Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part X.[1] The Kinetics of the Reactions of some Cyclic and Acyclic Dienes with μ-Hydrido-compounds

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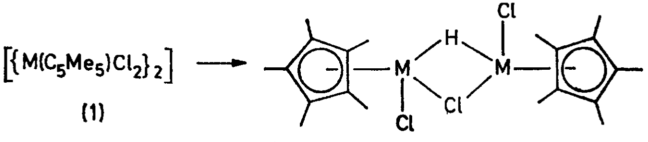
The μ-hydrido- complexes $[\{M(C_5Me_5)\}_2HCl_3]$ (2a; M = Rh) and (2b; M = Ir) react readily with cyclo-octa-1,3- and -1,5-diene, cyclohexa-1,3- and -1,4-diene, to give the cyclic η-allylic complexes which reductively decompose to give $[M^I(C_5Me_5)diene]$. The rate of the reaction of the hydride with a variety of cyclic and acylic dienes was shown to be first order in hydride and zero order in diene and to be independent of the nature of the diene. The rate-determining step is proposed to be opening of the metal-halide and *not* the metal-hydride bridge of (2). Cyclopentadiene gives a cyclopentenyl complex with (2), but this loses 2 H to give $[M^{III}(C_5Me_5)(C_5H_5)]^+$; norbornadiene gives a σ,η-norbornenyl complex that reductively eliminates to $[M^I(C_5Me_5)(norbornadiene)]$. The reactions of the hydrido-complexes (2) with dienes are compared with those of $[(MC_5Me_5Cl_2)_2]$ in alcohol-base.

IN the preceding paper [1] we discussed the reactions of a variety of acyclic dienes with the recently prepared bridged hydrides (2) [2] in dichloromethane, and with their dichloride dimer precursors (1) in ethanol–base. This paper extends the work to an examination of the reactions of (1), and particularly (2), with cyclic dienes and includes a kinetic study of the reactions of a variety of dienes with (2) which provides information on the formation of the initial η-allylic products. Parts of this work have appeared as preliminary communications.[3,4]

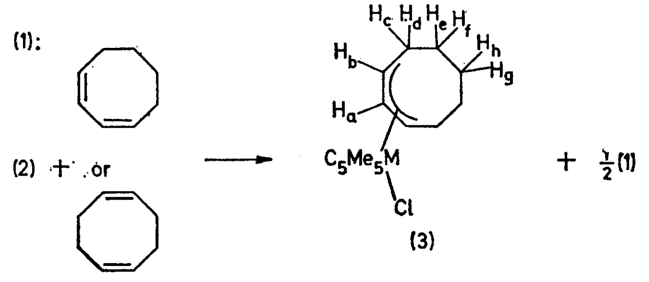


(1) (2)

a; M = Rh
b; M = Ir

RESULTS AND DISCUSSION

(i) *Cyclo-octa*-1,3- *and* -1,5-*diene*.—The hydrides (2a) and (2b) reacted with both cyclo-octa-1,3- and -1,5-diene in dichloromethane at 37 °C to give the 1—3-η-cyclo-oct-2-enyl complexes,[3] (3), and (1):



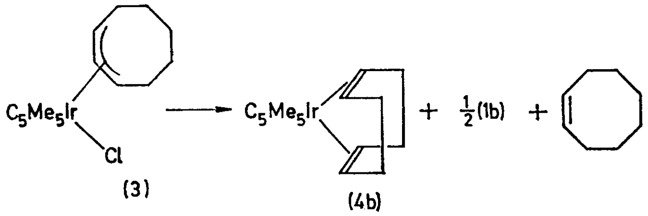
(3)

The 1—3-η-cyclo-oct-2-enyl complexes (3) were also obtained from reaction of cyclo-octa-1,3-, -1,4-, or -1,5-diene and (1) in ethanol–sodium carbonate (40—45 °C for Rh, 20—25 °C for Ir). The reactions of (1a) with cyclo-octa-1,3- and -1,5-diene were monitored by v.p.c. and it was found that there was no isomerisation of the excess of 1,3- to 1,5-diene or *vice-versa* during this stage.

The cyclo-oct-2-enyl complexes were characterised by n.m.r. spectroscopy; for example, for (3b) in $CDCl_3$, τ 5.75 [t, 1 H, H_a, $J(H_a - H_b) = 7$ Hz], 6.43 [dt, 2 H, H_b, $J(H_b - H_c) = J(H_b - H_d) = 7.5$ Hz], 7.4 (m, 2 H, H_c), 7.9 (m, br, 2 H, H_d), 8.14 (m, br, 6 H, H_e, H_f, H_g, H_h), and 8.55 (s, 15 H, C_5Me_5). This spectrum agrees with the cyclo-oct-2-enyl formulation but would not be expected for a cyclo-oct-3- or -4-enyl complex. The rhodium complex (3a) exhibited a similar spectrum but was poorly resolved owing to the overlapping of H_a and H_b [in benzene, τ 6.21 (m, 3 H, H_a, H_b), 7.88 (m, br, 2 H, H_d), 8.43 (m, 6 H, H_{e-h}), and 8.53 (s, 15 H, C_5Me_5)].

At somewhat higher temperatures (60—70 °C, 3—4 h, for Rh; 55—65 °C, 2—3 h, for Ir) (1) reacted with cyclo-octa-1,3- or -1,5-diene (and cyclo-octa-1,4-diene for Ir) to give the 1,2,5,6-η-cyclo-octa-1,5-diene complexes (4). They were characterised by n.m.r. spectroscopy [(4a): τ 7.05 (m, 4 H, olefinic), 7.24 (m, 8 H, CH_2), and 8.23 (s, C_5Me_5); (4b): 7.23 (m, 4 H, olefinic), 8.12 (m, 8 H, CH_2), and 8.13 (s, C_5Me_5)].

