Activation of Hydrogen by Rhodium Complexes containing Sulphide Ligands. Part II.[1] The Trichlorotris(diethyl sulphide)rhodium(III)-catalysed Hydrogenation of Maleic Acid

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$RhCl_3(Et_2S)_3$ has been found to catalyse the homogeneous hydrogenation of olefinic substrates in *NN'*-dimethylacetamide solution at *ca.* 70° and 1 atm. pressure. The kinetics have been interpreted in terms of an initial reduction to a rhodium(I) species, which with co-ordinated olefin then activates molecular hydrogen. The basic solvent plays an important role in initially promoting dissociation of a sulphide ligand from the rhodium(III) complex, and probably in enhancing an overall heterolytic splitting of the H_2 molecule in production of a rhodium(III) hydride intermediate.

EARLIER studies[2] have reported the homogeneous hydrogenation of olefinic compounds catalysed by chlororhodate(III) complexes in *NN'*-dimethylacetamide (DMA) solution. The systems involve initial reduction by hydrogen to rhodium(I), which is stabilised by complex formation with the olefin; subsequent reaction of the d^8 metal complex with hydrogen, probably *via* an oxidative addition reaction, gives the saturated product with regeneration of the rhodium catalyst:

$$\mathrm{Rh^{III}} + \mathrm{H_2} \longrightarrow \mathrm{Rh^{I}} + 2\mathrm{H^+} \qquad (1)$$

$$\mathrm{Rh^{I}} + \text{olefin} \longrightarrow \mathrm{Rh^{I}(olefin)} \qquad (2)$$

$$\mathrm{Rh^{I}(olefin)} + \mathrm{H_2} \longrightarrow [\mathrm{H_2Rh^{III}(olefin)}] \longrightarrow \mathrm{Rh^{I}} + \text{saturated product} \qquad (3)$$

This 'unsaturate route' for homogeneous hydrogenation[3] has been invoked for many catalytic systems involving metal complexes.[4,5]

We have undertaken a detailed study of ligand effects, solvent effects, substrate effects, *etc.*, in these rhodium-catalysed hydrogenations in order to learn more about the factors controlling reactions (1)—(3). Such studies on rhodium tertiary phosphine complexes have been reported by many workers[4,5] following the well-known work of Wilkinson's group on $RhCl(PPh_3)_3$;[6] these data have generally been discussed in terms of a 'hydride route', in which the dihydride is formed prior to reaction with olefin, although Candlin and Oldham[3] have shown that an 'unsaturate route' also exists for this system.

It is well known that sulphur compounds poison heterogeneous hydrogenations, and it was of interest to find that rhodium complexes containing sulphur ligands were effective homogeneous catalysts. A preliminary account of some of the work reported here has been published.[1]

A patent[7] has mentioned the use of the corresponding ruthenium compound $RuCl_3(Et_2S)_3$ for hydrogenation of olefin–acetylene mixtures, although the complex requires initial activation by treatment with lithium aluminium hydride. The only other sulphur containing complex reported to activate H_2 is a $PtCl_2(SPh_2)_2$–$SnCl_2$ mixture, which has been used to reduce polyolefins to the monoene stage.[8]

EXPERIMENTAL

Trichlorotris(diethyl sulphide)rhodium(III) was prepared according to the literature;[9] the compound had the correct m.p. of 127° and analysed correctly, but the visible and u.v. spectrum in ethanol gave peaks at 421 (ε 330) and 292 nm (20,100), somewhat different from those reported, 424 (ε 370) and 292 nm (25,800). Diethyl sulphide (Eastman Organic Chemicals) was used without further purification. *trans*-Cinnamic acid (Eastman Organic Chemicals) was purified by recrystallisation. Other compounds, solvents, and gases have been described previously.[2] Organic products were isolated by solvent extraction procedures after pumping off the DMA solvent.

