Transfer Hydrogenation of Ketones with $[Ru_4H_3(CO)_{12}]^-$ as the Precatalyst†

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The cluster $[N(PPh_3)_2][Ru_4H_3(CO)_{12}]$ **1a** has been found to be an efficient precatalyst for the transfer hydrogenations of ketones and α,β-unsaturated ketones. With substrates such as (5*S*)-carvone [2-methyl-5-(1-methylethenyl)cyclohex-2-en-1-one], (3*R*)-methylcyclopentanone and (3*R*)-methylcyclohexanone, moderate to high diastereoselectivities were observed for reduction of the conjugated olefinic and ketonic functionalities respectively. Aromatisation of carvone to 5-isopropyl-2-methylphenol and disproportionation of cyclohex-2-en-1-one to phenol and cyclohexanone have also been found to be catalysed by **1a**. Studies with radical inhibitors and other evidence suggest a radical mechanism for the transfer-hydrogenation and aromatisation reactions. In the transfer hydrogenation of cyclohex-2-en-1-one, the rate of conversion of **1a** into other soluble species can be modelled accurately if autocatalysis is assumed. The time-dependent concentration profiles of cyclohex-2-en-1-one, cyclohexanone and cyclohexanol are simulated well if autocatalytic formation of an active intermediate followed by consecutive reactions leading to the formation of products is assumed. Such a model is also consistent with the proposed radical mechanism.

Ruthenium carbonyl clusters have been used as precatalysts for a variety of transfer-hydrogenation reactions.[1] The potential synthetic importance of catalytic transfer hydrogenation of ketones is the origin of the work presented here. The salt $[N(PPh_3)_2][Ru_4H_3(CO)_{12}]$ **1a** has been chosen as the cluster precatalyst since its activity is greater than most other easily synthesised ruthenium clusters. The ability of **1a**, if any, to catalyse stereoselective transformations is obviously an important aspect of transfer hydrogenation reactions. In the present work this has been investigated in some detail. We have also attempted to grapple with a basic problem of many cluster-catalysed reactions, where the cluster precatalyst undergoes total conversion into other soluble species during the course of the reaction. Earlier we and others had reported attempts to evaluate the possible role of cluster intermediates in such reactions by studying the reactivities of isolated and fully characterised clusters.[1b,2] This methodology had to be adopted since the complexities of the overall reactions made conventional kinetic analyses extremely difficult. In this work we have evaluated the potential of kinetic modelling as a tool for studying such a complex reaction system. Kinetic and other evidence suggests that a radical-chain mechanism adequately accounts for all the observations. The conversion of **1a** into other soluble species is found to be an autocatalytic process. Part of this work has been communicated.[3]

Results and Discussion

(*a*) *Scope of the Reaction and General Observations.*—The relative catalytic efficiencies of complex **1a**, $[Ru_4H_4(CO)_{12}]$ **2**, $[Ru_3(CO)_{12}]$ **3**, $[Ru_4H_4(CO)_8(PBu^n{}_3)_4]$ **4** and $[N(PPh_3)_2][Ru_3H(CO)_{11}]$ **5** have been determined by testing them as precatalysts for the transfer hydrogenation of cyclohex-2-en-1-one with propan-2-ol as the donor. In all cases cyclohex-2-en-1-one is converted into cyclohexanone and then cyclohexanol in a sequential manner. From the data in Table 1 it is apparent that the anionic clusters are more efficient precatalysts than the neutral ones. Owing to its high activity, **1a** has been selected for detailed investigation. From Table 1 it is worth noting that the catalytic activity of **1a** increases significantly in the presence of a base as promoter. Similar effects of added HO^- ions have been observed in several other catalytic transfer-hydrogenation systems.[4] Indeed some of the most efficient catalytic systems for the transfer hydrogenation of ketones have been shown to be active *only* in the presence of added base.[4a–d] However, it is evident from Table 1 that **1a** is able to function as a reasonably active catalyst even in the absence of added base. While butan-2-ol is more or less as active as propan-2-ol as the donor solvent, *n*-propanol is noticeably less so.

Table 1 Transfer hydrogenation of cyclohex-2-en-1-one with different precatalysts and alcohols[a]

Catalyst	Donor	Conversion (%)[b]
1a	Propan-2-ol	100 (8, 92);[c] 40 (35, 5);[d] 90 (73, 17);[e] 98 (40, 58);[d,f] 100 (0, 100)[e,f]
	n-Propanol	10 (9, 1)[c]
	Butan-2-ol	95 (15, 80)[c]
2	Propan-2-ol	30 (18, 12)[c]
3	Propan-2-ol	25 (20, 5)[c]
4	Propan-2-ol	10 (9, 1)[c]
5	Propan-2-ol	65 (45, 20)[c]

[a] All reactions carried out with a catalyst (0.01 mmol) to cyclohex-2-en-1-one molar ratio of 1 : 100 in the donor (10 cm^3) at 82.4 °C. [b] Amount of cyclohex-2-en-1-one (cyclohexanone, cyclohexanol) consumed (formed). [c] Reaction time 8 h. [d] Reaction time 1 h. [e] Reaction time 3 h. [f] In the presence of NaOH (0.01 mmol).

The homogeneity of the catalytic system has been established by light scattering and the Collman test.[5] Thus, soluble acylated polystyrene can be transfer-hydrogenated using propan-2-ol as the donor and compound **1a** as the catalyst. This is evident from the intensity loss (> 20%) of the keto group of the acylated polystyrene.

During the course of the catalytic runs compound **1a** is converted almost completely into other soluble species. This is inferred on the basis of the changes in the solution IR spectra and the disappearance of the RuH signal in ^1H NMR spectra.

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† *Non-SI units employed*: ft = 12 in = 0.3048 m.

The conversion of **1a** into other species is dependent on the presence of the acceptor. Thus while no change in the IR spectrum of **1a** is observed when it is refluxed with propan-2-ol for about 3 h, in the presence of cyclohex-2-en-1-one (molar ratio of cyclohex-2-en-1-one to **1a** > 50:1) under identical conditions the rate of disappearance of **1a** is fast. At the end of a catalytic run only one of the species, $[N(PPh_3)_2][Ru_6(CO)_{18}]$ **6**, could be isolated in low yields (< 10%) by fractional crystallisation. When tested independently as a catalyst, it shows positive but much reduced activity compared with **1a**. In view of this it is unlikely that **6** plays any significant role during catalysis; rather it is one of the final organometallic products.

Efficient and elegant hydrogenation of α,β-unsaturated ketones with a polynuclear hydride-containing copper phosphine complex as the catalyst has recently been reported.[6] The applicability of **1a** as the precatalyst for the transfer hydrogenation of a variety of saturated and unsaturated ketones has been tested and the results are given in Table 2. The catalytic transfer-hydrogenation system based on **1a** has been found to be *inactive* for reducing 1,2- and 1,3-ketoesters such as methyl pyruvate, methyl acetoacetate and simple or conjugated olefins such as cyclohexene and hexa-1,3-diene. In Table 2 several points of interest may be noted. First, α,β-unsaturated ketones are more susceptible towards transfer hydrogenation than are their saturated counterparts. As we will see [section (*d*)], for the latter class of compounds peroxidic impurities in propan-2-ol initiate the reactions, while for the former the reactions proceed even in propan-2-ol completely free of peroxides [see sections (*d*) and (*e*)]. A comparison of the conversion data for isobutyl methyl ketone, cyclohexanone and menthone on the one hand [entries (ii), (ix) and (xiii)] and their α,β-unsaturated counterparts 4-methylpent-3-en-2-one, cyclohex-2-en-1-one and pulegone [*p*-menth-4(8)-en-3-one] [entries (v), (viii) and (xiv)] on the other makes it clear that for a fixed or similar time interval more conversion is achieved for the latter than for the former class of compounds. Secondly, the extent of conversions for both the saturated and unsaturated ketones diminish for sterically hindered substrates. Thus with *tert*-butyl methyl ketone and 3,5-dimethylcyclohexenone the extent of conversion is less than with isobutyl methyl ketone and 3-methylcyclohexenone, entries (iii), (xi), (ii) and (x) respectively. Finally, quite a few of the substrates contain centre(s) of chirality and/or, as a result of transfer hydrogenation, new centres of asymmetry are generated. Under suitable conditions the potential of **1a** to control chirality has therefore been investigated. These results are summarised in Table 3.

