Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part IX.[1] The Formation of η-Allyl-M^{III} and η-Diene-M^{I} Complexes from μ-Hydrido-compounds and Acyclic Dienes

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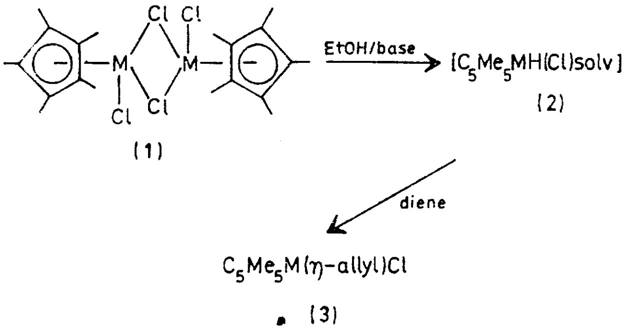
The reactions of the μ-hydrido-complexes $[H(MC_5Me_5)_2Cl_3]$ (4; M = Rh or Ir) with butadiene, penta-1,3-diene, isoprene, 1,1-dimethylallene, 2,3-dimethylbutadiene, *trans*-2-methylpenta-1,3-diene, and 2,5-dimethylhexa-2,4-diene are reported. η-Allylic complexes of varying stability are formed initially, but only the *syn*-1 (or 3-) alkyl isomer is formed where a choice is possible. The η-allylic complexes are of three types: (i) those that do not eliminate HCl under any conditions, (ii) those that eliminate HCl under forcing conditions, and (iii) those that eliminate HCl spontaneously to form the M^I(diene) complexes. The following conclusions are drawn: (a) the dienes react in the transoid form with these hydrides, and (b) in order for reductive elimination to occur, the η-allylic complex must have, or must easily be able to rearrange to a form bearing, an *anti*-1-alkyl group.

IN 1970 we published accounts of the reactions of di-μ-chloro-bis{chloro(pentamethylcyclopentadienyl)-rhodium and -iridum} (1a; M = Rh; 1b; M = Ir) with a variety of mono-, di- and tri-olefins in the presence of alcohol and base.[2,3] Two reactions with dienes were identified, the first leading to η-allylic complexes of M^{III} (3) and the second to η-diene complexes of M^I. In some cases the allylic complexes were shown to be intermediates in the formation of the diene complexes.

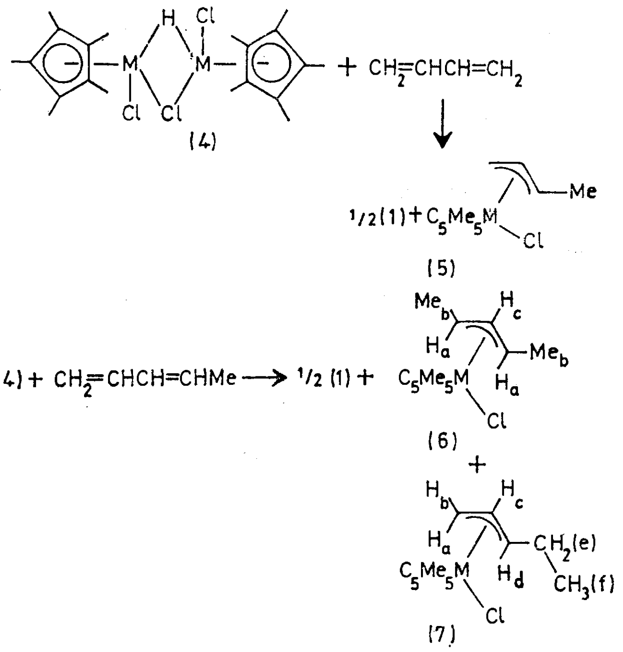
It was proposed that intermediate solvated hydride complexes (2) were formed from (1) which reacted with the dienes to give (3):



More recently we have been able to prepare hydrides of the type (4a, M = Rh) and (4b; M = Ir) by a number of routes, including the reaction of (1) with alcohol and base.[4] This paper describes the reactions of these hydrides with a number of acyclic dienes in deacidified dichloromethane † and compares the reactions with those of the dienes with the dichlorides (1) in ethanol/base. The following paper [5] includes a discussion of the reactions with cyclic dienes and the results of a kinetic investigation of the formation of the η-allylic complexes. Part of this work has appeared as a preliminary communication.[6]

RESULTS AND DISCUSSION

(i) *Buta*-1,3-*diene and Penta*-1,3-*diene*.—These dienes reacted with both (4a) and (4b) at 25 °C to give (1) and allylic complexes. Butadiene gave (5a) and (5b), while pentadiene gave (6a) and (6b), and (7a) and (7b), in the ratio 85 : 15 for both Rh and Ir.