The kinetic data were obtained by use of the previously described constant pressure gas-uptake apparatus.[2] Hydrogen solubility data have been given.[2]

RESULTS

Stoicheiometry and Kinetics.—Solutions of *ca.* 10^{-2}M-$RhCl_3(Et_2S)_3$ in DMA, yellow at room temperature and orange at 80°, were found to hydrogenate homogeneously αβ-unsaturated acids under an atmosphere or less of hydrogen. A three- to ten-fold excess of substrate was used.

Typical gas uptake plots are shown in Figure 1. The initial, more rapid uptake of hydrogen steadily decreased to a constant value which persisted up to regions approaching the end-point. At later stages (after *ca.* 5000 s for the lower curve), metallic rhodium appeared and this coincided with the observation of an unexpected increase in the hydrogenation rate, due to heterogeneous catalysis; no deviations from the linear rate were observed unless metal began to precipitate. The H_2 stoicheiometry corresponded to complete hydrogenation of the maleic acid (MA) to succinic acid, and reduction of Rh^{III} to Rh^{I}. In the absence of MA,

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[1] Part I, B. R. James, F. T. T. Ng, and G. L. Rempel, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 197.

[2] B. R. James and G. L. Rempel, *Discuss. Faraday Soc.*, 1968, **46**, 48.

[3] J. P. Candlin and A. R. Oldham, *Discuss. Faraday Soc.*, 1968, **46**, 60.

[4] R. S. Coffey, in 'Aspects of Homogeneous Catalysis,' ed. R. Ugo, vol. I, Carlo Manfredi, Milan, 1970, p. 3.

[5] B. R. James, in 'Organic Synthesis via Metal Carbonyls,' eds. I. Wender and P. Pino, vol. II, Wiley, New York, in the press.

[6] C. O'Connor and G. Wilkinson, *Tetrahedron Letters*, 1969, 1375, and references therein.

[7] F.P. 1,538,700 (*Chem. Abs.*, 1969, **71**, 83,317).

[8] J. C. Bailar, *Platinum Metals Rev.*, 1971, **15**, 2, and references therein.

[9] J. E. Ferguson, J. D. Karen, and S. Seevaratnam, *J. Chem. Soc.*, 1965, 2627.

the initial Rh^{III} complex was rapidly reduced by H_2 to the metal. No rhodium hydrides were detected in the course of these reactions.

The kinetics of the system were investigated in the initial region and in the subsequent linear region, and both show good first-order dependences on rhodium and hydrogen over a concentration range of (0·2—1·0) × 10^{-2}M in rhodium and (0·5—2·7) × 10^{-3}M in hydrogen; both rates are independent of the substrate concentration up to 0·1M (Table 1).

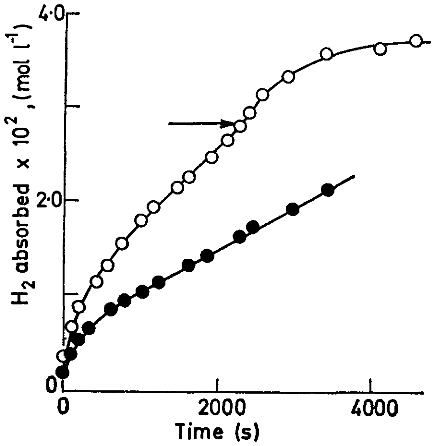

FIGURE 1 Hydrogen absorption plots for the $RhCl_3(Et_2S)_3$ catalysed hydrogenation of maleic acid at 80° in DMA, 725 mmHg H_2, 0·03M maleic acid; rhodium concentration: open circles, 8·80 × 10^{-3}M; filled circles 5·15 × 10^{-3} M; the arrow marks the point of metal precipitation

TABLE 1

Summary of kinetic data at 80° for the $RhCl_3(Et_2S)_3$ catalysed hydrogenation of maleic acid in DMA

[Rh] × 10^3 (M)	[H_2] × 10^3 (M)	[MA] × 10^{-2} (M)	k_1 ($mol^{-1}\,l\,s^{-1}$)	k_2 ($mol^{-1}\,l\,s^{-1}$)
2·54	2·32	3·0	1·53	0·45
5·15	2·32	3·0	1·85	0·36
7·64	2·32	3·0	1·81	0·33
8·80	2·32	3·0	1·90	0·33
10·20	2·32	3·0	1·90	0·31
5·15	0·62	3·0	2·30	0·36
5·15	1·22	3·0	1·87	0·34
5·15	1·70	3·0	2·50	0·33
5·15	2·32	3·0	1·83	0·36
5·15	2·70	3·0	1·83	0·36
5·15	2·32	2·0	1·80	0·34
5·15	2·32	10·0	1·87	0·34
5·15	2·32 [a]	3·0	1·68	0·34

[a] Using D_2.

