

Mono-substituted cyclopentadienyl half-sandwich transition metal complexes: ligand orientational effects

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Abstract

An analysis of crystal structures of the type $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{ML}_x$ ($x=1-5$) has been undertaken. A measure of the steric and electronic effects associated with L and R has been assessed from the arrangement of the L ligands relative to R and from the bending of R out of the cyclopentadienyl plane. The analysis revealed that when L and R were large, steric effects were dominant and the preferred conformer was such that L and R avoided each other as far as possible. Steric effects for small L and R were significant when x was large. For instance L groups were always staggered with respect to R for $x=4$ but for $x=2$ both staggered and eclipsed conformers were observed. Thus electronic factors were only dominant for a limited number of structures in which L, R and x were small. The results thus confirm an earlier proposal (N. J. Coville, K. E. du Plooy and W. Pickl, *Coord. Chem. Rev.*, 116 (1991) 1) that significant steric interactions are anticipated between the ring and the ligand set in $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{ML}_x$ complexes.

Introduction

Over the years, our research group has focused on the synthesis and study of mono-substituted cyclopentadienyl complexes of a range of transition metals. The NMR spectra of the complexes $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}$ have shown that the ligand set consisting of CO, L and I, adopt certain conformations relative to R in preference to others [1, 2]. Molecular mechanics calculations and crystal structure determinations established that the preferential conformations observed in solution are similar to those obtained in the solid state. We have thus come to the conclusion that, although electronic factors play a role, the preferred conformations in our complexes are *mainly* determined by steric factors. These steric considerations dictate that large R and L groups tend to adopt conformations in which they will be positioned away from each other. We wished to assess whether our findings could be related to a wider range of similar complexes. Herein we report the analysis of the crystallographic data available on a range of mono-substituted cyclopentadienyl transition metal half-sandwich complexes.

Some years ago, Muettterties *et al.* [3] published an analysis of $(\text{arene})\text{Cr}(\text{CO})_3$ type complexes. This study, which also summarised much earlier work in the area,

correlated orientational effects of the arene ring with the remaining ligands in the complex. Not unexpectedly, the orientation of the arene ring with respect to the three CO ligands (or other ligands) was shown to be dependent on intramolecular (electronic, steric) and intermolecular (crystal packing) effects. More recently Hunter and co-workers have analysed the arene planarity of ring substituted $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_3$ complexes and related the influence of substituent π donor/acceptor effects to this phenomenon [4].

In recent studies Poli [5] has analysed four-legged piano-stool structures of the type $(\eta^6\text{-C}_6\text{H}_6)\text{ML}_4$ and $(\eta^5\text{-C}_5\text{H}_5)\text{ML}_4$. A conformational analysis of the solid-state structures of $(\text{ring})\text{M}(\text{L})(\text{L}')(\text{PPh}_3)$ (ring = unsubstituted or substituted cyclopentadienyl or unsubstituted or substituted benzene) [6a] and metal diphosphine complexes [6b] has also been reported. The variation of bond distances and angles in metal-PPh₃ complexes has also been analysed [6c].

Since the pioneering work of Bürgi and Dunitz it has also been realised that crystallographic analyses can be used to obtain information on chemical transformations [7]. Examples of the analysis of crystal structures to obtain static and dynamic information for use in organometallic chemistry have also been reported over the years. Shambayati *et al.* used this approach to study Lewis acid carbonyl complexes, as well as to obtain conformations of π -bonding ligands in transition

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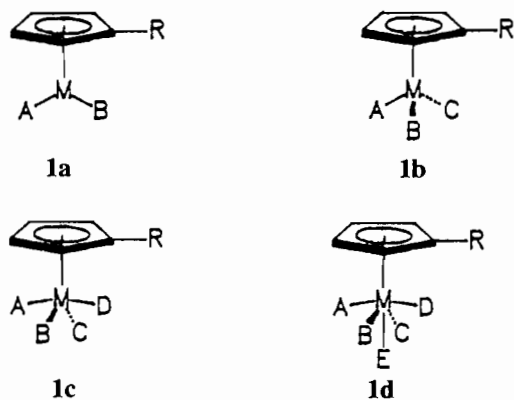
metal complexes [8]. Davies and co-workers [9] used crystal structures to undertake a conformational analysis of complexes containing the CpFe(CO)(PPh₃) auxiliary. The mechanism of the rearrangement of the metal framework in Au₂Ru₃ clusters was studied by Orpen and Salter [10] using this approach.

It is thus apparent that much information is available from the crystal structure determinations that have been reported over the decades.

Methodology

A search of the Cambridge Data File base was undertaken and all structures of the type (η^5 -C₅H₄R)ML_x (**1**) were accessed. A listing of many of these structures was recently reported [11] but no analysis of the data was undertaken. For a full listing of all (η^5 -C₅H₄R)ML_x structures published until mid 1992, see 'Supplementary material'.

This collection of structures is divided into subsets to facilitate comparisons (see Tables 1–4). Firstly the complexes were divided according to the number of ligands, L, attached to the metal, viz. (η^5 -C₅H₄R)ML₅, (η^5 -C₅H₄R)ML₄, (η^5 -C₅H₄R)ML₃ and (η^5 -C₅H₄R)ML₂ (see **1a–1d** below; here different ligands are shown attached to M). These groups were then subdivided, e.g. according to the number of carbonyl ligands (L=CO) present. The reason for this second subdivision will become apparent in the discussion below.



The analysis concentrated on structures that met the following criteria.

(a) The complexes should contain a transition metal, M.

(b) The complexes should contain a mono-substituted cyclopentadienyl ligand, i.e. a cyclopentadienyl ring with only one ring substituent.

(c) The cyclopentadienyl ring must be bonded via all five ring carbons to the metal, i.e. the η^5 -bonding mode.

(d) Complexes should contain only one η^5 -bonded cyclopentadienyl ring, i.e. half-sandwich complexes only were considered.

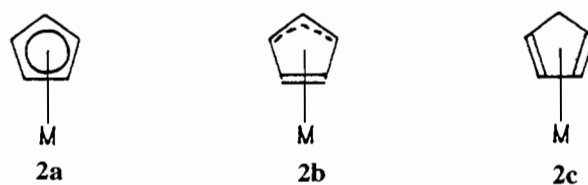
(e) Only complexes containing one (η^5 -C₅H₄R)M moiety were considered.

(f) To simplify the analysis, only ligands, L, coordinated to the metal through one atom, i.e. η^1 -bonding, were considered. (This excludes, for example, η^3 -allyl ligands and η^2 -diphosphine ligands).

The data contained in 'Supplementary material' do contain several compounds that do not meet the above criteria. Thus, chelating ligands have been excluded from the discussion that follows. Occasionally explicit mention will be made to these structures since they also provide information on bond lengths, bond angles, etc. A small number of crystal structures were not analysed due to apparent errors in the reported atomic coordinates, e.g. see ref. 49.

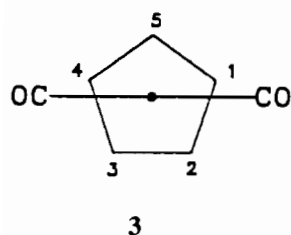
Results

The free C₅H₅⁻ ion is aromatic, with completely delocalised π -electrons. However, upon complexation of the cyclopentadienyl anion with an ML_x fragment, the aromaticity is affected [12]. Three possible modes for attaching the η^5 -bonded cyclopentadienyl ring to a metal are shown below (**2a–2c**).



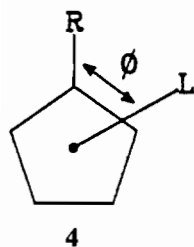
During a recent re-determination and analysis of the structure of (η^5 -C₅H₅)Mn(CO)₃, it was found that partial localisation of the cyclopentadienyl ring electrons occurred [12]. The (η^5 -C₅H₅)Mn(CO)₃ molecule was expected to be cylindrically symmetrical, but a number of structural features contradicted this expectation.

