Cluster Catalysed Selective Transfer Hydrogenation of α,β-Unsaturated Aldehydes

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$H_4Ru_4(CO)_8L_4$ (L = PBu^n_3) catalyses selective transfer hydrogenation of α,β-unsaturated aldehydes to α,β-unsaturated alcohols; kinetic and deuterium labelling studies indicate involvement of cluster intermediates and no participation by the cluster hydrides.

Various homogeneous hydrogen-transfer reactions are known to be catalysed by tri- and tetranuclear ruthenium clusters.[1] However, as for most other cluster-catalysed reactions, there is little direct evidence for the participation of cluster intermediates.[2] This uncertainty is accentuated by the fact that no unusual chemoselectivity, one of the possible indicators of cluster catalysis, has been reported for any of these reactions. We find that with isopropanol as the donor, $H_4Ru_4(CO)_8L_4$ (L = PBu^n_3) (**1**) catalyses the reduction of α,β-unsaturated aldehydes to the corresponding unsaturated alcohols, with high selectivities. Such high selectivities are rare both in homogeneous and heterogeneous catalysis and to our knowledge have not previously been observed in any catalytic hydrogen transfer system.[3] Preliminary kinetic and deuterium labelling studies indicate involvement of cluster intermediates and a passive role for the cluster hydrides.

Results of transfer hydrogenations of some α,β-unsaturated aldehydes and ketones using (**1**) as the catalyst are shown in Table 1. During reductions of α,β-unsaturated ketones, selective reduction of the ketonic functionality is not observed. Other ruthenium clusters such as $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and $[H_3Ru_4(CO)_{12}]^-$ are found to be far less active and selective than (**1**). With these clusters as the precatalysts, the conversions of crotonaldehyde were never more than 10% at 82 °C over 16 h and maximum selectivity to crotyl alcohol was about 50%. Furthermore, i.r. spectroscopic monitoring of the catalytic runs established that, apart from (**1**), all the clusters were converted into other carbonyl species. In contrast, (**1**) could be recovered quantitatively and reused.

With (**1**) as the catalyst, the rate of formation of crotyl alcohol from crotonaldehyde was found to be inhibited by the addition of L or application of CO pressure. The rate was found to be inversely proportional to the concentrations of added phosphine (Figure 1). Similarly, with increased CO pressure a limiting inhibited rate was reached. These observations indicate that the rate determining step is preceded by the rapid pre-equilibria involving dissociation of L and probably dissociation of CO, or, under CO pressure formation, of species such as $H_4Ru_4(CO)_9L_3$. The slopes (k_{obs}) obtained from rate *vs.* 1/[L] plots show linear dependence on the concentrations of (**1**) (Figure 2), crotonaldehyde, and isopropanol,[4] the rate expression is given in equation (1).

$$\text{Rate} = k[(\mathbf{1})]\,[\text{Crotonaldehyde}]\,[\text{isopropanol}]/[\text{L}] \qquad (1)$$

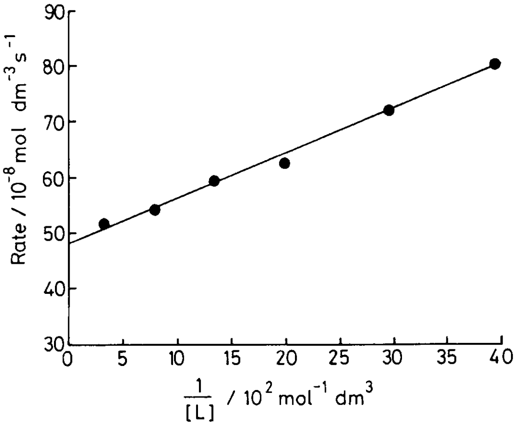

Figure 1. Plot of the rate of formation of crotyl alcohol *vs.* $[L]^{-1}$ at 82 °C.

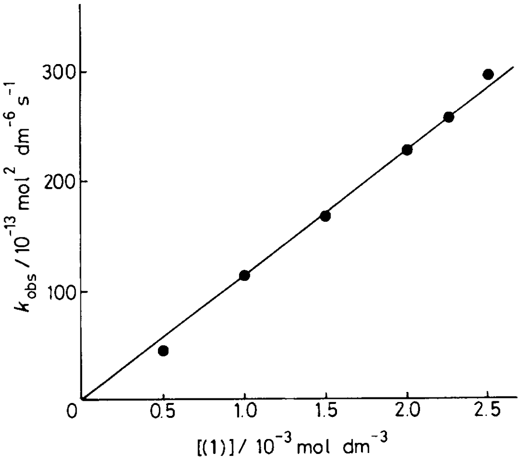

Figure 2. Plot of k_{obs}, slope of plot of Figure 1, *vs* [(**1**)] at 82 °C.

Table 1. Transfer hydrogenations with (**1**)[a]

Substrate	Conversion %	Products (%)[b]
Crotonaldehyde	75	Crotyl alcohol (90) n-butyraldehyde (4) n-butanol[c]
Cinnamaldehyde	55	Cinnamyl alcohol (80) 3-phenylpropanaldehyde (17) 3-phenyl propanol (3)
Pent-2-en-1-al	55	Pent-2-en-1-ol (70) n-pentanol (15) n-pentanol (15)
Mesityl oxide	15	Methylisobutylketone (70) 2-methyl pentan-4-ol (30)
Cyclohex-1-en-2-one	10	Cyclohexanone (90) cyclohexanol (10)

[a] All reactions carried out at 82 °C; (**1**) (0.01 mmol) and substrate (1.0 mmol) in propan-2-ol (15 ml); 16 h.

[b] Calculated as a percentage of the converted substrate, thus representing selectivity.

The first order dependence of the rate on the concentration of (**1**) eliminates the possibility of (**1**) breaking down to catalytically active species of lower nuclearities. A similar rate expression has previously been observed in a catalytic transfer hydrogenation system based on a ruthenium complex.[4] The rate expression shown in equation (1) obviously corresponds only to the phosphine dissociation pathway.

Under the catalytic conditions with $(^2H_8)$propan-2-ol as the donor, the hydride ions in (**1**) are found *not* to undergo isotopic exchange. This indicates that deuterium transfer from $(^2H_8)$propan-2-ol to crotonaldehyde proceeds without the formation of a metal deuteride intermediate. Alternatively, the rate of formation of such a deuteride is much slower than the rate of formation of $[^2H_2]$crotyl alcohol. This result is significant since in transfer hydrogenation reactions catalysed by mononuclear metal complexes isotopic exchange has been shown to be rapid.[5]

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