Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 16.[1] Homogeneous Hydrogenation Catalysts

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A number of pentamethylcyclopentadienyl-rhodium and -iridium complexes catalyse the hydrogenation of olefins under ambient conditions. The complexes $[\{M(C_5Me_5)X_2\}_2]$ (X = Cl, Br, or I, and M = Rh or Ir; M = Rh and X = NO_3), $[\{M(C_5Me_5)\}_2HX_3]$ (M = Rh and X = Cl or Br; M = Ir and X = Cl, Br, or I) and $[\{Ir(C_5Me_5)HX\}_2]$ (X = Cl or Br) are, in the presence of triethylamine, particularly efficient catalysts in propan-2-ol and, to a lesser extent, in dichloromethane. In the presence of base the μ-chloro-complexes $[\{M(C_5Me_5)Cl_2\}_2]$ (M = Rh or Ir) are more active than the μ-hydrido-complexes $[\{M(C_5Me_5)\}_2H_xCl_{4-x}]$ (M = Rh, x = 1; M = Ir, x = 1 or 2) and the tri-μ-hydrido-complex $[\{Ir(C_5Me_5)\}_2H_3]^+Cl^-$ is inactive. Dienes, acetylenes, and olefins bearing functional groups are readily reduced by $[\{M(C_5Me_5)\}_2HCl_3]$ (M = Rh or Ir) at 100 atm and 20 °C; the functional groups were not reduced. The results of preliminary kinetic studies on these systems suggest that alkene hydrogenations in the presence of $[\{M(C_5Me_5)Cl_2\}_2]$ (M = Rh or Ir) and $[\{Ir(C_5Me_5)HCl\}_2]$ involve monomeric active species whereas those carried out using $[\{M(C_5Me_5)\}_2HCl_3]$ (M = Rh or Ir) proceed *via* dimeric intermediates.

HOMOGENEOUS hydrogenation of organic compounds catalysed by transition-metal complexes continues to be a topic of both commercial and academic interest.[2] We have examined the catalytic activity of a number of pentamethylcyclopentadienyl-rhodium and -iridium complexes and we now report our results. Many of these compounds are very efficient hydrogenation catalysts; they are not reduced to metal under normal conditions and they are stable to air and are also soluble in a variety of solvents. Preliminary reports on olefin [3a,b] and arene [3c] hydrogenation have appeared.

In an effort to understand how these complexes function

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[1] Part 15, C. White, S. J. Thompson, and P. M. Maitlis, *J. Organometallic Chem.*, 1977, **136**, 87.

[2] For recent reviews on this topic see (*a*) G. Dolcetti and N. W. Hoffman, *Inorg. Chim. Acta*, 1974, **9**, 269; (*b*) B. R. James, 'Homogeneous Hydrogenation,' Wiley, New York, 1973.

[3] (*a*) C. White, D. S. Gill, J. W. Kang, H. B. Lee, and P. M. Maitlis, *Chem. Comm.*, 1971, 734; (*b*) P. M. Maitlis, C. White, J. W. Kang, and D. S. Gill, U.S.P. 1974, 3,849,459; (*c*) M. J. H. Russell, C. White, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1977, 427.

as olefin hydrogenation catalysts we have also carried out kinetic studies using the complexes $[\{M(C_5Me_5)Cl_2\}_2]$,* $[\{M(C_5Me_5)\}_2HCl_3]$, and $[\{Ir(C_5Me_5)HCl\}_2]$. These studies have added significance in that although there are many reports in the literature of dimeric compounds or bimetallic systems which catalyse the homogeneous hydrogenation of olefins,[2] few mechanistic studies of such systems have been carried out. Of those studied in detail, most appear to require conversion into an active monomeric form, for example $[\{Cr(C_5H_5)(CO)_3\}_2]$,[4] $[\{RuCl_2(C_6H_6)\}_2]$,[5] $[\{Rh(PPh_3)(dmgh)_2\}_2]$,[6,7] and $[\{MCl(C_8H_{14})_2\}_2]$.[8,9] Hydrogenations carried out in the presence of stearate complexes of the first-row transition-elements scandium(III) to zinc(II) were postulated to proceed *via* dimeric species; [10a] however, serious doubts have recently been expressed about this work.[10b] Active dimeric species have been shown to be involved in the $Rh_2(OCOMe)_4$-catalysed hydrogenation of olefins.[11]

RESULTS

The relative activities of various pentamethylcyclopentadienyl-rhodium and -iridium complexes were determined both in propan-2-ol and dichloromethane as solvents. Cyclohexene was used as the substrate and hydrogenation was carried out both with and without triethylamine as a co-catalyst. Hydrogenation proceeded readily at ambient temperature and atmospheric pressure and the initial rates of hydrogenation uptake are given in Table 1. For comparison the rates of hydrogen absorption were also measured for $[RhCl(PPh_3)_3]$ under similar conditions. The following conclusions may be drawn:

(*a*) The iridium complexes are always more active than the analogous rhodium ones.

(*b*) Taking account of the fact that a molecule of $[\{Rh(C_5Me_5)Cl_2\}_2]$ contains two rhodium atoms, this complex in propan-2-ol has an *activity per rhodium atom* twice that of $[RhCl(PPh_3)_3]$.

(*c*) The catalytic activities of the complexes are affected by the presence of a base, NEt_3. The complexes $[\{M(C_5Me_5)X_2\}_n]$ (M = Rh or Ir; $n = 2$; X = Cl, Br, or I; M = Rh, $X = NO_3$) are clearly activated by base suggesting that heterolytic activation of hydrogen is a predominant reaction in the catalytic cycle. Since these complexes are known to react with hydrogen in the presence of a base to give the hydrido-complexes (2),[12] it might at first be assumed that the initial step in the catalytic cycle in the presence of an olefin is still the formation of the monohydrido-complexes (2). This cannot be so, however, since examination of the data in Table 1 reveals that the halides (1) in the presence of NEt_3 are usually much more active catalysts than the corresponding hydrido-complexes, especially in propan-2-ol.

$$\underset{(1)}{[\{M(C_5Me_5)X_2\}_2]} + H_2 \rightleftharpoons \underset{(2)}{[\{M(C_5Me_5)\}_2HX_3]} + HX \quad (X = Cl, Br, or I)$$

The effect of NEt_3 on the other catalysts is not so clearly defined except for the acetate complexes where it retards hydrogenation.

