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A HYDROGEN-1 NUCLEAR MAGNETIC RESONANCE, MASS SPECTRAL AND EXTENDED HÜCKEL STUDY OF SOME OLEFIN COMPLEXES OF RHODIUM(I) AND IRIDIUM(I) AND THE CRYSTAL AND MOLECULAR STRUCTURE OF η^4-2,4-DIMETHYLPENTA-1,4-DIENE-(η^5-FORMYLCYCLOPENTADIENYL)RHODIUM(I)

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Summary

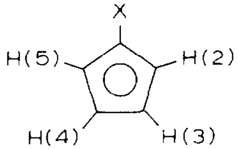
A ^{1}H NMR study of monosubstituted η-cyclopentadienyl-rhodium(I) complexes of type LLRh(C_5H_4X) and -iridium(I) complexes of type $L_2Ir(C_5H_4X)$ (L = ethene, LL = 1,3- or 1,5-diolefin; X = $C(C_6H_5)_3$, CHO, or $COOCH_3$) has been carried out. For complexes of both metals in which the neutral ligand is ethene or a non-conjugated diolefin the NMR spectra of the cyclopentadienyl protons are unusual in that H(2), H(5) resonate to high field either at room temperature or below.

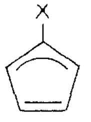
The corresponding NMR spectra for the cyclopentadienyl ring protons of complexes where the neutral ligand is a conjugated diene are, with one exception, normal.

A single crystal X-ray structural analysis of (η^4-2,4-dimethylpenta-1,4-diene)(η^5-formylcyclopentadienyl)rhodium(I) (which exhibits an abnormal ^{1}H NMR spectrum) reveals substantial localisation of electron density in the C(3)–C(4) Cp ring bond (1.283(33) Å) which may be consistent with a contribution from an 'allyl–ene' rotamer to the ring–metal bonding scheme. An extended Hückel calculation with self consistent charge iteration was performed on this complex.

The results predict a greater Mulliken overlap population for the C(3)–C(4) bond in the cyclopentadienyl ring and show that the localisation is dependent on both the Cp ring substituent and the nature of the diolefin. The mass spectral fragmentation patterns of some representative diene complexes of iridium(I) and rhodium(I) are presented.

Introduction





A previous ^1H and ^{13}C NMR study of some $(\eta^5\text{-}C_5H_4X)RhL_2$ and $(\eta^5\text{-}C_5H_4X)$-RhLL systems (L = CO or C_2H_4, LL = 1,3-,1,4-, or 1,5-diene; X = CN, $CO_2C_2H_5$, CO_2CH_3, $CO_2C_3H_7$, $COCO_2C_2H_5$ or CHO) [1] has indicated that assignments made for the H(2),H(5) and H(3),H(4) ring protons and the behaviour of these resonances with variation in temperature may be indicative of a significant contribution from an η^3-allyl-ene structure to the overall ring–metal bonding scheme. The expected diamagnetic anisotropic effect of substituent group X should cause H(2),H(5) to resonate to low field of H(3),H(4) in the ^1H NMR of all these complexes. This is the case for the 1,3-diene complexes with the exception of $(\eta^5\text{-}C_5H_4CHO)$ (*trans,trans*-1,4-diphenylbuta-1,3-diene)rhodium(I). For analogous complexes in which the neutral ligand is a non-conjugated diene or ethene and X is a moderately electron-accepting substituent such as CO_2R (R = CH_3, C_2H_5 or C_3H_7) or CN the rhodium complexes exhibit a normal ^1H NMR spectrum for the ring protons at ambient temperatures. On cooling a $CDCl_3$ or $(CD_3)_2CO$ solution of these complexes the signal assigned to H(3),H(4) moves downfield whereas that assigned to H(2),H(5) moves upfield so that at low temperatures H(3),H(4) invariably resonate to low field of H(2),H(5). A recent study of alkene rotational barriers in $(\eta^5\text{-}C_5H_4X)M(C_2H_4)_2$ (M = Rh, Ir; X = t-Bu, Me, H, CO_2R, CN, CHO and $COCO_2C_2H_5$) has shown that the electron-accepting character of the cyclopentadienyl ring substituent increases in the order $CO_2CH_3 = CO_2C_2H_5 = CO_2C_3H_7 = CN < CHO < COCO_2C_2H_5$ [2].

These findings are in accord with the fact that the NMR ring proton resonances for non-conjugated diene complexes in which X = CHO or $COCO_2C_2H_5$ always show the resonance for H(3),H(4) to low field of H(2),H(5). An X-ray study of one representative complex $(\eta^5\text{-}C_5H_4CO_2CH_3)(\eta^4$-1,5-cyclooctadiene)rhodium(I) was consistent with a contribution from an 'allyl-ene' structure [1].

In this work we have extended this study of other diene complexes of rhodium(I) and bis(ethene) complexes of iridium(I). A single crystal X-ray structure of the complex (η^4-2,4-dimethylpenta-1,4-diene)(η^5-formylcyclopentadienyl)rhodium(I) has revealed a more pronounced localisation of electron density within the cyclopentadienyl ring compared to that found in the cyclooctadiene complex. This is in agreement with the extended Hückel calculation with self-consistent charge iteration performed on this complex which predicts a greater Mulliken overlap population for the C(3)–C(4) bond in the cyclopentadienyl ring. The mass spectral fragmentation patterns for diene-rhodium complexes depend on the nature of the Cp ring substituent and differ from analogous iridium(I) complexes in which neutral ligand fragmentation is favoured over ligand loss.

Fragmentation patterns found for chloro-substituted 1,3-diene complexes show no evidence for single step diene loss and involve halogen transfer to the metal. Analysis of the mass spectra of alkyl-substituted diene complexes of rhodium(I)

TABLE 1

ANALYTICAL DATA FOR (η^5-C_5H_4CHO)Rh(diene) COMPLEXES

Diene	Colour	M.p. [a] (°C)	Analyses (Found (calcd.)(%)) C	H	M [b]
2-Chlorobuta-1,3-diene	red	oil	42.4 (42.2)	3.6 (3.5)	284/286
trans-1-Chlorobuta-1,3-diene	red	oil	42.2 (42.2)	3.5 (3.5)	284/286
2,3-Dichlorobuta-1,3-diene	yellow	64	37.7 (37.6)	2.7 (2.8)	318/320/322
trans,trans-Diphenylbuta-1,3-diene	yellow	181	65.3 (65.6)	4.8 (4.7)	402
2-Methylbuta-1,3-diene	yellow	51	50.0 (50.0)	5.0 (4.9)	264
Cyclooctatetraene [c]	orange	142	47.0 (47.4)	4.2 (3.9)	556

[a] Uncorrected. [b] Parent ion in mass spectrum. [c] (η^5-$C_5H_4CO_2CH_3)_2Rh_2(C_8H_8)$ complex.

indicated a fundamental difference between the fragmentation of analogous diene complexes of rhodium and iron.

Experimental

All manipulations involving air sensitive materials were carried out under an atmosphere of dry nitrogen and solvents were distilled from appropriate drying agents and stored under an inert atmosphere. Hydrogen-1 NMR spectra were recorded in $CDCl_3$ on Bruker WP-90 pulsed Fourier transform and Varian HR-220 instruments and shifts are quoted in ppm downfield from internal $SiMe_4$. Assignments of H(2),H(5) and H(3),H(4) cyclopentadienyl ring protons were made as previously described [1].

(η^5-Tritylcyclopentadienyl)(η^4-cycloocta-1,5-diene)rhodium(I) was prepared by the method of Lewis and Parkins [3] and (η^5-formylcyclopentadienyl)(η^4-2,4-dimethylpenta-1,4-diene)rhodium(1) was prepared as described previously [4]. All but six of the rhodium complexes have been characterised previously [4,5]. Analytical and NMR data for the new complexes are presented in Tables 1 and 2. Mass spectra were recorded with an AEI MS902 spectrometer with nominal electron energy of 70 eV. The high volatility of the samples permitted the use of low inlet system/ion source temperatures and there was no evidence for pyrolytic effects in any of the samples examined.

