Activation Energies for Molecular Tumbling and Cyclopentadienyl Rotation in $[M(\eta^5\text{-}C_5H_5)(\eta^4\text{-cod})]$ (M = Rh or Ir; cod = cyclo-octa-1,5-diene) and the *X*-Ray Crystal Structure of and Bonding in $[Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-cod})]$ †

Harry Adams, Neil A. Bailey,* Brian E. Mann,* Brian F. Taylor, Colin White, and Parvin Yavari
Department of Chemistry, The University, Sheffield S3 7HF

The *X*-ray structure of $[Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-cod})]$ (cod = cyclo-octa-1,5-diene) has been determined. The cyclopentadienyl ring is distorted in a manner consistent with an 'allyl-ene' structure. Carbon-13 and ^{103}Rh n.m.r. studies have been used to determine the activation energies for molecular tumbling and cyclopentadienyl rotation in $[M(\eta^5\text{-}C_5H_5)(\eta^4\text{-cod})]$ (M = Rh or Ir). Despite the 'allyl-ene' geometry, the activation energy for cyclopentadienyl rotation is the same as for ferrocene derivatives. The ^{13}C and ^{103}Rh chemical shift anisotropies were also determined.

There has been considerable discussion of the 'allyl-ene' geometry for the η^5-cyclopentadienyl ring.[1] The evidence for this bonding comes from *X*-ray structural investigations where typical bond lengths may be taken as those for $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$, (**1**), where the bond lengths support an 'allyl-ene' structure.[2] Support for the chemical significance of these observations is provided by the proposed mechanism of substitution of some cyclopentadienyl complexes, *e.g.* the reaction of $[M(\eta^5\text{-}C_5Me_5)(CO)_2]$ (M = Co or Rh) *via* $[M(\eta^3\text{-}C_5Me_5)(CO)_2L]$.[3]

If the localization of bonding is substantial, then it can be expected to restrict rotation of the cyclopentadienyl ring. It has been shown that ^{13}C nuclear magnetic relaxation data can be used to investigate such restricted rotation, provided that the molecule contains other CH groups.[4,5] The technique was applied to some monosubstituted ferrocenes, where localization of cyclopentadienyl bonding is not expected. In this work, the activation energies for molecular tumbling and cyclopentadienyl rotation are determined and the localized bonding is determined directly by *X*-ray diffraction analysis for $[Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-cod})]$ (cod = cyclo-octa-1,5-diene).

Preliminary structural data and powder-diffraction patterns obtained for $[Ir(\eta^5\text{-}C_5H_5)(\eta^4\text{-cod})]$ suggest that it is isomorphous with the present rhodium analogue, but the three-dimensional structure was not solved.[6]

Experimental

The n.m.r. technique employed has already been described.[5] The ^{13}C n.m.r. spectra were recorded at 100.62 MHz using a Bruker WH400 n.m.r. spectrometer using a 10-mm 43—170 MHz broad-band probe. The ^{103}Rh n.m.r. spectra were measured at 12.6 MHz using a 10-mm 12—50 MHz broad-band probe. Using this probe, the 90° pulse is 75 μs, but a 700-μs delay is required for the probe and electronics to recover after each pulse. As a result of the long 90° pulse, all measurements were performed on-resonance.

The complex $[Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-cod})]$ was prepared by the reaction of cyclopentadiene with $[\{RhCl(\eta^4\text{-cod})\}_2]$ in the presence of base as previously reported.[7] Sublimation of the product yielded pure crystals, which were used for the n.m.r. and *X*-ray studies. The complex $[Ir(\eta^5\text{-}C_5H_5)(\eta^4\text{-cod})]$ was prepared in 34.5% yield by a similar procedure using $[\{IrCl(\eta^4\text{-cod})\}_2]$; sublimation gave the product as white crystals.