TABLE 1

Hydrogenation of cyclohexene (11.8 mmol) using various rhodium and iridium complexes at 1 atm and 24 °C

			Initial H_2 uptake $cm^3\ min^{-1}$	
Complex [a]	Ref.	Et_3N mmol	Pr^iOH	CH_2Cl_2
$[RhCl(PPh_3)_3]$	19	Nil	4.3	4.2
$[\{Rh(C_5Me_5)Cl_2\}_2]$ [b]	*c*	7.2	9.8	2.3
$[\{Rh(C_5Me_5)Br_2\}_2]$ [b]	*d*	7.2	6.5	2.2
$[\{Rh(C_5Me_5)I_2\}_2]$ [b]	*c*	7.2	0.6	0.2
$[\{Rh(C_5Me_5)(NO_3)_2\}_n]$	*d*	Nil	0.7	0.2
		7.2	7.6	2.7
$[\{Rh(C_5Me_5)(OCOMe)_2(H_2O)\}_n]$	*c*	Nil	3.5	3.0
		7.2	0.6	0.5
$[\{Rh(C_5Me_5)\}_2HCl_3]$	12	Nil	2.7	0.5
		7.2	5.1	2.2
$[\{Rh(C_5Me_5)\}_2HBr_3]$	*d*	Nil	3.2	1.9
$[\{Rh(C_5Me_5)\}_2H(OCOMe)_2]$-$H(OCOMe)_2$	12	Nil		2.5
$[\{Rh(C_5Me_5)\}_2H(OCOMe)_2]$-$[PF_6]$ [b]	12	7.2	Nil	Nil
$[\{Ir(C_5Me_5)Cl_2\}_2]$ [b]	*c*	0.36	27.3	8.4
$[\{Ir(C_5Me_5)Br_2\}_2]$ [b]	*d*	0.36	14.6	5.6
$[\{Ir(C_5Me_5)_2I_2\}_2]$ [b]	*c*	0.36	7.2	7.3
$[\{Ir(C_5Me_5)\}_2HCl_3]$	12	Nil	7.1	1.5
		0.36	15.3	8.2
$[\{Ir(C_5Me_5)\}_2HBr_3]$	*d*	Nil	7.8	2.8
		0.36	9.7	2.2
$[\{Ir(C_5Me_5)\}_2HI_3]$	*d*	Nil	7.3	1.4
		0.36	8.0	0.7
$[\{Ir(C_5Me_5)HCl\}_2]$	*d*	Nil	12.7	4.2
		0.36	13.2	3.2
$[\{Ir(C_5Me_5)HBr\}_2]$	*d*	Nil	15.6	0.9

[a] 0.04 mmol in reaction mixture (20 cm^3), n assumed to be 2 for $[\{Rh(C_5Me_5)(NO_3)_2\}_n]$ and $[\{Rh(C_5Me_5)(OCOMe)_2(H_2O)\}_n]$; 0.08 mmol of catalyst used for $[RhCl(PPh_3)_3]$. [b] Inactive in the absence of NEt_3. The following complexes were inactive, even in the presence of NEt_3 (7.2 mmol) $[Rh(C_5Me_5)Cl_2(PPh_3)]$, $[Rh(C_5Me_5)(PMe_2Ph)_2Cl]X$ (X = Cl or BPh_4), $[\{Rh(C_5Me_5)\}_2(OH)_3][BPh_4]$ and $[\{Ir(C_5Me_5)\}_2H_3]X$ ($X = Cl^-$ or PF_6^-). [c] J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1969, **91**, 5970. [d] D. S. Gill and P. M. Maitlis, *J. Organometallic Chem.*, 1975, **87**, 359.

(*d*) Other ligands on the metal markedly modify the reactivities of the complexes. In both propan-2-ol and dichloromethane, in the presence of a base, the activity of $[\{M(C_5Me_5)X_2\}_2]$ decreases in the order $X = Cl > Br > I$. In these solvents in the *absence* of base reactivity increases on replacing a halogeno- by a hydrido-ligand (although $[\{Ir(C_5Me_5)\}_2H_3]Cl$ is inactive) but in the presence of an excess of base this trend is reversed for the chloro- and bromo-complexes and the catalytic activity now decreases

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* Unless specified M = Rh or Ir.

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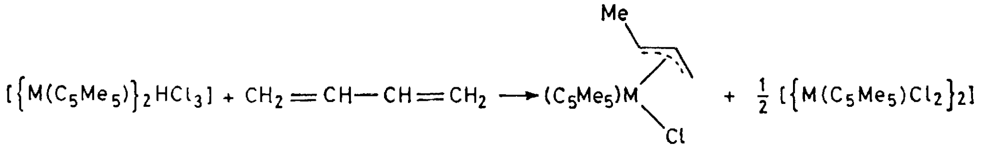
in the order, $[\{Ir(C_5Me_5)X_2\}_2] > [\{Ir(C_5Me_5)\}_2HX_3] > [\{Ir(C_5Me_5)HX\}_2] \gg [\{Ir(C_5Me_5)\}_2H_3]Cl$ (X = Cl or Br). This latter trend is also observed for the iodo-complexes in dichloromethane but in propan-2-ol the hydrido-complex $[\{Ir(C_5Me_5)\}_2HI_3]$ is slightly more active than the iodo-complex $[\{Ir(C_5Me_5)I_2\}_2]$ (Table 1).

(*e*) The phosphine complexes such as $[Rh(C_5Me_5)Cl_2(PPh_3)]$ and $[Rh(C_5Me_5)(PMe_2Ph)_2Cl]X$ (X = Cl or BPh_4) are inactive, even in the presence of NEt_3. We attribute this inactivity to the fact that these complexes are not dimers, as are the active catalysts listed in Table 1, and therefore they cannot readily generate an active site by bridge cleavage. Other co-ordinatively saturated monomeric rhodium(III) complexes have been reported to catalyse olefin hydrogenation {*e.g.* $[RhCl_3L_3]$, L = PPh_3,[13] $PPh(Me)Pr^i$ [14] and (biphenyl-4-yl)(1-naphthyl)(phenyl) phosphine [15]} but more forcing conditions than those used in this study were generally employed.

Addition of two equivalents of triphenylphosphine or triphenyl phosphite rendered the complexes $[\{M(C_5Me_5)\}_2XCl_3]$ (X = H or Cl) completely inactive even in the presence of triethylamine; this is presumably due to the formation of co-ordinatively saturated complexes, *e.g.* $[M(C_5Me_5)Cl_2(PPh_3)]$. *p*-Toluidine similarly deactivates $[\{Rh(C_5Me_5)Cl_2\}_2]$ but this complex retains 20% of its activity in the presence of eight equivalents of dimethyl sulphide.[16] The activity of $[\{Rh(C_5Me_5)\}_2HCl_3]$ in propan-2-ol is unaffected by addition of two equivalents of benzonitrile although more does lead to deactivation (*e.g.* 8 equivalents reduce the activity by *ca.* 80%).

The abilities of the catalysts $[\{M(C_5Me_5)\}_2HCl_3]$ to reduce a wide range of substrates was examined (Table 2). Under ambient conditions, both reduce mono-olefins whereas dienes and acetylenes are not reduced but react with these catalysts; *e.g.*



A number of such reactions have previously been reported.[17,18] Dienes, acetylenes and olefins with functional groups are hydrogenated relatively easily at 20 °C and 100 atm (Table 3). Functional groups (*e.g.* C=O) are not normally reduced under these conditions although acetone is slowly reduced to propan-2-ol. Functional groups in the olefin do, however, retard the reduction in varying degrees. As expected terminal olefins are reduced faster than internal ones but whereas $[RhCl(PPh_3)_3]$ reduces cyclohexene 50 times faster than 1-methylcyclohexene [19] the catalysts $[\{M(C_5Me_5)\}_2HCl_3]$ appear to be less selective in that the corresponding factor is approximately 3 for M = Rh and 7 for M = Ir. This may reflect a greater steric constraint in $[RhCl(PPh_3)_3]$ because of the bulky triphenylphosphine ligands.