Results and discussion

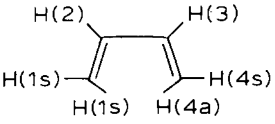
^1H NMR

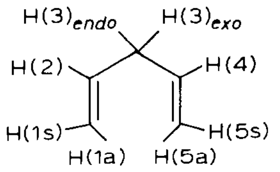
The ^1H NMR data for the complexes are presented in Table 2. Cyclopentadienyl ring proton assignments [1] were made through the aid of lanthanide shift reagents and selective deuterium labelling as described previously. The chemical shifts for the neutral diolefin protons were assigned in accord with the Immirzi designation [6].

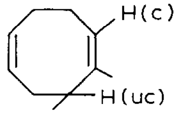
TABLE 2. PROTON CHEMICAL SHIFTS (δ, ppm) FOR (η^5-C_5H_4X)Rh(LL) AND (IN PARENTHESES) FOR (η^5-C_5H_4X)Ir(L)$_2$ COMPLEXES AT +40°C

No.	LL or L	X	H(2) and H(5) (Cp)	H(3) and H(4) (Cp)	X	H(1a)	H(1s)	H(2)	H(3)	H(4s) or H(4)	H(4a) or H(5s)	H(c) or H(5a)	H(uc)	C_2H_4
I	2,4-Dimethylpenta-1,4-diene [a,b]	CHO	5.21 (t)	5.56 (tq)	9.62 (s)	1.38 (d)	2.5 (t)	1.91 (s) (Me)	2.59 (tt) 2.46 (m)	1.91 (s) (Me)	2.5 (t)	1.38 (d)		
II	Cycloocta-1,3,5,7-tetraene [a,b,e]	$COOCH_3$	5.31 (t)	5.23 (td)	4.67 (s)							4.60 (d)		
III	Cycloocta-1,5-diene [a,c]	$C(C_6H_5)_3$	4.64 (t)	5.20 (td)	2.74 (m)							3.16 (m)	2.0 (m)	
IV	(Ethene	$COOCH_3$	5.64 (t)	5.44 (t)	3.80 (s)									0.89(m)) 2.75(m))
V	(Ethene [b]	CHO	5.45 (t)	5.77 (t)	9.75 (s)									0.95(m)) 2.87(m))
VI	2-Chlorobutadiene [b]	CHO	5.97 (m) 5.83 (m)	5.49 (m) 5.34 (m)	9.47 (s)	0.90 (td)	3.12 (tt)	Cl –	5.34 (m)	2.67 (qq)	0.45 (tt)			
VII	*trans*-1-Chlorobutadiene [b]	CHO	5.84 (m) 5.67 (m)	5.67 (m) 5.42 (m)	9.89 (s)	2.97 (qd)	Cl	5.1 (m)	4.7 (m)	2.64 (dm)	0.62 (td, td)			
VIII	2-Methylpenta-1,3-diene	CHO	5.74 (t)	5.50 (m) 5.27 (m)	9.62 (s)	0.59 (t)	2.67 (d)	2.04 (s) (Me)	4.97 (t)	2.45 (dd)	0.47 (tt)			
IX	2,3-Dichlorobutadiene [b,d]	CHO	5.95 (td)	5.50 (tq)	9.68 (s)	0.74 (t)	3.12 (dd)	Cl	Cl	3.12 (dd)	0.74 (t)			
X	*trans,trans*-Diphenylbutadiene [a,b]	CHO	4.69 (td)	5.10 (tq)	9.42 (s)	2.64 (dd)	7.30 (m) (ph)	5.60 (dd)	5.60 (dd)	7.30 (m) (ph)	2.64 (dd)			

[a] $^2J(^{103}Rh-H(2),H(5))$ 0.4 Hz, $^2J(^{103}Rh-H(3),H(4))$ 0.8 Hz. [b] $^5J(CHO-H(3),H(4))$ 0.4 Hz. [c] Previously prepared [3]. [d] $^2J(^{103}Rh-H(2),H(5))$ 0.7 Hz, $^2J(^{103}Rh-H(3),H(4))$ 0.9 Hz. [e] (η^5-$C_5H_4CO_2CH_3)_2Rh_2(C_8H_8)$ *complex*: s, *singlet*; d, *doublet*; t, *triplet*; m, *multiplet*; dd, *doublet of doublets*; td, *triplet of doublets*; tq, *triplet of quartets*; tt, triplet of triplets; qd, quartet of doublets; qq, quartet of quartets; dm, doublet of multiplets.







The 1,4-diene proton–proton coupling constants in complex I were essentially identical with CpRh(penta-1,4-diene) and other rhodium complexed alkylpenta-1,4-diene derivatives [7]. The geminal olefinic coupling is ^2J(H(1s)–H(1a) = ^2J(H(5s)–H(5a)) = -2.2 Hz whereas the value for uncomplexed penta-1,4-diene is 1.6 Hz. The change in this coupling would indicate an increase in sp^3 character for the terminal carbon atoms of the complexed diene. The vicinal couplings ^3J(H(1a)–H(2)) = ^3J(H(5a)–H(4)) = 11.5 Hz and ^3J(H(1s)–H(2)) = ^3J(H(5s)–H(4)) = 7.5 Hz are not directly comparable with those of the free ligand which exists mainly in the *s-trans* conformation. [8].

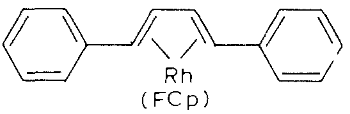
Complexation to rhodium confers a chemical shift difference between $H(3)_{endo}$ (δ 2.59 ppm) and $H(3)_{exo}$ (δ 2.46 ppm) and $^2J_{gem} = -12.5$ Hz. Both atoms show additional coupling to H(2)H(4)(^3J($H(3)_{endo}$–H(2)) 9.0 Hz) and (^3J($H(3)_{exo}$–H(2)) 2.0 Hz) which would imply that the respective dihedral angles are ca. 10° and ca. 70°. $H(3)_{endo}$ gave additional long range coupling to H(1*s*)H(1*a*) ($^4J \sim 1.0$ Hz) whereas $H(3)_{exo}$ showed coupling only to H(1*a*) ($^4J \sim 1.5$ Hz). ^{103}Rh–^{1}H couplings were not resolved. The spectra for the dimeric cyclooctatetraene complex II gave ^2J(^{103}Rh–H(c)) 1.8 Hz which is similar to the value reported [9] for $[(COT)RhCl]_2$. The assignments made for the 1,3-diene protons in complexes VI–X were as described previously and they show a deshielding effect in all cases relative to unsubstituted Cp derivatives which arises through the presence of electron-accepting groups on the Cp ring [10].

The spectra for the cyclopentadienyl ring protons appear as an A_2X_2 set of triplets with additional coupling to ^{103}Rh and in the case of formyl substituted [11] rings, the substituent proton. Complex I gives an 'abnormal' pattern for these resonances over the temperature range -80 to $+100$°C in that H(3),H(4) always resonates to low field of H(2),H(5). Replacement of the ring substituent by a more weakly electron-accepting group such as CO_2Me with retention of a non-conjugated diene system as in II results in a 'normal' ring proton spectrum at 40°C and above. As the temperature is decreased the H(2),H(5) signal moves upfield while that assigned to H(3),H(4) moves downfield. Coalescence occurs at 0°C and at lower temperature the assignment order is reversed.

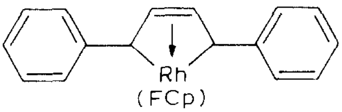
A similar result is found for the iridium(I) derivatives IV and V. In the former case 'coalescence' occurs at -50°C whereas the latter complex shows an abnormal spectrum over a wide temperature range. The tritylcyclopentadienyl complex III gave a similar result to I and V which suggests that the trityl group has a stronger electron-accepting influence than a CO_2R substituent. This is not, however, reflected in the chemical shifts of the system as a whole due to the anisotropic effect of the phenyl groups.

The conjugated diene complexes VI–VIII gave multiplet patterns for the Cp ring protons due to asymmetry in the 1,3-diene. The ring proton assignments made for complexes VI–IX clearly indicated a 'normal' pattern in that H(2),H(5) resonate to low field of (H3),H(4). Clearly this effect is governed by both the nature of the ring substituent and the counter diene or bis(ethene) ligand.

