APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 393–397
DOI:10.1002/aoc.444

Chemical applications of topology and group theory: 37. Pentalene as a ligand in transition metal sandwich complexes[†‡]

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Received 6 December 2002; Revised 7 January 2003; Accepted 15 January 2003

The η^8-$C_8H_6{}^{2-}$ pentalene ligands in the recently discovered sandwich compounds (η^8-C_8H_6)$_2$M (M = Ti, Zr) can be derived either by transannular 'pinching' of the cyclooctatetraene dianion, $C_8H_8{}^{2-}$, or by edge-sharing fusion of two cyclopentadienyl ligands $C_5H_5{}^-$. This paper depicts the relationship between the molecular orbitals in $C_8H_6{}^{2-}$, $C_8H_8{}^{2-}$, and $2C_5H_5{}^-$. In addition, this paper shows that the d_{z^2} orbital of the central metal atom is of suitable symmetry for δ bonding in the D_{2h} complexes (η^8-C_8H_6)$_2$M (M = Ti, Zr) unlike in the D_{8h} complexes (η^8-C_8H_8)$_2$M derived from cyclooctatetraene. This can account for the fact that the cyclooctatetraene sandwich compounds of stoichiometry (C_8H_8)$_2$M have unsymmetrical (η^8-C_8H_8)(η^4-C_8H_8)M structures in the case of the d-block metals titanium and zirconium in contrast to perhapto structures (η^8-C_8H_8)$_2$An in the case of the actinides (An = Th, Pa, U, Np, Pu) where metal f orbitals are available for metal–ring bonding. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: pentalene; sandwich complexes; topology; transition metals; cyclooctatetraene; titanium; zirconium

INTRODUCTION

One of the major landmarks in transition metal organometallic chemistry was the discovery of ferrocene, (η^5-C_5H_5)$_2$M (**I**: M = Fe),[1,2] by two independent research groups in 1951; for several historical articles on the discovery of ferrocene see Ref. 3. Ferrocene was the first example of a metal sandwich complex (Fig. 1). Among the metallocenes, ferrocene is particularly stable because of the 18-electron rare-gas configuration for the central metal atom. A few years later Fischer and Hafner[4] discovered the isoelectronic dibenzenechromium, (η^6-C_6H_6)$_2$M (**II**: M = Cr). However, attempts to extend this series of sandwich compounds to the isoelectronic 18-electron bis(cycloheptatrienyl)titanium, (η^7-C_7H_7)$_2$Ti (**III**: M = Ti) or its zirconium homologue have always failed. Thus, the reaction of $ZrCl_4$ with cycloheptatriene and sodium amalgam, which might have been expected to give (η^7-C_7H_7)$_2$M (**III**: M = Zr), instead was found to give the 16-electron (η^6-C_7H_8)$_2$M (**IV**: M = Zr).[5] Examples of other 16-electron titanium sandwich compounds include (η^6-C_6H_6)$_2$M (**II**: M = Ti)[6] and (η^5-C_5H_5)(η^7-C_7H_7)M (**V**: M = Ti).[7,8] In addition, cyclooctatetraene, rather than giving (η^8-C_8H_8)$_2$Ti analogous to 'uranocene', (η^8-C_8H_8)$_2$M (**VI**: M = U),[9,10] was found to give the 16-electron complex (η^8-C_8H_8)(η^4-C_8H_8)M (**VII**: M = Ti).[11]

In view of the difficulty in obtaining sandwich compounds of the types (η^7-C_7H_7)$_2$M (**III**: M = Ti) and (η^8-C_8H_8)$_2$M (**VI**: M = Ti), the 1997 report[12] of bis(pentalene)titanium, (η^8-C_8H_6)$_2$M (**VIII**: M = Ti) is of particular interest. Simple electron counting suggests this to be a 20-electron complex, i.e. eight electrons for each neutral η^8-pentalene ligand and four electrons for the neutral titanium atom, rather than a complex with the favored 18-electron configuration. However, a theoretical analysis of the available pentalene and titanium orbitals[13] suggests that (η^8-C_8H_6)$_2$Ti is actually an 18-electron complex. This short paper examines this relationship in greater detail, as well as the relationship between the pentalene, cyclooctatetraene, and cyclopentadienyl ligands.

