

MOLECULAR ORBITAL CALCULATIONS ON η^3 - AND η^5 -HEXADIENYL COMPLEXES OF THE PLATINUM METALS; AN ANALYSIS OF THEIR CONFORMATIONAL PREFERENCES AND FLUXIONAL CHARACTERISTICS

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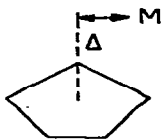
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Summary

Extended Hückel molecular orbital calculations are reported for the η^3 - and η^5 -platinum metal complexes $[\text{Pt}(\eta^3\text{-C}_6\text{H}_7)(\text{PH}_3)_2]^+$ and $[\text{Pt}(\eta^5\text{-C}_6\text{H}_7)(\text{PH}_3)_2]^+$. The η^3 -geometry is found to be only 0.56 eV more stable than the η^5 -geometry. This leads to a low energy fluxional process in these molecules. The stereochemistry of this fluxional process is rationalised in terms of the conformational preferences of the $[\text{Pt}(\eta^5\text{-C}_6\text{H}_7)(\text{PH}_3)_2]^+$ ions.

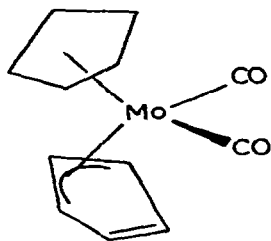
In recent publications we have demonstrated how molecular orbital calculations based on the extended Hückel approximation may be used to account for the electronic origins of the "slip" distortion in metallocarboranes [1–4]. A "slip" distortion being defined as the lateral displacement of the metal atom away from a central position above the pentagonal face of a carborane ligand, e.g. $\text{C}_2\text{B}_9\text{H}_{11}$, and as defined by the distance parameter, Δ , in I.



(I)

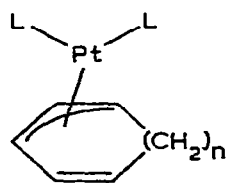
Our attention has focussed particularly on the $\text{ML}_2(\text{C}_n\text{B}_{11-n}\text{H}_{11})$ complexes based on the icosahedron [2,3] and it has been established that the magnitude and even the sign of Δ can be influenced by the electronic configuration of the metal, the π -acceptor characteristics of the ligands, L, and the substituents on

the open pentagonal face of the carborane ligand. These "slip" distortions are also observed in conventional organometallic compounds, e.g. $M(\eta\text{-C}_5\text{H}_5)(\eta\text{-1-3-C}_5\text{H}_5)(\text{CO})_2$ (II), and have been sensibly rationalised in terms of the requirements of the 18 electron rule [5]. However, this line of argument does

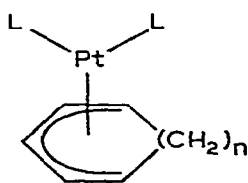


(II)

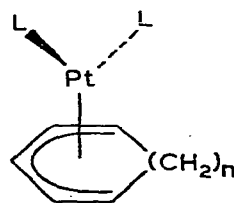
not account for the observation that complexes of the type $[\text{Pt}(\eta\text{-cyclohexadienyl})\text{L}_2]^+$ and related cyclic species take up a $\eta^3\text{-16-electron}$ ground state structure as illustrated in III rather than a $\eta^5\text{-18-electron}$ structure as illustrated in IV [6].



(III)



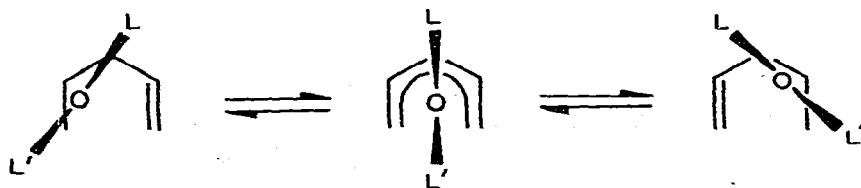
(IV)



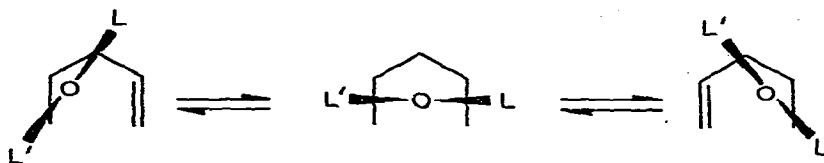
(V)

In an idealised sense it can be appreciated that III is related to IV by a "slip" distortion of the metal atom away from a central position above the pentagonal face towards the central carbon atom of the localised allylic fragment of III. In reality, the distortion is more complex because the degree of freedom introduced by the $(\text{CH}_2)_n$ chain permits an additional torsional distortion about the C—C bond joining the allylic and olefinic components of the π -system in III [7].

