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Substituted cyclopentadienyl compounds

II *. Molecular orbital study of ring slippage in some rhodium(I) derivatives and the X-ray structure of η^5-phenylcyclopentadienylbis(η^2-ethene)rhodium(I)

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Abstract

The X-ray structure of $(\eta^5\text{-}C_5H_4\text{-}C_6H_5)Rh(\eta^2\text{-}C_2H_4)_2$ has been determined. The substituent on the cyclopentadienyl ring crosses a double bond of the complexed ethene, *i.e.* relative to the rhodium atom it is *transoid* to the second olefinic double bond. The geometry of related systems is such that olefinic functions parallel the bond between the cyclopentadienyl ring and substituent. CNDO/U molecular orbital calculations have been performed on a series of these systems. The former orientation is often associated with a small contribution from an η^4-diolefin-η^1-alkyl rotamer while the latter is associated with an η^3-allyl-η^2-ene rotamer. The reasons for the preference for one of these structures in substituted cyclopentadienyl-rhodium(I)bis(olefin) compounds are discussed.

Introduction

Slip-fold distortion from η^5- towards η^3-coordination is perhaps best exemplified by certain transition metal-indenyl compounds [2], and it is well known that many $[(\eta^5\text{-indenyl})ML_n]$ systems display enhanced reactivity towards both S_N1 [3] and S_N2 [4] substitution reactions, compared with their cyclopentadienyl analogues. Nevertheless, there has been considerable discussion of the 'allyl-ene' geometry for the η^5-cyclopentadienyl ring [5]. The chemical significance of this

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* For Part I see ref. 1.

slippage has been demonstrated by the proposed mechanism of reaction of mono-substituted cyclopentadienyl-rhodium(I)- [6] and cobalt(I)-carbonyls [7] with tertiary phosphines. In these reactions it has been assumed, but not proved, that the substitution is facilitated in each case by some contribution from an allyl-ene rotamer. Similarly, the chemistry of a wide variety of transition metalcyclopentadienyl systems has been discussed in terms of slippage from η^5- to η^3- η^2- and η^5- to η^1-ring–metal bonding modes [8]. Crabtree *et al.* have also assumed that the reaction of the phenylcyclopentadienyl complex, $[(\eta^5\text{-PhC}_5H_4)IrHL_2]^+$ with PMe_3 involves the intermediacy of an allyl-ene slippage [9].

In contrast, the alternative η^4-diene-η^1-alkyl or 'diene-yl' slip-fold distortion has been scarcely mentioned since the discovery by Shaver *et al.* [10] that several cyclopentadienylrhodium(I)-olefin compounds show a contribution from this rotamer to the ring-metal bonding scheme. Bönnemann subsequently noted that analogous (Y–Co(1,5-COD) (Y = substituted cyclopentadienyl) showed one of two alternative orientations of diolefin and cyclopentadienyl ring [11]. The first involves a parallel orientation of diolefin functions with the cp ring C–X bond (X is the substituent). We noted that this is associated with related rhodium(I) systems which show a small degree of allyl-ene slippage [12]. In the second, the diolefin groups 'cross' the C–X bond, *i.e.* both orientations are related by a 90° rotation. The latter orientation has been found in association with the diene-yl slippage [10]. The distinction is less clear when the cp ring is unsubstituted [13] or polysubstituted [14].

Butler *et al.* performed a highly precise X-ray analysis of $(\eta^5\text{-C}_5H_5)Mn(CO)_3$ which was subsequently corrected for librational motion of the ring about the molecular axis [15]. They concluded that the observed inequalities in the ring C–C and metal–carbon distances arose from a population weighted average of both diene-yl and allyl-ene rotamers. Although Byers [16] noted allyl-ene slippage in $(\eta^5\text{-C}_5Me_5)Co(CO)_2$, analogous distortions in pentaphenyl- [17] or pentamethoxycarbonylcyclopentadienyl-transition metal complexes [18] have not yet been found. Bönnemann [11] noted that steric effects may sometimes by responsible for an observed conformation, *e.g.* in $(\eta^5\text{-C}_5H_4CPh_3)Rh(1,5\text{-COD})$ the olefin functions are parallel to the ring–substituent bond which minimises interaction between the diolefin and bulky trityl group.

