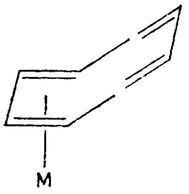
Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part XI.[1] 1—4-η- and 1,2;5,6-η-Cyclo-octatetraene Complexes and their Protonation Reactions

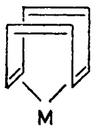
By **Anthony K. Smith** and **Peter M. Maitlis**,* Department of Chemistry, The University, Sheffield S3 7HF

The reaction of $[\{M(C_5Me_5)Cl_2\}_2]$ (1a; M = Rh) and (1b; M = Ir) with $K_2C_8H_8$ (C_8H_8 = cyclo-octatetraene) gave $[M(C_5Me_5)(C_8H_8)]$. The 1—4-η-C_8H_8 isomers (2) were formed at low temperatures and isomerised to the 1,2:5,6-η-C_8H_8 isomers (3) when warmed in solution. The protonation of co-ordinated cyclo-octatetraene in (2a) and (3a) was investigated using CF_3CO_2H and CF_3CO_2D and was shown to proceed by different paths; (2a) was protonated *exo* while (3a) was protonated *endo* to the metal. In both cases two isomers of $[Rh(C_5Me_5)(C_8H_9)]^+$ were formed, namely (2—6-η-bicyclo[5.1.0]octadienyl)(pentamethylcyclopentadienyl)rhodium, (8a), and (1—3:6,7-η-cyclo-octatrienyl)(pentamethylcyclopentadienyl)rhodium, (9a). Compound (8a) isomerised in solution to (9a). The protonation of the iridium analogue (2b) gave only (8b), while protonation of (3b) gave a mixture of (8b) and (9b), which did not isomerise.

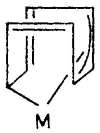
THE reactions of (pentamethylcyclopentadienyl)-rhodium and -iridium halides with a number of unsaturated hydrocarbons have been reported previously.[1,2] This work has now been extended by an investigation of the reaction of $[\{M(C_5Me_5)Cl_2\}_2]$ (1a; M = Rh) and (1b; M = Ir) with the cyclo-octatetraene dianion.



(A) M = $Fe(CO)_3$
$Ru(CO)_3$
$Os(CO)_3$



(B) M = $Mo(CO)_4$
$Co(\eta-C_5H_5)$
$Rh(\eta-C_5H_5)$
$Ir(\eta-C_5H_5)$
$PdCl_2$



(C) $Os(CO)_3$

Three *tetrahapto* modes of co-ordination for cyclo-octatetraene are known; 1—4-η, (A), 1,2:5,6-η, (B), and 1—3:6-η (C);[3] examples are shown below. It is apparent that the nature of the metal and the other ligands strongly influences the mode of co-ordination of cyclo-octatetraene but the precise electronic or steric reasons are still not clear. We here report a novel type of isomerisation between forms (A) and (B) as well as studies on the protonation of both forms with the same metal and other ligands.

Different modes of proton attack on co-ordinated cyclo-octatetraene have been reported. For example, the protonation of $[Fe(1—4-\eta-C_8H_8)(CO)_3]$ occurs by an *exo*-attack of the proton,[4] whereas for $[Mo(1—6-\eta-C_8H_8)(CO)_3]$[5] and $[M(C_5H_5)(1,2:5,6-\eta-C_8H_8)]$ [M = Co, Rh, or Ir][6] the attack is *endo*.

RESULTS AND DISCUSSION

1,2:5,6-η- and 1—4-η-Cyclo-octatetraene Complexes.—The reaction of the cyclo-octatetraene dianion with ruthenium(II) halides has been shown to lead to cyclo-octatetraeneruthenium(0) complexes.[7] We now report that the reaction of (1a) or (1b) with $K_2C_8H_8$ gave low yields of the univalent complexes $[M(C_5Me_5)(C_8H_8)]$. Two isomeric forms were initially produced in a ratio depending on the temperature at which the reaction and

---

[1] Part X, H. B. Lee, K. Moseley, C. White, and P. M. Maitlis, *J.C.S. Dalton*, 1975, 2322.