Table 1. Atomic positional parameters with estimated standard deviations (e.s.d.s) for $[Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-cod})]$

Atom	*X/a*	*Y/b*	*Z/c*
Rh(1)	0.210 86(3)	0.180 34(6)	0.203 36(4)
C(1)	0.044 9(5)	0.271 0(11)	0.118 4(7)
C(2)	0.113 9(6)	0.406 6(10)	0.110 2(7)
C(3)	0.162 6(6)	0.453 3(9)	0.232 1(7)
C(4)	0.125 5(5)	0.350 8(9)	0.316 5(6)
C(5)	0.054 5(5)	0.232 4(10)	0.248 0(7)
C(6)	0.209 3(5)	−0.089 8(8)	0.172 0(7)
C(7)	0.256 9(5)	−0.055 5(9)	0.295 5(6)
C(8)	0.374 4(7)	−0.074 6(12)	0.342 1(8)
C(9)	0.433 6(5)	0.092 4(12)	0.331 4(7)
C(10)	0.375 8(5)	0.213 0(10)	0.233 5(8)
C(11)	0.338 4(5)	0.164 0(11)	0.111 2(7)
C(12)	0.354 6(6)	−0.015 5(13)	0.061 4(7)
C(13)	0.267 7(7)	−0.143 9(11)	0.073 9(8)

Crystallography.—Crystal data. $[Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-cod})]$, $C_{13}H_{17}Rh$, $M = 276.18$, obtained by sublimation as yellow, elongated plates, crystal dimensions 0.33 × 0.80 × 0.05 mm, monoclinic, $a = 12.977(9)$, $b = 7.693(5)$, $c = 11.208(5)$ Å, $\beta = 101.86(5)°$, $U = 1\,095(1)$ Å^3, $D_c = 1.675$ g cm^{-3}, $Z = 4$, space group $P2_1/c$ (from systematic absences), Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 14.93 cm^{-1}, $F(000) = 560$.

Three-dimensional *X*-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the omega-scan method: 1 523 independent reflections (of 1 929 measured) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarization effects. The structure was solved by standard Patterson and Fourier-transform techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions (C–H 0.95 Å); their contributions were included in structure-factor calculations ($B = 8.0$ Å^2) and limited optimization of positional parameters was permitted. Refinement converged at R 0.0332 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of the rhodium atom. Table 1 lists atomic positional parameters with estimated standard deviations.

Scattering factors were taken from the literature;[8] unit weights were used throughout the refinement. Computer programs form part of the Sheffield *X*-ray system.

Results and Discussion

The structure is illustrated in Figure 1 with the atom labelling used in Table 2, which gives bond lengths and angles with estimated standard deviations.

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† η-Cyclo-octa-1,5-diene(η-cyclopentadienyl)rhodium(I).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: cal = 4.184 J.

Table 2. Bond lengths (Å) and angles (°) with e.s.d.s. for [Rh(η^5-C_5H_5)(η^4-cod)]

Rh–C(1)	2.278(8)	Rh–C(6)	2.107(7)
Rh–C(2)	2.273(8)	Rh–C(7)	2.112(7)
Rh–C(3)	2.233(8)	Rh–C(10)	2.112(8)
Rh–C(4)	2.265(7)	Rh–C(11)	2.128(8)
Rh–C(5)	2.223(7)	C(6)–C(7)	1.420(10)
C(1)–C(2)	1.390(11)	C(7)–C(8)	1.515(11)
C(2)–C(3)	1.428(11)	C(8)–C(9)	1.514(12)
C(3)–C(4)	1.391(10)	C(9)–C(10)	1.513(11)
C(4)–C(5)	1.407(10)	C(10)–C(11)	1.409(11)
C(5)–C(1)	1.462(11)	C(11)–C(12)	1.519(12)
Rh···H(6)	2.55	C(12)–C(13)	1.527(12)
Rh···H(7)	2.60	C(13)–C(6)	1.516(11)
Rh···H(10)	2.58		
Rh···H(11)	2.58		
C(5)–C(1)–C(2)	107.1(7)	C(13)–C(6)–C(7)	125.2(6)
C(1)–C(2)–C(3)	106.8(7)	C(6)–C(7)–C(8)	121.6(6)
C(2)–C(3)–C(4)	111.2(7)	C(7)–C(8)–C(9)	112.4(7)
C(3)–C(4)–C(5)	106.0(6)	C(8)–C(9)–C(10)	113.2(7)
C(4)–C(5)–C(1)	108.9(6)	C(9)–C(10)–C(11)	124.2(7)
		C(10)–C(11)–C(12)	123.7(7)
		C(11)–C(12)–C(13)	113.2(7)
		C(12)–C(13)–C(6)	112.2(7)

