endo-H and *exo*-H-(Cyclopentadienyl)(pentamethylcyclopentadiene)rhodium(I) and the Relative Reactivities of *endo*- and *exo*-Substituents

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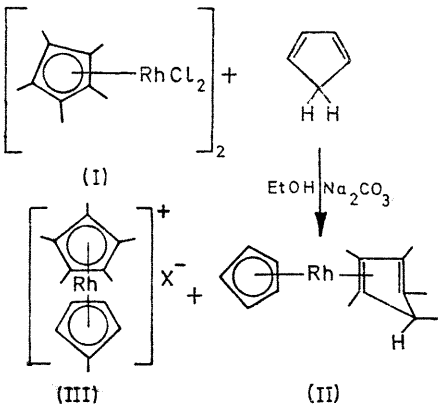
Summary In the two isomers of $C_5H_5RhC_5Me_5H$, the *exo*-substituent is more reactive than the *endo*-substituent. The *endo*-H is postulated to react *via* an intramolecular transfer to the other ring.

EXAMPLES of *endo,exo*-isomerism in the organic ligands of metal π-complexes are still rare because of synthetic difficulties. We report here an example of such isomerism and of the very unusual differences in reactivity of the two isomers.

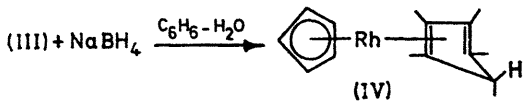
We recently described the synthesis of (cyclo-octa-1,5-diene)(pentamethylcyclopentadienyl)rhodium from μ-dichloro-dichlorobis(pentamethylcyclopentadienyl)dirhodium (I)[1] an example of a general reaction, full details of which will be reported shortly. The reaction of (I) with cyclopentadiene in ethanol in the presence of sodium carbonate is of special interest since it leads largely (54%) to the unexpected product (II) (cyclopentadienyl)(pentamethylcyclopentadiene)rhodium. A by-product (19%) here, which was the only product (76%) from this reaction in aqueous tetrahydrofuran, was (cyclopentadienyl)(pentamethycyclopentadienyl)rhodium (III) characterised as the hexafluorophosphate salt (X = PF_6)† [^{1}H n.m.r., τ 4·51 (5H, d, J_{H-Rh} 1·0 c./sec.) and 7·87 (15H, s)].

The complex (II) was identified spectroscopically as the *endo*-H isomer. In particular the low frequency ν_{CH} (at *ca.* 2750 cm.$^{-1}$), characteristic of complexes of this type with *exo*-H substituents,[2] was absent from its i.r. spectrum. The ^{1}H n.m.r. spectrum confirmed the structure and showed resonances at τ 5·12 (5H, d, J_{Rh-H} 1·0), 7·29 (1H, q, J_{H-Me} 6), 7·96 (6H, s), 8·57 (6H, s) and 9·67 (3H, d, J_{Me-H} 6 c./sec.).



† Satisfactory analyses and molecular weights, where appropriate, were obtained for all new compounds described.

The *exo*-H isomer (IV) was obtained (93%) as shown; there was no evidence for the formation of isomers in this reaction or that leading to (II).



The i.r. spectrum of (IV) was very similar to that of (II), except for the presence of an intense ν_{CH} band at 2750 cm.$^{-1}$ due to the *exo*-H. The ^{1}H n.m.r. spectrum of the complex in $CDCl_3$ showed resonances at τ 5·05 (5H, d, J_{H-Rh} 1·0), 7·18 (1H, q, broad, J_{H-Me} 6), 7·90 (6H, s), 8·69 (3H, d, J_{Me-H} 6·5), and 8·84 (6H, d, J 0·8 c./sec.). This solution slowly decomposed (5 hr at 40°) with regeneration of (III), which was identified by its n.m.r. spectrum.

$$(IV) + CDCl_3 \rightarrow (III;\ X = Cl) + CHDCl_2$$

A similar reaction occurred very readily when (IV) was treated with *N*-bromosuccinimide (NBS) in methanol:[3]

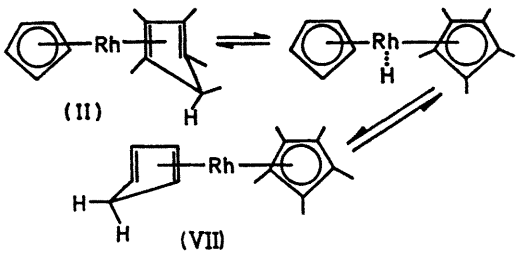
$$(IV) + NBS \xrightarrow{MeOH} (III;\ X = Br) + \text{succinimide}$$

By contrast, the *endo*-H isomer (II) was quite stable to $CDCl_3$ and reacted slowly with NBS to give products in which one ring had been cleaved off:‡

$$4\ (II) + 4NBS \xrightarrow{MeOH} [C_5Me_5RhBr_2]_2 + [C_5H_5RhBr_2]_2$$

The difference between (II) and (IV) is also elegantly displayed by their mass-spectroscopic cracking patterns. Both isomers show small peaks at *m/e* 304, corresponding to the parent ion $[C_5H_5RhC_5Me_5H]^+$. The *exo*-H isomer (IV), however, shows the base peak at *m/e* 303 $[C_5H_5RhC_5Me_5]^+$; this is weak for (II). The *endo*-H isomer's base peak is at *m/e* 289, which corresponds to $[C_5H_5RhC_5Me_4H]^+$ and inplies that loss of the *exo*-methyl is the favoured process for (II). This peak is weak in (IV).

The last result shows that when the *exo*-substituent is a methyl cleavage of this C–methyl rather than a C–H bond is preferred, and that it is indeed quite hard to remove an *endo*-substituent. One way in which this could be accomplished is by a transfer of the *endo*-H stereospecifically from one ring to another, perhaps *via* a transient Rh–H species:



This process is probably quite ready, and may well occur during the reactions leading to (V). The formation of (II) can also be interpreted in terms of a kinetically controlled formation of (VII) which is then transformed, by the reverse of the above reaction, to the thermodynamically more stable isomer, (II).

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‡ Approximately equal amounts of (V) and (VI) were obtained. The reactions of (II) and (IV) with HCl and halogens proceeded entirely analogously to those with NBS.

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