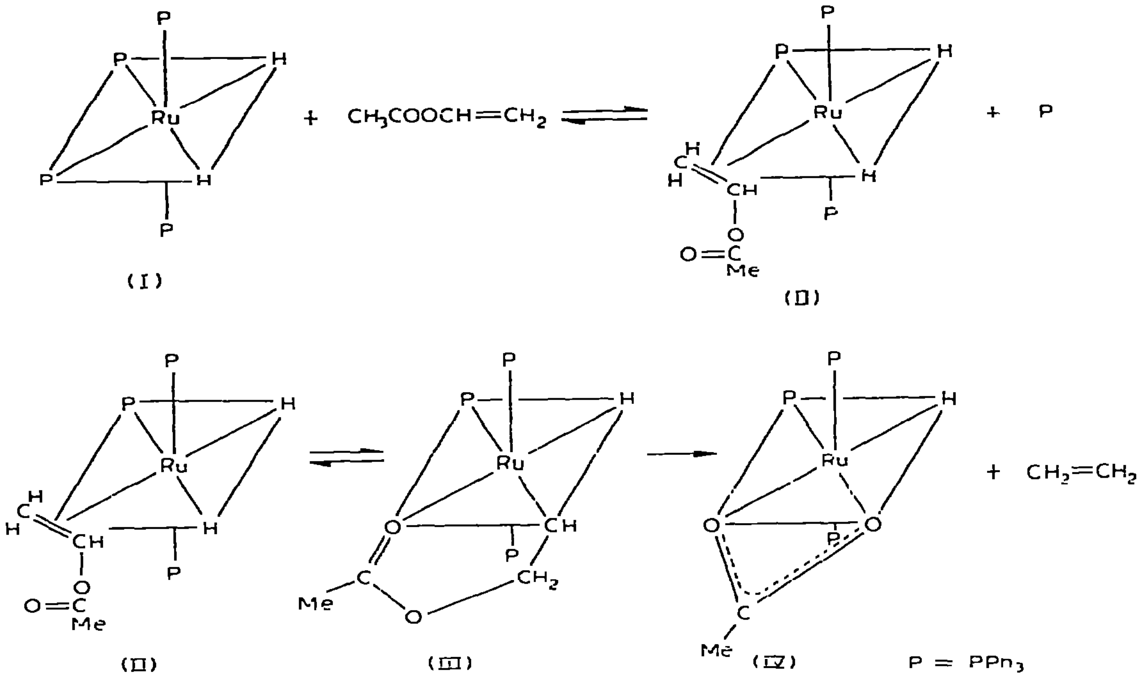
TABLE 1

REACTIONS OF TRANSITION METAL HYDRIDES WITH ALKENYL AND ALKYL CARBOXYLATES AT ROOM TEMPERATURE

Hydrido complex	Concentration (mmol)	Substrates	Volume (ml)	Reaction time (day)	Gas evolved [i] (mmol)	Product [j]
$RuH_2(PPh_3)_4$	0.0076	VAc [c]	5	1	C_2H_4(0.0837) + C_2H_6	$RuH(OAc)(PPh_3)_3$ [l]
$RuH_2(PPh_3)_4$	0.114	VPr [d]	2	1	C_2H_4(0.0863) + C_2H_6	$RuH(O_2CEt)(PPh_3)_3$ [l]
$RuH_2(PPh_3)_4$	0 536	AllAc [e]	4	1	C_3H_6 + C_3H_8	$RuH(OAc)(PPh_3)_3$ [l]
$RuH_2(PPh_3)_4$	ca 0.1	EtAc [f]	2	1		no reaction
$RuH_2(PPh_3)_4$	ca. 0.1	AmAc [g]	2	1		no reaction
$RuH_2(PPh_3)_4$	ca 0.1	PhAc [h]	2	1		no reaction
$RuH_2(PPh_2Me)_4$	ca. 0.1	VAc	2	2		no reaction
$RuH_2(PPh_2H)_4$	ca. 0.1	VAc	2	2		no reaction
$RuHCl(PPh_3)_3$	0 384	VAc	2	7	C_2H_4(0 161)	$RuCl(OAc)(PPh_3)_3$
$RhH(PPh_3)_4$	0 633	VAc	2	1	C_2H_4(0.430)	$Rh(OAc)(PPh_3)_3$ [l]
$RhH(PPh_3)_4$	0 0017	VPr	1	1	C_2H_4 + C_2H_6	$Rh(O_2CEt)(PPh_3)_3$ [l]
$RhH(PPh_3)_4$	0.112	AllAc	1	1	C_3H_6 + C_3H_8	$Rh(OAc)(PPh_3)_3$
$PdH_2(PCy_3)_2$ [a]	0 222	VAc	2	7	C_2H_4(0 018) + C_2H_6(0.086)	$Pd(PCy_3)_2$ [m]
$FeH_2(N_2)(PPh_2Et)_3$	0.477	VAc	2	7	N_2(0.431) + C_2H_4(0.115) + C_2H_6(0.035)	$Fe(OAc)_2$ [k]
$FeH_2(dpe)_2$ [b]	ca. 0.2	VAc	2	7		no reaction
$CoH(N_2)(PPh_3)_3$	0 352	VAc	2	1	N_2(0.409) + C_2H_4(0.177) + C_2H_6	Co(OAc) [k]
$CoH(dpe)_2$	ca. 0.1	VAc	2	7		no reaction
$NiHCl(PCy_3)_2$	ca. 0.2	VAc	2	2		no reaction