The decomposition of the cyclo-oct-2-enyl complexes (3) to the cyclo-octa-1,5-diene complexes (4) was studied under a variety of conditions, by-products being monitored as well (Table 1). The iridium complex (3b) gave the simplest reactions, which were of two types. (i) When heated in the absence of base (3b) gave a 1 : 1 mixture of (4b) and (1b) and the only volatile product detected was cyclo-octene:



(3) (4b)

(ii) In ethanol at 65 °C in the presence of triethylamine as base the reaction gave (4b) quantitatively; no (1b) or cyclo-octene were detected, but triethylammonium chloride was also formed. In benzene (at 75 °C) containing one equivalent of triethylamine (3b) was converted into (4b) and (1b); triethylammonium chloride and cyclo-octene were also formed. No reaction

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[1] Part IX, H. B. Lee and P. M. Maitlis, *J.C.S. Dalton*, preceding paper.

[2] A. J. Oliver, C. White, and P. M. Maitlis, *J.C.S. Dalton*, 1973, 1901.

[3] K. Moseley, J. W. Kang, and P. M. Maitlis, *Chem. Comm.*, 1969, 1155.

[4] H. B. Lee and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1974, 601.

occurred in the cold, even in the presence of base. When these reactions were carried out in the presence of an excess of cyclo-octa-1,3- or -1,5-diene no isomerisation of the free diene was observed.

The decomposition of the cyclo-octenylrhodium complex (3a) was more complex but followed a basically similar pattern, and no reaction occurred below *ca.* 65 °C. When the solid was heated *in vacuo*, or as a solution in benzene, with or without base, the products were again (4a) and (1a) (in a 1 : 1 ratio) and cyclo-octene; however, cyclo-octa-1,3-diene was also detected as a by-product. These products were also obtained in ethanol in the presence of a large excess of cyclo-octa-1,5-diene but in the absence of base. However, in ethanol–sodium carbonate, while the volatile products were still the same and again *ca.* 0.5 equivalents of (4a) were formed, the other organometallic product was an amorphous purple solid that could not be characterised but which had a composition corresponding to [$\{RhC_5Me_5\}_n$]. The same products, together with some (1a), were obtained from decomposition of (3a) in ethanol–triethylamine, but this time the yield of (4a) was higher. In ethanol–sodium carbonate in the presence of cyclo-octa-1,5-diene the only complex isolated was (4a) but there was substantial isomerisation of the cyclo-octa-1,5- to the -1,3-diene.

TABLE 1

Reaction $[M(C_5Me_5)(C_8H_{13})Cl] \longrightarrow [M(C_5Me_5)(\text{cyclo-octa-1,5-diene})]$
(3) (4)

Starting complex (3) (mmol)	Conditions	Products	
		(4) (mmol)	Others (mmol)
(3a) 0.23	*In vacuo*/110 °C/8 h	(4a) 0.11	(1a) (0.06); C_8H_{14} + 1,3-cod [b] (4 : 1)
0.17	C_6H_6/80 °C/8 h	0.08	(1a) (0.043); C_8H_{14} (0.032) + 1,3-cod (0.05)
0.18	C_6H_6–Et_3N (0.17 mmol)/80 °C/8 h	0.09	(1a) (0.048); C_8H_{14} (0.027) + 1,3-cod (0.06)
0.13	C_6H_6–pyridine (0.14 mmol)/80 °C/6 h	0.06	[$Rh(C_5Me_5)Cl_2(py)$] (0.06)
0.20	Light petroleum/90 °C/3.5 h	0.06	(1a) + unknown polymer; C_8H_{14} (0.06) + 1,3-cod (0.10)
0.24	Light petroleum–Et_3N (0.29 mmol)/90 °C/3.5 h	0.06	(1a) + unknown polymer; C_8H_{14} (0.065) + 1,3-cod (0.12) + 1,5-cod (0.01)
0.13	EtOH–1,5-cod (0.82) mmol/70 °C/9 h	0.06	(1a) (0.06); 1,5-cod (0.8) + 1,3-cod (trace) [a] + C_8H_{14} (trace) [a]
0.45	EtOH–Na_2CO_3/65 °C/9 h	0.24	$[RhC_5Me_5]_n$ (0.19); C_8H_{14} (0.06) + 1,3-cod (0.03)
0.13	EtOH–Et_3N (0.15 mmol)/73 °C/13 h	0.09	(1a) (0.02); $[RhC_5Me_5]_n$ (0.02); Et_3NHCl (0.12); C_8H_{14} (0.02) + 1,3-cod (0.005)
0.20	EtOH–Na_2CO_3/1,5-cod (0.33 mmol)/60 °C/5 h	0.18	1,5-cod (0.10) + 1,3-cod (0.14) + C_8H_{14} (0.03)
(3b) 0.11	*In vacuo*/95 °C/5.5 h	(4b) 0.064	(1b) (0.026) + C_8H_{14} [a]
0.22	C_6H_6/80 °C/19 h	0.11	(1b) (0.05) + C_8H_{14} (0.09) + 1,3-cod (trace)
0.10	C_6H_6–Et_3N (0.11 mmol)/75 °C/18 h	0.085	(1b) (0.015) + C_8H_{14} + Et_3NHCl
0.11	EtOH–Na_2CO_3/65 °C/4.5 h	0.11	C_8H_{14} (trace) [a]
0.11	EtOH–Et_3N (0.11 mmol)/60 °C/24 h	0.11	Et_3NHCl

[a] Detected but not estimated quantitatively. [b] 1,3-cod = cyclo-octa-1,3-diene; 1,5-cod = cyclo-octa-1,5-diene; C_8H_{14} = cyclo-octene.

These results can be understood in terms of the basic reactions:

$$[M(C_5Me_5)(C_8H_{13})Cl] \longrightarrow [M(C_5Me_5)(C_8H_{12})] + HCl \qquad (A)$$

$$[M(C_5Me_5)(C_8H_{13})Cl] + HCl \longrightarrow \tfrac{1}{2}[\{MC_5Me_5Cl_2\}_2] + C_8H_{14} \qquad (B)$$

The iridium reactions proceed cleanly in this sense, and in the presence of base reaction (B) is repressed. The rhodium reactions also follow this path but (3a) is more susceptible to attack by weak acids; for example, in benzene, and to a lesser extent in ethanol, even amine hydrochlorides attack (3) to give (1) and cyclo-octene. This was checked by treating (3a) with pyridinium chloride in pyridine and benzene; the only product detected was (1a).

