Tetranuclear Ruthenium Cluster catalysed Transfer Hydrogenation of α,β-Unsaturated Aldehydes†

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With propan-2-ol as the donor, phosphorus ligand-substituted ruthenium clusters, $[Ru_4H_4(CO)_8L_4]$, [L = PBu^n_3, $P(OEt)_3$, $P(OMe)_3$, PMe_3 or PPh_3], act as catalysts for the transfer hydrogenation of α,β-unsaturated aldehydes. High selectivities for the reduction of aldehydic functionalities rather than the olefinic ones are observed. Kinetic analyses indicate the existence of a dissociative and a non-dissociative pathway where the latter accounts for more than 99% of the reactions. On the basis of analytical solutions of the rate equations, a computer-assisted error-minimisation procedure yielded the optimum values of the different rate constants. With $[^2H_8]$propan-2-ol as the donor, the cluster hydrides do not undergo any isotopic exchange and no isotope effect is observed for the non-dissociative pathway. From Arrhenius plots, activation energies for different ligand-substituted clusters are found to be in the order $P(OMe)_3 > P(OEt)_3 > PBu^n_3$.

Homogeneous transfer hydrogenation reactions using $[Ru_3(CO)_{12}]$ **1** as a precatalyst have been the subject of several recent publications.[1] We have reported our attempt to evaluate the possible role of cluster intermediates in these reactions by studying the reactivities of the isolated and fully characterised clusters. This methodology had to be adopted since the complexities of the overall reactions made conventional kinetic analyses extremely difficult.

Here we report catalytic transfer-hydrogenation systems consisting of propan-2-ol as the donor, α,β-unsaturated aldehydes as the acceptors and $[Ru_4H_4(CO)_8L_4]$ [L = PBu^n_3, **2a**; $P(OEt)_3$, **2b**; $P(OMe)_3$, **2c**; PMe_3, **2d**; or PPh_3, **2e**] as the catalysts. In these reactions the clusters do not undergo irreversible conversion into other soluble species. This allows elucidation of the mechanistic details, to a reasonable extent, through kinetic studies. The preferential reduction of the aldehydic functionality, a phenomenon rare both in homo- and hetero-geneous catalysis, is observed in almost all the cases.[2] Within the framework of the empirical rate law, solutions of the rate constants are obtained by an optimisation method. Measurements of the activation energies of reactions catalysed by **2a**–**2c**, and deuterium-exchange studies are also described. Part of this work has been communicated.[3]

Results and Discussion

Scope of the Reaction.—Conversion and selectivity data for the reductions of a few representative α,β-unsaturated aldehydes, with complex **2a** as the catalyst are shown in Table 1. The parent cluster $[Ru_4H_4(CO)_{12}]$ **3**, **1** and $[Ru_4H_3(CO)_{12}]^-$ **4** have also been tested as precatalysts and found to be unsatisfactory. The conversions in these cases are considerably less (< 10%) and extensive degradations of the precatalysts occur. In contrast there are no observable changes in the IR and NMR spectra of **2a**–**2e** during the catalytic runs. At the end of such runs the starting clusters could be recovered quantitatively by column chromatography.

High selectivities for the reductions of aldehydic functionalities are observed with all the substrates (Table 1). In the case of citral, carbon-carbon double bond reduction leading to the formation of citronellol (3,7-dimethyloct-6-en-1-ol) is not observed. However, in the case of α,β-unsaturated ketones such as mesityl oxide and cyclohex-2-en-1-one, the olefinic double bond rather than the carbonyl group is preferentially reduced. The extent of reaction in these cases is less compared to that for the aldehydic substrates. It should be noted that while complexes **2a**–**e** are stable and do not undergo any change in the transfer hydrogenation of α,β-unsaturated ketones, **1**, **3** and **4** undergo autocatalytic transformations into other soluble species.[4] With secondary alcohols other than propan-2-ol somewhat diminished conversions are obtained. There is a drastic reduction in the conversion when propan-1-ol is used as the donor alcohol.

