Reactivity of Co-ordinated Ligands. Part XXII.[1] Protonation of (η-Cyclo-octatetraene)(η-cyclopentadienyl)-cobalt(I), -rhodium(I), and -iridium(I)

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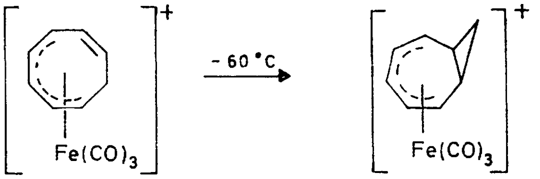
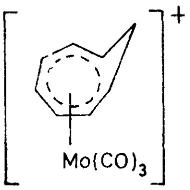
The protonation of (η-cyclo-octatetraene)(η-cyclopentadienyl) complexes [$(C_8H_8)M(cp)$] [(V; M = Co^I, Rh^I, and Ir^I) has been studied. The stable [$(C_8H_9M(cp)]^+$ cation, (VI), generated at room temperature has been shown to contain the C_8H_9 moiety co-ordinated to the metal atom *via* both an η-allyl– and an olefin–metal bond. In the case of M = Co or Rh, a bicyclic cation, (VIa), is produced initially; this subsequently undergoes isomerisation to a monocyclic form, (VIb). At low temperatures, protonation of the Ir complex yields a metal hydride species [$(C_8H_8)IrH(cp)]^+$, (VIII). Mechanisms of proton attack and the ensuing rearrangements are discussed and it is proposed that the proton attacks with *endo*-stereospecificity.

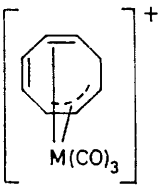
REACTIONS of co-ordinated oligo-olefins with protonic acids have been the subject of a number of recent studies.[2] Examples are known of proton addition occurring with *exo*-[3] and *endo*-stereochemistry[4] and at co-ordinated[2] and unco-ordinated[5] double bonds. In particular the protonation of tricarbonyl[η-(2-methylcyclo-octatetraene)]iron has been shown[5] to proceed at the unco-ordinated diene fragment and the n.m.r. spectrum interpreted[2] in terms of *exo*-proton addition. Recent n.m.r. spectral studies[6] have demonstrated that at low temperatures proton attack on tricarbonyl(η-cyclo-octatetraene)iron generates tricarbonyl(1—5-η-cyclo-octatrienylium)iron (I) which rearranges to (2—6-η-bicyclo[5.1.0]octadienylium)tricarbonyliron (II) at −60 °C. Structures similar to (I) have been reported for the C_8H_9 moieties in [(cp)Fe-(C_8H_9)][7] and (1,2:3,4-η-cyclo-octatetraene)(1—5-η-cyclo-octatrienylium)cobalt,[8] and a bicyclic C_8H_9 structure similar to (II) has been proposed for the protonation product of (η-buta-1,3-diene)carbonyl(1,2:3,4-η-cyclo-octatetraene)iron.[9] In contrast, protonation of tricarbonyl-[10] and tetracarbonyl-(η-cyclo-octatetraene)-molybdenum occurs with *endo*-addition to afford homoconjugated tricarbonyl(1—6-η-cyclo-octatrienylium)-molybdenum, (III). Bicyclic cations analogous to (II) are also initially formed by proton addition to tricarbonyl(η-cyclo-octatetraene)-ruthenium and -osmium,[12] but these undergo subsequent rearrangement to give the corresponding (1—3:6,7-η-cyclo-octatrienylium) cations, (IV).



(I) (II)



(III)



(IV) M = Ru or Os

It is apparent from these studies that the metal atom strongly influences the course of protonation reactions. This paper reports the modes of protonation of (η-cyclo-octatetraene)(η-cyclopentadienyl)-cobalt(I), -rhodium(I), and -iridium(I) complexes, (V).

RESULTS AND DISCUSSION

(η-Cyclo-octatetraene)(η-cyclopentadienyl)-cobalt(I) and -rhodium(I), (V), are known to form unstable solutions in concentrated sulphuric acid.[13] We found that using the less-vigorous protonic acid CF_3CO_2H the stable cationic species [$(C_8H_9)M(cp)]^+$, (VI), may be produced. Protonation of complex (V; M = Co) in CF_3CO_2H initially yielded two isomeric forms, (VIa) and (VIb), of the protonated species [$(C_8H_9)Co(cp)]^+$ in the ratio *ca.*

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[1] Part XXI, R. Edwards, J. A. S. Howell, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 2105.