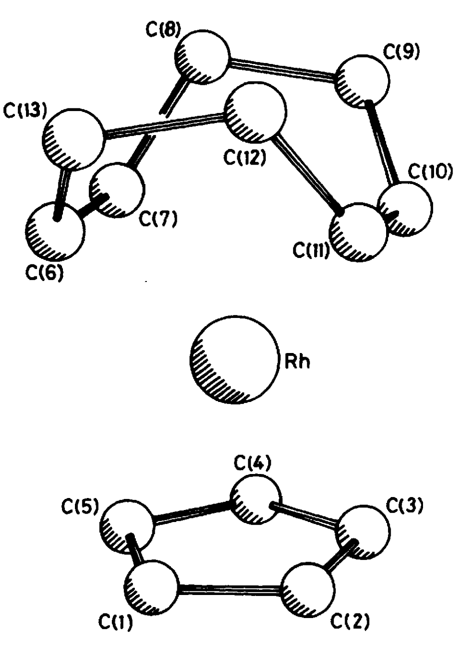

Figure 1. The molecular structure of [Rh(η^5-C_5H_5)(η^4-cod)] with the atom labelling

The cyclopentadienyl group, which is closely planar [root mean square (r.m.s.) deviation from mean plane 0.012 Å], is η^5-bonded to the rhodium atom; the slightly shorter rhodium–carbon distances to C(3) and C(5) reflect a 'pinching' of the ring across this line rather than a non-coplanarity or tilting of the ring. The ring bond lengths show an irregularity which can be either interpreted as a tendency to an 'allyl-ene' type of bonding, with atom C(4) as the central atom of the allylic fragment, or to a diene type geometry with C(1)–C(2) and C(3)–C(4) as the olefinic bonds. The rhodium atom lies 1.906 Å from the mean plane of the cyclopentadienyl ring and all hydrogen atoms are displaced from the ring plane in a direction away from the metal.

The cyclo-octa-1,5-diene is bonded to the rhodium atom in the normal η^4 mode; all four rhodium–carbon distances are essentially equal and the ligand adopts a slightly twisted-boat conformation [atoms C(6), C(7), C(10), and C(11) deviate by 0.043 Å from their mean plane and the torsion angles about bonds C(8)–C(9) and C(12)–C(13) are −24.3 and −21.5° respectively].

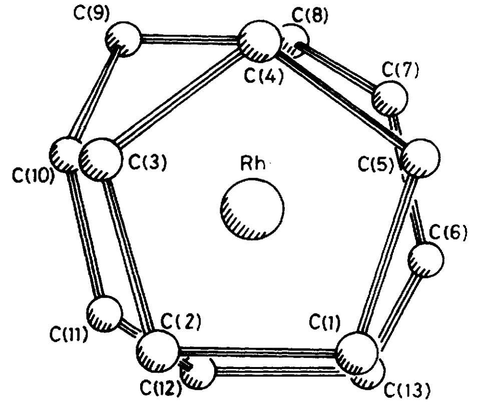

Figure 2. A view of the structure of [Rh(η^5-C_5H_5)(η^4-cod)] through the cyclopentadienyl group showing the relative orientations of the cyclic ligands

Wholly symmetric cyclopentadienyl and cyclo-octa-1,5-diene ligands of D_{5h} and C_{2v} symmetries, respectively, could adopt relative orientations such that, at most, there is coincidence of only one σ_v plane of each ligand. However, in view of the twisted nature of the cyclo-octadiene ligand, a relative orientation of the two ligands is possible in which two σ_v planes of the cyclopentadienyl are closely aligned with the two directions which, in the untwisted cyclo-octadiene, were its σ_v planes. This conformation is adopted in the present structure (see Figure 2). In order to determine the geometric distortions expected in the cyclopentadienyl group, resulting from the lesser symmetry of the *trans* ligand, it is necessary to consider the orbital overlaps between 'valence' metal orbitals and the π orbitals of both ligands, in each of the two unique relative orientations. Such a treatment has been previously reported[3] for the observed, symmetry-constrained, structure of [Co(η^5-C_5Me_5)$(CO)_2$], but consideration was given only to cobalt *d*-orbital involvement.