Empirical Kinetic Studies.—With complex **2a** as the catalyst the rate of formation of crotyl alcohol (but-2-en-1-ol) from croton aldehyde is found to be inhibited by the addition of PBu^n_3 or application of CO pressure. The rate is found to be inversely proportional to the concentration of added phosphine (Fig. 1). Similarly with increased CO pressure a limiting rate is reached. At CO pressures > 35 lb in^{-2} (*ca.* 2.41 × 10^5 Pa) the changes in the IR spectra of the catalytic solution indicate formation of the known[5] cluster $[Ru_4H_4(CO)_9(PBu^n_3)_3]$. From these observations it is inferred that the rate-determining step is preceded by pre-equilibria involving dissociation of phosphine and, under CO pressure, formation of $[Ru_4H_4(CO)_9L_3]$, catalytically a less-active species. For experimental convenience the effect on the observed rate of the concentration of externally added phosphine rather than applied CO pressure has been studied in detail.

The slope (k') and intercept (k'') obtained from plots of rate *vs.* $1/[PBu^n_3]$ are indicative of two independent pathways for the formation of crotyl alcohol. That involving an equilibrium between complex **2a** and a phosphine-dissociated species $[Ru_4H_4(CO)_8L_3]$ **2f** is characterised by k' while the pathway characterised by k'' does not involve phosphine dissociation. The latter gives a measure of the residual rate that prevails when the dissociative pathway is totally suppressed. Its magnitude is more than an order higher than that of k', in other words the non-dissociative pathway accounts for more than 99% of the observed rate.

Both k' and k'' show a linear dependence on the con-

† *Supplementary data available* (No. SUP 56856, 3 pp.): derivation of analytical solution to aldehyde consumption with time. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: cal = 4.184 J.

Table 1 [a] Transfer hydrogenations with complex **2a**

Acceptor	Donor	Conversion [b] (%)	Products [c] (%)		
Crotonaldehyde	Propan-2-ol	40	Crotyl alcohol	*n*-Butyraldehyde	Butan-1-ol
	Butan-2-ol	30	92	4	4
	Octan-2-ol	28	95	3	2
	4-Methylpentan-2-ol	30	96	2	2
	Pronan-1-ol	5	92	6	2
			95	5	0
			Cinnamyl alcohol	3-Phenylpropanal	3-Phenylpropanol
Cinnamaldehyde	Propan-2-ol	35	80	17	3
			Pent-2-en-1-ol	Pentanal	Pentan-1-ol
Pent-2-en-1-al	Propan-2-ol	55	70	15	15
	Butan-2-ol	45	75	15	10
			Nerol [d]	Geraniol	Citronellol
Citral	Propan-2-ol	46	43	57	0
	Butan-2-ol	26	31	69	0
			Methylisobutyl ketone		4-Methylpentan-2-ol
Mesityl oxide	Propan-2-ol	15	70		30
			Cyclohexanone		Cyclohexanol
Cyclohex-2-en-1-one	Propan-2-ol	10	90		10

[a] All reactions carried out at 82.5 °C; **2a** (0.01 mmol) and substrate (1.0 mmol) in the donor (15 cm^3) as solvent for 16 h. [b] All conversion values are averages for two or three runs as opposed to the ones reported in ref. 3 which were based on single runs. [c] Calculated as a percentage of the converted substrate thus representing selectivity. [d] 3,7-Dimethylocta-2,6-dien-1-ol.

