DIENE AND DIENYL COMPLEXES OF TRANSITION ELEMENTS

III *. PROTONATION OF η-CYCLOPENTADIENYL-η-DIENOL-RHODIUM AND -IRIDIUM COMPLEXES: SYNTHESIS OF CATIONIC COMPLEXES CONTAINING OPEN CHAIN PENTADIENYL LIGANDS

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Summary

The protonation of several dienol complexes of rhodium and iridium, $[M(\eta^4\text{-}R^1CH=CR^2CH=CHCHOHR^3)(\eta^5\text{-}C_5H_5)]$, (M = Rh, Ir), ($R^1$ = Ph; R^2 = H or Me; R^3 = Bu^t or Aryl) has been investigated using ^1H NMR spectroscopy. Initially the proton adds to the carbon atom of the diene system adjacent to the alcohol function to yield η^3-enyl derivatives. Deuteration studies indicate that this addition occurs stereospecifically *endo*. This reaction is followed by elimination of water to afford cationic complexes, $[M(\eta^5\text{-}R^1CHCH^2CHCHCR^3)(\eta^5\text{-}C_5H_5)]^+$, which were isolated as BF_4^- or PF_6^- salts. The open chain substituted pentadienyl ligands in the cations where R^3 = Aryl adopt an unsymmetrical structure, probably *cis syn anti*, in contrast to the corresponding pentadienyltricarbonyliron derivatives, in which the ligand is symmetrical (*cis syn, syn*).

Introduction

Apart from the well known η^5-pentadienyltricarbonyliron salts first reported by Mahler and Pettit [2], there are very few examples of the coordination of open chain η^5-pentadienyl ligands to transition elements [3]. The standard method of preparation of pentadienyltricarbonyliron salts is by protonation of dienoltricarbonyliron complexes [2,4]. In a preliminary communication, the synthesis by this method of the salts $[M(\eta\text{-}C_5H_5)(\eta^5\text{-}C_5H_6Me)]^+BF_4^-$ (M = Rh, Ir) from (η-cyclopentadienyl)(η-hexa-2,4-dien-1-ol)-rhodium and -iridium was described [5]. Extension to other dienol complexes of rhodium and iridium

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* For part II see ref. 1.

has now yielded further substituted pentadienyl salts. These reactions, however, show novel features which differ appreciably from those of the corresponding tricarbonyliron derivatives.

Results and discussion

The general method used for the preparation of the complexes [M(η^4-dienone) (η-C$_5$H$_5$)] has been described previously [6]. This involves treatment of [M-(cyclooctene)$_2$Cl]$_2$ with excess of the dienone in ether or hexane, affording [M(dienone)$_2$Cl], followed by reaction of this with thallium cyclopentadienide in methylene chloride. The desired complex is then separated from free dienone ligand by chromatography on silica gel. Analytical and spectroscopic data for new compounds of the types [M(dienone)$_2$Cl] and [M(dienone)(C$_5$H$_5$)] are listed in Tables 1, 2 and 3.

The dienol complexes were prepared by reduction of the corresponding dienone or dienol derivative. Whereas sodium borohydride in aqueous methanol smoothly reduces [M(η^4-hexa-2,4-dien-1-al)(C$_5$H$_5$)] (M = Rh, Ir) to the alcohols, it is without effect on the dienone complexes which have an aryl or tert-butyl group adjacent to the keto function. These, however, can be converted into the dienol by lithium aluminium hydride in ether/toluene. This method has been used for reducing free 1,5-diarylpenta-2,4-dien-1-ones [7]. Analytical and spectroscopic data for new compounds [M(dienol)(C$_5$H$_5$)] are given in Tables 4 and 5. The sorbyl alcohol complexes Ia, Ib have been mentioned in previous papers [5,6].

When a solution of Ia or Ib in diethyl ether is shaken with dilute aqueous tetrafluoroboric acid, the organometallic compound is extracted into the aqueous layer. After separation of this layer and concentration, addition of aqueous

TABLE 1

ANALYTICAL AND INFRARED DATA FOR THE COMPLEXES [M(η^4-R^{1}CH=CR^{2}CH=CHCOR^3)$_2$Cl]

M	R^1	R^2	R^3	Yield (%)	m.p. (°C)	Analysis (%) Found (calcd.)		ν(CO) (cm^{-1})
						C	H	
Rh	Ph	Me	Ph	94	173—174	68.2 (68.1)	5.4 (5.1)	1640
Ir	Ph	Me	Ph	93	202—204 dec.	59.7 (59.7)	4.5 (4.5)	1664 1643
Rh	Ph	H	Ar [a]	99	159—162	64.3 (64.8)	4.8 (4.8)	1647 1637
Rh	Ph	Me	Ar [a]	93	154—156	65.3 (65.7)	5.2 (5.2)	1633
Ir	Ph	Me	Ar [a]	91	175—177	58.2 (58.2)	4.6 (4.6)	1654
Rh	Ph	H	Bu^t	88	158 dec.	49.3 (48.6) [b]	5.0 (5.4) [b]	1666
Ir	Ph	H	Bu^t	95	152 dec.	55.0 (54.9)	5.5 (5.5)	1682

[a] Ar = p-MeOC$_6$H$_4$-; [b] Calcd. for 1 mol H$_2$O of crystallisation, indicated by infrared spectrum.

TABLE 2

ANALYTICAL AND SPECTROSCOPIC DATA FOR THE COMPLEXES [M(η^4-R^{1}CH=CR^{2}CH=CHCOR^3)-(η-C$_5$H$_5$)]

M	R^1	R^2	R^3	Yield (%)	m.p. (°C)	Analyses (%) Found (calc.)		ν(CO) (cm^{-1})
						C	H	
Rh	Ph	Me	Ph	58	140	66.6 (66.4)	5.2 (5.1)	1633
Ir	Ph	Me	Ph	42	133	54.6 (54.6)	4.2 (4.2)	1637
Rh	Ph	H	Ar ^{a}	81	150	64.6 (63.9)	5.1 (4.9)	1629
Rh	Ph	Me	Ar ^{a}	70	152	65.1 (64.6)	5.1 (5.2)	1646
Ir	Ph	Me	Ar ^{a}	28	164	53.9 (53.8)	4.4 (4.3)	1649
Rh	Ph	H	Bu^t	61	111—113			1680
Ir	Ph	H	Bu^t	56	118	50.9 (50.9)	4.95 (4.9)	1664

^{a} Ar = p-MeOC$_6$H$_4$-.

