Protonation of Cyclo-octa-1,5-diene- and Cyclo-octa-1,3,5-triene-cyclopentadienylrhodium(I) : Novel Versatility of Metal Co-ordination

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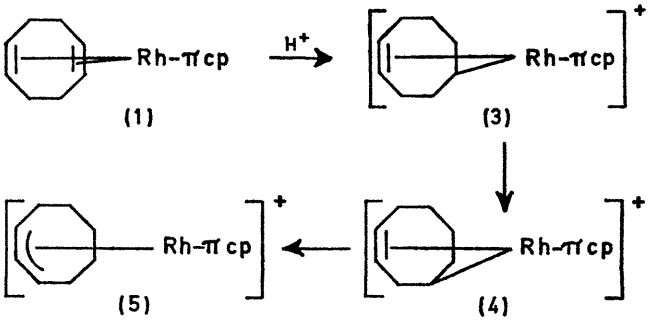
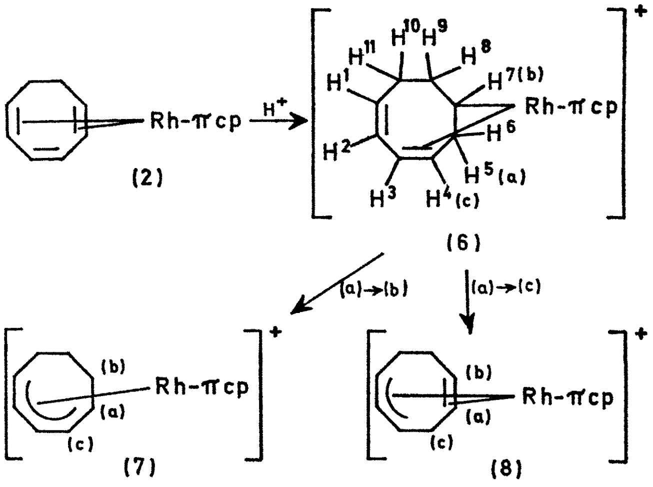
Summary The variation in reactivity of cyclo-octa-1,5-diene and cyclo-octa-1,3,5-triene complexes of d^8 metals is considered with particular reference to protonation of the cyclopentadienylrhodium(I) derivatives; the systems show a remarkable facility for prototopic rearrangements producing a variety of organic isomers.

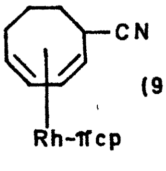
CONSIDERING the Dewar–Chatt model of the metal–olefin bond, it would be expected that the reactivity of the co-ordinated olefin would be dependent upon the electronegativity of the metal. For an isoelectronic system higher oxidation states would be expected to facilitate nucleophilic attack whilst low oxidation states favour electrophilic attack. For the (cyclo-octa-1,5-diene$M^{II}X_2$) systems (M = Pt or Pd, X = Cl or Br), the olefin has been shown to be activated towards a variety of nucleophiles to give σ–π–olefin complexes; conversely, it has been found that tricarbonylcyclo-octa-1,5-dieneiron(0)[2] is reactive towards electrophiles involving, for instance, hydride ion abstraction by trityl tetrafluoroborate to give an allyl–olefin complex. An isomeric diene has been formed by hydride abstraction from tricarbonylcyclo-octa-1,3-dieneiron(0)[2] and also by protonation of tricarbonylcyclo-octa-1,3,5-trieneiron(0).[3] The rhodium(I) complexes provide an interesting intermediate oxidation state between these two extremes in behaviour.

Cyclo-octa-1,5-dienecyclopentadienyrhodium(I)[4] (1) is inert to nucleophilic attack; however hydride abstraction occurs readily giving an allyl–olefin co-ordinating pattern.[5] Protonation of complex (1) has now been shown to give the σ–π bonding species (3). A related bonding pattern was also formed in the protonation of cyclo-octa-1,3,5-trienecyclopentadienylrhodium(I), (2) to yield the complex (6). The n.m.r. spectrum in $CDCl_3$ indicates that the complex (2) involves bonding as a 1,5-diene derivative. Subsequent prototopic rearrangements occur leading to isomerisation, for both series of complexes.