[2] K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc.* (*A*), 1970, 2875; K. Moseley and P. M. Maitlis, *ibid.*, 1970, 2884; C. White and P. M. Maitlis, *ibid.*, 1971, 3322; H. B. Lee and P. M. Maitlis, *J.C.S. Dalton*, 1975, 2316.

[3] See, for example, M. L. H. Green, 'Organometallic Compounds: The Transition Elements,' Methuen, London, 1968, vol. II, pp. 197—200; M. A. Bennett, *Adv. Organometallic Chem.*, 1966, **4**, 353.

[4] M. Brookhart and E. R. Davis, *Tetrahedron Letters*, 1971, 4349; D. F. Hunt, G. C. Farrant, and G. T. Rodeheaver, *J. Organometallic Chem.*, 1972, **38**, 349; M. Brookhart, E. R. Davis, and D. L. Harris, *J. Amer. Chem. Soc.*, 1972, **94**, 7853.

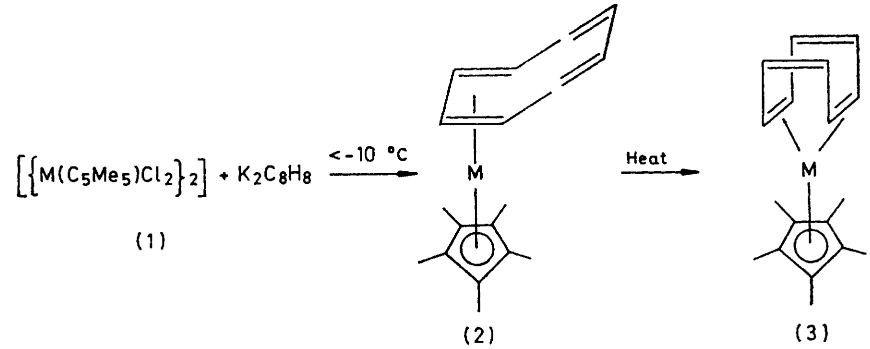
[5] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, 1965, **87**, 3267.

[6] J. Evans, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1974, 2375.

[7] R. R. Schrock and J. Lewis, *J. Amer. Chem. Soc.*, 1973, **95**, 4102; M. A. Bennett and A. K. Smith, unpublished results.

subsequent isolation of the product was carried out. When the temperature of the reaction and the isolation were kept below -10 °C, $>90\%$ of the isomers $[M(C_5Me_5)(1\text{—}4\text{-}\eta\text{-}C_8H_8)]$, (2a) and (2b), were obtained. The ^1H n.m.r. spectrum of (2a), in $CDCl_3$, showed resonances at τ 5.02 [d, C_8H_8, J(H–Rh) 0.7 Hz] and 8.00 [d, C_5Me_5, J(H–Rh) 0.4 Hz], while that of (2b), in $CDCl_3$, showed resonances at τ 5.08 (s, C_8H_8) and τ 7.98 (s, C_5Me_5). No changes in the spectra were observed on cooling the solutions to -50 °C. This is consistent with a $1\text{—}4\text{-}\eta\text{-}C_8H_8$ mode of co-ordination (type A) where a low-energy barrier to the fluxional behaviour of the C_8H_8 ring makes all eight protons equivalent on the n.m.r. time scale even at low temperature.[8]

Supporting evidence for this mode of co-ordination was provided by the i.r. spectrum of (2b) which showed a band at 1 560 cm^{-1} which has been assigned in other $1\text{—}4\text{-}\eta\text{-}C_8H_8$ complexes to ν(C=C) of the unco-ordinated conjugated double-bonds.[9] For example, in $[Fe(1\text{—}4\text{-}\eta\text{-}C_8H_8)(CO)_3]$ this vibration occurs at 1 562 cm^{-1}.



a; M = Rh; b, M = Ir

After 48 h in solution at 20 °C, both (2a) and (2b) had isomerised irreversibly to the $1,2{:}5,6\text{-}\eta\text{-}C_8H_8$ isomers (3a) and (3b). Sublimation (100 °C/0.1 mmHg) of the rhodium complex (2a) yielded only (3a), but the sublimate of the iridium complex (2b) contained *ca.* 10% of (2b) and 90% of (3b) (by n.m.r. spectroscopy).