The co-ordinate system used and the rhodium valence orbitals, together with the donor and acceptor orbitals of the cyclopentadienyl and cyclo-octadiene ligands, are illustrated in Figure 3 with their irreducible representations under the point group C_{2v}. Forward donation from the a_1 and e_1^+ molecular orbitals of the cyclopentadienyl group and from the two filled olefinic bonding molecular orbitals of the cyclo-octadiene, in additive and subtractive linear combinations, utilize the rhodium s, p_x, p_z, and d_{xz} atomic orbitals and donation from the cyclopentadienyl e_1^- molecular orbital utilizes a suitable $(d_{yz} + p_y)$ hybrid orbital.† The d^8 configuration of Rh^I occupies d_{xy}, $d_{x^2-y^2}$, d_{z^2} and the reverse $(d_{yz} - p_y)$ hybrid orbital.† Of these latter σ-non-bonding orbitals, d_{xy} and $d_{x^2-y^2}$ can only engage in δ-back donation to the π^* orbitals of either or both of the ligands and this interaction can be neglected as inconsequential. The d_{z^2} orbital remains essentially non-bonding since the anti-nodes of the ligand molecular orbitals lie close to its conical nodal plane. The $(d_{yz} - p_y)$ hybrid† lies parallel to, and between, the olefinic bonds of the cyclo-octadiene ligand and can engage in back bonding to the lowest lying π^* orbital of that ligand.

Although no molecular antibonding orbitals are occupied, the existence of this occupied B_2 hybrid orbital, with a p_y com-

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† The hybrid, written as a linear combination, is not meant to imply the magnitudes of the coefficients on each of the components.