(*b*) *Stereoselectivity of the Reaction*.—The potential of the catalytic system in conjunction with a chiral ligand such as diop[(−)-3,4-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane] has been evaluated for the asymmetric reduction of a ketone functionality. Acetophenone and octan-2-one were used as the prochiral acceptors and propan-2-ol as the donor. The efficiencies of the catalytic systems as judged by the extent of conversion over a fixed time are drastically reduced in the presence of diop. By increasing the reaction time sufficient conversions for reliable optical purity measurements could be obtained. On the basis of optical rotation measurements the enantiomeric excess in both cases have been estimated to be ≈20% (see Table 3). Other chiral phosphines such as chiraphos [(2*S*,3*S*)(−)-bis(diphenylphosphino)butane], binap [(*R*)(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] and prophos [(*R*)(+)-1,2-bis(diphenylphosphino)propane] in combination with **1a** do *not* give a catalytically active system.

Two other methods for influencing the chirality were tried. The ruthenium cluster has been used as the salt of a chiral cation. The extent of conversion of acetophenone into phenethyl alcohol with this catalyst, (*S*)(−)-$[Me_3NCH_2CH(OH)CH_2Cl][Ru_4H_3(CO)_{12}]$ **1b**, is similar to that obtained with **1a** but only a poor enantiomeric excess (≈10%) is achieved. As already mentioned, butan-2-ol is active as the donor (Table 1) solvent. However, other easily available chiral alcohols such as α-[1-(dimethylamino)ethyl]benzyl alcohol, methyl lactate or methyl phenylglycolate have no activity as the donor. In any case, as shown in Table 3, even with optically pure (*R*)(−)-butan-2-ol, acetophenone could be reduced with only about 10% enantiomeric excess.

The usefulness of homogeneous catalytic hydrogenation in directed asymmetric syntheses has recently been reviewed.[7] We have evaluated the potential of compound **1a** as a diastereospecific transfer-hydrogenation catalyst for a few of the chiral substrates. Stereochemical selectivity can be seen in the conversion of racemic 3,5-dimethylcyclohex-2-en-1-one (Table 2) exclusively to *trans*-3,5-dimethylcyclohexanone. With optically pure (1*R*)(+)-camphor [(1*R*)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one] and (5*R*)(+)-pulegone low diastereomeric excesses of (1*R*,2*R*)(−)-isoborneol (bornan-2-ol) and (2*S*,5*R*)(−)-menthone are obtained (see Table 3). With carvone [2-methyl-5-(1-methylethenyl)cyclohex-2-en-1-one] however the stereochemistry at C^5 shows a noticeable influence on the chemo- and diastereo-selectivities of the reactions. Thus with (5*S*)-carvone both dihydrocarvone and dihydrocarveol-(*p*-menth-8-en-2-ol) are formed. The (2*R*,5*S*) isomer of dihydrocarvone is formed with a diastereomeric excess of about 70% over the (2*S*,5*S*) isomer.

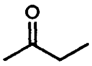
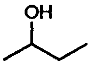
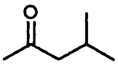
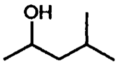
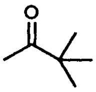
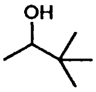
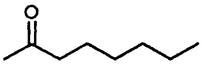
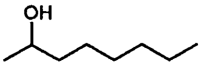
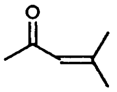
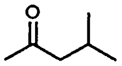
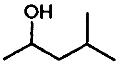
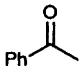
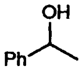
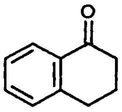
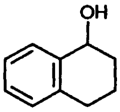
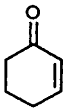
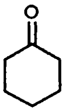
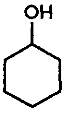
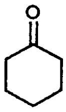
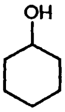
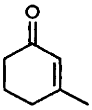
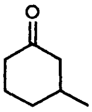
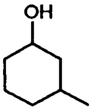
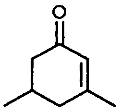
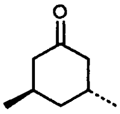
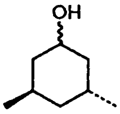
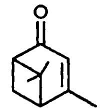
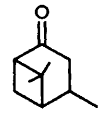
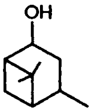
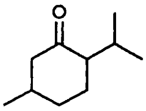
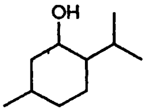
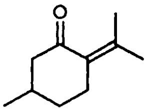
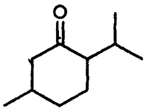
In contrast the conversion of (5*R*)-carvone into dihydrocarvone shows very little diastereoselectivity. More striking however is the fact that while dihydrocarveol is formed from (5*S*)-carvone, no such reaction is observed with the (5*R*) isomer; the reaction stops at the dihydrocarvone stage. This difference in reactivity of the diastereomers of dihydrocarvone is probably due to increased steric hindrance in isomers with *R* stereochemistry at the 5 position. With both (5*R*)- and (5*S*)-carvones a catalytic isomerisation pathway competes with the transfer-hydrogenation one, and 5-isopropyl-2-methylphenol is obtained in moderate yields. The facile aromatisation of the six-membered ring is probably a result of the radical mechanism [see sections (*d*), (*e*) and Scheme 3] of the transfer-hydrogenation process.

High diastereoselectivity is observed in the transfer hydrogenation of (3*R*)-methylcyclopentanone and (3*R*)-methylcyclohexanone. In both cases only one diastereoisomer can be seen in NMR experiments with shift reagents and by gas chromatography–mass spectrometry (GC–MS). These results taken in conjunction with the optical rotation value measured by polarimetry (see Experimental section) indicate that (1*R*,3*R*)-methylcyclopentanol and (1*S*,3*R*)-methylcyclohexanol are formed in > 95% diastereomeric excess.

(*c*) *Disproportionation of Substrates*.—As already mentioned, during a catalytic run the conversion of compound **1a** into other soluble species depends on the presence of the acceptor. This prompted us to study the interaction of **1a** with catalytic amounts of the acceptors in some detail. When cyclohex-2-en-1-one is heated with **1a** at 82 °C a mixture of cyclohexanone, cyclohexanol and phenol is obtained. Similarly, from isobutyl methyl ketone a mixture of 4-methylpent-3-en-2-one and 4-methylpentan-2-ol is obtained. However, under similar conditions, there is no reaction of **1a** with either cyclohexanone or acetophenone. The disproportionation reactions of cyclohex-2-en-1-one occur to only a small extent. Typically with a 50:1 acceptor to **1a** molar ratio, about ten turnovers are obtained over 3–5 h of reaction. The relevance of these observations to the proposed mechanism is discussed below.