The ^1H n.m.r. spectrum of (3a) showed resonances at τ 4.33 and 6.82 (broad, C_8H_8) and τ 8.24 [d, C_5Me_5, J(H–Rh) 0.4 Hz], while that of (3b) showed resonances at τ 4.36 and 6.80 (broad, C_8H_8) and 8.20 (s, C_5Me_5). These data are consistent with a $1,2{:}5,6\text{-}\eta$ non-fluxional mode of co-ordination of the C_8H_8. Additional evidence for this mode of co-ordination is provided by the presence of a band at 1 628 cm^{-1} in the i.r. spectrum of (3a). This band may be assigned to ν(C=C) for the unco-ordinated, non-conjugated, double-bonds in the C_8H_8 ring, by analogy to other $1,2{:}5,6\text{-}\eta\text{-}C_8H_8$ complexes.[9]

The assignment of the indicated structures to (2) and (3) is supported by the ^{13}C n.m.r. spectra. For example, (2b) [in CD_2Cl_2–CH_2Cl_2 at 0 °C] showed resonances at δ 91.0 (s, C_8H_8), 88.8 (s, C_5Me_5), and 10.6 p.p.m. (s, C_5Me_5). On cooling to -60 °C the C_8H_8 resonance broadened while the C_5Me_5 resonances remained sharp, while at -90 °C the C_8H_8 resonance had almost merged into the baseline. Unfortunately, solubility problems precluded the observation of spectra at lower temperatures.

By comparison, the spectrum of (3a) [$CDCl_3$/25 °C] showed resonances at δ 135.0 (s, C_8H_8 unco-ordinated), 75.5 [d, C_8H_8 co-ordinated, J(C–Rh) = 12 Hz], 97.0 [d, C_5Me_5, J(C–Rh) = 4.5 Hz], and 9.0 (s, C_5Me_5).

The isomerisation of a co-ordinated C_8H_8 ring from $1\text{—}4\text{-}\eta$ to $1,2{:}5,6\text{-}\eta$ is novel. However, the osmium complex $[Os(1\text{—}3{:}6\text{-}\eta\text{-}C_8H_8)(CO)_3]$ (C) isomerised in boiling hexane to $[Os(1\text{—}4\text{-}\eta\text{-}C_8H_8)(CO)_3]$.[10] A reversible coalescence of the C_8H_8 proton signals in the ^1H n.m.r. spectrum of $[Co(C_5H_5)(1,2{:}5,6\text{-}\eta\text{-}C_8H_8)]$ on heating to >100 °C has been reported.[11] This phenomenon may be due to an intramolecular process involving a $1\text{—}4\text{-}\eta\text{-}C_8H_8$ intermediate or transition state but it is more likely to involve an exchange reaction in which solvent participates.

Protonation.—Lewis *et al.* have shown [6] that protonation (in CF_3CO_2H) of $[M(C_5H_5)(1,2{:}5,6\text{-}\eta\text{-}C_8H_8)]$, (4), gave initially the η^5-bicyclo[5.1.0]octadienyl cation (5; M = Co or Rh), which then isomerised to the $1\text{—}3{:}6,7\text{-}\eta$-cyclo-octatrienyl cation (6). For (4; M = Ir) both (5; M = Ir) and (6; M = Ir) were initially produced and no further rearrangement was detected.

Their studies with CF_3CO_2D in place of CF_3CO_2H showed that the H^+ (D^+) attacked the ring *endo* to the metal to give (5) and that the stereochemistry was retained in (6). Furthermore, low-temperature studies indicated the formation of a metal-protonated species for (4; M = Ir) $[HIr(C_5H_5)(C_8H_8)]^+$, (7), which was a precursor of (5) and (6) (M = Ir). From the low-temperature ^1H spectrum of this species Lewis *et al.* suggested that the C_8H_8 was $1\text{—}4\text{-}\eta$-bonded (7a) and that a change in bonding had occurred on protonation. However, their published -50 °C spectrum of (7) can also be interpreted in terms of a non-fluxional, non-exchanging, rigid structure with $1,2{:}5,6\text{-}\eta\text{-}C_8H_8$, with

---

[8] F. A. Cotton, *Accounts Chem. Res.*, 1968, **1**, 257; ' Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, p. 403.

