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NMR studies of some η^4-diene-rhodium(I) and main group metal derivatives of functionally substituted cyclopentadienes

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Abstract

The carbon-13 NMR spectra of twenty four acyclic and cyclic η^4-1,3-, 1,4- and 1,5-diene-rhodium(I) complexes of type η^5-C_5H_4XRh (η^4-diene), (X = H, Cl, Ph, CO_2CH_3 or CHO) are described. Each diene type can be easily distinguished from the values of its ^{103}Rh–^{13}C coupling constants and olefin–carbon coordination shifts. The effects of methyl substituents on the relative chemical shifts of the acyclic η^4-1,3-diene carbon atom are broadly similar to that in analogous η^4-dienetricarbonyliron systems, but the metal–carbon coupling constants imply a greater degree of retrodative bonding in the case of the rhodium complexes. The largest coordination shifts are found for the β olefin carbons of the 1,4-diene complexes. The unusual metal–carbon coupling in these complexes are a reflection of the strained conformation adopted on bonding to rhodium, and do not suggest conjugative interaction between the two alkene functions. The spectra of the 1,5-diene complexes show the expected trend resulting from a reduction in strain energy relative to that for the previous case. The spectra of the η^5-cyclopentadienyl groups in these complexes are discussed in terms of a small contribution from either an η^3-allyl-η^2-ene or a η^4-diolefin-η^1-alkyl rotamer to the metal–ring bonding scheme; the rotamer type is governed by the cyclopentadienyl ring substituent and counter diene ligand. Several functionally-substituted cyclopentadienide salts have been examined by variable temperature hydrogen-1 and carbon-13 NMR spectroscopy. The fluxional behaviour of $Tl^I(C_5H_4NO_2)$ and $K(C_5H_4CHO)$ demonstrate how the Lewis acid character of the metal ion and the electron-accepting nature of the ring substituent control the structural preference for a form in which the substituent is either co-planar or orthogonal with respect to the cyclopentadienide group. Two dimensional ^1H–^{13}C NMR spectra and simulation techniques permitted unambiguous assignment of ring nuclei. The chemical ionisation and fast atom bombardment mass spectra of several of the thallium(I) complexes reveal considerable association in the vapour state.

Introduction

Although a large number of η^4-diene-rhodium(I) complexes are known and the mechanism of η^4-diene isomerisation has been studied [1] there are few reports of any systematic investigations of complexes of type $(\eta^5C_5H_4X)Rh(\eta^4\text{-diene})$ (X = Cl, Ph, CO_2Me, CHO; diene = acyclic or cyclic 1,3-; 1,4-; or 1,5-diene) by carbon-13 NMR spectroscopy. Some spectra–structure correlations have been made by Powell and Russell [2] for $(\eta^5\text{-}C_5H_5)Rh(\eta^4\text{-}L)$ (L = η^4-1,3-dienol, dienal or dienone ligand) while Gibson and Ong [3] carried out a comprehensive carbon-13 NMR study of $(\eta^4\text{-1,3-diene})Fe(CO)_3$ complexes.

In this latter study it was concluded that metal–olefin retrodative bonding was of little importance. Our results for related rhodium(I) complexes of η^4-1,3-dienes indicate that such bonding is of considerable importance in these systems. The result is not unexpected in view of the relative π acidities of the carbonyl and cyclopentadienide ligands. While there has been some carbon-13 NMR analysis of η^4-1,5-diene complexes of rhodium(I) [4,5], the corresponding η^4-1,4-diene complexes scarcely feature in the literature [6]. Our spectral assignments indicate that the largest coordination shifts are experienced by the internal olefin carbon atoms of the acyclic 1,4-diene complexes. The unexpected result presumably stems from the conformational changes which accompany complexation [7] and the proximity of the two π-systems of the diene, which results in unusual anisotropic shielding effects. Lock and Powell have previously reported [8] a correlation between $\delta(^{13}C)$ and the strength of the metal-alkene interaction for several rhodium-η^4-2,3 dimethoxycarbonylbicyclo[2.2.1]heptadiene complexes. While this type of correlation is reasonable within a closely related series it cannot be used as a means of distinguishing 1,4- and 1,5-diene–metal interaction.

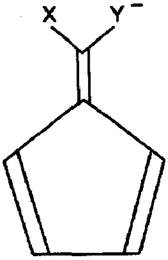
A clear distinction of diene type can, however, be made on the basis of the relative magnitude of the metal-olefin carbon coupling constants. We also present data for the η^5-cyclopentadienyl (Cp) counter ligand which exhibits a small degree of ring slippage [9] in all of the complexes. We have previously demonstrated that the nature of this slippage is controlled by the presence of electron accepting groups in the Cp ring and the type of counter ligand from ^1H NMR and single crystal X-ray studies [7,10]. Our present results indicate that consideration of $^{13}C-^1H$ coupling constants for the Cp ring is useful in the distinction of contributions from η^3-allyl-η^2-ene and η^4-diolefin-η^1-alkyl rotamers to the metal–Cp bonding scheme. We also report the $^1H/^{13}C$ analysis of several main group metal cyclopentadienide salts. Boche et al. [11], studied the fluxional behaviour of several monosubstituted cyclopentadienides of lithium and concluded that ion pair effects were of no decisive importance in determining the nature of the species in solution. Our present and previous results [12] for related derivatives of thallium(I), sodium and potassium clearly demonstrate that all the species exist as tight ion pairs even in solvents of high donor number such as dimethylsulphoxide, and that the preference for the planar form (A) or orthogonal form (B) is determined by the electron accepting

Table 1

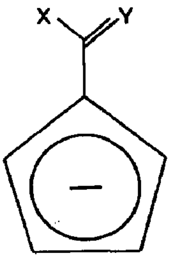
Analytical data for (η^5-C_5H_4X)Rh(η^4-diene) complexes

Diene	X	Colour	M.p. [a] (°C)	Analyses (Found (calcd) (%))		M [b]
				C	H	
2,3-Diphenylbuta-1,3-diene	CHO	yellow	130	65.3 (65.7)	4.6 (4.7)	402
trans,trans-Diphenylbuta-1,3-diene	CO_2Me	orange	154	63.5 (63.9)	4.7 (4.9)	432
2,4-Dimethylpenta-1,3-diene	CO_2Me	red	oil	52.0 (52.2)	5.9 (6.0)	322
Penta-1,4-diene	CHO	red	oil	49.7 (50.0)	6.2 (4.9)	264
2,5-Dimethylhexa-1,5-diene	Ph	yellow	73	64.2 (64.4)	6.3 (6.5)	354
2,5-Dimethylhexa-1,5-diene	Cl	yellow	65	50.1 (49.9)	6.0 (5.8)	312/ 314
1,5-Cyclooctadiene	Cl	yellow	96	50.2 (50.2)	5.1 (5.1)	310/ 312

[a] Uncorrected. [b] Parent ion in EI mass spectrum



(A)



(B)

ability of the ring substituent and the Lewis acidity of the metal cation. These two effects explain why some of the complexes are fluxional ((**A**) ↔ (**B**)) while other adopt exclusively form (**A**) or (**B**). It is generally assumed that thallium(I) cyclopentadienides are monomeric and exhibit predominantly covalent characteristics in the vapour state [13]. We present chemical ionization (CI) and FAB mass spectral data for several thallium(I) derivatives that indicate that the solid state chain structure is not completely fragmented in the vapour phase.

