One-step Formation of Methyl Acetate with Methanol used as the Sole Source and Catalysis by Ru^{II}–Sn^{II} Cluster Complexes

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Ru^{II}–Sn^{II} cluster complexes $[Ru(SnCl_3)_5L]^{3-}$ (L = MeCN, PPh_3) have been found to be effective for the catalytic conversion of methanol to methyl acetate in a single step.

Acetic acid is an important chemical and one of the main processes for its production is carbonylation of methanol (the Monsanto process). An alternative route from methanol to acetic acid proceeds *via* the isomerization of methyl formate; this reaction is useful where methyl formate is obtained as an undesirable by-product (*e.g.* in butane oxidation) or can be made cheaply.[1]

Since liquid-phase dehydrogenation of methanol to methyl formate is known,[2–4] we have considered dual functional catalysis (dehydrogenation then isomerization) to convert methanol directly into acetic acid in a one-pot reaction using Ru^{II}–Sn^{II} cluster complex catalysts $[Ru(SnCl_3)_5L]^{3-}$ (L = MeCN, PPh_3).† The choice of catalyst was based on the catalytic activity of Ru^{II} complexes for methanol dehydrogenation[2–4] and the following characteristics of the $SnCl_3^-$ ligand.[6] (i) It prevents the reduction of central transition metal ions to metal due to its high π-acceptor ability which removes electron density from the central metal ion; this is desirable under the present reducing conditions (methanol substrate). (ii) It renders the *trans* ligand labile and is also quite labile itself, easily providing vacant coordination sites.

Fig. 1 shows the time course for the formation of methyl acetate and methyl formate, a small amount of which was constantly present. The methyl acetate would be formed from acetic acid *via* a concomitant esterification reaction with methanol. The turnovers for methyl acetate formation reached to 9.2 (65 °C) and 5.4 (40 °C) over a reaction time of 120 h, which confirms that the reaction is catalytic. The results obtained under various conditions are summarized in Table 1.‡

Table 1 Formation of methyl acetate from methanol with $[Ru(SnCl_3)_5L]^{3-}$ catalysts[a]

		Turnover number			
		65 °C		40 °C	
L	Solvent[b]	10 h	100 h	10 h	100 h
MeCN	$MeNO_2$	1.9	7.8	1.0	4.7
	MeCN	1.2	1.6	0.6	4.1
PPh_3	$MeNO_2$	8.0	15.7	3.2	6.8
	MeCN	2.4	5.0	0.6	2.6

[a] Under N_2 atmosphere. [Catalyst] = 0.050 mmol dm^{-3}. [b] 200 cm^3 (methanol/solvent = 1 : 1 v/v).

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† All operations were performed under an inert atmosphere. Both of the anionic complexes were isolated and purified as Et_4N^+ salts. The MeCN complex was synthesized according to the literature,[5] and the PPh_3 complex was obtained by a ligand-exchange reaction with PPh_3.

‡ No other products were detected in the solution (GLC). The column packings used were PEG-6000, Porapak T and TCEP [1,2,3-tris(2-cyanoethoxy)propane]; Porapak T is convenient for the analysis of formaldehyde, and TCEP is suitable for the separation of methyl formate and formaldehyde dimethyl acetal.

Table 2 Conversion of paraformaldehyde catalysed by $[Ru(SnCl_3)_5(MeCN)]^{3-}$[a]

Catalyst/mmol	Solvent	Products/mmol			
		$MeCO_2H$	HCO_2Me	MeCOCOMe	MeOH
0.20	MeCN[b]	0.224	0.014	0.009	0.062
0.10	DMF[c]	0.113	0.006	0.016	0.089

[a] Under Ar atmosphere at 100 °C with [HCHO]/[Ru] = 20. Reaction time, 24 h. [b] An autoclave was used with a solvent volume of 50 cm^3. [c] A glass reaction vessel was used with a solvent volume of 25 cm^3. DMF = *N,N*-dimethylformamide.

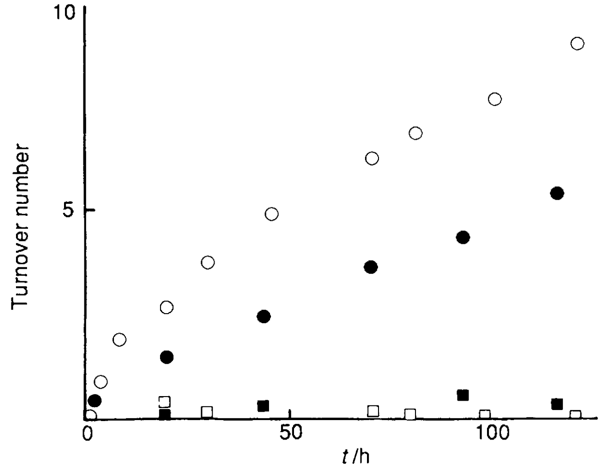

Fig. 1 Time course for the conversion of methanol to methyl acetate (○, ●) and methyl formate (□, ■) with $[Ru(SnCl_3)_5(MeCN)]^{3-}$ as catalyst, for reaction mixtures containing 0.050 mmol dm^{-3} catalyst in the solvent (200 cm^3, $MeOH/MeNO_2$ = 1 : 1 v/v) under N_2 (1 atm); reaction temperatures: 65 °C (○, □) and 40 °C (●, ■)

The reaction mechanism appears to involve a methyl formate intermediate for the acetic acid formation, for the following reasons. (i) There is a constant low concentration of methyl formate during the reaction (Fig. 1). (ii) Its isomerization to acetic acid has been found to be possible using the same homogeneous catalysts.[7]

It is noteworthy that in some cases trace amounts of formaldehyde dimethyl acetal (methylal) were detected during the reaction. Since formaldehyde should be the primary reaction product, it could be converted to methyl formate through a Tishchenko-type reaction. Ru^{II} and some other transition metal complexes are reported to be catalytically active for this reaction under essentially neutral conditions.[8–10] Table 2 shows the results for experiments with formaldehyde (paraformaldehyde) as the reactant; the main product is acetic acid and some methyl formate is also produced. This supports the reaction sequence ($HCHO \rightarrow HCO_2Me \rightarrow MeCO_2H$) postulated above. The formation of diacetyl (butane-2,3-dione), which is also formed from formaldehyde over lead silicate catalyst,[11] would indicate the presence of an acetyl intermediate.

The coordination of an oxygen or nitrogen base to the Sn^{II} ligand is very common in the corresponding transition metal mixed cluster systems.[6] Therefore, a multi-centre interaction with oxygen-containing substrates may be important in the catalysis here. Attempts to improve the catalytic activity are in progress.

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