There is some uncertainty in the initial rate data for k_1 but the kinetic dependences seem well established. The rate laws can thus be written as k_1 (or k_2) [H_2][Rh] with k_1 and k_2 representing the bimolecular rate constants for the initial and linear rates, respectively, incorporating all parameters except the hydrogen and rhodium concentrations. Average values of k_1 and k_2 at 80° were 1·92 and 0·35 l mol^{-1} s^{-1}, respectively. Rate measurements using deuterium indicated small isotope effects (k_1^H/k_1^D *ca.* 1·1 and k_2^H/k_2^D *ca.* 1·05). The deuteriosuccinic acid obtained from deuterium reduction showed sharp i.r. bands at 8·10 and 8·39 μm, consistent with a mixture of *meso*-symmetrically dideuteriated and unsymmetrically dideuteriated succinic acid.[10]

Added diethyl sulphide slows down the initial rate but did not essentially affect the linear rate (Table 2); the initial rate decreases rapidly at first with added sulphide and then tends to level off. It is interesting to note that the reactions at 0·15 and 0·20M, added sulphide thus give essentially linear uptake plots throughout, which in themselves incorrectly suggest an overall simplified mechanism.

TABLE 2

Effect of added diethyl sulphide and chloride on the catalytic hydrogenation; [Rh] = 5·15 × 10^{-3}M, [MA] = 3·0 × 10^{-2}M, [H_2] [a] = 2·32 × 10^{-3}M, at 80°

[Et_2S] (M)	[Cl^-] × 10^2 (M)	[ClO_4^-] × 10^2 (M)	k_1 ($mol^{-1}\,l\,s^{-1}$)	k_2 ($mol^{-1}\,l\,s^{-1}$)
0·00	0·00	0·00	1·85	0·36
0·02	0·00	0·00	1·32	0·41
0·05	0·00	0·00	0·97	0·40
0·10	0·00	0·00	0·64	0·43
0·15	0·00	0·00	0·50	0·42
0·20	0·00	0·00	0·37	0·40
0·00	0·12	0·38	1·18	0·36
0·00	0·25	0·25	0·77	0·38
0·00	0·50	0·00	0·56	0·36
0·00	1·00	0·00	0·54	0·38
0·00	30·00	0·00	0·54	0·45
0·00	0·00	30·00	1·75	0·55
0·00	30·00	30·00	0·51	0·47

[a] Assumed to be unaffected by added salts.

Addition of lithium chloride also decreases k_1 without substantially affecting k_2 (Table 2); the levelling-off tendency at lower k_1 values occurs, however, at added concentrations of *ca.* 5 × 10^{-3}M, some 10 times smaller than with added sulphide, and in fact, at a Rh : Cl^- ratio of 1 : 1. The k_1 inhibition is not a salt effect since addition of lithium perchlorate did not affect k_1. Some noted small variations may be due to small differences in hydrogen solubility. k_1 and k_2 were independent of addition of up to 0·05M-toluene-*p*-sulphonic acid (a strong acid).

Table 3 lists values of k_1 and k_2 determined at other temperatures.