The complexes (6a) and (6b) were isolated and purified by fractional crystallisation from ether–light petroleum and were assigned the structures shown based on their spectra (Table 1). The methyl groups in (6a) and (6b) were both *syn*- as shown by the coupling constants, J(a,c) = 10 Hz (6a) and 9 Hz (6b), which are close to the value expected and, in particular, to that reported (11.5 Hz) for the *syn*, *syn*-1,3-dimethylallyltris(trimethyl phosphite)nickel cation.[6]

The minor isomers (7a and b) could not be isolated pure but their structures follow clearly from the n.m.r. spectra of the mother liquors remaining after (6) had partly been crystallised out, and which contained *ca.*

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† It was found necessary to add one equivalent of triethylamine to the reactions in which HCl was liberated in order to ensure a clean reaction. The amine had no effect on the hydride–diene reactions.[5]

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

[2] K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2276.

[3] K. Moseley and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2284.

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

[5] H. B. Lee, K. Moseley, C. White, and P. M. Maitlis, following paper.

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

30% of (7). Thus the spectrum of (7b) showed resonances at τ 5.84 (m, 1 H, H$_c$), *ca.* 7.0 (m, 2 H, H$_b$ and H$_d$), 7.96 [d, 1 H, H$_a$, J(H$_a$-H$_c$) = 10, J(H$_a$-H$_b$) = 0], *ca.* 8.2 (m, 2 H, CH$_2$), 8.25 (s, 15 H, C$_5$Me$_5$), and 8.86 (t, 3 H, CH$_3$, J = 7 Hz) and is consistent with a 1-ethylallylic but not with a *syn, anti*-1,3-dimethylallylic ligand. The geometry of (7b), with ethyl *syn*, was assigned by comparison of the chemical shifts with those of the closely related (6b).

The complexes (6) and (7) were also obtained in the same ratios from the dichlorides (1) and penta-1,3-diene in ethanol/base at 65 °C, or in isopropyl alcohol/base at 25 °C. There was no evidence for any isomerisation (6) ⟶ (7) or the reverse.

Neither in the reactions with butadiene nor in those with pentadiene were any M^I–diene complexes produced, nor could such complexes be obtained from the allylic complexes (5), (6), or (7) under any of the conditions tried, including treatment with base in a variety of solvents including alcohols and for prolonged periods of time. These complexes remain unknown.

(ii) *Isoprene.*—Isoprene reacted with (4a) and (4b) in dichloromethane at 37 °C to give both the allylic complexes (8) and the η-isoprene complexes (10); the ratios were 55 : 45 for Rh and 30 : 70 for Ir. The complexes were separated by chromatography and identified by their n.m.r. spectra (Tables 1 and 2) and mass spectra.

The complexes (8) and (10) were also obtained from reaction of isoprene with the dichlorides (1) in ethanol in the presence of sodium carbonate (25 °C, 12 h); under more vigorous conditions (65 °C, 24 h) only the η-isoprene complexes (10a) and (10b) were formed.

The allylic complexes (8a) and (8b) could also be converted into the η-isoprene complexes when heated in an alcohol in the presence of base. In dichloromethane or benzene (25 °C, 48 h) in the presence of triethylamine, no η-isoprene complexes were formed and in benzene–sodium carbonate (65 °C, 24 h) the yields were only 20% for (10a) and <5% for (10b).

These results indicate that the η-isoprene complexes can be formed from the η-allylic complexes (8), particularly in polar solvents at higher temperatures, but that the allylic complexes are quite stable in less polar solvents, even in the presence of base, at 25 °C. This

TABLE 1

^{1}H n.m.r. spectra of η-allylic complexes in CH$_2$Cl$_2$ (τ) [a, b]

