

The Nature of Seat-ligand Fitting in Coordination Space.

V. Steric Hindrances and Reaction Mechanisms – a Further Discussion on the Structure and Chemistry of Compounds Containing Three π -Bonded Cyclopentadienyl Groups

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Abstract

Spherical trigonometry is introduced for the first time to describe the ligand movement in the coordination sphere. The steric hindrance is quantitatively analysed in order to explain the behaviour of triscyclopentadienyl uranium hydrocarbyls in thermolysis, photochemical decomposition, ligand rearrangement and carbon monoxide insertion. The results are in good agreement with the experimental observations.

Introduction

Steric hindrance is well recognized as an important factor in determining reaction mechanisms. Nevertheless it has not been studied quantitatively. In coordination and organometallic chemistry, a general question concerning steric hindrance is how the ligands (when regarded as geometrical entities) enter, leave, migrate and couple in the coordination sphere and how the ligand steric factors favour certain pathways to others.

In our previous paper [1], we suggested a method of estimating whether a specified bonding is stable or not by comparing the required and the available space. This method can be extended to study the reaction pathways on the basis that when the inert coordination environment is sterically overcrowded and the available space is smaller than that demanded by a reaction intermediate, steric hindrance will be encountered. The difference between the required and the actually available space offers a quantitative estimation of steric hindrance.

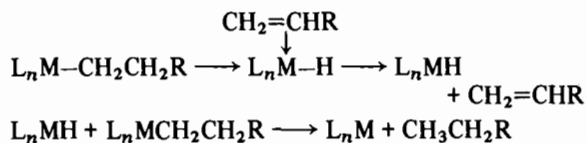
In this paper, by further discussion of the structure and chemistry of compounds containing three π -bonded cyclopentadienyl groups, we present a detailed geometrical description of ligand movements and demonstrate the steric resistance by showing

how the ligands move in various ways and how the reaction mechanisms are influenced.

Results and Discussion

1. Steric Hindrance in Thermal Decomposition of Metal–Carbon σ Bonds

A general thermal decomposition pathway of metal–carbon σ bonds is β -hydride elimination [2]:



This mechanism, however, does not take place for UCp_3R and ThCp_3R compounds. The RH molecule is released and the source of the hydrogen atom is the cyclopentadienyl ring. Marks has suggested that the β -elimination is more endothermic than that for middle and late transition metal complexes [3]. The energetic inaccessibility of the highly crowded olefin–hydride intermediate is also a reason for the strong resistance of UCp_3R towards β -elimination [4].

β -Elimination proceeds in two steps: (1) the β -hydrogen atom moves to coordinate to the metal; (2) the β -hydrogen atom transfers to the metal to give the olefin–hydride state.

In the first step before the β -hydrogen atom moves closer and interacts with the metal, the distance between the β -hydrogen and the α -carbon atoms should remain unchanged (Fig. 1a).

$$\begin{aligned}
 D_{\text{C}_\alpha-\text{H}_\beta} &= AB = (AC^2 + BC^2 + 2AC \cdot BC \cos \sphericalangle ACB)^{1/2} \\
 &= 2.16 \text{ \AA}
 \end{aligned}$$

Here AC , BC are the standard carbon–carbon and carbon–hydrogen distances and $\sphericalangle ACB$ is the standard bond angle for sp^3 hybridization.

The β -hydrogen atom moves towards the metal centre in three possible modes depending on the coordination environment.

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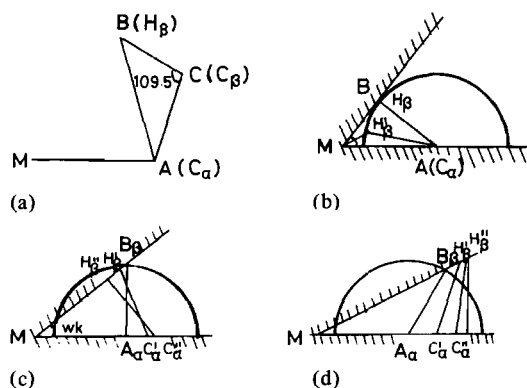


Fig. 1. β -Hydrogen movement towards the metal centre. (a) Distance between α -carbon and β -hydrogen remain unchanged during the process of β -hydrogen coordination. (b) Facile β -hydrogen coordination, there is no steric hindrance. (c) Hindered β -hydrogen coordination, when H_β moves closer to the metal, the α -carbon has to move away. (d) Difficult β -hydrogen coordination, both hydrogen and carbon atoms have to move away first from the metal in order to turn around.

(a) Facile β -hydrogen coordination

The β -hydrogen moves closer to the metal while the position of the α -carbon atom remains unchanged. In this way the C_α - C_β midpoint also moves towards the metal in favouring the metal-olefin π -bonding. There is a net gain in bond interactions.

In this route the required space, described as the bite between the β -hydrogen and the α -carbon atoms, is greater than or equal to b_o (Fig. 1b). By assuming $MA = 2.5 \text{ \AA}$

$$b_o = \sin^{-1} \left(\frac{AB}{MA} \right) = 60^\circ$$

(b) Sterically hindered hydrogen coordination

Whereas the β -hydrogen moves closer to the metal centre, the α -carbon has to move away from the metal. There is a gain in the metal-hydrogen interaction while there is a loss in the metal-carbon bond interaction.

The required space for the second mode of hydrogen coordination is less than b_o , but it should be greater than the second critical value b_h (Fig. 1c).

$$b_h = \tan^{-1} \left(\frac{AB}{MA} \right) = 41^\circ$$

(c) Seriously hindered β -hydrogen coordination: bond scission and hydrogen abstraction from the neighbouring ligands

When the available space is even less than b_h , the hydrogen atom cannot move towards the metal in spite of the α -carbon atom moving away from the metal (Fig. 1d). There is a net loss in the metal-

carbon bond interaction. One cannot expect that the alkyl group, once it has left the metal centre, will turn round for the β -hydrogen atom to coordinate to the metal. It is more likely that the alkyl group, on leaving, will abstract a hydrogen atom from the neighbouring ligands, which hindered its movement.

In the hydrogen coordination step, the bite actually available for the compounds MCp_3R is shown in Fig. 2. The three cyclopentadienyl groups comprise the inert coordination environment and hinder the β -hydrogen moving to coordinate to the metal. There are gaps between the three rings, *i.e.* Cp_1 - Cp_2 , Cp_2 - Cp_3 , Cp_1 - Cp_3 . The β -hydrogen and the α -carbon atoms should fit into the gaps until they contact the cyclopentadienyl groups. In this way the maximum reaction space can be achieved. These processes are described in the unit coordination sphere shown in Fig. 2b, which is further translated to the language of spherical trigonometry in Fig. 2c. Each point of the spherical triangle represents the centre of a ligand and each side of that triangle represents a bond angle, which should be greater than the sum of the fan angles of the two ligands, provided that there is no steric repulsion. The reactions taking place in the coordination sphere thus can be transformed into the problem of solving the maximum side of the corresponding triangles. In our example of the compounds MCp_3R , the questions are: (i) whether or not the maximum bite of the β -hydrogen and α -carbon atoms is satisfactory as b_o or b_h ; and (ii) how the triangle changes so that $H_\beta C_\alpha$ becomes satisfactory.

