Reactivity of Co-ordinated Ligands. Part XIII.[1] Electrophilic Substitution Reactions of Cyclohexa-1,3-diene Complexes of Rhodium(I) and Iridium(I)

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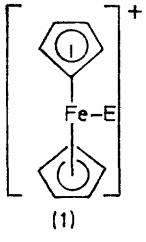
Protonation and deuteriation studies were carried out on complexes (cyclohexa-1,3-diene)(π-cyclopentadienyl)M[I] where M = Rh or Ir. In acid media proton exchange was shown to occur at the *endo*-methylene positions of the cyclohexadiene ligand *via* interaction with the metal. Reaction with Ph_3CBF_4 formed co-ordinated cyclohexadienium cations which were susceptible to nucleophilic attack to form the *exo*-derivatives. Acetylation of the rhodium complex yielded the product of acetyl substitution on the π-cyclopentadienyl ring. Acid solutions of this complex exhibited proton exchange both with the *endo*-hydrogens of the co-ordinated cyclohexadiene and with the hydrogens at the 2,3,4, and 5 positions of the substituted π-cyclopentadienyl ligand.

THE role of the metal in determining the course of electrophilic substitution reactions on co-ordinated organic ligands is still uncertain. The observation that ferrocene in strong acid produces an iron-protonated species [2,3] led Richards [4] and Rosenblum [5] to postulate that electrophilic substitution reactions of ferrocenes proceeds *via* initial attack of the electrophile on the essentially non-bonding E_{2g} orbital of the metal. The mechanism they propose involves rate-limiting transfer of the electrophile from a complexed cation (1)



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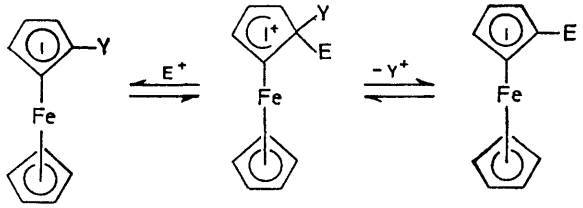


(2)

to the π-cyclopentadienyl ring, followed by fast removal of a proton. However isotopic rate studies and solvolysis studies led Mangravite and Traylor [6] to propose a course of reaction (2) which excludes the need to invoke metal participation. The following study of the protonation of (cyclohexa-1,3-diene)(π-cyclopentadienyl)-rhodium(I) (3), its derivatives, and cobalt and iridium analogues, demonstrates conclusively the ability of the metal to direct the entering electrophile *endo* to the co-ordinated organic ligand.

[1] Part XII, preceding paper.
[2] M. Rosenblum and J. O. Santer, *J. Amer. Chem. Soc.*, 1959, **81**, 5517.
[3] T. C. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *J. Amer. Chem. Soc.*, 1960, **82**, 5249.
[4] J. H. Richards, Abstr. 135th Nat. Meeting, Amer. Chem. Soc., April 1959, p. 86.
[5] M. Rosenblum, J. O. Santer, and W. G. Howells, *J. Amer. Chem. Soc.*, 1963, **85**, 1450.

RESULTS AND DISCUSSION

Preparation of the Diene Complexes $(C_6H_8)M(\pi\text{-}C_5H_5)$ (M = Co, Rh, Ir).—(Cyclohexa-1,3-diene)(π-cyclopentadienyl)rhodium(I) (3) was prepared using the general method of Cramer.[7] The analogous iridium complex was obtained from the reaction of sodium chloroiridate and cyclohexa-1,3-diene in aqueous ethanol, followed by treatment of the precipitated bridged dichloride $(C_6H_8IrCl)_2$ with cyclopentadienidethallium(I).[8] A solution of $(\pi\text{-}C_5H_5)Co(CO)_2$ and cyclohexa-1,3-diene in nonane heated under reflux yielded the cobalt complex.[9]

