Kinetically Controlled Displacement Reactions of Conjugated Dienes with Rhodium(I) and Iron(0) Complexes

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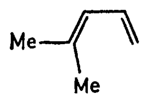
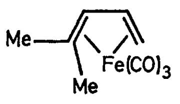
Summary The products of reaction of methyl substituted conjugated dienes with $(C_2H_4)_2Rh(acac)$ and with $Fe(CO)_5$ are determined by kinetic rather than thermodynamic factors.

THE use of iron pentacarbonyl in the isomerization of dienes is well known. An example is the formation of co-ordinated *trans*-2-methylpenta-1,3-diene (III) by reaction of 4-methylpenta-1,3-diene (I) with $Fe(CO)_5$. The driving force for the isomerization is believed to be the relief of steric strain between the *anti*-methyl substituent of (I) and the metal atom and the *anti*-hydrogen atom on the other terminal carbon atom in the proposed chelate intermediate (II).[1,2] However, *cis-trans*-hexa-2,4-diene (IV) reacts with retention of configuration to give a chelate wherein the same steric forces apply.[2] The differing behaviour of these two isomeric dienes remains unexplained. We here report a difference in reaction of the same two dienes with bis(ethylene)rhodium(I)acetylacetonate (V) and suggest an explanation which accounts also for the reactions with $Fe(CO)_5$.



(I)



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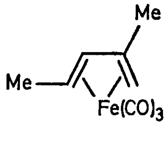
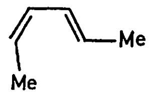
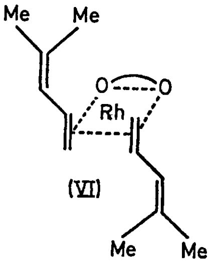


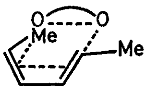
(III)



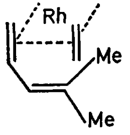
(IV)



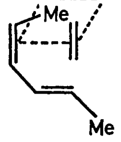
(VI)



(VII)

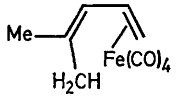


(VIII)

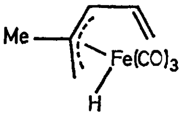


(IX)

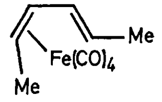
Reaction of (I) with (V) yields exclusively (whatever the reactant proportions) the complex (VI) in which two molecules of diene are co-ordinated in a monodentate fashion, each by the unsubstituted double bond. In contrast, reaction of (VI) with (V) yields exclusively (again independently of reactant ratio) the complex (VII) in which one molecule of diene is co-ordinated bidentately. Steric strain in (VII) is not expected to be any less than it would be in an analogous chelate complex of (I), so the failure of the latter to form is unlikely to be due to an intrinsically lower thermodynamic stability. While we were unable to isolate an intermediate it is probable that the two molecules of ethylene are displaced successively.[3] Because alkyl substituents destabilise metal–olefin complexes[3,4] the first step in the reaction sequence will be displacement of one ethylene by the unsubstituted end of (I) to form the intermediate (VIII). The second step may involve substitution of the second molecule of ethylene either by the free (substituted) double bond of the diene (in the cisoid form) or by the unsubstituted end of a second diene molecule. In the case of (I) the former pathway is rendered unfavourable by the steric repulsion between the *anti*-methyl group and the metal.



(X)



(XI)



(XII)

The two olefinic groups of (IV) have the same degree of substitution and therefore might be expected to co-ordinate with equal ease. However, one has a *cis*-, and the other a *trans*-, configuration, and there is evidence from stability constant measurements on Ag^I [4] and Rh^I [3] complexes that *cis*-olefins form the stronger bonds. Thus, (IX) is the expected intermediate in this case. Once (IX) is formed there is little or no steric repulsion from the metal atoms to the close approach and subsequent co-ordination of the free olefinic double bond since its methyl substituent now has a *syn*-configuration.

We can now explain the reactions of the same two dienes with $Fe(CO)_5$ if we assume, in the case of (I), an intermediate (X) in which the diene is monodentate rather than the chelate intermediate (II).[1] Evidence for an intermediate of type (X) is available[5] for the reaction of cyclo-octa-1,5-diene with $Fe(CO)_5$. Indeed, where the diene has two *anti*-substituents, as in 2,5-dimethylhexa-2,4-diene which also isomerizes with $Fe(CO)_5$,[2] a chelate intermediate would present an unacceptable degree of steric strain. A cisoid conformation in (X) brings the *anti*-methyl hydrogens very close to the metal and allows for a synchronous loss of CO, transfer of hydrogen and formation of a π-allylic bond (XI). It is important to note that the *trihapto*-group originates from the unco-ordinated double bond. A reversed metal–carbon hydrogen transfer in (XI), to the other terminal carbon atom, yields the product (III) *via* the mechanism proposed by Pettit *et al.*[1] Following the same arguments used for the Rh^I complexes, the intermediate for the case of diene (IV) is (XII). Here, the methyl substituent of the unco-ordinated olefinic group has a *syn*-configuration and the hydrogen transfer necessary for isomerization cannot readily occur.

The foregoing considerations are fully consistent with results for the reactions of other alkyl-substituted dienes with (V) and with Fe $(CO)_5$. Thus, for example, *cis*-penta-1,3-diene which with (V) forms a complex of type (VI), also isomerizes in the presence of $Fe(CO)_5$ to the *trans*-compound; with (V) the latter gives a chelate of type (VII).

Structures were deduced from ^1H n.m.r., i.r., and mass spectra and from elemental analyses.

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