TABLE 3

ANALYTICAL AND SPECTROSCOPIC DATA FOR THE COMPLEXES [M(η^4-R^{1}CH=CR^{2}CH=CHCH-(OH)R^3)(η-C$_5$H$_5$)]

M	R^1	R^2	R^3	Yield (%)	m.p. (°C)	Analyses (%) Found (calcd.)		ν(OH) (cm^{-1})
						C	H	
Rh	Ph	H	Ph	38	156—157 dec	64.7 (65.3)	5.2 (5.2)	3570w 3420(br)
Ir	Ph	H	Ph	58	171—174 dec	53.7 (53.5)	4.25 (4.3)	3575w 3420(br)
Rh	Ph	Me	Ph	48	124—125	66.8 (66.0)	5.55 (5.55)	3600w 3330(br)
Ir	Ph	Me	Ph	71	153—154	54.4 (54.4)	4.6 (4.6)	3590vw 3340(br)
Rh	Ph	H	Ar ^{a}	62	149—151 dec	63.9 (63.6)	5.4 (5.35)	3560w 3450(br)
Rh	Ph	Me	Ar ^{a}	63	124	64.35 (64.3)	5.8 (5.6)	3555s
Ir	Ph	Me	Ar ^{a}	50	145—146	54.7 (53.6)	5.1 (4.7)	3550s 3420(br)
Rh	Ph	H	Bu^t	78	136—137 dec	62.35 (62.5)	6.6 (6.6)	3575m
Ir	Ph	H	Bu^t	65	155	50.7 (50.7)	5.3 (5.3)	3565m
Rh	Me	H	H	97	57—58	49.4 (49.6)	5.5 (5.7)	3420(br)
Ir	Me	H	H	85	85—86	37.3 (37.2)	4.2 (4.25)	3420(br)
Rh	Me	H	Ph	62	102—104	59.8 (59.7)	5.6 (5.6)	3560w 3525w 3410(br)

^{a} Ar = p-MeOC$_6$H$_4$.

TABLE 4

HYDROGEN-1 NMR SPECTROSCOPIC DATA FOR THE COMPLEXES [M(R¹CH=CR²CH=CHCOR⁵)-(C₅H₅)] AND [M(R¹CH=CR²CH=CHCH(OH)R⁵)(C₅H₅)] [a]

M	Chemical shift (ppm)								
	R¹	R²	R³	R¹	H¹·	R²	H³	H⁴	H⁵
Rh	Ph	Me	Ph	7.24m	1.67s	2.37s	5.91d	2.42dd J 2.0 [c]	
Ir	Ph	Me	Ph	7.20m	2.11s	2.40s	5.86d	2.48d	
Rh	Ph	H	Ar [b]	7.3—7.0m	2.53dd J 2.0	5.52dd	5.99dd	2.68dd J 1.0	
Rh	Ph	Me	Ar	7.25m	2.46d J 2.0	2.36s	5.89d	~2.4	
Ir	Ph	Me	Ar	7.21m	2.08s	2.39s	5.84d	2.45d	
Rh	Ph	H	Buᵗ	7.16m	1.95dd J 1.8	5.73dd	5.47dd	2.44dd J 1.8	
Ir	Ph	H	Buᵗ	7.14m	1.91d	5.65dd	5.37dd	2.03d	
Rh	Ph	H	Ph	7.17m	1.97dd J 1.8	5.28dd	~5.02	1.65td J 2.5	
Ir	Ph	H	Ph	7.14m	1.78d	5.14dd	~4.98	1.14dd	4.15dd
Rh	Ph	Me	Ph	7.2m	1.80s	2.26s	4.94d	1.50m	4.30dd
Ir	Ph	Me	Ph	7.16m	1.54s	2.30s	4.85d	1.04dd	4.16dd
Rh	Ph	H	Ar	7.17m	2.18dd J 2.2	5.29dd	5.02dd	1.66td J 2.4	4.24dd
Rh	Ph	Me	Ar	7.20m	1.77d J 0.9	2.25s	4.89d	1.53td J 2.6	4.30dd
Ir	Ph	Me	Ar	7.16s	1.53s	2.29s	4.77d	1.02m	4.11dd
Rh	Ph	H	Buᵗ	7.22m	2.18dd J 2.0	5.22dd	5.0dd	1.53m J 2.0	2.71dd
Ir	Ph	H	Buᵗ	7.14m	1.74d	4.89dd	5.08dd	0.95m	2.67dd
Rh	Me	H	H	1.38s	1.4m	4.73m	4.73m	1.4m	3.54d
Ir	Me	H	H	1.42d	0.8m	4.73m	4.73m	0.8m	3.61d
Rh	Me	H	Ph	1.37d	~1.4m	4.93—4.69m		~1.4m	4.22dd

[a] In CDCl₃ relative to tetramethylsilane, $\delta = 0$ ppm. For numbering see Scheme 2. [b] Ar = p-methoxyphenyl
[c] J(Rh—C—H).

ammonium hexafluorophosphate afforded the salts IIa and IIb. The success of this experimental procedure must indicate that IIa and IIb are much less susceptible to addition of nucleophiles than the corresponding methylpentadienyltricarbonyliron salts, which are rapidly attacked by water [8]. When a few drops of trifluoroacetic acid are added to a solution of either Ia or Ib in CDCl₃ at room temperature, the proton NMR spectrum shows immediate formation of the cation. The NMR data also clearly indicate that the pentadienyl group adopts the cis structure present in the tricarbonyliron derivative.