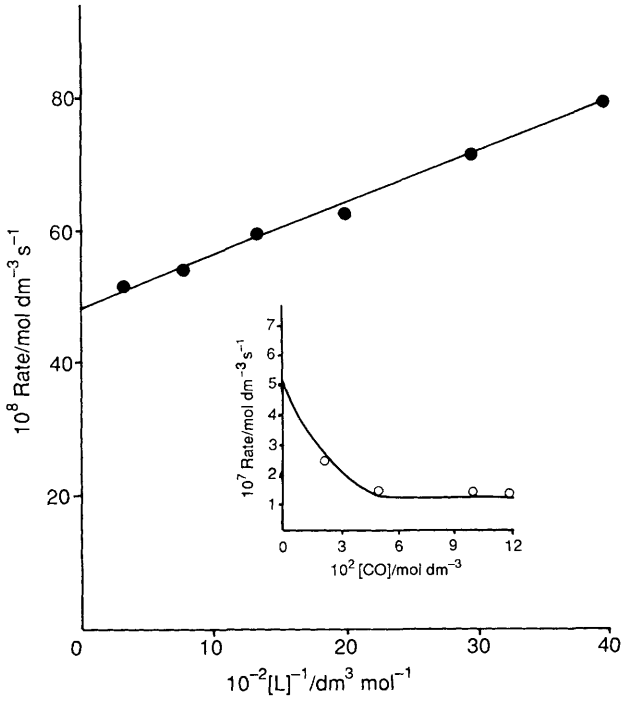


Fig. 1 Plot of the rate of formation of crotyl alcohol *vs.* $[L]^{-1}$ at 82.5 °C. Inset: Plot of the rate of formation of crotyl alcohol *vs.* [CO] at 82.5 °C

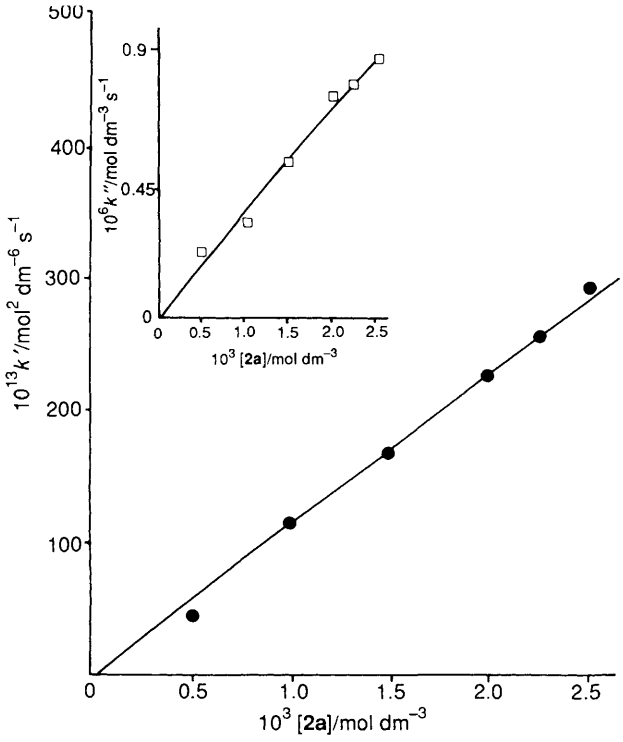


Fig. 2 Plot of k', slope of Fig. 1, *vs.* [**2a**] at 82.5 °C. Inset: Plot of k'', intercept of Fig. 1, *vs.* [**2a**] at 82.5 °C

centrations of **2a**, crotonaldehyde and propan-2-ol. Representative plots are shown in Fig. 2. The reactions and a rate expression consistent with these findings are given by equations (1)–(4) where A, AH_2, D and DH_2 represent crotonaldehyde,

$$\mathbf{2a} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathbf{2f} + L \quad (1)$$

$$A + DH_2 \xrightarrow{k_3} AH_2 + D \quad (2)$$

$$A + DH_2 \xrightarrow{k_4} AH_2 + D \quad (3)$$

$$\text{Rate} = \frac{k_1k_3}{k_2} \cdot \frac{[\mathbf{2a}][A][DH_2]}{[L]} + k_4[\mathbf{2a}][A][DH_2] \quad (4)$$

crotyl alcohol, acetone and propan-2-ol respectively. Reactions (2) and (3) are catalysed by **2f** and **2a** respectively.