The *trans,trans*-diphenylbuta-1,3-diene complex X gave the only anomalous result in the case of 1,3-diene complexes. The chemical shifts for this complex indicate a more strongly bonded Cp ring at the expense of the 1,3-diene and the ring proton assignments indicate an 'abnormal' spectrum. This may result from the preference for structure (**a**) over (**b**) since the latter will entail a conjugation loss between the phenyl rings [12]. This in turn will entail a reduction in π back bonding which may lead to a lack of competitive overlap between ψ_3 (the LUMO of the 1,3-diene) and the e_1^- ring orbital for the metal d_{xz} orbital. The effect should enhance the stability difference between e_1^- and e_1^+ Cp ring orbitals and may result in a more localised bonding scheme for the Cp ring.



(a)



(b)

(FCp = formylcyclopentadienyl

Some evidence for localisation may be obtained from the ^{103}Rh–ring proton coupling constants. The value $^2J(^{103}Rh–HCp)$ for unsubstituted cp Rh (olefin) complexes is invariably 0.9 Hz a value consistent with the important contribution of π back bonding to the ring-metal bonding scheme [10].

The introduction of an electron-accepting ring substituent results in two types of metal-proton coupling depending on the nature of the counter olefin. In conjugated diene complexes such as IX $^2J(^{103}Rh–H(2,5))$ 0.6–0.8 Hz and $^2J(^{103}Rh–H(3,4))$ 0.8–1.0 Hz. The respective values for complexes in which the counter ligand is a non-conjugated diene, ethene or *trans,trans*-diphenylbutadiene are 0.4 and 0.8 Hz. There is a consistency in that the difference between the two couplings is larger in complexes that show 'abnormal' spectra. This may be associated with a contribution from an 'allyl-ene' structure for the Cp ring since the direction of movement of H(2),H(5) upfield in these systems is towards the chemical shift region found for π-allyl rhodium(I) systems [13] and the decrease in rhodium–proton coupling is consistent with the finding that [14] the ^{103}Rh–H$_{syn}$ coupling is less than 0.5 Hz for these allyl systems. The corresponding coupling for H(3),H(4) would then be expected to come within the range 0.5–2.8 Hz which is found for olefin rhodium systems [10]. The associated downfield shift of this resonance may also indicate that this part of the ring is more weakly coordinated which has been confirmed for (η^5-$C_5H_4CO_2Me$)Rh(1,5-COD). A recent NMR study of the dependence of ^{103}Rh chemical shifts in CpRh(olefin) complexes has shown that the shielding of the metal nucleus follows the order 1,3-diene > 1,4-diene $\sim$ 1,5-diene [15]. The $\delta(^{103}Rh)$ values for conjugated diene complexes were found to be in the same region as $[(Cp)_2Rh]^+$ in which an essentially delocalised ring–metal bonding scheme should apply. These findings were suggested to arise through less efficient *p,d* overlap in the case of the metal complexes with non-conjugated dienes but may also be indicative of localisation in the Cp ring.

TABLE 3

ATOM COORDINATES ($\times 10^4$) FOR $[(\eta^5\text{-}C_5H_4CHO)Rh(\eta^4\text{-}C_6H_{10})]$ WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*
Rh	8054(1)	4947(1)	2931(1)
C(1)	9062(26)	3701(13)	1861(19)
C(2)	9004(25)	3303(13)	3037(19)
C(3)	10079(27)	3937(13)	3736(22)
C(4)	10673(28)	4709(15)	3143(22)
C(5)	10040(26)	4603(13)	1880(20)
C(6)	8021(35)	3189(17)	835(25)
C(7)	7767(23)	6648(12)	2397(17)
C(8)	6654(23)	6184(11)	2030(17)
C(9)	5123(23)	5799(12)	2453(18)
C(10)	5636(21)	4814(12)	3167(17)
C(11)	6581(22)	4944(14)	4265(17)
C(12)	6766(30)	6216(15)	710(22)
C(13)	4900(28)	3768(14)	2799(20)
O	8153(32)	3580(16)	−200(24)

Crystal structure of $(C_6H_{10})Rh(C_5H_4CHO)$

Crystal data. $C_{13}H_{17}ORh$, $M = 292.2$. Monoclinic, a 8.661(1), b 12.529(3), c 11.341(2) Å, β 96.35°, U 1223.28 Å^3, d_m 1.53 g cm^{-3} (by flotation), d_c 1.586 g cm^{-3}, $Z = 4$, $F(000) = 592$. Space group $P2_1/c$. Mo-K_α radiation, λ 0.71069 Å; μ(Mo-K_α) 12.35 cm^{-1}.

Measurements. A suitable crystal was obtained by slow recrystallisation from

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) IN I WITH e.s.d.s IN PARENTHESES

Rh–C(1)	2.217(22)	Rh–C(4)	2.245(17)
Rh–C(2)	2.229(28)	Rh–C(5)	2.217(17)
Rh–C(3)	2.272(24)		
C(1)–C(2)–C(3)	105.0(19)	C(5)–C(1)–C(2)	109.8(15)
C(2)–C(3)–C(4)	107.8(16)	C(5)–C(1)–C(6)	119.3(20)
C(3)–C(4)–C(5)	113.9(20)	C(2)–C(1)–C(6)	130.7(20)
C(4)–C(5)–C(1)	103.3(20)	C(1)–C(6)–O	116.3(25)
C(1)–C(2)	1.400(25)	C(5)–C(1)	1.428(21)
C(2)–C(3)	1.477(26)	C(6)–C(1)	1.529(23)
C(3)–C(4)	1.283(34)	C(6)–O	1.276(39)
C(4)–C(5)	1.425(21)		
Rh–C(7)	2.085(25)	Rh–C(10)	2.156(13)
Rh–C(8)	2.152(21)	Rh–C(11)	2.148(15)
C(7)–C(8)–C(9)	118.7(13)	C(7)–C(8)–C(12)	112.0(15)
C(8)–C(9)–C(10)	102.4(14)	C(9)–C(10)–C(13)	117.9(16)
C(9)–C(10)–C(11)	117.1(20)		
C(7)–C(8)	1.421(18)	C(10)–C(11)	1.424(18)
C(8)–C(9)	1.521(20)	C(8)–C(12)	1.505(21)
C(9)–C(10)	1.518(33)	C(10)–C(13)	1.546(40)

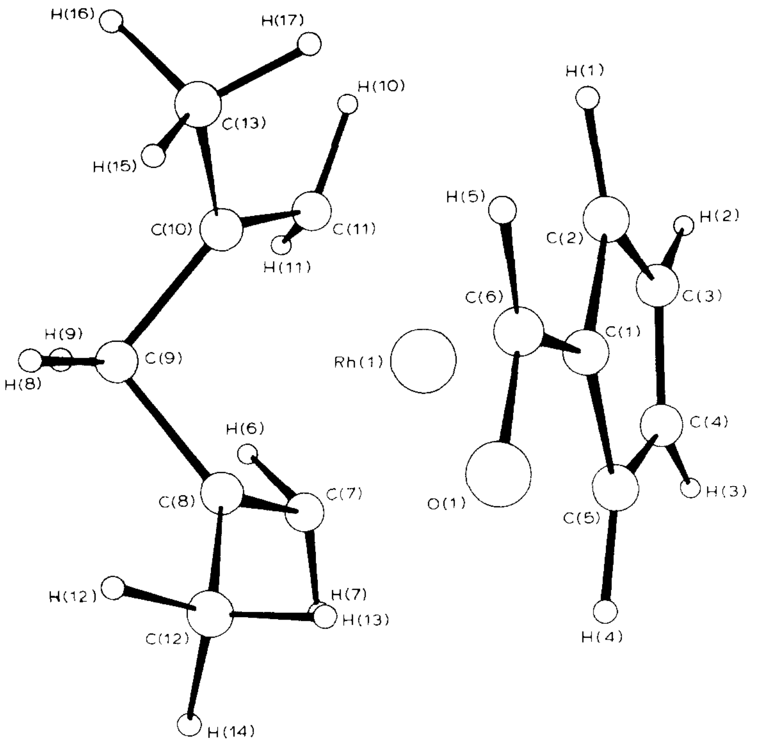


Fig. 1. The structure of η-formylcyclopentadienyl(η-2,4-dimethylpenta-1,4-diene)rhodium(I).

hexane at 0°C. A crystal with dimensions $0.2 \times 0.2 \times 0.4$ mm was sealed in a Lindemann capillary and space group and cell dimensions were determined using Weissenberg photographs. The intensities of 2051 reflections for which $2 \leqslant \theta \leqslant 22°$ were measured on a CAD-3 diffractometer. Three intensity standards were measured every 100 reflections and found to show significant deviations. θ–2θ scans were used for all measurements.