Experimental

All reactions were carried out under nitrogen in dry oxygen free solvents. Dienes were purchased from Aldrich or Wiley Organics Limited and used without further purification. All but seven of the rhodium complexes have been previously characterised [7]; analytical Data for the new complexes are presented in Table 1.

Preparation of cyclopentadienide salts

Thallium(I) nitrocyclopentadienide was prepared in 82% yield by aqueous metathesis in aqueous solution involving equimolar amounts of thallium(I) acetate and sodium nitrocyclopentadienide [14]. The product was purified by sublimation at 10^{-3} mmHg * and 100 °C to give an orange solid which decomposes at 152–155 °C. (Found: C, 19.3; H, 1.4. $C_5H_4NO_2Tl$ calcd.: C, 19.1, H, 1.3%), $\nu(NO_2)$ 1510 and 1342 cm^{-1}. Thallium(I) ethoxycarbonylformylcyclopentadienide was obtained in 15% yield by metathesis involving aqueous solution of the corresponding sodium salt [15] and thallium(I) acetate. Sublimation as before gave a yellow solid m.p. 70–72 °C. (Found: C, 29.6; H, 2.6. $C_9H_9O_3Tl$ calcd.: C, 29.2; H, 2.4%). $\nu(CO)$ at 1710 cm^{-1}.

The thallium(I) salts of chlorocyclopentadiene [16] phenylcyclopentadiene [12], methoxycarbonylcyclopentadiene [17] and cyclopentadiene [18] were prepared and characterised as previously described. Infrared spectra were recorded on a PE 577 instrument and mass spectra on a Kratos MS 80 instrument. Chemical ionisation mass spectra were determined with ammonia as ionising reactant, and FAB spectra were obtained with a dimethylsulphoxide-glycerol matrix of the sample. ^1H and ^{13}C NMR spectra were recorded with Bruker WP 80, AC-P 250, and AM-500 MHz instruments equipped with an Aspect 3000 Data system. The simulation study of $K(C_5H_4CHO)$ and $Na(C_5H_4COCO_2Et)$ was performed with resolution enhancement using the 'PANIC' (Parameter Adjustment in NMR by Iterative Calculation) programme. The nuclei were assumed to be weakly coupled at 500 MHz and line shapes was taken to be Lorentzian (line width = 0.3 Hz).

Results and discussion

The ^{13}C NMR data for the acyclic alkyl substituted η^4-1,3-diene complexes are presented in Table 2. Comparison of the spectra of II, III and IX indicates that the α effect is more pronounced when the terminal methyl group is in a *syn* compared to an *anti* position and is largest when *gem* dimethyl groups are present on the diene terminus. The presence of central methyl groups also results in a pronounced deshielding of C(2) and C(3) in complex IV. Comparison of the data for IV and V shows that although all the diene carbon atoms are affected by an increase in the π-acid character of the counter ligand, the deshielding effect is most obvious for the central carbon atoms. This is consistent with a contribution from the diene LUMO (ψ_3) to the bonding scheme. The β, γ and δ effects in these complexes parallel those reported by Gibson and Ong [3], and illustrate the importance of the influence of steric factors on the δ values for the complexed diene carbon atoms. There has been some controversy over the relative importance of the diene LUMO (ψ_3) to the metal–olefin bonding scheme in this type of complex. In the case of (η^4-1,3-diene)$Fe(CO)_3$ systems the strongly π-acidities of the counter ligands would be expected to result in minimal metal–diene retrodative bonding. The extreme example [19] of [(η^4-hexakis(trifluoromethyl)benzene)-η^5-cyclopentadienylrhodium(I)] illustrates the importance of such bonding on variation of ligand and transition metal. There is ample evidence that retrodative bonding has an important role in η^4-1,3-diene-Rh^I Cp complexes when electron accepted groups are present on the central carbon atoms (C(2) and C(3)) of the diene [20]. Powell and Russell [2] have suggested that consideration of the $^1J(^{13}C-^1H)$ and $^1J(^{103}Rh-^{13}C)$ coupling con-

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* Non SI unit employed: 1 mmHg = (101325/760) Pa.

stants should assist the qualitative interpretation of the relative importance of σ-donor-π-acceptor interactions. In complex I the ${}^1J({}^{13}C-{}^1H)$ couplings for C(1) and C(2) are 158 and 167 ± 0.5 Hz, respectively. In complex VIII the corresponding values are 160 and 168 ± 0.5 Hz. Retrodative bonding should be more important for I since involvement of the diene LUMO (ψ_3) in VIII will entail loss of conjugative interaction between the phenyl substituents. It is apparent that the ${}^{103}Rh-{}^{13}C$ coupling constants (Table 2) provide a more sensitive indication of bonding in these complexes. The ${}^{103}Rh-{}^{13}C$ coupling constants for σ-bonded mononuclear alkyl compounds vary from 17–26 Hz [21,22] while those for formally isolated η-bonded olefinic groups vary between 6–16 Hz [23]. The results in Table 2 do indicate a correlation between upfield shifts of the inner and outer diene carbon atoms and the metal–carbon coupling. For complexes in which retrodative metal–diêne bonding is expected to be important the metal-outer carbon coupling constants vary from 16.2 to 17.6 Hz, whereas the corresponding variation for the inner carbons is 6.2–8.0 Hz. In complexes II, III, VII and IX the different metal carbon couplings reflect the strength of metal–diene bonding. The bonding between rhodium and the olefin carbon atoms is expected to be asymmetric in these complexes mainly because of steric factors, but the results are consistent with those of Lock and Powell who found a similar correlation between ${}^{103}Rh-{}^{13}C$ couplings and metal–carbon bond strength for substituted η^4-norbornadiene derivatives [8]. The data for complexes II, VII and IX demonstrates that metal–carbon coupling is transmitted through an extra carbon atom when an *anti* methyl group is present on the diene. The anomalous results for complex VIII in which the ${}^1J({}^{103}Rh-{}^{13}C)$ values are 14.7 and 8.0 ± 0.3 Hz for the outer and inner diene carbons, show that when retrodative bonding is less important the difference in both coupling constants and chemical shifts for the two types of diene carbon atoms is appreciably reduced. Complex VI provides a significant contrast to VIII. The data shows that retrodative bonding is particularly important in the former case.

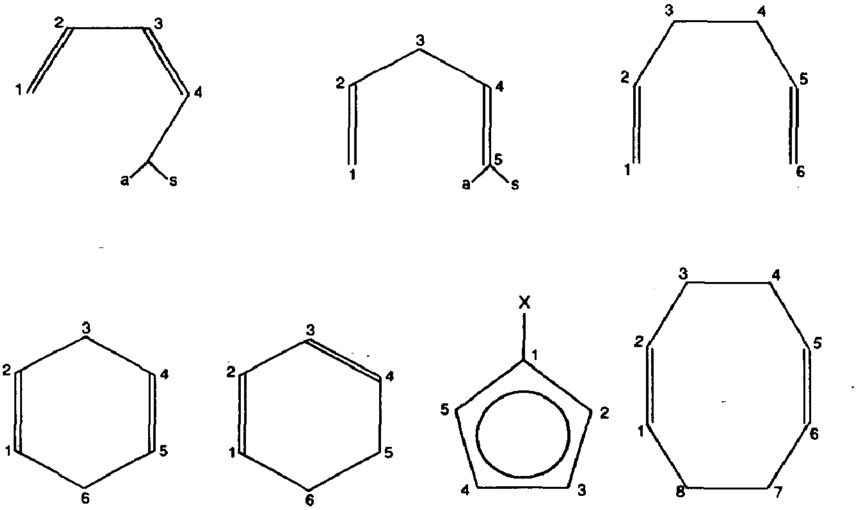


Fig. 1. Numbering system used for the ($\eta^5 C_5H_4X$)Rh(η^4-diene) and M(C_5H_4X) complexes.