We assume that the hydrogen atom is as far as 2.5 \AA from the metal centre (this distance is greater than the sum of the Van der Waals radius of hydrogen and the ionic radius of the metal. It is therefore safe to assume that there is no metal-hydrogen pre-bonding interaction) ($FA_H = 29^\circ$). The metal-carbon distance is assumed to be 2.7 \AA , which is much longer than the normal bond length between the metal and carbon ($FA_C = 43^\circ$). The sides CpH and CpC are the sum of the fan angles of the cyclopentadienyl and the hydrogen or carbon atom.

According to the available X-ray results [6], the sides Cp - Cp should be 117° . The available bite C_α - H_β in the triangle $CpH_\beta C_\alpha$ (Fig. 2c) can be calculated to be 33.7° based on the above parameters. This value is less than the critical value, b_h , indicating that the access of the β -hydrogen atom to the metal centre is completely hindered by the cyclopentadienyl group.

There are various routes along which the cyclopentadienyl groups can migrate to give more space for the β -hydride to coordinate to the metal. First, one of the cyclopentadienyl groups is pushed to migrate towards the C_{3v} axis (Fig. 2, route I). In this route the bond angle between the moving cyclopentadienyl, Cp_1 , and the other two cyclopenta-

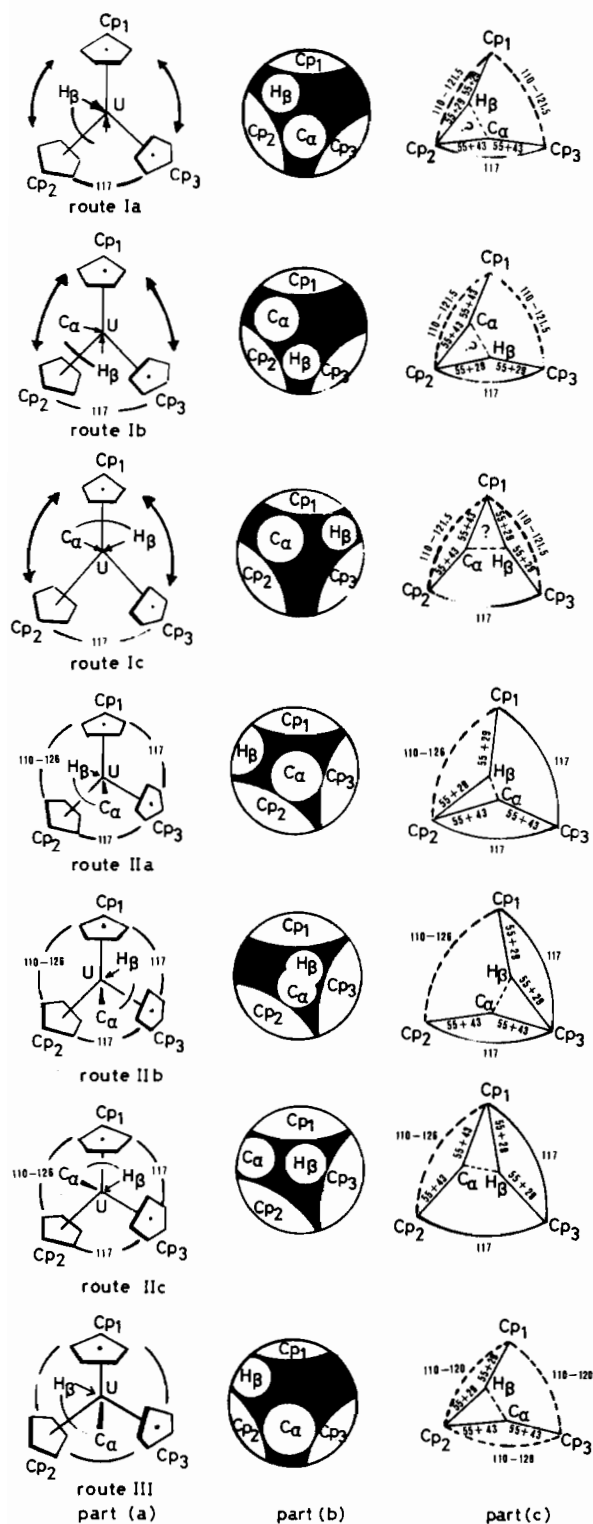


Fig. 2. Ligand movement on the surface of the coordination sphere. The α -carbon and β -hydrogen atoms are held in between the gaps of the cyclopentadienyl groups to achieve maximum bites. Part a: reaction intermediates; part b: projection on the unit sphere; part c: corresponding expression in the spheroid triangles for calculation.

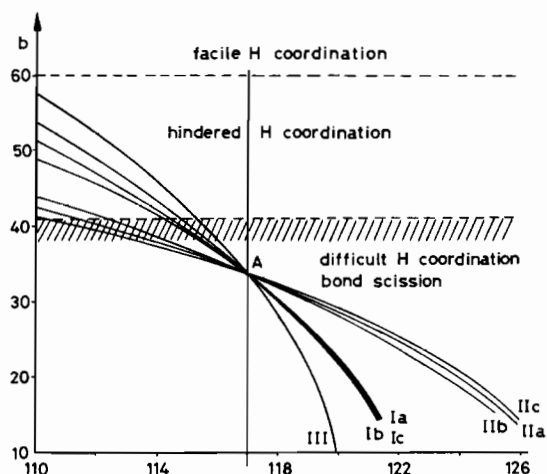


Fig. 3. A comparison of the available space with the required space for hydrogen coordination when the cyclopentadienyl groups move according to the routes shown in Fig. 2. The horizontal axis describes the bond angles between the moving Cp and the other Cp' groups.

dienyl groups will change, while the bond angle between the two stationary cyclopentadienyl groups, Cp₂ and Cp₃, remains 117°. The bond angles Cp₁-M-Cp₃ and Cp₁-M-Cp₂ thus range from 110° to 121.5°, depending on whether the three rings contact or are in the equatorial plane. There are three isomeric arrangements corresponding to the relative positions of the β -hydrogen and the α -carbon atoms (Fig. 2, Iabc). Each arrangement gives the independent available spaces which are shown in Fig. 3. The horizontal axis represents the bond angle between the moving cyclopentadienyl and the stationary cyclopentadienyl groups, while the vertical axis represents the available bite offered during the movement. The two critical values b_o and b_h are presented as required bites dividing the whole region into three parts.