Structure analysis. Processing of the measured data gave 1145 reflections for which $|F| \geqslant 2\sigma|F|$. No correction was made for absorption. The structure was solved and refined by the usual Patterson, difference-Fourier, and least squares methods. In the final full matrix refinement, anisotropic temperature factors were used for the rhodium atom only and all hydrogen atoms were placed in calculated positions. Unit weights were used. Refinement converged with $R = 0.0588$ and $R^1 = 0.0655$. The programs SHEL-X, XANADU and PLUTO (courtesy of Dr. G. Sheldrick, University of Göttingen) were used for all calculations and the Trinity College DEC-2060 computer was used throughout. Final positional parameters, together with standard deviations, are given in Table 3 Bond lengths and angles are given in Table 4 and least squares planes in Table 5. Final anisotropic thermal parameters and hydrogen parameters are given in Supplementary Publication No. SUP (4 pages).

Discussion of the structure

The molecule is illustrated in Fig. 1 together with the atomic numbering scheme. The metal atom is bonded to the four olefinic carbons of the 1,4-diene Rh–C, 2.085(25)–2.156(13) Å and to the five cyclopentadienyl carbon atoms (Rh–C, 2.213(23)–2.275(24) Å). The cyclopentadienyl ring is planar (Table 5) with some significant differences in the C–C and Rh–C distances. The C(3)–C(4) distance of 1.283(33) Å is very short and indicative of localisation of electron density in the C(3)–C(4) bond. Similar results have been found for $CpRh(C_2F_4)(C_2H_4)$ [16] and $CpRh(C_4H_4Cl_2)$ [17] in which the corresponding ring C–C bond lengths are 1.286(12) and 1.310(27) Å, respectively. While the differences between the remaining carbon–carbon and metal–carbon distances are similar, the observed pattern corresponds to that found in several other η^5-cyclopentadienylrhodium complexes in which a small contribution from an allyl-ene structure is apparent [1,18].

The data is not consistent with a significant contribution from a diolefin structure in which the cyclopentadienyl ring is generally non planar [19,20]. The CHO ring substituent is almost coplanar with the cyclopentadienyl ring and the C(1)–C(6) distance of 1.534(24) Å tends to eliminate delocalisation over ring and substituent.

The bonds from the four olefinic carbons of the 1,4-diene to the metal are somewhat shorter than those to the cyclopentadienyl ring and are within the range reported for [pivaloylmethanato-1,2,4,5-(1,2-bis(trifluoromethyl)-4-methyl-3-(prop-2-ylidene)-penta-1,4-diene)rhodium(I)] [21] and [η^4-3-methoxycarbonylcyclohexa-1,4-diene)(η^5-cyclopentadienyl)rhodium(I)] [22]. These complexes show olefin–metal bond lengths of 2.07(15)–2.2(15) and 2.125(13)–2.138(12) Å, respectively. Of considerable interest is the fact that although the four olefinic carbons are almost coplanar (Table 5) and symmetrically located with respect to the metal atom, the two double bonds are not parallel (angle of intersection 21.2°) and the C(8) and C(10) end of the pentadiene is tipped away from the plane of the cyclopentadienyl ring (angle of intersection 9.00°). According to the Dewar–Chatt–Duncanson model, maximum overlap would be achieved by having the olefinic double bonds parallel. This is found to be the case for other 1,4-diene complexes of rhodium where the two alkene functions are more constrained. For example, in (η^5-pentamethylcyclopentadienyl)(dibenzylideneacetone)rhodium(I) the metal atom is not symmetrically located with respect to a given double bond and the intramolecular contact between the terminal *anti* hydrogen atoms is 1.76 Å [23a]. The fact that the dibenzylideneacetone molecule maintains its parallel double bonds entails severe crowding of the hydrogen atoms which was suggested as a possible reason for the catalytic activity of this complex. In the present case the fact that the olefinic double bonds are not parallel presumably results in reduced steric crowding of the terminal olefin *anti* hydrogen

TABLE 5

LEAST SQUARES PLANES

(Distance of atoms from the planes are given in Å. Atoms not contributing to the planes are marked with an asterisk)

Plane 1: C(1) −0.02, C(2) 0.02, C(3) −0.01, C(4) −0.00, C(5) 0.01, Rh* 1.89
Plane 2: C(7) 0.01, C(8) −0.02, C(10) 0.02, C(11) −0.01, Rh* −1.49 Angle between planes 9.0°

TABLE 6

MULLIKEN OVERLAP POPULATIONS AND NET GROUP CHARGES ON (η^5-C_5H_4X)Rh(2,4-dimethylpenta-1,4-diene) (X = CHO or H)

Overlap population p(r − s)

X *r − s*:	1–2	2–3	3–4	4–5	5–1
CHO	1.0326	1.0452	1.0602	1.0449	1.0353
H	1.0557	1.0294	1.0741	1.0294	1.0557

Net group charges q(R)

X	R = Rh	R = C_5H_4X	R = C_6H_{10}
CHO	0.240	−0.300	+0.060
H	+0.209	−0.181	−0.029

atoms. Thus strain within the coordinated 1,4-diene is reduced at the expense of less favourable overlap with the metal orbitals. This finding may account for the thermal isomerisation of acyclic 1,4-diene complexes of rhodium(I) to give 1,3-diene products [5]. A similar isomerisation also occurs for cyclohexa-1,4-dienerhodium complexes which lack *anti* hydrogen substituents.

The driving force in this case is presumably due to increase in strain energy of the coordinated diene because of the adoption of a boat conformation [22]. In contrast the very stable norbornadienerhodium(I) systems result from minimal conformational change and reduction in strain energy upon complexation of the 1,4-diene [23b].

Molecular orbital theory of localisation in the cyclopentadienyl ring

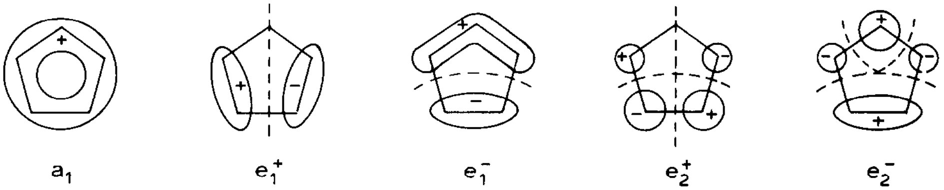
An extended Hückel (EH) calculation with self-consistent charge iteration [24] was performed on (η^5-C_5H_4CHO)Rh(2,4-dimethylpenta-1,4-diene) using the double-zeta exponents Rh suggested by Summerville and Hoffmann [25] and the VSIP parameters of Baranovskii and Nikolskii [26]. The results predicted a greater Mulliken overlap population for the C(3)–C(4) bond in the cyclopentadienyl (Cp) ring than for the other ring C–C bonds (Table 6). That this does not necessarily arise from the CHO substituent in the Cp ring is shown by the results of a similar calculation on the unsubstituted compound (where the local symmetry of the η^5-C_5H_5Rh portion possesses a five-fold axis) in which the distortion seems to be retained. Thus there are two possible sources of the observed and calculated distortion in the molecule (η^5-C_5H_4X)RhLL arising from the effects of (1) the ring substituent X with its particular ring conjugative and/or electron-accepting properties, and (2) the complexing, via the Rh atom, to the diolefin LL. Although too far from the Cp ring for effective overlap, LL may sufficiently lower the local symmetry of the Rh atom as to render its orbitals inequivalent in the x and y directions, and thus communicate a distortion to the ring system.

These effects should be examined separately in order to ascertain the conditions for one of them to be dominant.

(1) The ring substituent X. In order to arrive at an understanding of the essential factors through which X may distort the Cp ring we shall firstly confine our attention to the system of the C_5 ring alone. This is consistent with the common assent that bond length variations in aromatic compounds are predominantly a feature of the π system [27].

If the Rh complex were ionic, with a net charge of −1 on the Cp ring, both e_1^+

and e_1^- components of the doubly-degenerate MO e_1 with their respective nodal properties, would be fully occupied. (In an unsubstituted ring the charge distribution from the two components would then complement one another to produce five equal bond orders.)



