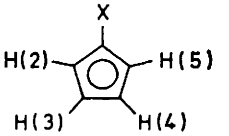
A Hydrogen-1 and Carbon-13 Nuclear Magnetic Resonance Study of the Bonding in some Monosubstituted Cyclopentadienyl Complexes of Rhodium(I) and the Crystal and Molecular Structure of Cyclo-octa-1,5-diene(η-methoxycarbonyl-cyclopentadienyl)rhodium(I)

By **Michael Arthurs** and **S. Martin Nelson,*** Department of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland
Michael G. B. Drew,* Department of Chemistry, The University, Whiteknights, Reading RG6 2AD

The ^1H and ^{13}C n.m.r. spectra of a series of monosubstituted η-cyclopentadienylrhodium(I) complexes of the types [$RhL_2(C_5H_4X)$] and [$Rh(LL)(C_5H_4X)$] are described (L = ethylene or CO; LL = a 1,3-, 1,4-, or 1,5-diene; X = Me, CMe_3, CO_2Me, CO_2Et, CO_2Pr^i, CHO, $COCO_2Et$, or CN). For complexes where the substituent X is electron-withdrawing in nature and where the neutral ligand is ethylene or a non-conjugated diene the ^1H spectra of the cyclopentadienyl ring protons show a novel temperature dependence (+40 to −60 °C) in $CDCl_3$ involving a chemical-shift cross-over without line broadening of the H(2), H(5) and H(3), H(4) resonances. In contrast, the n.m.r. behaviour of the complexes of conjugated dienes is normal. The unusual spectra observed for the non-conjugated alkene complexes are attributed to unequal barriers for the rotation of the cyclopentadienyl ring leading, at the lower temperatures, to preferential population of a particular rotamer state. A single-crystal *X*-ray structure determination of [Rh(cyclo-octa-1,5-diene)($C_5H_4CO_2Me$)] (1) suggests that the preferred rotamer in solution may be one in which the C_5 ring is bonded to the metal as an η-allyl *via* C(2), C(1), and C(5) [2.230(8), 2.256(6), 2.226(5) Å] with a weaker interaction *via* an alkene function localized between C(3) and C(4) [2.303(8), 2.294(7) Å]. A simple bonding model is proposed which relates the n.m.r. spectra of solutions to the structure of the solid and which accounts for the differences in behaviour between complexes of conjugated dienes on the one hand and those containing isolated double bonds on the other.

Crystals of (1) are triclinic, space group $P\bar{1}$, $Z = 2$, with a = 7.051(8), b = 8.390(8), c = 12.660(10) Å, α = 100.16(9), β = 101.33(8), γ = 105.95(11)°. The structure was solved by Patterson and Fourier methods from 2 023 independent reflections collected by counter methods and refined to R 0.039.

DURING the course of a study[1] of the isomerization of 1,4-dienes complexed to rhodium(I) in the complexes [Rh(1,4-diene)(η^5-C_5H_4X)] a novel temperature dependence of the ^1H n.m.r. spectra of the C_5H_4X ring protons was observed. This consisted in a chemical shift cross-over without line broadening of the H(2), H(5), and H(3), H(4) proton resonances.



The effect was noted to be dependent on the nature of the ring substituent X and on the nature of the co-ordinated diene. The present paper describes the results of a more systematic study of both the ^1H and ^{13}C n.m.r. spectra of a wider range of compounds which include ethylene, carbon monoxide, and 1,3-dienes as associated ligands. In order to assist the interpretation of the spectra a single *X*-ray structure determination of one representative complex was undertaken.

RESULTS AND DISCUSSION

The complexes investigated are of the types [RhL_2-(C_5H_4X)] or [$Rh(LL)(C_5H_4X)$] where L = ethylene or CO, LL = a symmetrical 1,5-, 1,4-, or 1,3-diene, and X = CHO, COOR (R = Me, Et, Pr^i), $COCO_2Et$, CN, Me, or CMe_3. Preparations are described in the Experimental section or in previous publications.[1,2]

*Hydrogen-*1 *N.M.R. Spectra.*—In the $CDCl_3$ spectra of rhodium(I) complexes of unsubstituted η^5-C_5H_5 the five ring protons are equivalent, appearing as a doublet, due to coupling with ^{103}Rh ($I = \frac{1}{2}$), in the τ 4—5 region. The ^{103}Rh–H coupling is independent of the nature of L and LL, being constant at 0.9 Hz. The signal moves slightly downfield on cooling to −60 °C but there is no change in the coupling and no broadening of the signal; as is general with η^5-C_5H_5 complexes the barrier to rotation of the ring about the metal–ring axis is small.[3]

For spectra of the complexes of monosubstitued η^5-C_5H_4X rings the ^1H n.m.r. spectra at 40 °C consist of two pseudo-triplets in the τ 4—5 region. One of the two resonances shows greater splitting than the other, occurring usually as a pseudo-triplet of doublets (Figure 1). For some of the complexes the more split resonance occurs to high field, with respect to the other, while in others it occurs to low field at this temperature. For some of the complexes, particularly those where L = ethylene and LL = an unconjugated diene, there are appreciable chemical-shift changes with temperature

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[1] M. Arthurs, M. Sloan, M. G. B. Drew, and S. M. Nelson, *J.C.S. Dalton*, 1975, 1794.

[2] S. M. Nelson, M. Sloan, and M. G. B. Drew, *J.C.S. Dalton*, 1973, 2195.

[3] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 114.

(Table 1). Invariably, the more-coupled resonance moves downfield on cooling to −60 °C while the other resonance moves, less rapidly, upfield. This applies irrespective of the relative chemical-shift positions of the more-coupled and less-coupled signals. For those cases where the more-coupled resonance occurs to high field at 40 °C there is therefore a convergence of the two resonances as the temperature is decreased. In some cases there is actually a chemical-shift cross-over. This occurs without line broadening or signal collapse. There are, however, certain changes in spectral complexity as coalescence is approached. In the 220 MHz spectra both signals assume an AB pattern near to coalescence while at the actual coalescence temperature the spectrum appears as a simple ^{103}Rh-split doublet. As the signals separate on further cooling the pattern approaches that of an AX system. This is illustrated in Figure 1 for the case of $[Rh(C_2H_4)_2(C_5H_4CO_2Me)]$. While signal coalescence and cross-over was observed for several of the complexes within the temperature range studied (+40 to −60 °C) it was clear that the spectra of several other complexes approach the coalescence condition at some higher or lower temperature. It was noted also that the temperature dependence is greater in the polar solvents, acetone and chloroform, than in *o*-dichlorobenzene or decalin (Figures 2 and 3). There were also small chemical-shift changes as the solvent was varied. Thus, the coalescence temperatures are solvent dependent. However, the direction of movement of a particular resonance as temperature was decreased was the same in all four solvents.

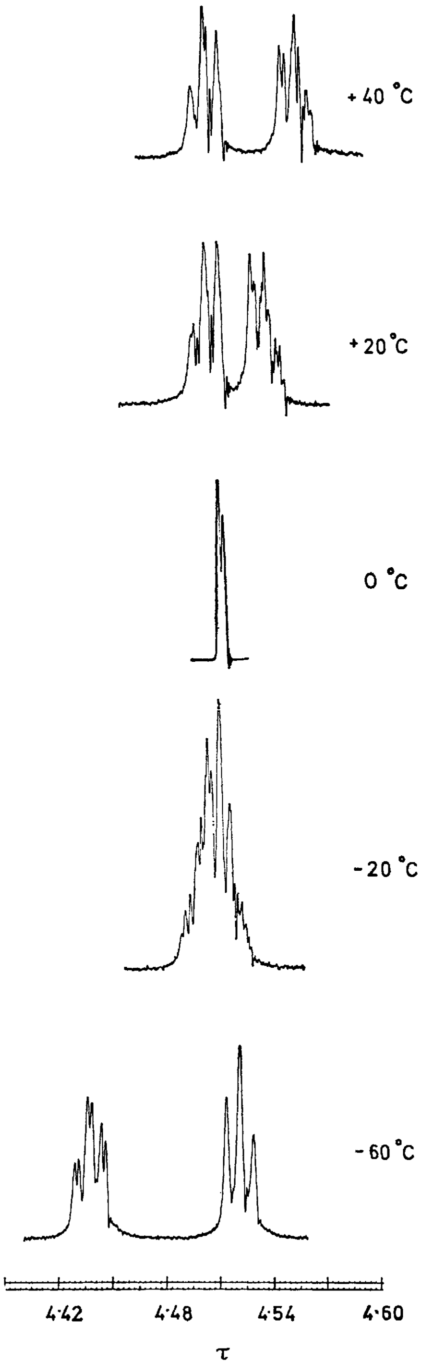

FIGURE 1 Hydrogen-1 n.m.r. spectra (220 MHz) in $CDCl_3$ of the cyclopentadienyl ring protons in $[Rh(C_2H_4)_2(C_5H_4CO_2Me)]$ at 40, 20, 0, −20, and −60 °C