Complex	C$_5$Me$_5$	H$_a$	H$_b$	H$_c$	H$_d$	H$_e$	H$_f$
[RhC(C$_5$Me$_5$)(1,3-dimethylallyl)] (6a)	8.37s	6.68dq J(a,b) = 6.5 J(a,c) = 10.0	8.43d J(b,a) = 6.5	6.28td J(c,a) = 10.0 J(Rh,c) = 2.0			
[IrCl(C$_5$Me$_5$)(1,3-dimethylallyl)] (6b)	8.31s	7.08dq J(a,b) = 6.0 J(a,c) = 9.0	8.49d J(b,a) = 6.0	6.07t J(c,a) = 9.0			
[RhCl(C$_5$Me$_5$)(1-ethylallyl)] (7a)	8.30s	7.25d J(a,c) = 11.0	*ca.* 6.6m	6.02m	*ca.* 6.6m	*ca.* 8.2m	8.84t J(f,e) = 7.0
[IrCl(C$_5$Me$_5$)(1-ethylallyl)] (7b)	8.25s	7.69d J(a,c) = 10.0	*ca.* 7.0m	5.84m	*ca.* 7.0m	*ca.* 8.2m	8.86t J(f,e) = 7.0
[RhCl(C$_5$Me$_5$)(1,2-dimethylallyl)] (8a)	8.34s	6.60q J(a,b) = 6.5	8.47d J(b,a) = 6.5	8.30d J(Rh,c) = 1.5	7.25s J(d,e) ≈ 1.0	6.77s J(e,d) ≈ 1.0	
[IrCl(C$_5$Me$_5$)(1,2-dimethylallyl)] (8b)	8.29s	7.00q J(a,b) = 6.0	8.53d J(b,a) = 6.0	8.25s	7.66s J(d,e) ≈ 1.0	6.92s J(e,d) ≈ 1.0	
[IrCl(C$_5$Me$_5$)(1,1-dimethylallyl)] (9b)	8.29s	8.99s	8.27s	5.89dd J(c,d) = 10.0 J(c,e) = 7.0	7.35dd J(d,c) = 10.0 J(d,e) = 1.0	6.96dd J(e,c) = 7.0 J(e,d) = 1.0	
[IrCl(C$_5$Me$_5$)((1,1,2-trimethylallyl)] (11b)	8.33s	9.00s	8.47s	8.25s	7.22d J(d,e) = 1.0	6.85d J(e,d) = 1.0	
[RhCl(C$_5$Me$_5$)(1,1,3-trimethylallyl)] (13a)	8.41s	8.93s	8.40s				
[IrCl(C$_5$Me$_5$)(1,1,3-trimethylallyl)] (13b)	8.37s	8.94s	8.28s	6.05d J(c,d) = 10.0	6.67m J(d,c) = 10.0 J(d,e) = 6.0	8.50d J(e.d) = 6.0	
[RhCl(C$_5$Me$_5$)(1-ethyl-2-methylallyl)] (14a)	8.36s	7.28s	6.80s	8.30d J(Rh,c) = 1.5	6.69t J(d,e) = 7.0	8.16m	8.88t J(f,e) = 7.0

[a] At 100 MHz. [b] Coupling constants in Hz.

TABLE 2

^{1}H n.m.r. spectra of η-diene complexes in CH$_2$Cl$_2$ (τ)

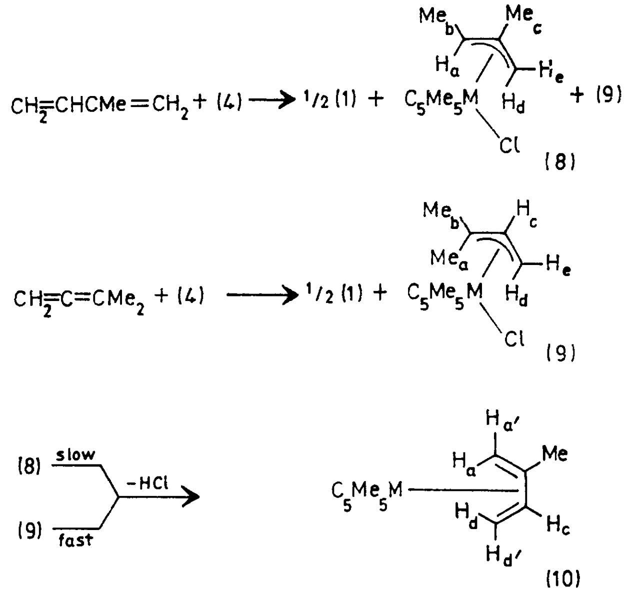
Complex	C$_5$Me$_5$	H$_a$	H$_{a'}$	H$_b$	H$_c$	H$_d$	H$_{d'}$	Others
[Rh(C$_5$Me$_5$)(isoprene)] (10a)	8.07s	9.85m	8.51m	8.22s	5.77t J(c,d) = 7.0 J(c,d') = 6.0	9.92m	8.40m J(d',c) = 6.0	
[Ir(C$_5$Me$_5$)(isoprene)] (10b)	8.04s	10.20m J(a,a') = 2.0	8.30dd J(a',a) = 2.0 J(a',c) = 1.0	8.16s	5.86dd J(c,d) = 6.5 J(c,d') = 6.0	10.41dd J(d,c) = 6.5 J(d,d') = 2.0	8.21dd J(d',c) = 6.0 J(d',d) = 2.0	
[Rh(C$_5$Me$_5$)(2,3-dimethylbutadiene)] (12a)	8.13s	9.93m J(a,a') ≈ 1.0	8.49s,br J(a',a) ≈ 1.0	8.22s				
[Ir(C$_5$Me$_5$)(2,3-dimethylbutadiene)] (12b)	8.09s	10.27m J(a,a') = 1.5	8.34d J(a',a) = 1.5	8.18s				
[Rh(C$_5$Me$_5$)(2-methylpenta-1,3-diene)] (15a)	8.14s	9.97m	8.63m	8.24s	5.91d J(c,d) = 7.0	9.40m		H$_e$: 8.84d J(e,d) = 6.0
[Ir(C$_5$Me$_5$)(2-methylpenta-1,3-diene)] (15b)	8.08s	10.28m J(a,a') = 2.0 J(a,c) ≈ 1.0	8.24m J(a',a) = 2.0 J(a',c) ≈ 1.0	8.18s	6.04d J(c,d) = 6.0	10.00qn J(d,c) = 6.0 J(d,e) = 6.0		H$_e$: 8.83d J(e,d) = 6.0
[Rh(C$_5$Me$_5$)(2,5-dimethylhexa-1,3-diene)] (17a)	8.14s	9.54m	8.46m	8.25s	5.74d J(c,d) = 8.0	9.20td J(d,c) = 8.0 J(d,e) = 8.0 J(Rh,d) = 2.0		H$_e$[c] H$_f$: 8.91d and 8.85d J(f,e) = 8.0
[Ir(C$_5$Me$_5$)(2,5-dimethylhexa-1,3-diene)] (17b)	8.07s	10.26m	8.42dd J(a',a) = 2.0 J(a',c) ≈ 1.0	8.18s	5.92d J(c,d) = 6.0	10.12dd J(d,c) = 6.0 J(d,e) = 8.0		H$_e$[c] H$_f$: 9.01d and 8.98d J(f,e) = 6.0

