The Nature of Seat-ligand Fitting in Coordination Space.
IV. Steric Requirements for a Molecular Fragment to Accommodate Additional Ligands; the Structure and Chemistry of Complexes Containing Three π-Bonded Cyclopentadienyl Groups

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Abstract

By comparing the residual space available in a molecular fragment with the space demanded by the additional ligands, structural and chemical properties of compounds containing this fragment can be studied quantitatively in the light of steric factors. This method is described in detail with the complexes of MCp_3 (where Cp is cyclopentadienyl) as an example.

Introduction

Organometallic compounds containing three π-bonded cyclopentadienyl groups are a characteristic of f-block and group IVB transition metals, comprising a class of the most important compounds for which the electron count exceeds 18. Their structure and chemistry has been reviewed [1–3] and their electronic structure has been discussed recently [4, 5].

In these compounds the orbital interactions between the metal and ligand are weak, and, to our understanding, non-directional. Ligand steric factors should be dominant in determining the structure and chemistry of this class of compounds. We have recently found that both in applying the uniform packing rule and in the seat-ligand least fitting method the structure of compounds of the type MCp_3L or MCp_3X (where Cp is cyclopentadienyl) can be well predicted [6–8].

The present paper is a further development of our research on the nature of seat-ligand fitting in local coordination space, applied to complexes with three π-bonded cyclopentadienyl groups.

Results and Discussion

(1) Residual Space and the Frontier Seats

In the coordination space of the MCp_3 fragment, the part which is not occupied by the three cyclopentadienyl groups is termed the residual space. The solid angle factor of the residual space is constant, *i.e.* $1 - 3SAF$(Cp), regardless of the positions of the rings. Nevertheless the vacant seats contained in the residual space can be varied. Whether or not the MCp_3 fragment could combine with additional ligands depends not only on the bonding between them, but also on the steric fitting between the vacant seats and the additional ligands. By analogy with the concept of frontier orbitals, the few largest vacant seats contained in the residual space are called frontier seats. The 'frontier seat' differs from a 'hole' [9], in that the former could be organized in different shapes whereas the latter is simply an empty cone.

(2) The Combination of the MCp_3 Fragment with Simple Cone Shaped Ligands

The simple cone ligands are termed type A ligands. Examples are Cp^-, Cl^-, F^- and some rod-like ligands such as NCS^-. The molecular structures of MCp_3AA' are formed under the geometrical conditions that there are corresponding frontier seats S_A and S'_A which could accommodate these ligands (Fig. 1).

The symbol α is used to describe the angle between the cyclopentadienyl group and the C_{3v} axis,
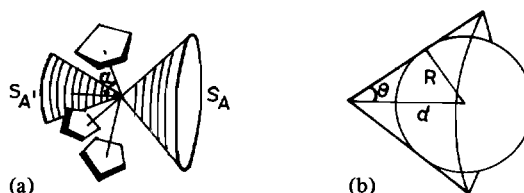

Fig. 1. Combination of the MCp_3 fragments with the simple cone shaped ligands: (a) frontier seats described by shaded cones; (b) donor atoms contained in the frontier seat.

TABLE I. Frontier Seats in the MCp₃ Fragment and the Corresponding Metal–Donor Atom Distances in Taking the Full Seat

Ring opening angle, α (°)	Bond angle Cp–M–Cp 2β (°)	Bond angle Cp–M–S_A (°)	S_A (°)	d_A for atom Cl⁻ (Å) R⁻	d_A for atom O (Å)	d_A for atom N (Å)	d_A for Cp⁻ (Å)	S'_A (°)
0	0	180	125					
10	17.3	170	115					
20	34.4	160	105					
30	51.4	150	95					
40	67.6	140	85	1.81	1.41	1.51		
50	83.2	130	75	1.86	1.45	1.55		
60	97.2	120	65	1.99	1.54	1.65		5
65	103.4	115	60	2.08	1.62	1.73	2.00	10
70	109	110	55	2.20	1.71	1.83	2.43[a]	15
75	113.6	105	50	2.34	1.83	1.96	2.91	20
80	117.0	100	45	2.55[a]	1.98	2.12	3.47	25
85	119.2	95	40	2.80	2.18	2.33	4.14	30
90	120	90	35	3.13	2.44	2.61[a]	4.96	35
95	119.2	85	(30)	3.60	2.80	3.00	6.00	40
100	117	80	(25)	4.26	3.31	3.56	7.40	45

[a]Metal–ligand distances at the normal bonding.

and 2β is used to describe the angle between two cyclopentadienyl groups (Fig. 11a):

$$\text{Angle Cp–M–Cp} = 2\sin^{-1}\left(\frac{\sqrt{3}}{2}\sin\alpha\right) = 2\beta \quad (2.1)$$