When the available bite is larger than b_o , there will be facile H coordination. When the available bite is larger than b_h but smaller than b_o , the hydrogen coordination will be hindered by the inert ligands, and when the available bite is much less than b_h , hydrogen coordination will be seriously hindered. It can be clearly seen that: (1) When the moving cyclopentadienyl group, starting from the reference structure (point A) in Fig. 3, is leaving the two stationary cyclopentadienyl groups, *i.e.* the bond angle becomes greater, the available space becomes smaller. When the moving cyclopentadienyl group is approaching the stationary cyclopentadienyl groups, the available space becomes greater. (2) When the hydrogen atom is situated in between the two stationary rings, the available bite is greater than in the other two isomeric routes. This phenomenon might be generalized as: when the small atom fits into the

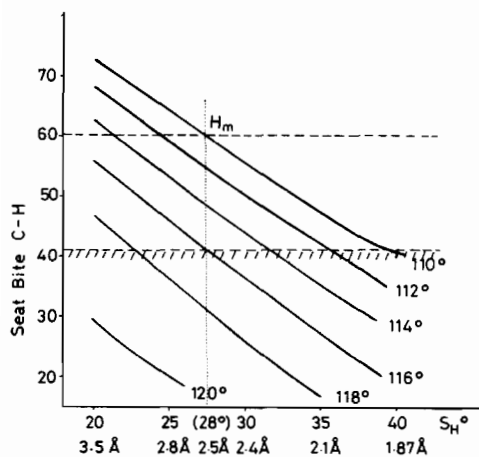


Fig. 4. Separation between the β -hydrogen and the carbon atoms described as $C_{\alpha}-H_{\beta}$ bites. Due to the limited residual space of the UCp_3 fragment, the closer the hydrogen approaches to the metal centre the closer it has to be bent over towards the carbon. The $Cp-M-Cp$ bond angle is given with each curve. Available space decreases when the bond angle is large.

large gap and the large atom fits in the small gap, the separation between them is greater than in the opposite case. (3) Even when the moving cyclopentadienyl group finally contacts the two stationary cyclopentadienyl groups the available space is still not large enough for facile hydrogen coordination, *i.e.* $b_{av} < b_o$.

In the second route, two cyclopentadienyl groups move in such a way that two bond angles remain 117° whereas only one bond angle changes. There are also three isomeric ways of arranging the hydrogen and the carbon atoms (Fig. 2, routes II). These provide even less available space than the previous routes. The ligand arrangements and the spherical trigonometry equivalences are shown in Fig. 2. The calculated reaction spaces are shown in Fig. 3.

In the third mode of ligand movement, the three cyclopentadienyl groups migrate synchronically keeping the C_{3v} symmetry unchanged. When they begin to contact, *i.e.* the bond angles between them are 110° , the maximum available space achieved is 58° , still less than b_o .

In Fig. 4 we have calculated how close the hydrogen atom can approach the metal atom provided that the carbon atom remains at a distance 2.7 \AA from the metal. It is clearly seen that when the bond angle $Cp-U-Cp$ becomes smaller the reaction space becomes larger. However, even when the cyclopentadienyl groups contact each other, the hydrogen atom is still 2.5 \AA from the metal ($FA_H = 28.5^\circ$) and it cannot move closer to the metal.

From the first step of hydrogen coordination to the second step of the olefin-hydride state it is

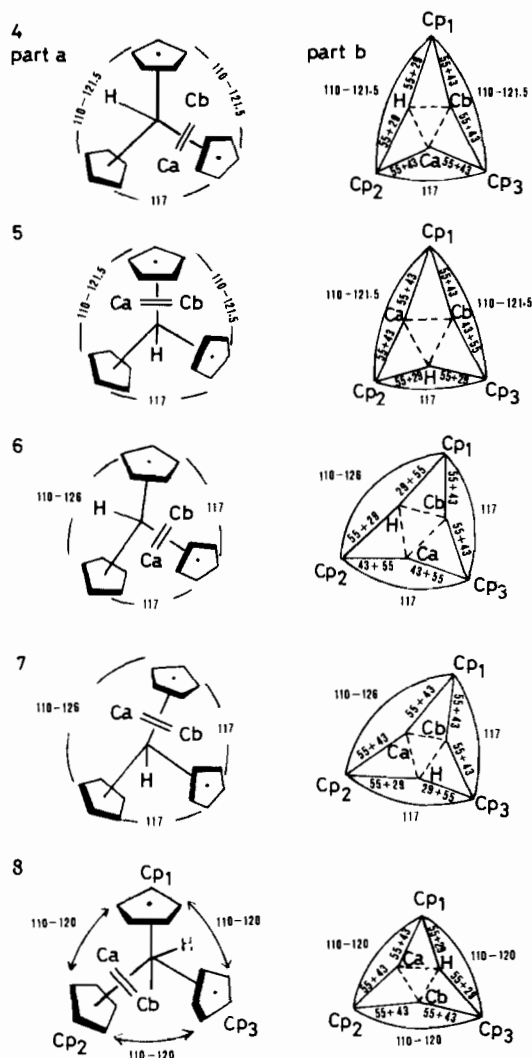


Fig. 5. The olefin-hydride state in the β -hydride elimination reaction. Part a: reaction intermediate; part b: expression in spherical triangles for calculation.

assumed that there are no instantaneous changes in the $M-H$ and $M-C$ bond lengths. Thus the fan angle of hydrogen is still 29° and the fan angle of carbon is still 43° . Since the hydrogen atom is now non-bonded to the carbon atom in the olefin, the bite between the hydrogen and the carbon atoms should be close to the sum of their fan angles. The available bite between the two carbon atoms should be greater than the actual bite of ethylene ligands. The ligand arrangement in the reaction intermediate state and their triangle equivalences are shown in Fig. 5. The calculated $C-H$ and $C-C$ bites are shown in Fig. 6, in which the sum of the corresponding fan angles, $FA_H + FA_C$ and $FA_{C=C}$, are drawn in horizontal lines as the required bites. It is clearly indicated that the available space is less than the required space. When the cyclopentadienyl groups

