Homogeneous Catalytic Hydrogenation of Carboxylic Acid Esters to Alcohols

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Summary The homogeneous catalytic hydrogenation of activated and simple aliphatic carboxylic acid esters to their corresponding primary alcohols has been accomplished under mild conditions [90 °C; 620 kPa (gauge) of hydrogen] using a novel anionic ruthenium hydride complex.

Carboxylic acid esters can be hydrogenated to their corresponding alcohols using heterogeneous metal oxide-based catalysts.[1,2] Reaction conditions are usually quite severe; commonly used copper–chromite catalysts generally require high temperatures (200—250 °C) and 13 000 to 21 000 kPa of hydrogen pressure. As far as we are aware, the hydrogenation of simple aliphatic esters using soluble metal-complex catalysts has thus far not been described. Ruthenium complexes have previously been reported to catalyse the hydrogenation of carboxylic acid anhydrides and dicarboxylic acids to lactones which were not, however, hydrogenated further to the di-alcohols.[3–5] We recently reported that the anionic tris-phosphine ruthenium hydride complex (**1**) is an effective homogeneous catalyst for the hydrogenation of a variety of polar organic compounds, including activated esters such as dimethyl oxalate and 2,2,2-trifluoroethyl trifluoroacetate,[6] but it is not effective for simple aliphatic esters. We have now prepared a metal complex which can in fact catalyse the hydrogenation of such esters to alcohols.

$$(Ph_3P)_2Ph_2P(\overline{C_6H_4)R}uH_2^-K^+(Et_2O)\cdot C_{10}H_8$$

(**1**)

$$[(Ph_3P)(Ph_2P)RuH_2^-K^+\cdot \text{ diglyme}]_2$$

(**2**)

The complex was prepared by the reduction of $[HRuCl(PPh_3)_2]_2$[7] with potassium naphthalide (mol. ratio Ru : K = 1 : 2) at low temperatures (−80 °C) in tetrahydrofuran (THF). After slow warming to room temperature, a THF-soluble, diethyl ether-insoluble, red-brown solid (**2**) was isolated from the reaction mixture. The solid was purified by crystallization from toluene solutions containing a small amount of diglyme ($MeOCH_2CH_2OCH_2CH_2OMe$). The elemental composition, n.m.r. and i.r. spectra and chemical properties of (**2**) are consistent with its formulation as the anionic phosphine-phosphido ruthenium dihydride complex, $[(Ph_3P)(Ph_2P)RuH_2^-K^+\cdot\text{diglyme}]_2$, ^1H n m.r. τ (Me_4Si) (M–H): 23·0, 23·74, 25·64, and 26·75; ^{31}P n m.r. (85% H_3PO_4) δ −143·4, −109·0, −102·3, and −101·7 p.p.m.; i.r. ν (M–H) 1745m, 1775m, and 1830m cm^{-1}. Reaction of crystalline (**2**) with HCl in THF gave 2 mol of H_2/Ru, and also a red solid which was shown by ^{31}P n.m.r. spectroscopy to contain both triphenylphosphine and diphenylphosphine. Elucidation of the detailed molecular structure of (**2**) will require *X*-ray crystallographic studies.

TABLE Catalytic hydrogenation of esters to alcohols [a]

Substrate	Catalyst	% Ester conversion[b]	Reaction time/h	Products[c]
MeOAc	(2)	22	20	EtOH, EtOAc, MeOH
MeOAc[d]	(2)	5	20	EtOH, EtOAc, MeOH
MeOAc[e]	(2)	0	20	—
EtOAc	(2)	8	20	EtOH
$EtCO_2Me$	(2)	5	20	Pr^nOH, $EtCO_2Pr^n$, MeOH
CF_3CO_2Me	(1)	10	20	CF_3CH_2OH, MeOH
CF_3CO_2Me	(2)	88	20	CF_3CH_2OH, MeOH
$CF_3CO_2CH_2CF_3$	(1)	100	12	CF_3CH_2OH
$CF_3CO_2CH_2CF_3$	(2)	100	4	CF_3CH_2OH
$(CO_2Me)_2$	(1)	10	20	$HOCH_2CO_2Me$, MeOH
$(CO_2Me)_2$	(2)	70	20	$HOCH_2CO_2Me$, MeOH

[a] Glass reactor, magnetic stirring, 620 kPa (gauge) H_2 90 °C, solvent (3 ml) toluene except where noted, ester (5 3 mmol), catalyst (0 017 mmol) [b] Actual ester conversion to hydrogenation products (note in some cases additional ester is consumed by transesterification) [c] Analyses by g c , 4 m, 3 2 mm i d stainless steel column (Porapak P 80/100 mesh) programmed 70 to 220 °C, 30 °C/min [d] THF solvent [e] Added 18-crown-6 (0 076 mmol)

Toluene solutions of (**2**) catalyse the hydrogenation of methyl acetate under mild conditions to yield a mixture of ethanol, ethyl acetate, and methanol [equation (1)] (typically a molar ratio of ethanol to ethyl acetate is 1 1 4) The ethyl acetate arises from the transesterification of the starting ester with the product ethanol (*cf* Table) Throughout the reaction the solutions remain clear we saw no

$$\mathrm{MeCO_2Me} \xrightarrow[\text{cat}]{\mathrm{H_2},\ 90\ ^{\circ}\mathrm{C}} \mathrm{EtOH} + \mathrm{MeCO_2Et} + \mathrm{MeOH} \tag{1}$$

evidence for precipitated metal † The hydrogenation of methyl acetate with (**2**) is effective only when carried out in a relatively non-co-ordinating solvent Use of a THF medium instead of toluene, or the addition of 18-crown-6, largely suppress the reaction Neat methyl acetate is not hydrogenated From the experiment with 18-crown-6, it appears that a relatively unsolvated alkali metal counter-ion is necessary to activate the ester towards hydride transfer from the anionic ruthenium catalyst Ethyl acetate and methyl propionate are also hydrogenated but with more difficulty Aromatic esters (*e g* methyl benzoate) are not hydrogenated under the same conditions For the hydrogenation of activated esters, complex (**2**) is a much more active catalyst than (**1**) (*cf* Table)

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† Group 8 metals are generally not effective as catalysts for the hydrogenation of simple aliphatic esters (ref 8)

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