[2] D. F. Hunt, G. C. Farrant, and G. T. Rodeheaver, *J. Organometallic Chem.*, 1972, **38**, 349 and refs. therein.

[3] B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *J.C.S. Dalton*, 1972, 456.

[4] B. F. G. Johnson, J. Lewis, and D. Yarrow, *J.C.S. Chem. Comm.*, 1972, 235.

[5] M. Brookhart and E. R. Davis, *Tetrahedron Letters*, 1971, 4349.

[6] M. Brookhart, E. R. Davis, and D. L. Harris, *J. Amer. Chem. Soc.*, 1972, **94**, 7853.

[7] A. Greco, A. Carbonaro, F. Cambisi, and G. Dall'Asta, *Chimica e Industria*, 1970, **52**, 49.

[8] A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 285.

[9] A. Carbonaro and F. Cambisi, *J. Organometallic Chem.*, 1972, **44**, 171.

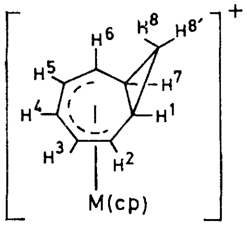
[10] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, 1965, **87**, 3267.

[11] H. D. Kaesz, S. Winstein, and C. G. Kreiter, *J. Amer. Chem. Soc.*, 1966, **88**, 1319.

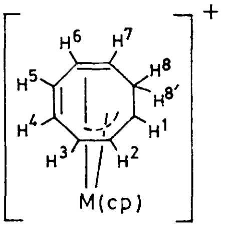
[12] M. Cooke, P. T. Draggett, M. Green, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *Chem. Comm.*, 1971, 621.

[13] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4821.

1 : 1. The ^{1}H n.m.r. spectrum of a freshly prepared solution of complex (V; M = Co) in CF_3CO_2H exhibited resonances at τ 1·74 (t, H_4, $J_{H_4-H_5} = J_{H_3-H_4}$ 7·0), 4·58 (s, cp), 4·5—4·8 (complex m, H_2, H_3, H_5, and H_6), 7·76 (m, H_1 and H_7), 8·60 (q, H_8, $J_{H_8-H_{8'}}$ 5·0, $J_{H_1-H_8} = J_{H_7-H_8}$ 5·0), and 8·94 (triplet of doublets, $H_{8'}$, $J_{H_8-H_{8'}}$ 5·0, $J_{H_1-H_8} = J_{H_7-H_{8'}}$ 8·2) which may be interpreted in terms of the 2—6-η-bicyclo[5.1.0]octadienylium structure (VIa). In addition, resonances which may be attributed to the 1—3:6,7-η-cyclo-octatrienylium isomer (VIb) (see below) were also present. After 48 h in solution isomer (VIa) isomerised irreversibly to (VIb), which was also obtained as the only product of reaction of (V) (in diethyl ether) and aqueous HPF_6. The n.m.r. spectrum of complex (VIb) (PF_6^- salt in liquid SO_2) showed absorptions at τ 4·1—4·3 (complex m, H_6 and H_3), 4·28 (s, cp), 4·70 (dd, H_4, $J_{H_3-H_4}$ 2·4, $J_{H_4-H_5}$ 8·0 Hz), 4·94 (dd, H_5, $J_{H_5-H_6}$ 4·0, $J_{H_4-H_5}$ 8·0), 5·48 (t, H_2, $J_{H_2-H_3} = J_{H_1-H_2}$ 8·0), 5·94 (q, H_7, $J_{H_6-H_7}$ 8·0, $J_{H_5-H_7} = J_{H_7-H_8}$ 8·0), 6·54 (quartet of doublets, H_1, $J_{H_1-H_2}$ 8·0, $J_{H_1-H_8} = J_{H_1-H_{8'}}$ 8·0, $J_{H_1-H_3}$ 3·0), and 7·90 (m, H_8 and $H_{8'}$). These assignments were fully corroborated by double-irradiation experiments.



