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Steric control of a ruthenium-catalysed alkyne hydrogenation reaction

Bongani S. Nkosi, Neil J. Coville *,
Department of Chemistry, University of the Witwatersrand, Johannesburg, P O Wits 2050 (RSA)

Michel O. Albers, Craig Gordon, Marjorie M. Viney and Eric Singleton
NCRL, CSIR, P O Box 395, Pretoria 0001 (RSA)

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Abstract

The cations $[RuHL'_5]^+$ and $[RuHL''_3L'_2]^+$ have been used in a study of the effect of variation of group 15 donor ligands (L'', L') on the hydrogenation reaction of alkynes. $[RuHL'_5]^+$ was found to catalyse hydrogenation of both alkynes and alkenes, the course of the reaction being dependent on the size of the ligand L'. The rate of hydrogenation of alkynes catalysed by $[RuHL'_5]^+$ was found to increase with the cone angle, θ, until ca 120° and then decrease as θ is raised still further. When the cone angle of L' < 120° no alkene hydrogenation occurs. Addition of excess PMe_3 (10 equiv.) to reaction solutions containing $[RuH(PMe_3)_5]^+$ was found to increase the selectivity of the alkyne hydrogenation reaction, with concomitant decrease in the hydrogenation rate. Addition of a range of other ligands L' (2–3 equiv.) to solutions of $[RuH(COD)L''_3]^+$ (L'' = PMe_3, PMe_2Ph) also resulted in a decrease in the rate of the alkyne hydrogenation, but the decrease was dependent on the size of L'. The $[RuHL''_3L'_2]^+$ complexes were found to catalytically hydrogenate alkynes exclusively when the sum of the cone angles for the L' and L'' ligands was $5\theta = 610 \pm 20°$. No correlation between electronic parameters and the reaction rate and product selectivity is apparent from our results. Mechanistic features of the catalysed hydrogenation of alkenes and alkynes in the presence of these ruthenium complexes are discussed.

Introduction

We recently reported on the homogeneous hydrogenation of alkenes and alkynes catalysed by $[RuH(COD)(PMe_2Ph)_3]^+$ (COD = 1,5 cyclooctadiene) [1]. The study revealed that addition of PMe_2Ph to reaction solutions containing either alkynes and/or alkenes resulted in a change in the product distribution in the sense that a

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decrease in the rate of alkene hydrogenation and an increase in that of alkyne hydrogenation occurred with increase of the amount of PMe_2Ph added (0–2 equiv.). Indeed addition of more than 2 equiv. of PMe_2Ph resulted in the generation of a stable active catalyst that hydrogenated alkynes exclusively [2].

These findings suggested that it might be possible to fine-tune the catalyst by variation of the ligands surrounding the Ru cation. We report here a comprehensive investigation of the alkyne/alkene hydrogenation reaction in the presence of a range of $[RuHL'_5]^+$ and $[RuHL'_2L''_2]^+$ (L′ = group 15 donor ligand; L″ = PMe_3, PMe_2Ph) complexes. These complexes were prepared in situ (by known procedures [3]) either by addition of 5 equiv. of L′ to $[RuH(COD)(NH_2NMe_2)_3]^+$ or 2 equiv. of L′ to $[RuH(COD)L''_3]$. In a previous report, preliminary data on the use of $[Ru(dppb)_2]^+$ (dppb = diphenylphosphinobutane) as a catalyst for alkyne hydrogenation reactions were also presented [4]. The results presented now provide an overall reaction scheme that accounts for the observations reported in this and our earlier publications [1,2,4].

Experimental

The complexes $[RuH(COD)(PMe_2Ph)_3][PF_6]$, $[RuH(COD)(PMe_3)_3][PF_6]$, and $[RuH(COD)(NH_2NMe_2)_3][PF_6]$ were synthesized by published procedures [3,5]. All other complexes were prepared by the in situ addition of ligands L to the above starting materials. Alkynes were purchased from various sources and were passed through an alumina column and then degassed by freeze/thaw techniques before use. The ligands, purchased from various sources, were used without further purification. All solvents were dried and degassed before use. Reactions were monitored by hydrogen uptake [6] and/or gas chromatography (GC) techniques. The 1-heptyne and the (non-interfering) internal standard hexane were purified by passage down a short silica gel column, then subjected to several freeze thaw cycles under vacuum to remove air.