A further complication in the rhodium system is that cyclo-octa-1,3-diene is liberated in all the reactions. The decomposition (3) ⟶ (4) requires that an isomerisation from 1—3-η-cyclo-oct-2-enyl to 1,2,5,6-η-cyclo-octa-1,5-diene takes place, presumably by a stepwise path.* The first step must involve the formation of either a dihapto- or a tetrahapto-cyclo-octa-1,3-diene metal hydride intermediate; our evidence shows that in the rhodium complex this is more labile than in the iridium analogue and therefore elimination of the 1,3-diene proceeds for Rh but is not detected for Ir. In the absence of an excess of diene in ethanol–base it appears that HCl is also eliminated, to leave the uncharacterised [$\{RhC_5Me_5\}_n$], while in the presence of an excess of cyclo-octa-1,5-diene the cyclo-oct-2-enyl complex is presumably reformed *in situ* and again decomposes by the two reaction paths; an overall isomerisation of cyclo-octa-1,5- to -1,3-diene, but not the reverse, is, therefore, observed.

I was also found that the complexes (4a) and (4b) in ethanol–base catalysed the reaction of cyclo-octa-1,5- to the -1,3- and the -1,4-diene and to cyclo-octene. This reaction was accompanied by the formation of substantial amounts of acetaldehyde and its diethyl

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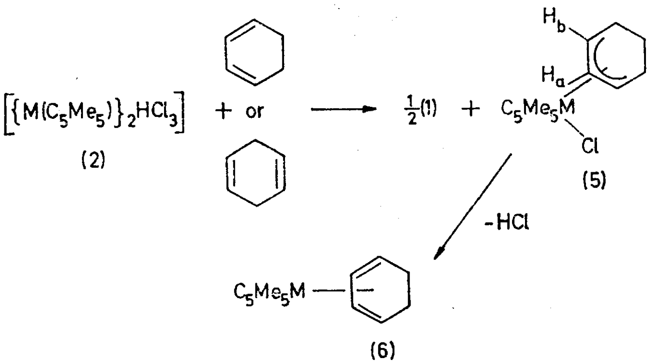
* N.m.r. evidence for stepwise isomerisation has been briefly reported for protonated 1,2,5,6-η-cyclo-octa-1,5-diene(cyclopentadienyl)rhodium.[5]

[5] J. Evans, B. F. G. Johnson, and J. Lewis, *Chem. Comm.*, 1971, 1253.

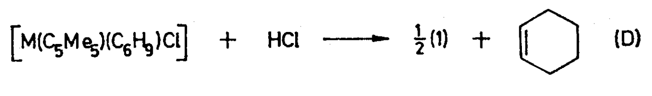
acetal, indicating that metal hydride species were again involved, but it was very much slower than the processes described above, and is clearly not related to them.

(ii) *Cyclohexa*-1,3- and -1,4-*diene*.—The hydrides (2a) and (2b) reacted with both cyclohexa-1,3- and -1,4-diene in deacidified dichloromethane at 37 °C to give (1) and the 1—4-η-cyclohexa-1,3-diene complexes (4).[6] When the reactions were followed by ^{1}H n.m.r. spectroscopy evidence was obtained for an unstable intermediate in both cases from the appearance of a transient C_5Me_5 resonance (τ 8.31 for Rh and 8.28 for Ir). These intermediates could not be isolated nor could the spectra be fully resolved owing to their low concentrations; however, in the iridium reactions a low-field triplet associated with the above C_5Me_5 resonance was observed in the spectrum [τ 5.97, J ($H_a - H_b$) = 6 Hz, H_a], which suggested the presence of a 1—3-η-cyclohexenyl (5) rather than a 1,2,4-η- or a σ-cyclohexenyl complex. The same intermediate was detected from both cyclohexa-1,3- and -1,4-diene.



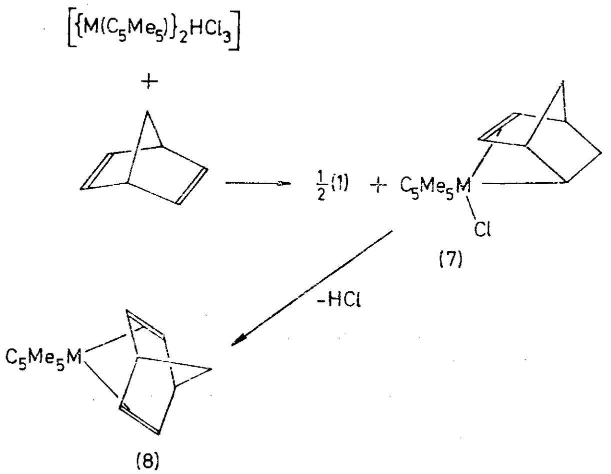
The structure shown was assigned to (5) on the basis of the evidence cited; a number of other 1—3-η-cyclohexenyl complexes, both of Rh and Pd, are known which all show the characteristic triplet (J = 6 Hz) in this region of the n.m.r. spectrum.[7] The complexes (5) readily decomposed to (6), particularly in the presence of a base such as triethylamine, when triethylammonium chloride was observed as the other product. In the presence of base, the formation of (1) and (6) was stoicheiometric, but in its absence a preponderance of (1) was observed owing to the competition of reactions (C) and/or (D).

$$[\{M(C_5Me_5)\}_2HCl_3] + HCl \longrightarrow (1) + H_2 \qquad (C)$$



(D)

(iii) *Norbornadiene*.—The reactions of (2a and b) with norbornadiene followed the same pattern as with the cyclohexadienes. The final products were (1) and the 2,3,5,6-η-norbornadiene-rhodium(I) and -iridium(I) complexes (8),[8] and when the reactions were studied by n.m.r. unstable intermediates were detected by their C_5Me_5 resonances [τ 8.30 (Rh) and 8.32 (Ir)]. By analogy to the other reactions described, these intermediates are assigned the 2,3,5-η-norbornenyl structures shown, (7); a norbornenylpalladium complex has been reported.[9]



Again, the reductive elimination reaction (7) → (8) was considerably accelerated in the presence of base; under these conditions (7) could not be detected and (1) and (8) were obtained in equivalent amounts.