In an attempt to examine the electronic effect of a ring substituent, we have restricted our study to cp–Rh(olefin) systems in which the ring is monosubstituted with a sterically innocent substituent. Although the accuracy of the X-ray data for $(\eta^5\text{-C}_5H_4C_6H_5)Rh(\eta^2\text{-C}_2H_4)_2$ is insufficient to demonstrate diene-yl slippage conclusively, the presence of this rotamer form is suggested by molecular orbital analysis. We report the results of some CNDO/U calculations on a series of monosubstituted cyclopentadienyl-rhodium(I)(olefin) systems. Our objective was to establish the relative importance of the ligand orientation and electronic nature of the ring substituent in the induction of a slip-fold distortion.

Experimental

X-ray crystallography: $(C_6H_5C_5H_4)Rh(C_2H_4)_2$

Crystal data: $C_{15}H_{17}Rh$, $M = 300.0$. Orthorhombic, a 5.762(7), b, 13.321(11), c 16.722(15) Å, U 1264.2 Å^3, D_m 1.60 g cm^{-3}, O_c 1.58 g cm^{-3}, $Z = 4$, $F(000) = 608$. Space group $P2_1nb$ (non-standard No. 33), $\mu(\text{Mo-}K_\alpha)$ 12.84 cm^{-1}, λ 0.7107 Å.

Table 1

Atomic coordinates ($\times 10^4$) for $(\eta^5\text{-}C_5H_4C_6H_5)Rh(\eta^2\text{-}C_2H_4)_2$

Atom	x	y	z
Rh	2500	5402(1)	2909(1)
C(1)	3844(29)	5777(17)	4117(10)
C(2)	1939(27)	5156(14)	4256(11)
C(3)	2573(32)	4256(14)	3856(11)
C(4)	4718(26)	4219(15)	3543(12)
C(5)	5638(28)	5235(17)	3711(12)
C(11)	6535(30)	8334(16)	4538(17)
C(12)	6205(28)	7427(16)	4265(12)
C(13)	4283(28)	6833(14)	4421(10)
C(14)	2497(33)	7263(15)	4908(10)
C(15)	2975(32)	8256(16)	5210(13)
C(16)	4981(31)	8771(15)	5027(16)
C(21)	1200(29)	6857(14)	2653(10)
C(22)	3324(25)	6792(16)	2269(12)
C(31)	2075(30)	4623(15)	1807(13)
C(32)	−75(29)	4798(17)	2099(13)

Measurements. Crystals of $C_{15}H_{17}Rh$ suitable for crystallography were obtained as yellow needles from hexane solution. A crystal of approximate dimensions $0.25 \times 0.3 \times 0.3$ mm was set up to rotate about the a axis on a Stoe Stadi diffractometer and data were collected *via* variable width ω scan. Background counts were for 20s and a scan rate of 0.0333°/s was applied to a width of $(1.5 + \sin \mu/\tan \theta)$. 1286 independent reflections were measured of which 891 with $I > 2\sigma(I)$ were used in subsequent refinement. The structure was determined by the heavy atom method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the cyclopentadienyl and phenyl rings were included in calculated positions. Hydrogen atoms on the ethene groups were located in a difference Fourier map and refined in constrained positions. The structure was given a weighting scheme of the form $w = 1/[\sigma^2(F) + 0.003F^2]$. Two structures were refined with opposite signs of coordinates and the structure with the lower R

Table 2

Selected bond lengths (pm) and angles (°) for $(\eta^5\text{-}C_5H_4C_6H_5)Rh(\eta^2\text{-}C_2H_4)_2$

Rh–C(1)	221.9(19)	Rh–C(2)	229.8(18)
Rh–C(3)	218.5(18)	Rh–C(4)	227.3(19)
Rh–C(5)	226.2(17)		
C(1)–C(2)–C(3)	102.0(16)	C(5)–C(1)–C(2)	111.1(18)
C(2)–C(3)–C(4)	117.1(17)	C(5)–C(1)–C(13)	120.1(15)
C(1)–C(5)–C(4)	106.5(15)	C(2)–C(1)–C(13)	128.4(16)
C(3)–C(4)–C(5)	103.0(16)		
Rh–C(21)	209.4(18)	Rh–C(22)	216.6(19)
Rh–C(31)	212.1(22)	Rh–C(32)	215.9(19)
C(1)–C(2)	138.7(25)	C(5)–C(1)	142.7(26)
C(2)–C(3)	140.5(27)	C(4)–C(5)	146.2(28)
C(3)–C(4)	134.4(25)	C(1)–C(13)	149.7(28)
C(21)–C(22)	138.4(21)	C(31)–C(32)	135.2(24)

