Protonation of (Cyclohexadiene)(cyclopentadienyl)rhodium(I). Evidence for *endo*-Proton Addition

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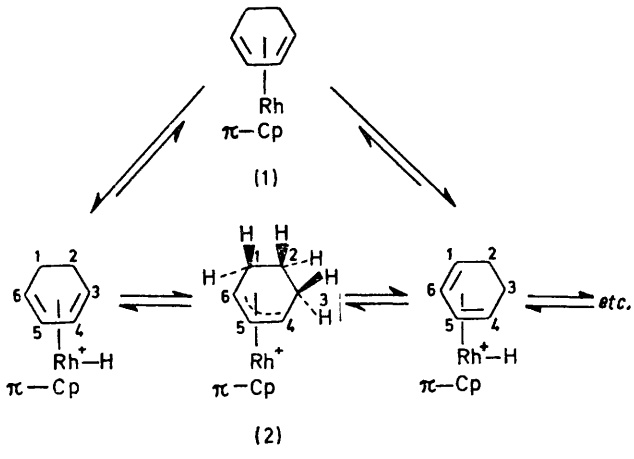
Summary The protonation of (cyclohexadiene)(cyclopentadienyl)rhodium(I), has been shown to proceed with metal–hydrogen interaction *via* a π-allylic cation to yield the *endo*-substituted product; the stereochemistry of the product has been established by deuteriation, coupled with studies on trityl and hydride ion atttack on the diene and dienyl salt, respectively.

THE path by which proton addition occurs to co-ordinated olefins is of obvious interest as a general example of the mechanism of electrophilic attack but until now has been little investigated.[1,2] We report here studies of the protonation of (cyclohexadiene)(cyclopentadienyl)rhodium(I), (**1**), and present evidence that this proceeds *via* interaction with the metal to yield the *endo*-protonated cation.

The ^{1}H n.m.r. spectrum (100 MHz) of a solution of (**1**) in CF_3CO_2H exhibited three resonances, τ 4·20 (s, 5H), 6·14 (m, 6H), 12·05 (m, 3H). A similar spectrum was observed for a freshly prepared solution of (**1**) in CF_3CO_2D, except that the signal at τ 12·05 was reduced in relative intensity from three to two protons. Significantly, however, on standing under ambient conditions this signal slowly decreased in intensity until after one hour it had disappeared. These observations may be rationalised by the equilibrium represented in the Scheme. As shown, a sufficiently rapid exchange will equilibrate three protons between the *endo*-methylenic and metal–hydride environments *via* a cationic π-allylic grouping (**2**) and hence account for the high field signal. The absorption at τ 6·14 due to six protons, is then explained by the protons per-

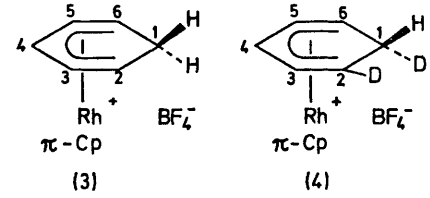
manently bonded to the six-membered ring being equilibrated between the allylic and *exo*-methylene environments. Slow exchange of H^+ or D^+ with the solvent and the metal hydride species would lead to collapse of the signal at τ 12·05 in CF_3CO_2D solution. Furthermore, treatment of (**1**) in ether with HPF_6 precipitated a yellow crystalline salt of composition $C_6H_9RhCpPF_6$. The ^1H n.m.r. (100 MHz, liq.SO_2) of this species was similar to that described above, indicating that the exchange is intra- rather than inter-molecular in origin. At −50 °C only slight broadening of the resonances was observed.



SCHEME.

Complex (**1**) was regenerated in quantitative yield on quenching the CF_3CO_2H solution with H_2O and neutralising with sodium bicarbonate. [^{2}H]-(**1**) was recovered from CF_3CO_2D solution, and in agreemeent with the suggested mechanism the two deuterium atoms were shown by n.m.r. to be incorporated at the methylene positions. However, the above mechanism also implied that the deuterium atoms would be *endo*, and the following study was undertaken to confirm this fact.

Solutions of (**1**) and [^{2}H]-(**1**) in CH_2Cl_2 were treated with 1 mol equiv. of Ph_3CBF_4 and the dienyl salts (**3**) and (**4**) were precipitated, respectively. The n.m.r. of (**3**) (100 MHz, liq.SO_2, Me_4Si): τ 3·12 (t,1H, 4-H), 4·14 (s, 5H, C_5H_5), 4·40 (t, d.d. overlap, 2H, 3- and 5-H); 5·68 (t, d.d. overlap, 2H, 2- and 6-H), 7·06 (quintet, 1H, 1-H_{endo}), 7·37 (d, 1H, 1-H_{exo}), is similar to those reported for analogous cations.[4,5] If the previous assignments of these spectra are accepted then the upfield doublet at τ 7·37 may be assigned to 1-H_{exo} and the lower field quintet at τ 7·06 to the absorption of 1-H_{endo}. The coupling constants J(1-H_{endo}, 1-H_{exo}) = 12, J(1-H_{endo}, 2-H) = J(1-H_{endo}, 6-H) = 6 Hz, accounts for the multiplicity of the latter signal. In the n.m.r. of (**4**) (100 MHz, liq.SO_2, Me_4Si): τ 3·12 (t, 1H,



4-H), 4·14 (s, 5H, C_5H_5), 4·40 (m, 2H, 3- and 5-H), 5·68 (d. 1H, 2- or 6-H), 7·37 (s, 1H, 1-H_{exo}), the resonance of 7·06 had completely disappeared. Such a change is interpreted in terms of specific deuterium incorporation at the *endo*-position,† and provides confirmatory evidence for the suggested mechanism of *endo* electrophilic attack. The observation of (**4**) as the only product indicates that attack by Ph_3CBF_4 was stereospecific. The n.m.r. assignments given above imply that (**4**) is the product of trityl attack at the *exo*-hydrogen as would be anticipated from steric considerations. In contrast, reduction of (**3**) with borodeuteride gave the neutral diene which reacted with Ph_3CBF_4 to yield an equimolar mixture of (**3**) and the *exo*-monodeuterium dienyl salt, characterised by the n.m.r. assignments used above. This indicates that nucleophilic attack by hydride ion occurs to give a product of the alternative stereochemistry to proton attack and in keeping with all other studies on nucleophilic addition to co-ordinated organic groups may be assigned as the *exo*-derivative.

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† A solution of (acetylcyclopentadienyl)(cyclohexadiene)rhodium(I) [the product of Friedel–Craft acetylation of (**1**)] in CF_3CO_2D was found to incorporate deuterium both at the *endo*-methylene positions and the 2,3,4,5 positions of the cyclopentadienyl ring. The electron-withdrawing character of the acetyl group has presumably activated the cyclopentadienyl protons to protonic substitution.

[1] M. A. Haas, *Organometallic Rev.*, 1969, *A*, **4**, 307.
[2] D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 6968.
[3] R. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217.
[4] D. Jones, L. Platt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4458.
[5] G. E. Herberich and J. Schwartzer, *Angew. Chem. Internat. Edn.*, 1968, **8**, 143.