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Substituted cyclopentadienyl compounds

IV *. NMR spectra of chloro-substituted (η^5-cyclopentadienyl)-rhodium-(η^4-diene) compounds and the crystal structure of (η^5-chlorocyclopentadienyl)-(η^4-2,3-dimethoxybutadiene)rhodium(I)

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Abstract

The molecular structure of (η^5-C_5H_4Cl)Rh(η^4-$C_4H_4(OMe)_2$) (I) has been determined. The orientation of the ligands is one in which the cyclopentadienyl ring substituent bond lies in a mirror plane that bisects the two terminal carbon–carbon bonds of the butadiene ligand. This conformation is associated with population of a cyclopentadienyl rotamer of η^4-diolefin-η^1-alkyl character. Extended Hückel molecular orbital calculations show that this rotamer is preferred to the alternative η^3-allyl-η^2-ene form in **I**. The ^{1}H NMR data for **I** and related compounds suggest that the metal-coupling patterns reflect the variation in charge density within the substituted cyclopentadienyl ring.

Key words: Rhodium; Cyclopentadienyl; Nuclear magnetic resonance; Crystal structure; Extended Hückel calculations

1. Introduction

In Part III [1] we presented the crystal structure of [(η^5-C_5H_4CHO)Rh(η^4-2,3-dimethoxybutadiene)] and reported on the value of CNDO/U molecular orbital calculations and solution NMR spectroscopy in the identification of conformational preferences in carboxyl-substituted cyclopentadienyl compounds of rhodium. Herein we report on X-ray, Extended Hückel molecular orbital calculations, and NMR studies of chloro-substituted analogues.

2. Experimental details

NMR spectra were recorded on a Bruker AC-250 spectrometer. C–H correlated spectra were obtained by routine procedures [2]. 2D HCC relay spectra [3] were obtained by 128 measurements, each measurement with 128 FIDs, and a 2D data matrix of 2 K by 256 W, with a total recorded time of *ca.* 70 h.

All compounds were prepared in high yield by reaction of thallium(I) chlorocyclopentadienide [4] with the appropriate chloro-bridged rhodium-diene precursor

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* For Part III, see ref. 1.

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and characterised as reported previously [5]. The complex [(η^5-C_5H_4Cl)Rh(η^4-$C_4H_4(OMe)_2$)], (I) was obtained in 75% yield as yellow needles, m.p. 64–66°C, MS: $m/e = 316/318$ (M^+). Anal. Found: C, 41.50; H, 4.63. $C_{11}H_{14}ClO_2Rh$ calc.: C, 41.69; H, 4.42%, and [(η^5-C_5H_4Cl)Rh(η^4-$C_4H_4(C_6H_5)_2$)] (II), was obtained similarly in 70% yield as an amorphous yellow solid, m.p. 158–160°C, MS: $m/e = 408/410$ (M^+). Anal. Found: C, 59.00; H, 5.42. $C_{23}H_{24}ClO_2Rh$ calc.: C, 58.66; H, 5.10%. The yellow (norbornadiene)Rh(η^5-C_5H_4Cl) (III) was obtained in 82% yield, m.p. 79–80°C, MS: m/e 294/296 (M^+). Anal. Found: C, 49.02; H, 4.31. $C_{12}H_{12}ClRh$ calc.: C, 48.89; H, 4.07%.

3. Crystal structure determination for I

3.1. X-ray crystallography: [C_5H_4Cl]Rh[$C_4H_4(OMe)_2$]

Crystal data: $C_{11}H_{14}O_2ClRh$, $M = 316.6$. Monoclinic, $a = 11.366(2)$ Å, $b = 9.305(2)$ Å, $c = 12.423(2)$ Å. $\beta = 113.70°(1)$, $U = 1203.03$ Å^3. $D_c = 1.75$ g cm^{-3}, $Z = 4$, $F(000) = 632$. Space group $P2_1/c$, μ(Mo-Kα) 1.60 cm^{-1}, $\lambda = 0.71073$ Å.