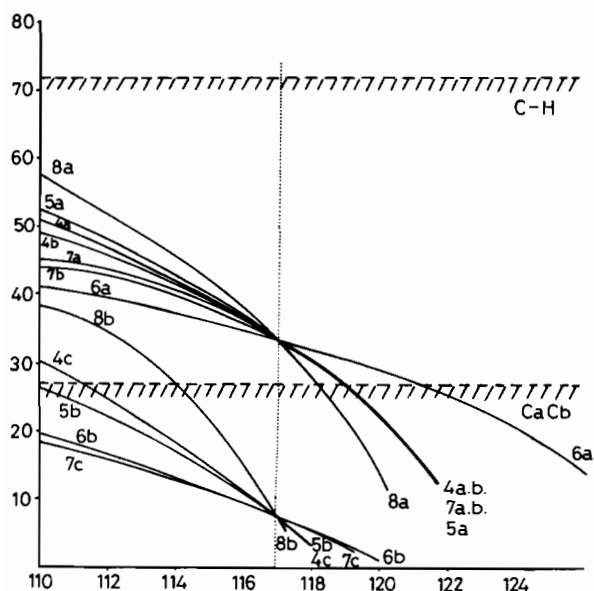


Fig. 6. A comparison between the available space and the required space for the olefin-hydride state. The upper group of curves refer to the maximum available hydrogen-carbon separation to compare with the line C-H. The lower group of curves refer to the maximum available carbon-carbon separation to compare with line CaCb. The available spaces are apparently smaller than the required ones.

are moving closer to give a larger reaction space, there seems to be nearly sufficient room to coordinate the olefin. However the hydrogen and the olefin are strongly rejected from coming together in the residual space of the UCp_3 fragment.

Meanwhile, we have calculated the intermediate state of $U(Me_5C_5)_2CIR$, and $TiCp_2R_2$. The results also suggest bond scission as the first step rather than hydrogen coordination. Unless the molecular fragment $M(Me_5C_5)_2R$ ($M = Th$) is produced as an intermediate, it is expected that β -hydrogen elimination will not be the favoured thermolysis route [7].

The β -elimination mechanism is, in contrast to the f- and the earlier d-transition organometallics, more general for the late transition ones. The spherical trigonometric equivalence for the reaction intermediates of a few well characterized elimination reactions are given in Fig. 7. Because the number of inert ligands are less and they can be packed in a more crowded manner than in the f-block organometallics, there are more spaces available for the reaction intermediates [7] due to coordination unsaturation.

2. Photochemical Reactions

Marks has reported that photochemical excitation of $ThCp_3R$ readily leads to β -hydride elimination. The key processes are ligand-to-metal charge-transfer promotion of the complex to a less coordinatively saturated excited state, $Th(\eta^5-Cp)_2(\eta^1-Cp)R$ or $Th(\eta^3-Cp)_2(\eta^3-Cp)R$ [4]. Our calculation based on the former structure has proved that there is sufficient space for the hydrogen coordination step and for the olefin-hydride intermediate state. The spherical trigonometric description of the intermediate state is shown in Fig. 8. The calculated available spaces are shown in Fig. 9 for the carbon-hydrogen separation, and Fig. 10 for the carbon-carbon separation. In comparison with the required separations,

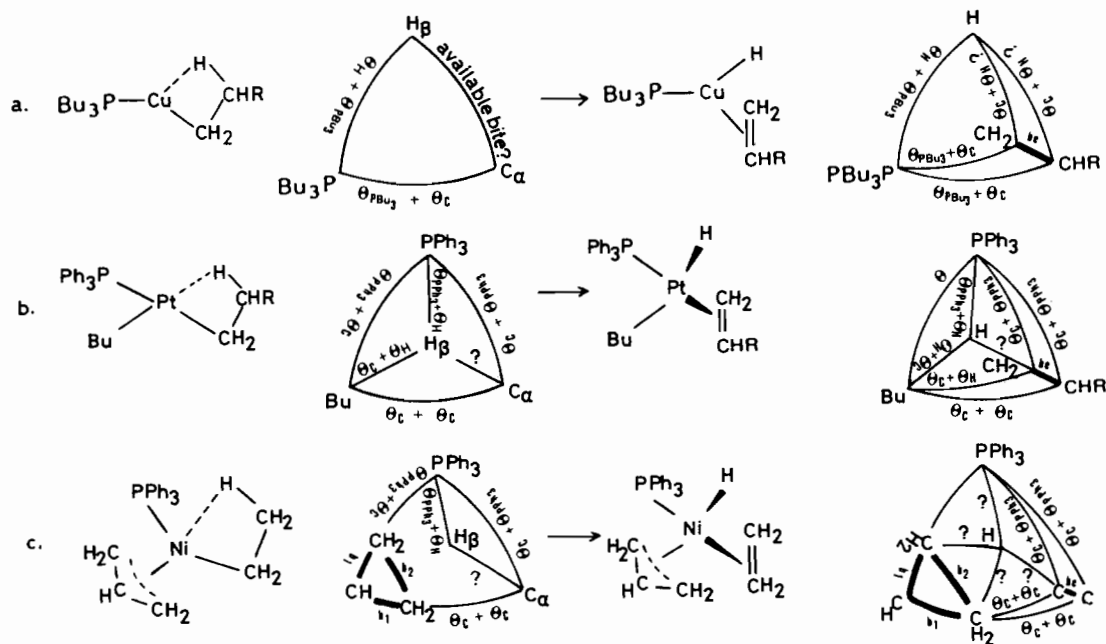


Fig. 7. Intermediate states and their spherical triangular equivalence for the β -hydrogen elimination processes of some organo-transition metal compounds: (a) $CuCH_2CD_2C_2H_5(PBu_3)_3$ [8], (b) $PtBu_2(PPh_3)_2$ [9], (c) $Ni(\eta^3\text{-allyl})(Et)(PPh_3)_2$ [10].

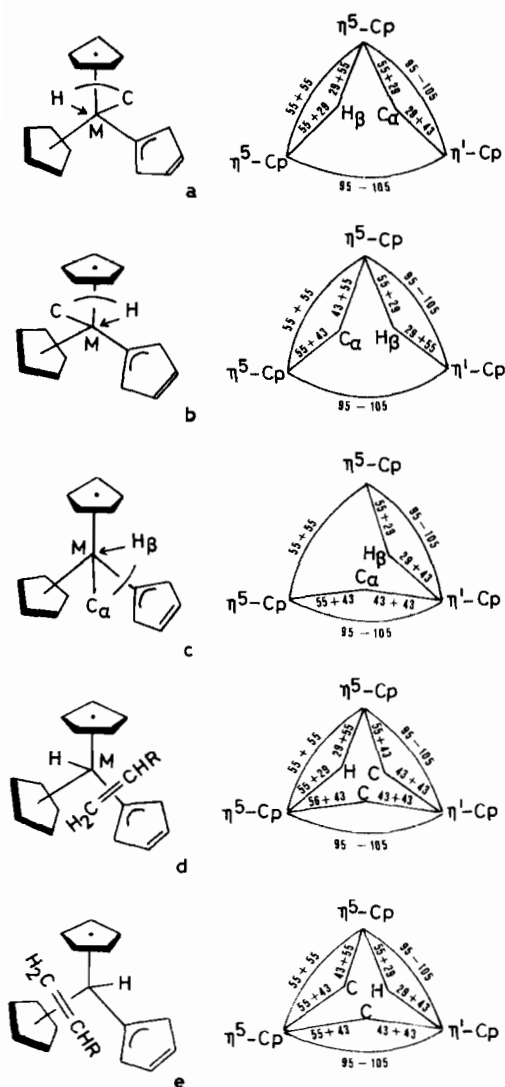


Fig. 8. Photochemical excitation of MCP_3R followed by the β -hydride elimination processes: reaction intermediates [11] and descriptions in spherical trigonometry. a, b, c: different C_{α} , H_{β} arrangements in the hydrogen coordination step; d, e: different arrangements in the olefin-hydride intermediate.