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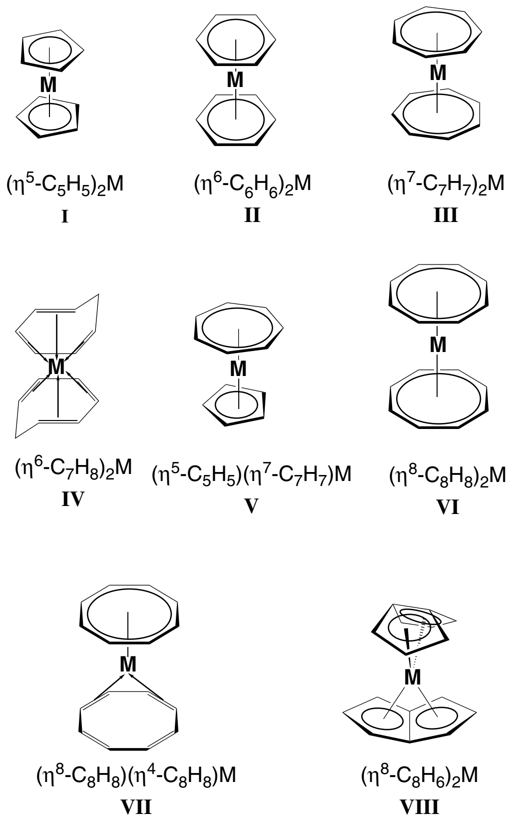
†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

‡For part 36 of this series see King RB. *J. Organometal. Chem.* 2002; **646**: 146.

Contract/grant sponsor: National Science Foundation; Contract/grant number: CHE-0209857.



$(\eta^5\text{-}C_5H_5)_2M$ I

$(\eta^6\text{-}C_6H_6)_2M$ II

$(\eta^7\text{-}C_7H_7)_2M$ III

$(\eta^6\text{-}C_7H_8)_2M$ IV

$(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)M$ V

$(\eta^8\text{-}C_8H_8)_2M$ VI

$(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)M$ VII

$(\eta^8\text{-}C_8H_6)_2M$ VIII

Figure 1. The structures of the sandwich compounds discussed in this paper.

THE PENTALENE LIGAND

Relationship of the pentalene ligand to the cyclooctatetraene ligand

The pentalene ligand is related to the cyclooctatetraene ligand by a transannular 'pinching' in which the single eight-membered ring is converted into two equivalent five-membered rings (Fig. 2). This reduces the symmetry from D_{8h} to D_{2h} and lifts the degeneracies of the E_1, E_2, and E_3 orbitals of the C_8H_8 ring. However, the pentalene orbitals available for σ, π, and δ bonding to metal atoms are seen to be very analogous to those of cyclooctatetraene, except for the splitting of the degenerate orbitals (Fig. 2).

Relationship of the pentalene ligand to two cyclopentadienyl ligands

A pentalene ligand can also be generated from the edge-fusion of two cyclopentadienyl ligands (Fig. 3) similar to the generation of naphthalene from edge-fusion of two benzene molecules. The relationship between the molecular orbitals of the pentalene ligand and two cyclopentadienyl ligands is more complicated than that between the pentalene and cyclooctatetraene molecular orbitals discussed above, since edge fusion results in the loss of two carbon atoms and hence two molecular orbitals.

Figure 4 depicts in more detail than Fig. 3 the relationship between the pentalene orbitals and those generated from symmetric and antisymmetric combinations of two C_5H_5 orbitals of the same symmetry. Since pentalene has eight molecular orbitals and two C_5H_5 rings generate ten molecular orbitals, two must disappear during the edge-fusion process. If regions of opposite sign at the edge shared by the two C_5H_5 rings are assumed to cancel out, then the antisymmetric $2E_1[\pi^-]$ combination of apparent ϕ symmetry is seen to coalesce into the same $B_1[\sigma^-]$ pentalene π molecular orbital as the antisymmetric $2A[\sigma^-]$ combination from $2C_5H_5$, thereby eliminating one of the ten molecular orbitals from $2C_5H_5$ (Fig. 4). Similarly, the antisymmetric $2E_2[\delta^-]$ combination of apparent γ symmetry from $2C_5H_5$ is seen to coalesce into the same $A_2[\pi^-]$ pentalene δ molecular orbital as the antisymmetric $2E_1[\pi^-]$ combination, thereby eliminating a second $2C_5H_5$ molecular orbital.