TABLE 2

Rates of reduction of various substrates using $[\{M(C_5Me_5)\}_2HCl_3]$ in propan-2-ol at 1 atm and 24 °C [a]

Substrate	Rate of H_2-uptake $cm^3\ min^{-1}$ M = Rh	M = Ir
Hex-1-ene	7.1	1.9
Cyclohexene	5.1	7.1
4-Methylcyclohexene	3.5	5.6
1-Methylcyclohexene	1.7	0.9
Cyclopentene	5.0	5.1
4-Methylpent-1-ene	9.1	2.7
2-Methylpent-1-ene	2.8	4.2 [b]
cis-4-Methylpent-2-ene	2.6	3.8
trans-4-Methylpent-2-ene	1.4	2.4
Mesityl oxide	0.4	3.8
2,4-Dimethylpent-2-en-1-ol	0.1	0.4
Allyl benzene	0.4	0.5
Cinnamaldehyde	0.4	

[a] 20 cm^3 reaction mixture contained 0.04 mmol $[\{M(C_5Me_5)\}_2HCl_3]$, 11.8 mmol substrate and, for M = Rh only, NEt_3 (7.2 mmol). [b] Rapid fall off in hydrogen uptake due to isomerization to 2-methylpent-2-ene.

TABLE 3

Hydrogenations at 100 atm/20 °C of substituted olefins, dienes, and acetylenes using $[\{M(C_5Me_5)\}_2HCl_3]$ in propan-2-ol [a]

Substrate	Time [b] h M = Rh	M = Ir	Products
4-Vinylcyclohexene	0.75		Ethylcyclohexane
Norbornadiene [b]	1		Norbornane
Cyclo-octa-1,3-diene	3	1	Cyclo-octane
Allylbenzene	3.5	1	Propylbenzene
Hexa-1,5-diene	4	3	Hexane
Mesityl oxide	4		Isobutyl methyl ketone
2-Methylpent-4-en-2-ol	4		2-Methylpentan-2-ol
β-Methylstyrene	7.5		Propylbenzene
Vinyl acetate	10		33% Reduction to ethyl acetate
Crotonaldehyde	10		30% Reduction to n-butyraldehyde
Diphenylacetylene	10		Mixture of 70% *cis*- and *trans*-stilbene + 30% dibenzyl
Acetone [c]	20		3—4% reduction to propan-2-ol

[a] Reaction mixture contained $[\{M(C_5Me_5)\}_2HCl_3]$ (0.01 mmol), Pr^iOH (5 cm^3) and substrate (7.6 mmol). [b] Unless stated otherwise, no unchanged substrate remained after this period. [c] Acetone used as solvent in place of Pr^iOH.

cis-Olefins are reduced faster than *trans*-olefins by $[\{Rh(C_5Me_5)\}_2HCl_3]$. No definite inferences can be drawn for $[\{Ir(C_5Me_5)\}_2HCl_3]$ since it is a powerful catalyst for the isomerization of olefins and equilibrium is attained in a few minutes. With terminal olefins, initial rates are high but they fall off sharply, usually within 10 minutes, due to isomerization of terminal olefins to internal olefins which are then reduced at much slower rates.

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Kinetic Studies

Catalyst $[\{M(C_5Me_5)Cl_2\}_2]$.—(a) *Effect of triethylamine upon the catalytic activity.* These halide complexes catalyse hydrogenation of olefins only in the presence of base. Base therefore plays an important role in the generation of the active catalyst and the effect upon the rate of hydrogenation of cyclohexene of adding various amounts of triethylamine was studied. Triethylamine was chosen as a base since it did not form stable complexes with these complexes; other amines (*e.g.* $EtPr^i{}_2N$) and Na_2CO_3 appeared to promote hydrogenation to a similar degree.

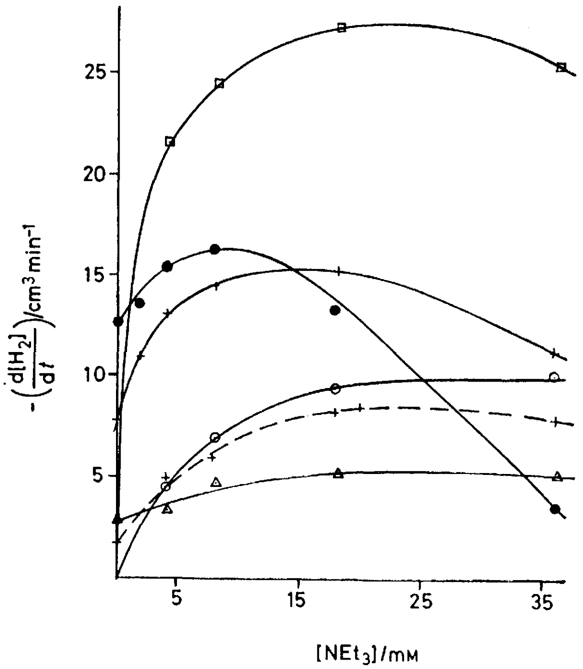


FIGURE 1 Initial rate of hydrogenation of cyclohexene as a function of triethylamine concentration in propan-2-ol using various catalysts: (○) $[\{Rh(C_5Me_5)Cl_2\}_2]$, (□) $[\{Ir(C_5Me_5)Cl_2\}_2]$, (△) $[\{Rh(C_5Me_5)\}_2HCl_3]$, (+) $[\{Ir(C_5Me_5)\}_2HCl_3]$ (—— propan-2-ol, — — — — dichloromethane), (●) $[\{Ir(C_5Me_5)HCl\}_2]$; [catalyst] = 2mM, [cyclohexene] = 0.592M, 24 °C

The most striking feature of the results (Figure 1) is that the rate of hydrogenation increases rapidly up to *ca.* 0.32 mmol (*i.e.* 8 equivalents) of triethylamine. Addition of more amine results in only a small further increase in rate and, in the case of $[\{Ir(C_5Me_5)Cl_2\}_2]$, a large excess of NEt_3 leads to a decrease in the rate of hydrogenation.

The main function of the NEt_3 in the catalytic process is probably to bind the HCl generated (Scheme) although we cannot exclude the possibility that it also facilitates bridge-cleavage or stabilises active intermediates.

The catalyst residues were examined by ^1H n.m.r. spectroscopy after completion of the hydrogenation reaction. In the case of $[\{Ir(C_5Me_5)Cl_2\}_2]$, $[\{Ir(C_5Me_5)HCl\}_2]$ began to be formed at low concentrations of triethylamine, whilst at higher concentrations $[\{Ir(C_5Me_5)\}_2H_3]^+$ was also formed especially when the hydrogenations were carried out in propan-2-ol rather than dichloromethane; no such di-μ-hydrido- or tri-μ-hydrido-complexes were detected in the rhodium system. Since the di-μ-hydrido-complex has a lower catalytic activity than $[\{Ir(C_5Me_5)Cl_2\}_2]$ (Table 1) and the tri-μ-hydrido-complex is completely inactive, this explains why $[\{Ir(C_5Me_5)Cl_2\}_2]$ in propan-2-ol is deactivated by addition of large excesses of triethylamine. In contrast, $[\{Rh(C_5Me_5)Cl_2\}_2]$ is not deactivated by an excess of triethylamine and this correlates with our inability to obtain the corresponding di-μ- and tri-μ-hydrido-rhodium complexes.