it is clearly seen that as long as the two η^5 -bonded and the η^1 -bonded cyclopentadienyl groups are close to each other, there will be a sufficiently large space for the β -elimination mechanism.

The ligand indenyl has two fan angles. The small one is the same as the simple cyclopentadienyl group. The larger one, on adding the phenyl ring, will be 66° *. Corresponding calculations have shown that

* $FA_{\text{indenyl}} = \arctan(b/d + l/d)$; b = ring centre (Cp)-ring centre (phenyl) distance; l = distance between ring centre and the hydrogen plus Van der Waals radii of hydrogen; d = metal-ring centre (Cp) distance.

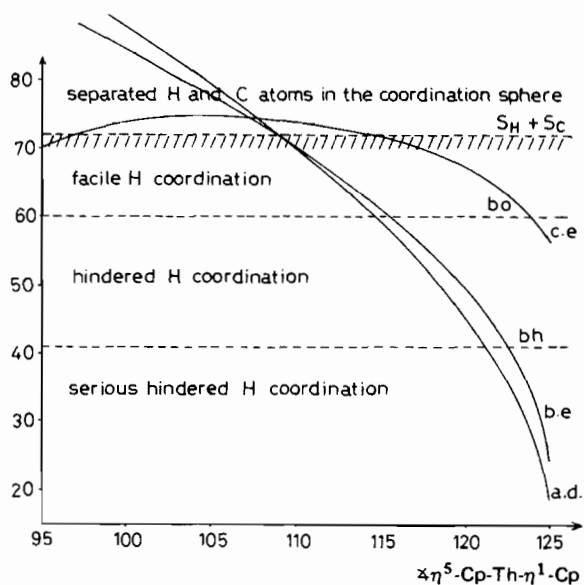


Fig. 9. The available space for C-H separation (the maximum bite) offered in the $M(\eta^5-Cp)_2(\eta^1-Cp)$ fragment. The horizontal axis represents the angle between the η^5 -bonded Cp and the η^1 -bonded Cp. Curves a, b, c, d, e refer to the corresponding arrangements in Fig. 8.

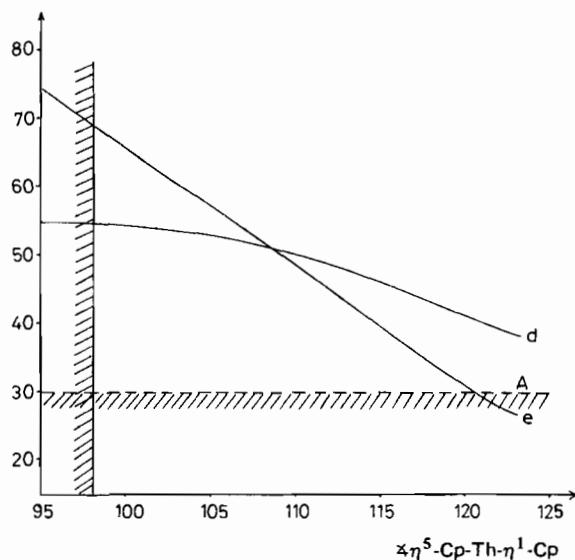


Fig. 10. The available space for the C=C bite offered by the $M(\eta^5-Cp)_2(\eta^1-Cp)$ fragment. Line A represents the required bite of the olefin in π -bonding to the metal at a distance $MC = 2.7 \text{ \AA}$.

the space is less than that required because the indenyl-U-indenyl bond angles are greater than the corresponding Cp-U-Cp angles.

3. Ligand Drifting Movement, Inter- and Intra-molecular Mechanisms for Isomerization Reactions

Organouranium(IV) systems of the general composition $U(C_5H_5)(C_5H_4R)(C_5H_4R')X$ have been in-



vestigated [12]. Stereoisomers were observed by means of ^1H NMR spectroscopy. In another type of tricyclopentadienyl uranium(IV) complex, UCP_3XY , rapid ligand rearrangement was suggested to explain the unusual curvature in the Δ^{iso} versus $1/T$ plots in the ^1H NMR spectrum [13]. So far theoretical discussions on ligand rearrangement reactions are mostly focussed on the initial and the final configurations and little is known about the intermediates [14, 15], *i.e.* the reaction mechanisms. Steric hindrance has been even less studied, yet it plays an important role in the isomerization reactions.

The intramolecular mechanism is normally followed in the ligand rearrangement for d-transition metal complexes. The detailed analysis of the steric hindrance, however, suggests that the above rearrangement might also follow the intermolecular mechanism.

Intramolecular rearrangement is closely related to the movement of the ligand drifting in the coordination sphere (Fig. 11). When the ligands are small so that one ligand can drift through the gap between two other ligands, the movement will lead to conversion from one stereoisomer to another. On the other hand, when the ligands are sufficiently large, such a 'drift' will be hindered, so that the ligands can oscillate only about their equilibrium positions; the structure is non-fluxional.

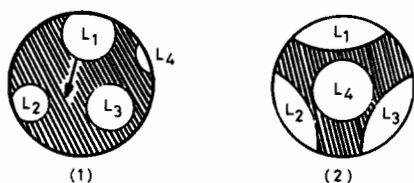


Fig. 11. Ligand migration movement in the coordination sphere: (1) when the ligands are sufficiently small, migration might lead to conversion of stereoisomer; (2) when the ligands are bulky they can oscillate only in the coordination sphere. There will be no isomer transformation.