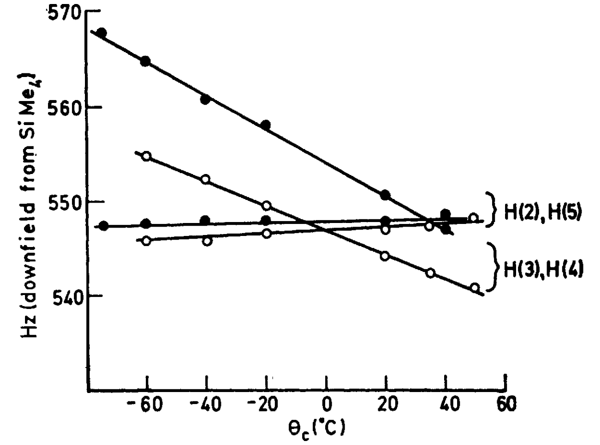

FIGURE 2 Temperature dependence of the chemical shifts of the H(2), H(5), and H(3),H(4) proton resonances of $[Rh(C_2H_4)_2(C_5H_4CO_2Me)]$ in $CDCl_3$ (○) and $[^2H_6]$acetone (●)

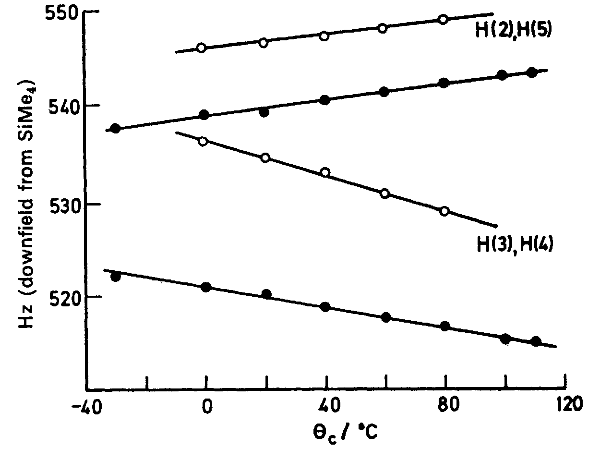

FIGURE 3 Temperature dependence of the chemical shifts of the H(2), H(5) and H(3), H(4) proton resonances of $[Rh(C_2H_4)_2(C_5H_4CO_2Me)]$ in *o*-dichlorobenzene (○) and decalin (●)

TABLE 1

Hydrogen-1 chemical shifts (τ) and ^{103}Rh–H coupling constants (Hz) for $[RhL_2(C_5H_4X)]$ and $[Rh(LL)(C_5H_4X)]$ complexes in $CDCl_3$ at 40 °C and (in parentheses) −60 °C

						a	
L (or LL)	X	H(2) and H(5)	H(3) and H(4)	Coalescence temperature (θc/°C)	$J[^{103}Rh–H(2),H(5)]$	$J[^{103}Rh–H(3),H(4)]$	$J[H(cp)–H(X)]$
C_2H_4	H	4.92	4.92		0.9	0.9	
	Me	4.68 (4.59)	5.04 (5.08)		0.8	0.6	0.4
	Bu^t	4.85 (4.80)	5.17 (5.17)		0.8	0.4	
	CO_2Me	4.48 (4.52)	4.58 (4.43)	0	0.4	0.8	
	CO_2Et	4.53 (4.57)	4.60 (4.45)	−20	0.4	0.8	
	CO_2Pr^i	4.56 (4.59)	4.66 (4.51)	−40	0.4	0.8	
	CHO	4.70 (4.72)	4.40 (4.28)		0.4	0.8	0.4 [H(3), H(4)]
	$COCO_2Et$	4.58	4.35		0.4	0.8	
	CN	4.48 (4.52)	4.58 (4.43)	0	0.4	0.8	
CO	H	4.36	4.36		0.9	0.9	
	Me	4.50 (4.42)	4.72 (4.74)		0.8	0.6	0.4
	CO_2Me	4.10 (4.12)	4.35 (4.25)		0.4	0.8	
	CHO	4.16 (4.17)	4.23 (4.17)	−60	0.4	0.8	0.4 [H(3), H(4)]
	$COCO_2Et$	3.83	4.18		0.4	0.8	
Penta-1,4-diene	H	4.70	4.70		0.9	0.9	
	CO_2Me	4.48 (4.52)	4.55 (4.41)	0	0.4	0.8	
	CHO	4.70	4.43		0.4	0.8	0.4 [H(3), H(4)]
3-Methylpenta-1,4-diene	H	4.80	4.80		0.9	0.9	
	CO_2Me	4.51 [b] (4.55) [b]	4.58 [b] (4.43) [b]	0	0.4	0.8	
		4.44 [c] (4.47) [c]	4.61 [c] (4.47) [c]	−60	0.4	0.8	
2,4-Dimethylpenta-1,4-diene	CO_2Me	4.61 (4.57)	4.61 (4.50)	40	0.4	0.8	
	CHO	4.79	4.44		0.4	0.8	0.4 [H(3), H(4)]
Hexa-1,5-diene	CO_2Me	4.64 (4.66)	4.80 (4.66)	−60	0.4	0.8	
	CHO	4.85	4.56		0.4	0.8	0.4 [H(3), H(4)]
2,5-Dimethylhexa-1,5-diene	CHO	4.93	4.53		0.4	0.8	0.4 [H(3), H(4)]
Cyclohexa-1,4-diene	CO_2Me	4.48 (4.51)	4.58 (4.43)	0	0.4	0.8	
	CHO	4.72	4.31		0.4	0.8	0.4 [H(3), H(4)]
	CN	4.50 (4.53)	4.59 (4.45)	0	0.4	0.8	
Cyclo-octa-1,5-diene	H	4.90	4.90		0.9	0.9	
Cyclo-octa-1,5-diene	CO_2Me	4.50 (4.54)	4.56 (4.41)	0	0.4	0.8	
		4.68	4.53		0.4	0.8	
	CHO	4.73	4.50		0.4	0.8	0.4 [H(3), H(4)]
Bicyclohepta-2,5-diene	CO_2Me	4.73 (4.75)	4.83 (4.76)	−65	0.4	0.8	
Cyclo-octa-1,3,5,7-tetraene	CO_2Me	4.55 (4.58)	4.58 (4.43)	−30	0.4	0.8	
Buta-1,3-diene	H	4.73	4.73		0.9	0.9	
	Me	4.78	4.90		0.6	0.4	0.4 [H(2), H(5)]
	Bu^t	4.83	4.83		0.6	0.6	
	CO_2Me	4.21	4.66		0.6	0.8	
	CHO	4.16 (4.14)	4.56 (4.58)		0.6	0.8	0.4 [H(3), H(4)]
2,3-Dimethylbuta-1,3-diene	CHO	4.33	4.62		0.6	0.8	0.4 [H(3), H(4)]
2,3-Dichlorobuta-1,3-diene	CO_2Me	4.16 (4.14)	4.56 (4.58)		0.7	0.9	
trans,trans-Hexa-2,4-diene	CO_2Me	4.53	4.88		0.8	0.9	
	CHO	4.66	4.66				
Cyclohexa-1,3-diene	H	4.79	4.79		0.9	0.9	
	CO_2Me	4.16	4.75		0.6	0.8	
	$COCO_2Et$	4.11	4.68		0.6	0.8	

[a] ±0.1 Hz. [b] *syn*-Methyl isomer. [c] *anti*-Methyl isomer.

