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Preliminary Communication

First use of methyl formate with no extra carbon monoxide in the hydroesterification of ethene catalysed by palladium complexes

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Abstract

The complex $[PdH(Cl)(PBu_3)_2]$, generated *in situ* by addition of one equivalent of $NaBH_4$ to $[PdCl_2(PBu_3)_2]$, is a good catalyst precursor for the addition of methyl formate to ethene. Extra carbon monoxide is not required, and methyl propanoate is produced with high selectivity.

Key words: Palladium; Hydroesterification; Ethene; Catalysis

Since the pioneering work of Sneeden and coworkers who discovered the direct addition of methyl formate to ethene catalysed by ruthenium complexes [1], several studies have concerned the substitution of the carbon monoxide–methanol couple by an alkyl formate to produce esters.

Two principal metals catalyse this reaction, ruthenium and palladium [2,3]. Surprisingly, all the reactions which involve palladium were rather slow and required CO pressure. In some cases, it was clearly shown by labelling experiments that the CO group which is incorporated in the ester function originates from the gas phase [3e].

Recently, Lin and Alper [3c] showed that zerovalent palladium complexes, such as $[Pd(PPh_3)_4]$ and $[Pd(dba)_2]$ with 1,4-bis(diphenylphosphino)butane (dba = dibenzylideneacetone or 1,5-diphenyl-1,4-pentadien-3-one) can catalyse the hydroesterification of ethene by methyl formate provided CO pressure is maintained during the reaction.

We have observed that $[PdH(Cl)(PBu_3)_2]$, previously described by Saito *et al.* [4] as an intermediate in the production of the stable hydrido-complex $[PdH(Cl)(PCy_3)_2]$ by metathesis of the tributyl phosphine ligands, is actually an active catalyst for the hydroesterification of ethene. Typically, an autoclave was charged with a 1/1.1 mixture of $[PdCl_2(PBu_3)_2]$ and $NaBH_4$ dissolved in 20 ml of methanol, 100 mmol methyl formate and pressurised to 3.5 MPa with ethene. A run carried out at 130°C for 3 h yielded 7% methyl propanoate (eqn. (1)) and a small amount of black palladium.

$$CH_2{=}CH_2 + HCOOCH_3 \xrightarrow{[Pd]} CH_3CH_2COOCH_3 \qquad (1)$$

As shown in Table 1, a first analysis of the reaction parameters revealed that methanol is an appropriate solvent, that the temperature should be near 130°C, and that a PBu_3/Pd ratio of 7 allowed us to transform 90% of the ethene in 3 h. No black palladium was observed, and the catalyst activity corresponded to a turnover frequency of 30 h^{-1}.

For a 75% conversion of methyl formate, the yield in methyl propanoate was 59%, and the yields of by-products were carbon monoxide (7%) and methyl acetate (4.5%). No pentan-3-one was detected, as previously observed by Sneeden for ruthenium [1]. We checked that $NaBH_4$ induces the decarbonylation of methyl formate to afford carbon monoxide, although even with 1.1 mmol of $NaBH_4$ the reaction proceeds slowly (24% during the first hour, compared with 1.2% with 7 mmol PBu_3) at 130°C. If in the reaction methyl formate is replaced by carbon monoxide (140 mmol or 3 MPa) with methanol as both solvent and reactant, the reaction yields 47% methyl propanoate (turnover 16 h^{-1}). Thus methyl formate is characterised by a turnover frequency twice that of the CO/MeOH mixture.

In addition, the nature of the phosphine is important. Indeed, less basic phosphines such as PPh_3 and $P(OMe)_3$, or very bulky phosphines such as PCy_3, show reduced activity. Trimethylphosphine shows a turnover frequency of 19 h^{-1}. This phosphine is less hindered [5] but more basic [6] than PBu_3, and should stabilise the hydride complex. However, PMe_3 which boils at 37.8°C should be present mainly in the gas phase.

Concerning the mechanism, we propose coordination of ethene to the hydridopalladium active species, followed by a 1,2-shift of the hydride to produce an

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TABLE 1. Hydroesterification of ethene by methyl formate catalysed by hydrido-complexes $[PdH(Cl)L_2]$ generated *in situ*

L	Solvent	*T* (°C)	L/Pd	*t* (h)	Yield in methyl propanoate (%)	Turnover frequency (h^{-1})
PBu_3	HCOOMe	100	2	14	traces	–
PBu_3	$HCONMe_2$	100	2	14	traces	–
PBu_3	MeOH	100	2	14	6	0.4
PBu_3	MeOH	130	2	14	14	1
PBu_3	MeOH	180	2	14	3.3	0.2
PBu_3	MeOH	130	5	3	58.4	19.4
PBu_3	MeOH	130	7	3	90.3	30.1
PBu_3	MeOH	130	10	3	43.9	14.6
PPh_3	MeOH	130	7	3	traces	–
PCy_3	MeOH	130	7	3	0.4	0.1
$P(OMe)_3$	MeOH	130	7	3	traces	–
PMe_3	MeOH	130	7	3	57.0	19.0

Experimental conditions: $[PdCl_2L_2] = 1$ mmol; $NaBH_4 = 1.1$ mmol; HCOOMe = 100 mmol; $C_2H_4 = 164$ mmol (3.5 MPa); solvent = 20 ml.

ethylpalladium species. This could cleave the CH bond of methyl formate as shown by Milstein for a rhodium complex, giving rise to a stable hydrido(methoxycarbonyl) species [7]. However, the alkoxycarbonylation pathway which involves CO insertion into the palladium–ethyl bond remains puzzling.

In conclusion, we report the first palladium system to catalyse the carbonylation of ethene in the absence of extra carbon monoxide. It is based on the formation of $[PdH(Cl)(PBu_3)_2]$ *in situ* by reaction of $[PdCl_2(PBu_3)_2]$ with $NaBH_4$. Turnover frequencies as high as 30 h^{-1} have been reached.

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