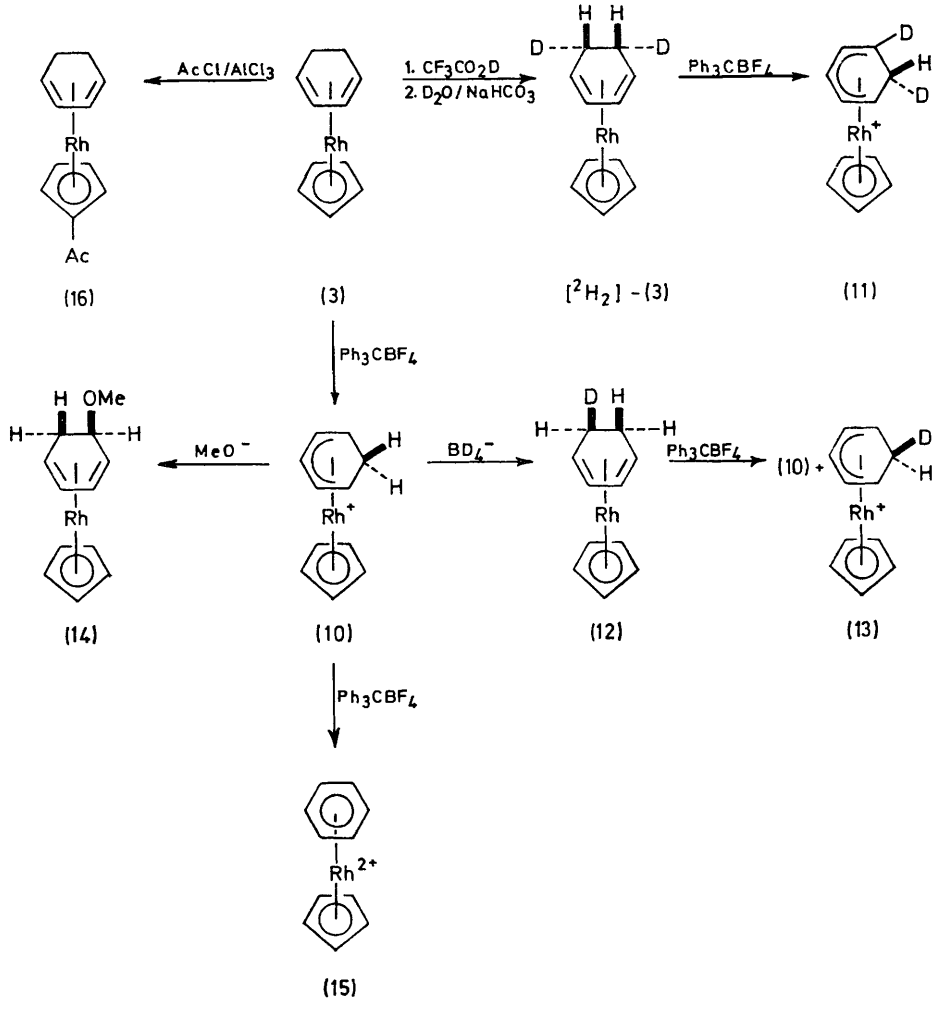
Protonation and Deuteriation of (Cyclohexa-1,3-diene)(π-cyclopentadienyl)rhodium(I) (3).—The ^1H n.m.r. spectrum (100 MHz) of a solution of (3) in CF_3CO_2H exhibited three resonances, τ 4·20 (5, 5H), 6·14 (m, 6H), and 12·05 (m, 3H). A similar spectrum was observed for a freshly prepared solution of (3) in CF_3CO_2D except that the signal at τ 12·05 was reduced in relative intensity from three to two protons. Significantly, however, when the solution was set aside under ambient conditions this signal slowly decreased in intensity until after 1 h it had disappeared. These observations are rationalised in Scheme 1. The mechanism postulated involves initial protonation of the metal followed by reversible transfer of the proton to the cyclohexadiene to form a cationic π-allylic complex (5). As indicated, a sufficiently rapid exchange will equilibrate three protons between *endo*-methylene and metal–hydride environments and hence account for the high-field signal. The absorption at τ 6·14 due to six protons is then explained by the protons permanently bonded to the six-membered ring being equilibrated between allylic and *exo*-methylene environments. The signal at lowest field is ascribed to the five protons of the π-cyclopentadienyl ring. Slow exchange of H^+ or D^+ with the solvent and metal hydride would lead to collapse of the signal at τ 12·05 in CF_3CO_2D solution. Furthermore, treatment of (3) in ether with HPF_6 precipitated a yellow salt of composition $C_{11}H_{14}RhPF_6$. The n.m.r. (100 MHz, liq. SO_2)