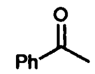
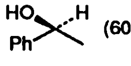
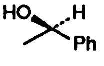
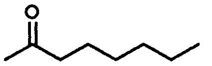
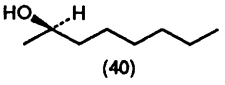
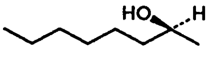
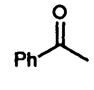
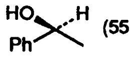
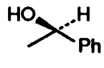
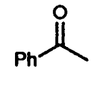
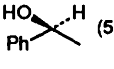
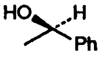
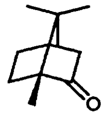
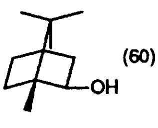
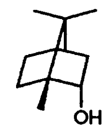
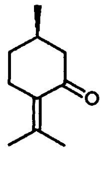
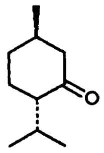
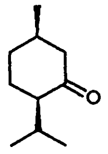
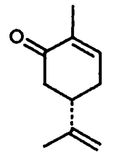
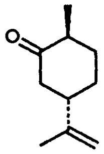
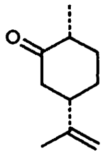
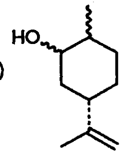
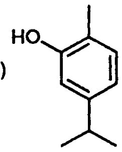
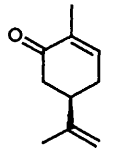
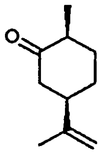
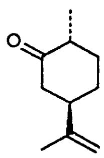
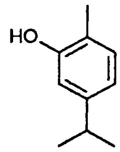
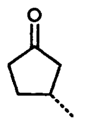
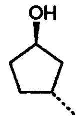
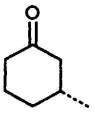
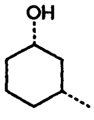
(*d*) *Evidence for a Radical Mechanism*.—The evidence indicative of a radical mechanism is briefly mentioned first and then discussed in detail. First the ability of propan-2-ol to act as the donor in the transfer hydrogenation of cyclohexanone is completely lost when it is entirely free of peroxidic impurities. This behaviour however is in contrast with that of cyclohex-2-en-1-one where even with peroxide-free propan-2-ol the hydrogen-transfer reaction proceeds smoothly. Secondly, in

Table 2 Transfer hydrogenation of different ketones with compound **1a** as the precatalyst and propan-2-ol as the donor[a]

Entry	Substrate	*t*/*h*	Conversion (%)[b]	Products (selectivity, %)
(i)		6	95	 (100)
(ii)		6	50	 (100)
(iii)		6	16	 (100)
(iv)		6	80	 (100)
(v)[c]		6	100	 (20)  (80)
(vi)		6	66	 (100)
(vii)		10	76	 (100)
(viii)[c]		5	100	 (20)  (80)
(ix)		6	85	 (100)
(x)[c]		6	70	 (64)  (36)
(xi)[c,d]		6	54	 (54)  (46)
(xii)[c]		50	60	 (90)  (10)
(xiii)		70	⩽10	 (100)
(xiv)		48	70	 (100)

[a] All reactions carried out with a catalyst to substrate molar ratio of 1 : 100 and **1a** (0.001 25 mol dm^{-3}) in propan-2-ol (10 cm^3) at 82.4 °C. [b] Amount of substrate consumed. [c] Selectivity measured by gas-liquid chromatography (GLC). [d] Proton NMR spectra of components separated by preparative GLC show the formation of only *trans*-3,5-dimethylcyclohexanone.

Table 3 Transfer hydrogenation of prochiral and chiral substrates

Catalyst	Substrate	Conversion (%)	Products (enantio- or diastereo-selectivity, %)
a		$100^{b,c}$	 (60)  (40)
a		$100^{b,c}$	 (40)  (60)
1b		$100^{c,d}$	 (55)  (45)
1a		$100^{c,e}$	 (55)  (45)
1a		$30^{c,f-h}$	 (60)  (40)
1a		$70^{c,f-h}$	 (55)  (45)
1a		$100^{c,f-h}$	 (7)  (48)  (33)  (12)
1a		$65^{c,f-h}$	 (34)  (28)  (38)
1a		$100^{c,f,h}$	 (≥95)
1a		$100^{c,f,h}$	 (≥95)

[a] diop salt of compound **1a** (see text). [b] Catalyst to substrate molar ratio of 1 : 160 with **1a** (0.001 25 mol dm^{-3}), (−)-diop (0.001 25–0.003 75 mol dm^{-3}) in propan-2-ol (10 cm^3) for 36 h. [c] Enantiomeric excess measured by polarimetry. [d] Catalyst to substrate molar ratio of 1 : 160 with **1b** (0.001 25 mol dm^{-3}) in propan-2-ol (10 cm^3) for 10 h. [e] Catalyst to substrate molar ratio of 1 : 160 with **1a** (0.000 62 mol dm^{-3}) in (*R*)(−)-butan-2-ol (2 cm^3) for 36 h. [f] Catalyst to substrate molar ratio of 1 : 100 with **1a** (0.002 mol dm^3) in propan-2-ol (10 cm^3) for 48 h. [g] Products separated by preparative GC. [h] Diastereomeric excess on the basis of GC–MS (isotopic abundance data) and ^{1}H NMR experiments with shift reagent.

rigorously purified propan-2-ol totally free of peroxidic impurities, transfer hydrogenation of cyclohexanone begins on addition of catalytic quantities of *tert*-butyl hydroperoxide. However, in the absence of **1a**, Bu^tO_2H is unable to initiate any transfer hydrogenation. Thirdly, carbon tetrachloride and 2,6-di-*tert*-butyl-*p*-cresol inhibit the transfer hydrogenation of cyclohex-2-en-1-one to varying degrees. Fourthly, an ESR signal is observed when **1a** is heated with neat cyclohex-2-en-1-one. Fifthly, when cyclohex-2-en-1-one is heated with trace quantities of water in the presence of catalytic quantities of **1a**, cyclohexanone, cyclohexanol and dioxygen are the products. Finally, the disproportionation of cyclohex-2-en-1-one under relatively mild conditions is easily explained by invoking a radical mechanism [see sections (*d*) and (*e*) and Scheme 3].

Unless rigorously purified, propan-2-ol is known to contain

Table 4 Effect of radical inhibitors on the observed rate of disappearance of cyclohex-2-en-1-one

(*a*) 2,6-Di-*tert*-butyl-4-methylphenol*	
Amount of inhibitor (mol)	Observed rate (mol dm^{-3} min^{-1})
0	0.003 8
0.000 1	0.003 55
0.000 45	0.002 23
0.000 9	0.000 5
(*b*) CCl_4	
Molar ratio of CCl_4 to **1a**	
0	0.001 65
0.5:1	0.001 5
1:1	0.000 88

* Molar ratio of cyclohex-2-en-1-one, compound **1a** (0.005 mmol) and propan-2-ol (70 μl) is 10:1:200.

trace quantities of peroxidic impurities.[8] When cyclohexanone is used as the substrate the interactions of such impurities with **1a** lead to the formation of catalytically active organometallic intermediate(s) capable of initiating a radical chain and the hydrogen-transfer reaction. It should be mentioned here that although other catalytic hydrogen-transfer systems requiring activation by exposure to dry air have been reported, a radical mechanism has not been considered.[4c,i]

In peroxide-free propan-2-ol addition of *tert*-butyl hydroperoxide generates the same or very similar catalytically active organometallic intermediate(s) from compound **1a** which can then initiate the radical chain. Other initiators such as aibn [2,2′-Azobis(isobutyronitrile)] are ineffective.

With cyclohex-2-en-1-one transfer hydrogenation proceeds even in peroxide-free propan-2-ol, presumably because the reaction between cyclohex-2-en-1-one and compound **1a** is sufficient for the formation of active organometallic intermediate(s). This is in accordance with the fact that **1a** catalyses the disproportionation of cyclohex-2-en-1-one but is inert towards cyclohexanone.