The magnitude of the temperature dependence of the chemical shifts was notably less for complexes in which the neutral ligand was CO, though coalescence was observed in one such case. In the case of complexes of conjugated dienes the chemical shifts were virtually independent of temperature. It is noteworthy, also, that in these spectra the more-coupled resonance always occurred to high field.

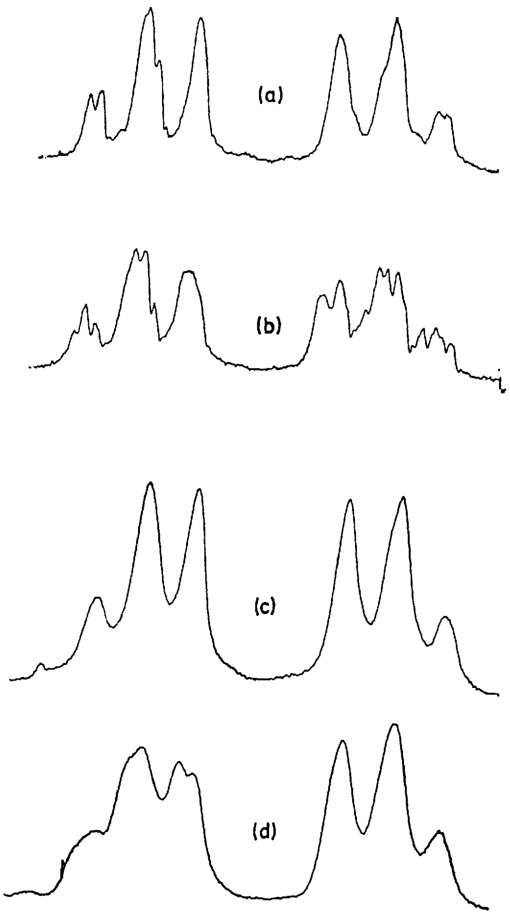

FIGURE 4 Normal [(b) and (d)] and ^{103}Rh-decoupled [(a) and (c)] spectra of [Rh$(C_2H_4)_2(C_5H_4CO_2Me)$] in $CDCl_3$ at 50 °C [(a) and (b)] and −60 °C [(c) and (d)]

Assignment of the ^{1}H *N.M.R. Spectra.*—Since the diamagnetic anisotropy effect of electron-withdrawing substituents such as $COCO_2Et$, CHO, CO_2R, and CN is expected to operate mainly at the 2- and 5-positions, as found for similarly substituted ferrocenes, cymantrenes, and cobalticenium salts,[4] it would be expected that the lower-field signal is due to H(2) and H(5). Also, since the electron-donating effect of an alkyl substituent is believed to operate mainly at the 3- and 4-positions,[5] the same relative ordering of the H(2), H(5) and H(3), H(4) chemical shifts would be expected. The situation is clearly more complex for several of the compounds described here. Before considering the assignment of the two resonances to particular pairs of protons it is first necessary to consider the origins of the small couplings.

In the simplest case where H(2) and H(5) on the one hand, and H(3) and H(4), on the other, are assumed to be equivalent, and where cross- and adjacent-coupling are assumed to be equal, the two resonances would be expected to appear as simple 1 : 2 : 1 triplets in the absence of any other coupling. It was apparent in most of the spectra that there was also unequal coupling of the two sets of protons to ^{103}Rh and that in some of the spectra (where X = CHO or CH_3) there was, in addition, coupling to substituent protons. Figure 4 compares the normal and ^{103}Rh-decoupled spectra at +50 and −60 °C. It can be seen that coupling to ^{103}Rh is greater for the protons which occur to high field at 50 °C, and to low field at −60 °C. It may be noted, further, that in the decoupled spectra the central line of each triplet is slightly split and scarcely more intense than the outside lines, indicating that cross- and adjacent-coupling of the ring protons are not equal.[6] We are indebted to Dr. R. J. Goodfellow of the University of Bristol for these measurements.

The complex [Rh(penta-1,4-diene)(C_5H_4CHO)] showed an apparent singlet at τ 0.22 for the formyl proton in $CDCl_3$ at 40 °C, a pseudo-triplet of quartets at τ 4.43 for one pair of ring protons [Figure 5(a)] and a pseudo-triplet at τ 4.70 for the second pair of protons. Irradiation at τ 0.22 produced a triplet of doublets for the lower-field resonance [Figure 5(b)] and only a slight sharpening of

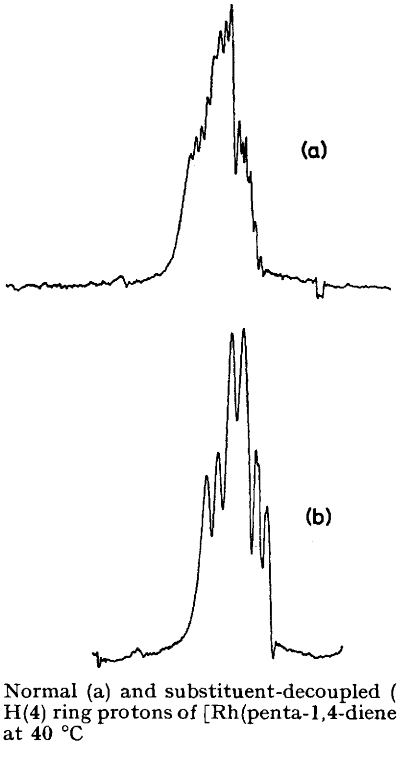

FIGURE 5 Normal (a) and substituent-decoupled (b) spectra of the H(3), H(4) ring protons of [Rh(penta-1,4-diene)(C_5H_4CHO)] in $CDCl_3$ at 40 °C

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[4] D. W. Slocum and C. R. Ernst, *Organometallic Chem. Rev. A*, 1970, **6**, 346.

[5] D. W. Slocum, C. R. Ernst, and W. E. Jones, *J. Org. Chem.*, 1972, **37**, 4278.

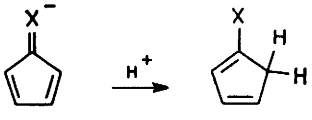
[6] D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, 1963, **38**, 470.

the components of the triplet at τ 4.70. Similarly, irradiation at τ 4.43 produced a sharpening of the ' singlet ' due to the formyl proton. Thus, the substituent coupling is greater to the same pair of protons that show the greater coupling to ^{103}Rh. It is worth noting that Kamezawa [7] has recently measured the substituent coupling in formylferrocene and found that the long-range coupling [to H(3) and H(4)] is larger than to H(2) and H(5), although the effect is small. If the same is true for the rhodium complex then the lower-field resonance is due to H(3) and H(4). However, more reliable criteria for assignment are considered later.

For the case of the methyl-substituted cyclopentadienyl complex $[Rh(C_2H_4)_2(C_5H_4Me)]$ irradiation at the methyl-group frequency produced a simplification of the lower-field resonance only. Again, this is the same signal that shows the greater ^{103}Rh coupling.