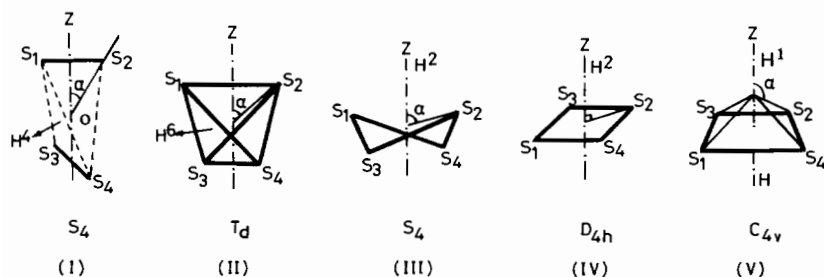


Fig. 12. Movement of four identical ligands along the route of increasing α will cause changes in symmetry leading to conversion of stereoisomers. This figure is to be read together with Table I and Fig. 13.

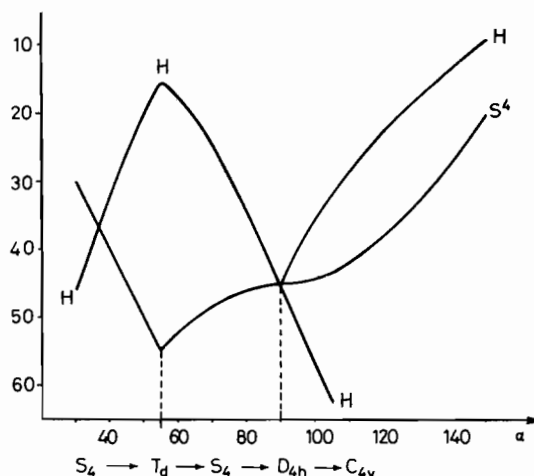


Fig. 13. Variation of the maximum available seats and the frontier seats in the processes of interconversion of MA_4 .

We present here a brief discussion on the intramolecular isomerization pathway concerning the four ligand packing and leave the general treatment for the following papers [16]. Tetrahedron, squeezed tetrahedron, square-planar and square-pyramid are the most popular structures. These structures can be realized stepwise assuming that the ligands move along a definite route with increasing α (Fig. 12).

If at certain geometries the available seats become smaller than the ligands, the movement will be sterically hindered. For example, when the sum of the fan angles (FAS) of the four ligands is less than 180° , the ligands can pass the square-planar state freely and there is no steric barrier at all. When the FAS of the ligands is more than 180° there will be a steric barrier ($\Delta = FAS - 180^\circ$) in the interconversion from T_d to D_{4h} .

We have given the geometrical analysis of the corresponding available seats and the holes of MA_4 species in Figs. 12, 13 and Table I. When the angle between the M-L bond and the improper axis, S_4 , increases, the available seats for the four ligands first increase, reaching the maximum at T_d symmetry and then begin to decrease. The ligand accommodated in a seat smaller than its fan angle is

TABLE I. Molecular Geometries in Accordance with Ligand Movement on the Surface of the Coordination Sphere

	I	II	III	IV	V
Structure	S ₄	T _d	S ₄	D _{4h}	C _{4v}
Symmetry	0 < α < 54.7	α = 54.7	54.7 < α < 90	α = 90	α > 90
Ligand position χ LOZ(α) (°)	α	54.7	$\cos^{-1}\left(\frac{\sqrt{2}}{2}\sin\alpha\right)$	45	$\sin^{-1}\left(\frac{\sqrt{2}}{2}\sin\alpha\right)$
Maximum seat available S _{max} ^a (°)	θ _L - α	θ _L - 54.7	$\theta_L - \cos^{-1}\left(\frac{\sqrt{2}}{2}\sin\alpha\right)$	θ _L - 45	$\theta_L - \sin^{-1}\left(\frac{\sqrt{2}}{2}\sin\alpha\right)$
Steric barrier ^a (°)	HOZ = ±α + θ + H	70.4	< HOZ = ±Z	+Z -Z	+Z
Position of frontier seat (°)	H ²	70.4 - θ	$\tan^{-1}\left(\frac{\cos\theta + \cos\alpha\cos(\theta + \alpha)}{\sin\theta + \cos\alpha\sin(\theta + \alpha)}\right)$	90 - θ	$\frac{\alpha - \theta}{180 - \alpha - \theta}$
Frontier seat ^b (°)			α - θ		

^aHere θ_L refers to the fan angle of ligands at the normal bond lengths.

^bWhen two frontier seats are given, they are not independent of each other.

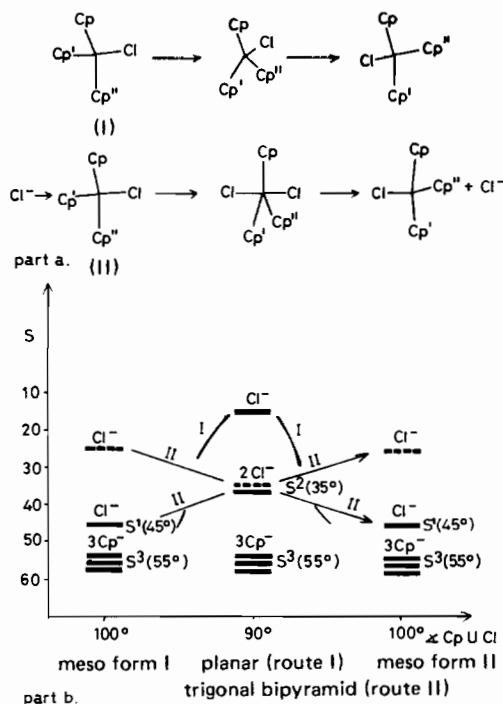


Fig. 14. Racemization reactions via intramolecular (I) and intermolecular mechanisms (II). Part a: the intramolecular and the intermolecular mechanism; part b: the steric barriers for these two mechanisms.

excited because it is subjected to the steric repulsion of other ligands. In such a seat the ligand has to move farther from the metal centre. Due to this reason, the metal–ligand bond distance is longer in spite of the stronger ligand field interaction in the square-plane than in tetrahedral case.

Going back to the two *meso* forms of compounds, UCp* Cp(R)Cp(S)Cl, if the isomer interconversion is via an intramolecular mechanism (route I, Fig. 14), the required space for the planar intermediate will be $FAS = 3FA_{Cp} + FA_{Cl} = 209^\circ$. Since the available is 180° only, on the assumption that the cyclopentadienyl group is more firmly bonded to the metal than the chloride, the available space for the latter would be $180^\circ - 3FA_{Cp} = 15^\circ$. This means that the chloride will be elevated to a distance $d = R_{Cl}/\sin 15^\circ = 7 \text{ \AA}$ from the metal. In fact, at such a distance the chloride is completely dissociated.