Recently, the crystal structure of (η^5 -C₅H₅)Co(CO)₂ was reported [13] and compared with the crystal structures of Cp*Co(CO)₂ (Cp* = η^5 -C₅Me₅, η^5 -C₅Bz₅, η^5 -C₅Ph₅). In these molecules, the aromaticity of the cyclopentadienyl ligands was disturbed. The cyclopentadienyl ring bonds which were eclipsed by the M–CO bonds were longer (C(3)–C(4), C(1)–C(2) = 1.424–1.429 Å) than those which were not eclipsed (C(2)–C(3), C(4)–C(5), C(1)–C(5) = 1.393–1.411 Å) (see 3).

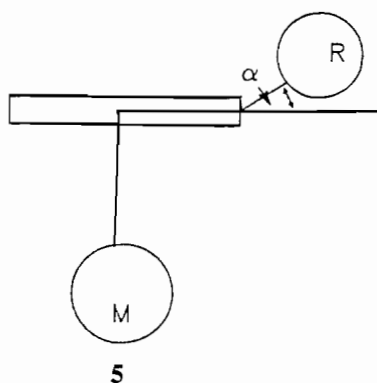


In the analysis of the crystal structures, discussed below, two particular features were deemed important.

(a) The conformations of the ligand set attached to the metal, as viewed down the cyclopentadienyl ring centroid–metal axis (4). The conformations are defined by the torsional angle ϕ (C–Cen–M–L) (C = cyclopentadienyl ring *ipso*-carbon, Cen = cyclopentadienyl ring centroid, M = metal, L = the atom through which the ligand is coordinated to M. Note: the torsional angles in Tables 1–4 are reported as negative or positive values. These values are defined relative to the ring substituents, with no implication with regard to chirality).



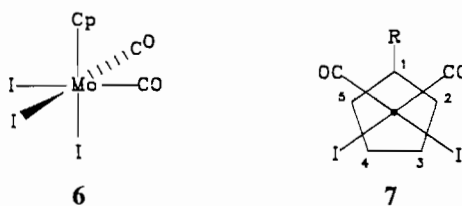
(b) The deviation, α (in degrees), of the cyclopentadienyl ring substituent from the cyclopentadienyl ring mean plane (5).



$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{ML}_5$ complexes

Only one crystal structure determination of a complex that falls in this category, $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{CO})_2\text{I}_3$ [14], has been reported (Table 1). If the cyclopentadienyl ring is considered as occupying *one* coordination site (instead of three), then the molecule can be described

as having a distorted octahedral geometry about Mo (6). The Mo atom is slightly lifted out of this plane, towards the cyclopentadienyl ring, and the CO groups are arranged in a *cis* configuration



When the molecule is viewed down the ring centroid–Mo axis (7), a conformation with the two CO groups on either side of the ring substituent, and the I groups away from the substituent, is observed. The cyclopentadienyl ring appears to deviate from complete aromatic delocalisation with the non-ligand eclipsed C–C bond shorter than the others (C(3)–C(4) = 1.387 versus the other C–C bond lengths of 1.413–1.434). An η^3 -allylic, η^2 -ene bonding type was proposed for this structure.

Steric crowding occurs due to the large number of ligands attached to the metal. Consequently, the centroid–Mo–L angles (L = equatorial ligands) are small (Cen–Mo–CO = 101–102°, Cen–Mo–I = 107°) when compared to $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{ML}_4$ complexes ($(\eta^5\text{-C}_5\text{H}_4\text{COMe})\text{V}(\text{CO})_4$: Cen–V–CO angles = 119–120° [15a]; $(\eta^5\text{-C}_5\text{H}_4\text{Pr})\text{WCl}_4$: Cen–W–Cl angles = 110–111° [15b]). The ring substituent, Me, consequently responds to this large steric interaction by bending out of the cyclopentadienyl ring plane, away from the metal, by a relatively large amount ($\alpha = 8.1^\circ$).

$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{ML}_4$ complexes

These complexes are considered as seven-coordinate, with the cyclopentadienyl ring occupying three coordination sites on the metal. A fairly wide range of crystal structures of complexes containing four L ligands have been reported (Table 2). To facilitate the discussion, the complexes in this group will be discussed according to the number of L = CO groups present in the structure.

$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_4$ complexes

Two extreme conformations are possible for these complexes when all the ligands, L, are the same: the 'eclipsed' and 'staggered' conformations, shown below (8).

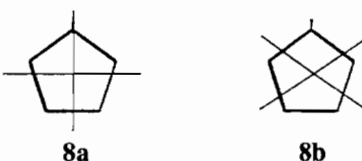


TABLE 1. (η^5 -C₅H₄R)ML₅ complexes

M	R $\alpha^{a,b}$	A $\phi^{b,c}$	B $\phi^{b,c}$	C $\phi^{b,c}$	D $\phi^{b,c}$	E	$d(M-C)^d$ $d(M-Cen)^d$	$d(C-C)^d$	$d(C-R)^d$	Ref. ^e
Mo	Me 8.1	CO 47	CO -47	I -5	I 132	I -138	2.301–2.375 1.998	1.387–1.434	1.496	14

For explanation of superscripts see footnotes to Table 3.

TABLE 2. (η^5 -C₅H₄R)ML₄ complexes

M	R $\alpha^{a,b}$	A $\phi^{b,c}$	B $\phi^{b,c}$	C $\phi^{b,c}$	D $\phi^{b,c}$	$d(M-C)^d$ $d(M-Cen)^d$	$d(C-C)^d$	$d(C-R)^d$	Ref. ^e	
(i) (η^5 -C ₅ H ₄ R)M(CO) ₄ complexes										
V	COMe -0.7	CO 32	CO -58	CO 121	CO -149	2.231–2.293 1.920	1.402–1.440	1.490	15a	
(ii) (η^5 -C ₅ H ₄ R)MCl ₄ complexes										
W	¹ Pr 3.4	Cl 136	Cl 46	Cl -44	Cl -134	2.304–2.348 1.995	1.388–1.422	1.507	15b	
(iii) (η^5 -C ₅ H ₄ R)M(CO) ₃ X complexes										
Cr	CHO -2.3	CO 49	CO 151	CO -58	AuPPh ₃ -135	2.164–2.230 1.838	1.37–1.42	1.45	17a	
Mo	Me 2.9	CO 36	CO 132	CO -60	HgCl -144	2.31–2.35 2.00	1.35–1.42	1.51	17b	
Mo	CHO -2.2	CO 32	CO 145	CO -65	AuPPh ₃ -140	2.310–2.392 2.012	1.401–1.428	1.448	17c	
Mo	COMe 0.8	CO 32	CO 139	CO -61	Me -141	2.305–2.380 2.01	1.403–1.427	1.478	17d	
W	COMe 2.3	CO 32	CO 127	CO -143	Me -55	2.30–2.41 2.012	1.34–1.49	1.47	17d	
W	CH ₂ OCOMe 7.7 6.8	CO -129 -134	CO -37 -42	CO 52 46	Cl 142 137	2.300–2.411 2.006 2.308–2.377 1.994	1.410–1.472	1.486	18	
W	C ₂ X ^e 5.6	CO 91	CO -75	CO -170	Me 10	2.310–2.385 2.003	1.406–1.417	1.427	19	
(iv) (η^5 -C ₅ H ₄ R)M(CO) ₂ (X)(Y) complexes										
Mo	Me 6.3 ^f	CO 38	CO -135	HgI -48	AsPhMe ₂ 129	2.28–2.40 1.991	1.381–1.499	1.439 ^f	20	
Mo	Me 0.7	CO 38	CO -142	I -57	P(OMe) ₃ 127	2.288–2.2411 2.020	1.376–1.476	1.518	21	
Mn	Me 0.0	CO 166	CO -14	GeCl ₃ -106	GeCl ₃ 80	2.109–2.149 1.757	1.379–1.451	1.513	22	
Mn	Me 3.2	CO 0	CO 179	SiCl ₃ -90	SiCl ₃ 88	2.112–2.165 1.772	1.389–1.419	1.503	23	
Mn	Me 3.6	CO 67	CO -46	SnPh ₃ -140	H 156	2.120–2.138 1.769	1.370–1.437	1.474	24	
Mn	Me 3.5	CO 15	CO 131	Si(F)Ph ₂ -78	H -135	2.123–2.142 1.757	1.411–1.430	1.497	25	
Mn	Me 3.5	CO 21	CO 131	SiCl ₃ -77	H -138	2.115–2.139 1.759	1.383–1.425	1.491	23	
Mn	Me 4.0	CO 14	CO -102	Si(Me)(Ph)(1-Np) 120	H ^g	2.10–2.14 1.76	1.38–1.46	1.49	26	
(v) (η^5 -C ₅ H ₄ R)M(CO)(X)(Y)(Z) complexes										
Mn	Me 3.8	CO -28	PMe ₃ -139	SiHPh ₂ 69	H 127	2.106–2.144 1.767	1.376–1.405	1.480	25	