[6] J. A. Mangravite and T. Traylor, *Tetrahedron Letters*, 1967, 4461.
[7] R. Cramer, *Inorg. Chem.*, 1962, **1**, 722; *J. Amer. Chem. Soc.*, 1964, **86**, 217.
[8] F. A. Cotton and L. T. Reynolds, *J. Amer. Chem. Soc.*, 1958, **80**, 269.
[9] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3593.

of this species was similar to that described above, indicating that the exchange is intramolecular rather than intermolecular in origin. At −50 °C only slight broadening of the resonance was observed.

Complex (3) was regenerated in quantitative yield on quenching the CF_3CO_2H solution with H_2O and neutralising the solution with sodium hydrogen carbonate. Dideuterio-complex (3) was recovered from CF_3CO_2D solution, and in agreement with the proposed mechanism the two deuterium atoms were shown by n.m.r. to be incorporated at the methylene positions.

Some support for the proposed mechanism is obtained from the protonation of the iridium complex (6). The ^1H n.m.r. spectrum [100 M Hz, CF_3CO_2H (50 μl) in CD_2Cl_2 (150 μl)] at −20 °C exhibited resonances at τ 4·00 (m, 2H, inner diene), 4·05 (s, 5H, π-cyclopentadienyl), 5·29 (m, 2H, outer diene), 7·98 (m, 4H, methylenes), and 25·30 (t, 1H, metal-hydride) indicating a complex of structure (7), where the resonances of the protons of the cyclohexa-1,3-diene and π-cyclopentadienyl ring are moved downfield relative to the unprotonated complex (6). As the temperature was raised the signals were observed to broaden, and the coalescence temperature was reached at 82 °C. Above this temperature appreciable decomposition took place. The assumption that broadening of the resonances was caused by equilibration between species (6), (7), and (8) was confirmed by examining the n.m.r. spectrum of (6) in CF_3CO_2D at room temperature. In this case the broad resonance at high field disappeared and the broad methylene resonance centred at τ 7·98 decreased from relative intensity 4 to 2 after 1 h. Neutralisation of this acid solution in D_2O gave the product dideuterio-complex (6), analogous to the previously described dideuterio-complex (3), the n.m.r. spectrum revealing dideuterium incorporation at the methylene positions. The analogous cobalt complex (9) decomposed in acid solution.



Reactions with Ph_3CBF_4.—The mechanism of protonation postulated above, proposes that the proton is transferred from the metal to the cyclohexadiene ligand, and hence implies that the deuterium atoms incorporated in the recovered dideuterio-complex (3) and dideuterio-complex (6) will occupy the *endo*-methylene positions. Additional evidence for this mechanism was obtained as follows. The dienyl salts (10) and (11) were prepared

by addition of an equimolar amount of Ph_3CBF_4 to solutions of complex (3) and dideuterio-complex (3) in CH_2Cl_2. The n.m.r. spectrum of (10) is similar to those reported for analogous cations.[10,11] If the previous assignments of these spectra are accepted then the quintet at τ 7·06 may be assigned to the *endo*-methylene proton, and the upfield doublet at τ 7·37 to the absorption of the *exo*-methylene proton. The shift to high field of the *exo*- relative to the *endo*-proton is caused by shielding effects arising from its stereochemical position over the dienium system in the ring. The absence of a resonance at τ 7·06 in (11) is interpreted in terms of specific deuterium incorporation at the *endo*-position and provides confirmatory evidence for the proposed mechanism of *endo*-electrophilic attack.