To obtain evidence for a radical mechanism the effect of two known radical quenchers on the rates of the reactions have been studied. Finding a suitable quencher was not easy since it must not react with **1a** or, if it does react, the extent of reaction should be negligible so that any reduction in the rate of the catalytic transfer-hydrogenation reaction is not a result of the degradation of compound **1a**. This rules out the use of various thiols and radical quenchers containing amino groups.[9a] These substances react rapidly with **1a** even when used in less than molar quantities, *i.e.* the radical inhibitor:**1a** molar ratio is about 0.5:1.

The effect of two radical inhibitors CCl_4 and 2,6-di-*tert*-butyl-*p*-cresol have been studied in detail. The effect of the latter on the observed rate is pronounced. There is no reaction between it and **1a**, the cluster remains intact even after prolonged (> 3 h) heating with the cresol at 82 °C. Degradation of **1a** is therefore not responsible for any reduction in the rate of the hydrogen-transfer reaction. As can be seen from Table 4, addition of increasing amounts of the cresol is accompanied by a drop in the observed rate. However, to bring about a noticeable decrease large amounts are required.

Although CCl_4 reacts with compound **1a** when the molar ratio of CCl_4:**1a** is greater than 1:1, the extent of reaction as judged by the change in the IR spectrum of **1a** is negligible over the first hour. However, the effect of varying amounts of CCl_4 on the initial rates of cyclohex-2-en-1-one disappearance is noticeable. Transfer hydrogenation of CCl_4 to $CHCl_3$ with **3** as the catalyst and propan-2-ol as the donor was reported by us.[1b,h] This reaction is also catalysed by **1a** suggesting the involvement of Cl$^•$ and $CCl_3{}^•$ radicals in these cluster-catalysed reactions.

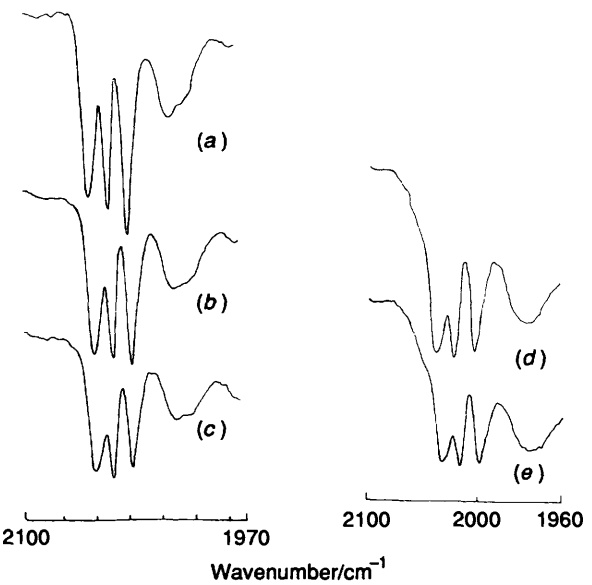


Fig. 1 Infrared spectra (2100–1960 cm^{-1}) of compound **1a** during catalytic transfer hydrogenation: (*a*) $t = 0$, with cyclohex-2-en-1-one (0.156 mol dm^{-3}), **1a** (0.001 25 mol dm^{-3}), propan-2-ol (10 cm^3) at 82.4 °C; (*b*) sample (*a*) after 65 min; (*c*) sample (*a*) after 135 min and 90% conversion; (*d*) cyclohexanone (0.102 mol dm^{-3}), **1a** (0.001 25 mol dm^{-3}), propan-2-ol (10 cm^3) at 82.4 °C for 65 min; (*e*) sample (*d*) after 200 min and 70% conversion

An isotropic ESR signal (*g ca.* 2.042 at 77 K) is observed when compound **1a** is heated with neat cyclohex-2-en-1-one (*ca.* 2 min). Several control experiments established that in the absence of **1a** no ESR signal is observed.

Quenching of organic radicals by water involving abstraction of hydrogen atoms is expected to generate hydroxy radicals which in turn should lead to the formation of small quantities of hydrogen peroxide and/or dioxygen and water.[9b] Thus when a mixture of compound **1a**, water and cyclohex-2-en-1-one is heated at 82 °C under argon for 4 h, cyclohexanone, cyclohexanol and dioxygen are detected as the products. Several control experiments have established that dioxygen is produced only in the presence of all the three reactants.

(*e*) *Kinetic Modelling and Proposed Mechanisms.*—The kinetic behaviours of the catalytic systems have been simulated by computer-assisted non-steady-state kinetic modelling.[10] The modelling studies were carried out mainly for the substrate, cyclohex-2-en-1-one. As already mentioned, the presence of peroxidic impurities in propan-2-ol is required to initiate the radical chain for the transfer hydrogenation of cyclohexanone and other saturated ketones, while cyclohex-2-en-1-one itself is capable of initiating the reaction. The proposed mechanisms for these two substrates are therefore similar but not identical. In both cases the conversion of **1a** into other soluble species may be monitored by infrared studies in solution. The overall changes in the inorganic carbonyl region are found to be nearly identical for both substrates, indicating that as a first approximation formation of the same or very similar organometallic intermediates may be assumed (Fig. 1). In both cases, complex profiles for the rates of disappearance of **1a** are observed. As shown in Fig. 2, for cyclohex-2-en-1-one transfer hydrogenation, when the order of the rate of disappearance of **1a** is varied from −1 to +2, marked discrepancies between the experimental points and the simulated curves result. This suggests a complex reaction sequence where the overall rate cannot be adequately modelled by a simple $-k[\mathbf{1a}]^n$ type expression with n having integral or fractional values. The simplest model which gives an excellent fit is based on the

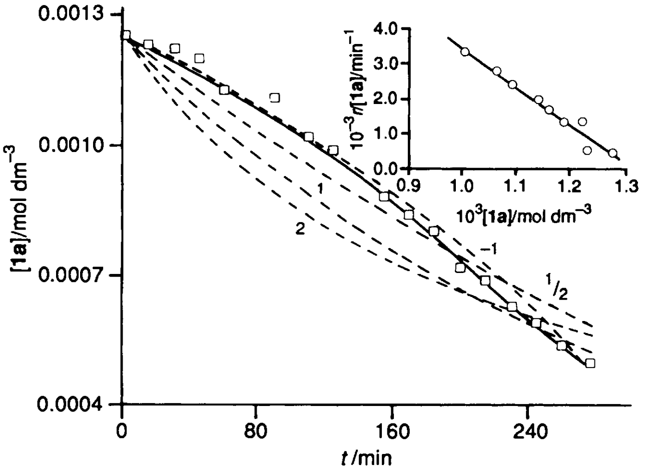


Fig. 2 Change in concentration of compound **1a** with time measured by IR spectroscopy (□). Experimental points with **1a** (0.001 25 mol dm^{-3}), cyclohex-2-en-1-one (0.3125 mol dm^{-3}) in propan-2-ol (10 cm^3) at 82.4 °C. - - -, Assuming that rate = $-k$[**1a**]^n labelled by respective *n*. ——, Autocatalysis, assuming reaction (1) and (2) of Scheme 1. Inset: plot of differential rate law (0.156 mol dm^{-3} cyclohex-2-en-1-one, other conditions same)