Table 3

Least squares planes

Plane 1: C(1) 2, C(2) 3, C(3) −2, C(4) 1, C(5) 1
Plane 2: C(11) −1, C(12) 0, C(13) 2, C(14) −2, C(15) 0, C(16) 1
Plane 3: Rh, C(21), C(22)
Plane 4: Rh, C(31), C(32)
Plane 5: Rh, cg [a], mp(2) [b], mp(3) [c]

Angles between planes: 1ˆ2 6.6°, 1ˆ3 40.7°, 1ˆ4 44.3°, 3ˆ4 84.8°, 1ˆ5 89.8°, 3ˆ5 88.8°, 4ˆ5 84.9°.

Deviations from the plane are given in pm. [a] Centroid of cyclopentadienyl ring. [b] Midpoint of C(21)–C(22) bond. [c] Midpoint of C(31)–C(32) bond.

value (R 0.064, R_w 0.067) was taken as correct. Calculations were carried out using SHELX-76 [19] and some of the programs on the Amdhal computer at the University of Reading. Positional parameters are given in Table 1 and molecular dimensions in the coordination sphere in Table 2. Least squares planes are given in Table 3.

Tables of anisotropic thermal parameters, H atom coordinates, structure factors and the remaining molecular dimensions (11 pages) are available from the authors.

Discussion

Structural considerations

The structure is shown in Fig. 1 together with the atomic numbering scheme. The rhodium atom is bonded to a cyclopentadienyl ligand and to two ethene groups. The Rh–C(cp) distances vary within the range 218.5(18)–229.8(18) pm while the Rh–C(ethene)distances lie between 209.4(18)–216.6(19) pm. The structure is best evaluated by least squares planes calculations (Table 3). Here it is apparent that the Rh, cg (centroid of the cyclopentadienyl ring), cm(2) and cm(3) (mid-points of the ethene bonds) form a plane within experimental error. Thus, the angles cg–Rh–cm(2) and cg–Rh–cm(3) are respectively, 131° and 134° while the angle cm(2)–Rh–cm(3) is 95°.

The C=C bonds of the ethene groups are approximately perpendicular to this plane. The angle between the cyclopentadienyl and phenyl rings is 6.6°. There are not intermolecular contacts less than the sum of the van der Waals radii. The planarity of the cyclopentadienyl ring and the associated bond lengths do not suggest an appreciable localisation of electron density within the pentagonal ring. However in related systems of this type a small degree of ring slippage is commonly observed [10,12]. A symmetrical pentahapto interaction between ring and metal would not be anticipated in view of the low symmetry of this type of complex [15]. However the thermal motion of the ring generally affects the accuracy of the data. Since bond angles are more amenable to deformation than bond lengths it is relevant to note that the C(5)–C(1)–C(2) bond angle is 111.1° and that the orientation of the two alkene groups is such that they 'cross' the C(1)–C(13) bond of the counter ligand. This arrangement has also been observed in closely related cp–rhodium(I) complexes in which the η^4-diolefin-η^1-alkyl slippage has been identified [10,20].

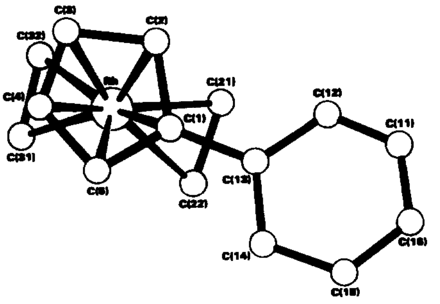


Fig. 1. The structure of $(\eta^5\text{-}C_5H_4C_5H_5)Rh^I(\eta^2\text{-}C_2H_4)_2$.

In contrast, the corresponding bond angle closes to 105° in those cp–rhodium(I) systems which have been shown to possess a contribution from an η^3-allyl-η^2-ene rotamer [12]. The two olefin functions are parallel to the C(1)–X (where X is the ring substituent) bond in this latter type of complex. Thus the nature of the ring substituent must affect the orientation of the two sets of ligands. Table 4 shows the slippage types observed for a series of rhodium(I) compounds.