R⁵	OH	C₅H₅	Coupling constants (Hz)				
			H¹H¹	H²H³	H³H⁴	H⁴H⁵	H⁵H⁶
8.10m 7.50m		4.90d J 0.9			7.3		
8.07m 7.50m		4.93s			5.9		
8.08d 6.94d 3.87s(OMe)		4.81d J 0.9	10	4	7.5		
8.08d 6.93d 3.87s(OMe)		4.89d J 1.2			7.5		
8.07d 6.90d 3.86s(OMe)		4.92s			5.9		
1.24s		4.83d J 1.0	7.5	5.0	8.0		
1.22s		4.87s	5.9	3.8	6.4		
7.4—7.1m	1.92d	5.06d J 0.6	8.0	4.6	8.0	7.6	3.2
7.4—7.2m	1.90d	5.06s	6.2	3.8	6.0	8.0	3.0
7.4m	1.96d	5.18d J 0.9			7.0	7.9	2.6
7.4m	1.94d	5.18s			5.9	8.2	2.4
7.37d 6.87d 3.80s(OMe)	1.88d	5.07d J 0.9	8.0	4.4	7.0	7.8	3.0
7.37d 6.88d 3.79s(OMe)	1.94d	5.17d J 0.9			7.0	7.9	2.6
7.36s 6.88d 3.79s(OMe)	1.90d	5.17s			5.6	8.2	2.6
0.97s	1.47d	5.08d J 0.9	8.5	4.0		9.5	1.8
0.97s	1.41d	5.06s	6.7	3.8	6.2	9.4	1.8
		5.18d J 0.9				5.9	
		5.35s				7.0	
7.4—7.2m	1.84d	5.26d J 0.9				7.9	3.0

(Ia, M = Rh;
  Ib, M = Ir)   (IIa, M = Rh;
  IIb, M = Ir)

TABLE 5

HYDROGEN-1 NMR SPECTRA OF PENTADIENYL SALTS [M^I($PhCH^1CH^2CH^3CH^4CH^5Bu^t$)]X

Chemical shifts [a] (ppm)

M^I	X	Ph	H^1	H^2	H^3	H^4	H^5	Bu^t	C_5H_5	Coupling constants (Hz)			
										H^1H^2	H^2H^3	H^3H^4	H^4H^5
RhC_5H_5	BF_4	7.6m	4.40d	6.63q	6.05m	5.80dd	3.71d	1.23s	5.68d [b]	13.3	6.8	5	12.6
IrC_5H_5	PF_6	7.42m	3.92d	6.40dd	6.80t	5.84dd	3.03d	1.21s	5.77s	9.4	6.2	5.9	10.3
$Fe(CO)_3$ [c]	BF_4	7.56m	4.38d	6.74dd	7.06t	6.06dd	4.05d	1.28s	—	7.5	7.5	7.5	13.0

[a] In CD_3NO_2, relative to TMS (δ = 0 ppm). [b] $J(^{103}Rh-^1H)$, 0.9 Hz. [c] Ref. 18.

Reduction of dienone complexes $[Fe(\eta^4\text{-}RCH=CHCH=CHCOR')(CO)_3]$ can lead to the formation of two diastereomeric alcohols [9,10], although the ψ-endo (RS) isomer [11] has been found to predominate. We also have obtained mixtures of diastereomers $[M(\eta^4\text{-}PhCH=CHCH=CHCH(OH)CH_3)(\eta\text{-}C_5H_5)]$ (M = Rh, Ir) from the sodium borohydride reduction of the corresponding dienones [12]. To avoid this complication in the protonation studies, dienones having bulky substituents (aryl or tert-butyl) adjacent to the keto group were chosen. In these cases the reduction was found to proceed stereospecifically to only one diastereomer, assumed to be that having the ψ-endo configuration.

The protonation of $[Rh(PhCH=CHCH=CHCH(OH)Bu^t)(C_5H_5)]$ (IIa) was followed by ^1H NMR spectroscopy. When trifluoroacetic acid is added to a solution of IIIa in $CDCl_3$ at $-60°C$, the yellow solution turns deep red. The red colour persists on warming to room temperature. The ^1H NMR spectrum of the product was assigned with the aid of double resonance experiments, and is consistent with protonation at carbon (IVa) (See Table 6 and Scheme 1). Proto-


(IIIa, M = Rh;   (IVa, M = Rh;   (Va, M = Rh;
IIIb, M = Ir)   IVb, M = Ir)   Vb, M = Ir)
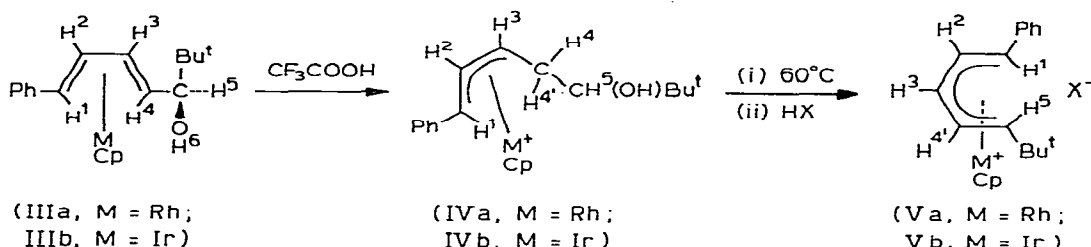
nation at carbon rather than at oxygen has also been found to occur with the complexes $[M(\eta^4\text{-}PhCH=CHCH=CHCOPh)(C_5H_5)]$ [1]. No signals to high field of tetramethylsilane were observed, indicating that the complex is not a metal hydride, and probably also eliminating any significant interaction between the metal centre and C^4 through the added hydrogen atom, such as has been found by Ittel and his coworkers in the protonation of dienetris(phosphite)iron complexes [13]. The value of the coupling constant $J(H^2H^3) \sim 7$ Hz shows that these two protons are cis, so that the $CH_2CH(OH)Bu^t$ substituent is anti.

When CF_3COOD is added to IIIa at $-60°C$, the NMR spectrum, run immediately after warming to ambient temperature shows a mixture of both protonated and deuterated forms of IVa. The former gradually disappears to be replaced by the latter. The two protons attached to C^4 give rise to multiplet signals centred at 2.12 ppm and 1.20 ppm in the protonated complex, while in the deuterated compound the higher field resonance is absent, as are its associated couplings.