The two major frontier seats, S and S', are *trans* to each other and are at the two ends of the C_{3v} axis:

$$\text{Angle Cp–M–}S_A = 180° - \alpha \quad (2.2)$$

$$\text{Angle Cp–M–}S_{A'} = \alpha \quad (2.3)$$

The magnitudes of the two seats are:

$$S_A = 180° - \alpha - \theta_{Cp} \quad (2.4)$$

$$S_{A'} = \alpha - \theta_{Cp} \quad (2.5)$$

The bond angles between cyclopentadienyl groups should not exceed 2β because the ligands cannot overlap. We adopt θ_{Cp} as 55°, which is the standard fan angle parameter for U(IV) [10] and for Eu(III) [11, 12]. α is thus limited to the range $70° \leqslant \alpha \leqslant 110°$.

Coordinating atoms with Van der Waals radii R, just fitting in the frontier seats without overlapping, should be put at the following distances

$$d_A = R/\sin S_A = R/\sin(\alpha + \theta_{Cp}) \quad (2.6)$$

$$d_{A'} = R/\sin S'_A = R/\sin(\alpha - \theta_{Cp}) \quad (2.7)$$

By comparing d_A and $d_{A'}$ with the normal bond lengths between the corresponding metal and the ligands, one can estimate whether or not the complexes MCp₃A and MCp₃AA′ will be formed and evaluate the corresponding bond angles. These are
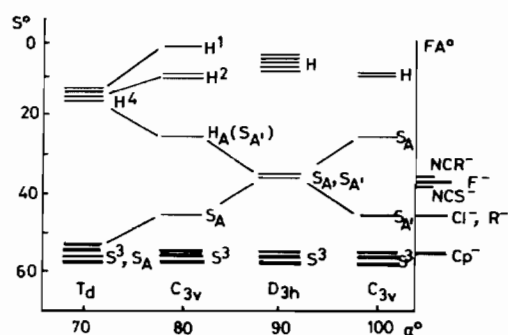

Fig. 2. Variation of frontier seats in accordance with the open angle α. Vertical axis: left, frontier seat; right, ligand size [10–13].

shown in Table I. Only those angles are significant which produce frontier seats close to the ligands.

The seat level diagram in Fig. 2 is shown to illustrate the dependence of frontier seats on the angle α. The seat levels are arranged according to the ordinate, whereas the angle α is given in the abscissa. On the left is the seat level diagram of the MCp₃ frame at the maximum compression ($\alpha = 70°$). The frontier seat S_A is 55°, just large enough to accommodate the fourth π-cyclopentadienyl to form MCp₄ or MCp₄⁻. The frontier seats cannot be larger than 55° unless the three cyclopentadienyls themselves are compressed, which will induce a great increase in the repulsion energy. Even in UCp₄ the U–Cp distance is longer than the normal bond distance [13]. The pentamethylcyclopentadienyl group takes a seat of 55° at the metal–ring centre distance of 3.3 Å. This means that steric repulsion occurs earlier than the orbital interaction. It is thus expected that the compound

$MCp_3(Me_5C_5)$ will not be easily prepared because of steric repulsion.

On the other hand, when α changes from $70°$ to $90°$, the seat $S_{A'}$ increases stepwise from $15.5°$ to $35°$. At first, seat $S_{A'}$ is not large enough to accommodate a second ligand. Nevertheless this seat would induce an association effect which has been observed in $UCp_3C(CN)_3$ [14]. Therefore, at the angle $\alpha = 80-85°$, only seat S_A, which is about $40-45°$, fits the fan angles of many ligands and the structure pattern MCp_3A is formed. The calculated bond angles are in good agreement with the observed X-ray results [6–8].

When α equals $90°$, the two frontier seats become equal and the fan angles of both are $35°$, which only properly fit small nitrogen donor ligands like NCR or NCS^-. Again many structures of this pattern have been experimentally observed [15, 16].

(3) The Combination of MCp₃ Fragments with Two Cone Combinations MCp₃B

Ligands which could be described as two cone combinations (type B) include classical bidentate ligands such as NO_3^- and $acac^-$ as well as the π-bonded ethylenes. They also apply to some reaction intermediates such as those shown below. Whereas the nature of the bond has been considered in the orbital interaction, the ligands are considered here only as cones with geometrical factors.