BIS(PENTALENE)METAL SANDWICHES: COMPARISON WITH OTHER SANDWICH COMPOUNDS

Metal–ring bonding in sandwich compounds

Figure 5 summarizes the 'classical' model of metal–ring bonding in sandwich compounds such as ferrocene and dibenzenechromium. In the case of sandwich compounds containing six-electron planar hydrocarbon ligands such as cyclopentadienide (in $(\eta^5\text{-}C_5H_5)_2Fe$) and benzene (in $(\eta^6\text{-}C_6H_6)_2Cr$) each metal–ring bond may be regarded as a triple bond with one σ component and two orthogonal π components. The metal orbitals available for the σ bonds are the s, p_z, and d_{z^2} orbitals and those are available for the π bonds are the $p(x, y)$ and $d(xz, yz)$ degenerate pairs. In addition, the $d(x^2 - y^2, xy)$ degenerate pair is available for δ back bonding (Table 1). Note that only eight of the nine metal orbitals of the sp^3d^5 manifold can participate in the metal–ring bonds in sandwich compounds of D_{nd} or D_{nh} symmetry (i.e. with parallel rings), since either of the metal s and d_{z^2} orbitals, but not both, can participate in the metal–ring bonding.

The limitations of the nine-orbital sp^3d^5 manifold for d-block transition metals become more apparent when considering ten-electron planar hydrocarbon ligands, of

Table 1. Metal orbitals available for ligand–metal bonding in metal–hydrocarbon complexes

Bond type	Symmetry group with a C_n ($4 \le n \le 8$) axis (e.g. D_4)	Symmetry group with no axis higher than C_2 (e.g. D_2)
$\sigma(\Gamma_\sigma)$	$A_1(s, z^2) + A_2(z)$	$A(s, z^2) + B_1(z)$
$\pi(\Gamma_\pi)$	$2E(x, y),(xz, yz)$	$2B_2(y, xz) + 2B_3(x, yz)$
$\delta(\Gamma_\delta)$	$B_1(x^2 - y^2) + B_2(xy)$	$A(x^2 - y^2, z^2) + B_1(xy)$

