Kinetics and mechanisms of homogeneous catalytic reactions. Part 2. Hydrogenation of cyclohexane catalysed by [RuH(CO)-(NCMe)₂(PPh₃)₂]BF₄

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Summary
Kinetic and mechanistic studies of the homogeneous hydrogenation of cyclohexane were carried out using the cationic complex [RuH(CO)(NCMe)₂(PPh₃)₂]BF₄ as the catalyst precursor, which was very efficient under mild reaction conditions in xylene solution. The experimental rate law was found to be \( r = \frac{K_1 K_3}{(1 + K_2 C_{\text{MeCN}}) + K_1 (1 + K_3 C_{\text{H₂}})} [\text{Ru}] [C_{\text{H}_2} C_{\text{H}10}] [H_2] \), which became \( K_{2+3}(1 + K_2) [\text{Ru}] [H_2] \) at high cyclohexane concentrations. The activation parameters were calculated. The kinetic data are consistent with a mechanism involving the oxidative addition of hydrogen as the rate-determining step of the catalytic cycle.

Introduction
The use of transition metal complexes in the homogeneous hydrogenation of olefins has been extensively studied in the last few years, mainly because this reaction is of great use in practical applications. The development of closely related fields such as the synthesis of dihydrogen complexes, oxidative addition–reductive elimination processes and the insertion of olefins into metal–hydride bonds has provided a deeper insight into the elementary steps of the catalytic cycle for this type of reaction. A further major contribution to this field is the study of kinetic and mechanistic aspects of such catalytic reactions.

Recently, this group published the first complete kinetic and mechanistic study of the hydrogenation of benzaldehyde catalysed by [RuH(CO)(NCMe)₂(PPh₃)₂]BF₄ (1)\(^{(1)}\). In this paper a kinetic and mechanistic investigation of the hydrogenation of cyclohexane, by use of (1) as the catalyst precursor, is reported.

Experimental
All manipulations were carried out with rigorous exclusion of air, which is required for successful hydrogenation. Cyclohexane was purified by distillation at reduced pressure. Solvents were dried by known procedures and distilled under an inert atmosphere prior to use. Complex (1) was prepared by this group's recently published procedure\(^{(13)}\). N.m.r. and i.r. spectra were recorded on a Bruker AM-300 spectrometer and Nicolet FT–i.r. 5DXC instrument, respectively.

Hydrogenation experiments
In a typical experiment the catalyst, cyclohexane and n-heptane (2.5 cm\(^3\)), dissolved in xylene (50 cm\(^3\) total volume), and a stirring bar were introduced into a glass-lined stainless steel autoclave (125 cm\(^3\)) fitted with a sampling valve and a high precision manometer. Air was removed by flushing three times with hydrogen, then the vessel was equilibrated for ca 30 min in a silicone–oil bath which was thermostatted at the reaction temperature, and subsequently charged to the desired pressure. During the catalytic run samples of the reaction mixture were periodically extracted via the sampling valve, and the total pressure of the system was continuously adjusted to a constant value by admitting hydrogen from a high pressure reservoir. The samples were cooled in a dry ice–acetone mixture and were immediately analysed by means of a 610 Series UNICAM gas chromatograph fitted with a thermal conductivity detector and a 3 m 10% SE-30 glass column using He carrier gas. The results were quantified with a UNICAM 4815 computing integrator using n-heptane as the internal standard.

When the hydrogenation was carried out in the presence of liquid mercury no effect on the initial rate was observed. Together with the high reproducibility of the results, this established that the catalytic reaction is truly homogeneous\(^{(16–18)}\).

Results and discussion
The complex [RuH(CO)(NCMe)₂(PPh₃)₂]BF₄ (1) proved to be an efficient catalyst precursor for the homogeneous hydrogenation of cyclohexane, in xylene solution, to give exclusively cyclohexane under mild conditions of temperature and pressure (373–413 K and ca 4 bar) according to Equation 1:

\[
\text{[RuH(CO)(NCMe)₂(PPh₃)₂]BF₄} + \text{H}_2 \rightarrow \text{hydrogenation products} (1)
\]

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Kinetics of the cyclohexane hydrogenation
In order to determine the rate dependence of Reaction 1 on the various reaction components, hydrogenation runs were performed at different concentrations of catalyst,
The concentration of complex (1) was varied in the 0.5-2.5 mM range, while the cyclohexane and dissolved hydrogen concentrations (1.0 and 1.7 x 10^{-2} M, respectively) and the temperature (403 K) were kept constant. The initial rates of hydrogenation of cyclohexane showed a direct dependence on catalyst concentration. A plot of log\( r_i \) versus log [Ru] (Figure 1) indicated first-order behaviour with respect to ruthenium concentration (log\( r_i \) = -1.89 + 1.06 log [Ru], \( r^2 = 0.992 \)).

Similarly, the effect of cyclohexane concentration on the hydrogenation rate was studied in the 0.1-1.2 M range, keeping the ruthenium concentration constant (1.5 x 10^{-3} M), likewise the dissolved hydrogen concentration (1.7 x 10^{-2} M) and the temperature (403 K). Figure 2 shows the dependence of the hydrogenation rate on the substrate concentration. The initial hydrogenation rate varies according to a saturation curve with increasing cyclohexane concentration, i.e. the dependence of the rate is nearly linear (log\( r_i \) = -4.77 + 0.92 log [C6H10], \( r^2 = 0.986 \)) when the substrate concentration is < 0.8 M, while >0.8 M the rate is independent of the initial olefin concentration. These experimental findings are similar to those reported for the hydrogenation of alkenes using tetra-acetate diruthenium complexes (1m and for homogeneous hydrogenation of crotonic acid in aqueous solution catalysed by m-sulphophenyl-diphenylphosphine ruthenium complexes (2)).

Figure 3 shows the dependence of the initial rate on the dissolved hydrogen concentration at 403 K, varied in the 1.3 x 10^{-2}-2.1 x 10^{-2} M range, at cyclohexane and catalyst concentrations of 1.0 and 1.5 x 10^{-3} M, respectively. The reaction is first order with respect to hydrogen concentration (log\( r_i \) = -2.94 + 1.12 log [H2], \( r^2 = 0.985 \)).

In view of the above, the catalytic hydrogenation of cyclohexane proceeds according to two experimental laws:

\[
\frac{r}{c} = k_{cat}[Ru][C_6H_{10.5}][H_2] \quad (2)
\]

\[
\frac{r}{c} = k_{cat}[Ru][H_2] \quad (3)
\]

which reproduce the behaviour of the reaction at low and high substrate concentrations, respectively. The equations allowed the average values of the rate constants at 403 K to be determined (\( k_{cat} = 0.73 \pm 0.02 \text{ M}^{-2} \text{s}^{-1} \) and \( k'_{cat} = 0.48 \pm 0.01 \text{ M}^{-1} \text{s}^{-1} \)). Addition of small amounts of acetonitrile (0.8 M) decreased the initial rate by approximately one order of magnitude (1.68 x 10^{-6} M s^{-1}).

The effect of the temperature on the rate constant was studied in the 383-413 K range at a cyclohexane concentration of 0.6 M, a ruthenium concentration of 1.5 x 10^{-3} M and a hydrogen concentration of 1.7 x 10^{-2} M. The plot...