TABLE 3

Variation of rate constants with temperature; [Rh] = 5·15 × 10^{-3}M, [MA] = 3·0 × 10^{-2}M, 1 atm. total pressure

T (°C)	k_1 ($mol^{-1}\,l\,s^{-1}$)	k_2 ($mol^{-1}\,l\,s^{-1}$)
70·5	1·07	0·17
75·0	1·37	0·25
80·0	1·85	0·36
85·0	2·34	0·61

Ethylene is also catalytically hydrogenated at 80° using a 1 : 1 C_2H_4–H_2 mixture at 1 atm with a 5 × 10^{-3}M-$RhCl_3(Et_2S)_3$ solution in DMA, but the kinetics of this system were not studied. No hydrogenation occurred using similar conditions in benzene solution at 50°; benzene-soluble solid substrates, such as *trans*-cinnamic acid, which was hydrogenated in DMA at a rate comparable to that of MA, were also not reduced in the benzene medium. Further, the rhodium complex itself is quite inert towards hydrogen in this solvent.

Spectrophotometry.—The initial u.v. and visible spectrum of $RhCl_3(Et_2S)_3$ in DMA at room temperature showed absorption peaks at 370 (ε 390) and 426 nm (310). With time, the peaks shift slightly and the extinction coefficients decrease somewhat to 370 and 270, respectively; this

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[10] C. R. Childs and K. Block, *J. Org. Chem.*, 1961, **26**, 1630.

constant spectrum is obtained rapidly on heating to 80°. When an excess of diethyl sulphide ($Et_2S : Rh = 10$) was added, the same initial spectrum resulted and this was invariant with time even at 80°.

When lithium chloride was added to the complex in ratios $\geqslant 1$ in DMA, a steady spectrum, with absorption maxima at 381 (ε 190) and 453 nm (160), and a shoulder at 530 nm (ε 50), was obtained on standing or heating to 80°.

No complexing was observed between the rhodium(III) complex and maleic acid.

The spectrum of a solution of $RhCl_3(Et_2S)_3$ and MA in DMA during the linear hydrogenation region showed only a shoulder at 430 nm (ε 220), typical of a rhodium(I) species [2]. Samples taken at different stages throughout this linear H_2 uptake region exhibited the same spectrum, showing the presence of the same catalytic species; the spectra remained unchanged on exposure to air for several days.

The visible spectrum of $RhCl_3(Et_2S)_3$ in benzene showed peaks at 370 (ε 425) and 429 nm (345), and this remained unchanged even when the complex was heated.

DISCUSSION

The results indicate that $RhCl_3(Et_2S)_3$ in DMA catalyses the homogeneous hydrogenation of maleic acid, cinnamic acid, and ethylene.

The data are consistent with the initial reaction involving reduction of rhodium(III) to rhodium(I), this being stabilised by complexing with olefin in a rapid step to prevent disproportionation to metal (equations 1 and 2). Reaction (3) accounts for the extended linear part of the uptake plot where hydrogenation to succinic acid occurs. The point of metal precipitation in the uptake experiments (Figure 1) indicates that the olefin complex is a 1 : 1 species; metal product probably occurs *via* reaction (4) rather than hydrogen reduction of rhodium(I).

$$2Rh^{I} \rightleftharpoons Rh^{0} + Rh^{II} \qquad (4)$$

The overall H_2 stoicheiometry supports this, and Wilkinson and his co-workers [11] have reported on the decomposition of rhodium(III) hydrides to a 1 : 1 ratio of metal and rhodium(II), presumably *via* rhodium(I):

$$Rh^{III}H \longrightarrow Rh^{I} + H^{+} \qquad (5)$$

Reduction of Rhodium(I).—The spectrophotometric data suggest that dissociation of a Et_2S ligand occurs in DMA but not in benzene solution; conductivity measurements indicated no measurable loss of chloride. Dwyer and Nyholm [12] have also demonstrated that dissociation of Et_2S from the complex in aqueous acid alcoholic solutions occurs more readily than chloride dissociation.

The kinetic results for the initial rate analyse well by assuming that H_2 reacts with an intermediate species only, produced by dissociation of the initial complex:

$$RhCl_3(Et_2S)_3 \overset{K}{\rightleftharpoons} RhCl_3(Et_2S)_2 + Et_2S \qquad (6)$$

$$RhCl_3(Et_2S)_2 + H_2 \xrightarrow{k} HRhCl_3(Et_2S)_2^{-} + H^{+},$$
$$\text{or} \qquad HRhCl_2(Et_2S)_2 + H^{+} + Cl^{-} \qquad (7)$$

(solvent molecules presumably complete octahedral co-ordination).