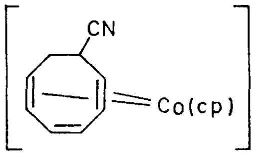
(VIa) M = Co, Rh, or Ir



(VIb) M = Co, Rh, or Ir

However, certain differences between the above spectrum and that of the isostructural complex (IV; M = Ru) are apparent.[6] In particular, the degeneracy of resonances arising from the allylic protons has been removed, and the resonances attributed to the allylic protons at τ 4·2 (outer allyl), 5·48 (t, centre allyl), and 6·50 (outer allyl) are more in common with those of other unsymmetrical η-allyl complexes. Such differences are not surprising as both changes in the electron density and the stereochemical configuration of the $C_8H_9^+$ moiety are to be expected between the complexes (IV) and (VI).

Cyanide-ion attack on the PF_6^- salt of (VIb) yielded air-sensitive orange crystals of [1,2:5,6-η-(8-cyanocyclo-octatriene)](η-cyclopentadienyl)cobalt, (VII). The ^{1}H n.m.r. spectrum (CS_2) exhibited seven resonances at τ 5·42 (s, 2H), 5·44 (s, 5H), 6·1 (m, 1H), 6·28 (m, 2H), 6·76 (m, 2H), 7·5 (m, 1H), and 8·2 (m, 1H). The resonance at τ 4·52 is ascribed to protons of an unco-ordinated double bond whose presence in the complex is indicated by an i.r. band at 1 638 cm^{-1}. The AB system at τ 7·5 and 8·2 is assigned to the geminal methylene protons and the resonance at τ 6·1 to the proton attached to the cyano-substituted carbon atom. In this case nucleophilic attack has occurred at the co-ordinated η-allyl group and is in contrast to cyanide addition to the co-ordinated olefinic bond observed with the analogous complex (IV; M = Ru).[6] Preferential reaction at the η-allyl group has also been observed for nucleophilic addition to cyclo-octa-2,5-dienyl complexes of cobalt, rhodium, and iridium.[14]



(VII)

Protonation of complex (V; M = Rh) in CF_3CO_2H produced a stable solution and the ^{1}H n.m.r. spectrum indicated formation of the cation (VIa) analogous to the bicyclic iron and osmium complexes. No isomeric forms of the species (VI; M = Rh) were observed on protonation in CD_2Cl_2–CF_3CO_2H at −50 °C. A stable orange salt was obtained on addition of aqueous HPF_6 to a diethyl ether solution of (V; M = Rh), and the n.m.r. spectrum (liquid SO_2) of this salt was similar to that recorded for the neutral complex in CF_3CO_2H solution. The n.m.r. spectrum (CF_3CO_2H, 29·5 °C) exhibited a resonance at τ 2·54 (t, 1H) assigned to the central proton, H_4, of the dienylium system ($J_{H_4-H_5} = J_{H_3-H_4}$ 6 Hz), and a band at τ 4·24 (m, 7H) due to overlap of resonances arising from H_3,H_5 and the cp protons. A signal at τ 4·58 (m, 2H) is assigned to the outer dienylium protons H_2,H_6. The bridgehead protons H_1,H_7 gave rise to a multiplet at τ 7·76 and the two non-equivalent methylene protons produced a quartet at τ 8·26 and a triplet of doublets at τ 8·64. The geminal coupling constant $J_{H_8-H_{8'}}$ 5·0 Hz and a similar value for the vicinal coupling constants $J_{H_7-H_8}$ and $J_{H_1-H_8}$ reproduce the observed quartet at τ 8·26 (H_8). The different coupling constant $J_{H_7-H_{8'}} = J_{H_1-H_{8'}}$ 8·0 Hz produces the observed triplet of doublets at τ 8·64 ($H_{8'}$), and suggests that the methylene hydrogen atoms make different dihedral angles with the bridgehead hydrogens.

There has been no structure determination of a bicyclic cation of this type, but if it is assumed that the methylene bridge is *exo* to the metal atom then molecular models suggest that the dihedral angle between H_7 and H_{endo} is *ca.* 0°, and that between H_7 and H_{exo} is *ca.* 140°. For these values the Karplus curve predicts vicinal coupling-constant values of 8·2 and 5·2 Hz respectively, in agreement with the work of Graham and Rogers [15] who showed that for substituted cyclopropanes the vicinal coupling constant for *cis*-protons was *ca.* 8·4 Hz, whilst that for *trans*-protons was *ca.* 5·7 Hz. On this basis the resonance at τ 8·64 is assigned to the *endo*-methylene hydrogen atom, $H_{8'}$, and the lower-field signal at τ 8·26 to the *exo*-hydrogen. It is reasonable to assume that the hydrogen atoms of the bridging methylene group are far enough removed from the dienylium system in the ring