The observation that (11) is the only product indicates that attack by Ph_3CBF_4 was stereospecific. The n.m.r. assignments imply that (11) is the product of trityl attack at the *exo*-hydrogen, as would be anticipated from steric considerations. In addition, reduction of (10) with sodium borodeuteride gave the neutral diene (12), which reacted with Ph_3CBF_4 to yield an equimolar mixture of (10) and the *exo*-monodeuterium dienyl salt (13) characterised by the n.m.r. assignments given in Tables 1 and 2. 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[12-14] on nucleophilic addition to co-ordinated organic groups is assigned as the *exo*-derivative.

The influence of certain substituent groups on both the π-cyclopentadienyl group and the cyclohexa-1,3-diene has also been investigated. Methoxide ion attack on the dienyl salt (10) produced (π-cyclopentadienyl)-(5-methoxycyclohexa-1,3-diene)rhodium(I) (14), which in CF_3CO_2H solution was reconverted into (10) and methanol. This reaction is probably facilitated by initial protonation at the lone pair of electrons of the oxygen, with the basicity of the methoxy-substituent precluding formation of a metal hydride species. The

TABLE 1

N.m.r. spectra of diene complexes *

Compd.	Proton(s)	Chemical shift (τ)	Relative intensity	Multiplicity	J(Hz)
(3)	π-Cp	4·77	5	s	
	inner diene	5·10	2	m	
	outer diene	6·37	2	m	
	endo-methylene	8·50	2	A part of AA'BB' spectrum	
	exo-methylene	8·78	2	B part of AA'BB' spectrum	
[$^2H_2$]-(3)	π-Cp	4·77	5	s	
	inner diene	5·10	2	m	
	outer diene	6·37	2	m	
	exo-methylene	8·78	2	s	
(12)	π-Cp	4·77	5	s	
	inner diene	5·10	2	m	
	outer diene	6·37	2	m	
	endo-methylene	8·50	2	m	
	exo-methylene	8·78	1	m	
(6)	π-Cp	4·84	5	s	
	inner diene	5·10	2	m	
	outer diene	6·54	2	m	
	methylenes	8·70	4	m	
[$^2H_2$]-(6)	As for (6), but in this case the resonance at τ 8·70 appears as a singlet of relative intensity 2.				
(14)	π-Cp	4·72	5	s	
	inner diene	4·98	2	m	
	outer diene	6·40	2	m	
	H^5 *endo*	6·72	1	m	
	$-OCH_3$	6·88	3	s	
	H^6 *endo*	7·94	1	m	
	H^6 *exo*	8·65	1	d	JH^6 *endo*, H^6 *exo* = 14
(16)	H^2, H^5	4·34	2	m	
	H^3, H^4	4·88	2	m	
	inner diene	5·13	2	m	
	outer diene	6·38	2	m	
	$-COCH_3$	7·82	3	s	
	methylenes	8·70	4	m	
[$^2H_6$]-(16)	inner diene	5·13	2	m	
	outer diene	6·38	2	m	
	$-COCH_3$	7·82	3	s	
	methylenes	8·70	2	s	

* All spectra were recorded in $CDCl_3$ with T.M.S. as internal standard, except for (16) and d^6-(16) which were recorded in CS_2 solution.

TABLE 2

N.m.r. spectra of cyclohexadienium salts *

Compd.	Proton(s)	Chemical shift (τ)	Relative intensity	Multiplicity	J(Hz)
(10)	H^3	3·12	1	t	JH^2, H^3 = 6
	π-(C_5H_5)	4·14	5	s	
	H^2, H^4	4·40	2	t	JH^2, H^3 = JH^1, H^2 = 6
	H^1, H^5	5·68	2	t	JH^1, H^2 = JH^1, H^6 *endo* = 6; JH^1, H^6 *exo* = 0
	H^6 *endo*	7·06	1	Quintet	JH^6 *endo*, H^6 *exo* = 12; JH^1, H^6 *endo* = 6
	H^6 *exo*	7·37	1	d	JH^6 *endo*, H^6 *exo* = 12
(11)	H^3	3·12	1	t	
	π-Cp	4·14	5	s	
	H^2, H^4	4·40	2	m	
	H^1	5·68	1	d	
	H^6 *exo*	7·37	1	s	
(10) + (13)	H^3	3·12	1	t	
	π-Cp	4·14	5	s	
	H^2, H^4	4·40	2	t	
	H^1, H^5	5·68	2	t	
	H^6 *endo*	7·06	1	m	
	H^6 *exo*	7·37	0·5	d	

* Spectra recorded in liq. SO_2 with Me_4Si as internal standard.