3.2. Measurements

A suitable crystal was obtained by slow recrystallisation from toluene : hexane (1 : 1) solution at 0°C. A yellow crystal of approximate size 0.72 mm × 0.58 mm × 0.20 mm was mounted on glass fibre. All geometric and intensity data were taken from this sample using an automated Nicolet R3mV four-circle diffractometer. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer. The ω–2θ technique was used to measure 2479 reflections, of which 2378 were unique in the range $5 < 2\theta < 50$. Three standard reflections were measured every 97 scans and showed no significant loss in intensity during data collection. Data were corrected for Lorentz and polarisation effects, and empirically for absorption. Processing of the measured data gave 1846 reflections with $I > 3.0\sigma(I)$ and these were used to solve and refine the structure in the monoclinic space group $P2_1/c$.

TABLE 1. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (η^5-C_5H_4Cl)Rh(η^4-$C_4H_4(OMe)_2$)

Atom	x	y	z	U_{eq} [a]
Rh	2163(1)	5520(1)	−112(1)	36(1)
Cl	1379(2)	5037(2)	−3135(1)	95(1)
O(1)	4325(3)	4189(3)	2140(3)	48(1)
O(2)	3347(3)	2432(3)	310(3)	53(1)
C(1)	1919(5)	6143(5)	−1911(4)	58(2)
C(2)	1108(5)	7040(6)	−1570(5)	68(2)
C(3)	1932(7)	7827(6)	−597(6)	76(3)
C(4)	3190(6)	7458(5)	−377(5)	67(2)
C(5)	3214(5)	6443(5)	−1193(4)	60(2)
C(6)	2175(5)	5350(4)	1600(4)	46(2)
C(7)	3033(4)	4312(4)	1463(3)	36(1)
C(8)	2501(4)	3360(4)	477(3)	39(1)
C(9)	1171(4)	3548(5)	−259(4)	48(2)
C(10)	4955(5)	5425(5)	2799(5)	59(2)
C(11)	2934(6)	1799(6)	−822(4)	77(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 2. Selected bond lengths (pm) and angles (°) with e.s.d.s. for (η^5-C_5H_4Cl)Rh(η^4-$C_4H_4(OMe)_2$)

Rh–C(1)	221.5(5)	Rh–C(2)	223.0(5)
Rh–C(3)	221.6(5)	Rh–C(4)	224.2(6)
Rh–C(5)	229.3(6)	Rh–C(6)	212.8(5)
Rh–C(7)	212.5(4)	Rh–C(8)	212.1(4)
Rh–C(9)	212.3(4)		
C(1)–C(2)	142.9(9)	C(2)–C(3)	140.1(8)
C(3)–C(4)	138.7(10)	C(4)–C(5)	139.4(8)
C(5)–C(1)	140.9(7)	C(1)–Cl	173.2(5)
C(6)–C(7)	143.1(7)	C(7)–C(8)	143.3(5)
C(8)–C(9)	142.9(5)	C(7)–O(1)	137.2(5)
C(8)–O(2)	136.8(6)		
C(1)–C(2)–C(3)	105.9(5)	C(2)–C(3)–C(4)	108.6(6)
C(3)–C(4)–C(5)	110.1(5)	C(4)–C(5)–C(1)	105.9(5)
C(5)–C(1)–C(2)	109.4(4)	Cl–C(1)–C(2)	124.4(4)
C(6)–C(7)–C(8)	116.5(3)	C(7)–C(8)–C(9)	116.4(4)