σ-bonding   π-bonding   agostic [27]

Reaction Intermediates
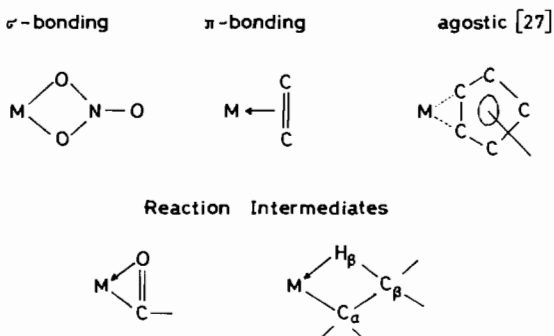
Such ligands could be described geometrically by three parameters: θ_a and θ_b for the two individual cones and b for their bite (Fig. 3). In the same way, the residual space of the MCp_3 fragment can be resolved into two seat combinations, which are described also by three parameters; S_a, S_b for the two individual seats and ω for their bite.

There are two conformations for the B type ligand to fit into the residual space. They could either take conformation **I**, for which the plane comprising the two coordination atoms and the metal centre extends through one of the M–Cp axes, *i.e.* plane MBB′ is approximately perpendicular to one of the Cp group
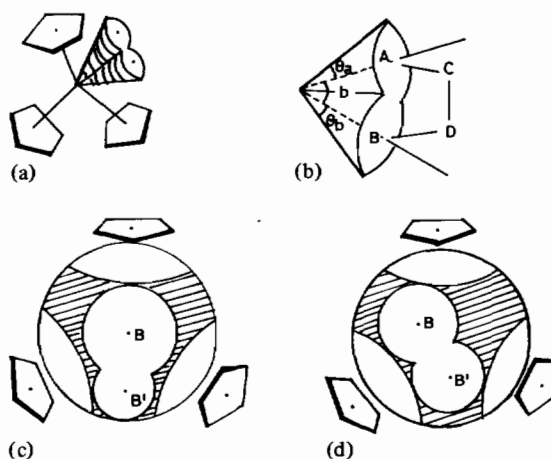

Fig. 3. Combination of MCp₃ fragments with bidentate ligands: (a) frontier seat described as a two cone combination; (b) steric parameters of two cone combinations; (c) conformation I; (d) conformation II.

planes; or they could take conformation **II**, for which the plane MBB′ is approximately parallel to one of the Cp group planes.

Whether or not the ligand B combines with the MCp_3 fragment and in which conformation depends on the fitting of the ligand to the combination seat of two cones.

When the two coordinating atoms are identical, one could resolve two single seats which are equal to the size of the individual coordinating atoms and examine whether the maximum bite of the two seats is greater than the bite of the ligand. The two conformations produce different results (Fig. 11b).

For the first conformation

$$\omega_1 = 360° - (\phi + \alpha + \theta_{Cp} + \gamma + S) \tag{3.1}$$

For the second conformation

$$\omega_2 = 2 \sin^{-1}\left(\frac{\sqrt{3}}{2} \sin(\phi + \gamma)\right) \tag{3.2}$$

Here α and β have the same meaning as that given in the second section and S is the fan angle of the single seat; γ, ϕ are given below

$$\gamma = \tan^{-1}\left(\frac{1}{2} \tan \alpha\right) \tag{3.3}$$

$$\phi = \cos^{-1}\left(\frac{\cos(S + \theta_{Cp})}{\cos \beta}\right) \tag{3.4}$$

When α is fixed, the bite decreases as the single seat increases.

The bite in the seat combination depends also on α, the opening angle of the cyclopentadienyl group. The smaller the value of α, the greater the bite of the two cones. The maximum bite is achieved at

the closest packing of the rings, *i.e.* $\alpha = 70°$. If, at this stage, the seat combination is still less than the corresponding ligands, stable structures of the type MCp_3B will not be obtained.

An example is the, as yet unknown, compounds composed of the $AnCp_3$ fragment and β-diketones or other bidentate chelates forming 6-membered rings. At the normal bond lengths of 2.4 Å, each oxygen atom of the diketone needs a seat of 36°, and the two atoms are overlapping negligibly so that their bite is only a little less than the sum of their fan angles, *i.e.* $b = 70°$. At the closest packing of three rings the largest bite for the two seat of 36° is attained at $\omega_2 = 59°$. Therefore it is apparent that the empty space on the MCp_3 fragment is not sufficiently large to coordinate a bidentate β-diketone.

Bagnall [17] attempted to prepare UCp_3(acac) but the product was UCp_2(acac)$_2$. Disproportionation of 'UCp_3(acac)' might just be due to problems of steric packing.