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

[15] J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, 1962, **84**, 2249.

to make shielding effects arising from the π-system negligible. Using the same criteria for the analysis of the n.m.r. spectrum of the ion $[(C_8H_9)Fe(CO)_3]^+$ reported by Wilkinson and his co-workers,[13] it may be shown similarly that for the methylene hydrogen atoms the *exo*-hydrogen gives rise to the resonance at lower field. In D_2SO_4 this resonance is absent, and this observation has been interpreted [2] in terms of *exo*-protonation of cyclo-octatetraene, in accord with the stereochemistry of protonation of tricarbonyl(η-cycloheptatriene)iron.[3] For the species $[(C_8H_8D)Fe(CO)_3]^+$ deprotonation with triethylamine has been shown [16] to generate exclusively $[(C_8H_8)Fe(CO)_3]$, indicating protonation and deprotonation are stereospecific and proceed in a similar manner. It has already been demonstrated [3] that deprotonation under these conditions removes the *exo*-proton.

The n.m.r. spectrum of complex (V; M = Rh) in CF_3CO_2D solution showed no resonance at τ 8·64, and the lower-field signal at τ 8·26 [H_8(*exo*)] existed as a triplet ($J_{H_1-H_8} = J_{H_7-H_8}$ 5·0 Hz). Hence the mechanism of protonation of this complex is different to that of the iron analogue, and proceeds *via endo*-attack of the proton. Similar stereospecificity has been reported [10] for proton addition to tricarbonyl(η-cyclo-octatetraene)molybdenum. The cation $[(C_8H_8D)Rh(cp)]^+$ could not be deprotonated. This bicyclic cation also slowly isomerised to a second complex ($t_{\frac{1}{2}}$ *ca.* 24 h at room temperature). The n.m.r. spectrum of this species indicated that it was the monocyclic cation (VIb; M = Rh), analogous to that finally observed in the cobalt system: (in 10% CF_3CO_2H in $CDCl_3$) τ 4·27 (s, 5H, cp), 4·32 (m, 2H, H_3 and H_6), 4·60 (m, 2H, H_4 and H_5), 5·03 (apparent q, 1H, H_1), 5·45 (asymmetric t, 1H, H_2), 6·02 (apparent q, 1H, H_7), 6·66 (m, 1H, $H_{8'}$), and 6·98 (m, 1H, H_8). When CF_3CO_2D was employed, the resonance at τ 6·66 was absent and loss of coupling was observed on the signals at τ 5·03, 6·02, and 6·98.

The structure of these complexes was confirmed by ^{13}C n.m.r. spectroscopy. A solution of complex (V; M = Rh) in $CDCl_3$ gave rise to three carbon resonances (shifts measured in p.p.m. downfield of Me_4Si), namely a singlet due to the unco-ordinated olefinic carbon atoms at −136 p.p.m., a singlet at −88 p.p.m. due to carbons of the cp ring, and a doublet at −68 p.p.m. ($J_{^{103}Rh-^{13}C}$ 12 Hz) attributed to the co-ordinated olefinic carbon atoms. Addition of CF_3CO_2H to this solution allowed observation of complex (VIa). The cp carbon atoms shifted slightly downfield to −88·8 p.p.m. (d, *J* 5 Hz) and five other resonances were observed at −102·6 p.p.m. (d, *J* 5 Hz) due to the central dienylium carbon atom, at −91·7 (d, *J* 10) and −88·3 p.p.m. (d, *J* 8 Hz) due to the other two pairs of dienylium carbon atoms, at −40·9 p.p.m. due to the bridgehead carbon atoms, and at −39·7 p.p.m. due to the bridging carbon atom. The ^{13}C n.m.r. spectrum of complex (VIb; M = Rh) in this solution was subsequently observed. The more complicated spectrum is indicative of the lower symmetry of the C_8H_9 moiety in this cation: −131·4(s) and −130·0(s) (C_4 and C_5), −89·8 (d, *J* 5, cp), −89·1 (d, *J* 10, C_3 or C_6), −82·9 (d, *J* 5, C_2), −77·8 (d, *J* 10, C_3 or C_6), −46·4 (d, *J* 5, C_1), −38·6 (d, *J* 5 Hz, C_7), and −19·1 p.p.m. (s, C_8). The assignments were made on the basis of selective irradiation of the individual proton resonances. The asymmetry in both the co-ordinated olefinic and η-allyl groups is highlighted by these observations. If the more probable assignments of C_3 at 89·1 p.p.m. and C_6 at 77·8 p.p.m. are assumed, then there are chemical-shift differences of 42·7 p.p.m. between the end of the η-allyl group and 39·2 p.p.m. between the co-ordinated olefinic carbon atoms. Close examination of molecular models indicates that the metal atom is closer to the ends of the co-ordinated groups adjacent to methylene groups. The higher shielding observed may therefore be attributed to two effects: first the increase in electron density and secondly greater shielding from the metal atom.