The structure was solved by direct methods and developed using alternating cycles of least-squares refinements and difference Fourier synthesis. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in idealised positions (C–H = 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08$ Å^2). The final cycle of least-squares refinement included 136 parameters for 1846 variables and did not shift and parameter by more than 0.001 times its standard deviation. The structure was assigned a weighting scheme of the form: $w = 1/[\sigma^2(F) + 0.000996F^2]$. The final R values were, $R = 0.033$ and $R_W = 0.037$, and the final difference Fourier was featureless with no peaks greater than 1.00 eÅ^{-3}. Calculations were carried out using the SHELXTL PLUS programme on the Micro Vax II computer at University College London. Table 1 gives the atomic coordinates, and Table 2 shows the bond distances and

TABLE 3. Least squares planes

Plane 1: C(1) 2, C(2) 1, C(3) 0, C(4) 1, C(5) 2, Cl 10, Rh* -189
Plane 2: C(6) 0, C(7)-0, C(8) 0, C(9)-0, Rh* 163
Angle between planes 13.2°

Distances of atoms from the planes are given in pm. Atoms not contributing to the planes are marked with an asterisk.

angles. The least-squares planes and deviations of atoms are given in Table 3. Tables of anisotropic thermal parameters, H atom coordinates, and a full list of molecular dimensions have been deposited with the Cambridge Crystallographic Data Centre.

4. Results and discussion

Figure 1 shows a general view of the molecular structure of **I** with the atom labelling. The projection of the cyclopentadienyl complex on to the 2,3-dimethoxybutadiene ligand is shown in Fig. 2. There are no intermolecular contacts below the sum of the van der Waals radii. The planarity of the cyclopentadienyl ring r.m.s. deviation from mean plane, 1.21 pm and the variations in C–C bond lengths within the pentagonal ring do not correspond to appreciable localisation of electron density. The rhodium atom, C(1) and its covalently bonded chlorine atom lie in the plane that bisects the two double bonds of the coordinated butadiene ligand as well as the C(3)–C(4) bond. This relative orientation of ligands has also been observed in $[(\eta^5$-C_5H_4-$C_6H_5)Rh(\eta^2$-$C_2H_4)_2]$ [6] and in $[(\eta^5$-$C_5(C_6H_5)_4Cl)Rh(\eta^4$-1,5-COD)] [7].

There are some significant differences in the metal-ring carbon bond distances in **I** which indicate a small degree of slippage towards an η^1-alkyl-η^2-ene, η^2-ene (usually referred to as 'diene-yl') rotamer. The structure of $[(\eta^5$-$C_5(C_6H_5)_4Cl)Rh(\eta^4$-1,5-COD) [7] shows that three types of metal-ring carbon bonds are present in the case of a marked slip-fold distortion. These are: (i) a very short Rh–C(1) bond 218.3(4) pm, (ii) intermediate Rh–C(2), Rh–C(3) bonds averaging 226.2(4) pm, and (iii) two longer Rh–C(4), Rh–C(5) bonds averaging 230.2(4) pm. In addition the cp ring is folded about the C(2)–C(5) vector by 4.2°. The corresponding bond distances in **I** are (i) Rh–C(1) 221.5(5) pm, (ii) average of Rh–C(2), C(3) 222.3(5) pm and (iii) average of Rh–C(4), C(5) 226.8(6) pm. A small degree of slippage of the diene-yl type is also reflected in the C(1)–Cl bond distance, which is 173.2(5) pm in **I**. In compounds in which this carbon is sp^2 hybridised, such as decachlororuthenocene [8], the C–Cl bond length is 170.3 pm, whereas in $(\eta^1$-$C_5Cl_5)Mn(CO)_5$, in which the carbon is considered to be sp^3 hybridised, the length is 179.8(6) pm [9]. There are no inequalities in the metal–carbon and carbon–carbon distances of the 2,3-dimethoxybutadiene ligand in **I**, and both are very similar to those observed in $[(\eta^5$-$C_5H_4CHO)Rh(\eta^4$-$C_4H_4(OMe)_2)]$ [1].