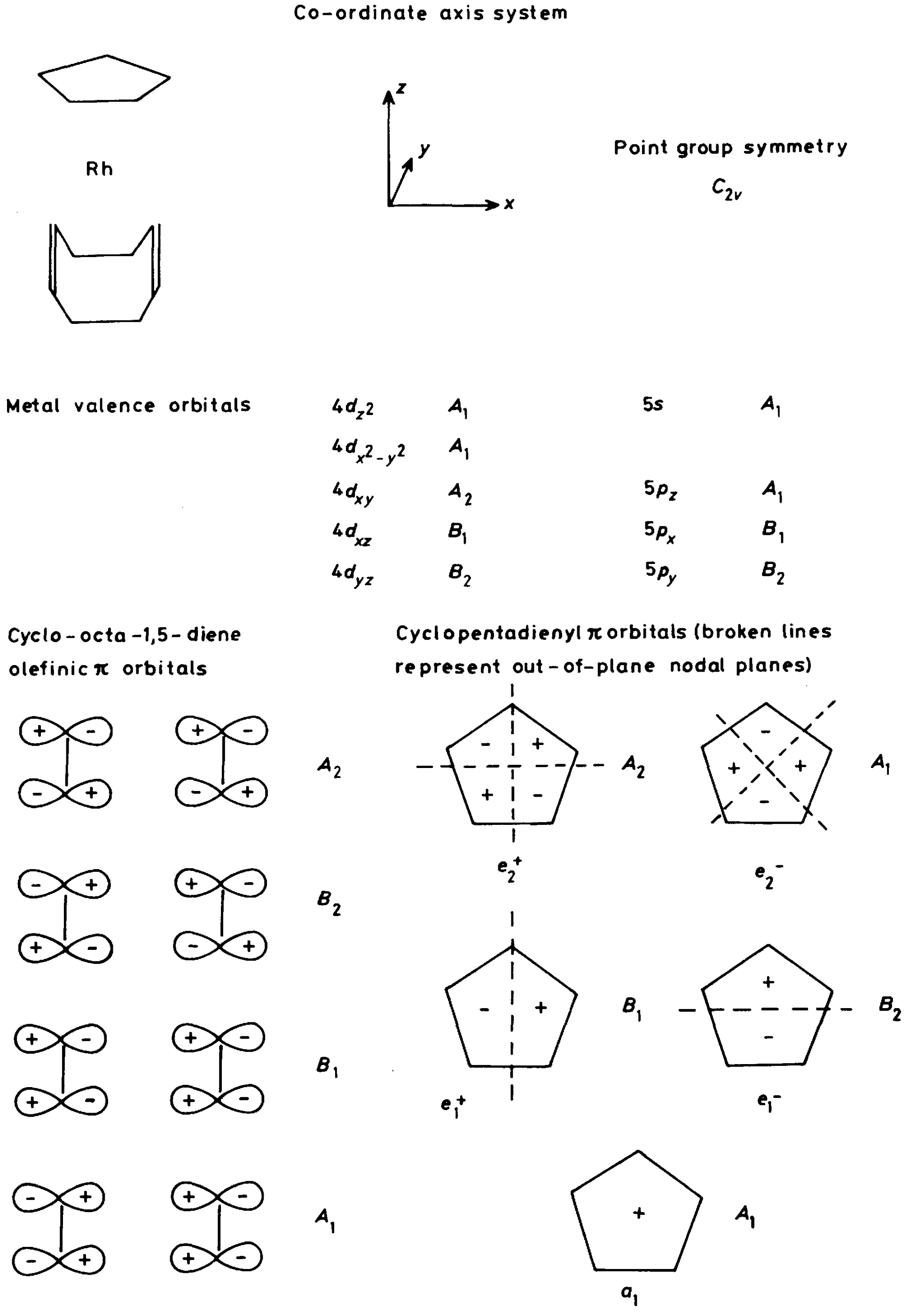

Figure 3. The metal valence atomic orbitals and frontier molecular orbitals of the two ligands, together with their irreducible representations under point group symmetry C_{2v}

ponent, at significantly higher energy than any occupied B_1 orbital is responsible for the loss of cylindrical symmetry and gives a lesser overall bonding for such B_2 interactions, thereby leaving the cyclopentadienyl ligand with a greater residual localization of its B_2 (e_1^-) molecular orbital and a consequential 'allyl-ene' geometry. If the cyclo-octadiene ligand were relatively twisted by 90° (or, equivalently 18°), then the cyclopentadienyl B_1 (e_1^+) orbital would have greater residual localization, leading to diene type geometry.

Thus the type of bond localization to be observed in the cyclopentadienyl ligand depends on which of the nodal planes of the e_1^+ and e_1^- molecular orbitals coincides with which of the σ_v planes of the Rh(η^4-cod) fragment of C_{2v} symmetry. There does not seem to be any clear reason to prefer either one or other orientation and it is likely that the small (18°) angular difference may be dominated by crystal-packing requirements or by crystallographically imposed symmetry constraints, leading to the appropriate localized geometry. In the present molecule, where the twist of the cyclo-octadiene ligand effectively reduces this 18° difference, it is not surprising that, even allowing for the marginal estimated standard deviations, a confused intermediate geometry results. In such circumstances,

Table 3. Carbon-13 and ^{103}Rh relaxation data for $[Rh(\eta^5-C_5H_5)(\eta^4-cod)]$ and $[Ir(\eta^5-C_5H_5)(\eta^4-cod)]$ in $[^2H_8]$toluene

(*a*) ^{13}C at 100.6 MHz

$[Rh(\eta^5-C_5H_5)(\eta^4-cod)]$				$[Ir(\eta^5-C_5H_5)(\eta^4-cod)]$		
Temperature/°C	T_1/s	$1 + \eta$	Assignment	Temperature/°C	T_1/s	$1 + \eta$
77.7	16.9	2.75	C_5H_5	73	15.8	2.71
	12.2	3.16	CH=CH		12.0	2.91
	6.9	3.25	CH_2CH_2		6.7	2.93
47	12.5	2.7	C_5H_5	50	11.4	2.71
	9.1	2.97	CH=CH		8.7	2.94
	5.0	2.99	CH_2CH_2		4.7	2.95
22	9.5	2.69	C_5H_5	22	9.1	2.72
	6.5	2.95	CH=CH		6.6	2.96
	3.8	2.98	CH_2CH_2		3.6	2.97
−9	5.5	2.67	C_5H_5	−5.5	5.2	2.68
	3.7	2.94	CH=CH		3.7	2.98
	2.0	2.95	CH_2CH_2		1.8	2.95
−27.5	3.2	2.66	C_5H_5	−27	3.3	2.65
	2.1	2.94	CH=CH		2.3	3.02
	1.1	2.93	CH_2CH_2		1.2	2.93

(*b*) $[Rh(\eta^5-C_5H_5)(\eta^4-cod)]$; ^{103}Rh at 12.6 MHz

Temperature/°C	T_1/s	$1 + \eta$	Temperature/°C	T_1/s	$1 + \eta$
66	12.7	1.11	−1.9	5.2	0.98
36.3	6.6	0.98	−33	2.4	0.99

Table 4. Calculated correlation times, τ_c, and cyclopentadienyl rotation times, τ_r, from ^{13}C n.m.r. data