A similar rate expression, corresponding to only the second term, has been observed in a catalytic transfer hydrogenation system based on a ruthenium complex.[6] The transfer hydrogenation of cyclohex-2-en-1-one by propan-2-ol with **2a** as the catalyst has also been found to be adequately described by the rate expression (4). This relatively simple kinetic behaviour should be contrasted with those of catalytic systems based on **1** or **4** as the precatalysts. In these cases radical mechanisms and complex rate profiles with autocatalytic

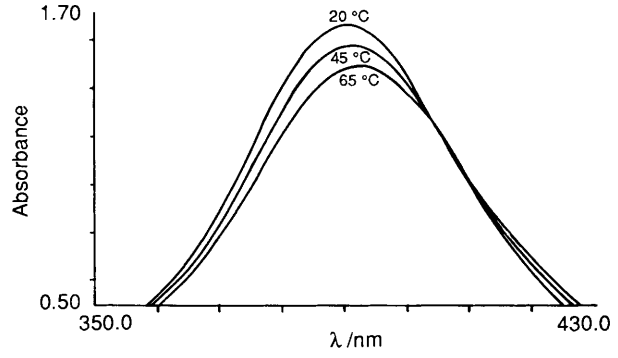


Fig. 3 The UV/VIS spectra of **2a** in propan-2-ol at three different temperatures

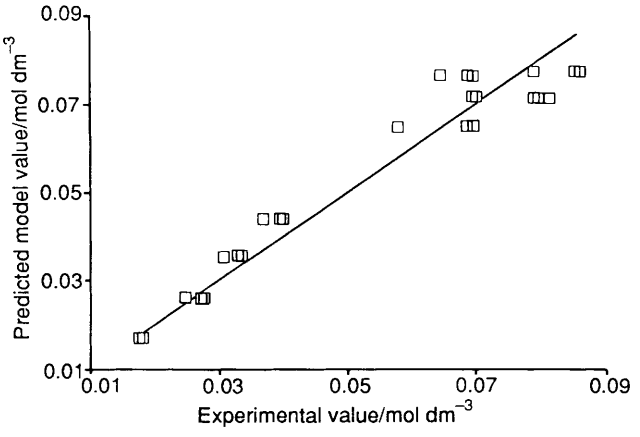


Fig. 4 Parity plot, *i.e.* plot of predicted values for the concentrations of croton aldehyde *vs.* experimental values

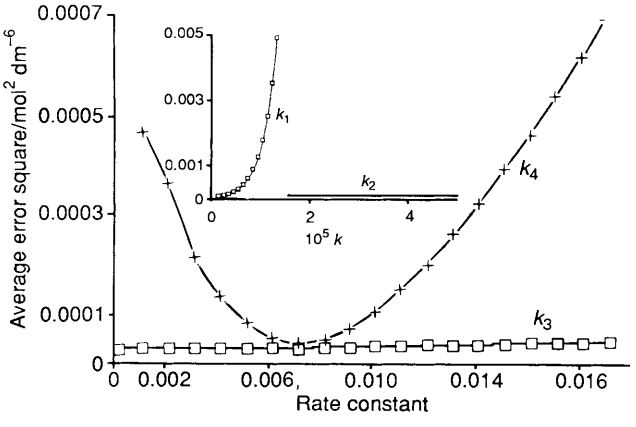
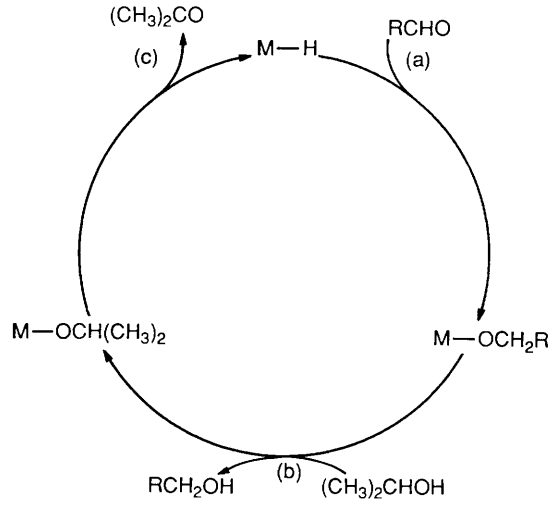