[a] Coupling constants in Hz. [b] In C$_6$H$_6$ solution. [c] Not observed due to overlapping with other signals.

implies that the η-isoprene complexes observed in the reaction of (4a) and (4b) with isoprene in dichloromethane at 25 °C cannot arise from (8a) or (8b), and must be formed by an alternative route.

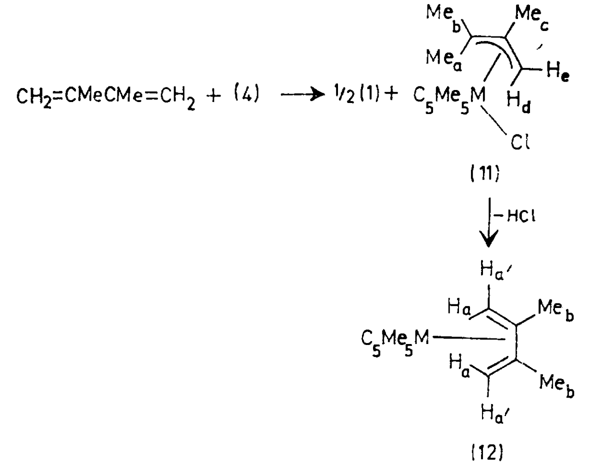
An n.m.r. study of the reaction of the iridium hydride (4b) with isoprene in the absence of triethylamine revealed an unstable intermediate (9b) which readily decomposed to (10b). The structure of this intermediate was inferred from its spectrum (Table 1) which showed two singlet methyl resonances at τ 8.27 and 8.99, suggesting the presence of *gem*-dimethyls, the higher field resonance being assigned to the *anti*-1-methyl. In the presence of triethylamine this intermediate could not be detected and only the formation of the η-isoprene complex (10b) was observed. The same intermediate was also observed in the reaction of 1,1-dimethylallene with (4b) (see below).

Although no intermediate could be detected from the reactions of the rhodium hydride (4a) with isoprene, a similar reaction must occur, since the only other way in which (10a) could be formed directly would be by reaction of a solvated ' C_5Me_5Rh ' species directly with isoprene. This can be ruled out since none of the appropriate diene complex is formed from either butadiene or pentadiene nor is the [Rh(C_5Me_5)(cyclo-octa-1,5-diene)] complex detected in the initial reactions of cyclo-octa-1,5-diene with (4a). It would be most surprising if isoprene alone reacted in this fashion.



(iii) 1,1-*Dimethylallene*.—This diene reacted with (4a) and (4b) in dichloromethane at 37 °C in the presence of triethylamine to give the η-isoprene complexes (10); in the absence of triethylamine the same intermediate (9b) was detected as had been observed in the isoprene reaction mentioned above. The complexes (10) were also obtained from 1,1-dimethylallene and the dichloro-complexes (1) in isopropyl alcohol–sodium carbonate at 25 °C.

(iv) 2,3-*Dimethylbutadiene*.—2,3-Dimethylbutadiene reacted with the hydrides (4a and b) under the above conditions to give (12a and b) identified by their n.m.r. and mass spectra. Again, an intermediate formulated as (11b) was observed in the reaction of (4b) in the absence of base, and a transient C_5Me_5 resonance (τ 8.36), presumably due to (11a), was detected during the same reaction with (4a).