In **1** the orientation is such that the C(cp)–Cl bond is crossed by an olefin function from 1,5-COD and a 'diene-yl' slippage is observed. It could be argued that this orientation arises from steric constraints but this seems unlikely since Bönnemann [11] noted that a parallel orientation was present in the related cobalt(I) complex, $(\eta^5\text{-}C_5H(C_6H_5)_4)Co(1,5\text{-}COD)$.

Although some degree of localised bonding would be expected in **2** and **7**, the reason for the nature of the slippage in **7** is not immediately obvious. The dynamic Jahn-Teller effects which might be expected for the isolated complex are probably supressed by the crystal lattice. Our solution NMR studies of **3** and **4** are in accord with some localised bonding and show that the electronic effects of a single chloro or phenyl substituent are closely matched [21]. Day *et al.* have shown that the 'diene-yl' slippage is present in **3** [10] and Bönnemann has found similar results in the X-ray analyses of $(BrC_5H_4)Co(1,5\text{-}COD)$ and $(ClC_5H_4)Co(1,5\text{-}COD)$ compounds [11]. The existence of this type of slippage in **4** is confirmed by our molecular orbital study and the reasons for the alternation are now discussed.

Table 4

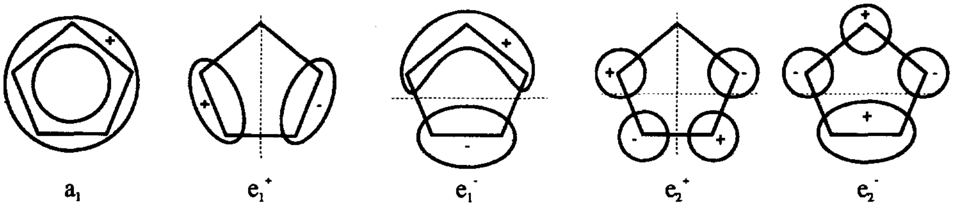
Observed alternation in ring slippage for several cyclopentadienylrhodium(I) complexes

Compound	Slippage type	Ref.
1 $C_5(C_6H_5)_4ClRh(C_2H_4)_2$	B	10
2 C_5H_5Rh(1,5-Cyclooctadiene)	A+B	13
3 $C_5H_4ClRh(C_2H_4)_2$	B	10
4 $C_5H_4C_6H_5Rh(C_2H_4)_2$	B [b]	
5 $C_5H_4CO_2CH_3Rh$(1,5-Cyclooctadiene)	A	12
6 C_5H_4CHORh(2,4-dimethylpenta-1,4-diene)	A	12
7 C_5Cl_5Rh(1,5-cyclooctadiene)	B	10

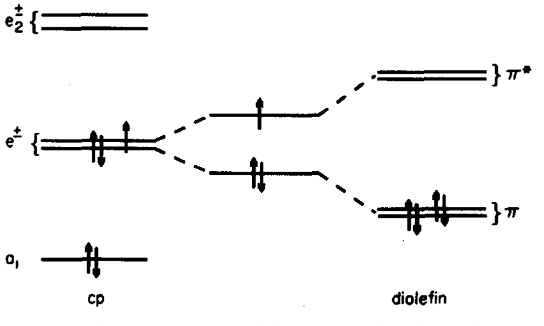
Type A slippage refers to 'allyl-ene' while type B slippage refers to 'diene-yl' bonding modes. [a] The (descending) order of the complexes reflects the increasing acceptance of the ring substituent(s). [b] Based on deformation in cp bond angles and relative orientation of ligands.

Molecular orbital theory of slippage in $(\eta^5\text{-}C_5H_4X)Rh(\text{diolefin})$ *compounds*

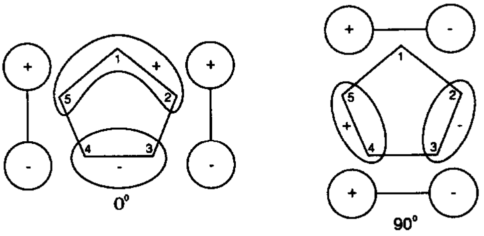
Qualitative aspects. 1. Consider the introduction of a rhodium ($4d^85s^1$) atom along the axis of the cp ring. Although this removes the symmetry plane of the ring, so that the cp MOs now have only approximate π character, the retention of the 5 fold symmetry axis implies that the nodal characteristics of the MOs will be similar to, and may be classified by, the orbital patterns of the C_{5v} point group.