Interestingly, the structure of UCp_3pz (pz = pyrazole) was an unexpected result [18]. The original attempt was to prepare the bridged structure **I**

I

II
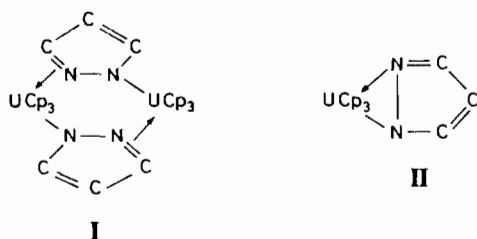
If such a structure really exists, there would be two independent nitrogen donor atoms present in the residual space of the UCp_3 fragment, the 'bite' between two independent donor atoms will be equal to or greater than the sum of their fan angles. Therefore a bite of 78° is needed for the two nitrogen seats in the bridged structure, which cannot be realized even on the closest packing of the three rings. However, in structure **II**, the two nitrogen atoms are held together by bonding, and the required space is much smaller.

It is clearly seen in Table II that the values of ω_2 are always greater than those of ω_1. Therefore, in the case of steric constraint, the ligands would adopt conformation **II**. This is exemplified in the structure of UCp_3pz [18]. The pyrazolate anion, at 2.383 Å from the uranium ion, is equivalent to two cones of $\theta_N = 39°$ combined at a bite of 32.9°. At the determined MCp_3 frame in UCp_3pz, the bond angles Cp–U–Cp are 114.3° with the corresponding value of $\alpha = 76°$. In this geometry the maximum bite for two seats of 39° is 29.3° in the first conformation and 33.1° in the second conformation. Consequently the pyrazole will only fit in the residual space of the UCp_3 fragment in the second conformation.

TABLE II. Maximum Bite of Two or Three Cone Combinations Fitted in the Residual Space of the MCp_3 Fragment ω_2/ω_1 (°)

θ_B	α				
	70	75	80	85	90
24					38.5
					(33.4)
26					31.4
					(27.2)
28					24.4
					(21.1)
30	75.1	63.4	49.6	34.1	17.4
	(69.7)	(57.4)	(44.0)	(29.8)	(15.0)
32	69.7	57.4	43.2	27.3	10.4
	(64.3)	(51.7)	(38.1)	(23.8)	(9.0)
34	64.2	51.4	36.7	20.5	3.5
	(58.8)	(46.0)	(32.3)	(17.9)	(3)
36	58.5	45.2	30.2	13.7	0
	(53.4)	(40.4)	(26.5)	(11.9)	0
38	52.9	39.1	23.6	6.9	
	(47.9)	(34.7)	(20.7)	(6)	
40	47.1	32.8	16.9	0	
	(42.4)	(29.0)	(14.8)	(0)	
42	41.2	26.5	10.2		
	(37.0)	(23.3)	(8.9)		
44	35.3	20.1	3.5		
	(31.5)	(17.6)	(3.0)		
46	29.2	13.5	−3.4		
	(25.9)	(11.8)	−6		
48	23.0	6.8			
	(20.3)	(5.9)			
50	16.7	0			
	(15.2)	(0)			
52	10.2				
	(8.9)				
54	3.5				
	(3)				

When the donor atoms are not identical, they will need different single seats for coordination. In the residual space one can resolve two seats, each of which is equal to one of the two donor atoms at the normal bond distances and see if the maximum bite of the two seats is equal to or greater than the bite of the ligand. The results of the comparison will decide whether the ligand can combine with the MCp_3 fragment or not. With $S_a = FA_a$ and $S_b = FA_b$, the bite is derived as follows:

$$\omega = \sin^{-1}(\sin \psi_a \sin \gamma) + \sin^{-1}[\sin \psi_b \sin(120° - \gamma)] \quad (3.5)$$

where

$$\psi_a = 180° - \gamma - \cos^{-1}\left[\frac{\cos(\theta_{Cp} + S_a)}{\cos \beta}\right] \quad (3.6)$$

$$\psi_b = 180° - \gamma - \cos^{-1}\left[\frac{\cos(\theta_{Cp} + S_b)}{\cos \beta}\right] \quad (3.7)$$

$$\gamma = \tan^{-1}\left(\frac{(\tan \psi_a/\tan \psi_b) - \cos 120°}{\sin 120°}\right) \qquad (3.8)$$

As an example the bidentate acyl group has a bite of 29.2° when the bond lengths U–C = 2.4 Å. U–O = 2.35 Å and C=O = 1.2 Å are assumed for the related structures [19]. The maximum bite at $\alpha = 70°$ will be 38.9°. At $\alpha = 73°$ and bond angle Cp–U–Cp = 110–113° there is a suitable seat of 29° for combination with the bidentate acyl group.