Complex (1) forms a red solution in $CF_3 \cdot CO_2H$. The ^1H n.m.r. spectrum is initially very broad, with several cyclopentadienyl singlets. After 30 min at *ca.* 30° the spectrum corresponds to a mixture of complexes (3) and (4). The complex (4) is the major product after 2 days at −15°, but (3) persists for periods up to 55 days when in addition to the complex (4) a further isomer (5) is produced. Treatment of an ethereal solution of the complex (1) with HPF_6 gives a yellow, unstable salt; the ^1H n.m.r. spectrum in $[^2H_6]$acetone is consistent with structure (5). The facility for prototopic rearrangements in these systems is emphasised by the ready reaction of compound (5) with triethylamine to yield (1).







(9)

Complex (2) dissolves in $CF_3 \cdot CO_2H$ to give a red solution, the ^1H n.m.r. spectrum of which indicates the formation of a new cationic structure (6). τ 3·78 (2,s, $H^1 + H^2$), 4·13 (5,s, C_5H_5), 5·35 (1,m,H^4), 6·77 (1,m,H^6), 6·96 (1,dd,H^5), 7·40 (1,m,H^3), 7·50 (1,m,H^7), and 7·9–8·3 (4,mH^{8-11}). Using CF_3CO_2D, the resonance due to H^5 is lost as is the coupling to H^4, H^6, and H^7. Double irradiation studies show that H^4 is coupled to H^3, H^5, and H^6 whilst H^7 is coupled to high field methylenic protons. When set aside, the complex (6) is converted ($t_{\frac{1}{2}}$ *ca.* 1 h at 24°) to a mixture of complexes (7) and (8). The spectrum of complex (7) is similar to that of tricarbonylcyclo-octa-2,4-dieniumiron(0)[3] cation whilst that of (8) corresponds to the analgous cobalt complex.[5] The deuterium atom at H^5 in the deuterio-complex (6) is specifically transferred to position (c) in complex (**8**) implying a 1–2 hydrogen shift. In contrast to the behaviour of the complex (**1**), treatment of an ethereal solution of (**2**) with HPF_6 gives a mixture of yellow salts of general formula $[C_8H_{11}Rh\text{–}\pi\text{–}C_5H_5]PF_6$. The composition of this mixture is markedly dependent upon the temperature of precipitation; at 20° the product is a mixture of complexes (**7**) and (**8**) in the ratio of 3 : 1 whilst at −10° (**6**) is the major product (50%) with 30% of (**7**) and 20% of (**8**). Triethylamine caused deprotonation of all these salts to yield compound (**2**).

In protonation of both compounds (**1**) and (**2**), σ–olefin complexes are formed first, with subsequent rearrangement to presumably thermodynamically preferred complexes, the rate being very dependent upon conditions. Protonation occurs initially at a co-ordinated double bond in both complexes, suggesting the primary involvement of metal as the electron-donor site. Direct evidence for the formation of a metal hydride has been obtained in the protonation of the related complex, cyclohexa-1,3-dienecyclopentadienylrhodium(I).[6]

Nucleophilic addition reactions to the ions $[C_8H_{11}Rh\text{–}\pi\text{–}C_5H_5]^+$ also yielded a series of products dependent upon the temperature of reaction. Thus whilst borohydride and cyanide attack cause some deprotonation to give compound (**2**), at −10°, cyanide reacts to yield solely compound (**9**); at 30° two other isomers are formed. Sodium borohydride reacts at −10° to give a mixture of mainly cyclo-octa-1,3-dienecyclopentadienylrhodium(I), (**10**), complex (**1**), and a third isomer, whilst at 20° none of the complex (**10**) is produced.

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[1] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2496; 3413.

[2] F. A. Cotton, A. J. P. Domingos, A. J. Deeming, B. F. G. Johnson, P. L. Jostly, J. Lewis, and S. S. Ullah, to be published *J. Amer. Chem. Soc.* 1971.

[3] W. McFarlane, L. Pratt, and G. W. Wilkinson, *J. Chem. Soc.*, 1963, 2162.

[4] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.

[5] J. Lewis and A. W. Parkins, *J. Chem. Soc.* (*A*), 1967, 1150.

[6] B. F. G. Johnson, J. Lewis, and D. J. Yarrow, submitted for publication.