[a] PCy_3: tricyclohexylphosphine. [b] dpe. 1,2-bis(diphenylphsophino)ethane. [c] VAc: vinyl acetate [d] VPr: vinyl propionate. [e] AllAc: allyl acetate. [f] EtAc: ethyl acetate. [g] AmAc: amyl acetate. [h] PhAc. phenyl acetate. [i] The amount of alkane evolved in parentheses is very small compared with that of alkene evolved. [j] Reaction product was identified by IR and NMR spectroscopic analysis, elemental analysis and chemical reactions. [k] Satisfactory elemental analysis was not obtained because of the difficulty of purification. Total displacement of the triphenylphosphine ligands was confirmed by IR analysis of the resulting complex. [l] Ref. 5. [m] Ref. 10.

SCHEME 1



The reaction may proceed as shown in Scheme 1.

The ruthenium complex I dissociates in polar solvents such as pyridine, dimethyl formamide and γ-picoline, as revealed by ^1H and ^{31}P NMR, liberating the triphenylphosphine ligand which was coordinated at the position *trans* to one of the hydrido ligands which are mutually in *cis* positions [6]*. In vinyl acetate solution, the olefin probably occupies this position giving the olefin-coordinated complex II in which the olefin is bonded through the double bond with ruthenium as shown in Scheme 1. This assumption of the interaction through the double bond is supported by the facts that I catalyzes the polymerization of vinyl monomers such as acrylonitrile, methacrylonitrile and methyl methacrylate whereas alkyl acetates such as ethyl and amyl acetate did not react with I at room temperature. However, by raising the temperature a decarbonylation reaction of amyl acetate by I takes place with liberation of hydrogen giving a yet unidentified ruthenium carbonyl complex with triphenylphosphine.

The predissociation of one of the phosphine ligands as a prerequisite to the reaction is also supported by the failure of complexes such as $RuH_2(PPh_2Me)_3$ [8] and $RuH_2(PPh_2H)$ [9] to react with vinyl acetate. The absence of the dissociation of the phosphine ligands in these complexes to any appreciable degree in solution has been established by NMR [10]. Hydrido complexes incorporating the bidentate ligand, 1,2-bis(diphenylphosphino)ethane, (dpe), such as $FeH_2(dpe)_2$ [11] and $CoH(dpe)_2$ [12] also failed to react with vinyl acetate presumably due to the absence of the dissociation of the bidentate ligand.

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* Similar compounds have been described by Meakin, Muetterties and Jesson [7].

The evolution of ethylene suggests that the vinyl entity in the vinyl acetate is inserted between one of the Ru—H bonds in I giving a σ-carbon-bonded ruthenium complex III as represented in Scheme 1. Probably the carbonyl group is also coordinated to ruthenium forming a chelate ring; the strain in the chelate ring or an electronic effect by the bonding of the ethylene entity to ruthenium may bring about the splitting of the C—O linkage yielding the (hydrido)acetatotris(triphenylphoshpine)ruthenium complex IV and liberating ethylene. The formation of a hydrido(propionate) complex, $RuH(OOCEt)(PPh_3)_3$, in the reaction of I with vinyl propionate and the formation of propylene and IV in the reaction of I with allyl acetate can be explained in a similar manner. The formation of ethane accompanying ethylene in the reaction of vinyl acetate with I may be due to the hydrogenation of the ethylene produced by its reaction with I, since ethylene reacts with the dihydrido complex I producing a zero-valent ruthenium complex and ethane [13]. If this is the case, the ratio of ethane to ethylene would reflect the rate difference in the reactions of I toward vinyl acetate and ethylene. Considerable variation was observed in the ethane to ethylene ratio when hydrido complexes other than I were used; $RhH(PPh_3)_4$ [1, 8] and $RuHCl(PPh_3)_3$ [14] gave only ethylene whereas $PdH_2(PCy_3)_2$ [15] and $FeH_2(N_2)(PPh_2Et)_3$ [16] produced considerable amounts of ethane in the reactions with vinyl acetate.