The kinetics of this isomerisation of complexes (VIa) and (VIb) (M = Rh) were followed in trifluoroacetic acid, between 52 and 67 °C, by observing the change in ^1H n.m.r. spectrum with time. The reaction was found to be first order with respect to (VIa) over three half-lives. Rates and standard errors were determined by a least-squares fit and an Arrhenius plot was obtained from these rates. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated using the Eyring equation. The kinetic data obtained are presented in the Table. The absence of a kinetic-isotope effect is consistent with the C–H(D) bond, once formed in the initial protonation, being retained during the isomerisation of (VIa) to (VIb). The high value of $\Delta S^{\ddagger}$ suggests that, during the rate-determining step, a transition state more disordered than (VIa) is produced. An electrocyclic ring-opening reaction would be consistent with this. A change in co-ordination to the metal atom is required during this reaction, so the nature of the metal will have a considerable effect on relative free energies of complexes of types (VIa) and (VIb) and the rates of any interconversions between them.

Solvent	θ_c/°C	$10^4k_{obs}/s^{-1}$
CF_3CO_2H	52	2·11 ± 0·04
CF_3CO_2D	52	2·18 ± 0·07
CF_3CO_2H	58·5	4·6 ± 0·1
CF_3CO_2H	62	8·0 ± 0·2
CF_3CO_2H	67	14·7 ± 0·8
E_a/kcal mol^{-1}		29 ± 1
$\Delta H^{\ddagger}$/kcal mol^{-1}		28 ± 1
$\Delta S^{\ddagger}$(325 K)/ cal K^{-1} mol^{-1}		12 ± 3

Evidence for metal involvement in directing the attacking proton on to the *endo*-face of the co-ordinated ligand was obtained from a study of the behaviour of complex (V; M = Ir) in acid solution. A white salt, (VIb; M = Ir) was precipitated when aqueous HPF_6 was added to a diethyl ether solution of complex (V), and the n.m.r. of this salt [$(CD_3)_2CO$, 29·5 °C] exhibited resonances at τ 3·94 (s, cp), 4·35 (complex m, H_3, H_4, and H_5), 4·74 (dd, H_6, $J_{H_5-H_6}$ 2, $J_{H_6-H_7}$ 7·5 Hz), 4·9—5·2 (m, H_1 and H_2), 5·72 (q, H_7, $J_{H_6-H_7}$ 7·5, $J_{H_7-H_8} = J_{H_7-H_{8'}} =$

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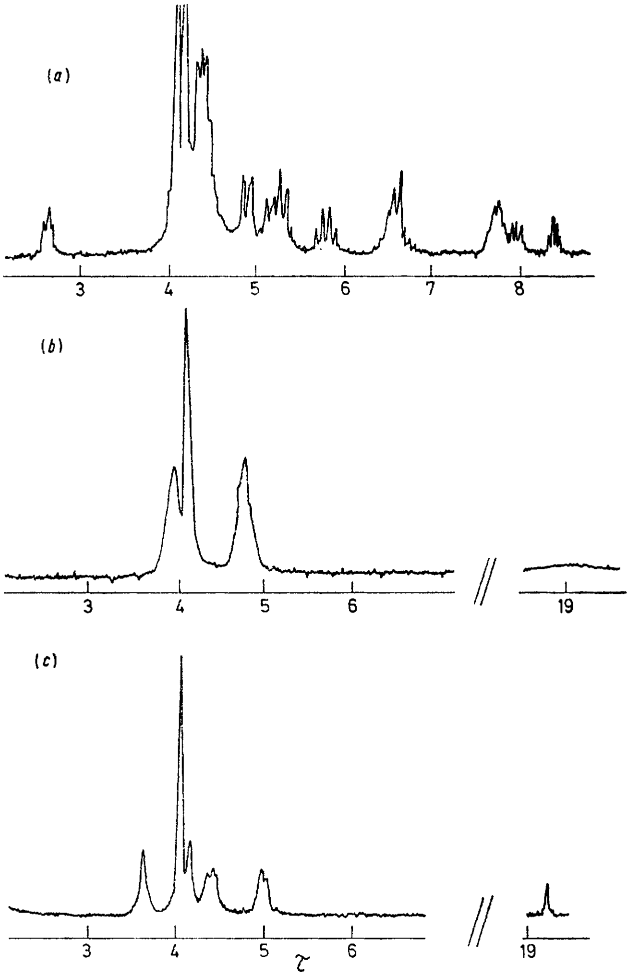
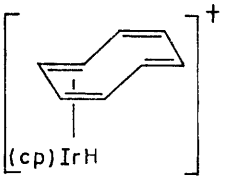
[16] R. Edwards, personal communication.