In a typical experiment the catalyst precursor $[RuH(COD)L''_3][PF_6]$ (1.0×10^{-4} mol), nitrogen degassed methanol (total volume made up to 50 ml), and a magnetic stirring bar were placed in a 300 ml Schlenk flask. The solution was frozen at $-196\,^{\circ}C$ and the flask evacuated to 1×10^{-1} torr. Hydrogen was admitted at 1 atmosphere and the solution warmed in a thermostatically controlled oil, or water, bath to the required reaction temperature ($\pm 0.1\,^{\circ}C$). Ligand L′ (2.0×10^{-4} mol) was added, followed after 5 minutes at the reaction temperature by the internal standard (5.0×10^{-3} mol) and alkyne (1.0×10^{-2} mol). The progress of the reaction was monitored at regular intervals by quantitative GC analysis using a Carlo Erba 4300 instrument fitted with a 2 m, 12% 1,2,3-tris(2-cyanoethoxy)-propane (TCEP) on Chromosorb P-AW column (operating temperature $70\,^{\circ}C$).

Results

Two types of complexes, $[RuHL'_5]^+$ and $[RuHL''_3L'_2]^+$, were used to examine the effect of the variation of L′ on the hydrogenation reaction.

$[RuHL'_5]^+$ catalysts

In the first set of experiments the required complex $[RuHL'_5]^+$ was generated in situ in THF by addition of five equivalents of L′ to $[RuH(COD)(NH_2NMe_2)_3]^+$,

Table 1

Hydrogenation of 1-hexene and 1-hexyne in the presence of $[RuH(COD)(NH_2NMe_2)_3]^+ + 5L$ [a,b]

L	Cone angle [c]		Electronic factor [c]	pK_a	Hydrogenation rate (mol min^{-1})	
	θ (deg.)	5θ	$\nu(cm^{-1})$		1-hexene	1-hexyne
$P(OMe)_3$	107	535	2079.5	2.60	0	0.16×10^{-5}
$P(OEt)_3$	109	545	2076.3	3.31	0	0.25×10^{-5}
PMe_3	118	590	2064.1	8.65	0	9.75×10^{-5}
PMe_2Ph	122	610	2065.3	6.5	0	10.83×10^{-5}
$PHPh_2$ [b]	128	640	2073.3	–	0	0
$P(O\text{-}i\text{-}Pr)_3$	130	650	2075.9	4.08	0	0.37×10^{-5}
$P(OMe)Ph_2$	132	660	2072.0	2.69	0	0.65×10^{-5}
$P(O\text{-}o\text{-}Tol)_3$	141	705	2084.1	−1.83	4.09×10^{-7}	2.09×10^{-5}
$P(i\text{-}Bu)_3$	143	715	2059.7	–	6.96×10^{-5}	$< 0.82\times10^{-5}$ [d]
PPh_3	145	725	2068.9	2.73	10.23×10^{-5}	$< 0.82\times10^{-5}$ [d]
PBz_3	165	825	2066.4	6.0	12.27×10^{-5}	$< 0.82\times10^{-5}$ [d]
PCy_3	170	850	2065.4	9.7	13.09×10^{-5}	$< 0.82\times10^{-5}$ [d]

[a] Reaction conditions: $T = 30.0 \pm 0.1$° C, tetrahydrofuran 25 ml, substrate 0.624 mol, catalyst 1.56×10^{-3} mol. [b] $PHPh_2$, PBr_3 and $PClPh_2$ formed precipitates; no catalysis observed. [c] Values obtained from ref. [8]. [d] Rate of hydrogenation; $P(i\text{-}Bu)_3 > PPh_3 > PBz_3 > PCy_3$.

and the hydrogenation of 1-hexyne and 1-hexene was studied by H_2 uptake procedures at 30 ° C and 1 atm pressure. The results are shown in Table 1.

The electronic effects of the ligand L′ (L′ = phosphine or phosphite), i.e. its electronegativity and electron accepting properties, can be associated with a number of parameters such as the pK_a of the ligand [7] and the ν(CO) stretching frequency of a series of $[Ni(CO)_3L']$ complexes [8]. The values are shown in Table 1. No correlation between either of the electronic parameters and the reaction rate is apparent. Arrangement of L′ according to the steric size of the ligand (measured by the ligand cone angle, θ [8]) is indicated in Table 1. It can be seen that the 1-hexyne hydrogenation rate increases with θ up to ca. 120 ° (PMe_3, PMe_2Ph) and then decreases as θ is raised still further. Remarkably no 1-hexene hydrogenation occurs when L has a cone angle below 120 °, but when $\theta > 120$ ° the reaction rate increases with increase in θ. This suggests that two processes are needed to rationalize the hydrogenation reaction data (see below).