Complexes of the type III and IV are in addition interesting because of their fluxional characteristics. Maitlis and his co-workers have studied the variable temperature NMR characteristics of the ions $[\text{Pd}(\eta\text{-1-3-C}_7\text{H}_9)(\text{PR}_3)_2]^+$ and have concluded that the fluxional process in these ions has a low activation energy ($\Delta G^\ddagger \sim 30 \text{ kJ mol}^{-1}$) [6] and proceeds through the symmetrical intermediate illustrated in IV in such a way that the phosphine ligands do not become magnetically equivalent, i.e.:



The alternative pathway involving an intermediate with the conformation illustrated in V, which would lead to an interchange of the phosphine ligands, is not



observed. In order to account for the ground state geometry of this type of complex, and the energetics and stereochemistry of the fluxional process we have completed calculations on the model compound $[\text{Pt}(\text{PH}_3)_2(\text{C}_6\text{H}_7)]^+$ with the idealised conformations illustrated in III, IV and V. Details of the computational methods and the geometrical parameters used in the calculations are given in the Appendix.

Results and discussion

The important valence orbitals of the angular $\text{Pt}(\text{PH}_3)_2$ and related fragments have been discussed in some detail elsewhere [1–3,8] and therefore only the important details will be reiterated here. In $\text{Pt}(\text{PH}_3)_2$ the platinum d orbitals show a relative simple splitting pattern, four of the orbitals having more than 95% metal d orbital character, i.e. xy , yz , $x^2 - y^2$, and z^2 * and the other has predominantly xz character but also has a small admixture of metal x orbital character. The sign of the mixing is such that it effectively hybridises the xz orbital away from the phosphine ligand as shown in Fig. 1. This molecular orbital is the highest occupied molecular orbital (HOMO) in the fragment. The lowest unoccupied molecular orbital (LUMO) is also hybridised away from the ligands, but it has a_1 symmetry and arises from an admixture of metal s and z orbitals.

The cyclohexadienyl fragment has π -molecular orbitals (see Fig. 2) which bear a close similarity to the π -molecular orbitals derived from simple Hückel molecular orbital theory for the pentadienyl radical [9]. The CH_2 bridge produces only minor perturbations on the π -molecular orbitals. The role of these secondary interactions in influencing the non-planarity of the hexadienyl ligand in organometallic complexes has been discussed in some detail by Hoffman and Hoffmann [10]. Having introduced the frontier orbitals of the individual fragments it is now possible to evaluate their mutual interactions for the different conformations illustrated in III–V above.

Table 1 summarises the computed total energies, i.e. within the extended Hückel approximation the sum of the energies of the occupied one electron energy levels, for $[\text{Pt}(\eta\text{-C}_6\text{H}_7)(\text{PH}_3)_2]^+$. The most stable geometry is that illustrated in (III), i.e. the η^3 -16 electron structure. This geometry is 0.56 eV (50 kJ mol⁻¹) more stable than the η^5 geometry illustrated in IV, which in turn is more stable by 0.28 eV (30 kJ mol⁻¹) than the alternative η^5 geometry illustrated in V. Such an order of stability would clearly account for the type of

* s , x , y , z , xz , yz , xy , $x^2 - y^2$ and z^2 are used to denote the corresponding ns , np and $(n-1)d$ atomic orbitals of the metal.

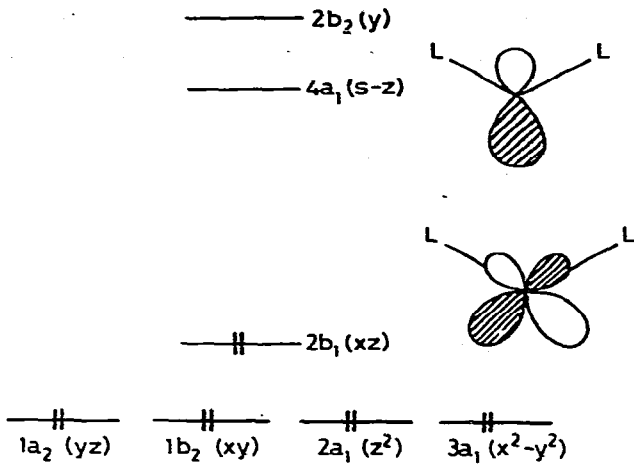


Fig. 1.