[10] D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4458.

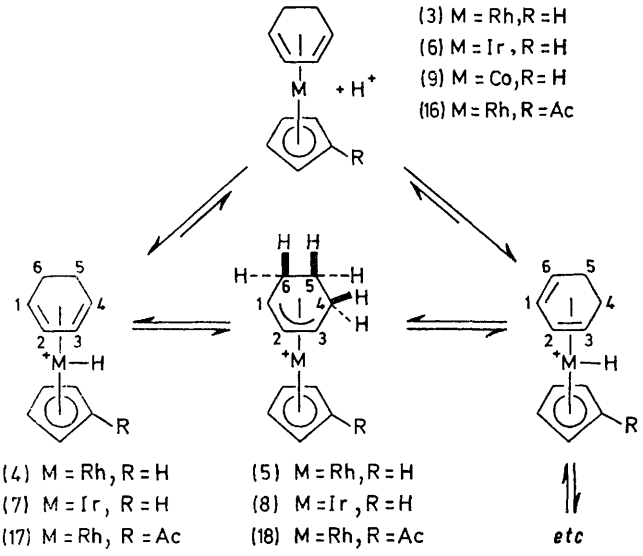
[11] G. E. Herberich and J. Schwartzer, *Angew. Chem. Internat. Edn.*, 1969, **8**, 143.

[12] P. L. Pauson, G. H. Smith, and J. H. Valentine, *J. Chem. Soc.* (*C*), 1967, 1057.

[13] P. E. Baikie, O. S. Mills, P. L. Pauson, G. H. Smith, J. Valentine, *Chem. Comm.*, 1965, 425.

[14] G. E. Herberich and R. Michelbrink, *Chem. Ber.*, 1970, **103**, 3615.

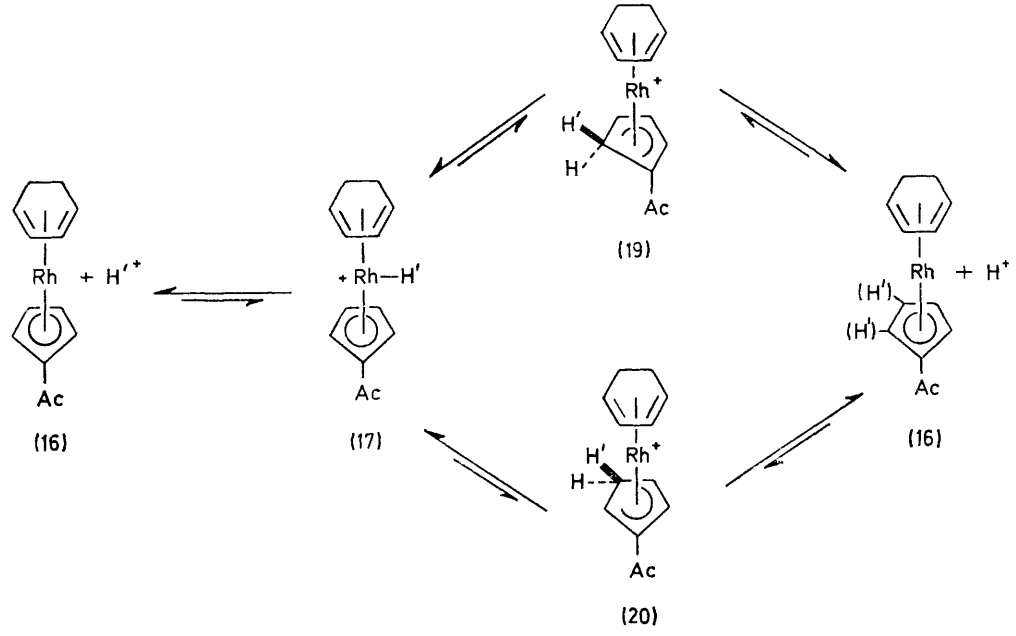
susceptibility of cation (10) to nucleophilic attack is in contrast to its electrophilic reaction with a further mole of Ph_3CBF_4 to yield the previously reported [15]