(iv) *Cyclopentadiene*.—Freshly cracked cyclopentadiene reacted rather differently with (2a and b). Unstable intermediates were again detected in both reactions which were assigned the 1—3-η-cyclopentenyl structures (9) based on their n.m.r. spectra {(9a): τ 5.67 (m, 1 H, H_a), 5.93 (m, 2 H, H_b), and 8.27 (s, 15 H, C_5Me_5) *; (9b): τ 5.73 [t, 1 H, H_a, J ($H_a - H_b$) = 3.0 Hz], 6.35 [m, 2 H, H_b, $J(H_b - H_c)$ or $J(H_b - H_d)$ = 0.5 Hz], 8.23 (s, 15 H, C_5Me_5), and 8.31 [t, 4 H, H_c and H_d, $J(H_c - H_d)$ = 18 Hz]}, but these intermediates were rapidly transformed into the pentamethyl-rhodicenium and -iridicenium cations (10),[8] particularly in the presence of base (triethylamine); when the reactions were followed by n.m.r. spectroscopy in $CDCl_3$ solvent, $CHDCl_2$ was detected as a by-product. No other products could be isolated and, in particular, no evidence was obtained for the formation of the known 1—4-η-cyclopentadiene(pentamethylcyclopentadienyl)iridium.[8]

Kinetics of the Reactions of (2a) *and* (2b) *with Diolefins*.—The rates of the reactions of (2a) and (2b) with diolefins in dichloromethane at ambient temperatures were such that they could conveniently be studied by following the rates of disappearance of the C_5Me_5 singlets due to (2a and b) in the n.m.r. spectra; these measure-

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* The resonances due to H_c and H_d were obscured by the signals of other species in the mixture.

[6] K. Moseley and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2884.

[7] R. Hüttel, H. Dietl, and H. Christ, *Chem. Ber.*, 1964, **97**, 2037; S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1964, 5002; D. Jones, G. W. Parshall, L. Pratt, and G. Wilkinson, *Tetrahedron Letters*, 1961, 48; C. A. Reilly and H. Thyret, *J. Amer. Chem. Soc.*, 1967, **89**, 5144; J. F. Nixon, B. Wilkins, and D. A. Clement, *J.C.S. Dalton*, 1974, 1993.

[8] K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2875.

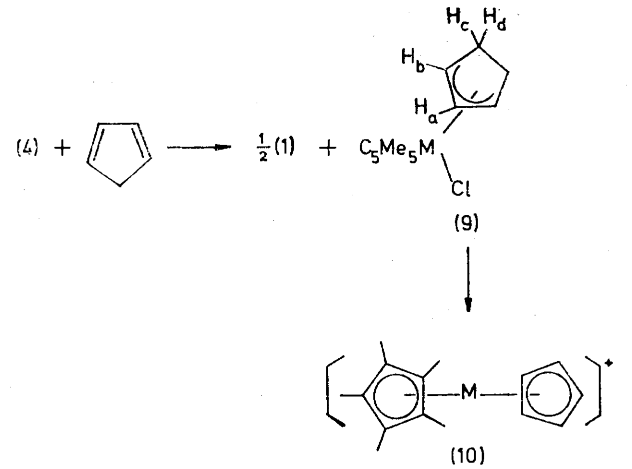
[9] J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, 1966, **88**, 5035.

ments were checked by observing the rates of appearance of the C_5Me_5 resonances of the products. All the reactions studied (Table 2) were found to be first order in the hydride and zero order in the diene. They were also independent of the nature of the diene within experimental error.* Typical plots are given in the Figure.

TABLE 2

First-order rate constants for the reactions of the hydrides, $[\{M(C_5Me_5)\}_2HCl_3]$, and deuterides $[\{M(C_5Me_5)\}_2DCl_3]$ with dienes in dichloromethane at 310 K, both in the presence and absence of triethylamine

Diene	Hydride/Deuteride	Et_3N (mmol)	$10^4k_1/s^{-1}$ Rh (±0.2)	$10^4k_1/s^{-1}$ Ir (±0.8)
Cyclo-octa-1,5-diene	$[\{M(C_5Me_5)\}_2HCl_3]$	0	1.5	7.5
		0.033	1.5	7.3
	$[\{M(C_5Me_5)\}_2DCl_3]$	0	1.4	7.4
Cyclo-octa-1,3-diene	$[\{M(C_5Me_5)\}_2HCl_3]$	0	1.3	7.2
Cyclohexa-1,4-diene	$[\{M(C_5Me_5)\}_2HCl_3]$	0	1.5	7.8
		0.017	1.5	
		0.033	1.5	7.8
		0.066	1.4	
		0.165		7.6
	$[\{M(C_5Me_5)\}_2DCl_3]$	0	1.6	7.8
Isoprene	$[\{M(C_5Me_5)\}_2HCl_3]$	0	1.3	7.4
		0.033	1.3	7.4
		0.066		7.5
	$[\{M(C_5Me_5)\}_2DCl_3]$	0	1.7	7.6
2,3-Dimethylbutadiene	$[\{M(C_5Me_5)\}_2HCl_3]$	0	1.4	8.0
	$[\{M(C_5Me_5)\}_2DCl_3]$	0	1.6	7.8

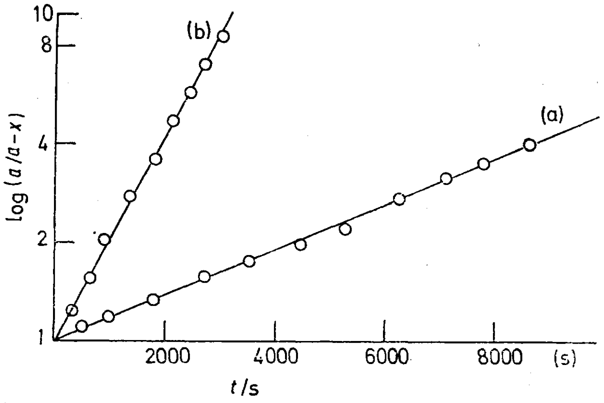


The average first-order rate constants, k_1, at 310 K were $1.4 \pm 0.2 \times 10^{-4}$ s^{-1} (Rh) and $7.6 \pm 0.8 \times 10^{-4}$ s^{-1} (Ir) corresponding to half-lives of *ca.* 5 000 s (Rh) and 910 s (Ir).