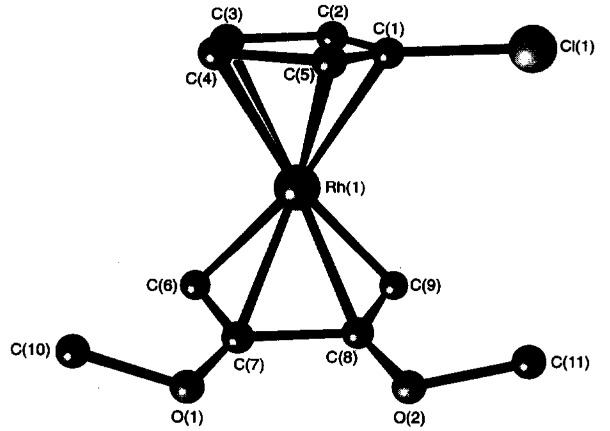

Fig. 1. The molecular structure of $(\eta^5$-$C_5H_4Cl)Rh(\eta^4$-$C_4H_4(OMe)_2)$ (**I**).

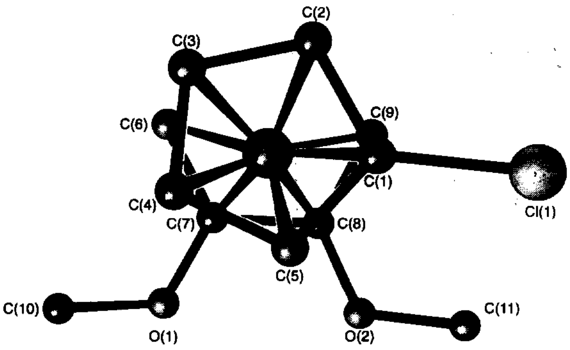

Fig. 2. A view of the structure of $(\eta^5$-$C_5H_4Cl)Rh(\eta^4$-$C_4H_4(OMe)_2)$ (**I**) through the cyclopentadienyl group, showing the relative orientations of the ligands.

The conformation associated with the ligands in **I** is linked with two important bonding interactions. If the cp ring lies in the *xy* plane, the bonding involves (i) the diene Ψ_2 MO and ring e_1^- MO competing for the empty metal d_{xz} hybrid orbital, and (ii) the diene Ψ_3 MO competing with the ring e_1^+ MO for the filled metal d_{yz} orbital. The character of the HOMO in this situation is e_1^+ and the electrons in this HOMO impose a diene-yl distortion upon the cp ring that is uncompensated by the e_1^- LUMO. As discussed in Part II [6]

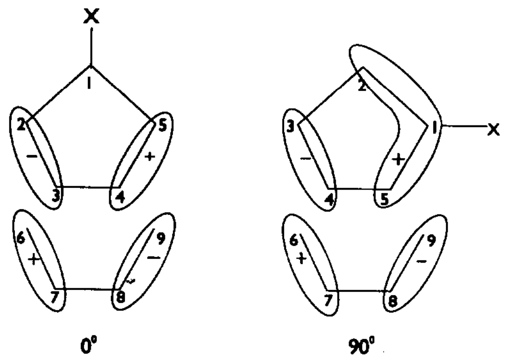

Fig. 3. Possible orientations of ligands in I.

TABLE 4. Mulliken overlap populations and total energies associated with 0° and 90° torsional orientations of the diene and ring in $[(\eta^5C_5H_4Cl)Rh(\eta^4\text{-}C_4H_4(OMe)_2)$ (I)

ϕ	p12	p23	p34	p45	p51	Energy (eV)
0°	1.0442	1.0272	1.0760	1.0272	1.0442	−957.9538
90°	1.0265	1.0555	1.0193	1.0699	1.0490	−958.4724

there are two possible ligand conformations found in substituted cyclopentadienyl-rhodium(olefin) compounds. These are associated with torsion angles $\phi = 0°$ and 90°, as depicted in Fig. 3. The former angle correlates with a tendency towards allyl-ene slippage, and the latter is associated with diene-yl slippage.