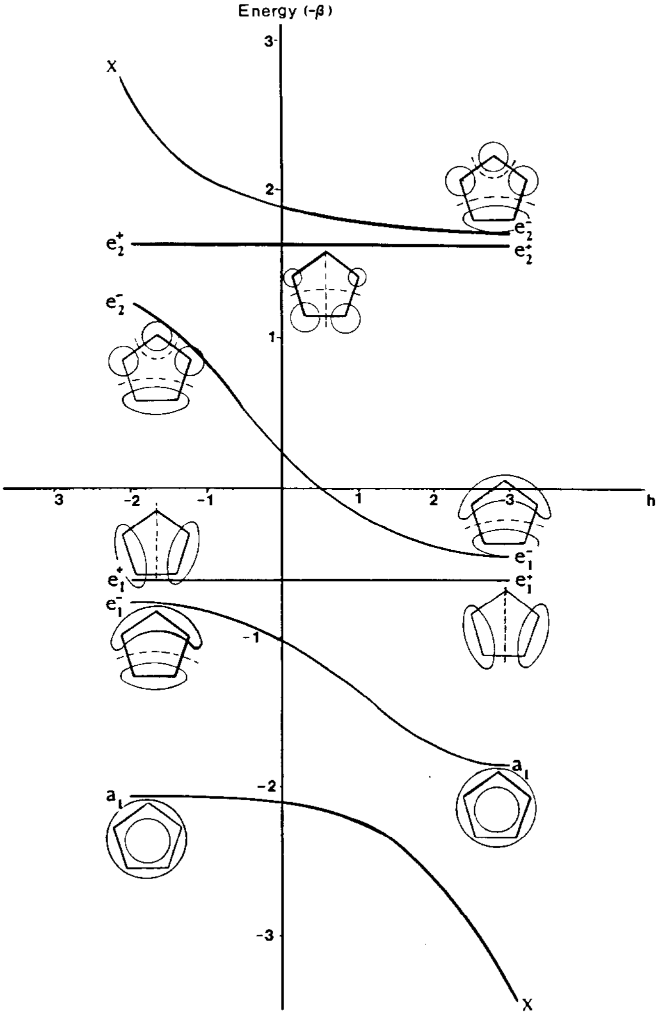


Fig. 2. The effect of varying the electronegativity parameter *h* of the substituent X on the MO energy levels of C_5H_4X. The labels are those of the approximate symmetries in the perturbed C_{5v} point group.

In fact the EH calculations described above indicate that the molecule is predominantly covalent (Table 6), the charge on the Rh atom being only $+0.21$ for $X = H$ (0.24 for $X = CHO$) while that on the 1,4-diene is very small.

The charges on the unsubstituted and substituted Cp ring are respectively -0.18 and -0.30; we therefore have fractionally more than five electrons to distribute among the MOs of the ring. The lowest, a_1, will be doubly occupied, leaving the remaining 3.2-electrons to occupy MOs which in the unsubstituted Cp ring are the doubly degenerate e_1 set.

The results of replacing a H atom in Cp may be discussed in two stages. (a) If X has orbitals capable of extending the π delocalisation of the ring it will remove the C_5 symmetry axis of the π electron system. The e_1^- MO of the substituted cp ring will therefore be stabilised, out the e_1^+ remains unaffected since it has a node through C(1). As the overlap between C(1) and X increases from zero the affected e_1^- MO loses its allyl-ene character but since the partially occupied e_1^+ MO retains its 'di-olefin' character and has higher population than e_1^- this distortion is conferred on the ring as the interaction between X and C(1) increases.

(b) Another way in which X can effect the π system of the ring is through its electron-withdrawing or -donating property. Figure 2 shows the effect, on the simple Hückel energy levels, of altering the electronegativity parameter h relating the coulomb integral of a heteroatom X to that of C via $\alpha_X = \alpha_C + h\beta$. In the limits $|h| \gg 1$, when the energies of the orbitals on X and C are very different so that very little interaction occurs, the levels form the energy level pattern a_1, e_1, e_2 expected for an unperturbed C_5 ring together with the energy of the group X. The curves have been so labelled for each limiting case.

In the region of $h \leq 0$ the orbital X has a high energy and the π system provides 5 electrons. These occupy MOs which have symmetries approximating a_1 and e_1^- for the unperturbed Cp, and partially occupy an e_1^+ MO which is unaffected by the presence of X. The results confers an overall e_1^- (i.e. an allyl-ene) distortion on the ring. If, on the other hand, the energy of the orbital on X is sufficiently low for the system to be described by the right hand portion of Fig. 2 there will be $5 + 2 = 7$ π electrons which will fill the MOs up to e_1^+ and partially occupy to MO which in these conditions has taken on the characteristic of an e_1^+ orbital. The contribution of the e_1^+ set to the ring is to impose a net e_1^+ symmetry i.e. the distortion is again di-olefin type.

As an electron accepting group, CHO falls into the second category, but the di-olefin distortion predicted in both (a) and (b), as well as by a charge-iterative all-valence-AO calculation on $[C_5H_4CHO]$ is not the one calculated (or observed) for (η^5-C_5H_4CHO)Rh(2,4-dimethylpenta-1,4-diene). We conclude that the simple mechanism given here for the effect of X on the system of the Cp ring is inadequate to described the distortion in the complex. This is consistent with the results displayed in Table 6 where we noted that Extended Hückel theory predicted an allyl-ene distortion in the Cp ring whether or not the ring is substituted. In fact Table 6 shows that this distortion should be more pronounced in the unsubstituted ring, agreeing with our expectation that CHO tends to impose the opposite distortion on the ring but that the distorting effect of the substituent is not the dominant one.

(2) Complexation to RhLL. We must now investigate the part played by the complexing of the ligand LL in the distortion of the Cp ring. A procedure which

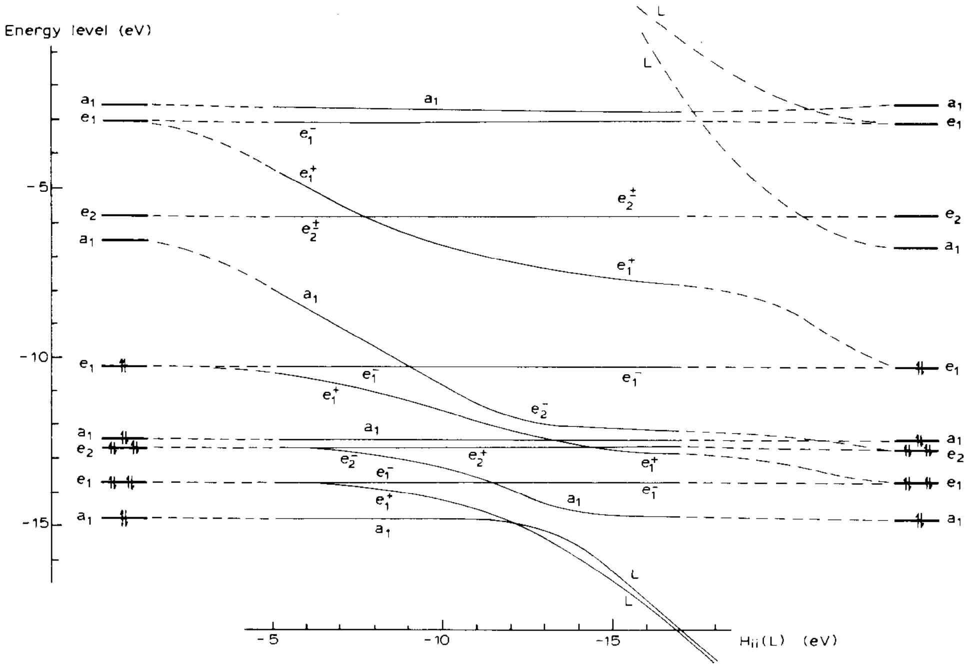


Fig. 3. MO energy levels of η^5-C_5H_5RhL (whose AOs and their interactions are described in the text) showing the effect of varying the electronegativity $H_{ii}(LL)$ of the AO in the ligand LL. The labels are those of the dominating symmetries at the particular $H_{ii}(LL)$ values at which they appear.

reduces the complexity of the problem to the probable essential interactions, and which is consistent with the π MO procedure in Fig. 3, is to consider the interaction between the π MOs of the Cp ring, the (4*d*, 5*s*, 5*p*) AOs on Rh and a single AO at each of the two dentate sites on LL. The energy of the AO on the LL is variable so that the dependence of the bonding on the nature of the ligand may be explored.