For explanation of superscripts see footnotes to Table 3

Only one structure of a mono-substituted cyclopentadienyl tetracarbonyl transition metal complex has been reported, namely $(\eta^5\text{-C}_5\text{H}_4\text{COMe})\text{V}(\text{CO})_4$ [15a] (Table 2(i)). The angles between the four CO groups and the centroid–metal axis (Cen–V–CO) are very similar (119–120°).

The torsional angles between the two CO ligands closest to the ring substituent (COMe), $\phi(\text{C-Cen-V-CO})$, are 32 and -58°C , respectively. One might have expected the CO groups to be more symmetrically arranged (e.g. **8b**), but the COMe group appears to be the cause of this asymmetric arrangement. This substituent is almost coplanar with the cyclopentadienyl ring. (The C of the COMe substituent deviates from the cyclopentadienyl ring mean plane by 0.7° , towards the metal. The methyl group is also bent towards the metal by 4° , and the O is turned away from the mean plane and the metal by 4°). The CO ligand with the larger C–Cen–V–CO torsional angle is on the same side as the larger COMe methyl group, a phenomenon observed with other related complexes (see below).

$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{MCl}_4$ complexes

The complex, $(\eta^5\text{-C}_5\text{H}_4\text{Pr})\text{WCl}_4$ [15b] (Table 2(ii)) has Cen–W–Cl angles of 110–111°, which are smaller than the Cen–V–CO angles reported for the structure discussed above.

The two Cl ligands on either side of the ring substituent are approximately equidistant from the substituent, corresponding to the most extreme ‘staggered’ conformation (**8b**). The Pr substituent is arranged in a way which minimises steric interactions with groups below the ring: the two methyl groups point in the direction away from the metal. As a result, this group only bends out of the cyclopentadienyl ring plane, away from the metal, by 3.4° .

The cyclopentadienyl ring C–C bond lengths indicate incomplete delocalisation, with the C(3)–C(4) bond being the shortest (1.388 Å), and the two bonds adjacent to the substituent, C(1)–C(5), and C(1)–C(2) the longest (1.420–1.421 Å) (see 7 for numbering scheme).

$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_3\text{X}$ complexes [17–19]

The crystal structures of seven complexes of this type have been determined (Table 2(iii)). For five of these complexes (M = Cr, Mo, W; R = Me, CHO, COMe, CH₂OCOMe; X = AuPPh₃, HgCl, Me, Cl), the X group occupies a position as far away from the ring substituent as possible ($\phi(\text{C-Cen-M-X}) = \pm 135$ to 144°), without the ring substituent being eclipsed by a CO group (smallest $\phi(\text{C-Cen-M-CO}) = \pm 32^\circ$). Although electronic effects may play a role here (for example with the small X = Cl ligand), in all instances [16] steric effects (X > CO) [16] can adequately explain the conformations. The ring substituent deviations from the

cyclopentadienyl ring plane, α , are normal for the coplanar CHO and COMe groups. The angle α is fairly large ($6.8\text{--}7.7^\circ$) for CH₂OCOMe. The long OCOMe chain points down slightly towards the M(CO)₄ moiety in the structure [18].

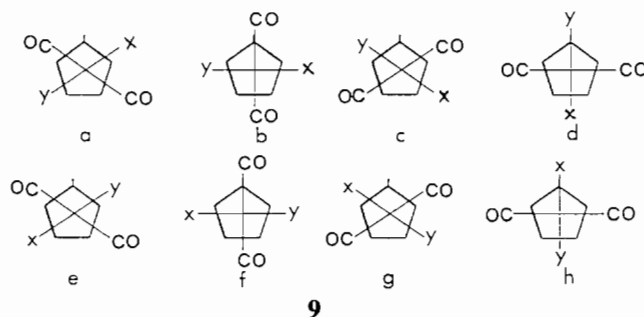
Of note is the relationship between the COMe group atoms (O,C) and the ligand set. For both $(\eta^5\text{-C}_5\text{H}_4\text{COMe})\text{M}(\text{CO})_3\text{Me}$ (M = Mo, W) the CO nearest to the ring substituent is closest to the O of the COMe group (see Table 2(i)).

For the remaining two structures, the X group (M = W, X = Me) gets as close as 10° [19] and 55° [17d] to the ring substituent. In the case of the latter structure [17d], disorder has been observed with regard to the Me position, where the positions of Me and one of the CO groups ‘trans’ to the ring substituent are interchangeable. The other complex in this series has X = Me at -141° [17d]. The small Me ligand thus shows no specific preferences with regard to its positions relative to a ring substituent.

$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_2(\text{X})(\text{Y})$ complexes [20–26]

The crystal structures of eight complexes are considered in this category (Table 2(iv)). Four of these complexes contain a hydride ligand ‘bridging’ the metal (M = Mn; X = Si(A)(B)(C) or SnPh₃; Y = H), and will be considered separately.

Interestingly, all four of the remaining structures (R = Me, M = Mo, Mn), are complexes which have a *trans* arrangement of the X and Y ligands of the metal ligand set. Eight extreme conformations (including mirror images) are possible for *trans*-($\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_2(\text{X})(\text{Y})$ complexes (**9a–h**). The rotational conformers which were *observed* for these complexes were those in which the bulky X or Y groups avoided positions close to the cyclopentadienyl ring substituent (smallest $\phi(\text{C-Cen-M-X/Y}) = 48$ to 88°).



The substituent deviation, α , ranged from 0.0 to 3.2° . (The deviation of 6.3° for $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{CO})_2(\text{HgI})(\text{AsPhMe}_2)$ [20] is not significant, see footnote to Tables). The positions of the CO groups, whether eclipsed or staggered with respect to R, did not seem to affect α significantly.

The $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_2(\text{X})(\text{H})$ complexes have the H and X ligands in a *cis*-configuration. The X ligand is situated away from the Me ring substituent in each case ($77\text{--}140^\circ$). The three ligands, other than H (2 CO and X), were all separated by dihedral angles of approximately 120° , which indicates the small effect of H on the conformers. The Me ring substituents bend away from the metal, and the cyclopentadienyl ring, by relatively small but similar amounts ($3.5\text{--}4.0^\circ$), regardless of the CO positions relative to R. It is to be noted that all C(ring)–C(Me) distances are shorter in these complexes ($\sim 1.49 \text{ \AA}$) than the average C(ring)–C(Me) distance ($\sim 1.51 \text{ \AA}$) found for all other $\eta^5\text{-C}_5\text{H}_4\text{Me}$ -containing complexes.

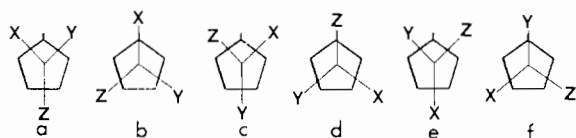
$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})(\text{X})(\text{Y})(\text{Z})$ complexes

Only one structure of this type, $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{M}(\text{CO})(\text{PMe}_3)(\text{SiHPh}_2)(\text{H})$ [25] (Table 2(v)), has been reported. A comparison with the similar structures above can be made since the structures are related by replacement of a CO ligand for the bulkier PMe_3 ligand. The predicted steric effects are observed. Thus, the conformation is staggered with respect to R (**8b**), with the larger PMe_3 and SiHPh_2 ligands positioned relatively far away from R ($\phi(\text{C-Cen-M-X/Y})$ are -139 and 69° , respectively). Not unexpectedly, the deviation of R from the cyclopentadienyl ring mean plane, α , is relatively small (3.8°).