Fig. 5 Variance *vs.* k_3 and k_4. Inset: variance *vs.* k_1 and k_2.

features are observed.[4] For reactions catalysed by **2a**–**2e** an externally added radical inhibitor, 2,6-di-*tert*-butyl-*p*-cresol has been found to have no effect on the reaction rates, excluding the possibility of a radical mechanism. Other evidence such as the absence of deuterium exchange by **2a** in deuteriated propan-2-ol (see later) is consistent with a non-radical mechanism.

Variable-temperature UV/VIS spectra of clusters **2a**–**2d** have been recorded (Fig. 3). In all cases the spectral changes are consistent with the existence of temperature-dependent equilibria between species such as **2a** and **2f**, *i.e.* reaction (1). However, with progressive dilution no apparent changes in the absorption band of **2a** could be observed. Addition of excess of phosphine to a solution of **2a** also does not lead to any spectral changes. This suggests that the dissociation constant, k_1/k_2, is small and its direct measurement by UV spectrophotometry is not possible. An alternative explanation based on the



Scheme 1

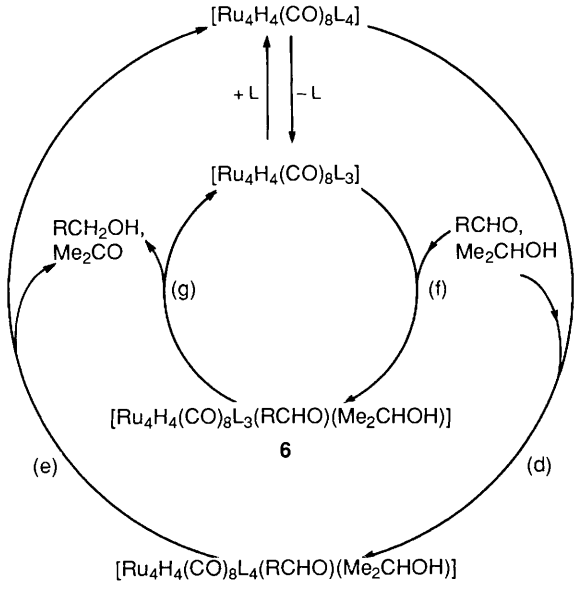
assumption that **2a** and **2f** have identical UV/VIS spectra with the same absorption coefficients is highly unlikely. Similar observations are made with clusters **2b**–**2d**.

Direct measurement of k_1/k_2 has not been possible also by ^{31}P NMR experiments. Thus at 25 °C, the spectrum of **2a** shows a single peak at δ 14.68 with respect to H_3PO_4. At this temperature in the presence of excess of phosphine (δ −31.41) the signal due to **2a** does not undergo any observable line broadening.

Estimation of the Rate Constants.—In the discussion so far it has been *assumed* that a rapid equilibrium leading to steady-state concentrations of complexes **2a** and **2f** precedes the product formation steps characterised by k_3 and k_4 *i.e.* a 'steady-state' approximation has been made. If this assumption is not made then the optimum estimates of k_1, k_2, k_3 and k_4 which satisfy the analytical solutions of the *four* differential rate equations derived from (1)–(3) could be sought through a computer-assisted optimisation procedure (see Experimental section). The predicted values for the concentrations of croton aldehyde at different time intervals with different initial concentrations of **2a** and PBu^n_3, are compared with the observed ones in a parity plot (Fig. 4). The predicted values agree reasonably well with the experimental ones; most points fall near the 45° line, the line where the prediction coincides with the experimental data. The errors associated with the model predictions as judged from the standard deviation are of the order of ± 10%.