In those reactions where η-allylic complexes were detected as unstable intermediates which decomposed to the η-diene complexes and HCl, one equivalent of triethylamine was added to minimise side-reactions such as (B), (C), and (D). This caused no change in the rate of formation of the η-allylic complexes though it did accelerate their decomposition to the diene complexes.

In addition to the rate constants listed in Table 2, semi-quantitative estimates of $t_{\frac{1}{2}}$ for the reactions of (2a) and (2b) with cyclohexa-1,3-diene, norbornadiene, cyclopentadiene, penta-1,3-diene, 1,1-dimethylallene, and *trans*-2-methylpenta-1,3-diene showed that here too the rates were independent of the concentration and nature of the diene. However, the reaction of (2b) with 2,5-dimethylhexa-2,4-diene was slower by a factor of *ca.* 3 than with other dienes, while the reaction of (2a) with dimethylhexadiene was too slow for study. Owing to its high volatility the reactions of butadiene with (2a and b) [1] were not further studied.

As the kinetics of the hydride–diene reactions showed no difference between various dienes, competition experiments were carried out wherein the hydrides were treated with an excess of two dienes and the products analysed. The results are given in Table 3 and within the limits of accuracy of the measurements (± 10%) there was no significant discrimination of the hydrides towards the dienes.



First-order plots for the reaction of $[\{M(C_5Me_5)\}_2HCl_3]$ (2) with cyclo-octa-1,5-diene in CH_2Cl_2 at 310 K. (a) Rh; (b) Ir; a = concentration of (2) at $t = 0$, x = concentration at time, t

The rates of reaction of four dienes with the deuterido-complexes, $[\{M(C_5Me_5)\}_2DCl_3]$, were also measured and found to be the same (Table 2), within experimental error, as those of the hydrides and there was no detectable isotope effect.

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* A reaction of the hydrides (2) with dichloromethane [to give (1)] competed. The rate for (2b) was very slow and not significant, however, (2a) reacted at a more comparable rate with dichloromethane ($k_s = 2.5 \pm 0.3 \times 10^{-5}$ s^{-1}) and allowance was made for this in all the calculations.

The choice of solvents for these reactions was limited by solubility problems to dichloromethane, deuteriochloroform, and benzene. More powerfully co-ordinating solvents such as dimethyl sulphoxide or pyridine reacted with the hydrides and deactivated them. The rates of reaction of (2a and b) with cyclo-octa-1,5-diene in chloroform at 310 K were also first order in complex and zero order in diene and were slower [$k_1 = 0.4 \pm 0.05 \times 10^{-4}$ (Rh) and $2.6 \pm 0.3 \times 10^{-4}$ s^{-1} (Ir)] than in dichloromethane. In benzene the rate of reaction of the rhodium hydride (2a) was too slow for convenient measurement at 310 K and the first-order rate constant of the reaction with the iridium hydride (2b) was estimated as 1.0×10^{-4} s^{-1} at 310 K. Although the data are limited, it appears that the rates decrease sharply in solvents of low polarity; qualitative observations bear this out since considerable rate enhancements are observed for related reactions in alcoholic solvents.

TABLE 3

Results of competition reactions in dichloromethane (310 K)

Reactants [a] (molar ratio)	Allylic and diene products [b] (molar ratio)
(2a) + isoprene + 1,5-cod + Et_3N (1 : 1.25 : 1.25 : 1)	(11a) + (12a) + (3a) (0.32 : 0.25 : 0.45)
(2a) + isoprene + 1,3-chd + Et_3N (1 : 1.25 : 1.25 : 1)	(11a) + (12a) + (6a) (0.30 : 0.25 : 0.45)
(2a) + isoprene + 1,3-pd + Et_3N (1 : 1.25 : 1.25 : 1)	(11a) + (12a) + (13a) + (14a) (0.29 : 0.20 : 0.42 : 0.09)
(2a) + isoprene + 2,3-dmbd + Et_3N (1 : 1.25 : 1.25 : 1)	(11a) + (12a) + (15a) (0.30 : 0.23 : 0.47)
(2b) + isoprene + 1,5-cod + Et_3N (1 : 1.25 : 1.25 : 1)	(11b) + (12b) + (3b) (0.14 : 0.34 : 0.52)
(2b) + isoprene + 1,3-chd + Et_3N (1 : 1.25 : 1.25 : 1)	(11b) + (12b) + (6b) (0.15 : 0.37 : 0.48)
(2b) + isoprene + 1,3-pd + Et_3N (1 : 1.25 : 1.25 : 1)	(11b) + (12b) + (13b) + (14b) (0.17 : 0.36 : 0.42 : 0.05)
(2b) + isoprene + 2,3-dmbd + Et_3N (1 : 1.25 : 1.25 : 1)	(11b) + (12b) + (15a) (0.15 : 0.37 : 0.48)

[a] 1,5-cod = cyclo-octa-1,5-diene; 1,3-chd = cyclohexa-1,3-diene; 1,3-pd = penta-1,3-diene; and 2,3-dmbd = 2,3-dimethylbutadiene. [b] (11) = [M(C_5Me_5)(*syn*-1,2-dimethylallyl)Cl]; [1] (12) = [M(C_5Me_5)(η-isoprene)]; [1] (13) = [M(C_5Me_5)(*syn,syn*-1,3-dimethylallyl)Cl]; [1] (14) = [M(C_5Me_5)(*syn*-1-ethylallyl)Cl]; [1] (15) = [M(C_5Me_5)(2,3-dimethylbutadiene)].[1]

The effects of temperature on the first-order rate constants of the reactions of both (2a and b) were investigated for one model diene, cyclo-octa-1,5-diene, and are given in Table 4. Since the general behaviour of the other dienes is very similar we presume that the activation parameters, calculated from a logarithmic plot of k_1 against $1/T$, will be the same. The activation parameters obtained are: $\Delta H^\ddagger$ 94 (Rh) and 90 (Ir) kJ mol^{-1} and $\Delta S^\ddagger$ −9.5 J K^{-1} mol^{-1} (for both Rh and Ir).