$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{ML}_3$ ($L = \text{A, B, C}$) complexes [1b, 2, 19, 27–63]

The $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{A})(\text{B})(\text{C})$ complexes (Table 3), can be divided into six different groups, based on the types of the ligands attached to the metal. The first and second subsets are those complexes containing the most symmetrical ligand sets ($\text{A} = \text{B} = \text{C} = \text{CO}$ or Cl), and are discussed first. Complexes with $\text{A} = \text{B} \neq \text{C}$ ($\text{A} = \text{B} = \text{CO}$ or $\text{A} = \text{B} = \text{other ligands}$), and finally, complexes with $\text{A} \neq \text{B} \neq \text{C}$ ($\text{A} = \text{CO}$ or other ligands), are then discussed.

Some of the different possible extreme conformations for $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{A})(\text{B})(\text{C})$ complexes are shown in **10**.



10

$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_3$ complexes

The crystal structures of eleven *substituted* cyclopentadienyl tricarbonyl transition metal complexes have been reported (Table 3(i)). In these complexes, the

ligands are regarded as occupying six coordination sites on the metal (the cyclopentadienyl ring occupies three sites). The structures can be described as having a distorted octahedral geometry, or ‘piano-stool’ structure. Consistent with the octahedral geometry, the OC–M–CO bonds of these complexes are typically $90\text{--}91^\circ$.

The complexes discussed here were found in both of the extreme ‘staggered’ and ‘eclipsed’ conformations depicted in **10a** and **10b** ($\text{X} = \text{Y} = \text{Z} = \text{CO}$), as well as other conformations between these two extremes. The large variations in the positions of CO indicate that both steric and electronic effects associated with R could determine the preferential conformations obtained. Significantly for $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_3$ ($\text{M} = \text{Mn, Re}$; $\text{R} = \text{CHO, COMe}$) the CO ligands adopt conformer **10a**. This must be determined specifically by electronic (electron withdrawal) effects. By contrast, when $\text{R} = \text{SiMe}_3$ ($\text{M} = \text{Re}$) a similar conformer is observed but in this instance steric effects must be dominant.

The largest values for α were found for complexes containing small metals and large ring substituents (e.g. $\text{M} = \text{Cr}$, $\text{R} = \text{PPh}_3$, $\alpha = 9.8$). The chiral C(H)(Me)(NHCOMe) substituent has a small α value (3.8°), despite the presence of an eclipsed CO at the ring substituent position. Further, there is no evidence of intramolecular interactions between the substituent and CO since the largest NHCOMe group is turned in the direction away from the $\text{M}(\text{CO})_3$ moiety [31].

$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{MCl}_3$ complexes

Only one crystal structure of this type has been reported, namely $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{VCl}_3$ [36] (Table 3(ii)). The Cl–M–Cl angles ($99\text{--}103^\circ$) are larger than the OC–M–CO angles ($\sim 90^\circ$) of the structures discussed above and the Me group does not deviate significantly from the cyclopentadienyl ring plane ($\alpha = 3.9^\circ$). The cyclopentadienyl ring *ipso*-carbon is eclipsed by one of the Cl ligands (conformation **10b**) ($\text{X} = \text{Y} = \text{Z} = \text{Cl}$) and is indicative of an electronic effect determining the conformer choice.

$(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M}(\text{CO})_2\text{X}$ complexes

Among the sixteen structures with $\text{Y} = \text{Z} = \text{CO}$ (**10**) that fall in this group (Table 3(iii)), a wide range of conformers, are obtained. It is observed that nine complexes have $\phi = 180 \pm 30^\circ$, three with $\phi = 120 \pm 30^\circ$ and four with $\phi = 60 \pm 30^\circ$. Only three complexes have conformer **10b** and in these complexes X (a carbene ligand) was attached to the metal via sp^2 -carbon atoms. This C atom can arrange in such a way as to minimise steric interactions with the cyclopentadienyl ring. Thus for most of the structures steric effects predominate and result in conformations where large X groups adopt positions away from R. This does not explain the conformational preferences of small groups such as NO

TABLE 3. ($\eta^5\text{-C}_3\text{H}_4\text{R}$) ML_3 complexes

M	R	A	B	C	$d(\text{M-C})^d$	$d(\text{C-C})^d$	$d(\text{C-R})^d$	Ref. ^e
	$\alpha^{\text{a,b}}$	$\phi^{\text{b,c}}$	$\phi^{\text{b,c}}$	$\phi^{\text{b,c}}$				
(i) ($\eta^5\text{-C}_3\text{H}_4\text{R}$) $\text{M}(\text{CO})_3$ complexes								
Cr ⁺	CHO	CO	CO	CO	2.191–2.253	1.322–1.428	1.423	27
	3.0	-65	55	174	1.934			
Cr	PPh ₃ ⁺	CO	CO	CO	2.183–2.249	1.394–1.452	1.751	28
	9.8	-43	79	-166	1.862			
	5.8	-52	75	-172	2.192–2.257	1.386–1.443	1.755	
Cr	SMe ₂ ⁺	CO	CO	CO	1.872			
	3.6	53	-71	171	2.172–2.46	1.418–1.438	1.743	29
Mn	COMe	CO	CO	CO	1.854			
	1.4	176	58	-60	2.133–2.143	1.418–1.427	1.47	30
Mn	C(H)(Me)(NHCOME) ^b	CO	CO	CO	1.764			
	3.8	0	-122	119	2.13–2.16	1.40–1.45	1.52	31
Mn	C(S→X)Ph ⁱ	CO	CO	CO	1.77			
	0.2	-75	45	165	2.133–2.153	1.393–1.431	1.453	32
Mn	Ti($\eta^5\text{-C}_3\text{H}_5$) ₂ X ⁱ	CO	CO	CO	1.769			
	8.2	12	-115	134	2.137–2.912	1.394–1.442	2.207	33
Mn	Fe($\eta^5\text{-C}_3\text{H}_5$)(CO)L	CO	CO	CO	1.988			
L=CO	7.1	1	-118	122	2.129–2.216	1.39–1.44	2.001	34
L=PPh ₃	5.4	-26	-143	93	1.783			
Re	COMe	CO	CO	CO	2.13–2.25	1.37–1.45	1.99	
	1.6	-168	65	-58	1.803			
Re	SiMe ₃	CO	CO	CO	2.268–2.285	1.377–1.405	1.50	30
	3.5	-60	60	180	1.947			
					2.26–2.40	1.30–1.54	1.79	35
					1.951			
(ii) ($\eta^5\text{-C}_3\text{H}_4\text{R}$) MCl_3 complexes								
V	Me	Cl	Cl	Cl	2.234–2.308	1.322–1.428	1.423	36
	3.9	-125	0	118	1.934			
(iii) ($\eta^5\text{-C}_3\text{H}_4\text{R}$) $\text{M}(\text{CO})_2\text{X}$ complexes								
Cr	CHO	CO	CO	NO	2.186–2.220	1.407–1.438	1.470	37
	1.5	63	-50	-175	1.842			
Cr	CN	CO	CO	NO	2.192–2.216	1.414–1.441	1.456	37
	2.8	58	-64	176	1.849			
Cr	NH ₂	CO	CO	NO	2.156–2.280	1.389–1.411	1.361	37
	7.2	97	-21	-144	1.849			
Mn ⁻	Me	CO	CO	GeH ₃	2.109–2.149	1.379–1.451	1.513	22
	0.0	-178	-44	64	1.757			
Mn	Me	CO	CO	PPh ₃	2.132–2.162	1.396–1.432	1.466	38
	1.5	87	-30	-154	1.776			
Mn	Me	CO	CO	$\eta^1\text{-S}=\text{C}(\text{Ph})\text{SCH}_2\text{C}(\text{S})\text{NMe}_2$	2.136–2.148	1.394–1.422	1.485	39
	3.1	68	-47	-169	1.778			
Mn	Me	CO	CO	$\eta^1\text{-O-N}_2\text{C}_6\text{H}_4\text{CF}_3$	2.104–2.155	1.374–1.428	1.516	40
	2.3	-159	93	-34	1.777			