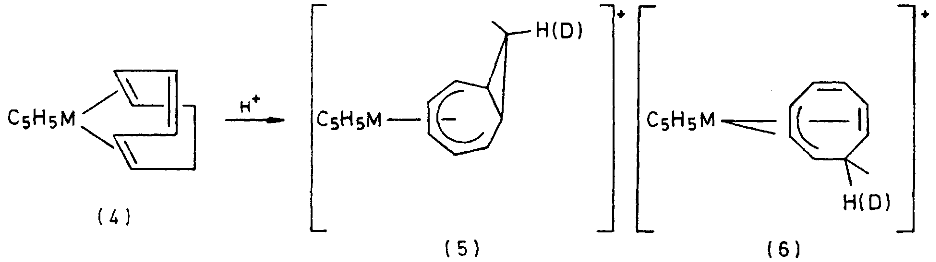
[9] R. T. Bailey, E. R. Lippincott, and D. Steele, *J. Amer. Chem. Soc.*, 1965, **87**, 5346; M. A. Bennett and J. D. Saxby, *Inorg. Chem.*, 1968, **7**, 321; A. Davison, W. MacFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 2821.

[10] M. I. Bruce, M. Cooke, and M. Green, *Angew. Chem. Internat. Edn.*, 1968, **7**, 639.

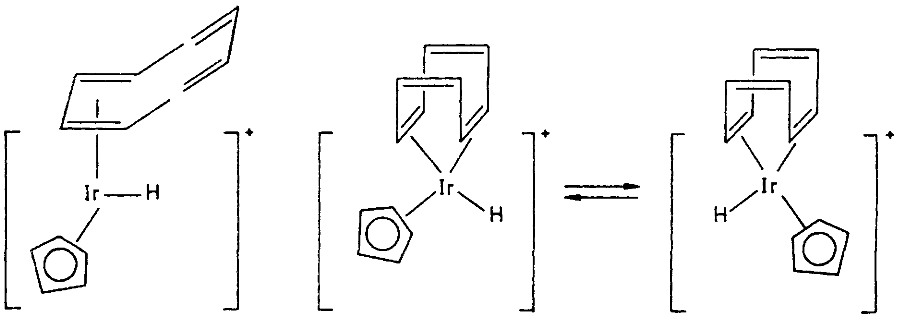
[11] S. Otsuka and A. Nakamura, *Inorg. Chem.*, 1966, **5**, 2059.

the proton occupying a defined co-ordination site on Ir, and which at -10 °C undergoes an (intramolecular) exchange between two sites, for example, (7b) $\rightleftharpoons$ (7c).