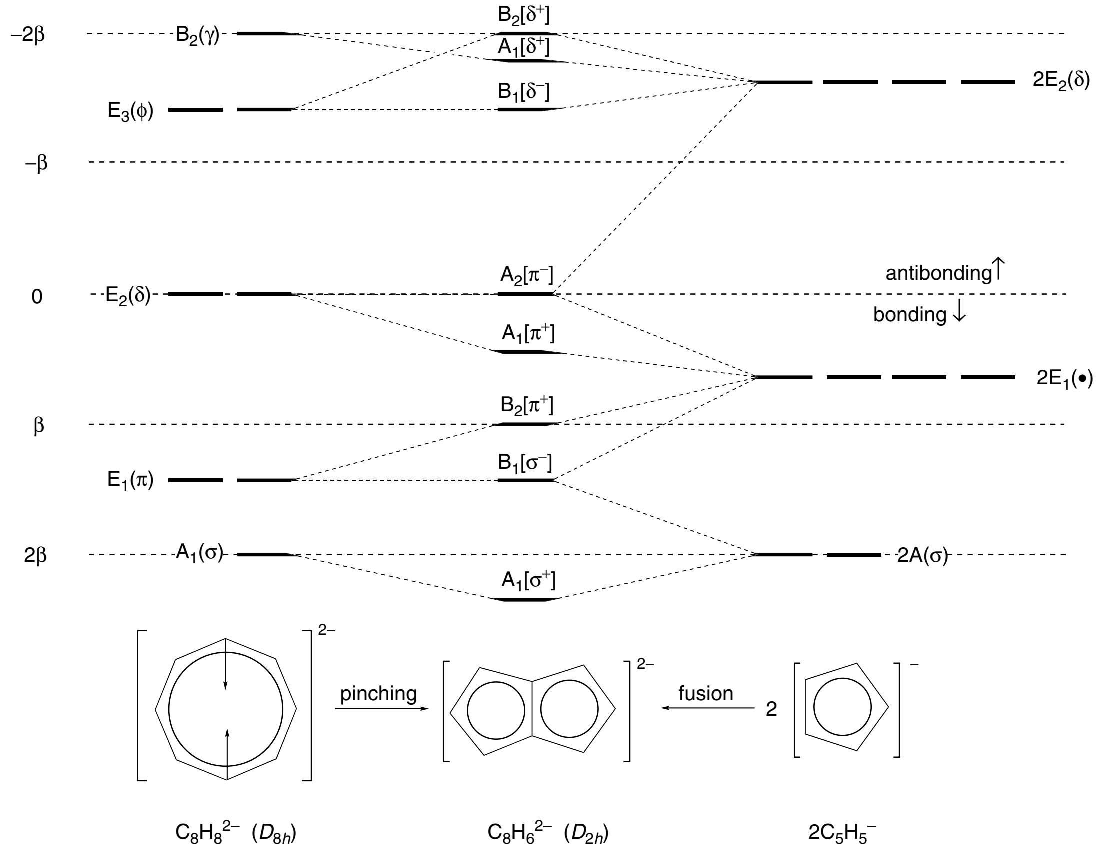


Figure 2. The relationship between the molecular orbitals in the $C_8H_8^{2-}$, $C_8H_6^{2-}$, and $2C_5H_5^-$ ligands.

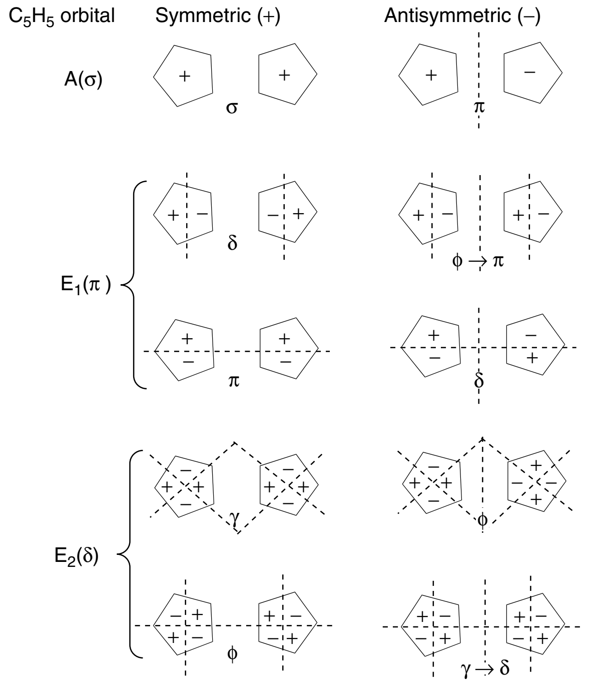


Figure 3. Fusion of the molecular orbitals in $2C_5H_5^-$ to give the $C_8H_6^{2-}$ molecular orbitals.

which $C_8H_8^{2-}$ is the best example. In such cases, full donation of the ten π electrons from the ring to the metal requires a metal–ring bond of order five, namely $\sigma + 2\pi + 2\delta$. For this reason, an $(\eta^8\text{-}C_8H_8)_2M$ (**VI**) complex where both $C_8H_8^{2-}$ rings donate ten π electrons each to the central metal atom is clearly not possible since the sp^3d^5 manifold has only nine orbitals to receive the 20 π electrons from the two C_8H_8 rings. Furthermore, for an $(\eta^8\text{-}C_8H_8)_2M$ complex involving d-block metals with parallel rings and eightfold (or even fourfold) ring symmetry (see Table 1) both of the A_1 orbitals, namely the s and d_{z^2} orbitals, cannot simultaneously participate in metal–ring bonding, since only one A_1 orbital can be involved in the ligand–metal bonding (see Table 1). This means that the total metal–ring bond order involving both rings cannot be any higher than eight, corresponding to a 16-electron $(C_8H_8)_2M$ complex (M = Ti). The titanium complex of this stoichiometry and its zirconium analogue thus adopt an unsymmetrical $(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)M$ (**VII**: M = Ti, Zr) structure[11] with a 16-electron configuration for the central metal atom. This contrasts with actinide complexes of the type $(\eta^8\text{-}C_8H_8)_2An$ (**VI**: An = Th, Pa, U, Np, Pu),[9] in which the availability of metal f orbitals, as well as metal s and d orbitals, allows the two $\eta^8\text{-}C_8H_8$ ligands to donate a total of 20 electrons to the actinide atom, leading to stable sandwich compounds with two parallel $\eta^8\text{-}C_8H_8$ rings.[14]