The maximum reaction rate occurred when L′ = PMe_3 or PMe_2Ph. These complexes were thus investigated in further detail in an attempt to optimize the reaction conditions. The alkyne and alkene hydrogenation data for $[RuHL_5']^+$ for L′ = PMe_2Ph have been described in detail elsewhere [1,2] and the remarkable influence of the PMe_2Ph concentration on the course of the reaction has been previously reported [2].

Similar studies were performed with $[RuH(PMe_3)_5]^+$. The influence of temperature on the reaction was ascertained from studies in methanol (Fig. 1). Thus the hydrogenation of 1-heptyne (20–60 ° C) revealed that increase in the temperature resulted in an increase in the alkyne hydrogenation rate but that this was also accompanied by an increase in the 1-heptene to 1-heptane hydrogenation rate. It should be noted, however, that the rate is faster at 40 ° C than at 60 ° C. This effect is related to the catalyst stability; at the higher temperature more rapid catalyst

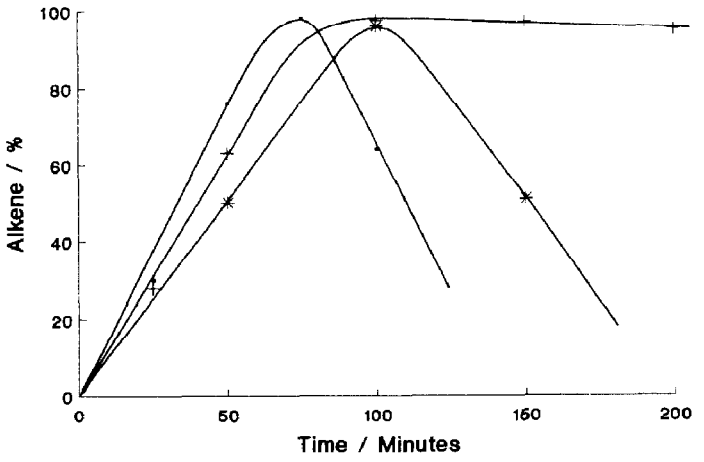

Fig. 1. Effect of temperature on the $[RuH(PMe_3)_5]^+$ catalysed hydrogenation of 1-heptyne (1 atm H_2, MeOH): +, 20 °C; ●, 40 °C; *, 60 °C.

deactivation/decomposition occurs, and this process is irreversible. Similar results were observed for the related $[RuH(PMe_2Ph)_5]^+$ catalyst system [1,2]. Furthermore at the higher temperature isomerisation of 1-heptene to *cis*- and *trans*-2-heptene was detected. The actual nature of the deactivated ruthenium complex was not investigated.

The influence of the solvent composition on the 1-heptyne reaction rate was also studied. As can be seen (Fig. 2) the hydrogenation rate was strongly influenced by the solvent, with acetone, tetrahydrofuran (THF), and methanol giving the fastest reaction rates.

In our previous study we observed that the addition of an excess of PMe_2Ph to $[RuH(PMe_2Ph)_5]^+$ stabilized the catalyst and enhanced the reaction rate and the catalytic selectivity of the ruthenium cation. To explore this finding further a similar study was carried out with $[RuH(PMe_3)_5]^+$. Addition of an excess of PMe_3 (10

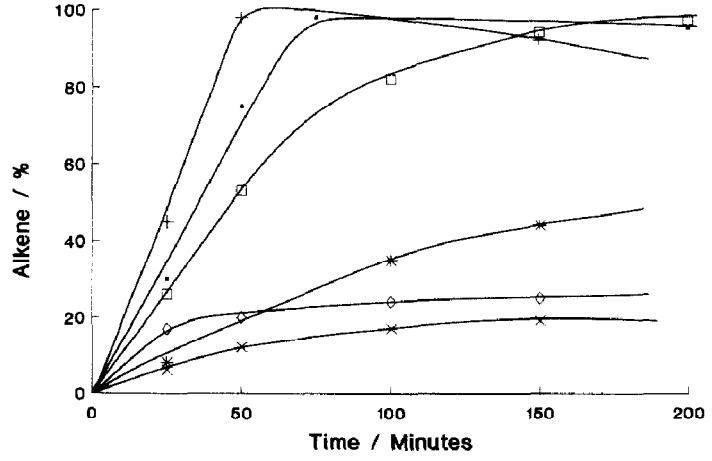

Fig. 2. Effect of solvent composition on the $[RuH(PMe_3)_5]^+$ catalysed hydrogenation of 1-heptyne (1 atm H_2; 40 °C); + MeOH; ●, acetone; □, THF; *, 1/1 MeOH/H_2O; ◇, MeOH+10% H_2O; ×, CH_2Cl_2.