TABLE 3. (continued)

M	R $\alpha^{a,b}$	A $\phi^{b,c}$	B $\phi^{b,c}$	C $\phi^{b,c}$	$d(M-C)^d$ $d(M-Cen)^d$	$d(C-C)^d$	$d(C-R)^d$	Ref. ^e
Mn	Me	CO	CO	=C(Me)NH ₂	2.149–2.169	1.37–1.43	1.53	41
Mn	2.3	7	128	-112	1.777			
Mn	Me	CO	CO	=C(OMe)C(Me)PMe ₃	2.122–2.233	1.372–1.450	1.477	42
Mn	3.1	-121	115	3	1.721			
Mn	Me	CO	CO	CHCH(PEt ₃)	2.14–2.22	1.41–1.51	1.52	43
Mn	1.5	-109	130	11	1.79			
Mn	5.3	-96	136	22	2.11–2.23	1.40–1.51	1.51	
Mn	Me	CO	CO	C ₃ Pb ₂ ^k	1.77			
Mn	3.7	35	-83	160	2.140–2.163	1.398–1.416	1.503	44
Mn	Me	CO	CO	Ge[(η^5 -C ₅ H ₄ Me)Mn(CO) ₂]	1.786			
Mn	3.7	7	-114	126	2.130–2.168	1.403–1.441	1.484	45
Mn	Me	CO	CO	Sb(SPh) ₃	1.767			
Mn	2.1	44	-75	162	2.124–2.159	1.391–1.437	1.531	46
Mn ⁺	Me	CO	CO	SMe ₂ Et	1.771			
Mn	3.9	-26	-142	99	2.113–2.179	1.368–1.431	1.463	47
Mn	C ₂ X ^l	CO	CO	PPh ₃	1.782			
Fe	-1.0	-37	82	-160	2.131–2.163	1.404–1.437	1.424	19
Fe	SiMeX ₂ ^m	CO	CO	Et	1.776			
Fe	-0.9	80	-52	-163	2.101–2.125	1.387–1.435	1.860	48
(iv) (η^5 -C ₅ H ₄ R)MX ₂ Y complexes								
Cr ⁿ	CO ₂ Me	NO	NO	Cl	2.196–2.251	1.391–1.442	1.465	49
Cr	-0.7				1.870			
Cr	CO ₂ Me	NO	NO	I	2.194–2.244	1.395–1.420	1.467	49
Mo	0.0	174	49	-69	1.864			
Mo	Me	Cl	(N ₂ C ₈ H ₄ <i>p-p</i> -F)	(N ₂ C ₈ H ₄ <i>p-p</i> -F)	2.284–2.446	1.360–1.447	1.489	50
Ru	5.4	26	-95	147	2.046			
Ru	C ₂ CO ₂ Me	PPh ₃	PPh ₃	Cl	2.191–2.225	1.401–1.453	1.440	51
Ru	-2.8	136	-94	24	1.926			
Ru	C ₃ H ₄	CO	PMe ₃	PMe ₃	2.206–2.428	1.387–1.434	1.496	52
Co	9.7	-116	-3	119	1.998			
Co	CO ₂ Me	PPh ₃	Me	Me	2.092–2.141	1.388–1.432	1.469	53
Co	1.2	171	-67	49	1.743			
(v) (η^5 -C ₃ H ₄ R)M(CO)(X)(Y) complexes								
Fe	Me	CO	I	2,6-Me ₂ C ₆ H ₃ NC	2.058–2.159	1.40–1.42	1.507	1(b)
Fe	3.8	-121	2	117	1.725			
Fe	Me	CO	I	P(OMe) ₃	2.077–2.123	1.399–1.400	1.46	1(b)
Fe	3.0	-47	-165	74	1.724			
Fe	Me	CO	I	P(C ₆ H ₁₁) ₃	2.087–2.161	1.355–1.44	1.46	1(b)
Fe	6.1	-154	-45	80	1.749			
Fe	tBu	CO	I	PPh ₃	2.091–2.123	1.385–1.425	1.522	2
Fe	8.8	-1	-116	121	1.731			
Fe	CHPh ₂	CO	I	PPh ₃	2.087–2.118	1.409–1.434	1.511	54
Fe	2.8	-73	44	166	1.721			

Fe	I	CO	I	PPh ₃	2.06–2.11	1.35–1.51	2.03	54
	4.2	-48	68	-167	1.71			
Fe	NEt ₂	CO	Br	PPh(OEt) ₂	2.034–2.304	1.397–1.425	1.332	55
	6.8	-127	-7	108	1.759			
Ru ^o	menthyl	CO	Cl	PPh ₃	2.207–2.250	1.382–1.442	1.519	56
	2.4	77	-46	-165	1.848			
Ru ^{p,q}	NM	CO	I	PPh ₃	2.189–2.261	1.37–1.44	1.51	57
	9.8	-9	-145	117	1.843			
Mn	Me	CO	NO	C(O)C(O) <i>p</i> -Tol	2.119–2.168	1.384–1.416	1.495	60
	-0.3	165	33	-88	1.785			
Fe	Me	CO	COMe	PPh ₂ Et	2.088–2.130	1.396–1.440	1.479	61
	4.0	31	149	-98	1.739			
Fe	Me	CO	COMe	PPh ₃	2.088–2.126	1.383–1.418	1.508	62
	2.2	33	-84	159	1.746			
Ru ^{q,r}	NM	CO	NCMe	PPh ₃	2.180–2.262	1.392–1.442	1.498	58
	6.1	58	-64	180	1.848			
Ru ^{q,s}	NM	CO	Me	PPh ₃	2.274–2.323	1.428–1.515	1.535	59
	7.6	-35	-148	96	1.922			
Ru ^{q,t}	NM	CO	SO ₂ Me	PPh ₃	2.215–2.293	1.361–1.465	1.535	59
	10.1	-45	72	-170	1.903			
	6.5	-57	58	178	2.200–2.248	1.365–1.408	1.542	
(v) (η ⁵ -C ₅ H ₄ R)M(X)(Y)(Z) complexes								
Mn	Me	CS	NO	I	2.137–2.189	1.388–1.438	1.492	63
	6.0	-25	100	-135	1.794			

^aValue given is the angle, α , by which the substituent R deviates from the mean plane defined by the cyclopentadienyl ring (Fig 5). A positive value indicates a deviation in the direction away from the metal and a negative value signifies bending towards the metal. ^bMultiple values are given if the structure determination shows more than one crystallographically independent molecule. ^cValue is the torsional angle, ϕ (C-Cen-M-L), where C is the substituent-carrying cyclopentadienyl ring carbon, Cen is the cyclopentadienyl ring centroid, M is the metal and L is the ligand A, B, C, D or E. Negative and positive values do not give information about the stereoisomerism of the molecules. They indicate relative positions only. With ligands bonding via more than one atom to the metal, the torsional angle given is either that of the centre between the two extreme atoms, or the torsional angles to each of the atoms bonded to M. ^d $d(M-C)$ is the metal to cyclopentadienyl ring carbon bond length range in Å; $d(M-Cen)$ is the metal to cyclopentadienyl ring centroid bond length in Å; $d(C-C)$ is the cyclopentadienyl C-C bond length range in Å; and $d(C-R)$ is the bond length from the cyclopentadienyl *ipso*-carbon to the ring substituent, R, in Å. ^eX = (η⁵-C₅H₄)Mn(CO)₂PPh₃. ^fDisorder was experienced with respect to the methyl ring substituent position, when the structure of this complex was determined, hence these values are not significant. ^gThe position of H was not determined by X-ray crystallography. ^h(+)-(R)- α -(N-acetylamino) ethyl cymantrene. ⁱX = (η⁵-C₅H₃)Mn(CO)₂. ^jX = (η⁵-C₅H₄)Mn(CO)₃. ^k1,2-Diphenylcyclopropane. ^lX = (η⁵-C₅H₄)W(CO)₃CH₃. ^mX = (η⁵-C₅H₄)Fe(CO)₂Et. ⁿThe published coordinates contained errors and hence an analysis could not be performed on this compound. ^oConfiguration at Ru is (S)-(+)-. ^pConfiguration at Ru is (R)-(-)-. ^qNM = neomenthyl. ^rConfiguration at Ru is (R)-. ^sConfiguration at Ru is (S)-. ^tConfiguration at Ru is (S)-(-)-.