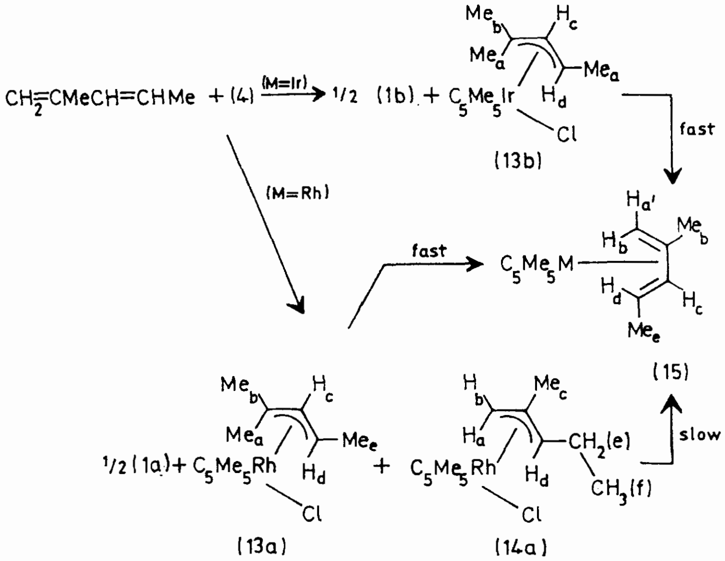
The rhodium complex (12a) was also obtained preparatively from reaction of (1a) with dimethylbutadiene at 25 °C in isopropyl alcohol–sodium carbonate; this, however, represented a poor route to (12b) which was better obtained by treating (1b) with stoicheiometric amounts of diene and isopropyl alcohol in benzene in the presence of sodium carbonate.

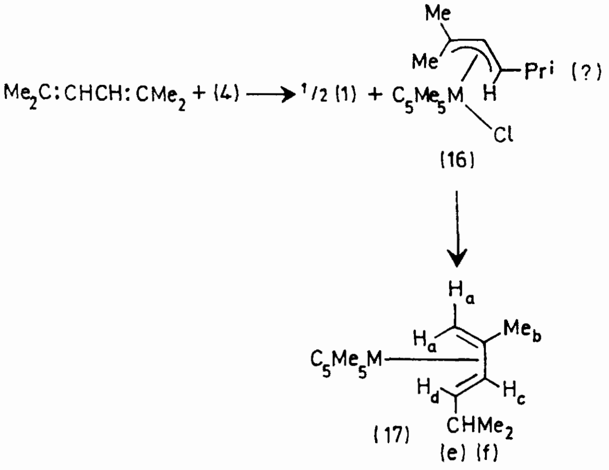
(v) trans-2-*Methylpenta*-1,3-*diene*.—*trans*-2-Methylpenta-1,3-diene reacted with the iridium hydride (4b) (CH_2Cl_2–Et_3N at 37 °C) to give the 2—5-η-4-methylpenta-2,4-diene complex (15b), together with (1b). When the reaction was followed by n.m.r. (no Et_3N) an unstable intermediate was detected which was assigned structure (13b) (Table 1).

In contrast, the rhodium hydride (4a) reacted (CH_2Cl_2–Et_3N at 37 °C) with 2-methylpenta-1,3-diene to give a mixture of (1a), (15a), and a new complex, (14a), in the ratio 2.5 : 4 : 1. In the absence of Et_3N it was possible to detect an unstable intermediate to which the structure (13a) was assigned, based on the observation of singlet methyl resonances at τ 8.40 (Me_b), 8.41 (C_5Me_5), and 8.93 (Me_a). The complex (14a) was isolated by chromatography and assigned the structure shown on the basis of its n.m.r. spectrum. This complex could also be converted into (15a), but only when heated in ethanol–sodium carbonate (18 h at 65 °C). Reaction of the dichloride (1a) with the diene in isopropyl alcohol–sodium carbonate (25 °C) gave (14a) and (15a), while (1b) gave only (15b) under these conditions.

(vi) 2,5-*Dimethylhexa*-2,4-*diene*.—Reaction of this diene with both (4a) and (4b) (CH_2Cl_2 at 37 °C) gave (1) and new diene complexes which were assigned structures (17a and b), based on their n.m.r. and mass spectra. Again, very unstable intermediates could be detected in both reactions by their C_5Me_5 resonances [τ 8.36 (Rh), 8.41 (Ir)], but these were never present in a concentration high enough for the other resonances to be resolved. It was therefore not possible to assign definitive structures to the intermediates, but, by analogy to the other systems, they were probably the allylic complexes (16).*

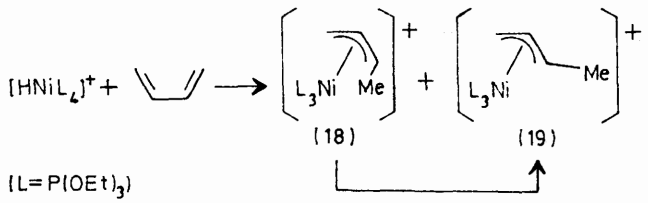
Mechanism of the Hydride-Diene Reaction.—All the seven dienes examined in this study reacted with the hydrides (4a and b) to give, in each case, η-allylic complexes arising by addition of M–H to a double bond.