In order to interpret the effect of the LL complexation on the π bonding of the Cp ring an Extended Hückel calculation was first of all performed on the molecule without LL i.e. on the fragment η^5-C_5H_5Rh. This is an open shell system with two electrons in a doubly degenerate e_1 MO; the normal charge-iterative procedure inherent in the method of calculation described for the complete molecule would consequently lift the degeneracies of the e_1 and e_2 MOs. Since our purpose is to explain the distorting power of LL on an axially symmetric system η^5-C_5H_5Rh it would be wrong to compare the results with those obtained for a fragment which was already distorted by the effects of an open-shell MO. We therefore performed a non-iterative calculation on this fragment, but used coulomb terms H_{ii} calculated from a charge distribution obtained from the self-consistent charge iterative computation already described for the complete molecule (η^5-C_5H_4CHO)Rh(2,4-dimethylpenta-1,4-diene). This procedure preserved the e_1 and e_2 degeneracies while at the same time using realistic atomic orbital energies. The MO energy levels thus calculated for η^5-C_5H_5Rh and their symmetry labels are shown on both the left and right edges of Fig. 3, together with their occupancies by the 14 electrons associated with the reduced system of AOs considered here. Note that the highest occupied level is doubly degenerate and is incompletely filled. Between these two sets of levels are displayed the energy curves obtained from a set of similar calculations conducted on η^5-$C_5H_5RhL'_2$ where L′ is a pseudo-atom, the energy of whose single AO, H_{ii} (L′), was varied between −5 and −20 eV. In the limits of high and low H_{ii}(L′) values these levels tend to those of the fragment η^5-C_5H_5Rh, together with a set of pure L′-AO levels. The diagram therefore allows the career of a particular MO to be followed, in both energy and symmetry aspects, between the two extrema. The symmetry labels on the curves indicate the approximate symmetry of a particular MO in the local 5-fold symmetry environment, as revealed by the LCAO coefficients. As H_{ii} (L′) changes so also may the approximate symmetry of the MO before correlating with the appropriate level of η^5-C_5H_5Rh at the opposite edge of the diagram.

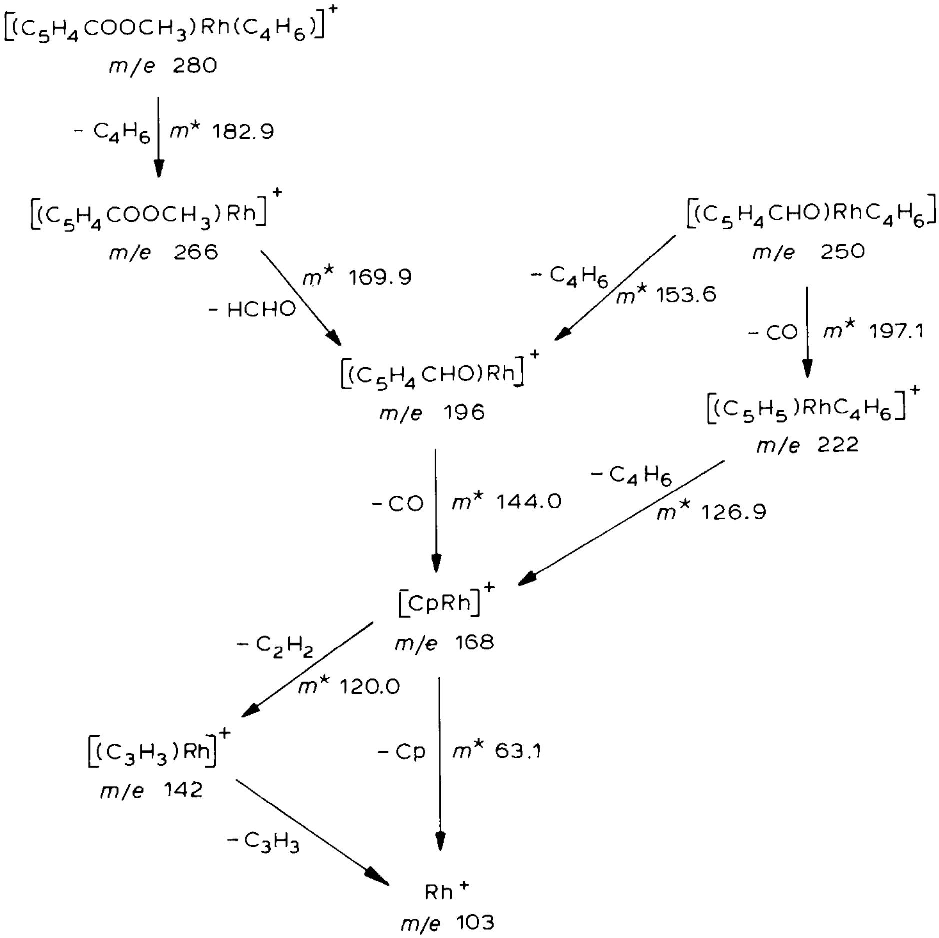
In deciding the electron occupancy of the MO scheme in Fig. 3 we have to decide whether the AO of the pseudo-atom L′ modelling the 1,4-diene ligand is to function as a donor or an acceptor orbital. If the Rh AOs interact primarily with the unoccupied π^* orbitals of the diene the number of electrons to be fed into the levels is the same as for η^5-C_5H_5Rh: the bonding scheme would be that appearing for low H_{ii}(L′) values, say between −5 and −9 eV. The splitting of the e_1 MO at −10.25 eV would cause the two electrons which previously filled this level to occupy the lower component $e_1{}^+$ resulting in the configuration $a_1{}^2e_1{}^4a_2{}^4(e_1{}^+)^2$. The molecule, having a small HOMO–LUMO gap would be kinetically unstable (and the Cp ring would have a di-olefin distortion).

If it is the occupied π MOs which dominate the complexing of the diene ligand, the additional 4 electrons which they contribute to the MO levels in Fig. 3 would provide a kinetically stable system, since the $e_1{}^+$ and a_1 levels at −10 to −11 eV would be filled, leaving a large HOMO-LUMO gap of several eV. Now if the donating orbital of the diene has a sufficiently low energy (H_{ii}(L′) between −14 and −20 eV) the MO levels would be as they appear on the right-hand portion of Fig. 3. In this region the MOs have taken on the symmetry characteristics of the limiting set of levels on the right-hand edge of the Figure, and the electron configuration $(L'_2)^4a_1{}^2e_1{}^4e_2{}^4a_1{}^2(e_1{}^-)^2$. The electrons in the $e_1{}^-$ HOMO impose an allyl-ene distortion on the Cp ring which is uncompensated by the $e_1{}^+$ LUMO.

The simple method used in these calculations emphasizes the important features of the bonding and shows that, provided the ligand system LL is sufficiently electronegative, we should expect an allyl-ene distortion of the Cp ring. Because of the deliberate neglect of the σ orbitals on Cp it would not be sensible to use the method to try to estimate the geometry of the distortion and thus to confirm the abnormally short C(3)–C(4) bonds by the X-ray results. All we may conclude from the analysis in this section is that this bond should be shorter than the C(2)–C(3) and C(4)–C(5) bonds, and that the C(1)–C(2) and C(1)–C(5) lengths should have intermediate values.

Mass spectra

Butadiene complexes. The fragmentation patterns found for the CpCHORh and $CpCO_2MeRh$ derivatives are similar to that described for $[CpCo(C_4H_6)]$ in that the main process is conversion of the molecular ion to the bare Rh^+ ion by the routes shown in Scheme 1 [28].

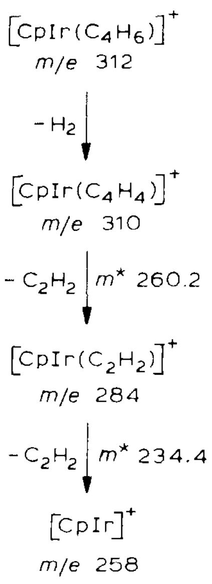


SCHEME 1

The parent ion in both complexes may lose butadiene in a single step to give $[(CpX)Rh]^+$ (X = CO_2Me or CHO). In the former case the base peak is the parent ion and subsequent fragmentation involves loss of the elements of formaldehyde followed by CO loss from the side chain. The subsequent decay pattern is similar to the scheme outlined for [CpRh-(1,5-cyclooctadiene)] by King [29]. The parent ion in the CpCHO complexes is $[(CpCHO)Rh]^+$ and there is competition between diene loss (major process) and CO loss from the side chain which is not in accord with the electron-accepting nature of the two cyclopentadienyl ring substituents and their relative effects on the π-contribution to the metal–1,3-diene bond [2]. The differing behaviour simply indicates a more facile elimination process in the case of the CpCHO complex.