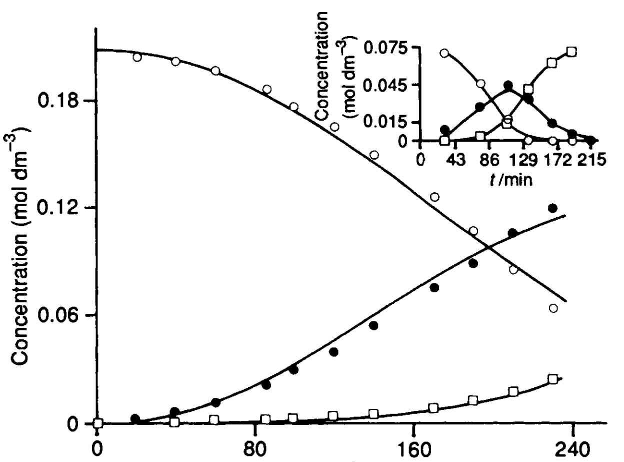


Fig. 3 Plots of concentrations of cyclohex-2-en-1-one (○), cyclohexanone (●) and cyclohexanol (□) measured experimentally *vs.* time; 0.001 25 mol dm^{-3} **1a**, 0.208 mol dm^{-3} cyclohex-2-en-1-one in propan-2-ol (10 cm^3) at 82.4 °C. ——, Simulated concentration profiles. Inset: **1a** (0.001 25 mol dm^{-3}), cyclohex-2-en-1-one (0.87 mol dm^{-3}) in propan-2-ol (10 cm^3) at 82.4 °C

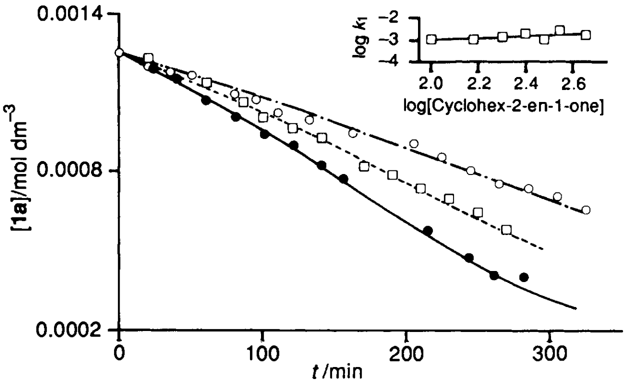


Fig. 4 Effect of initial concentration of cyclohex-2-en-1-one on the rate of disappearance of compound **1a** measured by IR spectroscopy: ○, □ and ● refer to experimentally measured concentrations of **1a** (initially 0.001 25 mol dm^{-3}) in propan-2-ol (10 cm^3) at 82.4 °C with initial concentrations of cyclohex-2-en-1-one of 0.104, 0.208 and 0.468 mol dm^{-3} respectively; –·–, – – – and —— refer to the simulated concentration profiles. Inset: plot of log k_1 *vs.* log [cyclohex-2-en-1-one]

assumption that **1a** is converted in an autocatalytic manner into carbonyl species of different nuclearities such as $[Ru_xH_y(CO)_n]$ **7** and $[Ru_{4-x}H_{3-y}(CO)_{12-n}]^-$ **8** [reactions (1) and (2) in Scheme 1]. Isolation of hexanuclear species such as **6** must be explained in terms of dissociation of **1a** into species having nuclearities less than four followed by recombination of two or more such species to generate stable clusters of six metal atoms. It is the first part of this process, *i.e.* dissociation of **1a** into clusters of lower nuclearities, that is autocatalytic.

$$[Ru_4H_3(CO)_{12}]^- \xrightarrow{k_1} \underset{\textbf{7}}{[Ru_xH_y(CO)_n]} + \underset{\textbf{8}}{[Ru_{4-x}H_{3-y}(CO)_{12-n}]^-} \quad (1)$$

$$[Ru_4H_3(CO)_{12}]^- + [Ru_xH_y(CO)_n] \xrightarrow{k_2} 2[Ru_xH_y(CO)_n] + [Ru_{4-x}H_{3-y}(CO)_{12-n}]^- \quad (2)$$

$$C_6H_8O + Me_2CHOH \xrightarrow{k_3} C_6H_{10}O + Me_2CO \quad (3)$$

$$C_6H_{10}O + Me_2CHOH \xrightarrow{k_4} C_6H_{12}O + Me_2CO \quad (4)$$

Scheme 1 C_6H_8O = Cyclohex-2-en-1-one, $C_6H_{10}O$ = cyclohexanone, $C_6H_{12}O$ = cyclohexanol; x and y are integers where $1 \leqslant x \leqslant 3$, $1 \leqslant y \leqslant 3$

The model is further extended by assuming that reactions (3) and (4) are catalysed by compound **7**. It is also reasonable to assume that these reactions are pseudo-zero order with respect to the concentration of propan-2-ol. The overall model consisting of reactions (1)–(4) for the transfer hydrogenation of cyclohex-2-en-1-one describes well the time-dependent concentrations of various species (see Fig. 3). It is possible that the other species **8** also acts as a catalyst. Indeed it is more than likely that there are other pathways catalytic or otherwise for the formation of the products. However, the reliability of kinetic modelling primarily lies in assuming as few reactions as possible and being able to predict accurately the time-dependent concentration profiles of the reactants and products. Inclusion of more steps *i.e.* rate constants increases the number of steps arbitrarily for which there is no empirical evidence. Furthermore inclusion of such steps does not improve the overall accuracy of the model in any significant manner.

The reaction of compound **3** with cyclohex-2-en-1-one is known[1i] to lead to the formation of a stable complex $[Ru_4(CO)_{12}(C_6H_6O)]$. The change in nuclearity from three to four in this case is also indicative of cluster fragmentation followed by the formation of a four-metal-atom cluster. The breakdown of **1a** may therefore be expected to be dependent on the presence of cyclohex-2-en-1-one. It is possible that co-ordination of cyclohex-2-en-1-one to the metal core involves displacement of one or more CO ligands. Unfortunately, the effect of applied CO pressure on the rate of reaction could not be studied since under these conditions **1a** is known[11] to undergo conversion into **5**. However, the rate constants k_1–k_4 (Scheme 1) for different concentrations of cyclohex-2-en-1-one can be determined on the basis of the model. As shown in Fig. 4, the rate of disappearance of **1a** is obviously a function of the concentration of cyclohex-2-en-1-one. The double logarithmic plot of k_1 against the concentration of cyclohex-2-en-1-one is approximately linear with a slope of 0.43. This may be taken as evidence for the dependence of the rate of breakdown of **1a** on the concentration of cyclohex-2-en-1-one in a kinetically detectable manner. A similar plot indicates k_2 to be considerably less sensitive (slope ≈0.18) to the concentrations of cyclohex-2-1-one.

In the case of cyclohexanone the breakdown of compound **1a** and formation of **7** or similar species are dependent on the

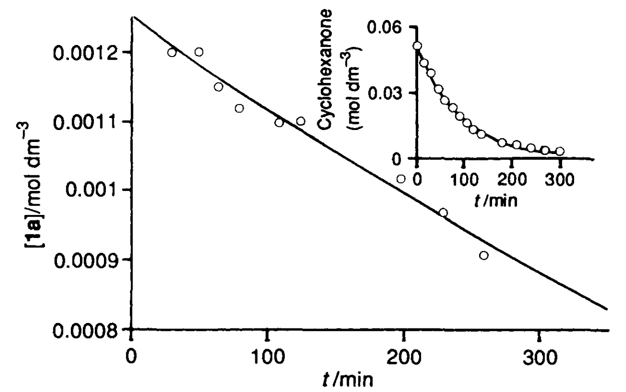


Fig. 5 Change in concentration of compound **1a** with time measured by IR spectroscopy: ○, experimental points with **1a** (0.001 25 mol dm^{-3}), cyclohexanone (0.204 mol dm^{-3}) in propan-2-ol (10 cm^3) at 82.4 °C; ——, autocatalysis, assuming reactions (1) and (2) of Scheme 1. Inset: ○, concentration of cyclohexanone measured experimentally; ——, simulated concentration profile

presence of peroxidic impurities. Obviously in this case the rate of disappearance of **1a** cannot be adequately modelled either by assuming integral or fractional order with respect to **1a**, or by assuming autocatalysis. This can be seen from the scatter of the experimental points in Fig. 5. However, reactions (1), (2) and (4) [(3) is redundant] of Scheme 1 can model the time-dependent concentration profile of cyclohexanone with accuracy. Thus, the generation of species such as, or similar to **7**, in a pseudo-autocatalytic manner by peroxy or hydroperoxy radicals seems to be involved.