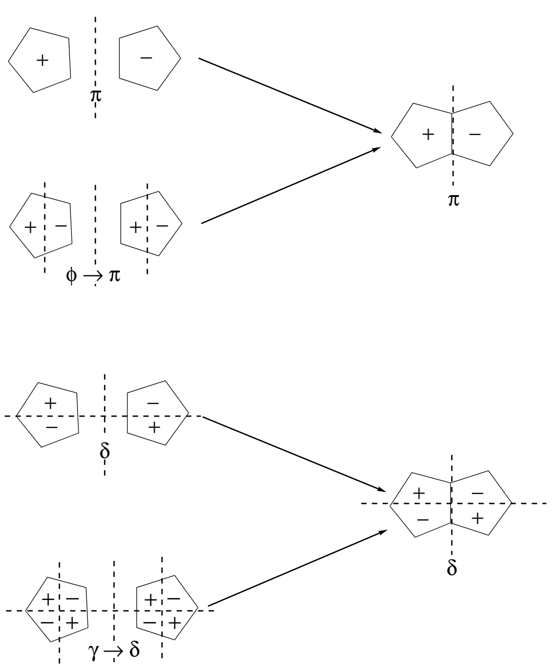


Figure 4. (a) Generation of a π orbital in $C_8H_6^{2-}$ ($B_1[\sigma^-]$ in Fig. 2) from either $2E_1(\pi)$ or $2A(\sigma)$ orbitals of $2C_5H_5^-$; (b) generation of a δ orbital in $C_8H_6^{2-}$ ($A_2[\pi^-]$ in Fig. 2) from either $2E_1(\pi)$ or $2E_1(\delta)$ orbitals of $2C_5H_5^-$.

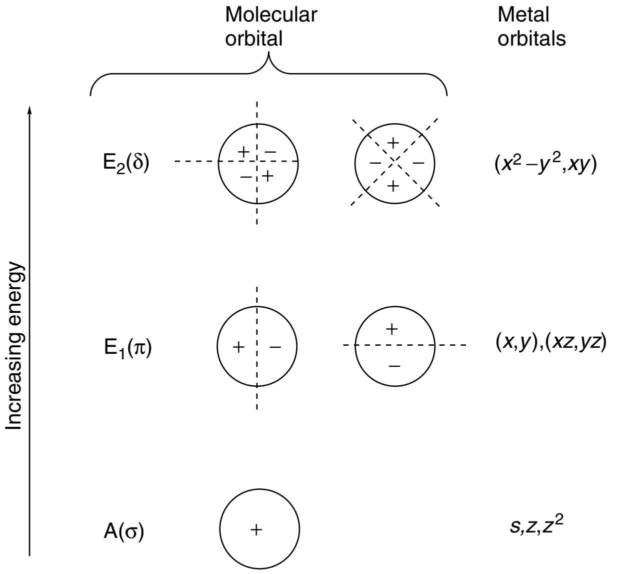


Figure 5. A generalized scheme for metal–ring bonding in $(\eta^n\text{-}C_nH_n)_2M$ ($5 \le n \le 8$) sandwich compounds showing the orbitals for σ, π, and δ bonding.

Metal sandwich complexes of pentalene

Conversion of a cyclooctatetraene ligand to a planar pentalene ligand involves reduction of the symmetry from D_{8h} to D_{2h}. In binding to a transition metal the pentalene ligand can fold at the edge shared by the two C_5 rings. This folding helps to maximize overlap between the pentalene molecular orbitals and the metal atomic orbitals. In $(\eta^8\text{-}C_8H_6)_2M$ (**VIII**: M = Ti, Zr)[12] the molecular symmetry is D_{2d} and the local metal–ligand ($\eta^8\text{-}C_8H_6Ti$) symmetry is C_{2v}. In this case the d_{z^2} orbital, as well as the other eight orbitals of the nine-orbital sp^3d^5 manifold, can participate in the bonding of the two pentalene ligands to the central metal atom. As a result, the two $\eta^8\text{-}C_8H_6^{2-}$ ligands donate a total of 18 electrons to the central M^{4+} atom (M = Ti, Zr) so that $(\eta^8\text{-}C_8H_6)_2M$ (**VIII**: M = Ti, Zr) are 18-electron complexes in accord with the analysis of Costuas and Saillard.[13] This analysis is also generally consistent with recently reported[15] density functional theory (DFT) calculations and photoelectron spectroscopic studies. However, the DFT calculations indicate global minima of C_1 symmetry for $(\eta^8\text{-}C_8H_6)_2M$ (**VIII**: M = Ti) and D_2 symmetry for $(\eta^8\text{-}C_8H_6)_2M$ (**VIII**: M = Zr, Hf) of somewhat lower energies than the ideal D_{2d} structures.