An extended Hückel calculation [10] was performed on **I** for both 0° and 90° orientations. The Mulliken bond orders and EH energies are given in Table 4. These results support the findings of the diffraction study relating to both orientation and distortion.

We have noted previously that substituents that can engage in effective conjugation with the cp ring, *e.g.* CHO, COMe, or COOMe are associated with the 0° orientation, while those that do not interact with the ring in this way are always associated with the 90° orientation [6].

5. ^1H and ^{13}C NMR spectra

Tables 5 and 6 give the ^1H and ^{13}C NMR data for several $[(\eta^5\text{-}C_5H_4Cl)Rh(olefin)]$ compounds according to the numbering scheme given in Fig. 4.

We had previously assigned the relative positions of H(2,5) and H(3,4) in chloro-substituted cyclopentadienyl-rhodium compounds on the basis that the latter should show a larger $^{103}Rh-^1H$ coupling constant by analogy with related rhodium compounds in which the cyclopentadienyl ring carries an electron accepting methanoyl or methoxycarbonyl group [11]. However, recent 2-D HCC relay spectroscopy studies [12] have shown that the opposite is the case, and in the chloro- and phenyl-substituted derivatives the H(2,5) nuclei show a typical metal coupling of 1.0 Hz while the H(3,4) nuclei generally show a smaller value ranging from 0.5 Hz in **V** to 0.8 Hz in **I**. This means that the resonance positions for the ring signals in all these compounds with the exception of **II** are those expected on the basis of the electron-accepting effect of this substituent. While an approximate correlation between these two metal-ring hydrogen couplings and population of an allyl-ene rotamer may be made for carboxyl-substituted rings [1], the situation is less clear for systems in which there is an appreciable population of the diene-yl rotamer, since the hydrogen atom pairs affected by slippage are now H(2,3) and H(4,5). It is apparent however, that in all these compounds the η^5-bonding mode is predominant, and that as a consequence of the differing inductive effects of carboxyl groups on the one hand and halogen and phenyl groups on the other, the relative ordering of these couplings may well reflect the variation in electron density at the corresponding carbon atom pairs. Substituent groups such as methanoyl tend to enhance the electron density at the C(2,5) ring positions at the expense of C(3,4),

TABLE 5. ^1H NMR spectral data for $[(\eta^5\text{-}C_5H_4Cl)Rh(diolefin)]$ with ^{103}Rh coupling constants in parentheses [a]

No.	Diolefin	H2 H5	H3 H4	$H6_a$ $H9_a$	$H6_s$ $H9_s$	H7 H8	(other)
I	2,3-dimethoxybutadiene	5.52 (td) (1.0)	5.21 (td) (0.8)	−0.02 (dd) (2.9)	2.50 (dd) (1.1)	3.47 (s, Me)	
II	t,t-1,4-diphenylbutadiene	4.53 (td) (1.0)	4.94 (td) (1.0)	2.45 (dd) (2.2)	7.30 (m, Ph)	5.46 (dd) (1.5)	
III	norbornadiene [b]	5.53 (td) (1.0)	4.96 (td) (0.6)		3.21 (m)	3.92 (m, H_{uc})	1.00 (t, H_b)
IV	2,5-dimethylhexa-1,5-diene [b]	5.30 (td) (0.9)	4.75 (td) (0.6)	1.63 (d)	2.56 (d)	1.78 (s, Me)	1.60–2.05 (m, H_{uc})
V	1,5-cyclo-octadiene	5.51 (td) (1.0)	4.90 (td) (0.5)		3.96 (m) (2.4)		2.18 (m, H_{uc})

[a] Recorded in $CDCl_3$ at 294 K relative to internal $SiMe_2$. [b] rhodium–diene coupling is less than 0.4 Hz; s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, td = triplet of doublets.