(4) Combination of the MCp₃ Fragment with Tridentate Ligands

Tridentate ligands could be described geometrically as a cone group composed of three simple cones. Thus the boron hydride group in $U(BH_4)_4$ at the normal bond lengths (B–H = 1.21 Å, U–B = 2.53 Å) could be described as three hydrogen cones, the fan angles of which are 29.7°. The bite between every two cones is 48.3° provided that the boron hydride is tetrahedral. Tridentate hydrotrispyrazolyl borate could be regarded as three nitrogen cones with their fan angles at about 36° (the fan angle of the nitrogen in the ligand might be in between the fan angles of a neutral nitrogen donor ligand and a negative pyrazole anion) and the bite between every two nitrogen atoms is about 70°.

Owing to the symmetry of the MCp₃ fragment in the residual space, the fitting of tridentate ligands is the same as the fitting of bidentate ligands in the second conformation. (There is an empty seat identical to the two seats occupied by the bidentate ligand (Fig. 4).)
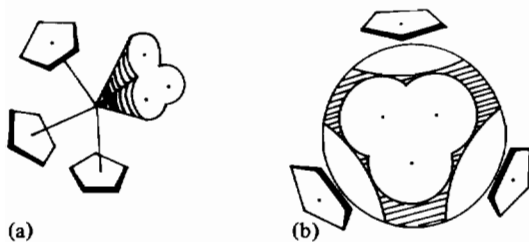

Fig. 4. Combination of the MCp₃ fragment with tridentate ligands: (a) S_T seat; (b) three donor atoms arranged in the coordination sphere.

The seat level diagrams for accommodation of tridentate ligands are given in Figs. 5 and 6. In Fig. 5 there is no overlapping among the three single seats, whereas in Fig. 6 the single seats overlap with each other. The former represent three small monodentate ligands closely packed in a hole. The latter represent coordination of a tridentate ligand. The seat combinations must be written together with the fan angles of its single seats and the bite among them. Thus tridentate boron hydride needs a seat combination S_T (29.7°, 48.3°) and the HBpz₃ ligand needs a seat com-

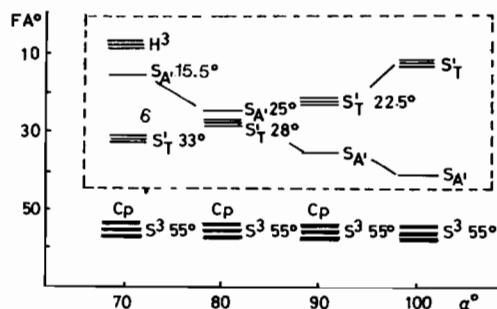Fig. 5. Seat level diagrams for the MCp₃ fragment. An S_T seat combination serves as the frontier seat. The bite of the S_T seat is the sum of the fan angles of the two seats. (In this way, there is no overlapping among the three single seats.) It should be noted that when α is less than 90°, the S_T seat is in the large hole of the MCp₃ fragment whereas the S_T seat is in the small hole when α is greater than 90°.
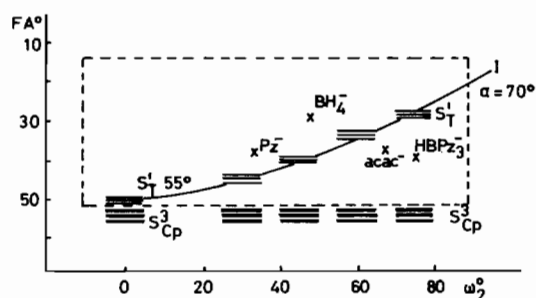

Fig. 6. Seat level diagrams for the MCp₃ fragment. The S_T seat varies with the bite of the single seats. Bidentate and tridentate ligands are plotted in the Figure as points (X). When the point is above the curve, the ligand could combine with the MCp₃ fragment.

bination S_T(36°, 70°). Bidentate ligand fitting in the first conformation needs an $S_B(\theta, b)$ seat, whereas it needs an $S_T(\theta, b)$ seat fitting in the second conformation.

It is clearly seen in Table II that the residual space in the MCp₃ fragment could accommodate tridentate tetrahydroborate when α is smaller than 80°. However, it could not accommodate tridentate HBpz₃ in any way. Experimentally, tridentate UCp₃BH₄ was established by Marks and Kolb [20], and disproportionation of the compounds 'UCp₃HBpz₃' was observed by Bagnall *et al.* [21].