If the unpaired electron on the Rh atom is considered to be extended into the cp ring, it will be fully associated with the $e_1^{\pm}$ levels, which may be regarded as not fully occupied. A bis-alkene or unconjugated chelating diolefin system, represented here by two ethene molecules with their C=C axes parallel, is added to the Rh–cp system so that the metal is sandwiched between the olefin functions and the cp ring. Of all the interactions between the three subsystems in cp · Rh · $(C_2H_4)_2$ we are interested in just those caused by the alkene ligands that will lift the degeneracy of the $e_1^{\pm}$ pair of levels. Now it is only those AOs on the intervening Rh atom which possess symmetries consistent with the MOs of diolefin (those discussed by, for example, Bailey *et al.*) that will communicate the perturbation from the diolefin to the cp ring [13]. As a result we can obtain a qualitative description of the effective interactions by considering HOMO–LUMO interactions between cp and diolefin subsystems.



The interaction of interest is that between the incompletely occupied $e_1^{\pm}$ orbitals on cp and the empty π^* levels on the diolefin. The orbital patterns on the left and right of the diagram make it clear that, for the $e_1^{\pm}$ nodal pattern depicted here, only the e_1^- orbital is stabilised by the interaction. The lifting of the degeneracy results in the full occupation of this component level at the expense of e_1^+ and consequently its nodal pattern imposes an 'η^3-allyl-η^2-ene' distortion on the cp ring, in which the C(3)–C(4) bond is shortened in comparison to C(2)–C(3) and C(4)–C(5). A similar effect is observed [16] and calculated [22] when transition metals are sandwiched between cp and two carbonyl ligands. As explained also by Bailey *et al.* [17], even if the cp is unsubstituted not all orientations of the olefin groups are equivalent with respect to the ring. In the above discussion we have selected a conformation in which the plane bisecting the bis-olefin (parallel to the C=C axes) passes through atom 1 and between atoms 3 and 4 in the pentagonal ring.



Next consider the rotation of the diolefin around the 5-fold axis of cp by an angle ϕ so that the bisecting plane is parallel to the C(3)–C(4) bond, but does not pass through a ring carbon atom. The smallest value of ϕ that will achieve this is 18°, but since the same structure is produced by a 90° rotation the two will be referred to as the 0° and 90° conformations. For the latter the diagram shows that it is the e_1^+ MO which is stabilised by the diolefin MOs, which should consequently impose an 'η^4-diolefin-η^1-alkyl' (or diene-yl) distortion on the cp ring, *i.e.* a shortening of the C(2)–C(3) and C(4)–C(5) bonds. At intermediate torsion angles ($0° < \phi < 18°$) there will be a different overlap between the Rh-mediated ligands: we might therefore expect the 0 and 90° conformations to describe energy minima in the rotation of the diolefin with respect to the cp ring. When one of the H atoms in the cp ring is replaced by a substituent X the nodal properties of the π-MO patterns are modified as shown in Fig. 2 of our earlier paper [12]. There we showed that while the e_1^+ MO is unaffected by the substitution, the e_1^- component is effectively raised in energy if X is an electronegative species and lowered if it is electropositive. Therefore unless the cp ring has a charge of -1.0, the nodal picture of π-MOs without the presence of the diolefin ligand would suggest that electronegative substituents would produce a diene-yl distortion, and less electronegative ones an allyl-ene distortion. This is what is observed [13], but we shall see in the next section that such a description is an oversimplification.

2. *Quantitative aspects.* Table 5 lists the Wiberg bond orders in the unsubstituted and substituted cp ring as calculated by CNDO/U [23], and also compares the total molecular energy for various torsion angles ϕ between 0° and 90°. The allyl-ene and diene-yl distortions in the unsubstituted ring for the energetically degenerate 0 and 90° conformations are revealed by the bond orders, and the Table shows that there is a very small energy barrier between these conformations. If the cp ring contains a substituent X in position 1 the bond orders show the ring distortions explained in Section 1, namely, that if the C=C bonds of the diolefin are parallel to C(1)–X the distortion is always allyl-ene and if perpendicular it is always diene-yl.