Three unsymmetrical 1,3-dienes were examined: penta-1,3-diene, isoprene, and 2-methylpenta-1,3-diene. Penta-1,3-diene added both Rh–H and Ir–H in the same way, 85% to the 1,2- and 15% to the 3,4-double bond. However, isoprene added Rh–H 45% 1,2- and 55% 3,4- while Ir–H added 70% 1,2- and 30% 3,4- and 2-methylpenta-1,3-diene added Rh–H 80% 1,2- and 20% 3,4- while Ir–H added 100% 1,2-. From these limited data it appears that terminal double bonds are attacked preferentially over internal double bonds but that Ir–H has some preference for addition to $-CMe{=}CH_2$. The distribution appears to be kinetically rather than thermodynamically determined and the ratios of (6) and (7) obtained from pentadiene were the same (within experimental error) starting from the hydrides (4) in CH_2Cl_2 at 25 °C as they were starting from the chlorides (1) in the presence of alcohol and base both at 25 and 60 °C.

Five of the seven dienes examined can, in principle, give allylic compounds with the 1- (and/or 3-) alkyl either *syn-* or *anti-*; for 1,1-dimethylallene and 2,3-dimethylbutadiene there is no alternative, and 1,1-dimethylallylic complexes are formed in which one methyl must be *syn* and one *anti*. In each case where an alternative is possible, it is experimentally observed that *only* the *syn*-isomer is obtained; the *anti*-isomer could never be detected. This result is in sharp contrast to other studies of hydride–diene reactions. For example, Tolman[7] observed that both the *anti-* and *syn*-1-methylallyl complexes (18) and (19) were obtained on reaction of $[HNi\{P(OEt)_3\}_4]^+$ with butadiene; the *anti*-isomer was kinetically favoured over the *syn*-isomer by a factor of 7.5. A slow (at 0 °C) isomerisation to the *syn*-isomer [(18) to (19)] then occurred:



Similar results have been obtained for the reaction of $[HNiL_4]^+$ with a variety of other 1,3-dienes,[7] for the reaction of $HCo(CO)_4$ with butadiene, penta-1,3- and

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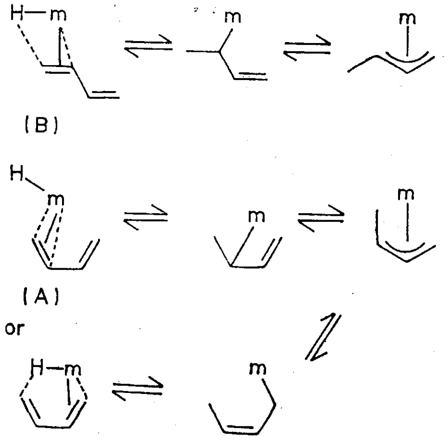
* The alternative structure for (16) with the 1-isopropyl group *anti-* rather than *syn-* can be excluded since on elimination of HCl this isomer of (16) would be expected to give the 2—5-η-2,5-dimethylhexa-2,4-diene complex and the *anti*-1-isopropyl isomer of (17); these were not detected.

[7] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 6785.

-1,4-diene,[8] and of $HRh(PF_3)_4$ with 1,3-dienes.[9] In each of these cases the *anti*-isomers appear to be kinetically, and the *syn*-isomers thermodynamically, favoured. In all cases the *anti*-isomers were easily detected; they were not found in the work described here, and we conclude that they are not formed.

From the predominance of the kinetically favoured *anti*-isomer (18) Tolman concluded that the acyclic 1,3-dienes react in the cisoid form (A). The results of the present work suggest that the hydrides (4a and b) must react with these dienes in the transoid form (B). Models indicate that it is unlikely that M–H can span a transoid 1,4-diene and therefore we propose that here the dienes react by 1,2-addition; it is, however, quite conceivable that the hydrides that give the *anti*-substituted allyls react by 1,4-addition.



The reason why these acyclic dienes react in the transoid rather than the cisoid form is probably steric since the transition state is likely to be very crowded.[4]

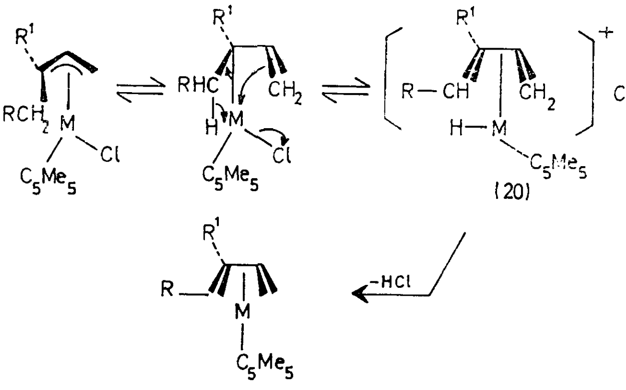
Decomposition of the η-Allylic Complexes.—The allylic complexes formed from reaction of the hydrides and acyclic 1,3-dienes may be divided into three groups based on their readiness to undergo reductive elimination of HCl to give the M-(diene) complexes.