7·5), and 7·60 (apparent t, H_8 and $H_{8'}$). Double-irradiation experiments established the sequence $CH_{(6)}\cdot CH_{(7')}\cdot CH_{(8)}H_{(8')}\cdot CH_{(1)}$, and the resonances of the protons of the unco-ordinated double bond, the existence of which was shown by an i.r. band at 1 658 cm^{-1}, were ascribed to a component of the low-field multiplet at τ 4·74.

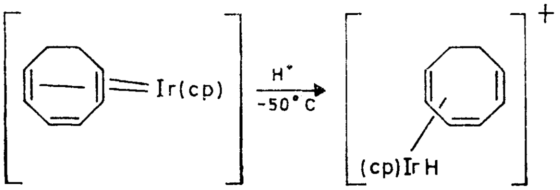
Low-temperature protonation was effected by the addition of a slight excess of CF_3CO_2H to a solution of complex (V) in CD_2Cl_2 at -50 °C. Under these conditions the n.m.r. spectrum [Figure (*c*)] exhibited a high-field signal at τ 19·2 (s, 1H) indicative of metal protonation. The hydrogen atoms of the cp ring resonated at τ 4·04 (s, 5H), and four absorptions were observed at τ 3·62, 4·15, 4·40, and 4·93 of relative intensity 2 : 2 : 2 : 2. The spectrum is consistent with structure (VIII), in which the cyclo-octatetraene ligand is bound through a co-ordinating 1,3-diene unit to the protonated metal atom. Protonation of (1,2:5,6-η-cyclo-octatriene)(η-cyclopentadienyl)iridium, (IX), has been shown[17] to proceed in a similar manner to generate the 1,2:3,4-η-cyclo-octatriene metal protonated complex (X). The change in the observed chelating mode of cyclo-octatetraene may presumably be correlated with pertubation of the iridium bonding orbitals on metal protonation, favouring 1,2:3,4-η-co-ordination of the ligand. On raising the temperature of the acid solution of complex (V) to -10 °C, the high-field resonance broadened and resonances attributed to protons of the cyclo-octatetraene ligand coalesced into two broad signals at τ 3·9 and 4·7 of relative intensity 4 : 4. Such a change may be interpreted in terms of a fluxional cyclo-octatetraene ligand. Valence tautomerism has been observed on monitoring low-temperature n.m.r. spectra of cyclo-octatetraene complexes of tricarbonyl-iron,[18] -ruthenium,[19,20] and -osmium.[21] It has been suggested that the process is *via* a 1,2-shift[22] mechanism in the ruthenium complex, but the validity of this analysis has been questioned.[21] The spectrum of the iridium complex obtained at -10 °C is not consistent with such a process. The 4 : 4 splitting of the eight protons best fits the unlikely 1,5-shift mechanism. But no mechanism solely involving the eight-membered ring need broaden the metal–hydride resonance. So the question of the mechanism of this exchange process is undecided at present. At room temperature no signal was observed at high field, and in addition to absorptions assigned to the η-allyl structure (VIb), resonances were also exhibited at τ 3·63 (t, 1H), 4·2 (s, 5H), 4·4 (m, 4H), 7·77 (m, 2H), 8·03 (q, 1H), and 8·42 (q, 1H) indicative of the isomeric bicyclic complex (VIa). The isomers appeared in the ratio 3 : 2 respectively, and no change in their relative abundances occurred at room temperature up to the limit of the stability of the sample (5 d).