Temperature/°C	$10^{12}\tau_c$/s	$10^{12}\tau_r$/s
(*a*) $[Rh(\eta^5-C_5H_5)(\eta^4-cod)]$		
77.7	4.2	2.9
47	5.6	3.8
22	7.6	4.2
−9	13.7	6.8
−27.5	24.1	11.3
(*b*) $[Ir(\eta^5-C_5H_5)(\eta^4-cod)]$		
73	3.9	3.3
50	5.6	4.7
22	7.4	5.0
−5.5	14.4	8.4
−27	21.4	10.6

the conclusions can be more simply expressed as a tendency for longer carbon–carbon bonds in the cyclopentadienyl ligand in positions most nearly opposite to π-accepting ligands: this argument is a manifestation of the well known *trans* influence.

The ^{13}C and ^{103}Rh nuclear magnetic relaxation data are collected in Table 3. The cyclo-octadiene carbon atoms show a full nuclear Overhauser enhancement (n.O.e.), showing that dipole–dipole relaxation is the only significant relaxation mechanism. For the CH_2 group, the spin–lattice relaxation time, T_1, is nearly half that of the cyclo-octadiene CH group. Qualitatively, the presence of two protons on the CH_2 group should halve its T_1 compared with the cyclo-octadiene CH group, but the average reduction is by a factor of 1.84. This discrepancy is better attributed to the shortened olefinic CH bond length rather than anisotropic tumbling. A small reduction in the bond length can have a much larger effect due to it being present to the sixth power in equation (1),[9] where μ_0

$$T_{1dd}^{-1} = \mu_0^2\gamma_I^2\gamma_S^2h^2S(S + 1)\tau_c/12\pi^2r^6 \qquad (1)$$

is the permittivity of a vacuum, γ_I is the gyromagnetic ratio of ^{13}C, γ_S is the gyromagnetic ratio of ^1H, h is Planck's constant, S is the spin quantum number of ^1H, τ_c is the molecular correlation time, and r is the carbon–hydrogen distance. This shortening is qualitatively consistent with the carbon–hydrogen bond-length change observed on going from ethane,[9] r_{CH} = 1.112 Å, to ethylene,[10] r_{CH} = 1.103 Å, or ferrocene,[11] r_{CH} = 1.104 Å. As a full n.O.e. is observed for the cyclo-octadiene carbon atoms, the condition $\omega^2\tau_c^2 \ll 1$ applies and equation (1) can be used to calculate the molecular tumbling time, see Table 4. Application of the Arrhenius and Eyring rate equations yields the following activation energies for molecular tumbling: for $[Rh(\eta^5-C_5H_5)(\eta^4-cod)]$, $E_a = 2.84 \pm 0.15$ kcal mol^{-1}, log $A = 13.18 \pm 0.54$, $\Delta H^‡ = 2.26 \pm 0.18$ kcal mol^{-1}, and $\Delta S^‡ = -0.18$ cal K^{-1} mol^{-1}; for $[Ir(\eta^5-C_5H_5)(\eta^4-cod)]$, $E_a = 2.85 \pm 0.12$ kcal mol^{-1}, log $A = 13.18 \pm 0.43$, $\Delta H^‡ = 2.29 \pm 0.12$ kcal mol^{-1}, and $\Delta S^‡ = -0.07 + 0.43$ cal K^{-1} mol^{-1}.

The T_1 for the cyclopentadienyl ring is considerably longer than for the olefinic carbon atoms of the cyclo-octadiene ring. This behaviour is attributable to an extra motional contribution due to intramolecular cyclopentadienyl rotation. The reduced n.O.e., η, in Table 3, shows that other mechanisms are operating, but the dipole–dipole contribution, T_{1dd}, can readily be calculated from equation (2). Equation (1) has been modified to include internal rotation by including X in equation (3),

$$T_{1dd} = 1.99T_1/\eta \qquad (2)$$

$$T_{1dd}^{-1} = \mu_0^2\gamma_I^2\gamma_S^2h^2S(S + 1)X\tau_c/12\pi^2r^6 \qquad (3)$$