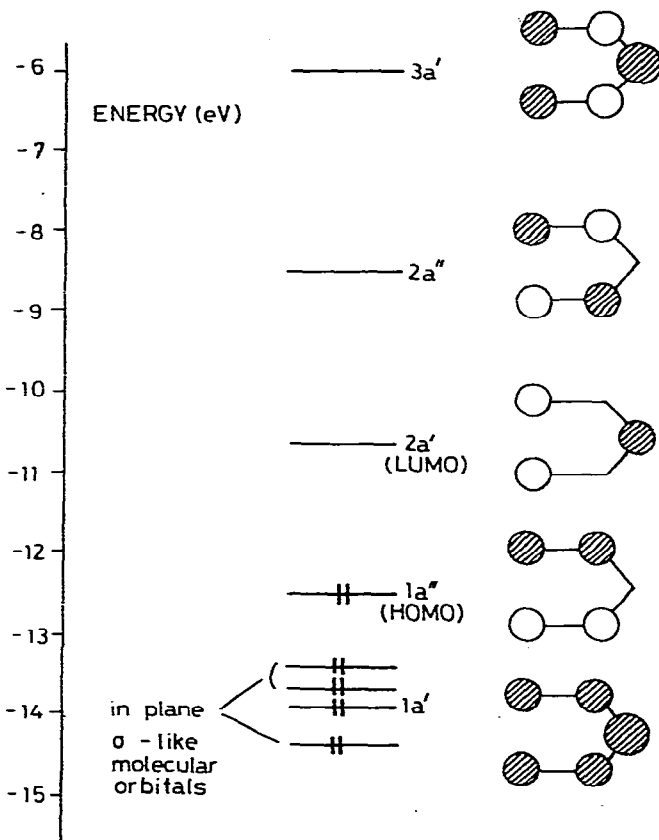


Fig. 2.

TABLE 1
COMPUTED TOTAL ENERGIES FOR $[\text{Pt}(\eta\text{-C}_6\text{H}_7)(\text{PH}_3)_2]^+$

Conformation	Total energy ^a (eV)	(kJ mol ⁻¹)
III	-930.886	-88,450
IV	-930.323	-88,400
V	-930.044	-88,370

rearrangement process which occurs in molecules of this type, furthermore the difference in energy between III and IV is close to experimentally determined activation energies for the fluxional process (30–67 kJ mol⁻¹ depending on the metal and the ligands coordinated to the metal). However, in view of the severe approximations involved in the extended Hückel method it is important to establish whether the observed energy differences have any basis in terms of symmetry or pseudo-symmetry arguments. Therefore, some attention will be given to trying to establish the important interactions which occur between the $\text{Pt}(\text{PH}_3)_2$ and hexadienyl fragments.

Figures 3, 4 and 5 illustrate schematically how the molecular orbitals of the two fragments interact in III, IV and V. From these figures and a more detailed analysis of the interfragment overlap integral and overlap populations [11,12] it can be seen that the most significant interactions involve the metal xz hybrid

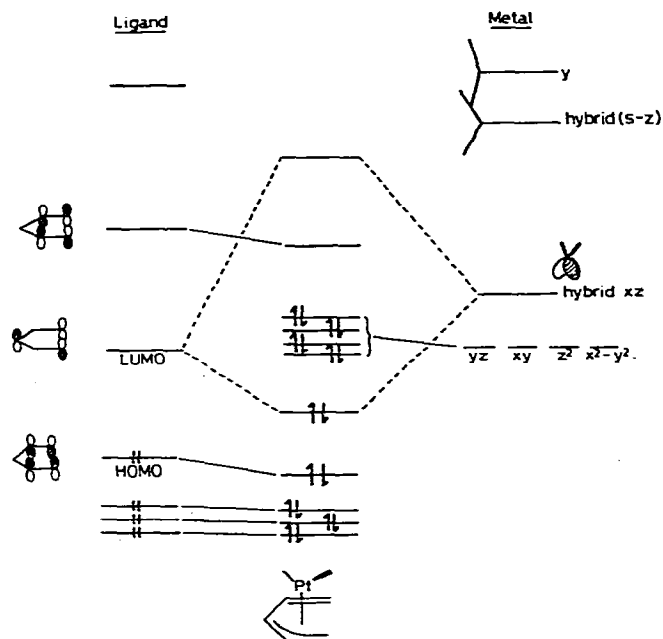


Fig. 3.