SCHEME 1

(benzene)(π-cyclopentadienyl)rhodium(I) ditetrafluoroborate (15).

a solvent shift of signals to lower field, broadening of resonances due to H^2, H^5 and H^3, H^4 of the substituted π-cyclopentadienyl ring and the appearance of a broad singlet in the methylene region of the spectrum. Significantly, however, on monitoring the n.m.r. spectrum of (16) in CF_3CO_2D, the resonance at τ 3·76 (assigned to H^2, H^5) disappeared after 5 min; the resonance at τ 8·36 (assigned to the methylene protons of the cyclohexadiene ligand) decreased from relative intensity 4 to 2 after 25 min in solution; and the signal at τ 4·12 (assigned to H^3, H^4) had completely collapsed after 90 min in solution. Neutralisation of this acid solution yielded hexadeuterio-complex (16). The n.m.r. of this species indicated specific deuterium incorporation at the 2,3,4, and 5 positions of the π-cyclo-pentadienyl ring and at two of the four methylene positions of the cyclohexadiene ligand. Deuterium incorporation was confirmed by mass spectrometry, a parent ion appearing at *m/e* 296, corresponding to $C_{13}H_9D_6ORh$, and a fragmentation ion appearing at *m/e* 214, corresponding to $C_7H_3D_4ORh$. The n.m.r. of complex (16) in acid solution may be explained, with regard to methylene exchange, by the equilibrium represented in Scheme 1 if the equilibrium (16) ⇌ (17) ⇌ (18) lies predominantly to the left. A proposition that may be correlated with the inability of complex (16) to produce



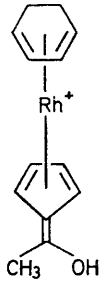
SCHEME 2

Preparation, Protonation, and Deuteration of (1-*Acetylcyclopentadienyl*)(*cyclohexadiene*)*rhodium*(I) (16).—Friedel–Craft acetylation of complex (3) yields the product of electrophilic substitution at the π-cyclopentadienyl ring (16). The n.m.r. of (16) in CF_3CO_2H is essentially the same as that of (16) in CS_2, apart from a salt on addition of HPF_6 to its ethereal solution, reflecting a decrease in basicity of (16) relative to (3). Alternatively the lifetime of the intermediates (17) and (18) may be too short ($<10^{-4}$ s) to be observed on the n.m.r. time scale.

Activation of the 1-acetyl-cyclopentadienyl ring to proton exchange in (16) is in contrast to the results obtained for substituted ferrocenes. 1-Acetylferrocene

[15] E. O. Fischer and R. D. Fischer, *Z. Naturforsch.*, 1961, **166**, 556.

has been shown[16] to undergo isotope exchange in deuterioacid at a slower rate than ferrocene itself, a fact explained by the electron-withdrawing properties of the acetyl group which reduces the susceptibility of the π-cyclopentadienyl ligand to electrophilic attack. In the case of complex (16) it appears to be the concomitant enhancement of acidity of the cyclopentadienyl protons that is the dominant factor in their reactivity. The greater rate of exchange of H^2, H^5 over H^3, H^4 is a reflection of the larger mesomeric effect exerted by the acetyl group on positions 2 and 5, and on the increased stabilisation of the intermediate (19) through extended delocalisation with the carbonyl chromophore. The proposed mechanism of π-cyclopentadienyl substitution is represented in Scheme 2, and involves initial proton attack either at the metal or the π-cyclopentadienyl ring. The protons of the substituted cyclopentadienyl ring may be regarded as having a residual positive charge, δ^+, which may be shared through delocalisation with the *d* orbitals of Rh^I. A situation then arises which will allow *exo*-protonation of the cyclopentadienyl ring (19) followed by proton transfer to the metal to give the intermediate cation (17). The observed n.m.r. spectra is explained if either the equilibrium lies predominantly towards (16) or the intermediate (17), (19), and (20) are very short-lived. The difference between the relative rates of isotopic exchange of (16) and 1-acetylferrocene may then be rationalised by the more ready transfer of a proton to Rh^I rather than Fe^{II}. The presence of the $COCH_3$ grouping in the π-cyclopentadienyl ligand does also provide an alternative site for proton attack. Although we regard such a mechanism as less likely it is possible that for the complex (16) the initial addition of H^+ occurs at the ketonic oxygen to generate the fulvene system (21). By this