These reactions are thought to be followed by the faster steps shown in equations (5) and (2), which is consistent with the invariance of initial rate with added acid. Activation of hydrogen [equation (7)] in this system will almost certainly involve an overall heterolytic splitting of the H_2 molecule, as discussed for the similar chlororhodate(III) system.[2]

Reactions (6) and (7) yield the rate law (8),

$$-d[H_2]/dt = Kk[H_2][Rh]/(K + [Et_2S]) \qquad (8)$$

k_1 can thus be identified with $Kk/(K + [Et_2S])$, and thus

$$\frac{1}{k_1} = \frac{1}{k} + \frac{[Et_2S]}{Kk} \qquad (9)$$

Equation (8) accounts for the observed dependencies; the plot shown in Figure 2 is in accord with equation (9) and gives a K value of 0·047M and a k value of 1·97 mol^{-1} l s^{-1} at 80°. The K value shows that the complex, at concentrations of about 5×10^{-3}M, is dissociated to the extent of *ca.* 90% in the absence of added diethyl sulphide, and the k_1 values (Table 1) determined under these conditions are close to that for reaction (7). The k_1 data in Table 3 give an excellent Arrhenius plot which yields the activation parameters $\Delta H_1^{\ddagger} = 12{\cdot}9 \pm 0{\cdot}1$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = -21 \pm 1$ e.u. for reaction (7).

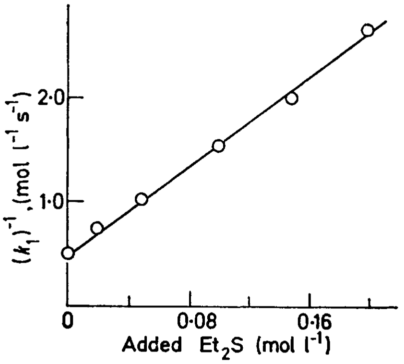

FIGURE 2 Inhibition of the hydrogen reduction of rhodium(III) by added diethyl sulphide, plotted according to equation (9); data in Table 2

The non-reduction of rhodium(III) by hydrogen in benzene solution shows that the solvent plays a critical role, with both polarity and co-ordinating ability probably being important here. Generally, reactions which produce ions are favoured in more polar solvents, and reactions such as (7) will clearly be favoured in the polar DMA (dielectric constant 38). Further, the dissociation reaction [equation (6)] is not observed in benzene, although it is essentially complete in the strongly co-ordinating DMA.[13] Solvent-assisted dissociation of octahedral complexes is well-substantiated.[14]

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[11] K. Thomas, J. A. Osborn, A. R. Powell, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 1801.

[12] F. P. Dwyer and R. S. Nyholm, *Proc. Roy. Soc., New South Wales*, 1944, **78**, 67.

[13] V. Gutmann, *Co-ordination Chem. Rev.*, 1967, **2**, 239.

[14] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1967, 2nd edn., pp. 134, 239, 585.

Chlororhodate(III) complexes are reduced by hydrogen in DMA at 80° at a rate very similar to that measured here for the sulphide complex, but the activation parameters for the chlorides ($\Delta H^{\ddagger} = 17{\cdot}3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9{\cdot}2$ e.u.[2]) on comparison with those noted above show that the similar rates result from a compensation effect in these parameters. The more negative $\Delta S^{\ddagger}$ value in the sulphur system can be attributed to formation of a polar transition state in reaction (7) between two neutral molecules.[15] The chloride system almost certainly involves activation of hydrogen by charged species.

The inverse chloride effect levelling off at Rh : Cl$^-$ *ca.* 1 suggests the formation of a less reactive species, presumably $RhCl_4(Et_2S)_2^-$; the shifting of the absorption peaks to higher wavelengths on addition of chloride indicates that higher chloro-complexes are present.[16] It should be noted that the data for the chloride variation do not analyse quantitatively for reaction by a mixture of the two complexes. The tetrachloro-species is seen to have *ca.* one third the activity of $RhCl_3(Et_2S)_2$; hence at $0{\cdot}25 \times 10^{-2}$M added chloride (Table 2), when roughly equal amounts of the two species are present, the composite k_1 value should be *ca.* 1·2 mol^{-1} l s^{-1} whereas the measured value is 0·8 mol^{-1} l s^{-1}.