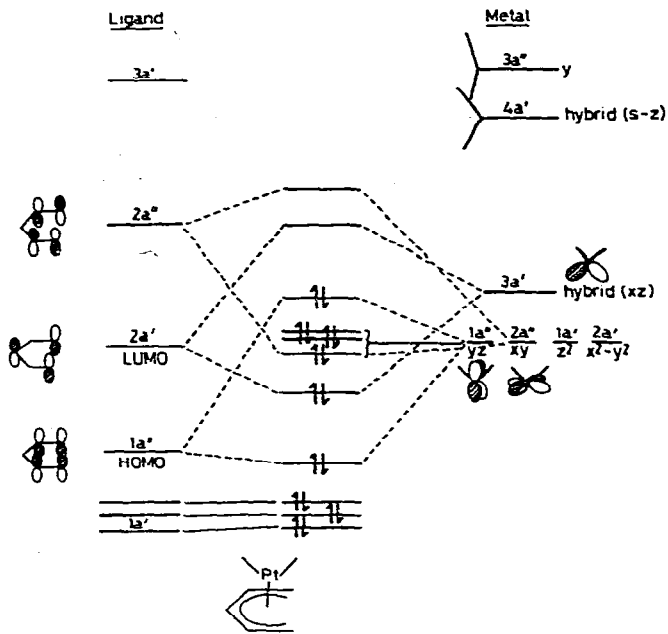


Fig. 4.

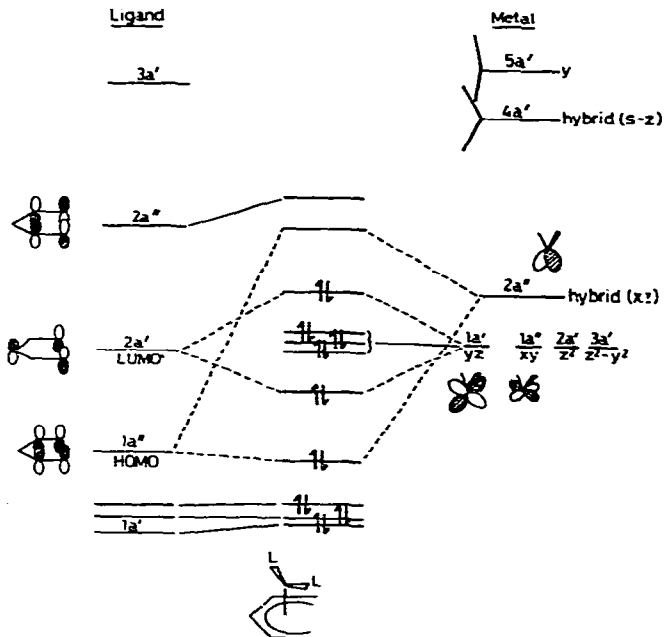


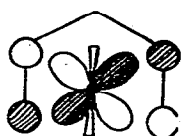
Fig. 5.

TABLE 2

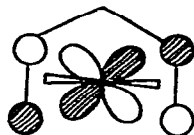
OVERLAP INTEGRALS, OVERLAP POPULATIONS AND ENERGY SEPARATIONS BETWEEN FRAGMENT ORBITALS IN $[\text{Pt}(\eta^5\text{-C}_6\text{H}_7)(\text{PH}_3)_2]^+$

	Overlap integral	Energy separation	Overlap population
<i>Orientation III</i>			
hybrid xz /ligand LUMO	0.1657	0.95 eV	0.2305
yz /ligand HOMO	0.0582	1.75 eV	0.0059
hybrid($s-z$) /ligand HOMO	0.1564		0.0469
<i>Orientation IV</i>			
hybrid xz /ligand LUMO	0.1506	0.95 eV	0.2157
yz /ligand HOMO	0.1047	1.75 eV	-0.0253
<i>Orientation V</i>			
yz /ligand LUMO	0.0899	0.15 eV	-0.0190
hybrid xz /ligand HOMO	0.1653	2.60 eV	0.1749

orbital, the metal yz orbital and the cyclohexadienyl cation's HOMO and LUMO. There are also supplementary bonding interactions between the empty metal $4a'$ (hybrid $s-z$ orbital) and the lower lying and filled ligand orbitals of a' symmetry and between the filled metal xy orbital and the empty ligand $2a''$ orbital. These interactions are important in stabilising the molecule but have little influence on the conformational preferences, the former for obvious reasons, the latter because the 90° rotation relationship between the nodal planes of the xy orbital coincides with the rotation relating the conformations as shown below:



(IV)



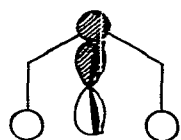
(V)

In the two η^5 conformations, IV and V, the ion has a plane of symmetry and therefore the important frontier molecular orbitals can be classified according to whether they are symmetric or antisymmetric with respect to this symmetry element in the following fashion:

Symmetry designation	Cyclohexadienyl orbitals	Metal orbitals	
		Conformation IV	Conformation V
a'	LUMO	hybrid xz	yz
a''	HOMO	yz	hybrid xz

Figures 4 and 5 illustrate the fact that these pairs of symmetry related orbitals give rise to two bonding and two antibonding combinations. Furthermore these four molecular orbitals are populated by six electrons because the electron populations of the separated fragments are; $\text{Pt}(\text{PH}_3)_2 \dots (yz)^2$ (hybrid xz)² and (cyclohexadienyl) \dots (HOMO)².