As already mentioned, many catalytic transfer-hydrogenation systems where added base has a beneficial and/or essential role have been reported.[4] In these reactions, the possibility of a base assisting in the formation of reactive organometallic hydrides which in turn can initiate a radical-chain mechanism should be considered.

The proposed radical steps constituting the mechanism of the **1a**-catalysed transfer hydrogenation are given in Scheme 2. The disproportionation of cyclohex-2-en-1-one in the absence of propan-2-ol and the isomerisation of carvone to thymol analogues (see Table 3) are also accounted for by these radical reactions (Scheme 3). The radical chain is initiated in a catalytic manner by the ruthenium hydrido carbonyl species **7**. Of the several possible propagation and termination steps, only the more likely ones are shown in Schemes 2 and 3. While for the transfer hydrogenation of cyclohex-2-en-1-one steps (5)–(11) are proposed, in case of cyclohexanone steps (5), (8) and (10) are obviously not involved.

Initiation:

$$\mathrm{C_6H_8O + [Ru_xH_y] \longrightarrow C_6H_9O^{\bullet} + [Ru_xH_{y-1}]} \quad (5)$$

$$\mathrm{[Ru_xH_{y-1}] + Me_2CHOH \longrightarrow [Ru_xH_y] + Me_2\dot{C}OH} \quad (6)$$

$$\mathrm{C_6H_{10}O + [Ru_xH_y] \longrightarrow C_6H_{11}O^{\bullet} + [Ru_xH_{y-1}]} \quad (7)$$

Propagation:

$$\mathrm{Me_2CHOH + C_6H_9O^{\bullet} \longrightarrow Me_2\dot{C}OH + C_6H_{10}O} \quad (8)$$

$$\mathrm{Me_2CHOH + C_6H_{11}O^{\bullet} \longrightarrow Me_2\dot{C}OH + C_6H_{12}O} \quad (9)$$

Termination:

$$\mathrm{Me_2\dot{C}OH + C_6H_9O^{\bullet} \longrightarrow Me_2CO + C_6H_{10}O} \quad (10)$$

$$\mathrm{Me_2\dot{C}OH + C_6H_{11}O^{\bullet} \longrightarrow Me_2CO + C_6H_{12}O} \quad (11)$$

Scheme 2 The CO groups associated with $[\mathrm{Ru_xH_y}]$ and $[\mathrm{Ru_xH_{y-1}}]$ are not shown for clarity. Formulation of propan-2-ol-derived radical based on literature[9b,c]

Disproportionation of cyclohex-2-en-1-one

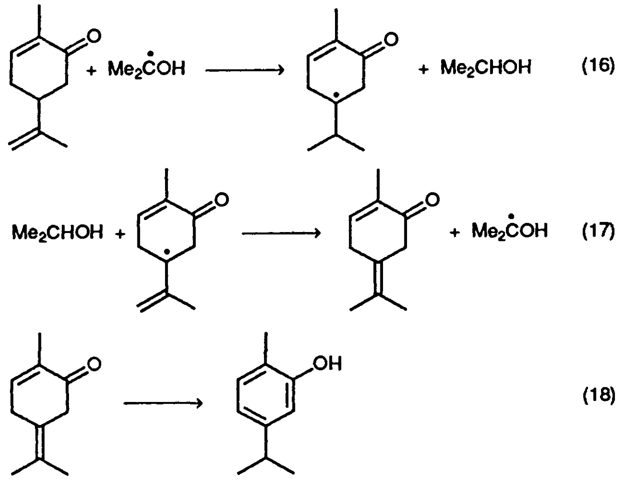
$$\mathrm{C_6H_8O + [Ru_xH_y] \longrightarrow C_6H_9O^{\bullet} + [Ru_xH_{y-1}]} \quad (12)$$

$$\mathrm{C_6H_8O + [Ru_xH_{y-1}] \longrightarrow C_6H_7O^{\bullet} + [Ru_xH_y]} \quad (13)$$

$$\mathrm{C_6H_8O + C_6H_7O^{\bullet} \longrightarrow C_6H_9O^{\bullet} + C_6H_6O} \quad (14)$$

$$\mathrm{C_6H_7O^{\bullet} + C_6H_9O^{\bullet} \longrightarrow C_6H_6O + C_6H_{10}O} \quad (15)$$

Isomerisation of carvone



Scheme 3 $\mathrm{C_6H_6O}$ = Phenol. $\mathrm{Me_2\dot{C}OH}$ has been taken as a representative radical catalysing the aromatisation of carvone. The keto–enol tautomerism and hydrogen-atom migration involved in step (18) are not shown explicitly

Finally it should be noted that steps (3) and (4) of Scheme 1 are obtained by summing steps (5), (6), (8), (10) and (6), (7), (9), (11) respectively of Scheme 2. The model could be refined, and meaningfully extended to include these steps only if the concentrations of one or more of the radical species could be empirically determined.

Conclusion

The anionic carbonyl cluster $[\mathrm{Ru_4H_3(CO)_{12}}]^-$ has been found to be an active precatalyst for the transfer hydrogenation of a wide variety of saturated and α,β-unsaturated ketones. With a few chiral substrates, conversions with moderate to high diastereoselectivities are obtained. Several observations indicate that a radical mechanism, rarely observed in cluster-catalysed reactions,[12] is involved. On the basis of kinetic modelling, initiation of the radical chain is considered to be catalysed by a hydrido carbonyl intermediate. The conversion of $[\mathrm{Ru_4H_3(CO)_{12}}]^-$ into this intermediate is found to be autocatalytic in nature.

Experimental

General Techniques and Materials.—All reactions and manipulations were carried out under an atmosphere of dry nitrogen or argon unless stated otherwise. All the ketones, diop, binap, chiraphos, prophos, (*R*)(−)-butan-2-ol, (*S*)(−)-(3-chloro-2-hydroxypropyl)trimethylammonium chloride, the shift reagent tris{3-[heptafluoropropyl(hydroxy)methylene]-D-camphorato}europium(III) and soluble polystyrene were purchased from Aldrich and used without further purification unless specified otherwise. Cyclohex-2-en-1-one and cyclohexanone were distilled twice before being used for the kinetic modelling studies. Propan-2-ol was made peroxide-free by treatment with $SnCl_2$ followed by reflux and distillation[8] over CaO. For cyclohex-2-en-1-one and other α,β-unsaturated ketones, freshly distilled propan-2-ol saturated with nitrogen was used. For cyclohexanone and other saturated ketones the distilled propan-2-ol was left under dry oxygen for 1 d then saturated with nitrogen.

Infrared and NMR spectra were recorded on Perkin Elmer 781 and Bruker 80 MHz Fourier-transform instruments. A Shimadzu GC 9A and JASCO DIP 140 polarimeter were used for routine gas chromatographic analyses and optical rotation measurements. The preparative GC experiments were carried out on a Philips Analytical 204 instrument. For the analysis and identification of dioxygen a Hewlett-Packard (HP) 5890A instrument with a molecular sieve 5 A column (6 ft × 1/8 in) with He as the carrier gas was used. A HP 5993B instrument was used for experiments requiring GC separation coupled with mass spectrometry. The ESR experiments were performed on a Varian E-112 instrument.