In the planar intermediate state the frontier seats in the axial direction are $90^\circ - FA_{Cp} = 35^\circ$. If the isomerization reaction takes place via the intermolecular mechanism (route II, Fig. 14), both the entering and the leaving chlorides, fitted in the axial seat, will be at a distance $d = R_{Cl}/\sin 35^\circ = 3.1 \text{ \AA}$ from the metal centre. The activation energy required for the ligand leaving the metal is actually the same as that needed in the dissociation which starts intramolecular mechanism. Since there will be an energy

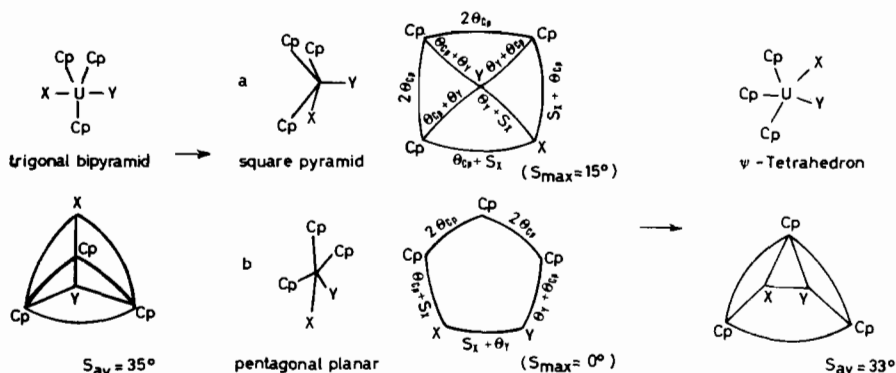


Fig. 15a. Ligand rearrangement from trigonal bipyramidal to the 'side on' species via the intramolecular mechanism. (a) square-pyramid; (b) pentagonal-planar.

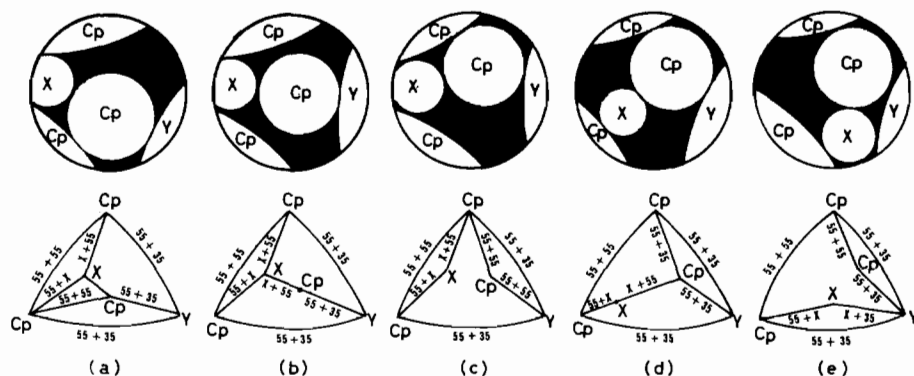


Fig. 15b. Cp-x position permutation movement leading to the ligand rearrangement.

gain for a new ligand entering the opposite seat, the intermolecular mechanism is thus more favourable than the intramolecular mechanism.

There are various routes for intramolecular ligand rearrangement mechanisms from trigonal bipyramid to the 'side on' species, e.g. via the pentagonal-planar, the square-pyramid or the Cp \rightleftharpoons X permutation (Fig. 15), or the other intermediates. For the pentagonal-planar one the required space is $\Sigma_i^5 FA_i = 231 - 243^\circ$ ($X = \text{NCR}$ or NCS^-) which is too large compared with the available space, 180° . It is thus expected that this intermediate is strictly forbidden. In the square-pyramid intermediate one of the axial ligands must drift through the Cp/Cp/Cp plane to reach the 'side on' configuration. In the instant of passing through this plane the required space will be $3FA_{\text{Cp}} + FA_X = 198 - 204^\circ$, ($X = \text{NCR}$ or NCS^-) whereas the maximum available space is 180° . One of the axial ligands has to be elevated to the smaller seat of 15° (Fig. 16a, route II), which corresponds to an M-X distance of 5.8 Å ($X = \text{NCR}$, NCS^-). Again the elevated ligand is actually dissociated.

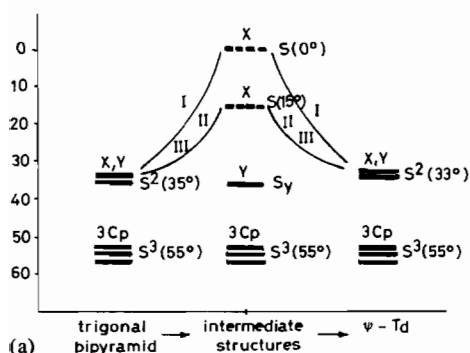
The Cp-X position permutation mechanism also demands space to turn round. The minimum requirement can be calculated according to the configuration shown in Fig. 15. The result is also shown in Fig. 16. Part of this route (c-d-e, Fig. 15b) will

lead the isomerization from trigonal-bipyramid to the 'side on' species. In the key step d the ligand X will be excited to a seat not greater than 15° .

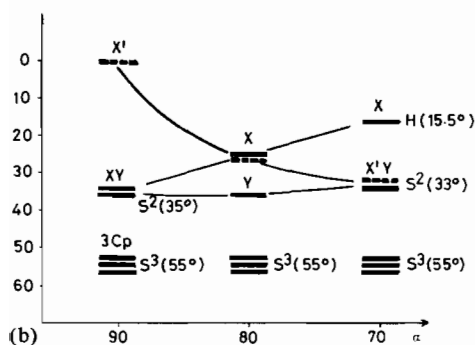
The intermolecular rearrangement mechanism is shown in Fig. 16. The leaving ligand in an axial position is excited to dissociation when the three cyclopentadienyl groups are turned over under the nucleophilic attack of the entering ligand X', and the excitation height is, in fact, the same as that in the intramolecular mechanism, which starts with dissociation. In the *cis*-position of the ligand Y, there are three single seats which reach a maximum of 33° (Fig. 17) when the cyclopentadienyl groups contact to each other. Therefore, in the 'side on' structure the two *cis*-ligands are accommodated in somewhat smaller seats than they are in the *trans*-positions of the trigonal-bipyramidal structure. The corresponding bond lengthening will be $R/\sin 33^\circ - R/\sin 35^\circ = 0.093 R$ (R is the Van der Waals radius of the donor atom). It is apparent that the 'side on' species is less stable than the trigonal-bipyramid.

4. Small Ligand Insertion in the M-R Bond

Following the above discussion, but in ligand integration reactions, the 'side on' species are less stable than the trigonal-bipyramid as regards steric repulsion. If, however, the two ligands, X and Y,



(a)



(b)

Fig. 16. Seat level analysis and steric barriers of inter- and intramolecular mechanisms for the trigonal bipyramidal \rightarrow ψT_d conversion. (a) the intramolecular mechanism; (b) the intermolecular mechanism. The ligand X leaves from the *trans*-position while the ligand X' enters the *cis*-position.