That this diolefin-orientation effect is more important than the nature of the substituent is seen from the comparison of the cases where X is a methoxycarbonyl, ethanoyl, methanoyl, chloro or fluoro group. In each case we get a distortion

Table 5

Wiberg bond orders on the monosubstituted cyclopentadienyl ring in bis(ethene)rhodium(I) complexes $[(\eta^5\text{-}C_5H_4X)Rh(\eta^2\text{-}C_2H_4)]$, as calculated by the CNDO/U method [23]. The total energy is also shown for various torsional orientations of the bis(olefin) and cp ring

X	ϕ ( )	p12	p23	p34	p45	p51	Energy (eV)
(Rh–cp)		1.3221	1.3221	1.3221	1.3221	1.3221	–
H	0	1.3281	1.1704	1.4395	1.1704	1.3281	–2599.4541
	9	1.3716	1.1525	1.4304	1.1994	1.2817	–2599.4385
	18 (or 90)	1.2374	1.4072	1.1465	1.4071	1.2374	–2599.4541
CH_3	0	1.3027	1.1681	1.4424	1.1668	1.3045	–2835.2197
	30	1.4065	1.1563	1.3582	1.2970	1.1652	–2835.1875
	60	1.3498	1.2713	1.2103	1.4258	1.1272	–2834.9609
	90	1.2079	1.4098	1.1485	1.4088	1.4088	–2835.1201
$COOCH_3$	0	1.2765	1.1952	1.4219	1.1934	1.2779	–4026.6885
	90	1.2044	1.4190	1.1452	1.4174	1.2057	–4026.5088
CHO [a]	0	1.2745	1.1947	1.4212	1.1933	1.2734	–3289.8809
	90	1.2026	1.4188	1.1451	1.4172	1.2029	–3289.7686
CHO [b]	0	1.2931	1.1714	1.4413	1.1714	1.2931	–3289.7744
	90	1.1975	1.4096	1.1494	1.4096	1.1975	–3289.7852
CHO [c]	0	1.2926	1.1738	1.4403	1.1738	1.2926	–3289.6523
	90	1.1992	1.4080	1.1541	1.4080	1.1992	–3289.4775
F	0	1.3153	1.1613	1.4485	1.1613	1.3153	–3332.0400
	90	1.2162	1.4072	1.1519	1.4072	1.2162	–3332.2129
$COCH_3$	0	1.2784	1.1921	1.4230	1.1911	1.2774	–3525.7354
	90	1.2043	1.4180	1.1449	1.4167	1.2064	–3525.5947
Cl [d]	0	1.3166	1.1619	1.4462	1.1619	1.3166	–3021.0918
	30	1.4165	1.1528	1.3612	1.2921	1.1784	–3020.9980
	60	1.3589	1.2689	1.2129	1.4224	1.1386	–3020.6240
	90	1.2184	1.4068	1.1506	1.4068	1.2184	–3021.1963

[a] CHO group coplanar with cp ring. [b] CHO group orthogonal to cp ring and oxygen atom *trans* to bis(ethene). [c] CHO group orthogonal to cp ring and oxygen atom *cis* to bis(ethene). [d] Electronic effect of Cl and C_6H_5 substituents are identical [21].

which depends only on the relative orientation of the diolefin group. The relative stabilities of the $\phi = 0$ and 90° conformers of the ring-monosubstituted species were then investigated. In the case of the Cl and F substituents the energy of the 90° conformer is slightly lower than that of the 0° conformer, resulting in a diene-yl distortion. For the substituents–$COOCH_3$, –$COCH_3$, and –CHO it is the 0° conformer that is more stable, resulting in the allyl-ene distortion. In each case these results support the findings of diffraction investigations relating to both conformation and distortion.

This indicates the influence of the ring substituent X on the conformation of the complex, and therefore on the type of ring distortion. However in the above series it is not only the electronegativity of X that is varied, but also the extension of electron delocalisation. We shall therefore examine each of these effects sepa-

Table 6

Effect of electronegativity of substituent X in $(\eta^5\text{-}C_5H_4X)Rh(\eta^2\text{-}C_2H_4)_2$ on the relative energies of the conformations