The small isotope effect observed indicates that the breaking of H–H bonds and making of Rh–H bonds occurs in a concerted process, although the detailed mechanism of reaction (7) remains unsubstantiated; the net hydride substitution reaction could involve oxidative addition to give a dihydride with subsequent loss of HCl, in the manner demonstrated for formation of monohydride complexes of some platinum(II) phosphine species.[17] Measured isotope effects in studies on hydrogen activation generally have been found to be small, and furnish little evidence for the mechanism of the activation.[5,18,19] We are currently studying ligand effects in reactions of the type shown in equation (7), in order to learn more of the activation process.

Hydrogenation of Olefins.—The catalytic hydrogenation reaction is outlined in equations (2) and (3), the constant spectrum measured during the linear uptake region being attributed to a square planar Rh^{I}–maleic acid complex. Reaction (1) must result in production of a labile species $Rh^{I}Cl_x(Et_2S)_y(DMA)_z$, where $x + y + z$ is probably 4. Compared to the $RhCl(PPh_3)_3$ system [3-6], the sulphur ligand is a weaker π-acceptor than the phosphine one and the rhodium(I) sulphide species is not so highly stabilised, as is seen by its ready reduction by hydrogen to the metal; a further co-ordinated π-acceptor olefin is necessary for stabilisation.

As discussed in some detail for the corresponding chloride system [2], hydrogenation likely proceeds by oxidative addition of H_2 followed by subsequent hydrometallation of the olefinic bond:

$$\begin{tikzcd} L_3Rh^{I}(\text{olefin}) + H_2 \arrow[r, "k_2"] & L_3Rh^{III}(\text{olefin})H_2 \arrow[d, shift left] \\ & L_4Rh^{III}(\text{alkyl})H \arrow[u, shift left] \arrow[ul, "+\text{ olefin}", "-\text{ saturated product}"'] \end{tikzcd} \qquad (10)$$

(L = Cl, Et_2S, or DMA)

The k_2 data in Table 3 give a good Arrhenius plot and the activation parameters $\Delta H_2^{\ddagger} = 21{\cdot}5 \pm 1{\cdot}0$ kcal mol^{-1} and $\Delta S_2^{\ddagger} = -1{\cdot}0 \pm 3{\cdot}0$ e.u. Activation entropies close to zero are expected for reaction between an ion and a neutral molecule,[20] and this could be consistent with the Rh^{I}–olefinic complex being $RhCl_2(Et_2S)(MA)^-$. Unfortunately we have not been able to isolate the rhodium(I)–maleic acid complex. Quite similar activation parameters ($\Delta H^{\ddagger} = 18$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6$ e.u.) were obtained for the hydrogenation of MA by chlororhodate(I) species in DMA.[2] The activity of the diethyl sulphide system is *ca.* one fifth that of the chloro-complex; this probably results from the relative σ-donor properties of the ligands since oxidative addition reactions are promoted by stronger σ-donors [21] ($Cl^- > Et_2S$).

The independence of the hydrogenation rate on added chloride up to 0·3M, and on added diethyl sulphide up to 0·2M, shows that the maleic acid ligand at 0·03M (Table 2) competes effectively with these ligands for a site on the square planar complex. The inhibition by added sulphide on the initial reduction of rhodium(III) was originally [1] incorrectly thought to be associated with the olefin hydrogenation step, and was rationalised in terms of a required dissociation of a Et_2S ligand from the rhodium(I) complex, comparable to dissociation of a phosphine ligand from $RhCl(PPh_3)_3$.[3-6]