The C-protonated allylic cation IVa is sufficiently stable to allow its isolation as the hexafluorophosphate. Addition of $HPF_6 \cdot (C_2H_5)_2O$ to a solution of IIIa in diethyl ether at $-40°C$, followed by gradual warming to room temperature gives deep red crystals. Recrystallisation from acetone/ether affords a solvate with 1 mol acetone of crystallisation, while use of acetonitrile/ether gives the unsolvated salt. The infrared spectra of both solvated and unsolvated forms show a strong band at 3485 cm^{-1}, assigned to O—H stretching. The presence of this band in both spectra indicates that it is not the overtone of the carbonyl stretching band of acetone. Weak interaction between the hydroxyl group with the rhodium atom in the acetone solvate might perhaps be indicated by the ^1H

SCHEME 1

(a) Possible mechanism for formation of pentadienyl cations by deuteration of alcohols III. (b) Favoured conformation about the C^4—C^5 bond in IV, assuming (i) *endo* addition of D^+ (consistent with NMR) and (ii) *exo*-addition. On *trans*-β-elimination of water from IV, deuterium on C^4 is retained in case (i), as observed when M = Ir.

(a)

(b)
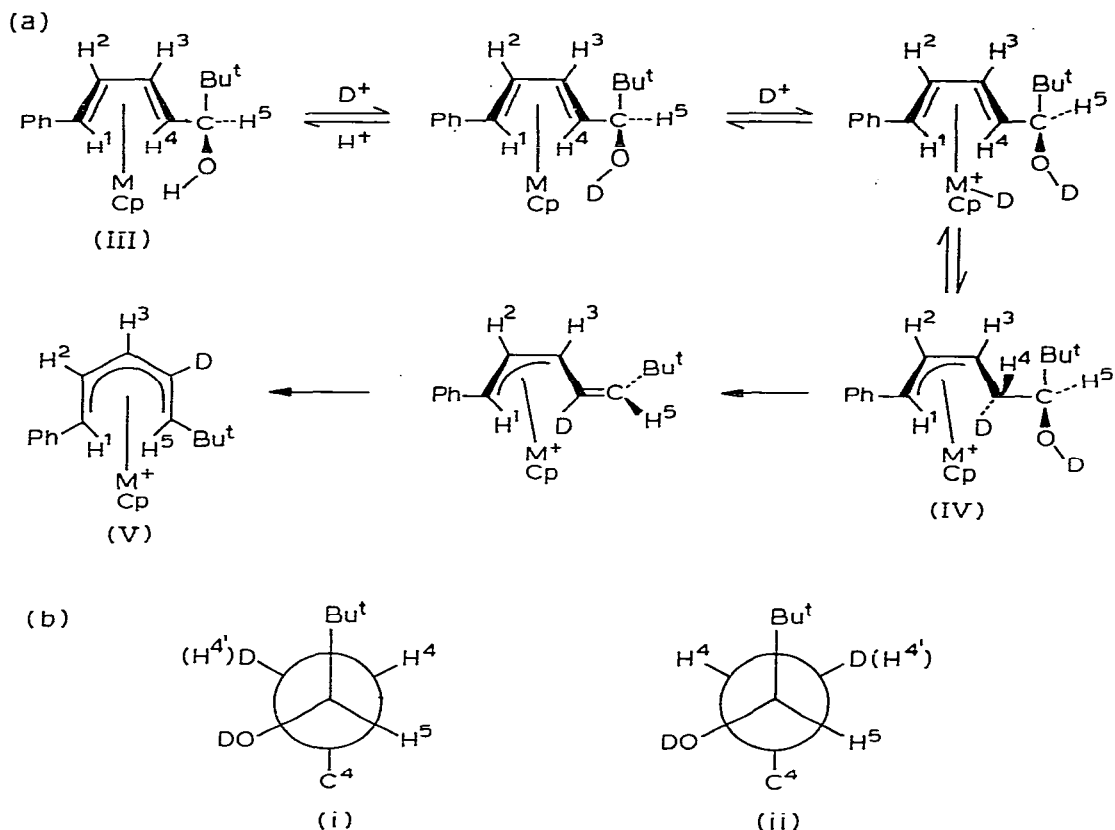
NMR spectrum of this complex in CD_3NO_2. This spectrum is identical with that of IVa in $CF_3COOH/CDCl_3$ or of the unsolvated species obtained by crystallisation from acetonitrile, except for an additional band at 5.02 ppm (t, J 2.5 Hz) and the change of the H^5 resonance from a doublet of doublets to a doublet of triplets (additional J 2.5 Hz). The band at 5.02 ppm is assigned to the OH proton. which is not observed in the protonation experiments, presumably on account of exchange with CF_3COOH. Its appearance as a triplet, rather than as a doublet is puzzling but could possibly be explained by coupling not only to H^5 (J 2.5 Hz) but also to rhodium-103 (J 2.5 Hz). It is not clear whether acetone is coordinated to rhodium in the crystalline solvate. The more strongly donating ligand, acetonitrile, was not taken up when the hexafluorophosphate was recrystallised from it. The CO stretching frequency of acetone in the solvate is 1684 cm^{-1} (Nujol mull) which is somewhat higher than in typical acetone complexes [14], but lower than in acetone itself.