AO energies		(like atom)	Total CNDO energy (eV)	
$E(s)$	$E(p)$		$\phi = 0°$	$\phi = 90°$
50.0	15.0	[a]	−3108.5068	−3108.5352
32.272	11.080	F	−3053.4893	−3053.5928
25.390	9.111	O	−3030.2637	−3030.3555
19.316	7.275	N	−3009.5098	−3009.6455
14.051	5.572	C	−2991.2979	−2991.4639
9.594	4.001	B	−2975.5322	−2975.6982
5.946	2.563	Be	−2962.0811	−2962.3428
3.106	1.258	Li	−2950.9004	−2951.2158

[a] Fictitious highly electronegative atom.

rately. Table 6 shows results of calculations on systems in which X is an (ns^{1-2} np^{0-5}) monatomic ring substituent whose electronegativity is varied by assigning $2s$ and $2p$ energies appropriate to the atoms shown in the third column. In this way the electronegativity is controlled in isolation since the nature of X precludes effective conjugation with the cp ring. It is clear that for such a substituent no reasonable electronegativity condition can lead to a preferential stability of the $\phi = 0°$ over $\phi = 90°$ configuration. The resulting structure must therefore be that in which the C–X bond is normal to the π-bonds of the bis(olefin) ligands, and the cp ring distortion is diene-yl. Both these features are observed experimentally in the X-ray structures of halo-substituted cp complexes of Rh^1 in which the counter ligand is 1,5-cyclooctadiene or bis(ethene) [10].

The result is also consistent with our earlier description [12] of an electronegative substituent as one which raised the energy of e_1^- over that of e_1^+, leaving the ring to be described by the nodal pattern of the latter. Ideally it would be desirable similarly to explore the effects of different extents of electron delocalisation in the cp substituent. Computer space limitations preclude the treatment of the required size of molecular system in a way that would be analogous to that described for the variation of the electronegativity. However we may make some qualitative observations on the effect of a conjugated substituent such as phenyl. Of the two rings in $\eta^5\text{-}C_5H_4\text{–}C_6H_5$ the cp is the more electronegative group. From the orbital patterns of $e^{\pm}$ and the presence of a node at the substituent position 1 the e_1^+ component would be expected to be preferentially stabilised leading to the 90° conformation and consequently to a diene-yl slippage. This conformation is observed in the crystal structure of $(\eta^5\text{-}C_5H_4\text{-}C_6H_5)Rh(\eta^2\text{-}C_2H_4)_2$.

Conclusions

Our calculations have shown that while the nature of the substituent X may influence the distortion in the cp ring, nevertheless when such a system contributes a π ligand of rhodium in cpX-Rh(diolefin) it is the orientation of the diolefin ligand relative to the cp ring that dominates the nature and extent of the slippage. The principal contribution to the slippage is the consequence of the interaction between the $e_1^{\pm}$ π MOs of cp and the appropriate $4d$ AOs on Rh, whose degeneracies are removed by interaction (principally) with the π^* MOs of the diolefin. We have shown that this orientation effect operates even when the ring is unsubstituted, leading to two almost degenerate conformations, one of which has an allyl-ene slippage, when the diolefin functions are parallel to a cp C–H bond, and the other a diene-yl, when the diolefin is normal to the corresponding C–H bond. The observed geometry [13] for the cp ring in cpRh(η^4-1,5-COD) may be interpreted as arising from a contribution from both forms of slippage.

Having established that the ring distortion is dominated by the diolefin orientation with respect to the C–X bond of the cp ring, it remains for us now to provide a qualitative explanation of the findings of the numerical calculations, that when X can participate in the ring π system the $\phi = 0°$ conformation is favoured, while otherwise the $\phi = 90°$ structure has the lower energy. Since we have already explained in Section 1 why the $\phi = 0°$ orientation stabilises the e_1^- on cp, it is apparent why this orbital is further stabilised by interaction with the π system of the substituent. If X is, for example Cl, no such additional π stabilisation is possible if $\phi = 0°$ since participation in the ring π system would raise the energy of the electron pair in the *3p* AOs. For $\phi = 90°$ the MO which is favoured is e_1^+, which has a node at the substituent position. We have already discussed why a π conjugated substituent also stabilises e_1^+.

In conclusion, we have shown how qualitative theory explains the characteristics of the distortion of the C–C bond lengths in ring substituted cp-Rh-diolefin systems. That the distortion is dominated by the relative orientation of the diolefin ligand with respect to the π plane containing a carbon atom, rather than by the ring substituent, is supported by experimental structures, and also by a series of calculations on a series of cpX-Rh-diolefin compounds.

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