(21)

means a second 'butadiene fragment' is produced offering an alternative site to the cyclohexadiene for a *second* proton addition. It is relevant that the protonation of tricarbonyl-1-acetylcycloheptatriene iron occurs at the ketonic oxygen,[1] and evidence for diprotonation of metal-olefin complexes has been reported.[17] However, in this case we can find no evidence to suggest that the acetyl-cyclopentadienyl grouping undergoes any change in its structure during the course of the reaction.

[16] M. N. Nefedova, D. N. Kursanov, V. N. Setkina, E. N. Pervealova, and A. N. Nesmeyanov, *Doklady Akad. Nauk S.S.S.R.*, 1966, **166**, 374.

EXPERIMENTAL

Microanalyses were carried out by the microanalytical department of this laboratory. N.m.r. spectra were measured on a Varian Associates HA 100 machine, and mass spectra were obtained from an A.E.I. MS 12 instrument. I.r. spectra were recorded using a Perkin-Elmer 257 spectrometer. M.p.s were measured in open capillary tubes on a Gallenkamp melting point apparatus. All reactions were carried out under pure dry nitrogen.

(Cyclohexa-1,3-diene)(π-cyclopentadienyl)rhodium(I) (3).—μ-Dichlorobiscyclohexa-1,3-dienerhodium(I) (1·4 g) and cyclopentadienidethallium(I) (1·7 g) were shaken in benzene (50 ml) for 12 h with exclusion of light. Insoluble thallium residues were filtered off and the yellow filtrate was evaporated *in vacuo* before chromatography through alumina with toluene as eluant. The yellow band that developed yielded, on evaporation, the product as yellow crystals (1·4 g, 90%) (Found: C, 53·15; H, 2·05. $C_{11}H_{13}Rh$ requires C, 53·2; H, 2·1%).

Protonation of Complex (3).—To a solution of complex (3) (200 mg) in ether (5 ml) was added HPF_6 dropwise to excess (*ca.* 0·5 ml). The orange-yellow precipitate so produced was immediately filtered off and washed with dry ether (3 × 10 ml). The salt was recrystallised from CH_2Cl_2 at −78 °C to yield the product (180 mg, 57%) (Found: C, 33·55; H, 3·6. $C_{11}H_{14}F_6PRh$ requires C, 33·5; H, 3·55%.) No ν(Rh–H) was observed in the i.r. region.

(Cyclohexadienium)(π-cyclopentadienyl)rhodium(I) *Tetrafluoroborate* (10).—To a stirring solution of (3) (320 mg) in CH_2Cl_2 (4 ml) solution was added an equimolar amount of Ph_3CBF_4 (420 mg) in CH_2Cl_2 (4 ml) solution. After 2 min the reaction was quenched with ether (6 ml) and the yellow precipitate was filtered off and recrystallised from CH_2Cl_2 at −78 °C, to yield the product (345 mg, 81%) (Found: C, 39·9; H, 3·75. $C_{11}H_{12}BF_4Rh$ requires C, 39·55; H, 3·7%.)

$NaBD_4$ *Reduction of Complex* (10).—Complex (10) (146 mg) was suspended in a rapidly stirred mixture of water (5 ml) and benzene (5 ml) and $NaBD_4$ (10 mg) were added. The solution was stirred for 10 min and the benzene fraction was then separated, dried ($MgSO_4$), and evaporated *in vacuo* to give a yellow crystalline product (12) (110 mg, 98%). An i.r. spectrum in CCl_4 solution showed C–D at 2118 cm^{-1}; *M* (mass spec) 249 corresponding to $C_{11}DH_{12}Rh$.