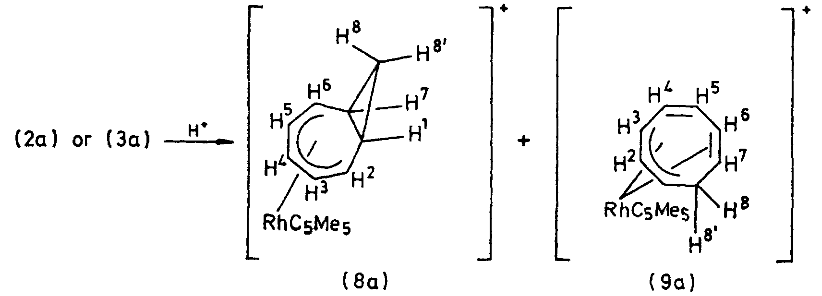
The studies described here were already in progress at the time of the appearance of the paper by Lewis *et al.*, and the results complement and extend their studies. We find that protonation of $[Rh(C_5Me_5)(1,2{:}5,6\text{-}\eta\text{-}C_8H_8)]$ (3a) followed the pattern described for (4; M = Rh) to give (8a) and (9a) in a 4 : 1 ratio at -50 °C; when warmed (8a) isomerised to (9a). The complexes were identified by their ^1H n.m.r. spectra which were assigned by analogy to (5) and (6) {(8a) τ 3.04 [t, H^4, $J(H^4\text{–}H^5) = J(H^4\text{–}H^3) = 6$ Hz], 4.8—5.4 (m, H^2, H^3, H^5, H^6), 7.8 (m, H^1, H^7), 8.35 [q, H^8(*exo*), $J(H^8\text{–}H^7) = J(H^8\text{–}H^1) = J(H^8\text{–}H^{8'}) = 5$ Hz], 8.75 [dt, $H^{8'}$(*endo*), $J(H^{8'}\text{–}H^8) = 5$; $J(H^{8'}\text{–}H^7) = J(H^{8'}\text{–}H^1) = 8$ Hz], and 7.98 (d, C_5Me_5); (9a), τ 4.57 (m, H^3, H^6), 5.30 (m, H^4, H^5), 5.86 (m, H^1, H^2), 6.5—6.8 [m, H^7, $H^{8'}$(*endo*)], 7.15 [m, H^8(*exo*)], and 8.05 (d, C_5Me_5)}.



(4) (5) (6)



(7a) (7b) (7c)



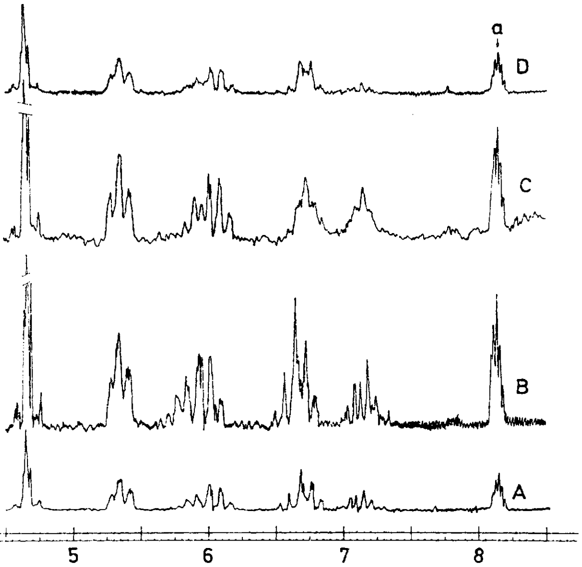
(8a) (9a)

A sample of the 1—4-η-C_8H_8 rhodium complex (2a) was also protonated in CF_3CO_2H at -50 °C to give (8a) and (9a) in a 3 : 2 ratio.

Owing to the difficulty of preparing substantial amounts of the iridium complexes (2b) and (3b) their protonation reactions were only briefly studied. However, it was ascertained, (i), that at -80 °C (3b) gave a high-field resonance at τ 19.7 ascribed to an IrH^+ species [by analogy with (7)]; and, (ii) that on warming to >-40 °C (3b) gave a spectrum very similar to that reported for the mixture of (5) and (6) (M = Ir) and which did not change when set aside or warmed. The latter species were characterised by C_5Me_5 resonances at τ 7.94 and 8.02 in the ratio of 4 : 3 which we ascribe to the iridium analogues of (8a) and (9a) respectively. In contrast, (2b) gave only one C_5Me_5 resonance at τ 7.94, which we therefore suggest is the bicyclo[5.1.0]octatrienyl complex (8b).