When IVa is heated with CF_3COOH to 70°C for several hours, further reaction occurs which can be monitored by NMR. On adding the reaction mixture to a solution of tetrafluoroboric acid in ether, yellow crystals of the salt Va were

TABLE 6

HYDROGEN-1 NMR SPECTRA OF THE ALLYLIC COMPLEXES $[M(R^1CH^1CR^2CH^3CH^4H^{4'}CH^4(OH)R^5)(C_5H_5)]^+$

M	\multicolumn{3}{c}{}	Chemical shifts [a]									Coupling Constants (Hz)					
	R^1	R^2	R^5	R^1	H^1	R^2	H^3	H^4	$H^{4'}$	H^5	R^3	C_5H_5	H_{12}	H_{23}	H_{34}	H_{45}	$H_{4'5}$	$H_{44'}$
Rh	Ph	H	But	7.55m 7.37m	4.7d	6.15ddd J 2.6 [b]	6.48q	2.03m	1.27m	4.02dd	0.89d	5.35d J 0.6	12.0	7.0	7.5	12.3	3.5	~14
Ir	Ph	H	But	7.31m	4.20d	6.58dd	5.91td	1.96qd	1.38m	3.81dd	0.89s	5.30s	10.8	0.5	8.5	12.6	4.3	13.0
Rh	Ph	H	Ph [c]	7.35m	4.88d	6.03ddd J 2.5	6.32q	2.24m	1.36m	5.03dd	7.35m	5.25s	11.7	7.5	~7	?	?	?
Rh	Ph	Me	Ph	7.40m	5.03s	2.17d J 2.0	6.20t	2.20m	1.37m	5.00dd	7.63m 7.26m	5.34d J 0.6	—	—	7.8	12.3	3.5	14.2
Rh	Me	H	Ph	2.13d	4.11 sextet	5.20ddd J 2.6	6.06q	2.15m	1.24m	4.93dd	7.27m 7.05m	5.42d J 0.6	12.0	7.0	7.9	12.2	3.5	13.0

[a] In CDCl$_3$ relative to TMS (δ = 0 ppm). [b] J refers to $J(^{103}Rh–C–^1H)$. [c] At –30°C.

isolated. The ^{1}H NMR spectrum of Va, in particular the observation of two high field doublets at 4.40 and 3.71 ppm assigned to H^1 and H^5, is consistent with the *cis* structure of the pentadienyl ligand (Table 5).
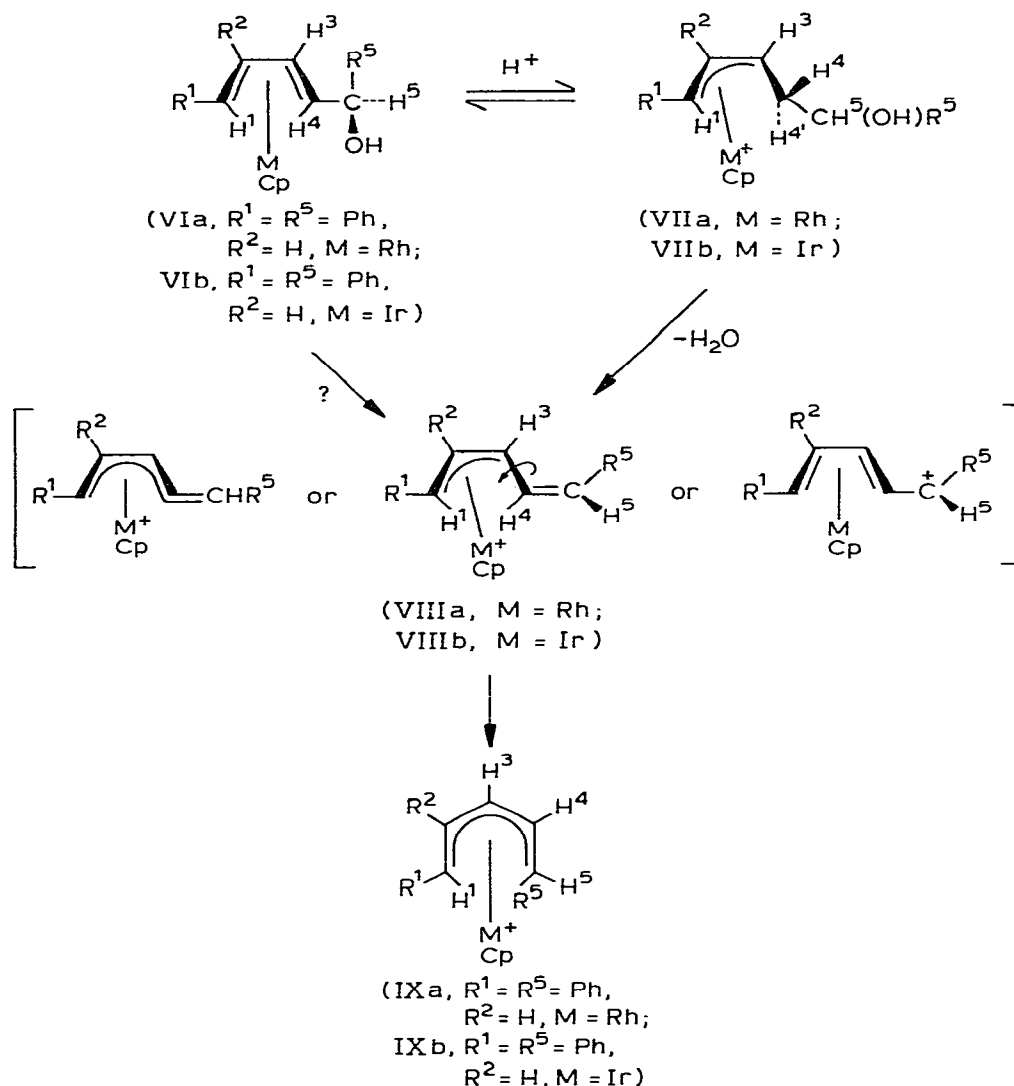
The iridium complex IIIb behaves in a similar manner to its rhodium analogue on protonation, except that both stages, which yield IVb and Vb, respectively, occur more rapidly (Scheme 1). For this reason the intermediate allylic cation was not isolated. The deuteration experiments here were particularly informative. Exchange of H for D to give IVb (H$^{4'}$ = D) was effectively complete after mixing IIIb and CF$_3$COOD in CDCl$_3$ at —60°C and warming to room temperature. In the final product, the pentadienyl cation Vb, H^4 was essentially replaced by deuterium, e.g. the resonance from H^5 (3.03 ppm) appeared as a singlet. In the case of the rhodium complex this exchange was also observed but was much less complete. The deuteration experiments shed light on the mechanism and stereochemistry of the reactions. First, the initial formation of the protonated form of IVb on addition of CF$_3$COOD could indicate intramolecular transfer of H from the OH group to C^4, perhaps via the metal atom, or perhaps a large kinetic isotope effect for transfer of H from the acid [15], by a two step mechanism to C^1. Secondly, the absence of only one of the two high field signals (H^4, H$^{4'}$) in the deuterated complex IVb shows that the addition is stereospecific. Protonation of coordinated organic ligands is usually *endo* [16], although instances of *exo*-addition have also been reported [17]. Our results are consistent with exclusive *endo* protonation (Scheme 1). The precursor alcohols (IIIa, IIIb) are assumed to have the ψ-*endo* configuration, by analogy with tricarbonyliron complexes [9]. In IVa or IVb H^4 and H$^{4'}$ can be distinguished by NMR by considering the favoured conformation about the C^5—C^4 bond. The vicinal coupling constants J(H^{4}H^5) and J(H$^{4'}$H^5) depend on the dihedral angles between the planes containing the relevant hydrogen atoms. In the *trans* orientation J(HH) is ~10—13 Hz, while in the *cis*, it is ~2—5 Hz [18]. We observe coupling constants of 3.5 Hz and 12.3 Hz for the rhodium compound IVa and 4.3 Hz and 12.6 Hz for the iridium compound IVb. In each case it is the larger (*trans*) coupling which disappears on deuteration. The Scheme shows that this is consistent with *endo* addition of D to C^4.