As already mentioned, considerations based on steady-state approximations indicate (3) to be by far the dominant pathway. The accuracy of the optimisation procedure is therefore expected to be largely dependent on the value of k_4. This can be seen in Fig. 5 where the variance as a function of k_4 shows a distinct minimum. The dependence of the variance on k_1 indicates a limiting value for this rate constant above which the variance rises steeply. However, over a wide range, the variance is an almost flat function of the other two rate constants k_2 and k_3. The 95% confidence limit values are $k_1 = (3 \pm 0.4) \times 10^{-6}$ s, $k_2 = (3 \pm 0.8) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}, $k_3 = (1 \pm 0.3) \times 10^{-4}$ dm^3 mol^{-1} s^{-1} and $k_4 = (6 \pm 0.7) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. It may be noted that k'/k'' obtained from the plot of rate *vs.* 1/[L] is of the same order as k_1k_3/k_2k_4, indicating reasonable accuracies for the estimated rate constants.

Deuterium Exchange and Related Studies.—Based on earlier literature,[6–8] a plausible and general mechanism for a transfer hydrogenation reaction is shown in Scheme 1. In step (a) hydride attack on the aldehydic functionality leads to the formation of a metal alkoxo species. This is followed by solvolysis by propan-2-ol resulting in the formation of an



Scheme 2

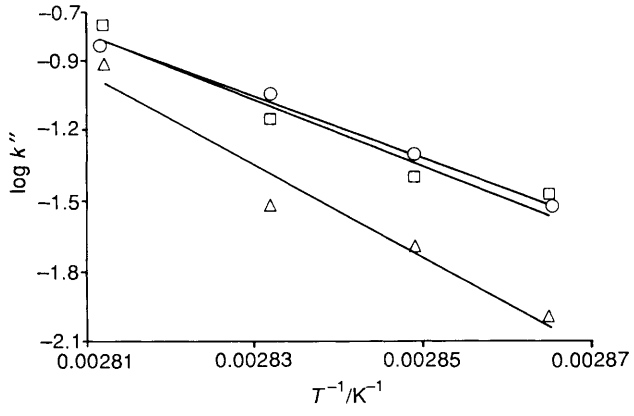


Fig. 6 Arrhenius plots for complexes **2a**, **2b** and **2c**; L = $P(OEt)_3$ (□), $P(OMe)_3$ (△) or PBu^n_3 (○)

isopropoxo complex and elimination of the alcoholic product. In step (c) the isopropoxo species undergoes β-hydride elimination yielding acetone and regenerating the metal hydride.

Under catalytic conditions with [$^2H_8$]propan-2-ol as the donor, croton aldehyde as the acceptor and complex **2a** as the catalyst, the hydride ions in **2a** are found to undergo negligible isotopic exchange. The intensity of the Ru–H NMR signal, a quintet at δ −16.98, is conveniently monitored with respect to added toluene as an internal standard. Simple calculations show that a mechanism such as that shown in Scheme 1 should result in a significant drop in the intensity of the hydride protons after only a few turnovers. Thus for the first, second and third turnovers the expected drops in intensity are 25, 44 and 64% respectively. Experimentally however after more than 20 turnovers only < 16% intensity loss is observed. A mechanism involving transfers and regenerations of the skeletal bridging hydrides of **2a** can therefore be ruled out. This behaviour is in contrast with what has been reported for the mononuclear transfer hydrogenation catalyst [$RhH(PPh_3)_4$], where rapid isotope exchange with the donor solvent is observed.[9]

The kinetic isotope effects using [$^2H_8$]propan-2-ol and $(CH_3)_2CHOD$ as the donors have also been measured. With the latter no effect is observed either on the slope (k')or the intercept (k'') of the plot of rate *vs.* 1/[L]. While $(CD_3)_2CDOD$ does not have any effect on k'', a primary isotope effect (k'_H/k'_D) of *ca.* 11 is observed for k'. Taking into account the kinetic, spectroscopic and isotope labelling evidence, the pathways shown in Scheme 2 are suggested.