^1H N.m.r. spectra for protonation of the complex (V; M = Ir) in CD_2Cl_2–CF_3CO_2H at (*a*) 29·5, (*b*) -10, and (*c*) -50 °C



(VIII)



(IX) (X)

Two possible mechanisms may be envisaged for form-

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[17] J. Evans, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 2668.

[18] C. G. Kreiter, A. Massbol, F. A. L. Anet, H. O. Kaesz, and S. Winstein, *J. Amer. Chem. Soc.*, 1966, **88**, 3444.

[19] M. I. Bruce, M. Cook, M. Green, and F. G. A. Stone, *Chem. Comm.*, 1967, 523.

[20] W. K. Bratton, F. A. Cotton, A. Davison, A. Musco, and J. Faller, *Proc. Nat. Acad. Sci. U.S.A.*, 1967, **58**, 1324.

[21] M. Cook, R. J. Goodfellow, M. Green, J. P. Mahler, and D. R. Yandle, *Chem. Comm.*, 1970, 565.

[22] F. A. Cotton, A. Davison, T. J. Marks, and A. Musco, *J. Amer. Chem. Soc.*, 1969, **91**, 6598.

ation of the cyclo-octatetraene protonated species (VIa) and (VIb) from the metal-protonated intermediate (VIII) on elevation of the temperature. The proton may be transferred directly from the metal atom to the ligand, resulting in *endo*-protonation, or a second proton may attack the cyclo-octatetraene with concomitant loss of the proton associated with the metal. Diprotonation of diene complexes has been reported previously,[23] although the stereochemistry of the second proton addition is uncertain.

Deuteriation of the iridium complex (V) at low temperature reproduced the spectrum described above in the region τ 0—10, with the expected absence of the high-field signal inferring metal deuteriation. The n.m.r. spectrum at room temperature indicated that deuterium was incorporated into the isomers (VIa) and (VIb) at the methylene position. It was hoped that analysis of the n.m.r. spectrum of the deuterium-incorporated bicyclic complex would provide an insight into the stereochemistry of proton attack as with the analogous bicyclic iron and rhodium cations. However the bicyclic C_8H_9 moiety of (VIa) exhibited the absorptions of the bridging methylene hydrogen atoms as quartets at τ 8·03 and 8·42 for which $J_{H_8-H_{8'}} = J_{H_1-H_8} = J_{H_1-H_{8'}} = J_{H_7-H_8} = J_{H_7-H_{8'}}$ 6 Hz, and no assignments of these resonances to either the *exo*- or *endo*-hydrogen atoms could be made on the basis of coupling-constant data. In CF_3CO_2D the resonance at τ 8·03 was absent and the higher-field resonance at τ 8·42 appeared as a triplet. For the analogous rhodium cation the signal at lower field was attributed to the *exo*-proton, and the disappearance of the absorption at higher field in CF_3CO_2D was interpreted in terms of *endo*-addition. A direct comparison on chemical-shift grounds would imply *exo*-protonation of the iridium complex. However it is not wise to make such a comparison on this basis, as a small conformational distortion of the bicyclic C_8H_9 moiety could greatly affect the chemical shift of the methylene hydrogen atoms by inclusion of shielding interactions from the dienylium system in the ring. The coupling-constant data demonstrate that the bicyclic ligands of the rhodium and iridium complexes are not structurally identical.

The results described above offer no definitive solution to the stereochemistry of proton attack on the cyclo-octatetraene ligand of the iridium complex. However *endo*-protonation of (1,2:3,4-η-cyclohexadiene)(η-cyclopentadienyl)iridium has been conclusively demonstrated,[24] and the observation of the metal-protonated intermediate at low temperatures favours a similar mechanism of proton addition *endo* to a co-ordinated olefinic bond.