(b) *Dependence on catalyst concentration.* Although plots of hydrogen uptake against $[\{M(C_5Me_5)Cl_2\}_2]$ were non-linear, on plotting hydrogen uptake against $[\{M(C_5Me_5)Cl_2\}_2]^{\frac{1}{2}}$ good linear plots were obtained for both M = Rh and Ir in dichloromethane and propan-2-ol (Figure 2).

(c) *Dependence on olefin concentration.* In propan-2-ol the rate of hydrogen uptake did not increase linearly with increasing cyclohexene concentration but approached an asymptotic value. However, the plot of the reciprocal of this rate against the reciprocal of the cyclohexene concentration was a straight line for the rhodium and iridium complexes (Figure 3). Similar plots were obtained when dichloromethane solvent was used.

(d) *Dependence on hydrogen pressure.* For the $[\{Ir(C_5Me_5)Cl_2\}_2]$-catalysed hydrogenation of cyclohexene in propan-2-ol or dichloromethane, plots of rate of hydrogen uptake against $p(H_2)$ showed marked deviations from linearity. Good straight lines were, however, obtained when the rates were plotted against $[p(H_2)]^2$ (Figure 4).

Catalyst $[\{M(C_5Me_5)\}_2HCl_3]$.—(a) *Effect of triethylamine upon the catalytic activity.* The mono-μ-hydrido-complexes even catalyse the reduction of olefins in the absence of a base; however, like the chloro-complexes $[\{M(C_5Me_5)Cl_2\}_2]$ the catalytic activity is enhanced by the addition of triethylamine. The effect of triethylamine is very dependent upon both the metal and the solvent. In dichloromethane the rate of reduction of cyclohexene with $[\{Ir(C_5Me_5)\}_2HCl_3]$ increases rapidly with increasing amounts of triethylamine but reaches a limiting value (Figure 1); the same catalyst in propan-2-ol is activated by addition of up to *ca.* 7 equivalents of triethylamine but the rate of hydrogenation then falls off with further addition of amine.

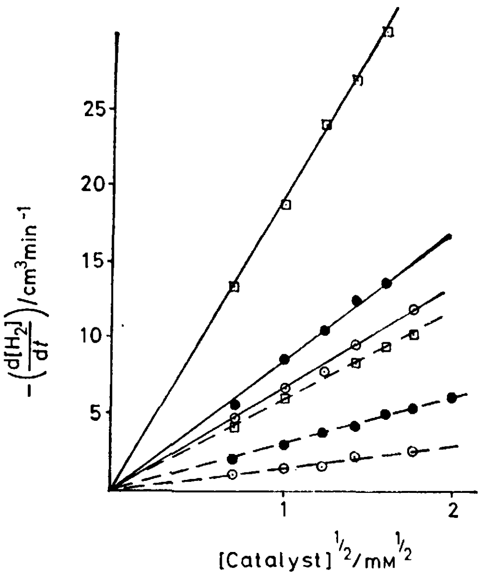


FIGURE 2 Plot of initial rate of hydrogenation of cyclohexene against the square root of catalyst concentration in propan-2-ol (——) or dichloromethane (— — — —): (○) $[\{Rh(C_5Me_5)Cl_2\}_2]$: NEt_3 = 1 : 180, (□) $[\{Ir(C_5Me_5)Cl_2\}_2]$: NEt_3 = 1 : 9, (●) $[\{Ir(C_5Me_5)HCl\}_2]$ no NEt_3 present; [cyclohexene] = 0.592M, 24 °C

In contrast, the rate of hydrogenation of cyclohexene with concentration of [$\{Rh(C_5Me_5)\}_2HCl_3$] increases with increasing amine concentration up to a maximum value for *ca.* 18 equivalents in dichloromethane or 8 equivalents in propan-2-ol; addition of further amine (up to 180 equivalents) produces no significant change in rate in either solvent.

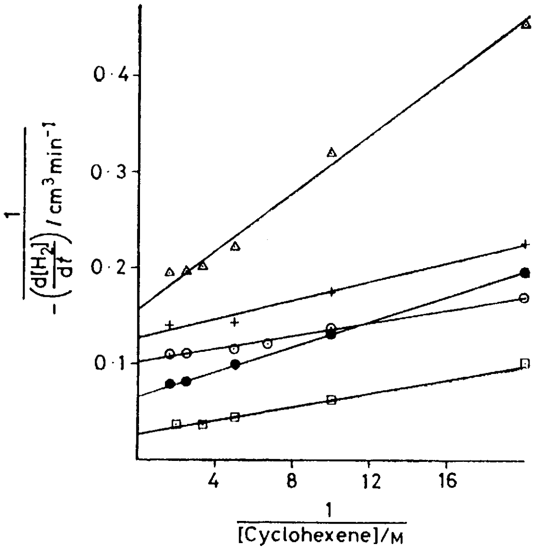


FIGURE 3 Plot of the reciprocal of the initial rate of hydrogen uptake against the reciprocal of the cyclohexene concentration in propan-2-ol at 24 °C. [Catalyst] = 2mM; (○) [$\{Rh(C_5Me_5)Cl_2\}_2$] : NEt_3 = 1 : 180, (□) [$\{Ir(C_5Me_5)Cl_2\}_2$] : NEt_3 = 1 : 9, (△) [$\{Rh(C_5Me_5)\}_2HCl_3$] : NEt_3 = 1 : 18, (+) [$\{Ir(C_5Me_5)\}_2HCl_3$] no NEt_3 present, (●) [$\{Ir(C_5Me_5)HCl\}_2$] no NEt_3 present

The fall off in catalytic activity of [$\{Ir(C_5Me_5)\}_2HCl_3$] in propan-2-ol at high amine concentration can again be attributed to formation of the less-active complex [$\{Ir(C_5Me_5)HCl\}_2$] and the inactive complex [$\{Ir(C_5Me_5)\}_2H_3$]Cl. Examination of the ^1H n.m.r. spectra of the catalyst residues after completion of the hydrogenation reaction showed the presence of both these species.

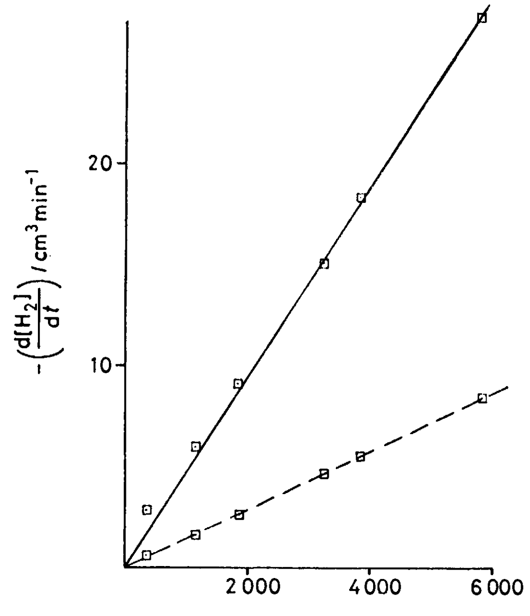


FIGURE 4 Dependence of initial rate of hydrogenation of cyclohexene on the square of the hydrogen pressure in propan-2-ol (—) or dichloromethane (— — — —) [$\{Ir(C_5Me_5)Cl_2\}_2$] = 2mM, [cyclohexene] = 0.592M, [NEt_3] = 0.018M, 24 °C

TABLE 4

Effect of solvent on the rate of hydrogenation of cyclohexene using [$\{M(C_5Me_5)\}_2HCl_3$] [a]

		Rate of H_2 uptake cm^3 min^{-1}	
Solvent	ε [b]	M = Rh	M = Ir
Benzene	2.28	0.5	1.0
Dichloromethane	9.08	0.1	1.5
t-Butyl alcohol	10.9	1.5	2.3
Propan-2-ol	18.3	2.7	7.1
Propan-1-ol	20.1	1.6	2.3
Acetone	20.7	1.0	3.6
Ethanol	24.3	0.8	1.9
Dimethyl sulphoxide	46.7	Nil	Nil

[a] 20 cm^3 reaction mixture contained 0.04 mmol catalyst and 1.2 cm^3 cyclohexene. [b] 'Handbook of Chemistry and Physics,' Chemical Rubber Company, Cleveland, 1972.