Since the orders of both the dissociative and the non-dissociative pathways are indicative of transition states involving the cluster, the aldehyde and propan-2-ol, species such as **5** and **6** are proposed as short-lived intermediates. The first-order dependence of the rate on the concentration of **2a** in both pathways rules out the possibility of the breakdown of the cluster to active species of lower nuclearities in a kinetically detectable manner.

The non-dissociative pathway, steps (d) and (e), accounts for more than 99% of the overall reaction and is characterised by the rate constant k_4. Since the use of [$^2H_8$]propan-2-ol has no effect on the magnitude of k_4, step (e) in which bonds to the isotopically labelled atoms are broken cannot precede or be the rate-determining step. However, for the dissociative pathway, a pathway of marginal importance to the overall rate, a large primary kinetic isotope effect is seen suggesting that step (g) either is or precedes the rate-determining step.

We are unable to provide direct evidence on whether or not multimetal activations of the substrate molecules take place. However, the proposed intermediates **5** and **6** have 64 and 62 valence electrons and would require to have four and five Ru–Ru bonds respectively. This suggests reversible metal–metal bond cleavage and co-ordination by RCHO and propan-2-ol to more than one metal atom. Co-ordination of both the substrate molecules to a single ruthenium centre would lead to a formal electron count of more than eighteen around that unique metal atom. Also, though it is clear that the bridging hydrides do not take part in catalysis, formation of transitory hydride species that do not exchange with the bridging hydrides cannot be ruled out.

It should be noted that the interaction through the aldehydic oxygen atom is expected to be sterically less demanding than that with either the conjugated olefinic functionality or the oxygen atom of a ketonic substrate. This may be one of the reasons for the preferential reduction of the aldehydic groups.

Comparative Activities of Complexes **2a**–**2d**.—The activities of the different phosphine-substituted clusters **2a**–**2e** are of the same order as judged from the overall conversion values for croton aldehyde. Under the conditions specified in Table 1 and with propan-2-ol as the donor, with different catalysts a conversion within the range 25–40% is usually achieved. To obtain a quantitative assessment of the relative efficiencies of **2a**–**2c**, activation energies corresponding to k'' have been measured. This required measurements of the intercepts (k'') of plots of rate *vs.* 1/[L] at different temperatures. The variations in temperature have to be confined within the narrow range of the boiling point (82.5 °C) of propan-2-ol and 76 °C, below which the rate becomes inconveniently small for measurements. This observation itself indicates a high activation energy (> 50 kcal) for the reaction. The activation energy for **2d** has not been measured because of the difficulty in handling small and accurate amounts of PMe_3. Cluster **2e** also had to be excluded from these studies due to its low solubility in propan-2-ol.

Owing to the narrow temperature range, rate measurements could be carried out only at four different temperatures at relatively small (2 °C) intervals resulting in large standard deviations (Fig. 6). The steep drop in reaction rates with lowering of temperature is reflected in the high activation energies obtained for all the catalysts. Clusters **2a** and **2b** are of comparable activities, the activation energies being 61 ± 3 and 64 ± 11 kcal mol^{-1} respectively. Cluster **2c** is an inferior catalyst with an activation energy of 89 ± 13 kcal mol^{-1}. While too much importance should not be attached to the actual numerical values of E_a, the high activation energies are indicative of catalyts having low efficiencies. However, a number of control experiments established that in the absence of **2a**–**2e** there is no reduction of crotonaldehyde. There does not seem to be any obvious correlation between the cone angles

and/or electronic parameters of the phosphorus ligands and the trend in the activation energies.