A zero-valent palladium complex, $Pd(PCy_3)_2$ [15], was not effective in causing the C—O bond cleavage of the vinyl acetate and presence of a hydride ligand seems to be required for initiating the reaction as suggested by Scheme 1.

In order to obtain further insight into the reaction mechanism, the reaction of vinyl acetate with $RuD_2(PPh_3\text{-}d_6)_4$ (V) in which two hydridic protons and *ortho* protons of PPh_3 in I are replaced by deuteriums, was carried out and the reaction products examined by IR and mass spectrometry. Examination of the ethylene produced in the reaction of 0.25 mmol of $RuD_2(PPh_3\text{-}d_6)$ (isotopic purity 87%) with 21 mmol of vinyl acetate revealed that the ethylene consisted of an isotopic mixture of $C_2D_2H_2/C_2DH_3/$ and C_2H_4 in a ratio of 5/21/74. The vinyl acetate recovered after the reaction contained ca. 2% of vinyl acetate-d_1, whereas the deuterium content in the ligand $PPh_3\text{-}d_6$ showed no appreciable decrease. Examination of the mass balance concerning the fate of the deuterium in $RuD_2(PPh_3\text{-}d_6)_4$ indicated that the hydridic deuteriums in V were incorporated into the ethylene and vinyl acetate. These results support Scheme 1 and provide further information regarding the detailed reaction mechanism: (1) Introduction of deuterium from the ruthenium deuteride V into vinyl acetate together with the H—D scrambling in the ethylene produced suggests that isotopic exchange is taking place between V and vinyl acetate presumably by insertion of the vinyl entity into one of the Ru—D bonds (II→III) and the reverse β-elimination (III→II). (2) The equilibrium reaction between II and III may be occurring faster than the C—O bond breakage which irreversibly leads to IV. This conclusion is in line with our observation in the hydrogenation of ethylene by I with D_2 that the isotopic exchange between ethylene and D_2 took place faster than the hydrogenation of ethylene. (3) The *ortho* hydrogens of the triphenylphosphine ligands do not participate in the hydrogen exchange and only the original hydridic deuterogens in V are involved.

In some cases the formation of carboxylates led to the total displacement of the phosphine ligands as observed in the reactions of the dinitrogen-coordinated complexes $FeH_2(N_2)(PPh_2Et)_3$ and $CoH(N_2)(PPh_3)_3$ [17] evolving dinitrogen in addition to ethylene and ethane and producing iron(II) and cobalt(I) acetate.

As Table 1 indicates, such cleavage of C—O bonds is common to Group VIII transition metal hydrides which are capable of producing a coordinatively unsaturated complex in solution.

In the production of vinyl acetate from ethylene and acetic acid a reaction mechanism involving the formation of a hydrido(acetato) complex which reacts with ethylene to give eventually vinyl acetate has been proposed [18]. The cleavage of the vinyl acetate described here can be regarded as the reverse process.

Experimental

All the reactions were carried out under nitrogen or in a vacuum. Solvents and reagents were purified by usual methods and stored under nitrogen before use. Alkenyl carboxylates were introduced by a trap to trap vacuum distillation into the reaction vessels containing the hydrido complexes. Analysis of evolved gas was carried out by mass spectrometry and gas chromatography after collecting the non-condensable gases at liquid nitrogen and Dry Ice/methanol temperature using a Toepler pump, by which the volume of the gas was measured. IR and NMR spectra were measured by a Hitachi EPI-G3 spectrometer and a JEOL 100 MHz NMR spectrometer. ^1H NMR signals are referred to TMS (τ 10) and $^{31}P\{^1H\}$ NMR signals to free triphenylphosphine signal, with downfield shifts positive.

Materials

All the hydrido complexes were prepared by methods reported previously.

Since the reaction conditions are more or less similar, the reaction of $RuH_2(PPh_3)_4$ with vinyl acetate as well as the characterization of the carboxylate complexes isolated are described below.