(b) *Effect of solvent.* Propan-2-ol as solvent consistently gave higher rates of hydrogenation than dichloromethane; in addition, as illustrated by the amine dependence discussed above, the behaviour of the catalyst often showed a solvent dependence. These observations led us to investigate further the effect of solvent on the activity and the data (Table 4) indicate that the hydrogenation appears to be favoured by polar and weakly co-ordinating solvents, particularly propan-2-ol. Hydrogen uptake was low in non-polar solvents and nil in dimethyl sulphoxide, a polar but co-ordinating solvent.

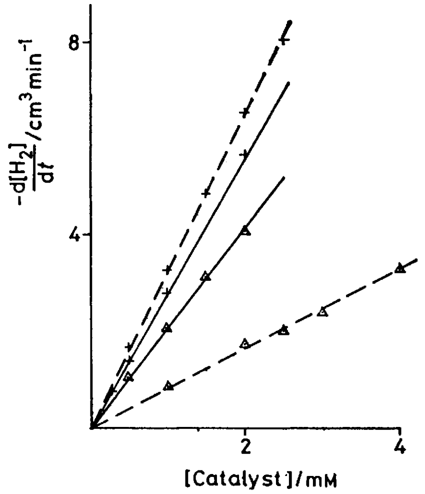


FIGURE 5 Initial rate of hydrogenation of cyclohexene as a function of catalyst concentration in propan-2-ol (———) or dichloromethane (— — — —): (△) [$\{Rh(C_5Me_5)\}_2HCl_3$] : NEt_3 = 1 : 18; (+) [$\{Ir(C_5Me_5)\}_2HCl_3$] : NEt_3 = 1 : 18 (CH_2Cl_2), no NEt_3 present in Pr^iOH; [cyclohexene] = 0.592M, 24 °C

(c) *Dependence on catalyst concentration.* Plots of rates of hydrogenation of cyclohexene against [$\{M(C_5Me_5)\}_2HCl_3$] gave good straight lines for both rhodium and iridium in dichloromethane and propan-2-ol (Figure 5). The first-order dependence on [$\{M(C_5Me_5)\}_2HCl_3$] suggests that this complex remains a dimer during the catalytic reaction, and this behaviour may be contrasted with the cases discussed above where the rates of hydrogen uptake varied linearly with $[\{M(C_5Me_5)Cl_2\}_2]^{\frac{1}{2}}$.

(d) *Dependence on olefin concentration.* The rate of hydrogenation of cyclohexene in either propan-2-ol or dichloromethane showed a first-order olefin dependence at low cyclohexene concentrations, but this became zero order at higher concentrations. Plots of the reciprocal of the rate against the reciprocal of the cyclohexene concentration were linear (Figure 3). A similar olefin dependence was observed for $[\{M(C_5Me_5)Cl_2\}_2]$.

(e) *Dependence on hydrogen pressure.* In contrast to $[\{M(C_5Me_5)Cl_2\}_2]$, $[\{M(C_5Me_5)\}_2HCl_3]$ gave linear plots of rate of hydrogen uptake against hydrogen pressure (Figure 6).

Catalyst $[\{Ir(C_5Me_5)HCl\}_2]$.—(a) *Effect of triethylamine on the rate.* Addition of up to 4 equivalents of triethylamine increased the rate of hydrogenation of cyclohexene by *ca.* 20%, this is to be contrasted with the complexes discussed previously where addition of 4 equivalents of triethylamine usually doubled the rate of hydrogenation. Addition of further amine to $[\{Ir(C_5Me_5)HCl\}_2]$ led to a marked decrease in activity (Figure 1). The ^1H n.m.r. spectra of the catalyst residues after hydrogenation in the presence of 9 equivalents of triethylamine showed that at least 85% of the catalyst remained unchanged and even in propan-2-ol less than 10% had been converted into the inactive $[\{Ir(C_5Me_5)\}_2H_3]Cl$. The drop in activity with increasing triethylamine concentration therefore cannot be entirely attributed to formation of the tri-μ-hydrido-species and indicates that the triethylamine is also hindering reaction in a different manner.

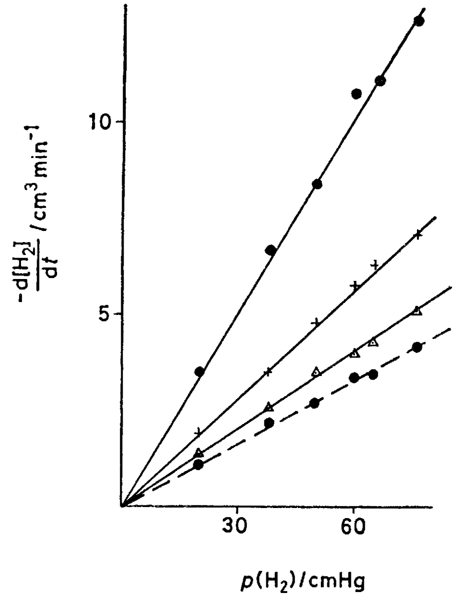


FIGURE 6 Plot of initial rate of hydrogenation of cyclohexene *vs.* hydrogen pressure in propan-2-ol (——) or dichloromethane (— — — —): [catalyst] = 2mM; (△) $[\{Rh(C_5Me_5)\}_2HCl_3]$: NEt_3 = 1 : 18; (+) $[\{Ir(C_5Me_5)\}_2HCl_3]$; (●) $[\{Ir(C_5Me_5)HCl\}_2]$; [cyclohexene] = 0.592mM, 24 °C

(b) *Dependence on catalyst concentration, hydrogen pressure, and olefin concentration.* In both propan-2-ol and dichloromethane in the absence of triethylamine, the rate of reduction of cyclohexene was dependent on $[\{Ir(C_5Me_5)HCl\}_2]^{\frac{1}{2}}$ and $p(H_2)$ (Figures 2 and 6). In propan-2-ol the olefin dependence was again first-order at low and zero-order at high cyclohexene concentrations; in dichloromethane, the rate was proportional to $[\text{olefin}]^1$ throughout the range examined (Figures 3 and 7).