where $X = \frac{1}{4}(3\cos^2\theta - 1)^2 + 18(5 + \sigma)^{-1}\sin^2\theta\cos^2\theta + \frac{9}{4}(1 + 2\sigma)^{-1}\sin^4\theta$; σ is the angle between the rotation axis and the C–H direction, $\sigma = (\tau_c + \tau_r)/\tau_r$, where τ_r is the rotation time of the group. For ferrocene, θ is known to be 85.4°, and the same angle is used for the two complexes in this paper. Application of equation (3) yields the value of τ_r given in Table 4, from which the activation energies for the cyclopentadienyl rotation can be calculated: for $[Rh(\eta^5-C_5H_5)(\eta^4-cod)]$, $E_a = 1.94 \pm 0.10$ kcal mol^{-1}, log $A = 12.66 \pm 0.35$, $\Delta H^‡ = 1.36 \pm 0.12$ kcal mol^{-1}, and $\Delta S^‡ = -2.51 \pm 0.37$ cal K^{-1} mol^{-1}; for $[Ir(\eta^5-C_5H_5)$-

Table 5. Temperature dependence of T_1(others) and the calculated chemical shift anisotropy for ^{13}C and ^{103}Rh for [Rh(η^5-C_5H_5)(η^4-cod)]

Temperature/°C	T_1(others)/s	$\sigma_{\parallel} - \sigma_{\perp}$/p.p.m.
(*a*) ^{13}C for the cyclopentadienyl group		
77.7	141	154
47	86	172
22	63	176
−9	34	182
−27.5	20	186
		average 174
(*b*) ^{103}Rh		
66	12.7	541
36.3	8.6	567
−1.9	5.2	467
−33	2.4	521
		average 524
(*c*) [Ir(η^5-C_5H_5)(η^4-cod)]; ^{13}C for the cyclopentadienyl group		
73	113	169
50	82	168
22	67	165
−5.5	34	178
−27	20	189

(η^4-cod)], $E_a = 1.69 \pm 0.17$ kcal mol^{-1}, log $A = 12.42 \pm 0.61$, $\Delta H^\ddagger = 1.12 \pm 0.18$ kcal mol^{-1}, and $\Delta S^\ddagger = -3.6 \pm 0.6$ cal K^{-1} mol^{-1}.

The most noteworthy feature of these results is that the *X*-ray structure of [Rh(η^5-C_5H_5)(η^4-cod)] shows bond localization in the cyclopentadienyl ring consistent with 'allyl-ene' bonding, yet the activation parameters are virtually identical with those for η-butylferrocene, where $E_a = 1.91 \pm 0.14$ kcal mol^{-1}, log A 12.74 ± 0.56, $\Delta H^\ddagger = 1.24 \pm 0.17$ kcal mol^{-1}, and $\Delta S^\ddagger = -2.5 \pm 0.7$ cal K^{-1} mol^{-1}.

It is clear that the 'allyl-ene' bonding has no significant effect on ring rotation. The n.m.r. and *X*-ray observations can be rationalized in terms of the speed of vibrations and rotations. The vibrational amplitude of a carbon–carbon bond in the ring will be similar to that for benzene,[12] 0.04 Å, which is approximately the same as the bond-length differences in the cyclopentadienyl ring.[2] Consequently, as the ring is rotating slowly compared with the speed of vibrations, the carbon–carbon bonds have ample time to re-adjust during the rotation.

The relaxation time of the cyclopentadienyl carbon atoms contains a second component other than the dipole–dipole mechanism discussed above, see Table 5. Paramagnetic relaxation is improbable as the sample was degassed, rhodium and iridium do not readily form paramagnetic complexes, and relaxation due to paramagnetic impurities should equally affect the cyclo-octadiene carbon atoms. The spin-rotation relaxation mechanism can be dismissed as the second relaxation component becomes more efficient with decreasing temperature, while the opposite is true for spin rotation. Scalar coupling relaxation can be dismissed for the rhodium complex as there are no quadrupolar nuclei present, and as the data for the iridium complex are so similar to the data for the rhodium complex the scalar coupling mechanism is also improbable for the iridium complex. This only leaves the chemical shift anisotropy mechanism and the chemical shift anisotropy is given in Table 5. The average value of 174 p.p.m. is not unreasonable in view of the literature values of 76 p.p.m. for ferrocene and 155 p.p.m. for [Ti(η^5-C_5H_5)$_2$Cl$_2$].

For ^{103}Rh, the theoretical maximum n.O.e. is 15.9 but in this work no enhancement was detected showing that no significant dipole–dipole relaxation occurs. Using a similar argument to that given above, it can be concluded that the relaxation mechanism is chemical shift anisotropy due to an anisotropy of 524 p.p.m.

Acknowledgements

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