TABLE 4

First-order rate constants for the reactions of [M(C_5Me_5)$_2$-HCl_3] (0.033 mmol) and cyclo-octa-1,5-diene (0.033 mmol) in CH_2Cl_2 at various temperatures

Rh		Ir	
T/K	10^4k_1/s^{-1}	T/K	10^4k_1/s^{-1}
324.0	6.0 ± 0.8	310.0	7.5 ± 0.8
322.5	5.0 ± 0.6	305.0	5.0 ± 0.5
318.5	3.3 ± 0.4	302.5	3.2 ± 0.3
314.5	1.9 ± 0.2	296.0	1.3 ± 0.2
308.0	1.0 ± 0.1	288.0	0.53 ± 0.08

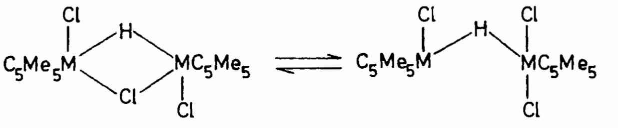
For technical reasons it was not possible to measure rates of decomposition of the allylic to the diene complexes but it was clear that a significant acceleration occurred in the presence of base.

Mechanism for the Formation of the η-Allylic Complexes and for their Reductive Elimination.—The kinetic data clearly show that the rate-determining step in the reactions of the hydrides with the dienes does not involve the diene since the rates are independent both of its concentration and, with the exception of one very sterically hindered diene, its nature. The primary step therefore involves only the hydride complex, and is presumably a dissociation to provide a site at which reaction can occur. The observed first-order dependence on [$(MC_5Me_5)_2HCl_3$] and the small negative $\Delta S^\ddagger$ show that dissociation,

$$[\{M(C_5Me_5)\}_2HCl_3] \rightleftharpoons [M(C_5Me_5)Cl_2(\text{solvent})] + [M(C_5Me_5)HCl(\text{solvent})]$$

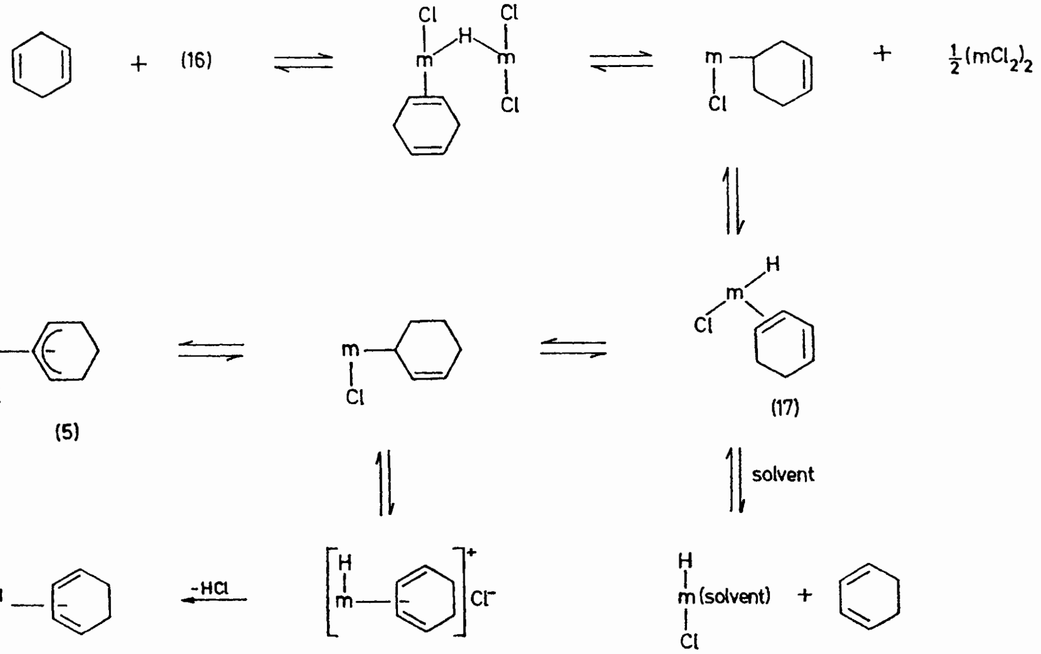
does not occur in dichloromethane, though such processes may occur in media of better solvating power. The most plausible way in which a vacant co-ordination site could be achieved is by the opening of either a M–H–M or a M–Cl–M bridge bond. No analogies to the former process have been reported, but it might be expected that opening the M–H–M bridge would give rise to a substantial isotope effect; in fact there was no detectable isotope effect when the deuteride, [$\{M(C_5Me_5)\}_2DCl_3$], was treated in place of the hydride. We therefore favour the rate-determining step to be the opening of the chloride bridge to give the singly bridged intermediate (16) which has a vacant site at one metal atom where co-ordination of the diene can occur prior to further fast reactions involving transfer of hydride giving first the σ- and then the π-allylic complex. The rate of bridge-opening is enhanced in solvents of higher polarity, because of better solvation of the intermediate (16), possibly involving weak binding of a solvent molecule at the vacant site.

Supporting evidence for this conclusion is provided from the reactions of the di-μ-hydrido-complex [$\{HIr(C_5Me_5)Cl\}_2$].[10] This compound shows no reactivity towards dienes in dichloromethane but reacts easily in



(2) (16)

better co-ordinating solvents such as acetone or ethanol, for example, with butadiene to give the 1—3-η-1-methylallyl complex. Opening of a M–H–M bridge, therefore, presumably only occurs when the solvation energy of the intermediate is sufficiently large to compensate for the extra energy needed in breaking the M–H bond.



SCHEME [m = Rh(C_5Me_5) or Ir(C_5Me_5)]

A further possibility that can be considered is that the rate-determining step in the reaction of (2a and b) is the ionisation of a terminal M–C to give an ion pair. Experimental difficulties have so far prevented us from testing this by measuring rates in the presence of added Cl^- in that no suitable chloride salt has been found which is soluble in dichloromethane and which neither reacts with the hydrides nor obscures the relevant region of the n.m.r. spectrum. Even if the experiments were more feasible, the interpretation of the results would be difficult, since added Cl^- would be expected to compete strongly for the vacant site in (16), as well as tending to repress any ionisation.