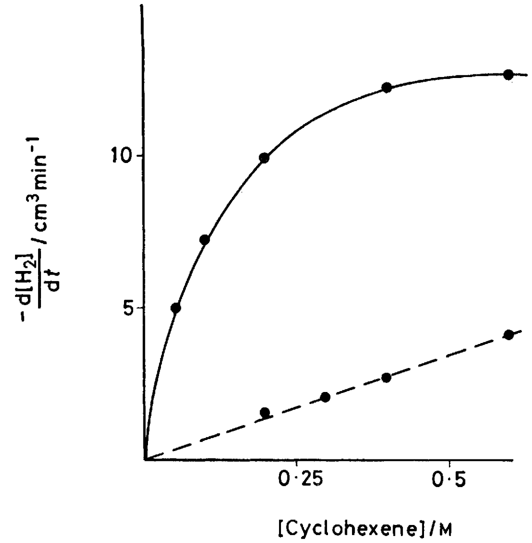


FIGURE 7 Initial rate of hydrogenation of cyclohexene as a function of cyclohexene concentration: (——) propan-2-ol, (— — — —) dichloromethane; $[\{Ir(C_5Me_5)HCl\}_2]$ = 2mM, 24 °C

Rate Equations.—The kinetic data obtained can be summarised by the following expressions; (i) for $[\{M(C_5Me_5)Cl_2\}_2]$ in propan-2-ol and dichloromethane:

$$\frac{-d[H_2]}{dt} = \frac{k[\{M(C_5Me_5)Cl_2\}_2]^{\frac{1}{2}}[p(H_2)]^2[\text{olefin}]}{1 + [\text{olefin}]} \qquad (1)$$

(ii) for $[\{M(C_5Me_5)\}_2HCl_3]$ in propan-2-ol and dichloromethane:

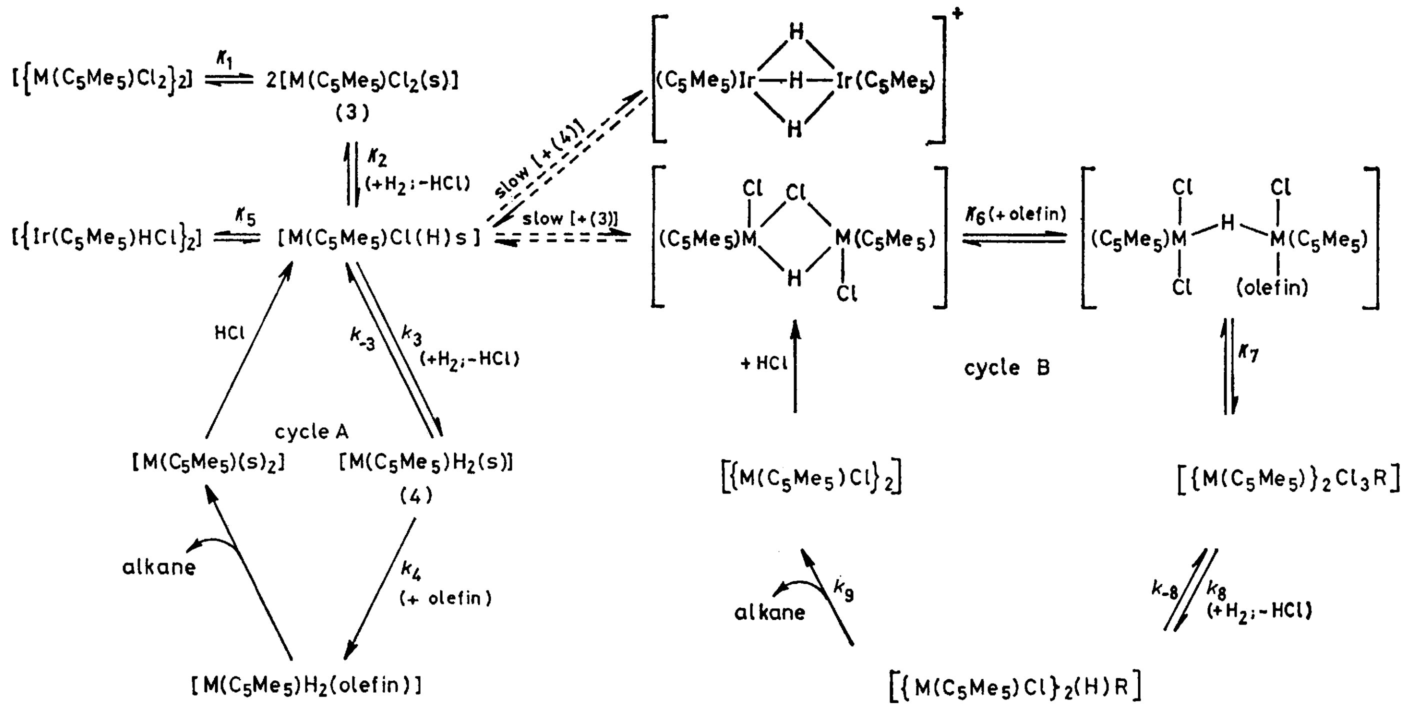
$$\frac{-d[H_2]}{dt} = \frac{k'[\{M(C_5Me_5)\}_2HCl_3][p(H_2)][\text{olefin}]}{1 + [\text{olefin}]} \qquad (2)$$

(iii) for $[\{Ir(C_5Me_5)HCl\}_2]$ in propan-2-ol:

$$\frac{-d[H_2]}{dt} = \frac{k''[\{Ir(C_5Me_5)HCl\}_2]^{\frac{1}{2}}[p(H_2)][\text{olefin}]}{1 + [\text{olefin}]} \qquad (3)$$

DISCUSSION

Mechanisms for Catalytic Hydrogenation.—These preliminary studies suggest that the detailed mechanisms of hydrogenation using these catalysts are exceedingly complex and our suggestions are summarised in the Scheme. In order to obtain even a limited understanding we have made the important assumption that two hydrogenation cycles exist (A and B in the Scheme) and that when the catalysts used are $[\{M(C_5Me_5)Cl_2\}_2]$ or $[\{Ir(C_5Me_5)HCl\}_2]$ cycle A is predominant and when $[\{M(C_5Me_5)\}_2HCl_3]$ are used the cycle B predominates. A similar proposal has recently been made for hydrogenations carried out using complexes of the type $[Rh(\text{diene})L_n]^+A^-$ (L = tertiary phosphine, arsine or phosphite, n = 2 or 3, $A^- = ClO_4^-$, BF_4^-, or PF_6^-) which are believed to proceed predominantly by one of three catalytic cycles, the cycle which predominates being



M = Rh or Ir; s = solvent

SCHEME

dependent upon the nature of the diene, L, and the solvent used.[20]

The evidence in favour of two distinct cycles A and B is that the characteristics of each group of catalysts, in both propan-2-ol and dichloromethane, are quite different as determined by their rates and their observed dependence on the reaction variables [equations (1)—(3)]. Against this must be set the observation that after hydrogenation involving one of the rhodium catalysts the ^{1}H n.m.r. spectra of the residues show the presence of both $[\{Rh(C_5Me_5)Cl_2\}_2]$ and $[\{Rh(C_5Me_5)\}_2HCl_3]$; similarly, after hydrogenation using one of the iridium catalysts the ^{1}H n.m.r. spectra show the presence of $[\{Ir(C_5Me_5)Cl_2\}_2]$, $[\{Ir(C_5Me_5)\}_2HCl_3]$, $[\{Ir(C_5Me_5)HCl\}_2]$, and $[\{Ir(C_5Me_5)\}_2H_3]Cl$. The relative amounts of the compounds obtained depends on the time of reaction, the solvent, and the amount of base; for the iridium catalysts the higher hydrides are present to larger extents in propan-2-ol and in the presence of base. It must be borne in mind, however, that the kinetic data are based on *initial* rates when presumably one species predominates.