In the iridium complex this deuterium atom is selectively retained during the final step in which the pentadienyl complex is formed. This observation is consistent with *trans* β-elimination of water. In the case of rhodium, however, the step seems to be rather unselective, suggesting that additional mechanisms may be operating. Protonation of IIIa at oxygen, followed by elimination of water could be one of these.

The behaviour of the rhodium and iridium complexes IIIa and IIIb on protonation contrasts sharply with that of the corresponding tricarbonyliron complex, which is rapidly converted at room temperature by CF$_3$COOH into the 1-phenyl-5-tert-butylpentadienyltricarbonyliron cation without evidence of intermediate C-protonation [19]. Dienetricarbonyliron complexes, however, which do not possess the alcohol function are converted into cationic η^3-enyl derivatives by acid [16]. Ittel and his coworkers have recently discussed the protonation of dienetris(phosphite)iron complexes [13]. In the protonated complex a bonding interaction between the iron centre and a hydrogen atom attached to the carbon atom adjacent to the allylic ligand has been detected

SCHEME 2

Suggested mechanism for the formation of η^5-diarylpentadienyl(η-cyclopentadienyl) cations of rhodium and iridium.

(VIa, $R^1 = R^5 = Ph$, $R^2 = H$, M = Rh;
VIb, $R^1 = R^5 = Ph$, $R^2 = H$, M = Ir)

(VIIa, M = Rh ; VIIb, M = Ir)

$-H_2O$

(VIIIa, M = Rh ; VIIIb, M = Ir)

(IXa, $R^1 = R^5 = Ph$, $R^2 = H$, M = Rh; IXb, $R^1 = R^5 = Ph$, $R^2 = H$, M = Ir)

by NMR spectroscopy. This interaction, which permits the iron atom to achieve an 18-electron configuration, is characterised by shifts to high field of tetramethylsilane and by evidence of exchange processes of *endo* protons adjacent to the alkenyl group in cycloalkenyl complexes. No such unusual NMR parameters are observed in our present work. It is well known that 16-electron complexes of rhodium(I) and iridium (I) are more favoured than those of iron(II). The 18-electron configuration of the metal in our η^3-allylic intermediates IVa and IVb, however, may still be achieved, as mentioned above, by coordination of the hydroxy group or, in the presence of CF_3COOH, by formation of a covalent trifluoroacetate.

TABLE 7

ANALYTICAL DATA FOR THE PENTADIENYL SALTS $[M(R^1CHCR^2CHCHCR^5)(C_5H_5)]X$

M	R^1	R^2	R^5	X	Colour	m.p. (°C)	Analyses (%) Found (calcd.)		Yield (%)
							C	H	
Ir	Me	H	H	PF_6^-	White	140 dec.	28.3(27.3)	2.7(2.8)	95
Rh	Ph	H	Bu^t	BF_4^-	Orange	211–213 dec.	51.0(52.9)	4.9(5.3)	43
Ir	Ph	H	Bu^t	PF_6^-	White	164–166 dec.	38.6(39.9)	3.9(4.0)	66
Rh	Ph	H	Ph	BF_4^-	Orange	160 dec.	55.7(55.7)	4.25(4.25)	76
Ir	Ph	H	Ph	BF_4^-	White	145 dec.	46.9(46.9)	3.6(3.6)	73
Rh	Ph	Me	Ph	BF_4^-	Orange	175–176	56.6(56.6)	4.5(4.55)	78
Ir	Ph	Me	Ph	BF_4^-	White	202–204 dec.	47.8(47.8)	3.8(3.85)	76
Rh	Ph	H	Ar	BF_4^-	Orange	158 dec.	53.4(54.8)	4.3(4.4)	71
Ir	Ph	Me	Ar	BF_4^-	Orange	164	55.3(55.6)	4.9(4.7)	68
Rh	Me	H	Ph	PF_6^-	Orange	141–142	43.0(43.4)	4.0(3.9)	77