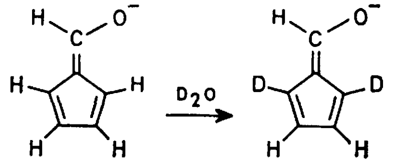
Effect of Lanthanide-shift Reagent.—Since the addition of paramagnetic lanthanide complexes is known to cause large chemical shifts in nuclei adjacent to an electronegative group, the use of such reagents in the present study should allow an unambiguous assignment of the spectra. The reagent $[Eu(fod)_3]$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione) was added incrementally to $CDCl_3$ solutions at 38 °C of several of the complexes, namely, those where $L = C_2H_4$ and $X = COCO_2Et$, CHO, and CO_2Me; $L = CO$ and $X = COCO_2Et$; and $LL = C_4H_6$ and $X = CHO$ and CO_2Me. In every case the resonance showing the smaller ^{103}Rh coupling moved downfield, the other resonance being relatively little affected. This was true irrespective of whether the shifted signal occurred to high or to low field. Thus, for $[Rh(C_2H_4)_2(C_5H_4X)]$ ($X = COCO_2Et$ or CHO) it was the upper-field signal at 38 °C which moved downfield, leading eventually, with further addition of $[Eu(fod)_3]$, to cross-over with the other resonance. These results provide strong evidence, in the case of rings with electron-withdrawing substituents, for assignment of the resonance with the smaller ^{103}Rh coupling to H(2) and H(5). As stated earlier, this resonance is sometimes found to high field with respect to H(3) and H(4), a situation which is the opposite to that reported for substituted ferrocenes and related systems.[4]

Deuterium Exchange Experiments.—It has been shown that protonation of the anion of nitro-,[8] methoxycarbonyl-,[9] formyl-,[10] and cyano-cyclopentadiene [8] yields only the isomer shown below. This suggests that



protons H(2) and H(5) are more susceptible to exchange. In fact, this has been verified experimentally for the case of $Na[C_5H_4NO_2]$.[8]

In the present study the potassium salt of formylcyclopentadienide was found to undergo slow exchange with D_2O to give $K[C_5H_2D_2CHO]$ ($t_{\frac{1}{2}}$ = *ca.* 12 h at 30 °C). On the basis of the work quoted above we conclude that the



exchange has occurred at the 2- and 5-positions. The exchanged salt was then allowed to react with $[\{Rh(C_2H_4)_2Cl\}_2]$ and with $[Rh(C_4H_6)_2Cl]$ to give, respectively, $[Rh(C_2H_4)_2(C_5H_2D_2CHO)]$ and $[Rh(C_4H_6)(C_5H_2D_2CHO)]$. For the former complex it was found, at 40 °C, that the ring-proton signal at higher field had almost disappeared whereas the reverse result was obtained for the latter complex. The diminished signals are, in each case, those which on the basis of the lanthanide-shifted spectra were assigned to H(2) and H(5). Thus, the lanthanide-shift and the deuterium-exchange experiments lead to the same conclusions in so far as the rings with electron-withdrawing substituents are concerned.

It was not possible to carry out deuterium exchange in D_2O with sodium or potassium salts of the alkyl-substituted cyclopentadienides because of hydrolysis; the thallium salts are insoluble in water. We are therefore unable to assign the ring protons by this method in these cases.

Summing up our conclusions with regard to ring-proton assignments for complexes with electron-withdrawing ring substituents, we have normal behaviour for all complexes where the neutral ligand is a conjugated diene. The term ' normal ' is used to describe a spectrum in which H(2) and H(5) resonate to lower field and neither the H(2) and H(5) nor H(3) and H(4) signals show any appreciable temperature dependence of the chemical shift, *i.e.* the spectra are analogous to those of similarly substituted ferrocenes.[4] The spectra of the ethylene and non-conjugated-diene complexes are anomalous in that at the lower temperatures the H(3) and H(4) protons are the more deshielded, though at the higher temperatures in some cases the situation is reversed. The carbonyl complexes appear to be intermediate in behaviour between that of the 1,3-diene complexes on the one hand and the ethylene complexes on the other. There is self-consistency in the assignments in that it is always the resonance with the greater ^{103}Rh coupling [attributed to H(3) and H(4)] which moves to lower field with decrease in temperature.

It is not possible on the basis of the available data to assign unambiguously the ring-proton spectra of the alkyl-substituted rings. However, it may be argued that, since ' normal ' spectra were obtained for rings with electron-withdrawing substituents whenever the neutral ligand is a 1,3-diene, the same should apply for alkyl-substituted rings. We propose, therefore, that the

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[7] N. Kamezawa, *J. Magnetic Resonance*, 1973, **11**, 88.

[8] R. C. Kerber and M. J. Chick, *J. Org. Chem.*, 1967, **32**, 1329.

[9] D. Peters, *J. Chem. Soc.*, 1959, 1761.

[10] L. Kaplan, L. A. Wendling, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, 1971, **93**, 3819.

lower field resonance is due to H(2) and H(5) in all these cases. This is the same assignment previously given for alkyl-substituted ferrocenes.[5] We note, however, that this means that ^{103}Rh (and the substituent proton, where applicable) is now more coupled to H(2) and H(5) than to H(3) and H(4).

The ^{13}C *N.M.R. Spectra.*—Chemical-shift data are given in Table 2 along with observed ^{103}Rh–^{13}C coupling constants. C(1), readily identified by its relatively low intensity, resonates at the lowest field in all cases except that where X = CN. Differentiation between the C(2),C(5) and C(3),C(4) resonances was achieved by selective proton decoupling. Thus, for the case of $[Rh(C_2H_4)_2(C_5H_4CO_2Me)]$, irradiation at the frequency of the low-field proton signal at τ 4.48 [assigned to H(2) and H(5)] caused collapse of the high-field ^{13}C resonance at δ 88.87, thereby identifying it as due to C(2) and C(5). Similarly, irradiation at the frequency of the low-field ^{1}H signal at τ 4.40 [assigned to H(3) and H(4)] of $[Rh(C_2H_4)_2(C_5H_4CHO)]$ caused collapse of the low-field ^{13}C resonance at δ 92.50. It follows that this resonance is due to C(3) and C(4). These assignments are once again supported by the europium-shifted spectra. Addition of [Eu(fod)$_3$] to $CDCl_3$ solutions of these complexes induced larger shifts of the signals assigned (as above) to C(2) and C(5).

TABLE 2

Carbon-13 chemical shifts (p.p.m.) and ^{103}Rh–^{13}C coupling constants (Hz) for $[RhL_2(C_5H_4X)]$ and $[Rh(LL)(C_5H_4X)]$ complexes in $CDCl_3$ at 40 °C and (in parentheses) −60 °C

					J(Rh–C)[d]		
L or LL	X	C(1)	C(2), C(5)	C(3), C(4)	C(1)	C(2), C(5)	C(3), C(4)
C_2H_4	H	87.11	87.11	87.11	3.6	3.6	3.6
		(87.28)	(87.28)	(87.28)			
	Me	91.73	83.05	83.05	7.7	5.1	5.1
	Bu^t		86.04	84.60	*a*	2.9	2.9
	CO_2Me	92.44	88.27	90.33	4.2	3.5	3.5
		(91.82)	(88.56)	(90.99)			
	CHO	103.30	87.80	92.50	4.1	3.5	3.8
		(102.40)	(87.81)	(93.51)			
	$COCO_2Et$	98.10	89.03	94.10	*a*	*a*	*a*
	CN	72.33	91.08	90.20	*a*	3.6	3.6
		(71.62)	(90.90)	(90.90)			
CO	H	87.79	87.79	87.79	3.5	3.5	3.5
		(88.27)	(88.27)	(88.27)			
	Me	106.00	89.52	87.75	3.2	3.8	3.5
		(105.82)	(90.06)	(87.97)			
	CO_2Me	97.80	87.34	92.18	4.1	2.9	3.5
		(97.62)	(86.94)	(92.93)			
	CHO	107.65	86.69	93.38	3.8	3.2	3.2
		(107.16)	(86.82)	(94.48)			
3-Methylpenta-1,4-diene	CO_2Me	91.92[b]	86.05[b]	88.25[b]	4.7[b]	4.1[b]	4.4[b]
		91.92[c]	86.38[c]	88.15[c]	4.7[c]	4.1[c]	4.1[c]
2,4-Dimethylpenta-1,4-diene	CHO	103.81	85.29	92.86	4.2	3.7	4.4
		(103.14)	(84.83)	(93.61)			
2,3-Dimethylbuta-1,3-diene	CO_2Me	92.70	85.40	85.61	4.9	2.2	2.8
		(92.03)	(85.30)	(85.86)			
	CHO	99.36	84.55	88.54	5.4	4.9	4.9
		(98.69)	(84.40)	(89.02)			
Hexa-1,5-diene	CO_2Me	93.13	88.15	90.26	4.2	3.6	3.6
		(92.90)	(87.97)	(90.52)			
Cyclo-octa-1,5-diene	CO_2Me	93.17	87.92	90.39	4.0	3.6	3.6
		(92.48)	(87.46)	(91.18)			

[a] Not observed. [b] *syn*-Methyl isomer. [c] *anti*-Methyl isomer. [d] ±0.3Hz.