From perturbation theory arguments it is clear that the extent of interaction between metal and ligand orbitals is decided primarily by the interfragment overlap integrals and the energy separations between these molecular orbitals which have non-zero overlap integrals [13]. The computed integrals given in Table 2 indicate that the metal hybrid- xz orbital, which has a greater degree of directional character, overlaps more effectively than yz with the cyclohexadienyl HOMO and LUMO. Furthermore, as the metal-cyclohexadienyl overlap integrals (given in Table 2) are similar for the two conformations, the observed conformational preference must be decided primarily by the relative energies of the interacting orbitals. The two electron bonding interaction between the hybrid- xz orbital and the cyclohexadienyl LUMO ($2a'$) is stronger than that with the cyclohexadienyl HOMO ($1a''$) because of the smaller energy separation in the former case. These bonding interactions which are illustrated schematically below will tend to stabilise conformation IV relative to conformation V.



hybrid xz - LUMO
(IV)



hybrid xz - HOMO
(V)

The calculated Mulliken overlap populations given in Table 2 confirm the preferred interaction between hybrid xz and the cyclohexadienyl LUMO.

The negative computed overlap populations for the metal yz orbital given in Table 2 arise because this metal orbital enters into a four-electron destabilising interaction with the cyclohexadienyl molecular orbital (see also Fig. 4 and 5). This antibonding interaction, as judged by the overlap populations in Table 2 is very similar for the two conformations and therefore has little influence on the relative stabilities of the conformations.

The antibonding nature of this interaction is slightly mitigated by a mixing of the metal y orbital character in the following way:



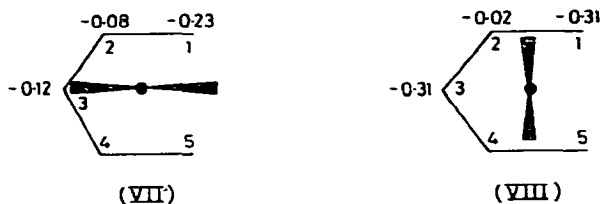
(VI)

This mixing rehybridises the orbital away from the hexadienyl ligand and thereby reduces its antibonding character. The effectiveness of this rehybridisation will depend markedly on the metal $d-p$ promotion energy, and the π -acceptor abilities of the other ligands coordinated to the metal. (The greater the π -acceptor ability the greater the rehybridisation) [13]. These effects will have an important influence on the relative stabilities of η^3 and η^5 coordinated modes and will be discussed in more detail below.

In conclusion the conformational preference for IV is decided primarily by the more favourable bonding interaction between the $\text{Pt}(\text{PH}_3)_2$ hybrid- xz

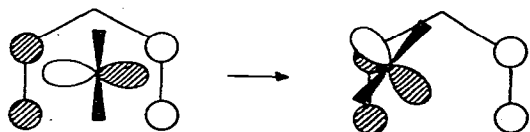
orbital and the LUMO of the cyclohexadienyl ligand. Similar conformational preferences have been noted for platinacarboranes and platinum dioxygen and olefin complexes and have been interpreted in a similar fashion.

The illustrations VII and VIII below give the computed charges for the two conformations and suggest strategies for influencing the relative stabilities of the two conformations.

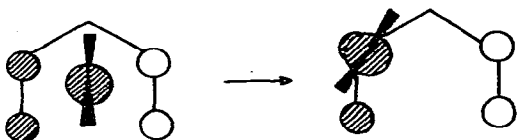


The larger negative charges at the 1, 3, and 5 positions for conformation V shown in VII above suggest that the introduction of strong electron-withdrawing groups at these positions, or the replacement of the carbon atoms by more electronegative elements, will lead to a stabilisation of conformation V relative to conformation IV. For a η^3 -hexadienyl complex such a substitution pattern could result in a preference for the alternative fluxional process illustrated above.