Table 2

Carbon-13 chemical shifts (δ(ppm)) relative to internal $SiMe_4$ for (acyclic-1,3-diene)Rh(CPX) complexes in $CDCl_3$ at 313 K with diene coordination shifts [a] and ^{103}Rh coupling constants [b]

Diene	η^4-1,3-Diene				Me	X	η^5-Cp		
	C(1)	C(2)	C(3)	C(4)			C(1)	C(2) and C(5)	C(3) and C(4)
Buta-1,3-diene	32.50	76.82	76.82	32.50		H			
(I)	(84.10)	(60.38)	(60.38)	(84.10)	–			85.40	
	[17.0]	[8.0]	[8.0]	[17.0]				[5.2]	
cis-Penta-1,3-diene	36.71	83.38	80.26	47.15	15.51	CO_2Me	89.81	85.94 85.75	87.11 86.37
(II)	(79.88)	(47.25)	(52.05)	(79.44)	(a)	51.32			
	[17.2]	[6.2]	[6.6]	[16.9]	[5.0]	166.61	[5.5]	[4.4] [4.4]	[5.0] [5.0]
trans-Penta-1,3-diene	34.31	76.74	81.98	52.94	20.92	CO_2Me	89.44	87.34	88.42 88.04
(III)	(80.14)	(60.84)	(50.92)	(76.78)	(s)	51.34			
	[17.6]	[8.2]	[7.5]	[16.2]		166.42	[4.8]	[4.8] [4.7]	
2,3-Dimethylbuta-1,3-diene	37.79	93.22	93.22	37.79	19.30	CO_2Me	92.70	85.61	85.40
(IV)	(75.36)	(50.1)	(50.1)	(75.36)		51.15			
	[16.2]	[7.8]	[7.8]	[16.2]		165.10	[5.0]	[4.5]	[5.1]
2,3-Dimethylbuta-1,3-diene	38.79	94.91	94.91	38.79	20.02	CHO	99.36	84.85	88.54
(V)	(74.36)	(48.4)	(48.4)	(74.36)		185.03			
	[16.6]	[7.8]	[7.8]	[16.6]			[5.1]	[4.6]	[4.6]

2,3-Diphenylbuta-1,3-diene	40.05	100.47	100.47	40.05	Ph	CHO	99.35	85.14	90.70
(VI)	(76.27)	(49.33)	(49.33)	(76.27)	138.81	185.61			
					130.73				
	[16.2]	[7.6]	[7.6]	[16.2]	127.47		[7.3]	[3.8]	[4.8]
					127.11				
cis-3-Methylpenta-1,3-diene	35.22	84.03	95.25	47.50	15.07	CO_2Me	90.45	86.14	87.11, 85.91
(VII)	(77.80)	(49.72)	(29.52)	(65.92)	(a)	51.08			
	[17.2]	[6.6]	[6.2]	[16.6]	[4.0]	165.61	[5.1]	[3.9]	[5.0]
					23.65				
					(Me_3)				
trans,trans-1,4-diphenyl-	56.65	77.24	77.24	56.56	Ph	CO_2Me	90.48	88.32	88.56
buta-1,3-diene	(72.67)	(55.56)	(55.56)	(72.67)	125.53	51.39			
(VIII)					128.43				
	[14.7]	[8.0]	[8.0]	[14.7]	143.56	165.70	[4.6]	[5.2]	[5.3]
2,4-Dimethylpenta-1,3-diene	36.91	96.47	85.03	61.35	21.84	CO_2Me	92.93	86.36 87.17	86.73 89.06
(IX)	(76.88)	(31.17)	(57.42)	(72.53)	(a)	51.08			
	(17.6)	[6.3]	[7.1]	[16.2]	[3.0]	165.98	[5.5]	[4.4]	[4.8]
					23.79				
					(s)				
					34.77				
					(2)				

[a] Values (ppm) given in parentheses. [b] Values (±0.3 Hz) given in square brackets.

Table 3

Carbon-13 chemical shifts (δ(ppm)) relative to internal $SiMe_4$ for (acyclic-1,4-diene) Rh(CPX) complexes in $CDCl_3$ at 313 K with diene coordination shifts [a] and ^{103}Rh coupling constants [b]

Diene	η^4-1,4-Diene					Me	X	η^5-Cp		
	C(1)	C(2)	C(3)	C(4)	C(5)			C(1)	C(2) and C(5)	C(3) and C(4)
Penta-1,4-diene	44.76	28.32	30.07	28.32	44.76		CHO	102.92	84.88	90.54
(X)	(68.08)	(105.14)	(6.89)	(105.14)	(68.08)		183.62			
	[14.7]	[8.4]	[2.6]	[8.4]	[14.7]			[4.5]	[4.3]	[4.0]
2-Methylpenta-1,4-diene	41.00	41.20	36.32	21.28	39.97	30.74	H	–	85.62	–
(XI)	(74.93)	(102.95)	(6.25)	(115.13)	(70.97)					
	[14.7]	[8.6]	[2.9]	[8.8]	[14.7]				[4.4]	
2-Methylpenta-1,4-diene	43.74	45.03	35.94	26.05	43.35	20.24	CO_2Me	92.93	86.95 86.36	89.96
(XII)	(72.2)	(99.11)	(6.62)	(110.36)	(67.59)		51.08			
	[15.1]	[8.8]	[2.9]	[8.8]	[15.1]			[5.0]	[4.0] [4.0]	[4.0]
2-Methylpenta-1,4-diene	45.65	48.16	35.94	28.05	45.00	30.15	CHO	103.46	85.10 84.90	92.21 91.21
(XIII)	(70.29)	(95.99)	(6.62)	(108.36)	(65.94)		183.33			
	[14.6]	[8.8]	[2.9]	[8.8]	[14.6]			[3.9]	[3.9] [3.9]	[4.4] [4.4]
3-Methylpenta-1,4-diene [c]	41.71	36.12	35.73	36.12	41.71	19.23	CO_2Me	91.92	86.05	88.25
(XIV)	(71.44)	(106.33)	(5.73)	(106.33)	(71.44)		51.08			
							165.53			
	[14.7]	[8.6]	[2.9]	[8.6]	[14.7]			[4.7]	[4.1]	[4.4]
2,4-Dimethylpenta-1,4-diene	45.74	47.99	41.65	47.99	45.74	30.61	CHO	103.81	85.29	92.86
(XV)	(66.37)	(95.57)	(5.73)	(95.57)	(66.37)		183.66			
	[14.7]	[10.3]	[2.9]	[10.3]	[14.7]			[4.2]	[3.7]	[4.4]
cis-1,4-Hexadiene	42.80	22.71	27.10	29.41	70.96	14.13	CHO	103.21	87.80 87.51	93.19 92.66
(XVI)	(71.72)	(102.34)	(4.16)	(98.19)	(66.0)		183.43			
	[15.1]	[8.4]	[2.9]	[14.6]				[5.0]	[3.6] [3.6]	[4.6] [4.6]

[a] Values (ppm) given in parentheses. [b] Values (± 0.3 Hz) given in square brackets. [c] Major isomer.