However, if an ionisation step were significant in the reactions of (2a and b) it should also occur for the di-μ-hydrido-complex [$\{HIr(C_5Me_5)Cl\}_2$], which would, therefore, be expected to react in dichloromethane at very nearly the same rate as (2b), since there appears no reason why a terminal Ir–Cl bond should not ionise equally easily in both complexes. The fact that the di-μ-hydrido-complex is inert towards dienes in dichloromethane and similar solvents, therefore inclines us to the view that ionisation is not important in non-polar solvents in either case.

It may also be noted that the crystal structure of (2a) reveals the angle RhCl(bridge)Rh′ to be only 73° and hence the bridge may be considered to be somewhat strained;[11] it is further clearly possible that some direct bonding occurs between the two metal atoms in (16).

The acyclic dienes discussed in the preceding paper[1] react with (16) in the transoid manner presumably for steric reasons. However, the cyclic *cis,cis*-dienes cannot react in this way and the low-field triplets in the n.m.r. spectra of (3b), (5b), and (9b) show that the $-(CH_2)_n-$ chains linking the ends of the η-allylic units must be attached in the expected *anti*-configuration in each case. Allylic complexes [or the equivalent for (7)] are formed in all the reactions of this type, both with cyclic and acyclic dienes and represent energy minima even where the metal(I)–diene complexes are the final products.

The observation of intermediates identified as 1—3-π-cyclohex-2-enyl complexes, in the reactions with the cyclohexadienes, and the fact that they are formed with equal facility from both the 1,3- and the 1,4-diene, necessitates revision of an earlier proposal concerning the mode of this reaction. For the reasons enunciated in the preceding paper,[1] it is not possible to propose [$M(C_5Me_5)(solvent)_n$] as an intermediate since, by analogy, it

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[10] D. S. Gill and P. M. Maitlis, *J. Organometallic Chem.*, 1975, **87**, 359.

[11] M. R. Churchill and S. W. Y. Ni, *J. Amer. Chem. Soc.*, 1973, **95**, 2150.

ought also to be present in reactions involving butadiene and hence to lead to the η-butadiene complex, a compound never isolated or detected. A modified mechanism for the reaction of the cyclohexadienes with the hydrides is shown in the Scheme.

Isomerisation of the 1,4- to the complexed 1,3-diene occurs by addition and elimination of M–H to give the intermediate (17); in the presence of a good solvent such as an alcohol there is competition between formation of the σ- and η-allylic intermediates and loss of cyclohexa-1,3-diene. The latter reaction then leads to the observed overall isomerisation of cyclohexa-1,4- to cyclohexa-1,3-diene in ethanol, a reaction that has not been detected in dichloromethane; however, in the latter solvent the intermediate η-cyclohexenyl complex is found. In the presence of a substantial amount of the 1,3-diene the equilibrium is displaced back to (17) and the π-diene complex results by β-hydride elimination from the σ-cyclohexenyl intermediate, simultaneous with ionisation of Cl^- and attack at the metal of the cyclohexenyl double bond, as has already been proposed.[1] The low stability of the cyclohex-2-enyl complex towards reductive elimination agrees well with these ideas.[1]

A similar process involving stepwise isomerisation *via* cyclo-octadienemetal hydride and cyclo-octenyl complexes will also explain the observed reaction of cyclo-octa-1,3-, -1,4-, or -1,5-diene to the 1—3-η-cyclo-oct-2-enyl complexes (3a and b) and their further decomposition to the 1,2,5,6-η-cyclo-octa-1,5-diene complexes (4a and b). It is surprising that the 1—3-η-cyclo-octenyl intermediates are so stable, since they are allylic complexes with two *anti*-substituents, and also that the 1,2,5,6-η-cyclo-octa-1,5-diene and not the 1—4-η-cyclo-octa-1,3-diene complexes result from the decomposition. However, few tetrahapto-complexes of the latter ligand have, to our knowledge, been made.[12] Presumably steric factors increase the activation energy needed for elimination of M–H from the cyclo-oct-2-enyl complex and once this barrier has been overcome the reaction proceeds further to the most stable product, (4).

The formation and ready decomposition of the norbornenyl (7) and the cyclopentenyl (9) complexes accord well with the proposed mechanism.[1] The former complexes behave normally to give the metal(I)–norbornadiene compounds (8) by reductive elimination of HCl, but the cyclopentenyl complexes give (10) by a path which involves loss of two hydrogen atoms, and no overall change in the formal oxidation state of the metal.

The close similarity in the products obtained from the reactions of the acyclic[1] and cyclic dienes with the hydrides (2a and b) in dichloromethane to those from the chlorides (1a and b) in ethanol–base suggest similar processes occur. However, we may by no means rule out that in the latter case an important active species is $[H(MC_5Me_5)Cl(solvent)]$ as was proposed earlier.[8]

EXPERIMENTAL

Details of the preparation and identification of the complexes (6) from cyclohexadienes, (8a) from norbornadiene, (10) from cyclopentadiene, and (11)—(15) from acyclic dienes have already been given.[1,6,8] The complexes obtained in the reactions described here were identified by their n.m.r. spectra and were also isolated and fully characterised, where appropriate. Olefins were distilled before use and stored under nitrogen in dark bottles at 0 °C. Their purity was checked by n.m.r. spectroscopy and v.p.c. and, where necessary, they were purified by preparative v.p.c. on a Carbowax column. Cyclo-octa-1,4-diene was prepared by the method of Craig *et al.*,[13] and was purified by preparative v.p.c.; the product used was better than 86% pure but contained 8% of the 1,3-isomer. The n.m.r. spectrum agreed with literature values.[14] All reactions were carried out under dry nitrogen.

Chloro(1—3-η-*cyclo-octenyl*)(*pentamethylcyclopentadienyl*)-*rhodium* (3a) *and -iridium* (3b).—Cyclo-octa-1,3-diene (0.40 g, 3.7 mmol) was added to a suspension of (1a) (0.22 g, 0.35 mmol) and anhydrous sodium carbonate (0.21 g) in absolute ethanol (5 ml) and the mixture was stirred (42 °C for 2 h). The volatile components were distilled off on a rotary evaporator and the deep red residue was extracted with ether. The ether solution was filtered and the solvent removed to leave deep red crystalline (3a) (0.26 g, 0.67 mmol, 96%; decomp. 127 °C) which was recrystallised from n-hexane [Found: C, 56.7; H, 7.3; Cl, 9.2%; *M*, 423 (osmometric in chloroform). $C_{18}H_{18}ClRh$ requires C, 56.5; H, 7.4; Cl, 9.3%; *M*, 383]. On treatment with hydrogen chloride in benzene the complex decomposed quantitatively to cyclo-octene and (1a). When (3a) (0.1 mmol) was treated with pyridinium chloride in pyridine (1.8 mmol) and benzene (3 ml) at 25 °C for 2 h, the only organometallic product detected was (1a), formed quantitatively.