More detailed analyses of data are presented below.

(i) Using $[\{M(C_5Me_5)Cl_2\}_2]$ as catalysts, the main catalytic pathway [cycle (A)] is:

$$[\{M(cp)Cl_2\}_2] \overset{K_1}{\rightleftharpoons} 2[M(cp)Cl_2(s)] \quad (cp = \eta^5\text{-}C_5Me_5,\ s = \text{solvent}) \tag{4}$$

$$[M(cp)Cl_2(s)] + H_2 \overset{K_2}{\rightleftharpoons} [M(cp)H(Cl)s] + HCl \tag{5}$$

$$[M(cp)H(Cl)s] + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [M(cp)H_2(s)] + HCl \tag{6}$$

$$[M(cp)H_2(s)] + \text{olefin} \xrightarrow[\text{slow}]{k_4} [M(cp)H_2(\text{olefin})] \tag{7}$$

$$[M(cp)H_2(\text{olefin})] \xrightarrow{\text{fast}} [M(cp)s_2] + \text{alkane} \tag{8}$$

$$[M(cp)s_2] + HCl \xrightarrow{\text{fast}} [M(cp)H(Cl)s] \tag{9}$$

From (4) and (5),

$$[M(cp)Cl_2(s)] = K_1^{\frac{1}{2}}[\{M(cp)Cl_2\}_2]^{\frac{1}{2}}$$

$$\text{and } [M(cp)H(Cl)s] = \frac{K_2[M(cp)Cl_2(s)][H_2]}{[HCl]}$$

Therefore

$$[M(cp)H(Cl)s] = \frac{K_1^{\frac{1}{2}}K_2[\{M(cp)Cl_2\}_2]^{\frac{1}{2}}[H_2]}{[HCl]} \tag{10}$$

Assuming a steady-state concentration of $[M(cp)H_2(s)]$

$$\frac{-d[M(cp)H_2(s)]}{dt} = k_4[M(cp)H_2(s)][\text{olefin}] + k_{-3}[M(cp)H_2(s)][HCl] - k_3[M(cp)H(Cl)s][H_2] = 0 \tag{11}$$

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[20] R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 1976, **98**, 2134.

Substituting for [M(cp)H(Cl)s] from (10) leads to

$$[\mathrm{M(cp)H_2(s)}] = \frac{k_3K_1^{\frac{1}{2}}K_2[\{\mathrm{M(cp)Cl_2}\}_2]^{\frac{1}{2}}[\mathrm{H_2}]^2}{(k_4[\mathrm{olefin}] + k_{-3}[\mathrm{HCl}])[\mathrm{HCl}]} \qquad (12)$$

Rate of hydrogen uptake = rate of alkane formation
= k_4[M(cp)H$_2$(s)][olefin]

Hence,

$$\frac{-\mathrm{d}[\mathrm{H_2}]}{\mathrm{d}t} = \frac{k_3k_4K_1^{\frac{1}{2}}K_2[\{\mathrm{M(cp)Cl_2}\}_2]^{\frac{1}{2}}[\mathrm{H_2}]^2[\mathrm{olefin}]}{[\mathrm{HCl}](k_4[\mathrm{olefin}] + k_{-3}[\mathrm{HCl}])} \qquad (13)$$

Equation (13) is in agreement with the observed rate equation (1) and is also entirely consistent with the observed dramatic activation by base.

(ii) With [{Ir(C$_5$Me$_5$)HCl}$_2$] as the catalyst, cycle A is again assumed to be the main catalytic pathway.

$$[\{\mathrm{Ir(cp)HCl}\}_2] \overset{K_5}{\rightleftharpoons} 2[\mathrm{Ir(cp)H(Cl)s}] \qquad (14)$$

(cp = η^5-C$_5$Me$_5$, s = solvent)

$$[\mathrm{Ir(cp)H(Cl)s}] + \mathrm{H_2} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{Ir(cp)H_2(s)}] + \mathrm{HCl} \qquad (6b)$$

$$[\mathrm{Ir(cp)H_2(s)}] + \mathrm{olefin} \underset{\mathrm{slow}}{\overset{K_4}{\rightleftharpoons}} [\mathrm{Ir(cp)H_2(olefin)}] \qquad (7b)$$

$$[\mathrm{Ir(cp)H_2(olefin)}] \xrightarrow{\mathrm{fast}} [\mathrm{Ir(cp)(s)_2}] + \mathrm{alkane} \qquad (8b)$$

$$[\mathrm{Ir(cp)(s)_2}] + \mathrm{HCl} \xrightarrow{\mathrm{fast}} [\mathrm{Ir(cp)H(Cl)s}] \qquad (9b)$$

Application of a steady-state approximation for the [Ir(cp)H$_2$(s)] species results in the rate law

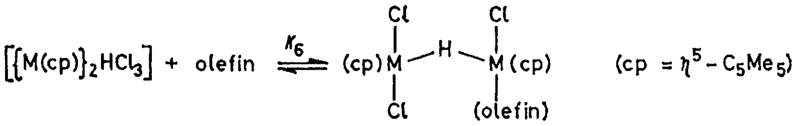
$$\frac{-\mathrm{d}[\mathrm{H_2}]}{\mathrm{d}t} = \frac{-\mathrm{d}[\mathrm{olefin}]}{\mathrm{d}t} = \frac{k_3k_4[\mathrm{Ir(cp)H(Cl)s}][\mathrm{H_2}][\mathrm{olefin}]}{k_4[\mathrm{olefin}] + k_{-3}[\mathrm{HCl}]} \qquad (15)$$

From (14) [Ir(cp)H(Cl)s] = $K_5^{\frac{1}{2}}[\{\mathrm{Ir(cp)HCl}\}_2]^{\frac{1}{2}}$
Hence

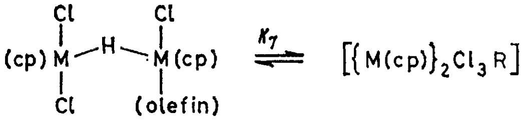
$$\frac{-\mathrm{d}[\mathrm{H_2}]}{\mathrm{d}t} = \frac{k_3k_4K_5^{\frac{1}{2}}[\{\mathrm{Ir(cp)HCl}\}_2]^{\frac{1}{2}}[\mathrm{H_2}][\mathrm{olefin}]}{k_4[\mathrm{olefin}] + k_{-3}[\mathrm{HCl}]} \qquad (16)$$

Equation (16) is in agreement with the observed rate equation (3) when propan-2-ol is used as the solvent and is also consistent with the observed activation by base. Further, it can be seen by comparing the rate equations (13) and (16) that the suggested mechanisms successfully account for the observation that the [{M(C$_5$Me$_5$)Cl$_2$}$_2$] catalytic systems are activated to a much higher degree than [{Ir(C$_5$Me$_5$)HCl}$_2$] by the addition of base. It is, however, not clear why the olefin dependence should differ in propan-2-ol and dichloromethane.