The protonation of several dienol complexes which possess an aryl substituent adjacent to the alcohol function has also been studied. These reactions also show evidence of initial C-protonation, followed by formation of a pentadienyl complex by elimination of water (Scheme 2). The C-protonated rhodium complexes are more stable to further reaction than the corresponding iridium ones. Müller, for example, has also noted the greater preference of rhodium(I) for the 16-electron configuration over iridium(I) [20]. The ^{1}H NMR spectra of some of these species are given in Table 6. As with compound IIIa, addition of CF$_3$COOD to VIa at —60°C followed by warming to —30°C gives initially the protonated product; subsequently the higher field proton resonating at 1.36 ppm is exchanged for deuterium, but at the same time the further reaction, which affords the pentadienyl complex, occurs. In general the C-protonated iridium complexes did not persist long enough to characterise by NMR. In some cases there was evidence of additional unidentified products on protonation below 0°C. On standing at room temperature or on gentle warming, water eliminated to yield substituted pentadienyl cations. In several cases (Table 7) these have been isolated as tetrafluoroborates, and characterised by elemental analysis. Their ^{1}H NMR spectra, however, are inconsistent with the *cis syn, syn* pentadienyl structure adopted by tricarbonyliron complexes. The *trans* ion structure VIIIa, VIIIb is one possibility, but this is considered unlikely on the basis of NMR results. In the iron systems, *trans* ions have been postulated as intermediates in the reactions of *cis*-pentadienyltricarbonyl iron cations with nucleophiles [22] (although this interpretation has been questioned [23]), and in the hydrolysis of esters of dienoltricarbonyliron complexes [4]. We suggest, however, that our cations possess the unsymmetrical *cis syn, anti* structure IXa, IXb which is derived from VIIIa, VIIIb by rotation about the C^3—C^4 bond. In the case of the tricarbonyliron complexes, such cations have been observed directly normally only at low temperatures, and they rearrange rapidly to *cis, syn, syn* cations [21]. The salts described here, however, are apparently indefinitely stable at room temperature; their rearrangement to the symmetrical *cis, syn, syn* ions has not yet been observed.

Detailed interpretation of the 90 MHz ^{1}H NMR spectra of the cations (Table 8) is hampered by the proximity of the low field resonances, which have been assigned to H^2, H^3 and H^5, to those of the aryl protons. Assignments have been aided in several cases, however, by double resonance experiments, H^1 is characterised by a signal at high field of the other resonances, and H^4 appears near the cyclopentadienyl signal. A complete analysis of the spectra of IXa and IXb was made at 400 MHz, including detailed double resonance measurements. The low field position of H^3 is characteristic of *cis*-pentadienyl complexes. Moreover the coupling constants are consistent with a *trans* coupling between H^1 and H^2, and *cis* couplings between H^2 and H^3, and H^3 and H^4.

The *anti*-phenyl group which is a feature of the proposed structure shows interesting NMR parameters. The two sides of the ring are magnetically inequivalent owing to the presence of a chiral centre at C^5. The *ortho* and *meta* protons on either side of the ring have very different chemical shifts. For example, in the spectrum of IXa, the *ortho* protons give rise to doublets at 7.79 and 6.42 ppm while the *meta* protons resonate at 7.63 and 7.42 ppm.

The ^{13}C NMR spectra of two complexes, VIIIa and VIIIb, were also found

TABLE 8

HYDROGEN-1 NMR SPECTRA OF PENTADIENYL SALTS $[M(R^1CH^1CR^2CH^3CH^4CH^5R^5)(C_5H_5)]^+BF_4^-$

M	R^1	R^2	R^3	Chemical shifts [a]								Coupling constants (Hz)			
				R^1	H^1	R^2	H^3	H^4	H^5	R^5	C_5H_5	H_{12}	H_{23}	H_{34}	H_{45}
Rh [f] (IXa)	Ph	H	Ph	7.28m 7.00m	2.84d	6.48ddd J 0.09	7.18t	5.68ddd J 1.8 [d]	6.65dd J 1.5	7.79d, 7.63m 7.44m, 7.15m, 6.42d	5.69d J 0.9 [d]	10.8	6.5	6.8	8.5
Ir [f] (IXb)	Ph	H	Ph	7.28m 6.95m	2.73d	6.51dd	7.38t	5.75dd	6.67d	7.73d, 7.61m 7.42m, 7.15t, 6.59d	5.80s	9.4	6.5	6.5	8.2
Rh	Ph	Me	Ph	7.29m	2.65s [b]	2.65s [b]	7.12d J 2.0	5.48t	6.58dd	7.54m 6.80m 6.5d	5.80d	—	—	7.0	8
Ir	Ph	Me	Ph	7.26m	2.62s	2.74s	7.31d	5.61dd	6.63d	7.6—7.2m 6.8—6.5m	5.96s	—	—	6.6	8.5
Rh	Ph	H	Ar [e]	7.29m	2.90s	c	7.08d	5.54t	c	7.7m, 7.1m, 6.7—6.3m	5.66d	10.8			
Rh	Ph	Me	Ar [e]	7.29m	2.64s [b]	2.64s [b]	7.07d [c]	5.45t	c	7.65m, 7.1m, 6.9—6.3m	5.77d J 0.9	—		8	8
Rh	Me	H	Ph	1.65d	1.67m	5.80dd	6.92d	5.57td	c	7.5—7.0m 6.4—6.2m	5.95d	10.6	6.7	8	7

[a] In CD_3NO_2 relative to TMS (δ = 0 ppm), 90 MHz. [b] Peaks resolved in $CDCl_3$ CF_3COOH + precursor alcohol. [c] Assignment uncertain. [d] J refers to $J(^{103}Rh-C-^1H)$. [e] Ar = p-methoxyphenyl. [f] 400 MHz, at Queen Mary College, London. ^{13}C NMR spectra (ppm from TMS, $J(Rh-C)$): Complex IXa: 104.0, 4.0 Hz (C^3); 94.3, 6.6 Hz (C^2); 89.6, 10.6 Hz (C^1), 86.4, 6.6 Hz (C^4); 76.1, 8.6 Hz (C^5) 93.2, 5.3 Hz (C_5H_5). Complex IXb: 100.3 (C^3); 84.6 (C^2); 78.4 (C^4); 72.7 (C^1); 56.8 (C^5); 87.8 (C_5H_5).

to be inconsistent with a symmetrical *cis syn, syn* structure for the 1,5-diphenyl-pentadienyl group (Footnote to Table 8). The resonances arising from C^1 and C^4 were identified by selective irradiation at the corresponding proton frequencies.

Experimental

Reactions were carried out under dry nitrogen. Microanalyses were by Butterworth Laboratories Ltd. Infrared spectra were determined by Nujol mulls on a Perkin-Elmer 257 spectrometer and were calibrated with polystyrene film. Hydrogen-1 and carbon-13 NMR spectra were recorded using a Bruker 90 MHz instrument at King's College, London. Some routine NMR measurements were made using a Varian EM 360 spectrometer at 60 MHz.