Recovery of Complexes from Acid Solutions.—Typically the acid solutions were decanted into H_2O or D_2O (10 ml) and $NaHCO_3$ was added until the solutions were neutral; the aqueous solutions were extracted with ether (3 × 5 ml). The combined ether extracts were dried ($MgSO_4$) and evaporated to yield the products. Complexes (3) and (6) were regenerated from CF_3CO_2H solution in quantitative yield.

(π-Cyclopentadienyl)(5-methoxycyclohexa-1,3-diene)rhodium(I) (14).—Sodium methoxide (120 mg) was dissolved in dry MeOH (8 ml) and the salt (10) (250 mg) was added. The solution was stirred for 5 min before decantation into water (20 ml) and extraction with ether (2 × 10 ml). The combined ether extracts were washed with H_2O and dried ($MgSO_4$); the evaporation *in vacuo* yielded yellow

[17] David A. T. Young, John R. Holmes, and Herbert D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 6968.

crystals. Recrystallisation from ether–pentane gave the product (120 mg, 61%). (Found: C, 51·6; H, 5·2. $C_{12}H_{15}ORh$ requires C, 51·8; H, 5·4%.)

(Benzene)(π-cyclopentadienyl)rhodium(I) *Ditetrafluoroborate* (15).—A stirred solution of (3) (0·5 g) in CH_2Cl_2 (5 ml) was treated with a two-fold excess of Ph_3CBF_4 (1·41 g) in CH_2Cl_2 (5 ml). After 15 min the reaction was quenched with ether (20 ml) and the off-white precipitate was filtered off and washed with acetone and then ether, to yield the product (800 mg, 96%) (Found: C, 32·15; H, 2·65. $C_{11}H_{11}B_2F_8Rh$ requires C, 31·45; H, 2·6%.)

(1-Acetylcyclopentadienyl)(cyclohexa-1,3-diene)rhodium(I) (16).—Complex (3) (140 mg) in CH_2Cl_2 (2 ml) was added dropwise to a stirred solution of aluminium trichloride (1·0 g) and acetyl chloride (0·8 ml) in CH_2Cl_2 (6 ml) at 0 °C. The reaction was stirred at 0 °C for 5 min and then the solution was decanted onto ice and water (20 ml). After hydrolysis the mixture was extracted into ether (3 × 8 ml), and the combined ether extracts were washed with water, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed through a silica column (2 × 20 cm). Toluene eluted a yellow solution which on evaporation yielded unchanged complex (3) (40 mg). Ethyl acetate–toluene (1 : 2) developed an orange band which on evaportion *in vacuo* produced orange-yellow crystals of the product (80 mg, 50%) (Found: C, 54·0; H, 5·1. $C_{13}H_{15}ORh$ required C, 53·8; H, 5·15%.) An i.r. spectrum in Nujol showed ν($COCH_3$) at 1668 cm^{-1}; m.p. = 67 ± 2 °C.

(Cyclohexa-1,3-diene)(π-cyclopentadienyl)iridium(I) (6).—Cyclohexa-1,3-diene (2 ml) and Na_2IrCl_6 (1·6 g) were heated under reflux in a solution of ethanol (20 ml) and water (10 ml) for 2 h. The white precipitate (1·0 g) produced when the mixture was cooled to 0 °C was shaken with cyclopentadienidethallium(I) (1·2 g) in benzene (50 ml) for 2 h with exclusion of light. The solution was filtered through Kieselguhr and the filtrate was evaporated *in vacuo* to produce a pale yellow residue. The residue was chromatographed through silica (2 × 20 cm); toluene eluted a colourless band which on evaporation *in vacuo* yielded the product as white crystals (350 mg, 32% yield from Na_2IrCl_6) (Found: C, 39·3; H, 4·1. $C_{11}H_{13}Ir$ requires C, 39·15; H, 3·85%.)

(Cyclohexa-1,3-diene)(π-cyclopentadienyl)cobalt(I) (9).—This complex was prepared from $C_5H_5Co(CO)_2$ and cyclohexa-1,3-diene by the method of King.[9]

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