Reactions of Bridged Rhodium and Iridium Hydrides with Dienes and the Reductive Elimination of the Resultant η-Allylic Complexes

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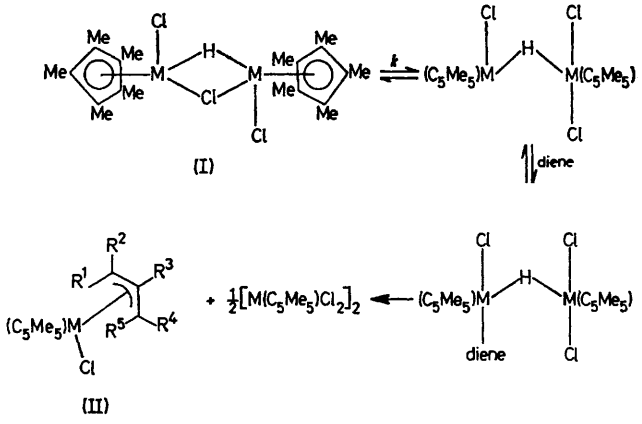
Summary The rate-determining step in the formation of the η-allylic complexes $[M(C_5Me_5)(all)Cl]$ (II), obtained by reaction of $[\{M(C_5Me_5)\}_2HCl_3]$ (I; M = Rh, Ir) with 1,3-dienes, is cleavage of the Cl bridge in (I); the ease with which complexes (II) undergo reductive elimination (−HCl) to give $[M^I(C_5Me_5)diene]$ depends on the positions of the substituents on the allyl ligand in (II).

REACTIONS of bridged metal hydrides do not appear to have been extensively examined. We report here on the stoicheiometric reactions of $[\{M(C_5Me_5)\}_2HCl_3]$ (I; M = Rh, Ir)[1] with 1,3-dienes to give the η-allylic complexes (II)[2] and $[M(C_5Me_5)Cl_2]_2$, and on the decomposition of (II) to $[M(C_5Me_5)(diene)]$.

In those cases where it was in principle possible to form either the *syn*-1- or the *anti*-1- substituted allyl, only the former was detected; for example, butadiene gave only (II; R^2 = Me) and no (II; R^1 = Me) on reaction with (I). The kinetics of the reactions (followed by ^1H n.m.r. spectroscopy) were found to be first order in (I) and zero order in a variety of dienes [isoprene, 2,3-dimethylbutadiene, cyclo-octa-1,3- and -1,5-diene, cyclohexa-1,4-diene, *etc.*]. The rates [k(Rh) $1{\cdot}4 \pm 0{\cdot}1 \times 10^{-4}$; k(Ir) $7{\cdot}5 \pm 0{\cdot}3 \times 10^{-4}$ s^{-1} in CH_2Cl_2 at 310 K] were independent of the nature of the diene and competition experiments, wherein two dienes were reacted with a deficiency of (I), showed that no discrimination occurred between them. The rates of reaction of dienes with the deuterio-complexes $[\{M(C_5Me_5)\}_2DCl_3]$, were also identical.

These data are consistent with a mechanism in which the rate-determining step is the opening of a chloride bridge in (I), to give a site at which the diene can bind before reacting further in fast subsequent steps (Scheme 1).



SCHEME 1

The activation parameters, determined from the reaction of (I) with cyclo-octa-1,5-diene,† were $\Delta H^{\ddagger}$ 93·3 (Rh) and 89·5 (Ir) kJ mol^{-1}; $\Delta S^{\ddagger}$ −18·4 (Rh) and −15·5 (Ir) J deg^{-1} mol^{-1}. The small negative values of $\Delta S^{\ddagger}$ are consistent with the formation of the bridge-opened intermediate postulated.

† Both cyclo-octa-1,3- and -1,5-diene gave the same products at the same rates; this was also true for cyclohexa-1,3- and -1,4-diene. Decomposition of the 1—3-η-cyclo-oct-2-enyl to the 1,2,4,5-η-cyclo-octa-1,5-diene complexes represents a special case which will be discussed elsewhere.

The allylic complexes (II) can be divided into three groups depending on the ease with which they undergo reductive elimination to give the $[M^1(C_5Me_5)(diene)]$ complexes:

(i) For (II; R^2 = Me or Et, and $R^2 = R^4$ = Me) no loss of HCl occurs and the diene complex could never be obtained, even under drastic conditions.

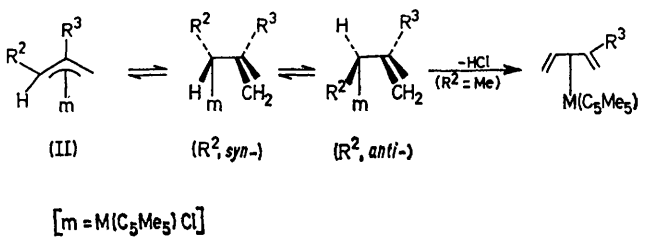
(ii) For (II; R^3 = Me and R^2 = Me or Et, and allyl = cyclo-oct-2-enyl†) loss of HCl occurs only on heating, particularly in the presence of base, to give the diene complexes.

(iii) For (II; $R^1 = R^2$ = Me, $R^1 = R^2 = R^3$ = Me, $R^1 = R^2 = R^4$ = Me, and allyl = cyclohex-2-enyl) loss of HCl occurs spontaneously (CH_2Cl_2; 130°) to give the diene complexes.

These observations lead to the following conclusions:

(a) In order for elimination of HCl to proceed easily the carbon skeleton of the allylic ligand in (II) must be a potential *cisoid* diene, *i.e.* R^1 (*anti*-) must be alkyl. This occurs for group (iii).

(b) If the allylic ligand in (II) has R^2 (*syn*-) and R^3 = alkyl, then elimination occurs, but with more difficulty [group (ii)]. This presumably proceeds *via* the formation of an intermediate σ-allyl complex which undergoes rotation about the C–C bond to give the intermediate where R^2 is now *anti* and in which condition (a) is fulfilled (for example, Scheme 2). The driving forces for this are the non-bonded repulsions between R^2 and R^3 in the intermediates; when these are small (R^3 = H), formation of $M^1(diene)(C_5Me_5)$ is energetically unfavourable.



SCHEME 2

(c) A consequence of the observation that butadiene, for example, gave only the allyl (II; R^2 = Me) on reaction with (I) and that no $[M(C_5Me_5)(\eta\text{-butadiene})]$ was detected either from this reaction or on decomposition of (II; R^2 = Me), is that acyclic 1,3-dienes must react in the *s-transoid* manner with (I), and presumably by a 1,2-addition of M–H. This may be contrasted with the behaviour of such dienes with $[HNiL_4]^+$, where the kinetically controlled allylic products have *anti*-1 substituents and where the diene evidently reacts in the *cisoid* form.[3]

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