Selective proton decoupling of the ^{13}C spectrum of $[Rh(C_2H_4)_2(C_5H_4CMe_3)]$ showed that the lower-field ^{1}H signal is associated with the lower-field ^{13}C resonance. Since we have tentatively assigned this proton resonance to H(2) and H(5) the lower-field ^{13}C resonance is assigned, equally tentatively, to C(2) and C(5). As with the proton spectra this assignment would be consistent with assignments previously reported for Bu^t-substituted ferrocene.[11]

The effect of cooling from +40 to −60 °C on the ^{13}C chemical shifts was small in most cases. Resonances assigned to C(1) and to C(2) and C(5) moved slightly upfield while those assigned to C(3) and C(4) moved slightly downfield for all cases where X = electron-withdrawing substituent. It is noteworthy that these are qualitatively the same effects as observed in the proton spectra. There is therefore a self-consistency in the effects of temperature on the ^{1}H and ^{13}C chemical shifts. Unlike the proton spectra, temperature variation within the +40 to −60 °C temperature range did not cause a cross-over of ^{13}C resonances though for X = CN in $CDCl_3$ the C(2),C(5) and C(3),C(4) resonances coalesce at −60 °C.

Table 2 includes data for the ^{103}Rh–C coupling constants. Values for C(2) and C(5) and C(3) and C(4) are the same to within experimental uncertainty while those for C(1) are somewhat larger in most cases.

Origin of the Temperature Dependence of the ^{1}H *N.M.R. Chemical Shifts.*—Chemical-shift coalescence without line broadening is unusual. The absence of line broaden-

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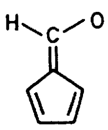
[11] A. A. Koridze, A. I. Mokhov, P. V. Petrovski, and E. I. Fedin, *Izvest. Akad. Nauk S.S.S.R.*, 1974, **9**, 2156.

ing and the fact of the cross-over precludes an explanation in terms of a rate-controlled or relaxation process. Secondly, the phenomenon, in the case of the ethylene complexes, cannot be connected with the changing rate of ethylene rotation [12] about the Rh–C_2H_4 bond axis with change in temperature since the effect is shown also by complexes of chelating 1,4-dienes not capable of dynamic behaviour of this kind. Nor is the effect attributable to particular orientations of the substituent groups with respect to the plane of the C_5 ring since it is exhibited also by complexes in which the substituent is the cylindrically symmetrical cyano-group.

The possibility of solvent-induced chemical-shift changes must be considered. Temperature-dependent ring-proton chemical shifts have been noted for pyrrole, furan, thiophen, and several *para*-substituted benzenes in polar and aromatic solvents.[13] In these cases a movement of the resonances of the α-protons to lower field with decrease in temperature was observed. The effects have been attributed [13] to weak hydrogen-bond interaction between solvent molecules and the ring C–H groups adjacent to the heteroatom or substituent. A smaller movement was observed for resonances due to the β-protons. The effects were negligible in inert solvents such as hexane or decalin.

In the complexes considered here the behaviour differs in two important respects. Firstly, the chemical shift movement with change in temperature is still apparent in decalin (Figure 3) and in hexane though the magnitude of the effect is smaller than in the polar solvents (Figure 2). Secondly, the resonances due to H(2) and H(5) move upfield, not downfield, with decrease in temperature. We conclude, therefore, that the process responsible for the anomalous temperature dependence of the proton spectra of ethylene and 1,4-diene complexes is not primarily due to interactions with solvent though it appears that the effect is more marked in polar solvents.

An explanation in terms of a fulvenoid structure such as



for the co-ordinated C_5H_4X group is rejected on the grounds that much more complex ^1H n.m.r. spectra are found for alkali-metal salts of monosubstituted cyclopentadienyl anions known to have the (asymmetrical) fulvenoid structure.[8] Moreover, it is difficult to see how such a structure could give rise to the kind of temperature dependence observed in the spectra of the rhodium complexes.

We now examine a model for the unusual properties of these complexes which is based on a localized bonding contribution to the metal–cyclopentadienyl interaction. It must be noted that completely π-delocalized bonding is not expected for these systems since they lack cylindrical symmetry, even in the case of the unsubstituted C_5H_5 complex. Departures from purely delocalized bonding will be greatest for those cases where the ring substituent has a strong electronic influence, *e.g.* $COCO_2$-Et and CHO. Thus, the degeneracy of the cyclopentadienyl e_1 orbitals is lifted. This, in turn, leads to unequal overlap with the metal d_{xy} and d_{yz} orbitals. This being so it follows that not all possible orientations of the substituted C_5 ring with respect to the associated neutral ligands L or LL are of equal energy, *i.e.* the rotating ring now experiences unequal energy barriers. We make the assumption that one particular orientation is more stable than all others. At high temperatures, *i.e.* where $\mathbf{k}T$ is large compared to the largest barrier height, the preferred rotamer state will not be appreciably more populated than others of higher energy and the metal–C_5H_4X bonding will approach the fully delocalized condition. At lower temperatures where $\mathbf{k}T$ is comparable in magnitude to the rotational barrier heights the proportion of molecules in the lowest-energy conformation becomes progressively greater. Since the rate of interconversion of the various rotamers is large compared to the n.m.r. time scale the observed spectra will be the averaged spectra of all rotamers weighted according to their populations.

In order to gain some insight into the nature of the preferred conformation a single-crystal *X*-ray structural determination of one representative complex which showed 'anomalous' ^1H n.m.r. behaviour was undertaken. It is assumed, here, that if one particular structure or conformation is preferred over all others in solution at low temperatures this preference will be reflected in the solid-state structure. The complex chosen for structure analysis was [Rh(cyclo-octa-1,5-diene)($C_5H_4CO_2Me$)], this being one of the few which are not oils at room temperature.

Crystal Data.—$C_{15}H_{19}O_2Rh$, $M = 334.2$, Triclinic, $a = 7.051(8)$, $b = 8.390(8)$, $c = 12.660(10)$ Å, $\alpha = 100.16(9)$, $\beta = 101.33(8)$, $\gamma = 105.95(11)°$, $U = 684.7$ Å^3, $D_m = 1.59(2)$ g cm^{-3}, $Z = 2$, $D_c = 1.61$ g cm^{-3}, $F(000) = 340$. Space group $P\bar{1}$ from the successful structure determination. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 12.1 cm^{-1}.

A crystal with dimensions *ca.* 0.60 × 0.45 × 0.10 mm was mounted with a^* parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. For the latter, 15 high-angle reflections were used in a least-squares procedure. The apparatus was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum *X*-radiation was used with the stationary-crystal–stationary-counter method and a counting time of 10 s. Individual backgrounds were taken from plots of background as a function of 2θ. Several standard reflections were monitored during the course of the experiment but no significant change in intensity was detected. Of 2 400 independent reflections measured with $2\theta < 50°$, 2 023 with

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[12] R. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217.

[13] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R. Spectroscopy,' Pergamon, 1968, vol. 2, p. 850.

$I > 3\sigma(I)$ were used in subsequent calculations. No extinction or absorption corrections were applied.

Structure Determination.—The rhodium-atom position was determined from the Patterson function and successive Fourier syntheses were used to locate the positions of the remaining atoms. The structure was refined by full-matrix least squares with all atoms except hydrogen given anisotropic thermal parameters. Hydrogen atoms were located from a difference-Fourier map. These were included in the structure-factor calculation with thermal parameters equivalent to those of the carbon atom to which they were bonded. The parameters of the eight hydrogen atoms closest to the metal were refined, those of the other eight were kept fixed. The final R was 0.039. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$, was $w^{\frac{1}{2}} = 1$ for $F_o < 21$ and $w^{\frac{1}{2}} = 21/F_o$ for $F_o > 21$. Calculations were made on a CDC 7600 computer at the University of London Computer Centre with programs described in ref. 14 and on a 1904S computer at Reading University. Atomic scattering factors were taken from ref. 15 as were the corrections for the real and imaginary part of the anomalous dispersion for rhodium. The anisotropic thermal factor is defined as $\exp(-2\pi^2\sum_i\sum_j h_ih_jb_ib_jU_{ij})$ $(i,j = 1,2,3)$ where b_i is the i'th reciprocal lattice dimension. The isotropic thermal parameter is defined as $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$. In the final cycle of refinement all shifts were $<0.10\sigma$. The final difference-Fourier map showed no serious peaks and the zero-weighted reflections showed no serious discrepancies. Final positional parameters, together with standard deviations, are given in Table 3. Bond distances and angles are given in Table 4. Final anisotropic thermal parameters and observed and calculated structure factors are listed in Supplementary Publication No. SUP 21924 (10 pp., 1 microfiche).*

Discussion of the Structure.—The molecule (1) is illustrated in Figures 6 and 7 together with the atomic numbering scheme. Figure 6 is a general view of the molecule while Figure 7 is a projection onto the cyclopentadienyl (cp) plane. The metal atom is bonded to the cyclopentadienyl ring [Rh–C, 2.226(5)—2.303(8) Å] and to the two double bonds in cyclo-octa-1,5-diene [Rh–C, 2.101(5)—2.129(5) Å]. The cp ring is planar and almost parallel to the plane containing the two double bonds in the diene (angle of intersection 3.6°). The CO_2Me substituent group is almost coplanar with the cp ring and the short C(1)–C(6) distance [1.437(10) Å] suggests the occurrence of some delocalization over ring and substituent.