Acyclic η^4-1,4-dienes

Carbon-13 NMR spectral data for this type of complex are rather sparse [6], since the conditions required for diene-metal interaction often result in the isomerisation of the 1,4-diene [24].

Data for representative alkyl-substituted acyclic-1,4-dienerhodium(I) complexes are presented in Table 3. The ^{13}C–^{103}Rh coupling constants for terminal and internal olefin carbons are 14.7, and 8.4–10.3 ± 0.3 Hz, respectively. Comparison of the value with those expected for diolefin-rhodium(I) complexes in which the chelating groups may be regarded as isolated, indicates that agreement is not good. In complexes such as $[\eta^5\text{-}C_5H_4COCH_3Rh(\eta^2\text{-}C_2H_4)_2]$ [12] the metal–alkene carbon coupling is 13.2 ± 0.3 Hz which is close to the corresponding values found for 1,5-diene complexes (Table 4). The results given in Table 3 show that the metal–olefin coupling constants are intermediate between those found for formally isolated and formally conjugated diolefin-rhodium systems. A recent structural analysis of uncomplexed penta-1,4-diene demonstrated that no conjugative interaction exists in this molecule [25]. The single crystal X-ray structure of XV [7] shows that the olefin C–C bond lengths are very similar to those found in related rhodium(I) complexes of butadiene [20], and cyclooctadiene [10]. The quality of the X-ray data for XV was insufficient to demonstrate any inequalities in rhodium–olefin bond lengths but they do show the highly strained nature of the complexed diene. The two alkene functions in this complex are non-parallel (angle of intersection 21.2°) which stems from the severe non-bonded interactions expected for the terminal *anti* hydrogen atoms in a structure in which these groups remained parallel. The $^1J(^1H$–$^{13}C)$ coupling constants for C(1), C(2), and C(3) in X are 156.3, 166.2, and 132.7 ± 0.5 Hz, respectively. These values do not correlate with appreciable conjugative interaction and a more likely explanation emerges from the single crystal X-ray and carbon-13 NMR analysis of dichloro(η^4-3-methylcycloocta-1,4-diene)palladium(II) by Wing et al. [27]. This study shows that the metal–olefin carbon bond length correlates with the upfield coordination shift. The β-carbon atoms of the 1,4-diene are appreciably closer to the metal and resonate to higher field of the corresponding α-carbons. Our assignment of α- and β-olefin carbons was made by selective decoupling experiments and the trend would suggest a similar asymmetric bonding arrangement. Of considerable interest is the small metal–allylic carbon coupling (2.7 ± 0.3 Hz) observed in the spectra of these complexes. A similar coupling was previously reported for norbornadienerhodium(I) complexes [28]. This coupling is of the through-space type which is also observed for *anti*-methyl groups in 1,3-dienerhodium complexes (Table 2). Table 4 shows the carbon-13 spectral data for some acyclic 1,5- and cyclic 1,3-, 1,4- and 1,5-diene complexes. The results for the acyclic (XVII–XIX) and (XX–XXII) 1,5-diene complexes are in direct contrast to those in Table 3. While the upfield shifts of the olefinic carbons are somewhat smaller than those found in the corresponding ethene derivatives [29], the ^{103}Rh–^{13}C couplings are remarkably similar and consistent with symmetrical metal–olefin bonding. The effect of alkyl substitution on the values for C(2) and C(5) in XVIII and XIX is very similar to that found in η^2-propene-rhodium(I) systems [30], and no metal–allylic carbon coupling was observed for the 1,5-diene complexes. Complex XXIII shows the largest coordination shift of this series, which is inconsistent with extent of olefin–metal interaction. The single crystal X-ray structure of η^5-(cyclopentadienyl) rhodium(I) (3-methoxy-carbonylcyclohexa-1,4-diene) demonstrates that the 1,4-di-

Table 4

Carbon-13 chemical shifts (δI(ppm)) relative to internal $SiMe_4$ for acyclic-1,5-diene, cyclic-1,3-diene, cyclic 1,4-diene and cyclic 1,5-diene complexes of type: (diene)Rh(CPX) in $CDCl_3$ at 313 K with diene coordination shifts [a] and ^{103}Rh coupling constants [b]

Diene	η^4-Diene		Me	X	η^5-Cp		
	C(olefin)	C(aliphatic)			C(1)	C(2) and C(5)	C(3) and C(4)
1,5-Hexadiene (XVII)	40.77, C(1,6) (74.07), [13.2] 68.20, C(2,5) (65.03) [13.2]	33.47, C(3,4)	–	CO_2Me 51.27 165.40	93.12 [4.3]	88.12 [3.7]	90.26 [3.7]
2,5-Dimethylhexa-1,5-diene (XVIII)	43.69, C(1,6) (66.09), [13.9] 82.05, C(2,5) (63.42) [13.8]	39.31, C(3,4)	31.98	Ph 125.80 126.14 128.53 134.49	106.37 [3.1]	87.63 [3.9]	89.47 [3.5]
2,5-Dimethylhexa-1,5-diene (XIX)	54.62, C(1,6) (64.26), [13.7] 83.59, C(2,5) (61.58), [13.6]	39.32, C(3,4)	29.92	Cl	100.14 [5.0]	87.68 [4.3]	90.47 [3.2]
1,5-Cyclooctadiene (XX)	66.45, C(1,2) (62.29), [13.9]	32.17, C(3,4)	–	CO_2Me 51.30 165.66	93.19 [4.0]	87.92 [3.7]	90.39 [3.7]
1,5-Cyclooctadiene (XXI)	64.27, C(1,2) (64.47), [13,9]	32.17, C(3,4)	–	CPh_3 126.27 126.92 130.69 147.26	116.65 [5.0]	85.68 [3.8]	89.34 [3.8]
1,5-Cyclooctadiene (XXII)	66.40, C(1,2) [62.84], [13.9]	32.21	–	Cl	98.67 [3.7]	84.67 [3.4]	86.99 [3.9]
1,4-Cyclohexadiene (XXIII)	32.84, C(1,2) (91.81), [10.3]	29.57 [2.7]	–	H		83.54 [4.9]	
1,3-Cyclohexadiene (XXIV)	55.20, C(1,4) (69.26), [16.4] 75.87m, C(2,3) (50.40), [7.6]	26.71	–	H		82.53 [5.2]	

[a] Values (ppm) in parentheses. [b] Values (± 0.3 Hz) given in square brackets.

ene assumes a boat conformation on complexation [31]. The high reactivity of cyclic and acyclic 1,4-diene complexes of rhodium towards isomerisation compared to the inertness of corresponding 1,5-diene compounds is derived from the pronounced Van der Waals interactions which arise on complexation. The apparent paradox that norbornadiene [32] forms an extremely stable olefin complex with rhodium(I) is resolved on the grounds that little conformational change occurs on complexation and relief of steric strain is expected for such systems. The isomerisation of η^5-Cp Rh(η^4-1,3-COD) to the η^4-1,5-COD analogue shows that the driving force for such rearrangement is not the attainment of a conjugated structure but is simply related to relief of steric strain [33].

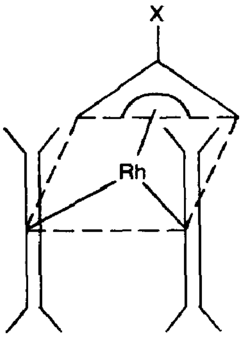
The abnormally large complexation shifts which occur for the olefin carbons of the 1,4-diene complexes stem mainly from steric rather than electronic effects.