The small isotope effect observed for k_2 is in line with previously determined values for dihydride formation *via* oxidative addition to square planar d^8 systems.[2,5,19,22] The production of the *meso*-dideuteriated succinic acid shows that hydrogen has been added *cis* to the maleic acid; such addition is usually operative in catalysed homogeneous hydrogenation,[5] and has been demonstrated for the $RhCl(PPh_3)_3$ catalyst system which also involves a $L_3Rh^{III}(olefin)H_2$ intermediate.[4,5] The presence of unsymmetrically dideuteriated succinic acid gives evidence for a stepwise transfer of the hydrogen through an alkyl hydride intermediate, and also requires the reversal of a deuteriated alkyl to co-ordinated olefin and hydrogen [equation (10), and step (2) in the Scheme]. The hydrogenation is not complicated by accompanying isomerisation to fumaric acid.[23] The hydrometallation

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[15] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1963, 2nd edn., p. 137.

[16] W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, 1963, **2**, 463.

[17] U. Belluco, M. Guistiniani, and M. Graziani, *J. Amer. Chem. Soc.*, 1967, **89**, 6494.

[18] J. Halpern, *Ann. Rev. Phys. Chem.*, 1965, **16**, 103.

[19] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1966, **88**, 3511.

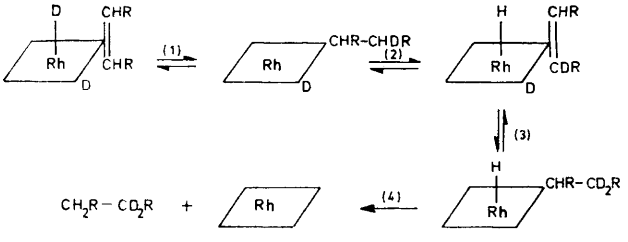
[20] Ref. 15, p. 147.

[21] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983, and references therein.

[22] C. O'Connor and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2665.

[23] B. R. James and F. T. T. Ng, to be published; Miss F. T. T. Ng, Ph.D. Thesis, University of British Columbia, 1970.

steps, (1) and (3), *via* a probable four-centre transition state, are expected to result in *cis*-addition of Rh–H(D) across the olefinic bond. To give overall *cis*-addition, the final displacement of carbon by the remaining coordinated hydrogen [step (4)] must occur with retention of configuration.



SCHEME

Further evidence that rhodium(I) catalysts are involved has been obtained by comparison with the activity of rhodium(I) species formed *in situ* from the cyclooctene dimer $[RhCl(C_8H_{14})_2]_2$ by addition of appropriate ligands.[23]

Detailed studies on the reduction of other unsaturated carboxylic acids using $RhCl_3(Et_2S)_3$ and other related sulphide complexes show basically the same overall processes, but are sometimes more complex because of an accompanying isomerisation, or a required dissociation of a ligand L from the L_3Rh^I(olefin) complex prior to reaction with hydrogen.

Other Related Systems.—Dichlorobis(2,5-dithiahexane)-rhodium(III) chloride[24] was found to be inactive for hydrogenation of maleic acid in DMA under similar conditions; the presence of the chelating sulphur ligand presumably makes dissociation according to a reaction such as (6) difficult, and reduction to rhodium(I) is not observed. Walton[24] also noted that the chelated complex is unable to form hydride species.

The *cis*- and *trans*-isomers of $IrCl_3(Et_2S)_3$[25] are inactive for olefin hydrogenation in DMA under the conditions noted for the *trans*-rhodium isomer,* although the *cis*-iridium complex* itself does react slowly with molecular hydrogen probably to give an iridium(III) hydride. Unlike their rhodium analogues, iridium(III) hydrides do not readily transform by equation (5) to the univalent state.[26]

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* In a recent paper (E. A. Allen, N. P. Johnson, and W. Wilkinson, *Chem. Comm.*, 1971, 804) a *trans*-configuration has been assigned to these complexes in contrast to the originally assigned *cis*-configuration.[9,25]

[24] R. A. Walton, *J. Chem. Soc.* (*A*), 1967, 1852.

[25] G. B. Kauffman, J. H. S. Tsai, R. C. Fay, and C. K. Jorgensen, *Inorg. Chem.*, 1963, **2**, 1233.

[26] A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc.* (*A*), 1966, 1670.