Clusters **1a**–**6** were synthesised by literature procedures.[13] Cluster **1b** was prepared by a method analogous to that employed[13a] for **1a**.

Test for Homogeneity of Catalytic Systems based on Compound **1a**.—Soluble polystyrene (4 g) was acylated in chloroform (50 cm^3) in the presence of $AlCl_3$ (5 g) by adding acetyl chloride (3 cm^3) at 0 °C over a period of 0.5 h followed by heating at 50 °C for 1 h. Addition of water and ice gave a white solid which was extracted with CH_2Cl_2–$CHCl_3$ (50:50). Addition of hexane precipitated acylated polystyrene [ν_{CO} at 1690vs cm^{-1}].

Acylated polystyrene (0.25 g) was heated in a mixture of propan-2-ol (10 cm^3) and 1,2-dichloroethane (10 cm^3) in the presence of compound **1a** (0.026 g) at 82.4 °C for 18 h. The polymer was precipitated by addition of hexane. The intensity ratio of the IR bands of the polymer at 1690 and 840 cm^{-1} was measured before and after the reaction. This showed a drop of $\geqslant$20%.

Experiments pertaining to Conversion and Optical Purity.—These experiments were carried out at 82.4 °C (reflux temperature of propan-2-ol) in a two-necked round-bottomed flask with compound **1a** (16 mg, 0.0125 mmol) and substrate (1.25 mmol) in propan-2-ol (10 cm^3) over different reaction times. The conversion and product selectivity were determined by GC.

The optical rotation measurements were carried out on samples separated by distillation under reduced pressure or column chromatography. The transfer-hydrogenated products of (1*R*)(+)-camphor, (5*R*)(−)- and (5*S*)(+)-carvone and (5*R*)(+)-pulegone were separated by preparative GC in which mixtures of diastereoisomers appeared as single peaks. The isotopic abundances of different stereoisomers were determined by GC–MS analyses where different peaks corresponding to different diastereoisomers could be seen. In the ^1H NMR spectra of 3-methylcyclopentanol and 3-methylcyclohexanol only one diastereoisomer could be seen before and after the addition of increasing amounts of shift reagent.

Literature rotation values were used for calculating the extent of enantio- or diastereo-specificity:[14] (*S*)(−)-*sec*-phenethyl alcohol, α[589.3 nm, 25 °C, 1.7 g in $CHCl_3$ (100 cm^3)] −37.5° (authentic sample from Aldrich); (1*R*,2*R*)(−)-isoborneol, α(589.3 nm, 20 °C, MeOH) −32.30°; (2*S*,5*R*)-(−)menthone, α(589.3 nm, 20 °C) −24.8°; (2*S*,5*S*)(−)-dihydrocarvone, α(589.3 nm) −19°; (1*R*,3*S*)(−)-3-methylcyclopentanol, α(589.3 nm) −5.55°; (1*R*,3*S*)(+)-3-methylcyclohexanol, α(589.3 nm) +20.91°. The values for (1*R*,3*R*)-3-methylcyclopentanol and (2*R*,5*S*)-dihydrocarvone could not be located in the literature. The measured values were α[589.3 nm, 25 °C, 1 g in MeOH (100 cm^3)] −7° and α[589.3 nm, 25 °C, 3 g in MeOH (100 cm^3)] +11° [from (5*S*)(+)-carvone]. The measured rotation of (1*S*,3*R*)(−)-3-methylcyclohexanol was α [589.3 nm, 20 °C, 1 g in MeOH (100 cm^3)] −19.5°.

Disproportionation of Cyclohex-2-*en*-1-*one and Experiments relating to the Radical Mechanism*.—These experiments were carried out with compound **1a** (6.5 mg, 0.005 mmol) and cyclohex-2-en-1-one (50 μl, 0.5 mmol) sealed in a small glass vessel under argon and heated at 82.5 °C for 5 h. The formation of cyclohexanone and phenol was established by GC and GC–MS analyses.

The effect of radical quenchers (CCl_4 and 2,6-di-*tert*-butyl-*p*-cresol) was studied using similar experimental set-ups with the exception of adding various quantities of $\mathrm{Pr^iOH}$ and the radical inhibitor. The reaction between cyclohex-2-en-1-one (0.2 cm^3), water (10 μl) and compound **1a** (13 mg, 0.01 mmol) was carried out for 4 h in a similar fashion. Formation of dioxygen was detected by GC analysis.

Experiments pertaining to Kinetic Modelling.—These experiments were carried out in refluxing propan-2-ol (82.4 °C, 10 cm^3). Various amounts of cyclohex-2-en-1-one and cyclohexanone and compound **1a** were used. Samples were withdrawn at suitable time intervals and subjected to GC and IR analyses. The rate of disappearance of **1a** was monitored by the loss in intensity of the strong band at 2000 cm^{-1}.

The Mathematical Basis.—The differential equation (19)

$$d[\mathbf{1a}]/dt = -k_1[\mathbf{1a}] - k_2[\mathbf{1a}][\mathbf{7}] \qquad (19)$$

$$[\mathbf{7}] = [\mathbf{1a}]_0 - [\mathbf{1a}] \qquad (20)$$

describes the consumption of compound **1a** (see Scheme 1)[15] where $[\mathbf{1a}]_0$ is the initial catalyst concentration. The cyclohexenone concentration does not appear on the right-hand side of equation (19) because it is in large excess in comparison to the concentration of **1a**, and hence is included in the rate constant k_1. Therefore step (1) in Scheme 1 becomes pseudo-first order with respect to the concentration of **1a**. Nevertheless, the initial concentration of cyclohexenone affects the rate of disappearance of **1a** (see text and Fig. 5). Substituting equation (20) into (19) and rearranging gives (21). Integrating equation

$$\frac{d[\mathbf{1a}]}{[\mathbf{1a}]} + \frac{d[\mathbf{1a}]}{(k_1/k_2) + [\mathbf{1a}]_0 - [\mathbf{1a}]} = -k_2\{(k_1/k_2) + [\mathbf{1a}]_0\}dt \qquad (21)$$

(21) and substituting the initial condition gives (22), where

$$\ln[\mathbf{1a}] - \ln\{(k_1/k_2) + [\mathbf{1a}]_0 - [\mathbf{1a}]\} = \alpha t + \{\ln[\mathbf{1a}]_0/(k_1/k_2)\} \qquad (22)$$

$\alpha = k_1 + k_2[\mathbf{1a}]_0$. On rearranging the time-dependent integral rate equation (23) for [**1a**] is obtained where $x = e^{-\alpha t}$. The

$$[\mathbf{1a}] = [\mathbf{1a}]_0\alpha x/(k_1 + k_2[\mathbf{1a}]_0 x) \qquad (23)$$

differential rate equation for [**1a**] is obtained by rearranging equations (19) and (20) where *r* is the rate.

$$r/[\mathbf{1a}] = \alpha - k_2[\mathbf{1a}] \qquad (24)$$

The differential equations for the consumption of cyclohex-2-en-1-one and cyclohexanone and generation of cyclohexanol [Scheme 1, section (*e*)] are (25)–(27).

$$d[C_6H_8O]/dt = -k_3[C_6H_8O][\mathbf{7}] \qquad (25)$$

$$d[C_6H_{10}O]/dt = k_3[C_6H_8O][\mathbf{7}] - k_4[C_6H_{10}O][\mathbf{7}] \qquad (26)$$

$$d[C_6H_{12}O]/dt = k_4[C_6H_{10}O][\mathbf{7}] \qquad (27)$$

Parameter estimation. The transfer-hydrogenation reaction involves four rate constants k_1–k_4 which can be estimated by fitting of the experimental data by the model. The rate constants k_1 and k_2 can be determined by two methods, either from the integrated equation (23) or from the differential rate equation (24). In the integral method the observed decrease in catalyst concentration with time was fitted by the model. The rate constants k_1 and k_2 were adjusted so that the sum of squares of the difference between the model prediction and experimental data were minimised. The minimisation procedure can be carried out by using a standard optimisation technique like Powell's method.[15] In the differential method, the rate constants k_1 and k_2 were determined by plotting r/[**1a**] against [**1a**] [equation (24)] which results in a straight line.