(i) Those that do not eliminate HCl under any conditions attempted comprise the *syn*-1-methyl-, (5), the *syn*, *syn*-1,3-dimethyl-, (6), and the *syn*-1-ethyl-allylic complexes (7).

(ii) Those that eliminate HCl only with difficulty on heating, except in a polar solvent in the presence of base. These include the *syn*-1,2-dimethyl- (8) and the *syn*-1-ethyl-2-methyl-allylic (14a) complexes.

(iii) The remaining complexes [*syn*, *anti*-1,1-dimethyl- (9) *syn*, *anti*-1,1,2-trimethyl- (11), *syn*, *anti*, *syn*-1,1,3-trimethyl- (13) and, presumably, the *syn*, *anti*-1,1-dimethyl-*syn*-3-isopropyl-allylic (16)] all eliminate HCl so rapidly that they are only just detectable in the absence of base and not at all in its presence.

A feature of the complexes in group (iii) is that they all possess *syn*-and *anti*-1-methyl groups and we suggest that the presence of the latter is a requirement for a ready reductive elimination, the reason being that if there is an *anti*-1-methyl or -methylene group the carbon skeleton is already cisoid and close to the conformation needed for formation of the *cis*-diene. The proposed mechanism is shown in Scheme 1.



SCHEME 1

The essential features are that in the σ-allylic transition state with RCH_2 *anti*- the C–H bond can break and the M–H can form concurrently with breakage of the M–C σ- and formation of an M–olefin π-bond. This process is aided by ionisation of Cl^- and attack of the other double bond to give a diene metal hydride cationic complex which then loses H^+. The suggested ionic intermediate (20) is very similar to intermediates that have been postulated to arise in the reverse process, the protonation of a cyclohexa-1,3-dienerhodium(I) complex,[10] and also explains why the reaction is favoured by very polar solvents such as ethanol [see below for the complexes of group (ii)].

The common feature of complexes of group (ii) which do reductively eliminate HCl, though with difficulty, is that they all possess alkyl groups in both the *syn*-1- and the -2-position. It is well-established that with increasing bulk of 1- and 2-substituents, the *anti*-1-isomers become thermodynamically more stable.[7] It is, therefore, logical to presume that compounds comprising this group which have relatively small substituents at the 1- and particularly at the 2-positions, need extra activation energy in order to form the *anti*-1-isomers, presumably *via* σ-1-allylic intermediates (Scheme 2), which then readily decompose to the η-diene complexes. The complexes in group (i) bear only hydrogen in the 2-position and the activation energy for this reorganisation may be expected to be prohibitively high and hence no reductive elimination occurs. This interpretation is also in accord with the results for the cyclic dienes discussed in the following paper, which belong to groups (ii) and (iii).

Our inability to obtain, for example, the η-butadiene

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[10] B. F. G. Johnson, J. Lewis, and D. Yarrow, *J.C.S. Dalton*, 1972, 2084.

TABLE 3

Analytical data (calculated values in parentheses)