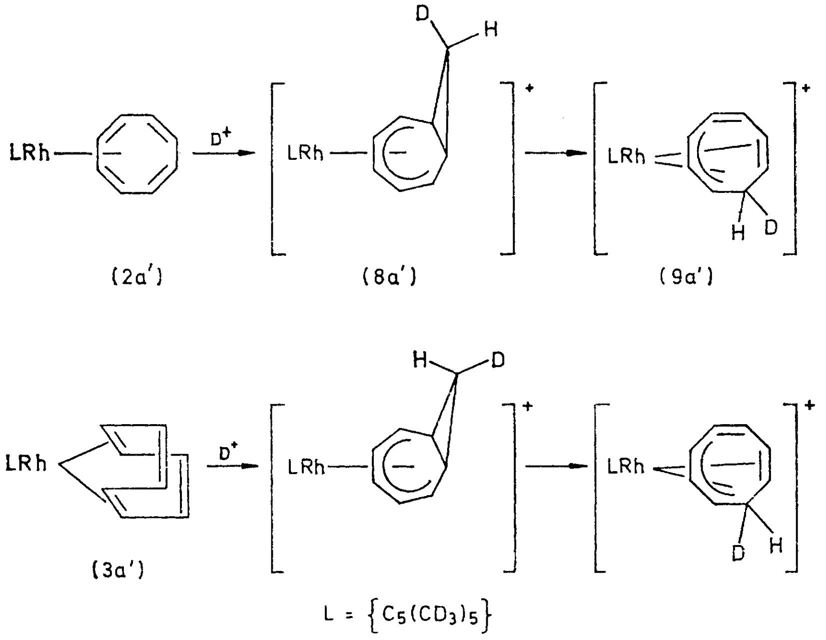
In order to simplify the interpretation of the ^1H n.m.r. spectra by removing the strong $[C_5(CH_3)_5]$ resonances, the perdeuteriomethyl compounds $[Rh\{C_5(CD_3)_5\}(1\text{—}4\text{-}\eta\text{-}C_8H_8)]$ (2a′) and $[Rh\{C_5(CD_3)_5\}(1,2{:}5,6\text{-}\eta\text{-}C_8H_8)]$ (3a′) were synthesised from $[\{Rh[C_5(CD_3)_5]Cl_2\}_2]$.[12]

One sample of each of the isomers (2a′) and (3a′) was treated with CF_3CO_2H at -30 °C and one sample of each was treated with CF_3CO_2D at -30 °C; to simplify the spectra further the resultant mixtures of (8a′) and (9a′) were allowed to warm to room temperature until all the bicyclic (8a′) had isomerised to the monocyclic isomer (9a'). As shown in the Figure, the samples from both C_8H_8 isomers and CF_3CO_2H gave identical spectra,



100 MHz ^1H n.m.r. spectra in $CDCl_3$ of $[Rh\{C_5(CD_3)_5\}(C_8H_9)]^+$, (A) from (2a') and CF_3CO_2H, and (B) from (3a') and CF_3CO_2H; and of $[Rh\{C_5(CD_3)_5\}(C_8H_8D)]^+$, (C) from (3a') and CF_3CO_2D, and (D) from (2a') and CF_3CO_2D. The signals labelled (a) are residual protons of the C_5Me_5 group

in which the resonances of H^8(*exo*) and $H^{8'}$(*endo*) were clearly present. The spectrum of (9a') from the 1—4-η-C_8H_8 complex (2a') and CF_3CO_2D still showed the presence of $H^{8'}$ (*endo*) but H^8 (*exo*) was almost completely absent. In contrast, the spectrum of (9a') from the 1,2: 5,6-η-C_8H_8 complex (3a') in CF_3CO_2D showed H^8 (*exo*) as a broad triplet owing to the removal of coupling to $H^{8'}$ (*endo*) and the multiplet (τ 6.5—6.8) containing H^7 and $H^{8'}$ was greatly reduced in intensity as well as simplified owing to the absence of resonances due to $H^{8'}$(*endo*).



These results clearly indicate that the 1—4-η- and the 1,2:5,6-η-C_8H_8 complexes are both protonated stereospecifically but in different ways. Lewis *et al.* have shown that the isomerisation of (5; M = Rh) to (6; M = Rh) is stereospecific and that when deuterium is incorporated at $H^{8'}$(*endo*) in (5) it appears only at $H^{8'}$ in (6). If we make the very probable assumptions that no interchange of H^8 and $H^{8'}$ has occurred in the isomerisation (5) ⟶ (6) and that a similar stereospecific relationship holds for (8a) and (9a), then we may conclude that the 1—4-η-complex (2a) is protonated stereospecifically *exo* while the 1,2:5,6-η-complex (3a) is protonated stereospecifically *endo*.