The occurrence of a four-electron destabilising interaction between the metal yz orbital and the ligand HOMO described above for conformation IV provides an important clue for understanding why the η^3 geometry is the preferred ground state structure for this type of molecule. Qualitatively it can be appreciated that a "slip" distortion of the metal atom across the face of the cyclohexadienyl ligand and in the sense illustrated below could reduce the antibonding character of this orbital:



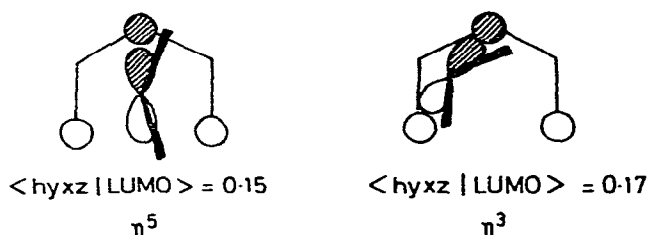
At the same time such a distortion permits the introduction of a two electron bonding interaction between the higher lying and empty metal ($s-z$) hybrid orbital and the ligand HOMO which was symmetry forbidden for the symmetrical η^5 structure, as shown below:



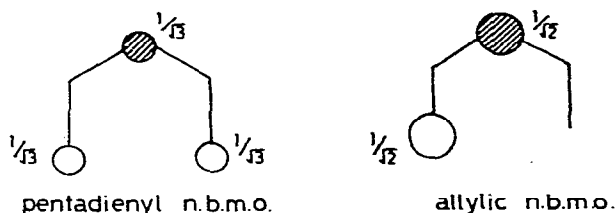
This view has been substantiated by the detailed calculations which have been completed and which are summarised in Table 2. The metal yz -hexadienyl HOMO overlap integral decreases from 0.1047 in IV to 0.0582 in III, and at the same time the metal hybrid ($s-z$) overlap integral increases from 0.000 to 0.1564. This reduction of antibonding character associated with the yz orbital

is clearly illustrated in Fig. 3 which shows that the yz orbital is essentially non-bonding in the η^3 complex.

The reduction in antibonding character of the metal yz orbital is not achieved at the expense of the important bonding interaction between the metal hybrid- xz orbital and the ligand LUMO, because the overlap integral calculations given in Table 2 indicate that for the η^3 geometry the overlap between this metal orbital and the $2p_z$ orbitals on the 1 and 3 carbon atoms of the hexadienyl ligand is superior to that for η^5 geometry (see below):



The overlap in the η^3 geometry is further improved by a torsion about the C(3)–C(4) bond which reduces the conjugation between the allylic and olefinic components of the hexadienyl ligand. In the limit of no overlap between these components the coefficients of the p_z orbitals at carbon atoms 1 and 3 would increase from approximately $1/\sqrt{3}$ to $1/\sqrt{2}$ (i.e. the coefficients of the non-bonding allylic molecular orbital as illustrated below [9]):

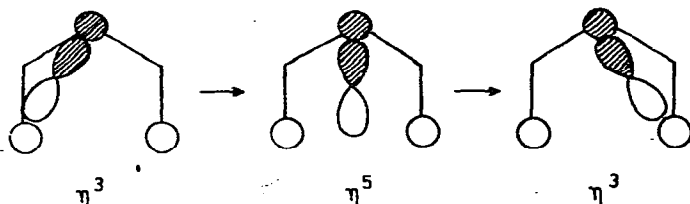


In summary the η^3 geometry is preferred for these cyclohexadienyl complexes because the important metal-hybrid xz -LUMO interaction is improved and the antibonding yz -hexadienyl interaction is reduced relative to those of the η^5 geometry.

Fluxional characteristics of η^3 -cyclohexadienyl complexes

Although a detailed investigation of the potential energy surface for the fluxional process in $[\text{Pt}(\text{PH}_3)_2(\text{C}_6\text{H}_7)]^+$ has not been made, an understanding of the bonding in these complexes and the factors influencing the relative stabilities of III, IV and V gained from the above analysis does enable us to account for trends in the activation energies of the fluxional process and predict results for future studies. These molecules clearly are fluxional because the slipping motion of the platinum atom across the face of the cyclohexadienyl ligand involves only small changes in the overlap integrals between the frontier orbitals of the constituent fragments. In particular the phase relationship between the $2p_z$ orbitals at the terminae of the haptotropic shift permits the retention of

consistently good overlap between the metal-hybrid xz orbital and hexadienyl LUMO orbital throughout the reaction coordinate as illustrated below:

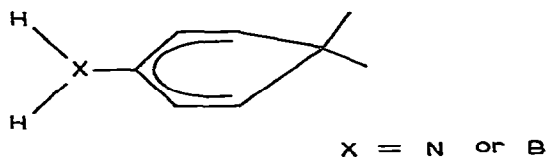


The importance of this phase relationship in understanding the fluxional characteristics of organometallic complexes containing the ML_2 unit has been stressed previously [14].