equiv.) was indeed found to increase product selectivity (i.e. no heptane was observed on hydrogenation of 1-heptyne) but the rate was also found to be reduced considerably. This type of behaviour is to be expected if the reaction rate depends on ligand (PMe_3) dissociation (see below). To examine further the difference between the effects of the presence of an excess of the ligand on the two catalysts $[RuH(PMe_2Ph)_5]^+$ and $[RuH(PMe_3)_5]$, 2–3 equiv. of ligands, L′, of varying cone angle were added to solutions of $[RuH(PMe_3)_5]^+$. In all the systems investigated (e.g. L′ = $P(OMe)_3$, $P(OEt)_3$, $P(O\text{-}o\text{-}MeC_6H_4)_3$) the rate fell, but the decrease varied with L′; the smaller L′, the slower the reaction. The possibility of ligand exchange is suggested by these results (see below). Thus addition of an excess of ligand L′ to the $[RuH(PMe_3)_5]^+$ catalyst does not cause rate enhancement under any conditions.

Finally it should be noted that the $[RuH(PMe_3)_5]^+$ cation can catalyse the hydrogenation of a range of alkynes, including acetylene and 2-heptyne.

$[RuHL''_3L'_2]^+$ catalysts

If the cone angles, θ, of the five ligands surrounding Ru in $[RuHL'_5]^+$ are added together then when $5\theta \sim 600°$ the rate and selectivity towards the alkyne hydrogenation reactions are at a maximum (Table 1). Above or below this value the alkyne hydrogenation rate falls with change in 5θ.

To "fine-tune" the catalyst further and provide confirmation of this steric control of the alkyne hydrogenation reaction a range of mixed ligand complexes with varying electronic and steric properties were prepared. These complexes were readily synthesized in situ from $[RuH(COD)L''_3]^+$ (L″ = PMe_3, PMe_2Ph) by addition of 2 equiv. of L′ (L′ = phosphines, phosphites, etc.) to yield the $[RuHL''_3L'_2]^+$ complexes. L″ was chosen as PMe_3 or PMe_2Ph so as to destablish more accurately the value of 5θ that would maximize the alkyne hydrogenation rate.

No attempt was made to isolate the mixed ligand complexes. In solution some ligand scrambling could also take place to yield $[RuHL''_3L'_2]^+$ and $[RuHL'L''_4]^+$ which would influence the overall reaction rate. However use of a Ru to ligand ratio (ligand = L′ + L″) of 1/5 suggests that the average cone angle will remain near constant and be determined primarily by the $[RuHL''_3L'_2]^+$ complex. It should also be noted that ligand inter-meshing was ignored in determining the value of 5θ [9].

(i) $[RuH(COD)(PMe_2Ph)_3]^+/L'$ catalysts. The catalysed hydrogenation of 1-heptyne was performed in acetone at 10 °C and 1 atm P and the reaction was monitored by GC. The results of the study are shown in Table 2. These results confirm the findings from the earlier study (Table 1) that established the dominance of the steric rather than the electronic effect of the ligand set on the alkyne hydrogenation reaction. This is highlighted by the data for $[RuH(PMe_2Ph)_3L'_2]^+$ where L′ = PMe_3, $P(OPh)_3$ and $P(O\text{-}i\text{-}Pr)_3$. 5θ for the above complexes varies from 590°–626° whereas the electronic property of the ligands covers the complete spectrum from that of a good nucleophilic ligand (PMe_3) to a good π acceptor/poor σ donor ligand ($P(OPh)_3$). It should also be noted that when L = PPh_3 ($5\theta = 656°$) the alkyne hydrogenation is rapid but simultaneously alkene hydrogenation (and isomerisation) has already commenced. There is thus a very narrow range of ligand steric size which will yield exclusive alkyne hydrogenation at a moderate rate namely $5\theta = 610 \pm 20°$.