or the carbenes. The NO ligand is often found in a position near *trans* to the cyclopentadienyl ring substituent, and it appears that an electronic effect operates in the case of this ligand. The carbene adopts conformations similar to **10b** (R=Me) again suggesting electronic effects are significant.

$(\eta^5-C_5H_4R)MX_2Y$ complexes

Comparisons between complexes in this series are difficult, since X differs substantially between complexes (Table 3(iv)). For example, X could be a small group such as NO, or a large ligand, such as PMe₃. Hence no specific conformational preferences with regard to the arrangement of the X and Y ligands were noted.

$(\eta^5-C_5H_4R)M(CO)(X)(Y)$ complexes

This series of complexes contains a set of ten complexes with X=halogen (M=Fe, Ru; Y=PR₃, P(OR)₃, RNC). The CO and halogen ligands did not exhibit any preferential positions with respect to the ring substituent, R ($\phi(C-Cen-M-CO)=1-154^\circ$, $\phi(C-Cen-M-halogen)=2-165^\circ$). However, the bulky ligand Y always occupied positions *away* from the ring substituent. The torsional angle, $\phi(C-Cen-M-Y)$, in these structures was in the range 74–167°. Interestingly, none of the ligands, CO, halogen or Y were found with torsional angles $\phi(C-Cen-M-L)=180 \pm 13^\circ$.

The deviation of R from the cyclopentadienyl ring mean plane, α , was in the direction away from the metal. For large R groups ('Bu, neomenthyl), α was large (8.8°, 9.8°, respectively). Large unsymmetrical R groups that could rotate in such a way as to minimise interactions with the metal–ligand set (e.g. CHPh₂) had a smaller α value (2.8°).

A further six complexes in this group (X halogen) also showed similar conformational preferences. Again, regions close to the cyclopentadienyl ring substituents were not occupied by the bulky Y ligands (Y=phosphines and COCO-*p*-Tol). The torsional angle range, $\phi(C-Cen-M-Y)$, was 88–180°, while for the other ligands, $\phi(C-Cen-M-L)$ was in the range 30–165°.

$(\eta^5-C_5H_4R)M(X)(Y)(Z)$ complexes

The crystal structure of only one complex of this type, $(\eta^5-C_5H_4Me)Mn(CS)(NO)(I)$, has been reported (Table 3(vi)) [63]. The methylcyclopentadienyl ring substituent deviated from the ring, and away from the metal–ligand set by 6.0°. The conformation had the CS group closest to, and NO furthest from, the ring substituent ($\phi(C-Cen-Mn-CS)=25^\circ$).

$(\eta^5-C_5H_4R)ML_2$ complexes

The crystal structures of only three complexes of this type have been determined (Table 4). However, an interesting analysis of the crystal structures of unsub-

stituted and pentasubstituted cyclopentadienyl dicarbonyl cobalt complexes has been carried out [13] (see above). In the analysis it was found that the bonds 'eclipsed' by an M–CO bond were longer than those that were not eclipsed [13].

Only two mono-substituted cyclopentadienyl complexes containing two carbonyl ligands, have been reported. For one of these (M=Co, R=PPh₃) [65], the ligands are arranged nearly symmetrically about the ring substituent ($\phi(C-Cen-Co-CO)=91, -96^\circ$). The shortest bond length is associated with a non-eclipsed bond (C(4)–C(5)=1.375 Å), which is *trans* to the ring substituent. This shows that ring substitution leads to a distortion of the delocalisation of the cyclopentadienyl ring. The PPh₃ ring substituent is bonded to the ring via a single bond, and the phenyl rings are arranged to minimise steric interactions. As a result the deviation from the cyclopentadienyl ring mean plane, α , is relatively small (4.8°).

The other complex containing two CO ligands (M=Rh, R=NO₂) [66], has a less symmetrical arrangement of the CO ligands ($\phi(C-Cen-Rh-CO)=72, -111^\circ$). The cyclopentadienyl C–C bond lengths do not vary significantly or show localisation. The N and two O atoms of the NO₂ ring substituent are approximately coplanar with the cyclopentadienyl ring plane, and N deviates from the ring mean plane, away from the metal ($\alpha=3.7^\circ$). The *ipso*-C of the ring and the NO₂ substituent are approximately coplanar and the NO₂ mean plane deviates from the mean plane of the other cyclopentadienyl ring carbons (C(2)–C(4)) by approximately 10°. This indicates that the cyclopentadienyl ring aromaticity has been disturbed.

Discussion

From the above analysis a number of conclusions can be drawn.

1. When L and R are small, electronic effect will determine the arrangement of the ligands with respect to R. Unfortunately very few structures are available with small L and R. From the limited data set it appears that

(i) for $(\eta^5-C_5H_4R)ML_4$ conformer **8b** rather than **8a** is favoured for both electron donating and accepting L and R (R=COMe, L=4×CO or L=3×CO, Me; R='Pr, L=4×Cl).

(ii) for $(\eta^5-C_5H_4R)ML_3$, conformer **10a** is favoured for R=electron withdrawing group (R=CHO, COMe; L=CO) whereas for R=electron donating group, conformer **10b** is favoured (R=CHR₂Me, R=CO, Cl). However if one of the ligands is NO then it can override the effect of R (e.g. R=Me, L=2×CO, NO) and result in **10a** as the preferred conformer.

TABLE 4. (η^5 -C₅H₄R)ML₂ complexes

M	R $\alpha^{a,b}$	A $\phi^{b,c}$	B $\phi^{b,c}$	$d(M-C)^d$ $d(M-Cen)^d$	$d(C-C)^d$	$d(C-R)^d$	Ref. ^e
Co	Cl 6.0	CO -123	=CO(C ₄ H ₆)Zr(η^5 -C ₅ H ₅) ₂ 55	2.072–2.130 1.734	1.382–1.417	1.730	64
Co	PPh ₃ 4.8	CO 91	CO -96	2.018–2.112 1.688	1.375–1.426	1.765	65
Rh	NO ₂ 3.7	CO 72	CO -111	2.244–2.29 1.926	1.39–1.42	1.44	66

For explanation of superscripts see footnotes to Table 3.

2. If either L or R (or both) are large then L and R will tend to be displaced from each other. This can be influenced by the number of ligands e.g. (η^5 -C₅H₄R)CoL₂ conformers appear to be dominated by electronic effects [67]). This has been confirmed in a number of reports. For instance both ring rotational studies [11] and molecular mechanics calculations [1] have revealed that the energy barrier to ring rotation is small. However, as the ligands and/or ring substituents become larger the interaction between the ring and the ligand set increases.

3. When more than two different L groups are attached to the metal or when L is a bridging ligand, predictions become more difficult.