(iii) When [{M(C$_5$Me$_5$)}$_2$HCl$_3$] is used as the catalyst the observed first-order dependence on [{M(C$_5$Me$_5$)}$_2$HCl$_3$] suggests that hydrogenation involves a dimeric species. A mechanism involving initial heterolytic activation of hydrogen must be ruled out since this would lead to [{M(C$_5$Me$_5$)HCl}$_2$] and, not only does [{Ir(C$_5$Me$_5$)HCl}$_2$]



(cp = η^5-C$_5$Me$_5$) (17)



(18)

$$[\{\mathrm{M(cp)}\}_2\mathrm{Cl_3R}] + \mathrm{H_2} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} [\{\mathrm{M(cp)Cl}\}_2\mathrm{(H)R}] + \mathrm{HCl} \qquad (19)$$

$$[\{\mathrm{M(cp)Cl}\}_2\mathrm{(H)R}] \overset{k_9}{\rightleftharpoons} [\{\mathrm{M(cp)Cl}\}_2] + \mathrm{alkane} \qquad (20)$$

$$[\{\mathrm{M(cp)Cl}\}_2] + \mathrm{HCl} \xrightarrow{\mathrm{fast}} [\{\mathrm{M(cp)}\}_2\mathrm{(H)Cl_3}] \qquad (21)$$

appear to dissociate into monomers, but it also has a lower activity than $[\{Ir(C_5Me_5)\}_2HCl_3]$ in the presence of base.

In contrast, strong support for a mechanism involving initial activation of olefin comes from the observation that of the complexes investigated, the complexes $[\{M(C_5Me_5)\}_2HCl_3]$ were the most efficient catalysts for the isomerisation of alkenes; that the rates of alkene isomerisation are comparable with the rates of hydrogenation is clearly demonstrated in the reduction of 2-methylpent-1-ene using $[\{Ir(C_5Me_5)\}_2HCl_3]$ where the rate of hydrogenation decreases sharply within the first few minutes due to the conversion of the starting olefin to 2-methylpent-2-ene (Table 2). It is also pertinent to note that at no time during our investigation of olefin isomerisation reactions with $[\{M(C_5Me_5)\}_2HCl_3]$ did we observe disproportionation into $[\{M(C_5Me_5)HCl\}_2]$ and $[\{M(C_5Me_5)Cl_2\}_2]$ which lends support to the proposal that olefins react directly with the dimeric complexes $[\{M(C_5Me_5)\}_2HCl_3]$.

No completely satisfactory detailed mechanism for cycle B can be given at this time, but we tentatively suggest that the reactions (17)—(21) take place when cyclohexene is hydrogenated in the presence of $[\{M(C_5Me_5)\}_2HCl_3]$.

Assuming a steady state concentration of $[\{M(cp)Cl\}_2H(R)]$ leads to the rate law

$$\frac{-d[H_2]}{dt} = \frac{d[alkane]}{dt} = \frac{k_8k_9[\{M(cp)Cl\}_2R(Cl)][H_2]}{k_9 + k_{-8}[HCl]} \quad (22)$$

From (17) and (18)

$$[\{M(cp)Cl\}_2R(Cl)] = K_6K_7[\{M(cp)\}_2HCl_3][olefin] \quad (23)$$

$$\frac{-d[H_2]}{dt} = \frac{k_8k_9K_6K_7[\{M(cp)\}_2HCl_3][H_2][olefin]}{k_9 + k_{-8}[HCl]} \quad (24)$$

Equation (24) is consistent with the observed activation by base and is in close agreement with the observed rate equation (2). It does not, however, predict the observed change over to zero olefin dependence at high olefin concentrations. To account for this it is necessary to assume that K_6 is large so that at high olefin concentrations all the $[\{M(C_5Me_5)\}_2HCl_3]$ is complexed with olefin but, unfortunately, we have been unable to obtain any evidence to support this assumption.

Conclusion.—The mechanisms of these reactions are clearly complex and a more detailed analysis must await further results. It is, however, clear that these compounds function as very efficient homogeneous catalysts towards alkenes. Kinetic studies based on initial rates suggest that two basic catalytic cycles operate and that hydrogenations in the presence of $[\{M(C_5Me_5)Cl_2\}_2]$ or $[\{Ir(C_5Me_5)HCl\}_2]$ involve active monomeric species whereas those carried out with $[\{M(C_5Me_5)\}_2HCl_3]$ involve active dimeric species.

Finally, it is worth re-emphasising the rather surprising result that when the catalysts operate under optimum conditions (*i.e.* in the presence of an appropriate amount of base) it is the chloro-complexes, $[\{M(C_5Me_5)Cl_2\}_2]$ rather than the μ-hydrido-complexes $[\{M(C_5Me_5)\}_2H_xCl_{4-x}]$. ($M = Rh$, $x = 1$, $M = Ir$, $x = 1$ or 2) which are the most active catalysts (Figure 1) and that the tri-μ-hydrido-complex $[\{Ir(C_5Me_5)\}_2H_3]^+$ is quite inactive. We believe that this is due to μ-chloro-bridges being more easily cleaved than μ-hydrido-bridges.

EXPERIMENTAL

The preparations of the complexes are described in the references listed in Table 1. For hydrogen reactions reagent-grade solvents were used and these were freshly distilled under nitrogen; dichloromethane was in addition deacidified by standing over sodium carbonate. All olefins were purified before use by passing them through an alumina column (60 cm × 4 cm) under nitrogen; they were then dried over calcium hydride and finally distilled under nitrogen immediately before use. Their purity was confirmed by n.m.r. and v.p.c.

Hydrogenation Studies.—All gas uptake measurements were made using a conventional constant pressure hydrogenation apparatus fitted with a 100 ml Pyrex flask having a side arm fitted with a tap and sealed with a serum cap. The side arm was used to introduce olefins into a closed system. The reaction flask was flattened on one side to accommodate a Teflon-coated magnetic stirrer which was driven by an electric motor so that it operated at the gas-liquid interface.

Measured amounts of the catalyst, solvent and, where necessary, triethylamine were added to the reaction flask and the whole apparatus alternately evacuated and filled with hydrogen several times. The stirrer motor was started and the solution was saturated with hydrogen for 10 minutes after which time stirring was stopped and a known amount of olefin was introduced through the side arm of the flask. The system was allowed to equilibrate for two minutes during which time the pressure inside the apparatus was adjusted to atmospheric pressure and the volume of hydrogen recorded. Stirring was re-commenced and the timer simultaneously started and, as the reaction proceeded, the hydrogen uptake was recorded at 1 or 2 min intervals, after the pressure of the system had been re-adjusted to atmospheric pressure. The initial rate of hydrogen uptake was obtained from the tangent to the plot of hydrogen uptake against time and the tabulated rates are generally the average of at least two determinations and are reproducible to ±5%.

After the hydrogenation reactions the liquid organic products were distilled off under reduced pressure and characterised by v.p.c. whilst the organometallic residues were characterised by ^1H n.m.r. spectroscopy.

High-pressure Hydrogenations.—Dienes, acetylenes, and olefins containing functional groups were hydrogenated in a glass-lined thick-walled steel bomb (9½ in × 2 in) at a hydrogen pressure of 1 500 p.s.i. Known amounts of the catalyst, olefin, solvent and, if necessary, triethylamine together with a small magnetic stirrer were put into the glass-liner. The liner was placed in the bomb which was connected to the hydrogen line and flushed with hydrogen several times before being filled to the required pressure.

The mixture was stirred through the bomb using a powerful magnetic stirrer. The reaction products, both organic and organometallic, were worked up as described above.

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