There are some significant differences among the Rh–C bond distances to the cp ring. The longest bonds are those from the metal to C(3) and C(4) [2.303(8) and

TABLE 3

Final positional parameters ($\times 10^5$ for Rh, $\times 10^4$ for C, $\times 10^3$ for H) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	*U*
Rh	35 049(7)	45 674(5)	19 073(4)	
O(1)	0 031(8)	7 080(8)	2 998(5)	
O(2)	3 045(8)	7 974(7)	4 260(4)	
C(1)	3 001(9)	7 102(7)	2 420(5)	
C(2)	2 177(12)	6 436(8)	1 256(6)	
C(3)	3 755(13)	6 395(9)	0 744(6)	
C(4)	5 591(12)	6 947(8)	1 572(7)	
C(5)	5 149(10)	7 347(7)	2 615(6)	
C(6)	1 855(10)	7 351(7)	3 222(5)	
C(7)	1 968(17)	8 224(15)	5 124(7)	
H(2)	088(12)	622(9)	088(7)	65(22)
H(3)	366(13)	598(11)	−006(8)	86(25)
H(4)	709(14)	708(11)	155(7)	90(27)
H(5)	618(13)	800(11)	338(7)	82(25)
C(11)	5 548(9)	3 269(8)	2 477(6)	
C(12)	4 507(12)	3 597(10)	3 260(6)	
C(13)	2 780(15)	2 238(14)	3 465(9)	
C(14)	0 826(15)	1 761(14)	2 662(9)	
C(15)	0 858(11)	2 486(9)	1 657(7)	
C(16)	1 870(10)	2 090(7)	0 852(6)	
C(17)	3 077(13)	0 844(9)	0 885(7)	
C(18)	5 106(12)	1 519(9)	1 698(7)	
H(11)	706(11)	412(9)	258(6)	64(20)
H(12)	523(11)	436(9)	395(7)	62(20)
H(15)	−027(12)	281(10)	156(6)	66(21)
H(16)	136(12)	219(10)	−003(7)	77(23)
H(131) *	321	110	353	90
H(132)	257	274	431	90
H(141)	019	037	238	90
H(142)	−029	218	306	90
H(171)	221	−030	107	80
H(172)	333	047	005	80
H(181)	670	184	214	80
H(182)	523	062	220	80

* Parameters of this hydrogen atom and subsequent ones were fixed in the refinement.

TABLE 4

Molecular dimensions; bond lengths (Å) and bond angles (°)

Rh–C(1)	2.256(6)	Rh–C(4)	2.294(7)
Rh–C(2)	2.230(8)	Rh–C(5)	2.226(5)
Rh–C(3)	2.303(8)		
C(1)–C(2)–C(3)	109.7(6)	C(2)–C(1)–C(6)	126.0(6)
C(2)–C(3)–C(4)	108.2(7)	C(1)–C(6)–O(1)	124.8(6)
C(3)–C(4)–C(5)	108.0(7)	C(1)–C(6)–O(2)	112.4(6)
C(4)–C(5)–C(1)	108.4(4)	O(1)–C(6)–O(2)	122.8(7)
C(5)–C(1)–C(2)	105.5(6)	C(6)–O(2)–C(7)	115.3(6)
C(5)–C(1)–C(6)	128.4(5)		
C(1)–C(2)	1.421(9)	C(6)–O(2)	1.337(7)
C(2)–C(3)	1.399(13)	O(2)–C(7)	1.466(13)
C(3)–C(4)	1.399(10)	C(2)–H(2)	0.89(8)
C(4)–C(5)	1.419(12)	C(3)–H(3)	1.00(10)
C(5)–C(1)	1.436(10)	C(4)–H(4)	1.04(10)
C(1)–C(6)	1.437(10)	C(5)–H(5)	1.04(7)
C(6)–O(1)	1.209(9)		
Rh–C(11)	2.125(7)	Rh–C(15)	2.101(5)
Rh–C(12)	2.104(8)	Rh–C(16)	2.129(5)
C(11)–C(12)–C(13)	123.6(7)	C(15)–C(16)–C(17)	123.5(7)
C(12)–C(13)–C(14)	115.4(10)	C(16)–C(17)–C(18)	114.9(6)
C(13)–C(14)–C(15)	115.3(9)	C(17)–C(18)–C(11)	115.1(7)
C(14)–C(15)–C(16)	125.1(8)	C(18)–C(11)–C(12)	124.8(6)
C(11)–C(12)	1.378(11)	C(17)–C(18)	1.482(10)
C(12)–C(13)	1.522(13)	C(18)–C(11)	1.530(10)
C(13)–C(14)	1.448(14)	C(11)–H(11)	1.08(7)
C(14)–C(15)	1.505(15)	C(12)–H(12)	0.93(7)
C(15)–C(16)	1.398(12)	C(15)–H(15)	0.90(9)
C(16)–C(17)	1.520(11)	C(16)–H(16)	1.13(9)

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* For details see Notices to Authors, No. 7, in *J.C.S. Dalton*, 1976, Index issue.

[14] '*X*-Ray System of Programs,' ed. J. M. Stewart, University of Maryland Technical Report, TR 67 58.

[15] 'International Tables for X-Ray Crystallography,' vol. 4, Kynoch Press, Birmingham, 1975.

2.294(7) Å, respectively] while the shortest bonds are to C(2) and C(5) [2.230(8) and 2.226(5) Å]. The Rh–C(1) distance [2.256(6) Å] is intermediate but closer in magnitude to Rh–C(2) and Rh–C(5). A similar variation in Rh–C bond lengths was noted previously[16] in the complex (η-cyclopentadienyl)(η-2,3-dichlorobutadiene)rhodium(I) in which the distances vary between 2.187(14) and 2.258(17) Å, on average 0.05 Å shorter than in (1). In $[Rh(C_2H_4)(C_2F_4)(C_5H_5)]$[17] the Rh–C(cp) distances range from 2.171 to 2.252 Å, again somewhat shorter than in (1). Differences in cp ring C–C distances are comparable with the standard deviations and little significance can be placed on them.