That other factors cannot totally be discounted is shown by the effect of adding group 15 donor ligands APh_3 (A = P, As, Sb, Bi) to a reaction solution containing

Table 2

Hydrogenation rates of 1-heptyne in the presence of $[RuH(COD)(PMe_2Ph)_3]^+ + 2L$ [a]

L	Cone angle [b]		Electronic factor [c] (cm^{-1})	pK_a	Rate of 1-heptyne hydrogenation (mol min^{-1})
	θ (deg.)	5θ			
PMe_3	118	602	2064.1	8.65	13.00×10^{-5}
PMe_2Ph	122	610	2065.3	6.50	10.83×10^{-5}
PPh_3	145	656	2068.9	2.73	3.17×10^{-5}
$P(t\text{-}Bu)_3$	182	730	2060.1	11.40	1.33×10^{-5}
$P(OMe)_3$	107	580	2079.5	2.60	2.17×10^{-5}
$P(OEt)_3$	109	584	2076.3	3.31	4.00×10^{-5}
$P(O\text{-}n\text{-}Pent)_3$	110 [d]	586	–	–	7.83×10^{-5}
$P(OPh)_3$	128	622	2085.3	−2.00	$\sim 8\times10^{-5}$
$P(O\text{-}i\text{-}Pr)_3$	130	626	2075.9	4.08	11.67×10^{-5}
$P(O\text{-}o\text{-}Tol)_3$	141	648	2084.1	−1.83	3.83×10^{-5}

[a] Reaction conditions: $T = 10.0 \pm 0.1$°C, acetone 25 ml, substrate 1.0×10^{-2} mol, catalyst 1.1×10^{-4} mol, P 0.8 bar. [b] Data obtained from ref. 8, for discussion of this parameter see also ref. 7. [c] Data obtained from ref. 8, for discussion of this parameter see also ref. 7. [d] Estimated ~110°C.

$[RuH(COD)(PMe_2Ph)_3]^+$. The hydrogenation of 1-heptyne using the above in situ mixture was monitored by GC and the results are shown in Table 3. Although it is clear that PPh_3 is the best ligand no trend relating to the steric size of the ligands in the series can be discerned.

(ii) $[RuH(COD)(PMe_3)_3]^+$/L' catalysts. The catalysed hydrogenation reaction of 1-heptyne in acetone at 10°C and 1 atm pressure was monitored by GC for reactions involving the above in situ generated catalyst. As observed with the related $[RuH(COD)(PMe_2Ph)_3]^+$ catalysts, exclusive alkyne hydrogenation occurs at an optimal rate when the added ligand L' and the PMe_3 ligand have a total cone angle 5θ of $610 \pm 20°$ (see Fig. 3). Similar results were obtained when the reaction was performed at 40°C in acetone (sequence of rates L' = $PMe_2Ph \sim PMe_3 < P(O\text{-}i\text{-}Pr)_3 < P(OEt)_3 < P(OMe)_3$).

Diphosphine systems

In a previous study the catalytic behaviour of $[RuH(dppb)_2]^+$ (dppb = diphenylphosphinobutane) was explored [4]. It is possible that these complexes may catalyse hydrogenation of alkynes by a route different from that for the monophosphine complexes, as has been found for related Ru complexes [10]. A series of experiments were performed, however, in which one equivalent of diphosphine ligand was added

Table 3

Effect on the hydrogenation of 1-heptyne of adding various ligands (L) to $[RuH(COD)(PMe_2Ph)_3]^+$ [a]

L	Rate [b]
PPh_3	3.17×10^{-5}
$AsPh_3$	0.83×10^{-5}
$SbPh_3$	1.92×10^{-5}
$BiPh_3$	1.33×10^{-5}

[a] Reaction performed in acetone at 10°C. [b] Initial rate: mol alkyne hydrogenated per min.