η^5-Cyclopentadienyl groups

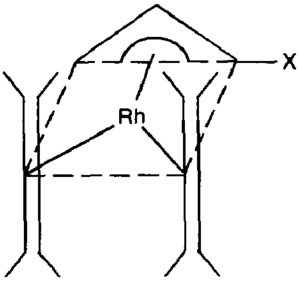
Carbon-13 spectral data is presented for the η^5-Cp species in Tables 2–4. A previous [10] ^{1}H NMR study of complexes of type η^5-$C_5H_4XRh(LL')$ (where X = CO_2Me, CN, CHO and $COCO_2Et$ and LL' = bis-η^2-ethene or chelating η^4-1,4- or 1,5-diene) in conjunction with several single crystal analyses [7,10] has indicated that there is a small contribution from an η^3-allyl-η^2-ene rotamer to the ring–metal bonding scheme. The relative values for the ring hydrogen nuclei and the variation in signal movement with temperature in conjunction with differences in ^{103}Rh–^{1}H couplings were found to be a valuable aid in assignment of the extent of localisation [7]. We now extend this study to include systems in which X = Cl or C_6H_5. In these latter systems it has been proposed that the preferred rotamer should be one involving ring slippage of the η^4-diolefin-η^1-alkyl type [12,34]. There has been considerable interest [35] in the design of analogous cobalt(I) systems as catalysts and extent of ring slippage of the η^3-allyl-η^2-ene type has recently been correlated with the nature of X for some η^5-XC_5H_4Co(1,5-COD) complexes [36].

We were interested in the potential application of ^{13}C NMR spectroscopy to the study of ring slippage in the rhodium(I) complexes. Kohler [37] originally proposed a correlation between $\delta(^{13}C)$ of the ring junction carbon atoms vs. indenyl hapticity in η^5-C_9H_7Rh(olefin) complexes. The degree of η^3-allyl-η^2-ene ring slippage in these indenyl complexes is considerably greater than that found for related cyclopentadienyl complexes [38]. Marder et al. have recently confirmed that the downfield shift of the ring junction carbons in (η-indenyl)RhL_2 (L = η-C_2H_4, CO or PMe_3) correlates with the counter ligand δ-donor/π-acceptor properties [39]. Inspection of the data for representative Cp complexes in Tables 1–3 shows that the δ values for C(3) and C(4) are to low field of C(2) and C(5) but little value can be placed on this since Watts et al. [40] find a similar result for analogous ferrocene derivatives. Nixon [41] found that the relative magnitude of the ^1J(Rh–C) coupling constants in the Cp ring of η^5-$C_9H_7Rh(\eta^2\text{-}C_2H_4)_2$ follow the sequence J(Rh–C(1)) > J(Rh–C(2)) > J(Rh–C(3)) where C(3) is the ring junction carbon. In the case of the data presented here the corresponding J value for C(1) is usually the largest but those for C(2) and C(3) are very similar. This result is not unexpected since the degree of ring slippage is small. On decreasing the temperature however, the signals assigned to C(1), C(2) and C(5) move slightly upfield while that assigned to C(3) and C(4) moves more rapidly downfield, a result consistent with increasing localisation. In view of the results of Day et al. [34] on η^5-chlorocyclopentadienylrhodium(I) complexes, we expected that complexes XVIII, XIX, and XXII might demonstrate a contribution from the η^4-diolefin-η^1-alkyl rotamer. Distinction between the two types of distortion using NMR is expected to be somewhat difficult since the qualitative effect on the C(2) and C(3) signal movement and ^1J(Rh–C) couplings is expected to be similar. In view of this we examined the $^1J(^1H\text{–}^{13}C)$ coupling constants for a series of complexes. The values of $^1J(^{13}C\text{–}^1H(2))$ and $^1J(^{13}C\text{–}^1H(3))$ for XIV and XVII are 175.5 and 176.5 ± 0.5 Hz while the corresponding results for XVIII and XXII are 174.4 and 182.2 ± 0.5 Hz. This latter finding would be in agreement with a small contribution from a diolefin rotamer in which this ordering of ^{13}C–^{1}H couplings is expected [2].

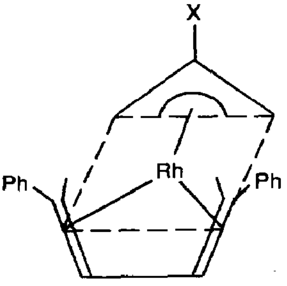
The origins of the preference for a particular rotamer may be found from examination of the conformation of the complex. Those systems which demonstrate a small contribution from an η^3-allyl-η^2-ene rotamer are, with the exception of the



(C)



(D)

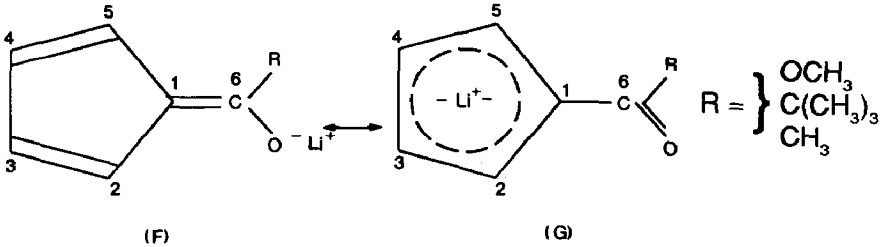


(E)

trans,trans-1,4-diphenylbuta-1,3-diene complexes, of type (η-C_5H_4X)Rh(η^4-diene) (where X = CO_2Me, CHO, CN, $COCO_2Et$, and diene = 1,4-, 1,5-diene or bis-ethene). Taking the ring to lie in the x, y plane the important bonding interactions between the CpRh fragment and the alkene functions will involve use of the metal d_{yz} and d_{xz} orbitals. The crystal structure of these complex [7,10] type shows that the alkene groups are almost parallel to the ring substituent group X as in **C**. The ring e_1+ and alkene π–π orbital combination will be involved in competitive overlap for d_{yz} while the other principal interaction involves competition between e_1- and $\pi^\star+\pi^\star$ for d_{xz} [42]. When X is electron accepting it is expected that the e_1- orbital will become stabilized with respect to e_1+ [43]. The net consequence is that there is a more effective competition between e_1+ and the alkene combination π–π for d_{yz}. The energy difference between $\pi^\star+\pi^\star$ and e_1- is increased and competitive overlap is diminished. The Cp ring then adopts more of the character of e_1- i.e. an η^3-allyl-η^2-ene distortion is imposed on the system. There is ample solution spectroscopic evidence that this distortion becomes more pronounced as the electron accepting nature of X increases [10,36]. This will result in a larger energy difference between $\pi^\star+\pi^\star$ and e_1- and so reduce competitive overlap for d_{xz}. The results of Day et al. [34] and Bönnemann [35] suggest that when X = C_6H_5 or Cl, conformation **D** is preferred. In this situation the alkene double bonds cross the ring substituent X and the principal interactions involve competition between π–π and e_1- for d_{yz} and between $\pi^\star+\pi^\star$ and e_1+ for d_{xz}. The more important interaction is expected to be the former and the ring adopts more of the character of e_1+, i.e. a η^4-diolefin-η^1-alkyl distortion is imposed. We find that the electron-accepting nature of the ring substituent increases in the order: H < Cl ~ Ph < CO_2Me ~ CN < COMe < CHO < $COCO_2Et$ [12]. If conformation **C** was common to all these systems then little Cp ring distortion would be expected for the chloro- and phenyl-substituted systems [40]. It is not clear why there is a preference for conformation **D** in these cases. The only conjugated diene complexes which exhibit abnormal ^1H NMR spectra are those of type: η^5-C_5H_4XRh(η^4-*trans,trans*-1,4-diphenyl-buta-1,3-diene) (X = CO_2Me, CHO) [7]. In conjugated diene complexes the principal bonding interactions involve the diene HOMO (ψ_2) and e_1+ for d_{yz} and the diene LUMO (ψ_3) and e_1- for d_{xz}. Clearly, the energy matching of the competing ligand orbitals will be closer than that expected for analogous non-conjugated diene complexes so there is little preference for a particular rotamer. However, in the case of **E** use of the diene LUMO is disfavoured due to the consequent loss in conjugation between the terminal phenyl groups. This means that there is little competition between ψ_3 and e_1- for the metal d_{xz} orbital and the η^3-allyl-η^2-ene distortion is imposed on the Cp ring.