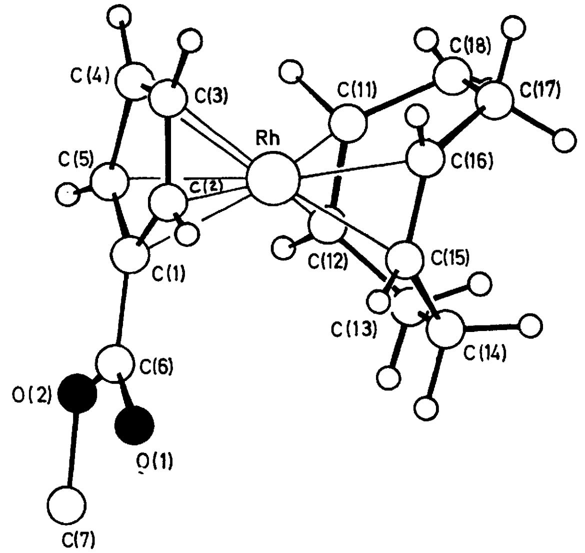

FIGURE 6 General view of the structure of $[Rh(cyclo\text{-}octa\text{-}1,5\text{-}diene)(C_5H_4CO_2Me)]$

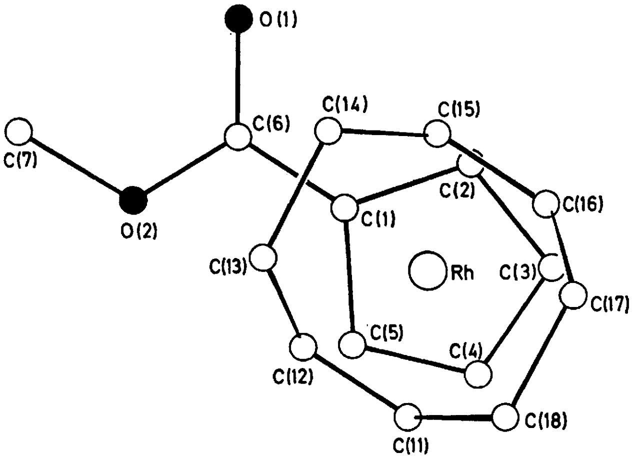

FIGURE 7 Projection of the structure of $[Rh(cyclo\text{-}octa\text{-}1,5\text{-}diene)(C_5H_4CO_2Me)]$ onto the cyclopentadienyl plane

The Rh–C bond lengths to the cyclo-octa-1,5-diene (cod) are also different, being 2.125(7) and 2.129(5) Å for Rh–C(11) and Rh–C(16) and 2.104(8) and 2.101(5) Å for Rh–C(12) and Rh–C(15). This means that the C(11), C(16) end of the cod ring and the C(3), C(4) end of the cp ring are tilted away from each other, both these ends lying furthest from the metal. The Rh–C(cod) distances in (1) are similar to, though slightly longer on average than, corresponding bond lengths in other complexes of Rh^I with this diene. Thus, in $[Rh_2(cod)Cl_2\{P(OPh)_3\}_2]$[18] and [Rh(cod)(acac)][19] the Rh–C(cod) distances are 2.10(2) and 2.103(7) Å, respectively (acac = pentane-2,4-dionate). In general, it seems that the Rh–C bonds in cod complexes are slightly shorter than in complexes where the alkene is ethylene: 2.167(2) Å in $[Rh(cp)(C_2H_4)(C_2F_4)]$,[17] 2.135(20) Å in $[Rh(C_2H_4)(acac)]$,[20] and 2.19(1) Å in $[Rh(C_2H_4)(C_2F_4)(acac)]$.[20] In [{Rh(4-methylpenta-1,3-diene)Cl}$_2$], in which the diene is bound only by the unsubstituted double bond, the Rh–C distances are 2.120(9) and 2.163(9) Å.[21]

In (1) the C(11)–C(12) and C(15)–C(16) bonds are equivalent at 1.388 Å, towards the lower end of the range of C=C distances observed in the ethylene and cod complexes quoted above. Variations in the lengths of co-ordinated C=C bonds are expected to arise, at least in part, from variations in the degree of back donation of metal d_π electrons, this in turn being influenced by the nature of the associated ligands. The degree to which olefin substituents are bent back out of the plane containing the co-ordinated olefin is often taken as a measure of the extent of metal d_π-to-p_π^* back co-ordination. Using the conventions of ref. 22 we calculate values of 46.6 and 38.3 for α, which may be compared to values of 43 and 26 for [Rh(cod)(acac)].[19] These values may be compared with those collected in ref. 17; but because of the occurrence of the two alkene functions in an eight-membered ring in the present case the values of α are somewhat different from those in less restrained molecules. Even so, the hydrogen atoms are a significant amount out of the plane of C(11), C(12), C(15), C(16)—by 0.57, 0.26, 0.39, and 0.50 Å, respectively.

In many structures the cod ligand has an asymmetric skewed conformation such that there is a significant difference between the C(14) $\cdots$ C(18) and C(13) $\cdots$ C(17) distances across the ring; this is 0.68 Å in the free molecule,[23] 0.43 Å in [Rh(cod)(acac)][19] but only 0.17 Å in (1) (distances 3.51 and 3.34 Å, respectively). We also note that the distance between the mid-points of the double bonds is 2.76 Å in (1), compared to 2.74 Å in [Rh(cod)(acac)][19] and 3.05 Å in the free ligand.[23] [The distance between the mid-point of the C(13)–C(14) and C(17)–C(18) bonds is 3.09 Å.] Tucker *et al.*[19] consider the more symmetrical the ligand conformation the more

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[16] M. G. B. Drew, S. M. Nelson, and M. Sloan, *J. Organometallic Chem.*, 1972, **39**, C9.

[17] L. J. Guggenberger and R. Cramer, *J. Amer. Chem. Soc.*, 1972, **94**, 3779.

[18] J. Coetzer and G. Gafner, *Acta Cryst.*, 1970, **B26**, 985.

[19] P. A. Tucker, W. Scutcher, and D. R. Russell, *Acta Cryst.*, 1975, **B31**, 592.

[20] J. A. Evans and D. R. Russell, *Chem. Comm.*, 1971, 197.

[21] M. G. B. Drew, S. M. Nelson, and M. Sloan, *J.C.S. Dalton*, 1973, 1484.

[22] J. K. Stalich and J. A. Ibers, *J. Amer. Chem. Soc.*, 1970, **92**, 5333.

[23] L. Hedberg and K. Hedberg, *Abstracts Amer. Cryst. Assoc.*, Summer Meeting, Bozeman, Montana, 1964.

strongly it is bound to the metal. Application of this idea to (1) may well explain why the Rh–C(cp) bonds are longer than expected, a strong Rh–cod interaction serving to weaken the Rh–cp interaction. Rh–C and C–C dimensions in (1) are also similar to those found recently for [Rh(cod){(*S*-methyl)dimercaptomaleonitrile}],[24] but full details for this complex have not yet been given.

There are a few short contacts between molecules; only nine (ignoring hydrogen) are <3.75 Å. These are given in Table 5. This small number reflects inefficient packing of the molecules.

TABLE 5

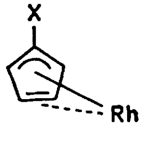
Intermolecular distances <3.75 Å,* excluding hydrogen atoms

$C(4) \cdots O(1^{I})$	3.25	$C(12) \cdots C(7^{IV})$	3.73
$C(5) \cdots O(1^{I})$	3.46	$C(14) \cdots C(7^{V})$	3.73
$C(11) \cdots O(1^{I})$	3.68	$C(16) \cdots C(16^{VI})$	3.73
$C(2) \cdots C(17^{II})$	3.71	$C(17) \cdots C(16^{VI})$	3.66
$O(2) \cdots O(2^{III})$	3.64		

* Roman numerals as superscripts refer to the following equivalent positions with respect to the *x,y,z* set in Table 1

I	$1 + x, y, z$	IV	$1 - x, 1 - y, 1 - z$
II	$x, 1 + y, z$	V	$-x, 1 - y, 1 - z$
III	$1 - x, 2 - y, 1 - z$	VI	$-x, -y, -z$

Discussion of the N.M.R. Behaviour in Relation to the Structure.—The structure described above clearly indicates that although the bonding of the metal to the cyclopentadienyl ring is predominantly of the type expected for a metal–π-cyclopentadienyl complex, there is evidence for a small but significant departure from fully symmetrical bonding. Important features of the structure are (*i*) the cp ring is planar, (*ii*) the substituent carbon and oxygen atoms are co-planar with the ring ruling out any interaction with the metal, (*iii*) the substituted cp ring is orientated with respect to the cod ligand such that the axis passing through C(1) and bisecting C(3)–C(4) is parallel to the axes of the double bonds of cod (Figure 7), (*iv*) the plane of the cp ring is tilted such that the substituted end lies closer to the plane containing the two double-bonds of cod, and (*v*) C(3) and C(4) lie significantly further from the metal than C(1), C(2), and C(5). These latter observations are suggestive of a small contribution from an η^3-allyl–alkene localized structure of the type proposed by Bennett *et al.*[25] A similar, and less formalized type of

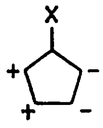


localization is that suggested by Cotton [26] in which there is gradation in carbon–carbon bond order which varies inversely with metal–carbon bond order.