Reaction of $RuH_2(PPh_3)_4$ with vinyl acetate

Vinyl acetate (5.0 ml) was introduced to $RuH_2(PPh_3)_4$ (112 mg, 0.0976 mmol) by a trap to trap distillation in a vacuum. The yellow heterogeneous system gradually became homogeneous at room temperature to produce a precipitate of a light yellow complex $RuH(OAc)(PPh_3)_3$ after a day. No hydrogenated product was detected by gas chromatography. Ethylene (0.0837 mmol) and a small amount of ethane were evolved but no hydrogen evolution was observed for 1 day. The precipitate was recrystallized from a mixture of tetrahydrofuran and diethyl ether, washed with n-hexane and dried in a vacuum. (Found: C, 70.1; H, 5.0. $C_{56}H_{49}O_2P_3Ru$ calcd.: C, 71.0; H, 5.2%.) Yield: 49%, (dec.): 250-251°. IR(KBr): ν(Ru—H) 2020; ν_{as}(OCO) 1530, ν_s(OCO) 1450 cm^{-1}. ^1H NMR: τ 27.4 (1H, quartet, Ru—H); 8.52 (3H, singlet, CH_3COO). ^{31}P NMR in CH_2Cl_2: 84.6 (triplet), 50.4 ppm (doublet).

Dry hydrogen chloride (24 ml, S.T.P.) reacted with $RuH(OAc)(PPh_3)_3$, (580 mg, 0.61 mmol) in diethyl ether for a day at room temperature to give acetic acid (0.73 mmol) and hydrogen (0.54 mmol).

Reaction of $RuD_2(PPh_3\text{-}d_6)_4$ with vinyl acetate

$RuD_2(PPh_3\text{-}d_6)$ was prepared by the exchange reaction of $RuH_2(PPh_3)_4$ with excess deuterium gas at 1 atm in benzene solution at room temperature for a week. The exchange reaction was repeated three times and the deuterated complex recovered. Isotopic purity was estimated as 87% by NMR analysis of triphenylphosphine oxide obtained after oxidation of the deuteride complex with hydrogen peroxide.

Vinyl acetate (2.0 ml) and $RuD_2(PPh_3\text{-}d_6)_4$ (300 mg) gave RuD(OAc)-$(PPh_3\text{-}d_6)_3$ and deuterated ethylenes (the ratio of $C_2H_4/C_2H_3D/C_2H_2D_2$ was 74/21/5). Vinyl acetate-d_1 was detected in the solution (yield of 0.36 mmol) and confirmed by mass spectroscopic analysis. The deuterium content in the triphenylphosphine ligands of $RuD(OAc)(PPh_3\text{-}d_6)_3$ was almost the same as that of the starting $RuD_2(PPh_3\text{-}d_6)_4$.

Product characterization of carboxylate complexes

$RuH(O_2CC_2H_5)(PPh_3)_3$. (Found: C, 71.2; H, 5.9. $C_{57}H_{51}O_2P_3Ru$ calcd.: C, 71.2; H, 5.4%.) (dec.) 261-263°. IR: ν(Ru—H) 2020; ν_{as}(OCO) 1525; ν_s(OCO) 1465 cm^{-1}. ^1H NMR: τ 29.8 (quartet, Ru—H); 9.50 (triplet, CH_3); 8.42 (quartet, CH_2). ^{31}P NMR: 84.6 (triplet); 50.4 ppm (doublet). Excess dry hydrogen chloride reacted with $RuH(O_2CC_2H_5)(PPh_3)_3$, (184 mg, 0.192 mmol) to give propionic acid (0.181 mmol) and hydrogen (0.197 mmol).

$Rh(OAc)(PPh_3)_3$. (Found: C, 71.0; H, 5.4. $C_{56}H_{48}O_2P_3Ru$ calcd.: C, 70.9; H, 5.1%.) IR: ν_{as}(OCO) 1600 s; ν_s(OCO) 1370 cm^{-1} s. ^1H NMR: τ 7.78 (s, CH_3). ^{31}P NMR: 24-26.5 ppm m. $Rh(OAc)(PPh_3)_3$ (199 mg, 0.210 mmol) reacted with excess dry hydrogen to give acetic acid (0.24 mmol).

$Rh(O_2CC_2H_5)(PPh_3)_3$. (Found: C, 70.5; H, 5.5. $C_{57}H_{50}O_2P_3Rh$ calcd.: C, 71.1; H, 5.2%.) IR: ν_{as}(OCO) 1600 s; ν_s(OCO) 1370 cm^{-1} s.

$RuCl(OAc)(PPh_3)_3$. (Found: C, 67.7; H, 4.9. $C_{56}H_{48}ClO_2Ru$ calcd.: C, 68.5; H, 4.9%.) IR: ν_{as}(OCO) 1520, m; ν_s(OCO) 1460 cm^{-1}, m.

Co(AOc). This was recrystallized from pyridine as a complex which can be formulated as $Co(OAc)(pyridine)_{0.5}$. (Found: C, 35.8; H, 4.4; N, 3.5. $C_{45}H_{55}CoN_{0.5}O_2$ calcd.: C, 34.3; H, 3.5; N, 4.4%.) IR: ν_{as}(OCO) 1620 (br); ν_s(OCO) 1420 cm^{-1} (br).

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