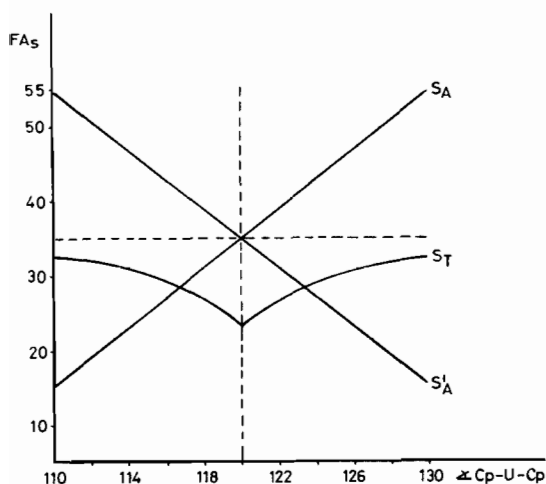


Fig. 17. Comparison of the frontier seats in the trigonal-bipyramidal and the 'side on' configurations. S_A and S'_A : frontier seats for ligand X and Y to adopt the *tbp* configuration; S_T and S'_T : frontier seats for ligand X and Y to adopt the side on configuration. S_T refers to three single seats non-overlapping each other, i.e. $S_T(\theta, 2\theta)$.

can be integrated into a new ligand, the reaction will be inverted, favouring its formation. Thus small ligands like carbon monoxide and carbon dioxide

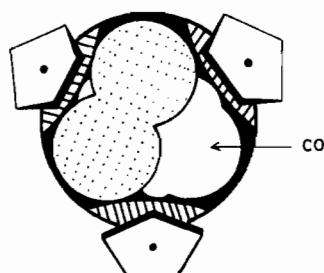


Fig. 18. Carbon monoxide insertion into the vacant seat adjacent to the secondary groups of hydrocarbyls. The shaded areas represent cyclopentadienyl groups. The dotted areas represent two methyl groups in an isopropyl group; note that the metal-carbon bond is only partially shielded.

[17], sulphur dioxide [18] and acetonitrile [19], insert into the metal-carbon σ -bonds.

There are three remarkable points which are closely related to the steric conditions of the tricyclopentadienyluranium(IV) fragment. First, the rate of insertion is greater for more sterically demanding hydrocarbyls. Recalling the combination of the UCp_3 fragment with ligands exerting second-order steric effects (part 5 of our last paper [1]), there are three secondary seats produced by the UCp_3 fragment. The secondary groups of the hydrocarbyl push the three cyclopentadienyl groups to near contact but there is still steric congestion. However, the steric congestion is not uniform, except in the case of the *t*- C_4H_9 group. The carbon monoxide will take one of the three secondary seats in the transient state of the side configuration (Fig. 18). It is clearly seen that the more unsymmetric and the more bulky the hydrocarbyl, the closer the carbon monoxide can approach to the primary carbon atom and to the metal centre. Once there is a nucleophilic attack on the opposite site of the hydrocarbyl, the three cyclopentadienyl groups will be triggered to close up, and push the carbon monoxide to fuse with the hydrocarbyl. The secondary groups in the hydrocarbyl cooperate with the cyclopentadienyl groups to increase the pressure on the carbon monoxide. In this way, hydrocarbyls which have two methyl groups in the secondary layer, such as *iso*- C_3H_7 and *sec*- C_4H_9 , will fuse with carbon monoxide more efficiently than those which have one alkyl group and two hydrogen atoms such as *n*- C_4H_7 , *neo*- C_5H_{11} . The methyl group is the least efficient to accept carbon monoxide and the insertion occurs at a slow rate.

Secondly, carbon dioxide and sulphur dioxide insert into the uranium(IV)-carbon bond more slowly or under more difficult conditions.

Unlike the carbon monoxide and acetonitrile reactions, carbon dioxide inserts into the metal-carbon bond to produce a four-membered ring at the first step. The oxygen-oxygen bite is more than

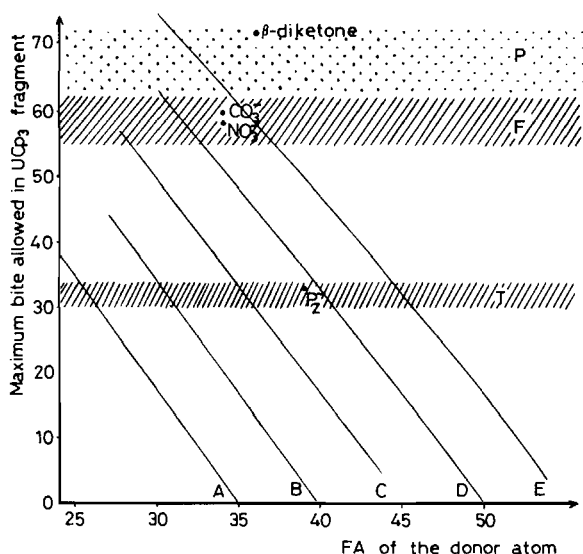
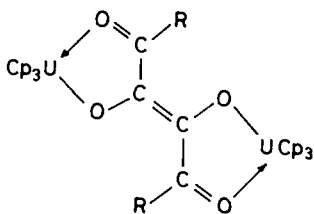


Fig. 19. The required space to bond bidentate ligands and the available space in the UCp_3 fragment. (1) Border T: critical border to form 3-membered rings; F: critical border to form 4-membered rings; P: critical border to form 5- and 6-membered rings. (2) Curve A: $\alpha = 90^\circ$, $Cp-U-Cp = 120^\circ$; curve B: $\alpha = 85^\circ$, $Cp-U-Cp = 119.2^\circ$; curve C: $\alpha = 80^\circ$, $Cp-U-Cp = 117.1^\circ$; curve D: $\alpha = 75^\circ$, $Cp-U-Cp = 113.5^\circ$; curve E: $\alpha = 70^\circ$, $Cp-U-Cp = 109.5^\circ$.

60° for a carboxylic acid. Compared with the available seat (Fig. 19), it is more critical to carry on the insertion.

Thirdly, there are no multi-insertions and dimerization to produce a five-membered ring, such as



A five-membered ring demands more space than a four-membered ring and so the reaction is seriously hindered.

Ligand dissociation and association reactions [20], and ligand exchange reactions of complexes containing three π -bonded cyclopentadienyl groups have been discussed elsewhere [21]. The error in introducing the spherical trigonometric method to describe ligand movement will be discussed in another paper.

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Note Added in Proof

After completion of this paper, the author had learned that the first $CpUXY$ complex to contain a four-membered ring, *i.e.*, $CpU[(NPh)(O)CCHP-(Ph)(R)(Me)]$ [22], has been determined.

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