The η^3-bonded allyl needs an S_T seat combination with three bites. The two short bites between the neighbouring carbon atoms are 27.4° at the normal bond lengths (C–C = 1.27 Å and U–C = 2.68 Å). The third bite between the two end carbon atoms is 53.2°. Comparing these values with the seat combinations given in Table II, η^3-bonded allyl would not be structurally stable. In fact σ-bonded η'-allyl was observed [22]. In ref. 4 and 23 it was argued that there is no steric problem because a π-bonded cyclopentadienyl group can even exist in the residual space. The fact is

that the allyl group demands a different seat from that required by the cyclopentadienyl group; the C–C–C bond angle (145° [24]) in the allyl group is much greater than those in the cyclopentadienyl group. Furthermore the metal–carbon distance is shorter than those in the corresponding cyclopentadienyls.

(5) Combination of the MCp₃ Fragment with Ligands Exerting Second-Order Steric Effect

In certain ligands, such as alkyls, ethers and amines, the coordinating atoms connect with more than two secondary atoms, which are not completely shielded by the donor atom. They are about 3–3.5 Å away from the metal centre, *i.e.* the same distance as the ring hydrogens. Therefore they also take seats in the coordination sphere. The whole ligand can be treated as a three cone combination (for OR_2) or a four cone combination (for CR_3^-). The coordinating

atom is the major cone whereas the secondary atoms are the side cones (Fig. 7).

Geometrical conditions for MCp_3R to form a stable structure (R = ligands with secondary steric effects) are that both the coordinating atom and the branch atoms should fit in the residual space of the MCp_3 fragment.

Fan angles of the secondary atoms, and their branch angles ψ_B from the C_{3v} axis, can be calculated as follows (Fig. 8)

$$FA_B = \sin^{-1}\left(\frac{R_B}{d_B}\right) \tag{5.1}$$

$$d_B = (d_A^2 + d_{AB}^2 - 2d_A d_{AB}\cos MAB)^{1/2} \tag{5.2}$$

$$\psi_B = \cos^{-1}\left(\frac{d_A^2 + d_B^2 - d_{AB}^2}{2d_A d_B}\right) \tag{5.3}$$

where R_B and d_B are the Van der Waal's radii and the M–B distance of the secondary groups (e.g. methyl) (Table III).

The branch angle of a triplet cone group seat, ψ_s, which fits the secondary groups is derived as follows (Table IV)

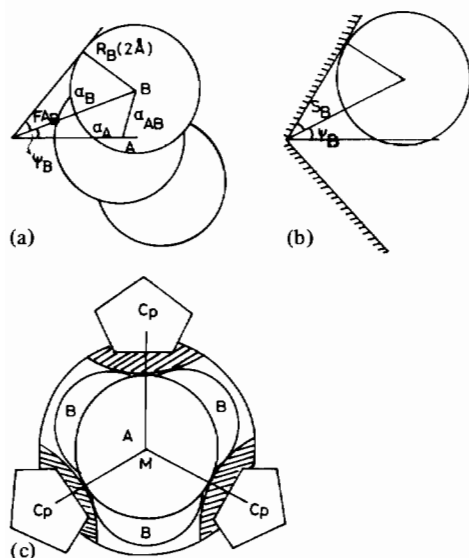$$\psi_S = 180° - \cos^{-1}\frac{\cos(\theta_{Cp} + S_B)}{\cos\beta} - \gamma \tag{5.4}$$

Fig. 7. The space needed by the secondary methyl group and the seats offered by the MCp_3 fragment: (a) calculation of FA_B and ψ_B; (b) calculation of S_B and ψ_B; (c) a four cone combination seat to accommodate CR_3^- in the residual space of the MCp_3 fragment, looking in the direction M–A.
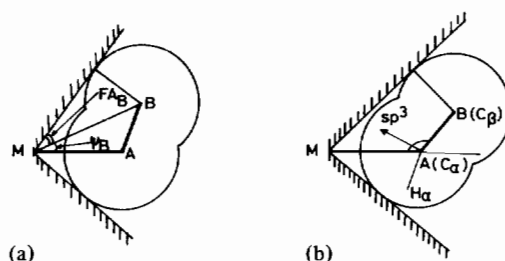

Fig. 8. Distortion of CHR^- in a smaller seat: (a) when the seat is large enough, the $M–C_\alpha$ bond coincides with the direction of sp^3 hybridization of α carbon atom; (b) in a smaller seat, the bond angle $MC_\alpha C_\beta$ is increased, whereas the bond angle $MC_\alpha H_\alpha$ should decrease.