Main group metal cyclopentadienide salts

In recent years much activity has been directed towards the synthesis and utilisation of functionally substituted cyclopentadienide salts of lithium, sodium, potassium and thallium(I) [44]. These compounds offer alternative high-yield and selective routes to many full or half-sandwich transition metal complexes which are difficult to obtain by direct electrophilic substitution. In 1982 Boche et al. reported the fluxional behaviour of several lithium derivatives in which the Cp ring carries a methoxycarbonyl or a 2,2′-dimethylpropanoyl subsitutent [11]. The fluxional process involves interconversion of the planar conformation **F** and orthogonal conformation **G**.



MNDO calculations indicate that the planar form is more stable than the orthogonal form by 17.6 kJ mol^{-1} for $Li(C_5H_4COCH_3)$ which did not show fluxional behaviour. The resonance stabilisation in these enolate species explains why they might be expected to demonstrate fluxional behaviour and why they are inherently more stable than the parent system. It was concluded from the study of the lithium species that ion pair effects are of little importance in determining rotation about the C(1)–C(6) bond [11]. In order to test the generality of this statement we extended this study to include analogous cyclopentadienide derivatives of thallium(I), potassium and sodium [12]. Table 5 gives the NMR data for some representative complexes. Introduction of a substituent into the Cp ring lowers the symmetry from D_{5h} to C_{2v}. The four ring hydrogen atoms give one of three possible splitting patterns which are determined by chemical and/or magnetic inequivalence:

(1) The simplest pattern is one involving two apparent triplets for the two sets of ring hydrogens H(2),H(5) and H(3),H(4). This pseudo-A_2X_2 pattern indicates a structural preference for the orthogonal form **G** in solution. Rapid rotation about the C(1)–C(6) bond results in the same chemical and magnetic environments for H(2) and H(5) as well as H(3) and H(4). Detailed observation of these triplet patterns at 250 MHz does not suggest that the spectra are deceptively simple AA′XX′ systems. The A_2X_2 pattern is found when either the ring substituent is weakly electron accepting e.g. in $Li(C_5H_4CH{=}CH_2)$ and/or when the metal ion is a soft Lewis acid [12] e.g. in $Tl^I(C_5H_4X)$ (X = Ph, Cl, CO_2Me, CN, CHO). The

Table 5

Hydrogen-1 [a] and carbon-13 chemical shifts (δ(ppm)) for M(C_5H_4X) salts [b] in $(CD_3)_2SO$ relative to DSS (sodium 4,4-dimethyl-4-silapentanesulphonate) as internal standard at 304 K

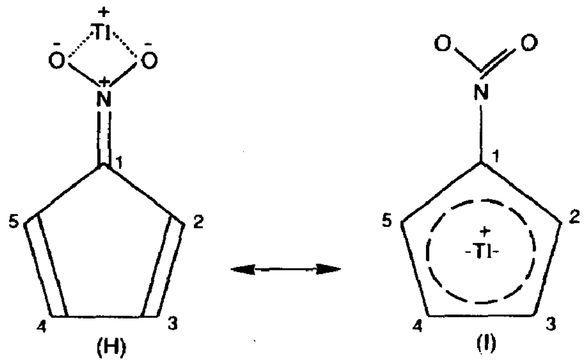
	^1H				X	^{13}C					X
	H(2)	H(5)	H(3)	H(4)		C(1)	C(2)	C(5)	C(3)	C(4)	
K(C_5H_4CHO) (XXV)	6.18	6.08	5.79	5.69	8.90 (s)	126.51	109.55	119.81	116.17	113.15	179.39
Na($C_5H_4COCO_2Et$) (XXVI)	6.36	6.21	5.86	5.74	4.21 (q) 1.26 (t)	120.65	113.24	118.46	117.16	114.83	15.83 60.79 170.51 174.63
(Tl(C_5HNO_2) (XXVII)	6.39		5.72			135.57	116.35		111.89		
Na($C_5H_4NO_2$) (XXVIII)	6.39		5.70			134.97	116.62		112.08		

[a] The cyclopentadienyl ring hydrogen atoms appear as multiplets in each case. [b] The numbering system for the ring nuclei is clockwise as shown in Fig. 3 and 5.

corresponding ^{13}C NMR spectra show a single peak for each of the atom pairs, C(2), C(5), and C(3), C(4).

(2) The second pattern approximates the ABCD situation in which four multiplets are observed for the ring hydrogens. This chemical and magnetic inequivalence stems from a preference for the planar form **F** in solution. The inherent asymmetry of the ring substituent in the case of XXV also gives one peak for each of the ring carbon nuclei. The conditions which favour this situation are the presence of a moderate to strongly electron-accepting ring substituent and/or a metal ion which has hard Lewis acid character e.g. $Tl^I(C_5H_4C(CN)=C(CN)_2$ [12], $K(C_5H_4X)$ ($X = COMe$, CHO) or $Na(C_5H_4COCO_2Et)$. The single crystal X-ray structure of $Na(C_5H_4COMe) \cdot THF$ supports the concept of an equilibrium between planar and orthogonal structures [46]. The coordination sphere sphere around each sodium ion comprises oxygen atoms from two C_5H_4COMe ligands, an oxygen atom from the THF molecule and an ion contact pair between the sodium and the five ring carbon atoms of the Cp ligand. Our observations [12] (on the fluxionality of $K(C_5H_4COMe)$, which has a coalescence temperature of 313 ± 3 K and an activation energy ($\Delta G^{\ddagger}$) for rotation about C(1)–C(6) of 61.4 ± 1 kJ mol^{-1}, are not in agreement with the conclusions of Boche et al. on the relative importance of ion pairs to this process. Alteration in hardness of the metal ion in this case gives the non-fluxional lithium and thallium(I) derivatives which show preference for the planar and orthogonal forms respectively. Compound XXV (Table 5) gives one sharp peak for each of the five ring carbon nuclei at 300 K in $(CD_3)_2SO$. Increase in temperature results initially in signal broadening for C(2), C(5) and C(3), C(4) while the nodal carbon C(1) and the substituent carbon C(6) give persistently sharp signals. Coalescence of C(2) and C(5) occurs at 363 K. The activation energy ($\Delta G^{\ddagger}$) for rotation about the C(1)–C(6) bond is estimated as 67.1 ± 1 kJ mol^{-1}, a value somewhat higher than that found for $K(C_5H_4COMe)$. The energy difference between planar and orthogonal forms in this latter case is expected to be smaller due to the decrease in electron-accepting character of the ring substituent. Compound XXVI also gives hydrogen-1 and carbon-13 spectral patterns which reflect a preference for the planar form **D** but we were unable to study the temperature dependence owing to the thermal instability in solution [15].