To date few theoretical studies have been published to assist in correlating the above ring substituent electronic (or steric) effects with ring–ligand conformations [68a–e]. From an analysis of (η^5 -C₄BH₄)M(CO)₃ and (η^5 -C₄NH₄)M(CO)₃ complexes [68b] it was suggested that the former complex would arrange the CO ligands to eclipse the B atom while the latter complex would arrange the ligands to be staggered with respect to the N atom. Thus, CO ligands would avoid atoms of high electronegativity. This would imply that if R was an electron withdrawing group in (η^5 -C₅H₄R)M(CO)₃ that an eclipsed arrangement of the CO groups would be expected. However, the structure of, for example, (η^5 -C₅H₄COMe)Mn(CO)₃ has a staggered geometry. The reason for this and other discrepancies is not known and perhaps could relate to the dominance of intermolecular packing forces.

Finally, a comparison between the above analysis and a series of (η^5 -C₆H₅R)Cr(CO)₃ complexes can be made. Hunter and co-workers [4] have convincingly indicated that when R is a π donating group on the arene ring that the substituent bends away from the ligand set, while if R is a π accepting ligand, R bends towards the ligand set. Steric effects are not believed to contribute in these findings. A comparison of data for the two types of complexes is shown in Table 5.

The data reveal that in general $d(C-R)$ is shorter in the cyclopentadienyl complexes. Care must be used

TABLE 5. A comparison of structural data for (η^5 -C₆H₅R)Cr(CO)₃^a and (η^5 -C₅H₄R)ML_x ($x=1-4$) complexes

Substituent	Arene complex		Cyclopentadienyl complex	
	$d(C-R)$ (Å)	α^b	$d(C-R)$	α^c
NEt ₂	1.356	5.89	1.33	6.8
NH ₂	1.369	5.78	1.36	7.2
OMe	1.357	1.90		
Me	1.501	-0.15	1.42–1.59	-0.3 → 6.1
SiMe ₃	1.891	-0.59	1.79	3.5
COMe	1.505	-1.04	1.47–1.50	-1.2 → 1.6
CO ₂ Me	1.493	0.40	1.46–1.47	-0.7 → 1.2
CH(tBu) ₂	1.523	11.84		
CHO			1.42–1.52	-2.2 → 3.0
NM ^d			1.50–1.54	6.1–10.1

^aData taken from ref. 8b. ^b α = angle between least-squares planes defined by the *ipso* and *ortho* carbon atoms of the arene and the least-squares plane defined by the *ortho* and *meta* carbon atoms of the arene. ^cSee text. ^dNM = neomenthyl.

in comparing data for the α values. The α values have been measured differently for the two sets of complexes. Further, the data for the new complexes are derived for a similar series of complexes whereas the same is not true for the cyclopentadienyl complexes. No obvious relationship between the two data sets is apparent. If a restricted set of complexes e.g. (η^5 -C₅H₄R)Fe(CO)₂(PPh₃)I (R = I, CHPh₂, tBu) are considered [54] it is found that α varies tBu (8.8°) > I (4.2°) > CHPh₂ (2.8°) which again does not correlate with the arene data.

Conclusions

The collected crystallographic data of (η -C₅H₄R)ML_x complexes have revealed that a wide range of complexes containing different substituents, metals and ligands has been reported. Prior to this work no comprehensive analysis of the data had been undertaken.

The analysis of the orientation of the ring substituent, R, with respect to ligands, L, below the ring plane has revealed that steric interactions between L and R are significant. These effects influence the final conformers observed in the solid state. Our study has also shown that when steric effects associated with L and R are small, conformational effects will be determined by a combination of electronic and inter-molecular packing effects. However, the data obtained to date do not appear to fit theoretical predictions. This could be a result of the limited data set presently available for testing the theory.

The aromatic character of the cyclopentadienyl ring was observed to be affected by the ring substituent. This was reflected in, for example, the cyclopentadienyl C–C bond lengths and non-planarity of the cyclopentadienyl ring. Not all the structures reflected these findings but this could relate to the quality of the X-ray crystallographic determinations. In this publication we have not investigated this phenomenon in any detail.

It is anticipated that half-sandwich complexes in which the ring contains more than one substituent would show even more dramatic steric effects. An analysis of these types of complexes may also further unravel the influence of steric and electronic effects on ligand conformational properties.

Supplementary material

Table 6 giving the X-ray crystallographic data for all (η^5 -C₅H₄R)ML_x complexes is available from the authors on request.

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References

- (a) P. Johnston, M. S. Loonat, W. L. Ingham, L. Carlton and N. J. Coville, *Organometallics*, **6** (1987) 2121; (b) P. Johnston, L. Denner, C. F. Marais, J. C. A. Boeyens and N. J. Coville, *J. Crystallogr. Spectrosc. Res.*, **18** (1988) 403.
- K. E. du Plooy, C. F. Marais, L. Carlton, R. Hunter, J. C. A. Boeyens and N. J. Coville, *Inorg. Chem.*, **28** (1989) 3855.
- E. L. Mutttert, J. R. Blecke, E. J. Wucherer and T. Albright, *Chem. Rev.*, **82** (1982) 499.
- (a) A. D. Hunter, V. Mozoi and S. D. Tsai, *Organometallics*, **11** (1992) 2251; (b) A. D. Hunter, L. Shilliday, W. S. Furey and M. J. Zaworotko, **11** (1992) 1550; (c) J. Li, A. D. Hunter,

- McDonald, B. D. Santarsiero, S. G. Bott and J. C. Atwood, *Organometallics*, **11** (1992) 3050
- R. Poli, *Organometallics*, **9** (1990) 1892.
- (a) H. Brunner, B. Hammer, C. Kruger, K. Angermund and I. Bernal, *Organometallics*, **4** (1985) 1063, (b) D. A. V. Morton and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, (1992) 641; (c) B. J. Dunne, R. B. Morris and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, (1991) 653.
- H.-B. Burgi and J. D. Dunitz, *Acc. Chem. Res.*, **16** (1983) 153
- S. Shambayati, W. E. Crowe and S. L. Schreiber, *Angew. Chem., Int. Ed. Engl.*, **29** (1990) 256
- B. K. Blackburn, S. G. Davies and M. Whittaker, in I. Bernal (ed.), *Chemical Bonds – Better Ways to Make Them and Break Them*, Elsevier, Amsterdam, 1989, p. 141.
- A. G. Orpen and I. D. Salter, *Organometallics*, **10** (1991) 111.
- N. J. Coville, K. E. du Plooy and W. Pickl, *Coord. Chem. Rev.*, **116** (1991) 1.
- P. J. Fitzpatrick, Y. Le Page, J. Sedman and I. S. Butler, *Inorg. Chem.*, **20** (1981) 2852.
- M. Yu. Antupin, Yu. T. Struchkov, A. N. Chernega, M. F. Meidine and J. F. Nixon, *J. Organomet. Chem.*, **436** (1992) 79.
- B. S. Erler, J. C. Dewan, S. J. Lippard and D. R. Tyler, *Inorg. Chem.*, **20** (1981) 2719.
- (a) M. Hoch and D. Rehder, *Chem. Ber.*, **121** (1988) 1541; (b) M. L. H. Green, J. D. Hubert and P. Mountford, *J. Chem. Soc., Dalton Trans.*, (1990) 3793.
- C. A. Tolman, *Chem. Rev.*, **77** (1977) 313
- (a) F. Edelmann, S. Tofke and U. Behrens, *J. Organomet. Chem.*, **309** (1986) 87; (b) M. Cano, R. Criado, E. Gutierrez-Puebla, A. Monge and M. P. Pardo, *J. Organomet. Chem.*, **292** (1985) 375; (c) B. N. Strunin, K. I. Grandberg, V. G. Andrianov, V. N. Setkina, E. G. Perevalova, Yu. T. Struchkov and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, **281** (1985) 599; (d) R. D. Rogers, J. L. Atwood, M. D. Rausch and D. W. Macomber, *J. Crystallogr. Spectrosc. Res.*, **20** (1990) 555.
- S. Tofke and U. Behrens, *J. Organomet. Chem.*, **331** (1987) 229
- C. Lo Sterzo and J. K. Stille, *Organometallics*, **9** (1990) 687.
- M. M. Mickiewicz, C. L. Raston, A. H. White and S. B. Wild, *Aust. J. Chem.*, **30** (1977) 1685.
- A. D. U. Hardy and G. A. Sim, *J. Chem. Soc., Dalton Trans.*, (1972) 1900.
- W. Gäde and E. Weiss, *Chem. Ber.*, **114** (1981) 2399.
- U. Schubert, K. Ackermann, G. Kraft and B. Wörle, *Z. Naturforsch., Teil B*, **38** (1983) 1488.
- U. Schubert, E. Kunz, B. Harkers, J. Willnecker and J. Meyer, *J. Am. Chem. Soc.*, **111** (1989) 2572.
- U. Schubert, G. Scholz, J. Müller, K. Ackermann, B. Wörle and R. E. D. Stansfield, *J. Organomet. Chem.*, **306** (1986) 303.
- F. Carré, E. Colomer, R. J. P. Corriu and A. Vioux, *Organometallics*, **3** (1984) 1272.
- F. Edelmann and U. Behrens, *Chem. Ber.*, **117** (1984) 3463.
- T. Debaerdemaeker, *Z. Kristallogr.*, **153** (1980) 221.
- V. G. Andrianov, Yu. T. Struchkov, V. N. Setkina, A. Zh. Zhakaeva and V. I. Zdanovich, *J. Organomet. Chem.*, **140** (1977) 169.
- T. L. Khotsyanova, S. I. Kuznetsov, E. V. Bryukhova and Yu. V. Makarov, *J. Organomet. Chem.*, **88** (1975) 351.
- N. M. Loim, Z. N. Parnes, V. G. Andrianov, Yu. T. Struchkov and D. N. Kursanov, *J. Organomet. Chem.*, **201** (1980) 301.

