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Preliminary communication

(h^4-Dibenzylideneacetone)pentamethylcyclopentadienylrhodium(I)

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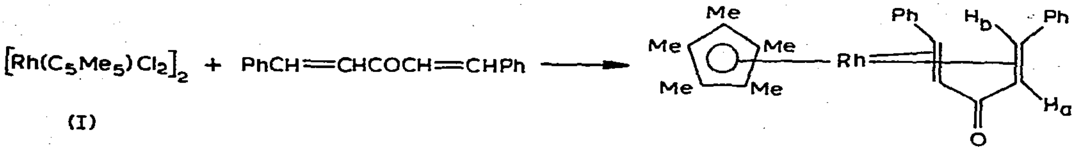
SUMMARY

Dibenzylideneacetone can act as a 1,4-diene in bonding to a single metal atom and this has been shown by the synthesis of (h^4-dibenzylideneacetone)pentamethylcyclopentadienylrhodium(I).

The current considerable interest[1–3] in complexes of dibenzylideneacetone (Dba) prompts us to report that this ligand can, in favourable circumstances, bond as a 1,4-diene to a single metal atom despite the large potential restraints arising from non-bonded interactions between the two hydrogens (H_b) on the double bonds. Recent X-ray studies on solvated $[Pd_2(Dba)_3]$ showed that in that complex one double bond of each Dba was coordinated to one palladium while the other double bond of each Dba was coordinated to the other palladium, both metal atoms being trigonally coordinated overall[4].

We have previously shown[5] that dichloro(pentamethylcyclopentadienyl)rhodium dimer (I) reacts with a wide variety of diolefins in alcohol-base to give h^4-diene complexes of Rh^I. In a similar manner I reacted with Dba in ethanolic sodium carbonate (two days at 55°) to give a 42% yield of red crystals of dibenzylideneacetone(pentamethylcyclopentadienyl)rhodium (II). The complex gave satisfactory analyses and its structure was established from its ^1H NMR spectrum. This showed, in addition to the phenyl hydrogens (τ 2.80 m) and the C_5Me_5 resonance (τ 8.81 s), doublets at τ 5.17 (H_a) and 6.47 (H_b) [$J(H_a{-}H_b)$ 11 Hz] which were further split ($J \approx 1$ Hz) by coupling to ^{103}Rh ($I = 1/2$, 100%).

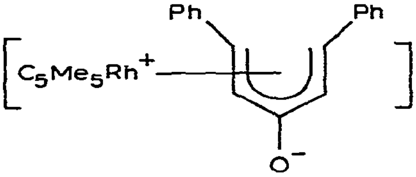
In uncomplexed Dba the resonances of H_a and H_b are observed at τ 2.22 and 2.92 and $J(H_a{-}H_b)$ is 16.5 Hz. The large upfield shift in these resonances on complexation together with the change in $J(H_a{-}H_b)$ as well as the observed coupling to Rh show that Dba is complexed to the metal through its double bonds. The simplicity of the spectrum indicates that both double bonds are complexed to the one metal atom*.



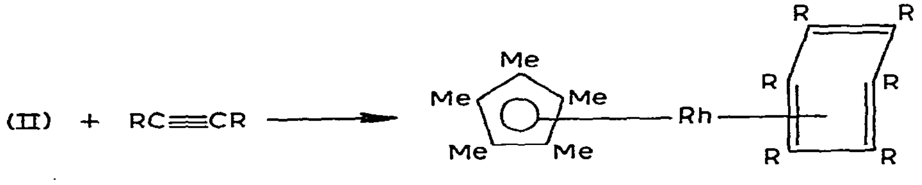
(I)

(II)

The IR spectrum of II showed a single very strong ν(CO) at 1562 cm^{-1} ($CHCl_3$ solution) which was at considerably lower frequency than in Dba. This suggests that there is some polarisation of the carbonyl bond and that a contributor to the structure of II is:



The complex II was moderately stable but it did slowly decompose in chloroform to give I and free Dba. On heating with cycloocta-1,5-diene (50°, 18 hours) decomposition occurred to give unidentified products; none of the known $[Rh(C_5Me_5)(1,5\text{-}C_8H_{12})]$ was obtained[5]. In contrast, II reacted with dimethyl acetylenedicarboxylate under these conditions to give a quantitative yield of the "bent benzene" complex, (III), which had previously been obtained from $[Rh(C_5Me_5)(OCOCH_3)_2]$ and the acetylene under hydrogen[6]:



(III) (R = COOMe)

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*Professor J.A. Ibers has informed us that the results of an X-ray determination on II confirm this structure.

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