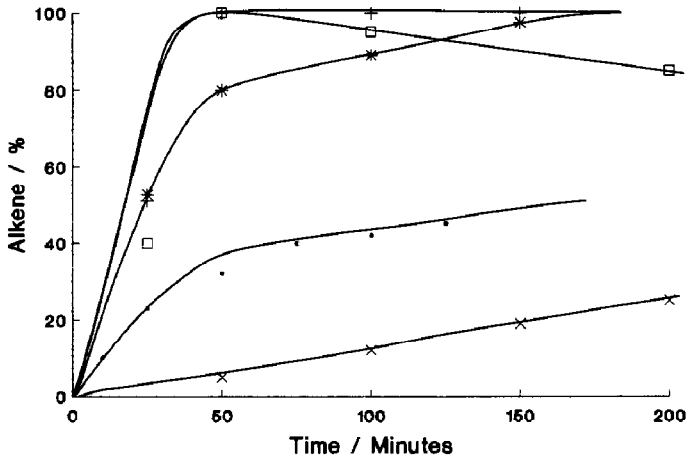

Fig. 3. Effect of the addition of ligand, L, to $[RuH(COD)(PMe_3)_3]^+$ on the hydrogenation of 1-heptyne (10 °C, acetone, 1 atm *P*); *, 2 equiv. $P(O\text{-}i\text{-}Pr)_3$; +, 2 equiv. $P(O\text{-}o\text{-}MeC_6H_4)_3$; ●, 2 equiv. $P(OPh)_3$; ×, 10 equiv. PMe_3; □, 5 equiv. PPh_3.

to $[RuH(COD)L''_3]^+$ ($L'' = PMe_3$, PMe_2Ph). In general good catalytic behaviour was observed, but the reaction was generally accompanied by secondary alkene hydrogenation.

Discussion

From the above results the following conclusions can be drawn:

(1) A wide range of $[RuHL'_5]^+$ and mixed ligand complexes $[RuHL''_3L'_2]^+$ (where L′ and L″ are group 15 donor ligands) can catalyse the hydrogenation of alkynes.

(2) The hydrogenation rate and selectivity is influenced by the steric size of the ligands surrounding the metal.

(3) The hydrogenation reaction is sensitive to the presence of excess ligand, temperature and solvent.

In an earlier publication we suggested that the selectivity of the hydrogenation reaction appeared to be influenced by the steric effect associated with the ligand set surrounding the ruthenium [1]. The new data not only confirm this proposal but reveal the narrow range of ligands of appropriate cone angles which can be used to optimize the reaction rate and selectivity. This is given by the value of 5θ, where θ is a measure of the cone angle of ligand L, and 5θ is the summation of the cone angles for the 5L ligands (which may be the same or different) that surround the Ru atom. Electronic properties associated with the ligand L must perturb the steric effect but the data clearly indicate the dominance of the steric over the electronic effect of L in determining the rate.

The further remarkable feature of the reaction is the increase in the rate of secondary reaction, the hydrogenation of the alkene, which occurs with ligands of large cone angle.

The accumulated data thus suggest that the overall reaction involves the ligand

dissociation process shown below:

$$[RuHL_5]^+ \rightleftharpoons [RuHL_4]^+ + L \rightleftharpoons [RuHL_3]^+ + L$$
$$(\text{or } [RuHL_3S]^+,\ S = \text{solvent})$$

(A)	(B)	(C)
(18e)	(16e)	14e (or 16e)

The data for the alkyne hydrogenation rate can be readily rationalized by assuming that **B** is the catalytically active species in solution. For large ligands L the equilibrium would lie towards **B**, and the possibility of Ru–alkyne bonding would be enhanced.

Rationalization of the rate of the competing alkene hydrogenation reaction requires the presence of another catalytically active species. Since alkyne–metal bonding is generally stronger than alkene–metal bonding [11] it seems unlikely that an increase in concentration of **B** (as L gets larger) would lead to a change in the bonding preference. For instance, even if the position of equilibrium $\mathbf{A} \rightleftharpoons \mathbf{B}$ were such that the complex existed exclusively as **B** (L bulky) the alkyne hydrogenation reaction should still be dominant. Our results indicate otherwise. We thus suggest that when L is bulky a second equilibrium, $\mathbf{B} \rightleftharpoons \mathbf{C}$, is set up in solution to form a new catalytically active species. To rationalize our rate data we propose that this complex, **C**, preferentially catalyses hydrogenation of alkenes rather than alkynes. A similar scheme [1] to rationalize the influence of added ligand on the ratio of the competing alkene and alkyne hydrogenations is completely consistent with this proposal.

Conclusion

A highly selective alkyne hydrogenation catalyst $[RuHL'_2L''_3]^+$ has been prepared in situ and the variations in the rate of hydrogenation of alkenes and alkynes can be accounted for in terms of the total cone angle, 5θ, of the 5 surrounding ligands (L', L'').

The major difficulties associated with the catalyst at present are its air sensitivity and temperature instability. Studies are in progress to address these problems. The studies to date have concentrated on the catalytic behaviour of the new ruthenium complexes. Non-catalytic studies are required to quantify the equilibrium concentrations of the various ruthenium species in solution.

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