- 32 V. G. Andrianov, Yu. T. Struchkov, P. V. Petrovskii, E. I. Fedin, D. N. Kursanov, S. P. Dolgova and V. N. Setkina, *J Organomet Chem*, 221 (1981) 183.
- 33 R. J. Daroda, G. Wilkinson, M. B. Hursthouse, K. M. A. Malik and M. Thornton-Pett, *J. Chem Soc., Dalton Trans.*, (1980) 2315.
- 34 A. S. Batsanov and Yu. T. Struchkov, *J Organomet Chem*, 266 (1984) 295.
- 35 W. Harrison and J. Trotter, *J Chem Soc., Dalton Trans.*, (1972) 678.
- 36 D. B. Morse, D. N. Hendrikson, T. B. Rauchfuss and S. R. Wilson, *Organometallics*, 7 (1988) 496.
- 37 R. D. Rogers, R. Shakir, J. L. Atwood, D. W. Macomber, Y-P. Wang and M. D. Rausch, *J Crystallogr Spectrosc. Res.*, 18 (1988) 767.
- 38 M. J. Zaworotko, R. Shakir, J. L. Atwood, V. Sriyonyongwat, S. D. Reynolds and T. A. Albright, *Acta Crystallogr., Sect. B*, 38 (1982) 1572.
- 39 H. G. Raubenheimer, G. J. Kruger, A. von A. Lombard, L. Linford and J. C. Viljoen, *Organometallics*, 4 (1985) 275.
- 40 C. F. Barrientos-Penna, F. W. B. Einstein, D. Sutton and A. C. Willis, *Inorg Chem.*, 19 (1980) 2740.
- 41 H. G. Alt, H. E. Engelhardt, E. Steinlein and R. D. Rogers, *J Organomet Chem.*, 344 (1988) 321.
- 42 W. Malisch, H. Blau and U. Schubert, *Chem Ber*, 116 (1983) 690.
- 43 R. D. Rogers, H. G. Alt and H. E. Maisel, *J Organomet Chem.*, 381 (1990) 233.
- 44 U. Kirchgassner and U. Schubert, *Organometallics*, 7 (1988) 784.
- 45 W. Gäde and E. Weiss, *J Organomet Chem*, 213 (1981) 451.
- 46 A. Lombard, G. Huttner and K. Evertz, *J Organomet. Chem*, 350 (1988) 243.
- 47 R. D. Adams and D. F. Chodosh, *J Am. Chem. Soc.*, 100 (1978) 812.
- 48 M. E. Wright and V. W. Day, *J Organomet. Chem*, 329 (1987) 43.
- 49 Y-P. Wang, Y-H Yang, S-L. Wang and F. L. Liao, *J Organomet Chem*, 419 (1991) 325.
- 50 F. J. Lalor, D. Condon, G. Ferguson and M. A. Khan, *Inorg. Chem*, 20 (1981) 2178.
- 51 M. I. Bruce, K. R. Grundy, M. J. Liddell, M. R. Snow and E. R. T. Tiekink, *J. Organomet. Chem*, 375 (1989) 131.
- 52 R. Boese, W. B. Tolman and K. P. C. Vollhardt, *Organometallics*, 5 (1986) 582.
- 53 Y. Wakatsuki and H. Yamazaki, *Nippon Kagaku Kaishi*, (1985) 586.
- 54 J. du Toit, D. C. Leventis, J. C. A. Boeyens, M. S. Loonat, L. Carlton, W. Pickl and N. J. Coville, *J. Organomet Chem*, 368 (1989) 339.
- 55 (a) P. Brun, P. Vierling, J. G. Riess and G. Le Borgne, *Organometallics*, 6 (1987) 1032; (b) J. Hartgerink, P. Vierling, J. G. Riess and G. Le Borgne, *Nouv. J. Chim*, 9 (1985) 5398.
- 56 E. Cesarotti, G. Ciani and A. Sironi, *J. Organomet Chem.*, 216 (1981) 87.
- 57 E. Cesarotti, A. Chiesa, C. F. Ciani, A. Sironi, R. Vefghi and C. White, *J. Chem. Soc., Dalton Trans*, (1984) 653.
- 58 E. Cesarotti, M. Angoletta, N. P. C. Walker, M. B. Hursthouse, R. Vefghi, P. A. Schofield and C. White, *J. Organomet Chem.*, 286 (1985) 343.
- 59 C. Lindsay, E. Cesarotti, H. Adams, N. A. Bailey and C. White, *Organometallics*, 9 (1990) 2594.
- 60 J. B. Sheridan, G. L. Geoffroy and A. L. Rheingold, *J Am. Chem. Soc.*, 109 (1987) 1584.
- 61 H. Y. Liu, M. Rahman, L. L. Koh, K. Eriks, W. P. Giering and A. Prock, *Acta Crystallogr., Sect. C*, 45 (1989) 1683.
- 62 H. Y. Liu, L. L. Koh, K. Eriks, W. P. Giering and A. Prock, *Acta Crystallogr., Sect. C*, 46 (1990) 51.
- 63 J. A. Potenza, R. Johnson, S. Rudich and A. Efraty, *Acta Crystallogr., Sect. B*, 36 (1980) 1933.
- 64 G. Erker, R. Lecht, C. Kruger, Y-H. Tsay and H. Bonnemann, *J. Organomet. Chem*, 326 (1987) C75.
- 65 N. C. Baenzinger, R. M. Flynn and N. L. Holy, *Acta Crystallogr., Sect. B*, 35 (1979) 741.
- 66 M. D. Rausch, W. P. Hart, J. L. Atwood and M. J. Zaworotko, *J. Organomet Chem*, 197 (1980) 225.
- 67 H. Bonnemann, *Angew. Chem., Int. Ed. Engl.*, 24 (1985) 248.
- 68 (a) C. Caletti, C. Furlani, C. Puliti and H. Werner, *J. Organomet. Chem*, 289 (1985) 417; (b) T. A. Albright and R. Hoffmann, *Chem. Ber*, 111 (1978) 1578; (c) J. Silvestre and T. A. Albright, *J. Am. Chem. Soc.*, 107 (1985) 6829; (d) *Nouv. J. Chim*, 9 (1985) 659; (e) M. Arthurs, H. Karodia, M. Sedgwick, D. A. Morton-Blake, C. J. Cardin and H. Page, *J. Organomet Chem.*, 291 (1985) 231.