The above findings show that the mode of co-ordination of the $C_8H_9^+$ moiety depends on a subtle balance of factors within the system. Although few generalisations can be made, it appears that the most-favoured bonding mode is the 1—3:6,7-η-structure, (VIb). The stereochemistry of proton addition is difficult to assess; however, the stereospecificity of such reactions is beyond doubt. The addition of a proton *exo* to the iron complex suggests that the metal atom is not involved in the reaction and that the proton attacks an unco-ordinated double bond from the least sterically hindered side of the molecule. The proposed *endo*-addition of a proton to the rhodium and iridium complexes implies some degree of metal involvement in the reaction. A metal-protonated species, (VIII), has been observed for the iridium complex at —50 °C, and a similar intermediate may exist at lower temperatures on protonation of (V; M = Rh). The study of complex (V; M = Ir) demonstrates that proton attack only occurs on cyclo-octatetraene when it is co-ordinated through a 1,3-diene unit. Initial attack of a proton on the 1,5-diene unit may be precluded because of formation of a high-energy transition state through the inability of the ligand to stabilise the resulting positive charge without extensive molecular rearrangement. Thus, for 1,5-chelating cyclo-octatetraene complexes of cobalt, rhodium, and iridium, interaction of a proton with the metal atom may be a prerequisite to tautomerism of cyclo-octatetraene to a 1,3-co-ordinating mode before proton addition occurs at the ligand. Such a reaction scheme may involve a lower-energy path for formation of a stabilised $C_8H_9^+$ moiety than direct protonation of the oligo-olefin. The mechanism also implies *endo*-protonation.

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained on a Varian HA 100 spectrometer using tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were recorded on a Varian XL 100-15 spectrometer employing solvent deuterium lock.

The cyclo-octatetraene complexes of tricarbonyl-ruthenium[25] and -osmium,[26] and of (η-cyclopentadienyl)-cobalt,[27] -rhodium,[28] and -iridium, (V),[29] were prepared by standard methods described in the literature.

Protonation of the Cyclo-octatetraene Complexes.—Low-temperature protonation was effected by adding a slight molar excess of CF_3CO_2H from a microlitre syringe to a solution of the appropriate complex in CD_2Cl_2 at —78 °C. PF_6^- Salts of the cations (VI) were obtained by adding 40% aqueous HPF_6 dropwise to a solution of the appropriate complex in diethyl ether until precipitation was complete. The precipitates were filtered off, washed with diethyl ether (3 × 10 cm^3) and anhydrous ether (3 × 10 cm^3), and dried *in vacuo* to give the salts in almost quantitative yield: $[(C_8H_9)Co(cp)]PF_6$, brown (Found: C, 41·45; H, 4·05. Calc. for $C_{13}H_{14}CoF_6P$: C, 41·7; H, 3·75); $[(C_8H_9)Rh(cp)]PF_6$, orange (Found: C, 38·05; H, 3·35. Calc. for $C_{13}H_{14}F_6PRh$: C, 37·3; H, 3·35); and $[(C_8H_9)Ir(cp)]PF_6$, white (Found: C, 29·8; H, 2·80. Calc. for $C_{13}H_{14}F_6IrP$: C, 30·75; H, 2·75%).

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[23] D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 6968.

[24] B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1972, 2084.

[25] M. Bruce, M. Cooke, and M. Green, *J. Organometallic Chem.*, 1968, **13**, 227.

[26] M. I. Bruce, M. Cook, M. Green, and D. J. Westlake, *J. Chem. Soc.* (*A*), 1969, 987.

[27] A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, 1960, **33**, 425.

[28] R. Cramer, *Inorg. Chem.*, 1962, **1**, 722.

[29] H. Yamazaki, *Bull. Chem. Soc. Japan*, 1971, **44**, 582.

Preparation of [1,2:5,6-η-(8-*Cyanocyclo-octatriene*)](*η-cyclopentadienyl*)*cobalt*.—NaCN (0·1 g) was added to a solution of the PF_6^- salt of complex (VI; M = Co) (0·12 g) in 50% aqueous acetone (5 cm^3). The mixture was stirred for 10 min and then decanted into water (15 cm^3) and extracted with diethyl ether (3 × 5 cm^3). The organic extracts were washed, dried ($MgSO_4$), and evaporated *in vacuo* to give an orange solid which was recrystallised from diethyl ether to yield the *product* as air-sensitive orange crystals (0·05 g, 63%) (Found: C, 66·15; H, 5·50; N, 5·25. Calc. for $C_{14}H_{14}CoN$: C, 65·9; H, 5·50; N, 5·50%); ν_{CN} at 2 222 cm^{-1} and $\nu_{C=C}$ at 1 638 cm^{-1} (Nujol).

Kinetics.—Kinetic runs were carried out on a Varian HA-100 instrument, using an ethylene glycol temperature standard. Complex (V; M = Rh) (80 mg) was dissolved in the appropriate acidic solvent (0·4 cm^3) and Me_4Si (0·05 cm^3) added. Protons H_4 of (VIa) and H_2 of (VIb) were integrated and the concentrations of the two isomers determined. The least-squares fits were carried out on a Hewlett-Packard 9100B calculator.

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