The activation energy for the fluxional process will be decided primarily by the relative stabilities of the two conformations III and IV, and from the discussion above these are determined primarily by the degree of hybridisation associated with the metal xz and yz orbitals. Increased participation of x in the hybrid xz orbital, which is promoted by good σ -donation ligands L , leads to a more favourable interaction with the cyclohexadienyl LUMO and a preferential stabilisation of the η^3 geometry. In contrast strong π -acceptor ligands, or metal atoms with small $d \rightarrow p$ promotion energies, will stabilise the η^5 geometry IV by reducing the antibonding interaction between the metal yz orbital and the cyclohexadienyl HOMO.

Mann and Maitlis have studied the fluxional process in $M(\eta^3-C_7H_9)L_2^+$ ($M = Pd$ or Pt) and have established that the activation energy for the process shows the following dependence on L $acac^* > en > Cl > AsEt_3 > PEt_3 > olefins$ [6] in broad general agreement with the theoretical analysis described above. Furthermore, they have noted that the platinum complexes have higher activation energies than the corresponding palladium complexes, which is consistent with the larger $d-p$ promotion energy of the heavier metal.

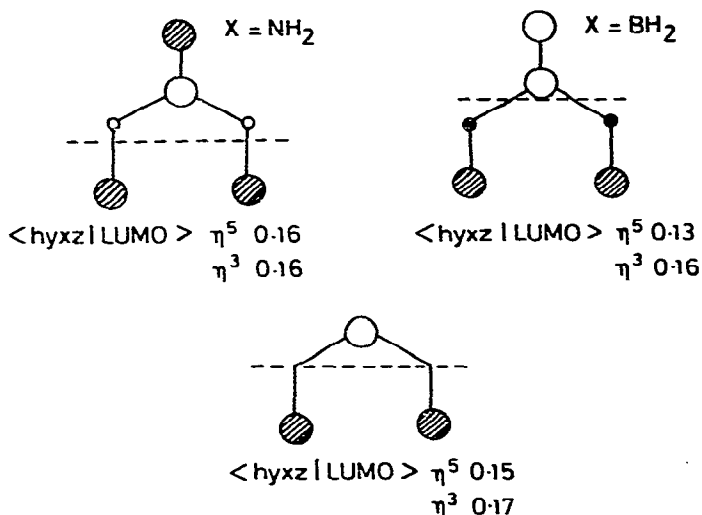
The effect of π -donating and π -withdrawing substituents in the 3 position of the cyclohexadienyl ligand have also been evaluated using the following model compounds:



The amino group is found to preferentially stabilise the η^5 conformation, the energy difference between the η^3 and η^5 geometries being reduced from 0.56 to 0.45 eV. On the other hand the boranyl group preferentially stabilises the η^3 geometry. The reason for this distinction can be traced to the slight changes in nodal characteristics of the LUMOs which accompany substitution and are

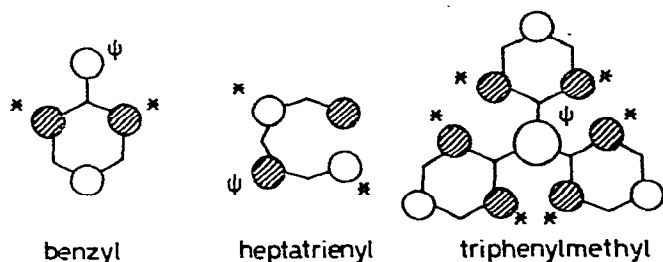
* $acac$ = acetylacetonate, en = ethylenediamine.

illustrated below:



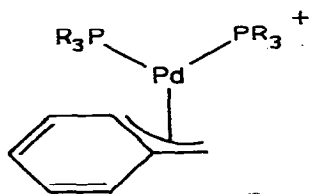
The shift in the nodal plane associated with the introduction of substituents increases the overlap between the hybrid αx orbital and ligand LUMO in the η^5 geometry for the aminocyclohexadienyl complex, but decreases it for the boranycyclohexadienyl complex. The underlying reasons for the change in sign of the coefficients at the 2 and 4 positions in the substituted derivatives can be easily traced using second order perturbation theory arguments [15].

The phase relationship of the carbon $2p_z$ orbitals at the terminae of the haptotropic shift is not unique to the cyclohexadienyl cation but is a consequence of the odd-alternant nature of the π -system in this molecule [9]. A similar phase relationship is found in the non-bonding molecular orbitals of the following cations which are capable of forming η^3 -complexes with ML_2 fragments.