These results therefore suggest that the 1—4-η-C_8H_8 complex is attacked directly by H^+ (D^+) at the cyclo-octatetraene while attack on the 1,2:5,6-η-C_8H_8 complex occurs *via* an M–H^+ intermediate. Evidence in support comes from the observation of the low-temperature protonation at the metal in both $[Ir(C_5Me_5)(1,2{:}5,6\text{-}\eta\text{-}C_8H_8)]$, (3b), and from (7), particularly if our suggestion is correct that the structure of the resultant species is (7b) rather than (7a).

These results would then also accord with the observations that $[Fe(1\text{—}4\text{-}\eta\text{-}C_8H_8)(CO)_3]$ is protonated *exo* at an unco-ordinated C_8H_8 carbon,[4] while $[Mo(1,2{:}5,6\text{-}\eta\text{-}C_8H_8)(CO)_4]$ is protonated *endo*.[5] However, while the formation of the 1—5-η-bicyclo[5.1.0]octadienyl cations and the subsequent isomerisation to the 1—3 : 6,7-η-cyclo-octatrienyl cations appears established for the cobalt and rhodium complexes, the formation of both initially for M = Ir without any sign of subsequent isomerisation is surprising. It must be presumed that two routes exist to the formation of the monocyclic cations.

EXPERIMENTAL

$[\{IrCl_2[C_5(CH_3)_5]\}_2]$, $[RhCl_2\{C_5(CH_3)_5\}]$, and $[\{RhCl_2[C_5(CD_3)_5]\}_2]$ were prepared by published methods.[12,13] Cyclo-octatetraene was distilled before use. All reactions were carried out in a nitrogen atmosphere. Typical preparations are described.

$[Rh(C_5Me_5)(C_8H_8)]$.—Potassium metal (0.4 g) in freshly distilled tetrahydrofuran (20 ml) was treated with cyclo-octatetraene (0.4 g) at −30 °C. The mixture was stirred while warming to room temperature until all the potassium had disappeared (*ca.* 2 h). The solution was cooled to −30 °C and $[\{RhCl_2(C_5Me_5)\}_2]$ (0.4 g) was added. After 1 h at −30 °C the solvent was removed *in vacuo* and the product was extracted with pentane (15 ml). Removal of the solvent gave an orange solid (yield, 10—20%).

This orange solid contained up to 90% (2a) and 10% (3a). On sublimation (100 °C, 0.1 mmHg), (3a) was obtained as a yellow solid, m.p. 127—130 °C (decomp.) (Found: C, 63.0; H, 7.0%; *M*, 342 (mass-spectrometric). $C_{18}H_{23}Rh$ requires C, 63.1; H, 6.8%; *M*, 342).

$[Ir(C_5Me_5)(C_8H_8)]$ was obtained as described above; (2b) was obtained virtually free of (3b) by keeping the temperature of the material in all operations below −10 °C. A mixture of (3b) (90%) and (2b) (10%) was obtained as a yellow solid by subliming the product (140 °C, 0.1 mmHg) (Found: C, 49.6; H, 5.5. $C_{18}H_{23}Ir$ requires C, 50.1; H, 5.4%).

Protonation of $[M(C_5Me_5)(C_8H_8)]$.—Solutions of $[M(C_5Me_5)(C_8H_8)]$ in $CDCl_3$ were treated with a slight excess of trifluoracetic acid at −78 °C. The solutions were analysed by n.m.r. spectroscopy at the appropriate temperatures.

We thank Dr. B. E. Mann for helpful discussions, the S.R.C. for support of this work, and I.C.I. Ltd. for a grant towards the purchase of chemicals.

[5/2424 *Received*, 12*th December*, 1975]

---

[12] J. W. Kang and P. M. Maitlis, *J. Organometallic Chem.*, 1971, **30**, 127.

[13] J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1969, **91**, 5970.