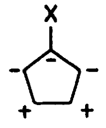
We now consider how such a structure accords the n.m.r. spectral observations. H(2) and H(5) would be expected to occur in the chemical-shift range characteristic of η-allylic protons in the *syn* position, *i.e.* at values appreciably higher than τ 4—5. In (π-allyl)cyclo-octa-1,5-dienerhodium(I) for example, the *syn* η-allylic protons resonate at τ 7.35 in $CDCl_3$.[27] Similarly, a weak interaction between the metal and C(3)=C(4) such as is implied by this structure is expected to result in a downfield shift, *i.e.* towards chemical-shift positions characteristic of non-co-ordinated olefinic protons.[28] It is surprising, perhaps, that coupling to ^{103}Rh is somewhat greater for H(3) and H(4) than for H(2) and H(5). The opposite might have been expected if C(3) and C(4) are more weakly bonded than C(1), C(2), and C(5). The movement upfield of the ^{13}C resonances of C(1), C(2), and C(5) [29] and the downfield movement of C(3) and C(4) [30] on cooling is also consistent with the model proposed.

It remains to account for the occurrence of a significant contribution from the localized bonding structure in those complexes where the neutral ligands are isolated double bonds (ethylene or non-conjugated dienes) but not in the case of conjugated dienes. We suggest that the explanation is to be found in the different symmetries of the π-acceptor orbitals of the neutral ligands with respect to the C_5H_4X moiety.

The introduction of a substituent into the $[C_5H_5]^-$ ring lowers the symmetry from D_{5h} to C_{2v}. Taking the ring to lie in the *x,y* plane the e_1 orbitals transform as a_2 and b_2.



a_2



b_2

If X is electron withdrawing in its influence then, since the values of the Hückel coefficients for $[C_5H_5]^-$ indicate that the b_2 orbital has the larger amplitude at the substituent position,[31] we expect that this orbital will become stabilised with respect to a_2. Neglecting the asymmetry in the substituent X the cod complex as a whole has merely a mirror plane of symmetry bisecting C(3)–C(4). In C_s symmetry the a_2 and b_2 reduce to a'' and a' respectively. Since the principal overlap interactions of a'' and a' are with d_{yz} and d_{xz}, respectively, the Rh–C_5H_4X bond will have more of the character of a' than of a'', a conclusion consistent with the structural model proposed for the lowest-energy rotamer.

However, the bonding description will be modified to the extent that d_{xz} and d_{yz} are involved in competitive overlap with π* orbitals of the neutral ligands. The crystal structure determination has shown, for the case

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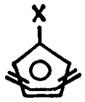
of the cod complex, that the axes of the C=C double bonds are approximately parallel to the C_2 axis of the C_5H_4X moiety (Figure 7). Thus, for this complex, and, prepresumably, all others containing non-conjugated dienes or ethylene, there is little or no competition for d_{xz} by π^* orbitals of the neutral ligand since they do not have the appropriate symmetry.

While the detailed geometry of the conjugated diene complexes considered here is unknown, it is probable that it is as illustrated below where C(1) of the cp ring



is *trans* to the internal bond of the 1,3-diene. A similar arrangement occurs in two unsubstituted cp complexes of the type [Rh(1,3-diene)(C_5H_5)].[16] If the same relative disposition of ligands applies in the present complexes we now have competition between a' and ψ_3 (the lowest unoccupied molecular orbital of the 1,3-diene) for the same metal orbital d_{xz}. The effect will be to diminish the stabilization of a' relative to a'', *i.e.* a more fully delocalized Rh–C_5H_4X bonding situation is approximated.

Results for the CO complexes suggest that the bonding in these is intermediate in character to those in the two groups of alkene complexes discussed above. However, without more information on the structure of these compounds further discussion of this point is unwarranted.

EXPERIMENTAL

All operations were carried out under an atmosphere of nitrogen and all solvents were dried and freed from oxygen before use. Dienes were purchased from Pfaltz and Bauer, Koch–Light, Aldrich, Chemical Samples Co. Ltd., or Phase Separations Ltd.

Preparation of Cylopentadienide Salts.—Thallium(I) cyclopentadienide was prepared as described by Hunt and Doyle [32] while thallium(I) methoxycarbonylcyclopentadienide and potassium formylcyclopentadienide were prepared as described in a previous publication from this laboraory.[1] The ethoxycarbonyl and isopropoxycarbonyl derivatives were similarly synthesized by esterification with, respectively, ethanol and isopropyl alcohol, of dicyclopentadienedicarboxylic acid. The esters of the di-acid were obtained as oils in 70% (R = Et) and 60% (R = Pr^i) yield. They were characterized by their i.r., n.m.r., and mass spectra, and by chemical analysis. The dimeric esters were cracked at 220 °C and 18 mmHg and passed directly into an aqueous solution of thallium(I) acetate and KOH as described previously for the methyl ester.[1] Tl[$C_5H_4CO_2Et$] was obtained as white needles in 65% yield, m.p. 80—82 °C (Found: C, 27.7; H, 2.7. $C_8H_9O_2Tl$ requires C, 28.1; H, 2.6%), ν(CO) at 1 675 cm^{-1}. Tl[$C_5H_4CO_2Pr^i$] was obtained as off-white needles in 60% yield, m.p. 101—102 °C (Found: C, 30.2; H, 3.2. $C_9H_{11}O_2Tl$ requires C, 30.3; H, 3.1%).

For the preparation of Tl[C_5H_4CN] dicyanocyclopentadiene was prepared and cracked as described by Webster.[33] The freshly cracked material (5 g) was added to an aqueous solution (150 cm^3) of Tl_2SO_4 (20 g) and KOH (7.5 g). The white suspension was vigorously agitated for 2 h. The resulting solid was filtered off, washed with water, ethanol, and hexane, and dried *in vacuo*. Recrystallization of 5 g portions from acetonitrile (500 cm^3) gave cyanocyclopentadienylthallium(I) (*ca.* 4 g) as off-white needles, m.p. 150—152 °C (decomp.), ν(CN) at 2 200 cm^{-1}; $m/e = 295$, 293; $M = 294.3$.

Ethoxalylcyclopentadienylsodium was prepared by the method of Thiele,[34] methylcyclopentadienylthallium(I) by the method of Reynolds *et al.*,[35] and t-butylcyclopentadienylthallium(I) by the method of Nesmeyanov.[36]

Preparation of the Rhodium(I) *Complexes.*—Several of the complexes have been described previously.[1,2] Those that are new were prepared by the same general methods. The carbonyl complexes were prepared by reaction of the appropriate cyclopentadienyl salt with [{Rh(CO)$_2$Cl}$_2$].[37]

The complexes were characterized by chemical analysis (data for C and H agreed with calculated values to within 0.4%) and by i.r., mass, and ^1H n.m.r. spectra (see Results and Discussion section). I.r. spectra were measured in the range 4 000—250 cm^{-1} (Perkin-Elmer 457 grating spectrophotometer) in KBr discs or as thin films between KBr or CsI plates. Spectra of the monosubstituted cyclopentadienyl complexes were very similar to those of the parent unsubstituted compounds except that lower intensity bands occurred near 1 420 and 1 100 cm^{-1}. In addition, the oxalate, ester, and formyl derivatives displayed a strong band at 1 600—1 700 cm^{-1} characteristic of the C=O stretch, while the cyano-derivatives had a strong band at *ca.* 2 200 cm^{-1}. All the diene and ethylene complexes showed two or three bands at 1 400—1 500 cm^{-1}.

^1H n.m.r. spectra were recorded in $CDCl_3$, *o*-dichlorobenzene, or, less commonly, decalin, hexane, pyridine, and acetone using Varian Associates A60D, HA100, and HR220 spectrometers fitted with variable-temperature accessories. The probe temperature was calibrated using methanol below ambient temperature and ethylene glycol above it.[38] Carbon-13 n.m.r. spectra were obtained using Bruker HX-90 and WX-90 Fourier-transform spectrometers, with complete proton decoupling. Mass spectra were recorded using A.E.I. MS902 and MS30 spectrometers at an ionizing voltage of 70 eV.

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