In the illustrations ψ represents the carbon atom which retains its bonding with the ML_2 unit throughout the migratory process and * the carbon atoms at terminae of the migratory process. Becker and Stille [16] have studied the variable temperature NMR characteristics of IX and related complexes with chiral carbon centres and established that in non-donor solvents the fluxional process does indeed proceed by a simple suprafacial rearrangement as indicated. In donor solvents, nucleophilic addition at the metal by the donor encourages a η^3 - η^1 transformation similar to that proposed earlier for $\text{Mo}(\eta\text{-C}_5\text{H}_5)$ -

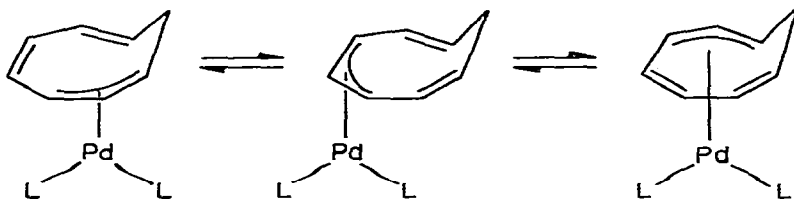
(η^3 -benzyl)(CO)₂ [17,18]. The non-bonding molecular orbital for a planar tri-



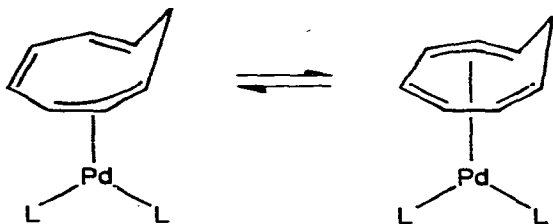
(IX)

phenylmethyl cation illustrated above suggests a facile fluxional process for this molecule involving six equivalent sites for the ML₂ fragment around the central carbon atom. However, the non-planarity of this species leads to two distinct fluxional processes, the lower energy process involves a suprafacial shift of the ML₂ unit about one phenyl ring similar to that noted above for the benzyl complex IX, and a higher energy process where the triphenylmethyl cation rotates with respect to the metal in the manner of a three bladed propeller. The second process leads to magnetic equivalence of all the *ortho*-carbons in the triphenylmethyl cation and has for example been observed in Pd(acac)(Ph₃C) [19].

For heptatrienyl complexes, e.g. [Pd(η^3 -C₈H₉)(PEt₃)₂]⁺ the following rearrangement processes are predicted on the basis of the non-bonding molecular orbital characteristics described above:



On the other hand the following suprafacial shift would be symmetry forbidden



In addition to the phase relationships discussed above clearly the distance between the carbon atoms at the terminae of the migratory process could have a significant influence on the activation energy for the suprafacial shift. Mann and Maitlis have noted that the activation energy for the fluxional process in [Pd(η^3 -C₈H₁₁)(AsEt₃)₂]⁺ is much larger than that observed for [Pd(η^3 -C₇H₉)-

$(\text{AsEt}_3)_2]^+$ and have ascribed this difference to the larger C—C distance in the former case [6].

Appendix

All calculations were performed on the ICL 1906A computer at Oxford using the extended Hückel (ICON8) and fragment molecular orbital analysis (FMD MK19) programs developed at Cornell University by Prof. R. Hoffmann and his coworkers [20–23]. The following geometric parameters were used throughout the calculations on $[\text{Pt}(\eta\text{-C}_6\text{H}_7)(\text{PH}_3)_2]^+$:

(a) Cyclohexadienyl fragment: pentadienyl C—C 1.40 Å, C—H, 1.08 Å; C—C—C angle 120°; CH₂ unit: C—CH₂ 1.50 Å; C—H 1.10 Å, H—C—H angle 109°; dihedral angle between pentadienyl and C—CH₂—C planes 40°.

(b) $\text{Pt}(\text{PH}_3)_2$ fragment: Pt—P 2.29 Å; P—H 1.42 Å; P—Pt—P angle 100°, Pt—P—H angle 109.5°.

The electronic parameters used in the calculations are summarised below:

Orbital	Exponent	H_{ii} (eV)
Pt 6s	2.554	-9.80
Pt 6p	2.554	-5.35
C 2s	1.625	-21.4
C 2p	1.625	-11.4
P 3s	1.600	-18.6
P 3p	1.600	-14.0
H	1.30	-13.6

Orbital	Exp. 1	Coeff. 1	Exp. 2	Coeff. 2	H_{ii} (eV)
Pt 5d	6.013	0.634	2.696	0.551	-10.61

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