The fragmentation pattern of $[CpIr(C_4H_6)]$ in contrast, is dominated by sequential hydrogen and ethyne loss from the parent ion (Scheme 2). The *m/e* values quoted in the text for ions containing iridium refer to ^{193}Ir.

In this case the parent is the base peak and there is no evidence for single step



SCHEME 2

butadiene loss. This type of fragmentation is consistent with the results found in the mass spectra of bis(ethene) complexes of iridium(I) and suggests a stronger olefin–metal interaction than in the case of rhodium(I) [30].

Chloro substituted buta-1,3-diene complexes. Table 7 gives the relative abundances and main processes involved in the fragmentation of the formylcyclopentadienyl derivatives of *trans*-1-chlorobutadiene and 2-chlorobutadiene. All relative abundances refer to an arbitrary value of 100 chosen for the base peak in each spectrum.

The fragmentation patterns for the two complexes are very similar but elimination of HCl is a more facile process for the 2-chlorobutadiene complex. This is a surprising result in view of the fact that a chlorine atom on the diene terminus might be expected to be more reactive. The product of this elimination is the species $[C_4H_4RhCpCHO]^+$ *m/e* 248 which fragments by initial loss of CO from the cyclopentadienyl ring to give $[(C_4H_4)RhCp]^+$ *m/e* 220. This ion decays by three competing processes which involve loss of H_2, C_2H_2 or C_4H_4, respectively. The first elimination product $[(C_4H_2)RhCp]^+$ *m/e* 1218 may contain a π complexed ethyne species. Loss of ethyne from $[(C_4H_4)M]^+$ species has previously [31] been cited as evidence against a π-cyclobutadiene structure although this is a controversial point [32] and in the present case such a structure seems unlikely.

No evidence was available for single step diene loss from the parent ion and the peak corresponding to $[(C_4H_5Cl)Rh]^+$ was absent. Low intensity peaks at *m/e* 231/233 corresponding to $[(Cl)RhCpCHO]^+$ arise through migration of halogen to the metal. This unusual process has been previously observed for $[(CO)_3Cr\text{-}\eta^6C_6H_5Cl]$ [33] and for metal complexes of halo-substituted pentane-2,4-dionates [34]. In the case of (η^5-cyclopentadienyl)trihalophosphinemanganese dicarbonyl compounds, the ion $[CpMnX]^+$ (X = F, Cl, Br) is formed by initial decarbonylation followed by loss

TABLE 7

RELATIVE ABUNDANCES, PRINCIPAL POSITIVE IONS AND METASTABLE TRANSITIONS ($m^\star$) IN (η^5-C_5H_4CHO)RhLL COMPLEXES

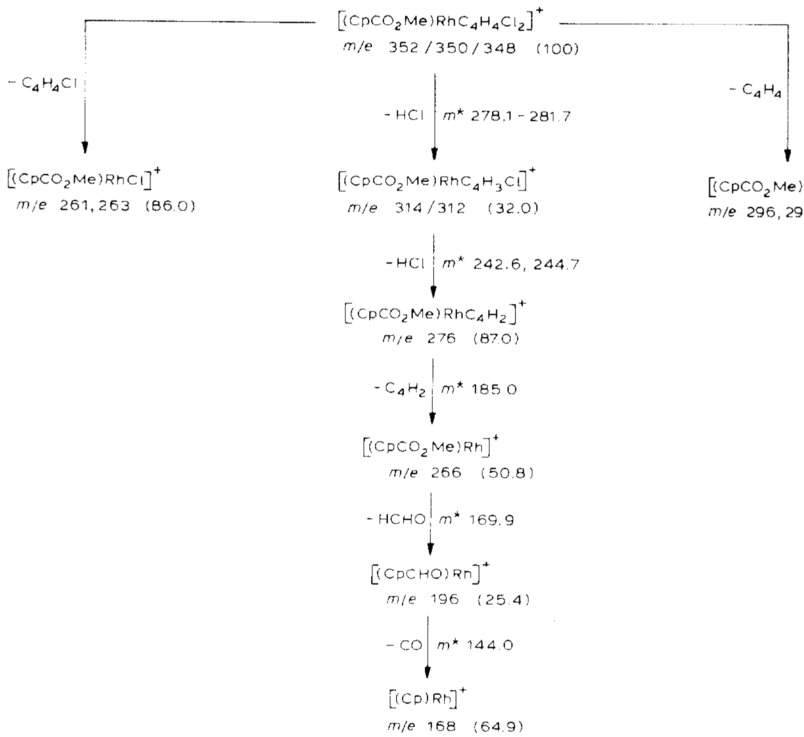
Ion [a]	Relative abundances		Metastable transitions $m^\star$	Process	Neutral fragment lost
	LL [b]	LL [c]			
$[(CpCHO)RhC_4H_5Cl]^+$	100.0	100.0	–	–	–
$[(CpCHO)RhC_4H_4]^+$	74.0	28.8	216.5 215.0	$[(CpCHO)RhC_4H_5Cl]^+ \rightarrow [(CpCHO)RhC_4H_4]^+$	HCl
$[(CpCHO)RhCl]^+$	3.0	5.8			
$[CpRhC_4H_4]^+$	11.6	6.8	195.1	$[(CpCHO)RhC_4H_4]^+ \rightarrow [CpRhC_4H_4]^+$	CO
$[CpRhC_4H_2]^+$	28.9	16.8	216.0	$[CpRhC_4H_4]^+ \rightarrow [CpRhC_4H_2]^+$	H_2
$[(CpCHO)Rh]^+$	31.6	20.0			
$[CpRhC_2H_2]^+$	16.1	7.5	171.0	$[CpRhC_4H_4]^+ \rightarrow [CpRhC_2H_2]^+$	C_2H_2
$[CpRh]^+$	97.0	95.0	144.0	$[(CpCHO)Rh]^+ \rightarrow [CpRh]^+$	CO
			128.3	$[CpRhC_4H_4]^+ \rightarrow [CpRh]^+$	C_4H_4
$[(C_3H_3)Rh]^+$	28.7	23.6	120.0	$[CpRh\}^+ \rightarrow [(C_3H_3)Rh]^+$	C_2H_2
$[(C_2H_2)Rh]^+$	3.4	4.3			
Rh^+	17.8	13.8	63.1	$[CpRh]^+ \rightarrow Rh^+$	Cp

[a] Ions having less than 3% relative abundance are not recorded. [b] LL = 2-chlorobutadiene. [c] LL = 1-chlorobutadiene.

of a dihalophosphine radical. In the present case the process is assumed to involve simultaneous loss of a C_4H_5 radical [35].

Scheme 3 shows the main fragmentation process for the methoxycarbonylcyclopentadienyl derivative of 2,3-dichlorobutadiene. Relative abundances are given in parentheses. The fragmentation pattern for this complex again gave no evidence for single step diene loss which apparently suggests that the chloro substituted butadienes are more firmly bonded to rhodium than butadiene itself in the parent ion. However as the π-accepting nature of the 1,3-diene increases, single step loss should be facilitated due to the weakening effect on the positive charge (located mainly on the rhodium) on the back bonding [28].

More facile fragmentation routes may therefore be available to these chlorodiene systems than single step diene loss. One such process involves stepwise loss of HCl which gives the highly abundant $[(CpCO_2Me)RhC_4H_2]^+$ (*m/e* 276) ion. The ion $[(CpCO_2Me)RhCl_2]^+$ (*m/e* 296, 298, 300) was observed in low abundance and presumably results from loss of a C_4H_4 radical with migration of two chlorine atoms to the metal. Loss of C_4H_4Cl and transfer of one chlorine atom represents a much more favourable process however. Fragment ions at *m/e* 232/230, 204/202, and 195 were observed in low abundance and assigned to $[(C_5H_4CO)RhCl]^+$, $[(C_5H_4)RhCl]^+$, and $[C_5H_4Rh]^+$, respectively. These unusual ions may be associated with decay of $[(CpCO_2Me)RhCl]^+$ (*m/e* 261, 263) but no metastable evidence was apparent.