The same complex (3a) was also obtained (96—98%) from either cyclo-octa-1,3- or -1,4-diene under the above conditions and from cyclo-octa-1,3- or -1,5-diene (80%) and (1a) in ethanol in the presence of triethylamine.

The cyclo-octenyliridium complex (3b) was obtained as yellow crystals (decomp. 95 °C) under the above conditions from either cyclo-octa-1,3- or -1,5-diene in ethanol–sodium carbonate at 25 °C (100%) or triethylamine in ethanol (50 °C for 3 h, 88%) [Found: C, 46.3; H, 6.0; Cl, 7.5%; *M*, 532. $C_{18}H_{28}ClIr$ requires C, 45.8; H, 6.0; Cl, 7.5%; *M*, 472].

(1,2,5,6-η-*Cyclo-octa*-1,5-*diene*)(*pentamethylcyclopentadienyl*)-*rhodium* (4a) *and -iridium* (4b).—A mixture of (1a) (0.20 g, 0.33 mmol), anhydrous sodium carbonate (0.2 g), and cyclo-octa-1,5-diene (0.35 g, 3.3 mmol) in absolute ethanol was stirred at 70 °C for 3 h. The volatile products were then removed *in vacuo* on a rotary evaporator and the residue was crystallised from ether at −78 °C to afford the cyclo-octa-1,5-dienerhodium complex (4a) (0.18 g, 0.53 mmol, 80%; m.p. 160—163 °C). The analytical sample was sublimed at 65 °C/10^{-3} mmHg [Found: C, 62.0; H, 7.8%; *M* (mass-spectrometric) 346. $C_{18}H_{27}Rh$ requires C, 62.4; H, 7.9%; *M*, 346].

The complex was obtained in similar yield using cyclo-octa-1,3- or -1,4-diene under the same conditions.

The cyclo-octa-1,5-dieneiridium complex (4b) (m.p. 163—166 °C) was obtained from either cyclo-octa-1,3-diene

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[12] E. Koerner von Gustorf and J. C. Hogan, *Tetrahedron Letters*, 1968, 3131; A. J. Deeming, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 2093.

[13] L. E. Craig, R. M. Elofson, and I. R. Rossa, *J. Amer. Chem. Soc.*, 1953, **75**, 480.

[14] S. Moon and C. R. Ganz, *J. Org. Chem.*, 1969, **34**, 465.

(85%) or cyclo-octa-1,5-diene (73%) by an identical procedure [Found: C, 50.2; H, 6.4%; *M* (mass-spectrometric) 434, 436. $C_{18}H_{27}Ir$ requires C, 49.6; H, 6.3%; *M*, 434, 436.]

Both (4a) and (4b) gave the dichloride complexes (1a) or (1b) on treatment with HCl.

Decomposition of the 1—3-η-*Cyclo-oct*-2-*enyl Complexes* (3a) *and* (3b) *to the* 1,2,5,6-η-*Cyclo-octa*-1,5-*diene Complexes* (4a) *and* (4b).—The complexes (3a) and (3b) were allowed to react under the conditions described in Table 1. In a typical experiment (3a) (75 mg, 0.2 mmol), anhydrous sodium carbonate (70 mg), and cyclo-octa-1,5-diene (40 μl, 0.33 mmol) were heated (60 °C for 5 h) in ethanol (2 ml) under nitrogen. The solvent and volatile products were carefully distilled off at 10^{-2} mmHg into a liquid nitrogen-cooled trap and were analysed by v.p.c. [9.5 ft × 1/8 in steel column packed with 20% Carbowax M on 60/70 chromosorb W, at 110 °C] with reference to standard sample mixtures. The solid residue was analysed by n.m.r. spectroscopy and the main products were also isolated and characterised. Similar analyses were also performed during the reaction of (1a) or (1b) to (3a) or (3b).

N.m.r. and Rate Measurements.—The reactions of the hydrido-complexes[2] (2a) and (2b) with the dienes were followed initially on a Varian HA-100 n.m.r. spectrometer; kinetic data were obtained on a Varian A-60 n.m.r. spectrometer fitted with a model V-6057 variable temperature system. The spectrometer probe was preset at a constant temperature which was calibrated with a copper-Constantin thermocouple. Rate data were obtained by following the change in intensity (estimated by electronic integration and measured twice) of the C_5Me_5 resonances of both the initial and product complexes until at least 85% of the reaction was complete. The spectra of product and intermediate complexes were identified by comparison with authentic samples as described.

All reactions were carried out in spectroanalysed dichloromethane which had been purified and deacidified from HCl by passage through an alumina column; it was stored in dark bottles over anhydrous sodium carbonate. For each experiment the hydride (2a or b) [0.003 mmol = 19.6 mg (M = Rh), and 25.0 mg (M = Ir)] was accurately weighed into the n.m.r. tube and was then dissolved in 0.40 ml of dichloromethane containing tetramethylsilane as internal standard. The required amount of diene was then added in the cold using a microsyringe together with triethylamine [4.6 μl, 0.033 mmol], for those reactions where the diene complexes were formed as final products. The tube was quickly sealed, vigorously shaken, and placed into the spectrometer probe. Details of the experiments are given in Tables 2—4.

Plots of log $(a/a - x)$ [a = initial concentration of hydride, x = concentration of hydride after time t] were linear over at least four half-lives for all the dienes investigated, indicating first-order dependence on the hydride [Figure]. Moreover, the observed reaction rates were unchanged for hydride to diene ratios over the range 1 : 10, 1 : 5, 1 : 2, 1 : 1, 1 : 0.5, and 1 : 0.25, showing the independence of reaction rate on the diene concentration.

We thank the National Research Council of Canada for supporting this work.

[5/019 *Received*, 6*th January*, 1975]