(3) The third pattern resembles the AA′XX′ case in which each set of ring hydrogens gives a symmetric ten line multiplet which shows that the planar form is preferred. This situation applies when the ring substituent is highly symmetric e.g. $Na(C_5H_4CN)$ [47], $Na(C_5H_4NO_2)$ [14] (XXVIII), and the unique case of $Tl^IC_5H_4NO_2$ (XXVII). Variable temperature NMR study of the sodium salt (XXVIII) of nitrocyclopentadiene shows that the energy difference between planar and orthogonal conformation is substantial as no appreciable change occurs from 298–373 K. Replacement of the sodium ion with the much softer thallium(I) ion gives the expected result. At ambient temperature XXVII gives two ten line multiplets at δ 6.39 and 5.72 ppm (Fig. 2). The lower field multiplet is slightly broadened. On warming a $(CD_3)_2SO$ solution to 333 K the centre portion of the lower field multiplet broadens appreciably while the intensity of the a, k and b, l [45] lines increases. A similar though less pronounced effect occurs for the upper field multiplet which is entirely consistent with the type of fluxional process. At 369 K the appearance of each multiplet is considerably simplified in that only five lines are observed for each half-spectrum and the intensity of the a, k and b, l lines is



now reduced relative to the centre portion. The spectral changes are similar to those reported by Roberts et al. [48] for certain primary Grignard reagents in which inversion of configuration at the CH_2Mg centre occurs rapidly at ambient temperature. Due to the chemical equivalence within each set of ring nuclei in XXVII, ^{13}C NMR spectrum gives only one signal each for C(1), C(2,5) and C(3,4). At 369 K the signal for C(1) is broadened while those assigned to C(2,5) and C(3,4) are split into asymmetric doublets. We interpret this evidence as an indication that near equal amounts of conformers **H** and **I** are present in solution at 369 K, and that conformer **H**, predominates at ambient temperature. There has been considerable controversy concerning the nature of the bonding in cyclopentadienylthallium(I) derivatives in the solid state and in solution [13,49]. It is certainly apparent that the ionic character in solution depends on the electron-accepting nature of the ring substituent [50,51]. Koridze et al. deduced that $Tl(I)C_5H_4CH(Me)Ph$ exists predominantly as tight ion pairs in THF and is less ionic in nature than the analogous potassium compound [52]. These conclusions emerged from consideration of the shielding of the ring carbon nuclei of the respective salts. The higher shielding found for the potassium compound was linked to a higher ionic nature in solution. Our results [12] for the thallium(I) and potassium salts of formyl- and ethanoyl-cyclopentadienide are in good agreement with those found by Koridze. Table 5 shows however, that when the ring substituent is strongly electron accepting the distinction is attenuated for XXVII and XXVIII. In considering the effects responsible for the fluxionality of several lithium Cp derivatives Boche et al. [11] concluded that ion pair effects were of little importance since the ^{13}C NMR spectral changes were almost the same when the solvent composition was altered from pure THF to the highly polar mixture THF · 2HMPT (HMPT = hexamethyl phosphoric triamide). We have not carried out any studies in moderately polar solvents like THF or CH_2Cl_2, but have specifically used a solvent of high donor number (DMSO) [53]. It is difficult to reconcile the trend in conformational preferences found for the lithium, sodium, potassium and thallium(I) cyclopentadienides with solvent-separated ionic species in solution. If such species were dominant in e.g. DMSO, then the role of the cation in controlling orthogonal/planar structural types should be minimal. It is clear however, that this is not the case and that there must be appreciable contribution from tight ion pair species even in highly polar solvents.

Assignment of NMR spectra of XXV and XXVI

Figure 3 shows the ^1H–^{13}C chemical shift correlation plot (HETCOR) of $K(C_5H_4CHO)$ in $(CD_3)_2SO$ at 304 K. In compounds of this type the ^{13}C δ values for C(2), C(5) usually resonate to low field of C(3) and C(4) and the chemical shift difference between C(2) and C(5) is invariably larger than that found for C(3) and C(4). [11,12]. Our results show a consistency with the latter observation for XXV and XXVI but not with the former. The ^1H NMR spectrum of freshly prepared solutions of XXV in D_2O closely resemble those found in $(CD_3)_2SO$. The former solutions exhibit a time dependence which involves preferential deuterium exchange at the C(2) and C(5) positions [12]. While the two lower field multiplets gradually decrease in intensity in the ^1H NMR spectrum, the corresponding ^{13}C NMR spectrum showed that (excluding the nodal carbon C(1)) the lowest and highest field ring carbon signals have decreased in intensity. This preferential deuterium exchange and the HETCOR plot thus permit assignment of the two sets of atom pairs. A similar situation exists for XXVI. The experimental and simulated spectrum for XXVI is presented in Fig. 4 and coupling constant data for XXV and XXVI are given in Fig. 5. The lower field multiplets (XXVI) appear as apparent quintets while the upper field multiplets resemble septets. Decoupling experiments were performed on XXV. Removal of the aldehyde coupling gave remarkably similar patterns for the ring hydrogens compared to XXVI. Unambiguous assignment of the ring nuclei

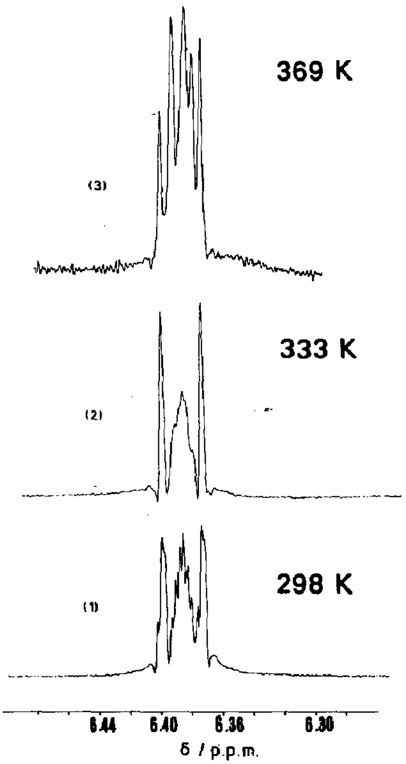


Fig. 2. The half-spectrum (250 MHz) of the AA′XX′ system of the ring hydrogen nuclei of $Tl^I(C_5H_4NO_2)$ at various temperatures in DMSO-d_6.