η-Cyclopentadienyl-η-hexa-2,4-dien-1-oliridium

η-Cyclopentadienyl-η-hexa-2,4-dien-1-aliridium [6] (1.10 g) in methanol (30 cm³) was treated with ice cold sodium borohydride (0.80 g) in water (10 cm³). The reaction mixture was stirred for 24 h. Water (40 cm³) was added and the product extracted with ether. The ether extracts were washed with water and dried (K_2CO_3). Removal of solvent followed by crystallisation from hexane gave the product as white flaky crystals (0.93 g, 85%), m.p. 85—86°C.

The rhodium complex was prepared similarly. Yield 90%, m.p. 57—58°C.

η-Cyclopentadienyl-η-1-phenylhexa-2,4-dien-1-olrhodium

η-Cyclopentadienyl-η-hexa-2,4-dien-1-alrhodium (0.50 g) in ether (10 cm³) was added dropwise with stirring to an ice-cold solution of phenyl magnesium bromide [from Mg (0.1 g) and bromobenzene (0.55 cm³)] in ether (10 cm³). A yellow precipitate was formed. After 1 h at 0°C, water (1 cm³) was added, and then toluene (3 cm³) and the mixture filtered through anhydrous potassium carbonate. The filtrate was passed through a silica gel column (10 cm × 1 cm) made up in 1% pyridine in ether. The eluate was evaporated to ca. 4 cm³, pentane (40 cm³) was added, and the mixture allowed to crystallise at —5°C. Yield (0.40 g, 62%), m.p. 103—104°C.

Preparation of dienone complexes of rhodium and iridium

The general method for the preparation of the dienone complexes from chlorobis(cyclooctene)-rhodium or -iridium, followed by treatment of the resulting complex [M(dienone)₂Cl] with TlC₅H₅ has been described previously [6]. Characterising data for these intermediate compounds are given in Tables 1 and 2.

Reduction of dienone complexes

A typical reaction is described.

(η-Cyclopentadienyl)(η-1,5-diphenylpenta-2,4-dien-1-one)iridium (0.19 g) in ether/toluene (1/1) (15 cm³) was cooled to 0°C and lithium aluminium hydride (30 mg) added. The mixture was stirred for 10 min, but the yellow colour of the ketone still remained. More LiAlH₄ (~20 mg) was added, and

the solution soon became colourless. Excess hydride was quenched by addition of ethyl acetate (2 cm³), and then with methanol (2 cm³). The mixture was filtered through anhydrous K_2CO_3 and the filtrate evaporated to dryness. Crystallisation of the residue from toluene/hexane gave white crystals (0.11 g, 58%), m.p. 172—174°C, dec.

(η-Cyclopentadienyl)(η-1-t-butyl-5-phenylpenta-2,4-dien-1-ol)rhodium (IIIa)

The ketone complex (0.30 g) was dissolved in ether, and lithium aluminium hydride (~50 mg) added in three portions over 20 min. The excess hydride was destroyed with ethyl acetate (1 cm³) followed by propan-2-ol (1 cm³). The reaction mixture was filtered through Florisil, which had first been deactivated with 1% pyridine in ether. The filtrate was evaporated to dryness leaving a brown oil, which was taken up in ether and passed through a silica column (10 cm X 1 cm) made up in 1% pyridine in ether. A yellow band was eluted with the same solvent mixture. Evaporation, addition of pentane and cooling to —5°C afforded yellow-orange crystals (0.234 g, 78%) m.p. 136—137°C, dec. Yields from these lithium aluminium hydride reductions were variable. They were usually in the range 30—75%.

(η-Cyclopentadienyl)(1-3-η-1-phenyl-5-hydroxy-6,6-dimethylheptenyl)-rhodium hexafluorophosphate

Compound IIIa (110 mg) in dry ether (50 cm³) was cooled to —40°C, hexa-fluorophosphoric acid diethyl ethereate (0.2 cm³) added, and the mixture stirred at —40°C for 30 min. It was then allowed to warm up to 10°C over 30 min. The red precipitate was filtered off, washed with ether (it became sticky), dissolved in acetonitrile and filtered. Ether was added to the filtrate, which was cooled to —5°C overnight, Deep red crystals (88 mg, 59%) separated, m.p. 117—120°C, Found: C, 45.0; H, 4.8; N, <0.2. $C_{20}H_{26}F_6OPRh$ calcd.: C, 45.3; H, 4.9%.

A similar preparation, crystallised from acetone/ether, gave the acetone solvate. (84 mg, 50%) m.p. 114—116°C, Found: C, 46.6; H, 5.3; F, 19.0. $C_{23}H_{32}F_6O_2PRh$ calcd.: C, 46.95; H, 5.5; F, 19.4%.

(η-Cyclopentadienyl)(1-5-η-1-phenyl-5-tert-butylpentadienyl)rhodium tetra-fluoroborate (Va)

The alcohol complex IIIa (150 mg) was dissolved in $CDCl_3$ in an NMR tube, cooled to —78°C, and trifluoroacetic acid (0.1 cm³) added. The tube was allowed to warm to room temperature and was sealed. The tube and contents were heated to 70°C for 12 h when the initially formed compound IVa had disappeared and was replaced by the product. The mixture was added to tetra-fluoroboric acid (40% aqueous solution) (0.5 cm³) in ether (50 cm³). The orange precipitate was filtered, washed with ether and recrystallised from nitromethane/ether. Yield 80 mg (45%), m.p. 211—213°C, decomp.

Preparation of (η-cyclopentadienyl)(arylpentadienyl)rhodium and iridium tetrafluoroborates

A typical procedure is described.

Compound VIa (82 mg) was dissolved in $CDCl_3$ in an NMR tube and cooled

to —60°C. Trifluoroacetic acid (0.1 cm³) was added and the sample allowed to warm up to ambient temperature. The ¹H NMR spectrum was recorded from time to time. After three days, no further change in the spectrum occurred. The solution was added to tetrafluoroboric acid (40% aqueous) (0.4 cm³) in diethyl ether (40 cm³). The resulting yellow precipitate was filtered off, dissolved in nitromethane, filtered and reprecipitated with ether. Yield 78 mg (78%), m.p. 175—176°C dec.

Acknowledgements

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