TABLE 6. ^{13}C NMR spectral data for $[(\eta^5\text{-}C_5H_4Cl)Rh(diolefin)$ with ^{103}Rh coupling constants in parentheses [a]

No.	Diolefin	C1	C2 C5	C3 C4	C6 C9	C7 C8	Me	C_{uc}
I	2,3-dimethoxybutadiene	98.37 (5.0)	84.51 (5.3)	81.13 (4.6)	19.81 (17.5)	123.49 (5.7)	56.77	
II	t,t-1,4-diphenylbutadiene	101.97 (5.9)	85.86 (6.2)	85.48 (5.2)	56.87 (14.9)	77.88 (7.7)	131.50 (Ph)	
III	norbornadiene	102.91 (6.0)	86.28 (3.9)	83.35 (5.2)	32.42 (8.9)			47.16 (C_b) [b] 57.68 (C_{uc}) (6.9)
IV	2,5-dimethylhexa-1,5-diene	100.14 (5.0)	90.47 (3.2)	87.68 (4.3)	54.62 (13.7)	83.59 (13.6)	29.92	39.32
V	1,5-cyclo-octadiene	98.68 (3.7)	86.99 (3.4)	84.67 (3.9)	66.45 (13.9)			32.17

[a] Recorded in $CDCl_3$ t 294 K relative to internal $SiMe_4$ [b] Bridgehead carbon

while chloro-, phenyl, and methyl substituents cause deshielding of C(2,5) relative to C(3,4) [13]. The larger metal–hydrogen coupling then tends to be associated with the hydrogen atom pairs that reside on the more deshielded carbon nuclei. CNDO/U calculations show that substituents which do not conjugatively interact with the cp ring tend to favour an orientation of ligands which increases the 'diene-yl' rotamer population. The ordering of these couplings may thus be considered as some indication of the nature of the slippage, and the differences between them tend to reflect the extent of a specific slip-fold distortion.

The ^1H NMR spectrum of **II** is unusual in that the H(2,5) nuclei resonate to high field of H(3,4). This is also observed [10] in the spectrum of $[(\eta^5\text{-}C_5H_4CHO)Rh(\eta^4\text{-}\textit{trans,trans}\text{-1,4-diphenylbutadiene})]$. In the latter case the phenomenon is associated with bonding characteristics of this diene and the presence of the strongly electron-accepting methanoyl group, which promote slip-fold distortion of the allyl-ene type. When the ring substituent is more weakly accepting, *e.g.* a methoxycarbonyl group, the ordering of these resonances is that expected on the basis of diamagnetic anisotropy [1]. Since a chlorine substituent is very weakly electron accepting it is difficult to account for the spectrum of **II** but it is noteworthy that the equal couplings to the H(2,5) and H(3,4) pairs are without precedent. This behaviour may be consistent with the relative orientation of the ligands in **II**, because the expected geometry is one in which the ring chlorine atom eclipses a phenyl group. Steric factors may then result in a modified orientation which is intermediate between the 0° and 90° conformers. The carbon spectra were assigned from C–H (HETCOR) correlation spectra, and the ordering of the C(2,5) and C(3,4) atom pairs is in agreement with that noted for analogous ferrocene derivatives [14].

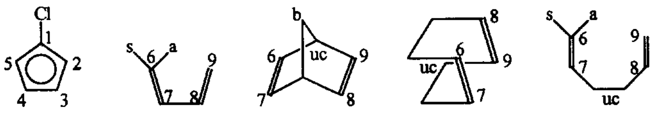

Fig. 4. The atom numbering system for Tables 5 and 6.

The results show that the relative magnitudes of rhodium–C(2,5) and C(3,4) couplings depend on the nature of the counter ligand. In carboxyl-substituted rhodium and iron-cyclopentadienyls, it is found that the C(3,4) atoms are associated with a larger metal–carbon coupling [15]. In accord with the change in substituent effect, the C(2,5) atoms show the larger coupling in **I** and **II**. However, the opposite occurs for **III**, **IV** and **V**, and this may be associated with a higher degree of localised bonding in the latter compounds.

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