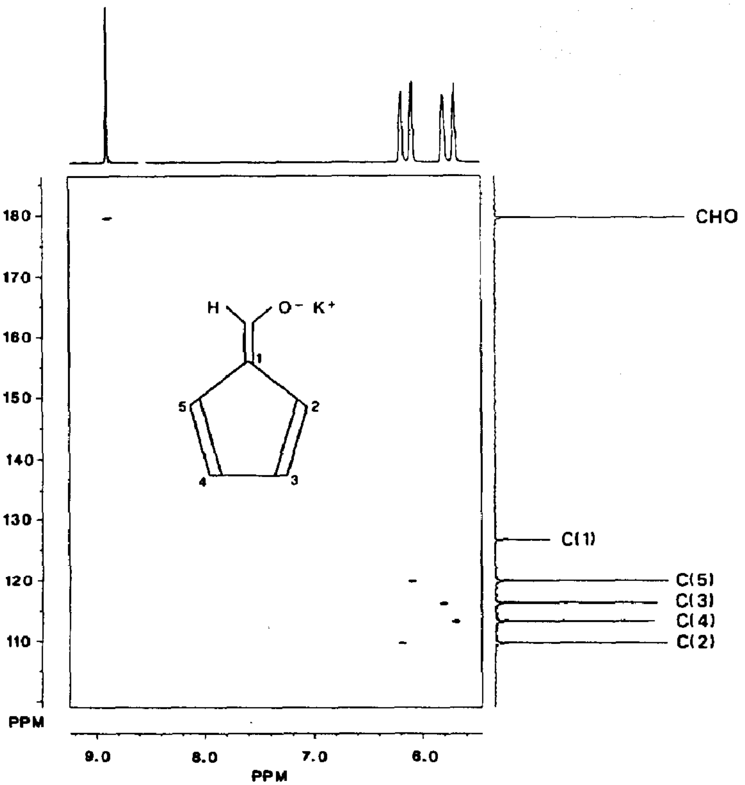


Fig. 3. The 2D 62.9 MHz ^{13}C-^{1}H chemical shift correlation plot (Hetcor) of $K(C_5H_4CHO)$ in DMSO-d_6 at 304 K.

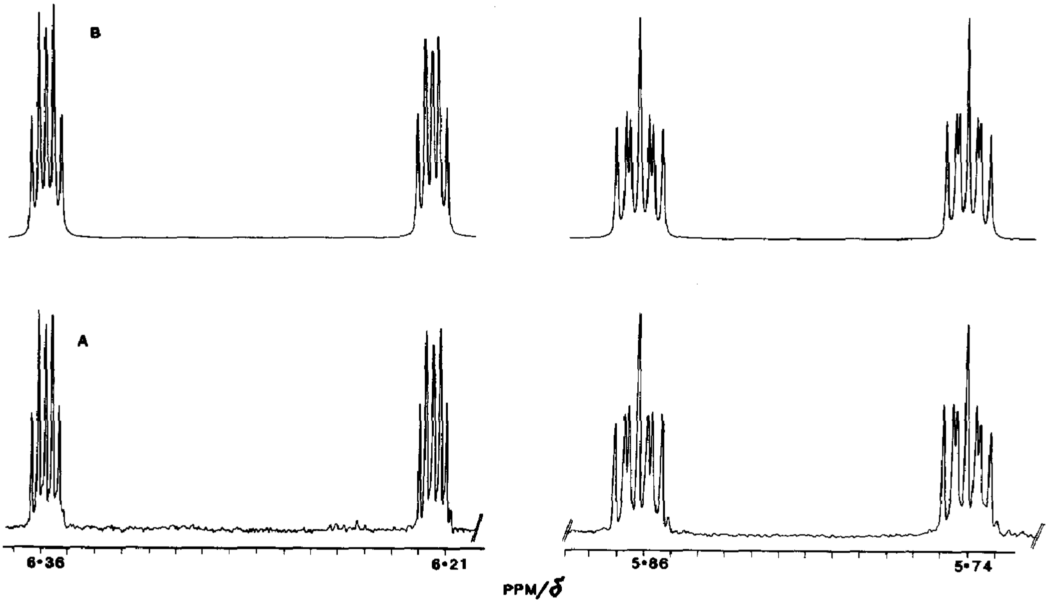
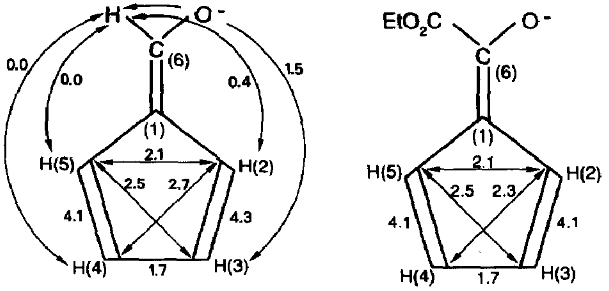


Fig. 4. Experimental (A) (500 MHz) and simulated (B) ^{1}H NMR spectrum of the ring nuclei of $Na(C_5H_4COCO_2Et)$ (XXVI).



(XXV) (XXVI)

Fig. 5. Coupling constant data for formylcyclopentadienide (XXV) and ethoxycarbonylformylcyclopentadienide (XXV) obtained from simulated spectra. (*J* ±0.05 Hz).

was effected by observing the aldehyde hydrogen-ring coupling pattern. In compounds with related fulvene structures such as 6-dimethylaminofulvene the substituent hydrogen exhibits appreciable coupling only to those ring hydrogens which have a *trans* relationship to it [54]. In these systems long range coupling from the substituent through five bonds is also found to exceed the corresponding four bond coupling. This latter finding does not required coplanarity of interacting nuclei as it occurs in (η^5-C_5H_4CHO)Rh^I(olefin) complexes in which there is a free rotation about the C(1)–C(6) ring bond. The former observation does however require a coplanar situation and is best understood on the basis of the extended W coupling mechanism. In the present case only H(2) and H(3) show appreciable coupling to the aldehydic hydrogen which permits assignment of the ring nuclei. Recent ^{1}H NMR studies on [($\eta^5C_5H_4Me$)Fe(CO)(L)I] (L = phosphine or phosphite) complexes show that the shapes of the four absorption envelopes found for the ring nuclei are controlled by the ^4J(H(2)–H(5)) and ^3J(H(3)–H(4)) couplings [55]. The spectra observed in the present case closely resemble those found for fulvene derivatives in which J(H(2)–H(3)) ≫ J(H(2)–H(4)).

Table 6

Characteristic mass spectral data for some $\eta^5C_5H_4XTl(I)$ complexes [a]

Complex	Ionisation mode [a]	*m/e* [b]	Relative intensity	Assignment
η^5-C_5H_5Tl	+CI	475	88.6	$[C_5H_5Tl_2]^+$
		271	13.1	$[C_5H_5TlH]^+$
		205	85.5	Tl^+
η^5-$C_5H_4COCO_2EtTl$	−EI/FAB	535	12.2	$[(C_5H_4COCO_2Et)_2Tl]^-$
		331	16.1	$[(C_5H_4COCO_2Et)_2H]^-$
		165	100.0	$[(C_5H_4COCO_2Et]^-$
		93	31.1	$[C_5H_4CHO]^-$
		65	45.5	$[C_5H_5]^-$
	+EI/FAB	751	1.4	$[C_5H_4COCO_2Tl_3]^+$
		575	11.8	$[C_5H_4COCO_2EtTl_2]^+$
		205	100.0	Tl^+
η^5-$C_5H_4NO_2Tl$	+CI	520	23.1	$[C_5H_4NO_2Tl_2]^+$
		316	39.3	$[C_5H_4NO_2TlH]^+$
		205	6.4	Tl^+

[a] *m/e* values quoted for Tl containing ions refer ^{205}Tl.

Mass spectra

The positive ion chemical ionisation and positive and negative ion fast atom bombardment mass spectra are presented for several representative thallium(I) compounds in Table 6. We have previously recorded the electron impact mass spectra of many analogous ($\eta^5C_5H_4X)Tl^I$ systems and noted that the sample is apparently monomeric in the vapour phase [56]. Our present results indicate that the zig-zag chain structure may not be entirely disrupted under less energetic conditions than electron impact. The production of $[CpXTl_2]^+$ species is most pronounced for the parent compound and the FAB spectra for (η^5-$C_5H_4COCO_2Et)Tl^I$ demonstrate the differing routes for chain degradation. It is quite likely that further studies of this type may reveal more highly associated species.

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