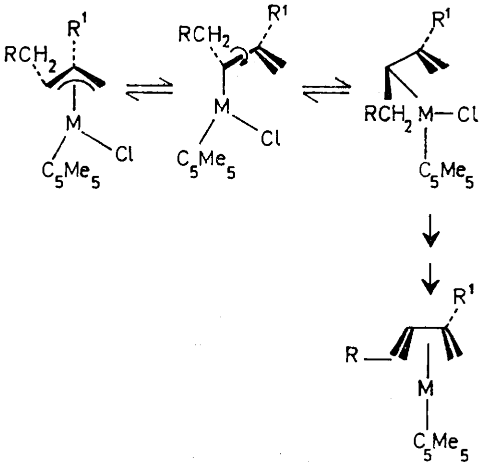
Complex	C	H	Cl	M.p. (t/°C)	Yield[a] (%)
[RhCl(C_5Me_5)(1,3-dimethylallyl)] (6a)	52.55 (52.55)	7.29 (7.06)	10.27 (10.35)	135—137[b]	62
[IrCl(C_5Me_5)(1,3-dimethylallyl)] (6b)	41.85 (41.68)	5.72 (5.60)	7.18 (8.21)	123—125[b]	60
[RhCl(C_5Me_5)(1,2-dimethylallyl)] (8a)	52.30 (52.55)	6.98 (7.06)	10.21 (10.35)	163—165[b]	50[c]
[IrCl(C_5Me_5)(1,2-dimethylallyl)] (8b)	41.76 (41.68)	5.49 (5.60)	7.50 (8.21)	152—155[b]	33[c]
[Rh(C_5Me_5)(isoprene)] (10a)	59.18 (58.83)	7.67 (7.57)		Oil at 25	50
[Ir(C_5Me_5)(isoprene)] (10b)	46.26 (45.55)	5.94 (5.86)		Oil at 25	65
[Rh(C_5Me_5)(2,3-dimethylbutadiene)] (12a)	60.07 (60.00)	7.86 (7.87)		50—52	80[c]
[Ir(C_5Me_5)(2,3-dimethylbutadiene)] (12b)	46.24 (46.92)	6.35 (6.15)		55—57	55[d]
[RhCl(C_5Me_5)(1-ethyl-2-methylallyl)] (14a)	54.32 (53.87)	7.23 (7.35)	9.73 (9.94)	145—147[b]	18[c]
[Rh(C_5Me_5)(2-methylpenta-1,3-diene)] (15a)	59.87 (60.00)	8.06 (7.87)		51—53	70
[Ir(C_5Me_5)(2-methylpenta-1,3-diene)] (15b)	46.09 (46.92)	6.15 (6.15)		57—59	65
[Rh(C_5Me_5)(2,5-dimethylhexa-1,3-diene)] (17a)	61.83 (62.06)	8.34 (8.39)		56—58[b]	75[c]
[Ir(C_5Me_5)(2,5-dimethylhexa-1,3-diene)] (17b)	48.90 (49.40)	6.61 (6.68)		62—65	65[c]

[a] Based on isolated yields from reactions of (1a) or (1b) with the diene in ethanol–sodium carbonate at 65 °C for 18 h. [b] Decomposed on melting. [c] In isopropyl alcohol/sodium carbonate at 25 °C for 18 h. [d] From reaction of (1b) and the diene in isopropyl alcohol–triethylamine in benzene (25 °C for 24 h).

complex either from the reaction of (1) or (4) with butadiene, or by reductive elimination of HCl from (5), implies that under these conditions the reaction

$$\text{(1) or (4)} \longrightarrow [\mathrm{M(C_5Me)_5HCl(solv)}] \longrightarrow \underset{(21)}{[\mathrm{M(C_5Me_5)(solv)}]} \xrightarrow{\text{diene}} [\mathrm{M(C_5Me_5)(diene)}]$$

does not take place, and in particular that species such as (21) are not present in significant concentration in any of these reactions.



SCHEME 2

EXPERIMENTAL

All dienes were distilled under nitrogen and stored under nitrogen at −10 °C before use. Typical reactions of the rhodium and iridium dichloride dimer complexes (1) with dienes in ethanol–base have already been described.[2,3] Analytical and n.m.r. data on the new complexes reported here are given in Tables 1—3.

The n.m.r. (60 and 100 MHz) experiments using the hydrides (4a) and (4b)[4] were carried out in deacidified dichloromethane as solvent and the spectra obtained were compared with those of the authentic samples prepared as above.

Mass spectra were determined for the M^I–diene complexes on a Hitachi–Perkin-Elmer RMU-6A spectrometer using an electron beam strength of 70 eV. The major ions together with their intensities in brackets, are: (10a): *m/e* 306 [75], 239 [10], 238 [100], 237 [12], 236 [18], 69 [22], and 41 [11]; (10b): *m/e* 396 [100], 394, [67], 393 [60], 391 [41], 379 [28], 377 [18], 323 [10], 322 [15], 133 [12], 91 [10], 55 [12], 53 [12], 41 [19], 39 [18]. (12a): *m/e* 320 [97], 238 [100], 237 [13], 236 [21], 235 [10]; (12b): *m/e* 410 [100], 408 [67], 407 [73], 405 [48], 393 [62], 391 [41], 324 [11], 323 [15], 322 [15], 321 [14], 320 [13], 319 [15], 91 [11]. (15a): *m/e* 320 [68], 239 [17], 238 [100], 237 [20], 236 [23], 235 [19], 234 [17], 233 [12], 232 [13], 119 [19], 103 [20], 67 [15]; (15b): *m/e* 410 [65], 408 [44], 407 [62], 405 [40], 393 [100], 391 [67], 324 [13], 323 [16], 322 [15], 321 [14], 320 [11], 319 [12], 269 [17], 133 [11].

(17a): *m/e* 348 [73], 238 [100], 237 [24], 236 [27], 235 [18], 234 [17], 233 [14], 232 [15], 231 [13], 230 [12], 103 [11]; (17b): *m/e* 438 [72], 436 [48], 419 [100], 417 [67], 325 [10], 324 [11], 323 [18], 322 [11], 321 [14], 320 [11], 119 [12].

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