Experimental

All reactions and manipulations were carried out under an atmosphere of dry nitrogen unless specified otherwise. Clusters **1**, **2a**–**2e** and **3** were synthesised by literature procedures.[5,10,11] α,β-Unsaturated carbonyl compounds, the phosphorus ligands and deuteriated propan-2-ol were purchased from Aldrich. Propan-2-ol was purified by refluxing over CaO and subsequent distillation. The aldehydes and phosphorus ligands used in the kinetic runs were distilled under reduced pressure, and clusters **2a**–**2e** were crystallised twice.

Infrared and NMR spectra were recorded on a PE 781 and a Brucker 80 MHz F.T. instrument. Temperature-programmed gas-chromatographic analyses were performed on a Shimadzu GC 9A instrument. The UV/VIS spectra were recorded on a Shimadzu UV-160 instrument.

The reactions were carried out in double jacketted vessels and constant temperature was maintained by circulating water at the desired temperature. In reaction mixtures consisting of propan-2-ol, crotonaldehyde, **2a** and PBu^n_3 in predetermined initial concentrations, the time-dependent concentrations of croton aldehyde and its transfer-hydrogenated products were measured by gas chromatography. The initial rates were determined at $<10\%$ conversions which depending on the concentrations of various reactants typically took 4–8 h. At low conversions all the consumed croton aldehyde is totally converted into crotyl alcohol and therefore pathways to butyraldehyde need not be considered. To determine the order of the reaction, the slopes and intercepts of straight lines obtained by plotting the observed initial rate against the reciprocal of the added phosphine concentrations were tested for linear correlation with the concentrations of each reactant.

Optimisation of k_1–k_4.—The differential equations relating concentrations and time for reactions (1)–(3) could be integrated by defining the initial conditions to get the analytical solution (5) for the changes in aldehyde concentrations with

$$[\text{aldehyde}] = [\text{aldehyde}]_0 e^{(A+B)t+C} \quad (5)$$

time (see SUP 56856) where, $A = -k_3[\text{catalyst}]_0$, $B = -(k_3 - k_4)\alpha_5$, $C = -[(k_3 - k_4)/k_2]$ ln $[(\alpha_6 - x)/(\alpha_6 - 1)]$, $x = e^{k_2(\alpha_4 - \alpha_5)t}$, $\alpha_6 = ([\text{catalyst}]_0 + \alpha_4)/([\text{catalyst}]_0 + \alpha_5)$ and α_4 and α_5 are roots of the quadratic part (right-hand side) of the first-order differential equation (6) for the time-dependent

$$d[\text{catalyst}]/dt = [\text{catalyst}]_0([\text{catalyst}]_0 + [L]_0) - ([\text{catalyst}]/[k_2])[k_1 + k_2(2[\text{catalyst}]_0 + [L]_0)] + [\text{catalyst}]^2 \quad (6)$$

concentration of **2a**. Here $[\text{aldehyde}]_0$, $[\text{catalyst}]_0$ and $[L]_0$ are the aldehyde, catalyst and ligand concentrations at time $t = 0$ (initial conditions). In other words $[\text{catalyst}]_0$ and [catalyst] are the concentrations of **2a** at zero time and after an interval of t.

The unknown rate constants k_1, k_2, k_3 and k_4 were estimated by fitting the model to a large number of observed results. Experiments were performed by changing the initial catalyst and ligand amounts. The parameter estimation consisted of an optimisation procedure, where the sum of the squares of the differences between the experimental data and the model values is minimised.[12] The optimisation in this case was carried out with 27 experiments.

Acknowledgements

The authors thank ICI India for financial support.

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Received 1*st August* 1991; *Paper* 1/04016B