TABLE III. Examples of the Ligands which Exert Second-order Steric Effects

Ligand	Assumed M–A distance (Å)	Bond length A–B (Å)	FA of the donor atom (°)	FA_B (°)	ψ_B (°)
CH_3^-	2.5	1.09	47.7	23.2	19.6
CR_3^-	2.5	1.54	47.7	36.7	25.6
NH_3	2.7	1.04	33.7	22.0	17.9
NR_3	2.7	1.47	33.7	35.1	23.4
OH_2	2.5	1.03	34.1	23.6	18.8
OR_2	2.5	1.43	34.1	37.7	24.3

TABLE IV. The Triplet Seats and their Branch Angle to the C_{3v} Axis of the MCp$_3$ Fragment, ψ_S (°)

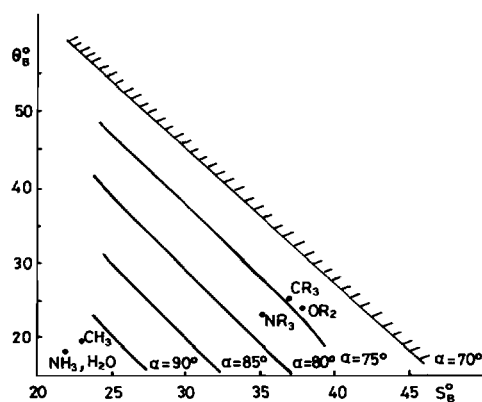| S_B (°)	α (°)				
	70	75	80	85	90
(Cp–M–Cp)	109.5	113.6	117	119.2	120
25	53.5	46.7	38.9	30.1	20.4
27.5	49.1	42.0	34.0	25.0	15.2
30	44.7	37.4	29.1	19.9	10.1
32.5	40.4	32.8	24.3	15.0	5.1
35	36.1	28.3	19.5	10.0	0
37.5	31.9	23.8	14.8	5.2	
40	27.6	11.2	10.0	0	

Fig. 9. Steric requirements for the MCp$_3$ fragment bound to bulky ligands. Horizontal axis: fan angle of the S_T individual seat. Vertical axis: branch angle of the S_B seats which each curve represents.

To compare the seat with the corresponding secondary group, the single seat S_B is assigned to be equal to the fan angle of the secondary group FA_B, if $\psi_S \geqslant \psi_B$, the whole seat group will fit the ligand (Fig. 7). On the other hand, if $\psi_S \leqslant \psi_B$, one requires a larger opening angle. Finally, when $\psi_S \ll \psi_B$ at $\alpha = 70°$, the bulky ligand should not coordinate to the MCp$_3$ fragment because of steric hindrance.

The seats required by the secondary atoms are listed in Table III for selected ligands at the normal bond lengths. For example, CR$_3^-$ needs a major seat, $S = 47.7°$, for the coordinating carbon atom and three side secondary seats (36.7°) which form a branch angle of 25.6° with the C_{3v} axis. At the normal bond angle Cp–U–Cp = 117°, $\alpha = 80°$, there is a major seat of 45° which is nevertheless close to the fan angle of the carbon atom in the residual space. However when the secondary seats are assigned to be equal to the fan angle of the methyl group, the maximum branch angle offered in the residual space of the MCp$_3$ fragment is 16° (Fig. 8) only, which is much less than that needed. Distortion is thus expected to occur for the unknown structure of UCp$_3$CR$_3$. Either the opening angle will be forced to be greater than 80°, or the uranium—carbon bond length will be longer than normal. With an asymmetric bulky ligand, e.g. CHR$_2^-$, the methyl group should be forced away from the normal metal centre and the M–C bonding should be forced away from the direction of sp^3 hybridization of the carbon atom. The structure of UCp$_3$CH$_2$R [25] does show the very large U–C$_\alpha$–C$_\beta$ bond angle of 128°. Similar bond angles are observed in LnCp$_3$thf [26]. Figure 9 can be used for a general examination of the seat-ligand fitting for bulky ligands. The fan angle of the secondary seat, S_B, is plotted on the X axis, whereas the branch angle of the secondary seat is plotted on the vertical axis. Each curve represents the dependence of ψ_S on S_B at a fixed angle α. Fan angles and branch angles of bulky ligands are plotted as points in Fig. 9. They are in between the curves for $\alpha = 70°$ and $\alpha = 80°$. This

means that there is sufficient space for their coordination.