Equations (25)–(27) were solved numerically by a fourth-order Runge–Kutta method.[16,17] The rate constants k_3 and k_4 were also estimated by the optimisation procedure described above, by minimising the sum of differences between the model and the observed concentrations of cyclohex-2-en-1-one, cyclohexanone and cyclohexanol.

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References

1 (*a*) S. Bhaduri, K. Sharma and D. Mukesh, *J. Chem. Soc., Dalton Trans.*, 1992, 77; (*b*) S. Bhaduri, N. Sapre, K. Sharma, P. G. Jones and G. Carpenter, *J. Chem. Soc., Dalton Trans.*, 1990, 1305; (*c*) Y. Blum and Y. Shvo, *J. Organomet. Chem.*, 1984, **263**, 93; (*d*) Y. Blum, D. Reshef and Y. Shvo, *Tetrahedron Lett.*, 1981, **22**, 1541; (*e*) Y. Shvo, Y. Blum and D. Reshef, *J. Organomet. Chem.*, 1982, **238**, C79; (*f*) M. Bianchi, U. Maffeoli, P. Frediani, G. Menchi and F. Piacenti, *J. Organomet. Chem.*, 1980, **240**, 59; **236**, 375; (*g*) M. Bianchi, U. Maffeoli, G. Menchi, P. Frediani, S. Pratesi, F. Piacenti and G. Botteghi, *J. Organomet. Chem.*, 1980, **198**, 73; (*h*) S. Bhaduri, N. Y. Sapre, K. R. Sharma and P. G. Jones, *J. Organomet. Chem.*, 1989, **364**, C8; (*i*) A. Basu, S. Bhaduri, K. Sharma and P. G. Jones, *J. Organomet. Chem.*, 1987, **328**, C34.

2 S. Bhaduri, H. Khwaja, N. Sapre, K. Sharma, P. G. Jones and G. Carpenter, *J. Chem. Soc., Dalton Trans.*, 1990, 1313; S. Bhaduri, K. Sharma and H. Khwaja, *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1989, **101**, 195; S. Han, J. Song, P. D. Macklin, S. T. Nguyen, G. L. Geoffroy and A. L. Rheingold, *Organometallics*, 1989, **8**, 2127.

3 S. Bhaduri, D. Mukesh and K. Sharma, *J. Chem. Soc., Chem. Commun.*, 1990, 1506.

4 (*a*) R. L. Chowdhury and J. E. Backvall, *J. Chem. Soc., Chem. Commun.*, 1991, 1063; (*b*) S. Gladiali, L. Pinna, G. Delogu, S. De Martin, G. Zassinovich and G. Mestroni, *Tetrahedron Asymmetry*, 1990, **1**, 635; (*c*) G. Zassinovich, R. Bettella, G. Mestroni, N. Bresciani-Pahor, S. Geremia and L. Randaccio, *J. Organomet. Chem.*, 1989, **370**, 187; (*d*) E. Farnetti, J. Kaspar and M. Graziani, *J. Mol. Catal.*, 1990, **63**, 5; (*e*) D. Muller, G. Umbricht, B. Weber and A. Pfaltz, *Helv. Chim. Acta*, 1991, **74**, 232; (*f*) S. De Martin, G. Zassinovich and G. Mestroni, *Inorg. Chim. Acta*, 1990, **174**, 9; (*g*) R. Marcec, Z. Raza and V. Sunjic, *J. Mol. Catal.*, 1991, **69**, 25; (*h*) S. Gladiali, G. Chelucci, F. Soccolini, G. Delogu and G. Chessa, *J. Organomet. Chem.*, 1989, **370**, 285; (*i*) G. Mestroni, G. Zassinovich, E. Alessio and M. Tarnatore, *J. Mol. Catal.*, 1989, **49**, 175; (*j*) G. Zassinovich and G. Mestroni, *J. Mol. Catal.*, 1989, **42**, 81; (*k*) C. Bianchi, E. Farnetti, M. Graziani, G. Nardin, A. Vacca and F. Zanobini, *J. Am. Chem. Soc.*, 1990, **112**, 9190; (*l*) G. Zassinovich and G. Mestroni, *J. Mol. Catal.*, 1987, **42**, 81.

5 J. P. Collman, K. M. Kosydaro, M. Bressan, W. Lamanna and T. Garrett, *J. Am. Chem. Soc.*, 1984, **106**, 2569.

6 W. S. Mahoney, D. M. Brestensky and J. M. Stryker, *J. Am. Chem. Soc.*, 1988, **110**, 291; W. S. Mahoney and J. M. Stryker, *J. Am. Chem. Soc.*, 1989, **111**, 8818.

7 J. M. Brown, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 190.

8 *Vogel's Textbook of Practical Organic Chemistry*, revised by B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith and A. R. Tatchell, 4th edn., Longman, London, 1978, p. 270.

9 (*a*) R. A. Sheldon and J. K. Kochi, *Metal Catalysed Oxidations of Organic Compounds*, Academic Press, New York, 1981, p. 29 and refs. therein; (*b*) *The Chemistry of Peroxides*, ed. S. Patai, Wiley, New York, 1983, p. 720; (*c*) K. Takeda, H. Yoshida, K. Hayashi and S. Okamura, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 1632.

10 B. V. Den Bosch and L. Hellinckx, *Am. Inst. Chem. Eng. J.*, 1974, **20**, 250; J. W. Moore and R. G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 1981, p. 318.

11 J. C. Bricker, C. C. Nagel, A. A. Bhattacharyya and S. G. Shore, *J. Am. Chem. Soc.*, 1985, **107**, 377.

12 D. M. Roundhill, M. K. Dickson, N. S. Dixit and B. P. Sudha-Dixit, *J. Am. Chem. Soc.*, 1980, **102**, 5538.

13 (*a*) J. W. Koepke, J. R. Johnson, S. A. R. Knox and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3947; (*b*) S. A. R. Knox, J. W. Koepke, M. A. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942; (*c*) C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. McPartlin and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 383; (*d*) F. Piacenti, M. Bianchi, P. Frediani and E. Benedetti, *Inorg. Chem.*, 1971, **10**, 2759; (*e*) B. F. G. Johnson, J. Lewis, P. R. Raithby and G. Suss Fink, *J. Chem. Soc., Dalton Trans.*, 1979, 1356.

14 *Dictionary of Organic Compounds*, 5th edn., Executive Editor J. Buchingham, Chapman and Hall, New York, 1982.

15 F. Mata-Perez and J. F. Perez-Benito, *J. Chem. Educ.*, 1987, **64**, 925.

16 A. C. Norris, *Computational Chemistry, An Introduction to Numerical Methods*, Wiley, New York, 1981.

17 G. Beech, *Fortran IV in Chemistry, An Introduction to Computer Assisted Methods*, Wiley, New York, 1978.

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