SCHEME 3

Alkyl substituted 1,3- and 1,4-diene complexes. The mass spectra of *cis*- and *trans*-1,3-pentadiene ligands show loss of a single hydrogen atom or methyl radical from the parent ion as important fragmentation processes [36]. This type of decay is also apparent in the spectra of other alkyl substituted penta-1,3-diene, penta-1,4-diene and hexa-2,4-diene ligands and is in accord with the even electron rule [37]. A study of the fragmentation patterns of [(η^4-diene)tris(trifluorophosphine)iron(0)] complexes (diene = buta-1,3-diene; isoprene; *cis* and *trans*-penta-1,3-diene, 2,3-dimethylbutadiene, *cis,trans* and *trans,trans*-hexa-2,4-diene, and 2,4-dimethylpenta-1,3-diene) has shown that formation of species such as $[(C_3H_6)Fe]^+$, $[(C_2H_2)Fe]^+$ and $[(C_3H_4)Fe]^+$ through loss of ethyne, propene or ethene from the ion $[(\text{diene})Fe]^+$ represent important processes [38]. In this work the fragmentation patterns of (η^5-C_5H_4X)Rh(diene) complexes were examined (X = H, CHO or $COOCH_3$; diene = *cis* and *trans*-penta-1,3-diene; penta-1,4-diene, isoprene, 2,3-dimethylbutadiene, *cis,trans*- and *trans,trans*-hexa-2,4-diene, *trans*-hexa-1,3-diene, *cis*-3-methylpenta-1,3-diene, 4-methylpenta-1,3-diene, *cis*- and *trans*-hexa-1,4-diene, 2-methylpenta-1,4-diene and 3-methylpenta-1,4-diene).

The spectra of the above complexes displayed more elaborate fragmentation processes in which the loss of C_2H_2, C_3H_6 or C_2H_4 from the complexed diene are not important decay routes. Loss of a radical or hydrogen molecule from the parent ion becomes apparent in the case of the rhodium complexes. In all cases diene fragmentation is followed by elimination of the Cp ring and in the case of $CpCo_2Me$ derivatives there is no evidence for transfer of the methyl group to the metal atom unlike the fragmentation of similarly substituted ferrocene and cymantrene systems [39].

The fragmentation patterns of the (η^5-C_5H_4CHO)RhC_5H_8 (C_5H_8 = *cis*- or *trans*-penta-1,3-diene, isoprene or penta-1,4-diene) complexes were virtually identical. In all cases the parent ion (*m/e* 264) loses the elements of CHO in presumably a consecutive process to give $[CpRhC_5H_7]^+$ (*m/e* 235, m^* 209.1). This indicates competitive fragmentation between the diene and side chain of the Cp ring. This ion then undergoes elimination of H_2 which gives $[CpRhC_5H_5]^+$ (*m/e* 233, m^* 231.0). A low abundance peak at *m/e* 233 also occurs in the mass spectrum of $[CpCHORh(C_2H_4)_2]$. This is tentatively assigned to $[(\eta^5\text{-}C_5H_5)_2Rh]^+$ which may be produced by pyrolysis within the instrument. The base peak in the spectrum of the bis(ethene) complex is $[(CpRh]^+$ (*m/e* 168) at ion source temperature of 90°C and at 180°C it is $[Cp_2Rh]^+$ (*m/e* 233). It is known that dissociation of ethene from cyclopentadienyl complexes occurs at temperatures above 115°C [40]. This may provide a route for formation of the rhodocenium cation but careful monitoring of source and inlet temperatures in the present study should reduce this contribution to

TABLE 8

RELATIVE ABUNDANCES, PRINCIPAL POSITIVE IONS AND METASTABLE TRANSITIONS (m^*) IN η^5-CpRh(η^4-3-methylpenta-1,4-diene)

m/e	Ion	Relative abundances	Metastable transition	Neutral fragment lost	m^*
250	$[CpRhC_6H_{10}]^+$	90.0			
248	$[CpRhC_6H_8]^+$	5.0	$[CpRhC_6H_{10}]^+ \rightarrow [CpRhC_6H_8]^+$	H_2	246.0
247	$[CpRhC_6H_7]^+$	23.0	–	–	–
235	$[CpRhC_5H_7]^+$	4.1	$[CpRhC_6H_{10}]^+ \rightarrow [CpRhC_5H_7]^+$	CH_3	220.9
233	$[CpRhC_5H_5]^+$	17.5	$[CpRhC_5H_7]^+ \rightarrow [CpRhC_5H_5]^+$	H_2	231.0
222	$[CpRhC_4H_6]^+$	4.0	$[CpRhC_6H_{10}]^+ \rightarrow [CpRhC_4H_6]^+$	C_2H_4	197.1
184	$[RhC_6H_9]^+$	1.0	–	–	–
182	$[RhC_6H_7]^+$	3.5	$[RhC_6H_9]^+ \rightarrow [RhC_6H_7]^+$	H_2	180.0
			$[CpRhC_6H_7]^+ \rightarrow [RhC_6H_7]^+$	Cp	
168	$[CpRh]^+$	100.0	$[CpRhC_6H_{10}]^+ \rightarrow [CpRh]^+$	C_6H_{10}	112.9
			$[CpRhC_6H_7]^+ \rightarrow [CpRh]^+$	C_6H_7	114.3
			$[CpRhC_5H_5]^+ \rightarrow [CpRh]^+$	C_5H_5	121.1
142	$[C_3H_3Rh]^+$	12.5	$[CpRh]^+ \rightarrow [C_3H_3Rh]^+$	C_2H_2	120.0
103	Rh^+	8.2	$[CpRh]^+ \rightarrow Rh^+$	Cp	63.1
			$[RhC_6H_7]^+ \rightarrow Rh$	C_6H_7	58.3

m/e 233 [41]. There was no evidence for single step diene loss in the above complexes.

The fragmentation pattern of [(CpCO$_2$Me)Rh(*trans*-penta-1,3-diene)] (*m/e* 294) in contrast give single step diene loss as major decay process. This is followed by subsequent fragmentation of the ring side chain and minor processes involve formation of [(CpCO$_2$Me)RhC$_5$H$_5$]$^+$ (*m/e* 291) and [CpRhC$_5$H$_5$]$^+$ (*m/e* 233). The nature of the Cp ring subsequent appears to be the deciding factor in the fragmentation of these complexes rather than the diene isomer. Table 8 gives the relative abundance and main processes involved in the fragmentation of [CpRh(η^4-3-methylpenta-1,4-diene)]. This complex gives a mass spectrum which is typical of the isomeric C$_6$H$_{10}$-dienerhodium complexes when the cyclopentadienyl ring does not carry a substituent. The main fragmentation process involves loss of diene from the parent ion to give [CpRh]$^+$ (*m/e* 168). Alternatively the parent ion may lose hydrogen to form the [CpRh(C$_6$H$_7$)]$^+$ (*m/e* 247) species which fragments by loss of C$_6$H$_7$ to give [CpRh]$^+$ (major process) or loss of C$_5$H$_5$ (minor process) to give the low abundance ion [Rh(C$_6$H$_7$)]$^+$ (*m/e* 182). The unusual loss of a methyl radical from the parent ion gives [CpRhC$_5$H$_7$]$^+$ (*m/e* 235) which decays by loss of H$_2$ to give the [CpRhC$_5$H$_5$]$^+$ (*m/e* 233) species. Loss of C$_2$H$_4$ from the parent ion is also observed and gives [CpRh(C$_4$H$_6$)]$^+$ (*m/e* 222) which may contain a π complexed butadiene ligand. In conclusion, the mass spectral decay pattern of CpRh(C$_6$H$_{10}$) shows some similarity to Cp derivatives of iron, manganese and cobalt in which ligands other than Cp are lost [42]. However, the formation of high abundance ions at *m/e* 247 and 233 by apparent radical loss is at variance with the preference for loss of even electron species from ions derived from π bonded compounds and unusual compared to the decay patterns of analogous (diene)iron tricarbonyl systems.

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