(6) The Molecular Structure of MCp$_3$; Combination of the MCp$_3$ Fragment with Additional Cyclopentadienyl Groups

The coordination space of the MCp$_3$ fragment is not saturated, so that the residual space needs to be filled. If there are no other ligands present, the η^5-bonded cyclopentadienyl group bonded to one metal ion has to fill the frontier seats of another MCp$_3$ fragment. In this way the compound should have a polymeric molecular structure. The frontier seat normally accommodates the fourth cyclopentadienyl group in the η^1 or η^2-mode. Interestingly, as the ionic radii of the lanthanides decrease, the bond lengths between the π-bonded cyclopentadienyl group and the metal ion decrease, whereas the bond lengths between the σ-bonded cyclopentadienyl group and the metal ion increase*. This fact is apparently due to the expansion of the three major seats and the enforced contraction of the frontier seat, which is fully explained in the seat analysis of the MA$_3$B pattern [8]. In Fig. 10 the metal—carbon distances are plotted on the horizontal axis while the fan angle demanded for the η^2-bonded cyclopentadienyl group, estimated according to the following equation:

$$\theta_{\eta^2\text{-Cp}} = FA_{\eta^2\text{-Cp}} = \sin^{-1}(R/d) + \tfrac{1}{2}\sin^{-1}(1/2d) \quad (6.1)$$

(Fig. 10), is given in curve I. The space demanded by the η^2-bonded cyclopentadienyl group decreases with increasing M–C distances. The seat offered by the MCp$_3$ fragment increases somewhat because the side seats fit better in the corner at longer distances. Each curve represents the corresponding seats at a fixed

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*The η^2-carbon atoms are semi-coordinated to the metal at distances from 3.3 to 3.7 Å [27].
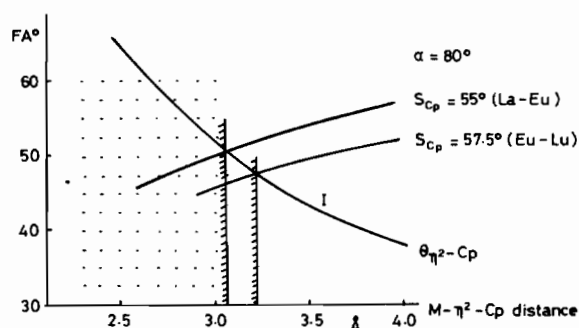
Fig. 10. Combination of the MCp$_3$ fragment with the fourth η^2-cyclopentadienyl. The cross points A and B indicate the minimum distance between the metal and the η^2-bonded carbons, at this point the residual space of LnCp$_3$ ($\alpha = 80°$) is just large enough to accommodate a η^2-cyclopentadienyl group.
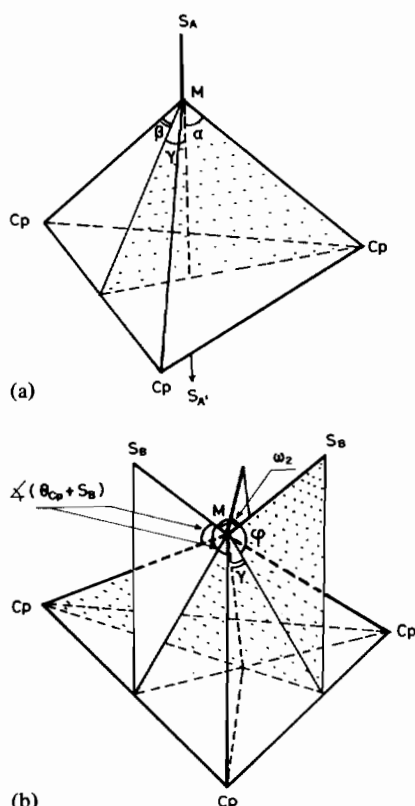

(a)

(b)

Fig. 11. (a) Calculation of the frontier seat S_A, $S_{A'}$; geometrical description of α, β and γ. (b) Calculation of seat bites for two seat groups; geometrical description of ϕ and ω_2.

opening angle, $\alpha = 80°$, offered by the MCp$_3$ fragment. The η^2-cyclopentadienyl group can be accommodated in the residual space only if $S_{Cp} \geqslant FA_{Cp}$. It can be seen that the carbon atom in the η^2-Cp group should be at least further than 3 Å from uranium and the middle lanthanides. For the heavier lanthanides the η^5-bonded cyclopentadienyl groups are bonded

closer so that the η^2-cyclopentadienyl group is extruded further away from the metal ion. Finally, the frontier seat becomes too small to accommodate σ-bonded ligands so an 'agostic' cyclopentadienyl group is held in the frontier seats [27]. For lutetium and scandium, the cyclopentadienyl group requires too large a seat so it becomes critical for the metal to hold three η^5-bonded cyclopentadienyl groups and the third cyclopentadienyl group is again converted to σ-bonding.

Conclusions

Using the MCp$_3$ fragment as an example, the present paper has suggested a general approach to the steric problems. By comparison of the space needed and the space available, the structure and chemistry of compounds of weak LFSE can be studied in detail. A further discussion concerning the reaction intermediates will be given in a following paper.

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