The details of the metal–ring bonding in D_{2d} $(\eta^8\text{-}C_8H_6)_2M$ (**VIII**: M = Ti, Zr) sandwich compounds have the s and p_z metal orbitals forming the two metal–ring σ bonds and the $p(x, y)$ and $d(xz, yz)$ metal orbital pairs forming the two sets of metal–ring perpendicular π bonds, as is the case for simple metal sandwich compounds such as $(\eta^5\text{-}C_5H_5)_2Fe$ and $(\eta^6\text{-}C_6H_6)_2Cr$ (Fig. 5). However, unlike the simple metal sandwich compounds, the three remaining d orbitals, $d^3(z^2, x^2 - y^2, xy)$ are all available for δ bonding so that the metal–ring bond order is four to one of the $C_8H_6^{2-}$ ligands and five to the other $C_8H_6^{2-}$ ligand in $(\eta^8\text{-}C_8H_6)_2M$ (**VIII**: M = Ti, Zr). The actual structure may be viewed as a resonance hybrid between the two possibilities, where the ligands with metal–ligand bond orders of four and five are interchanged. In terms of the underlying group theory (Table 1), when the symmetry is lowered so that all of the higher order rotation axes C_n ($n \ge 3$) disappear, then both the σ- and δ-bonding manifolds have orbitals belonging to the fully symmetric A irreducible representation. Therefore the d_{z^2} orbital, which belongs to the fully symmetric A representation in D_2, can participate in either σ or δ bonding in terms of its symmetry.

The ability for the d_{z^2} orbital to participate in metal–ligand δ bonding when the local metal–ligand symmetry is reduced from C_{4v} or higher to C_{2v} is depicted in Fig. 6. In a system having C_4 or higher order rotation axes, the interaction between the metal d_{z^2} and the positive region of the ligand δ orbital is exactly cancelled by the interaction between the metal d_{z^2} orbital and the negative region of the ligand δ orbital so that the net overlap is zero. However, if the symmetry is reduced from C_{4v} to C_{2v}, then the interactions of the metal d_{z^2} orbital and the positive and negative regions of the ligand δ orbital no longer cancel out so that there is some net overlap. This overlap is enhanced by folding the pentalene ligand towards the central torus of the metal d_{z^2} orbital of opposite sign to the two major lobes.

The situation involving the two $C_8H_6^{2-}$ ligands in $(\eta^8\text{-}C_8H_6)_2M$ (**VIII**: M = Ti, Zr) together donating to the central metal atom 18 electrons, rather than the theoretically

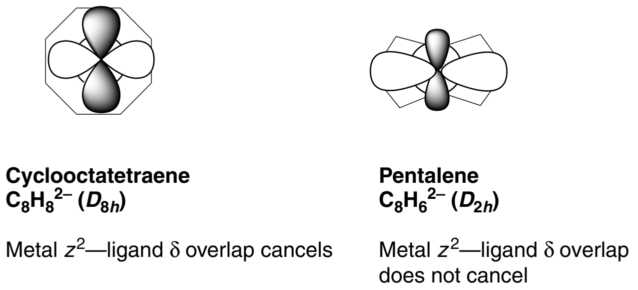


Figure 6. A comparison of the zero overlap between the metal d_{z^2} atomic orbital and a ligand δ molecular orbital in D_{8h} cyclooctatetraene metal complexes with the non-zero overlap between the metal d_{z^2} orbital and a ligand δ orbital in D_{2h} (or D_{2d}) pentalene metal complexes. The cylindrical symmetry of the d_{z^2} atomic orbital viewed along the z-axis is indicated by the circle behind the four lobes (two shaded and two unshaded) representing the δ molecular orbital of the $C_8H_8^{2-}$ or $C_8H_6^{2-}$ ligand.

possible 20 electrons because of symmetry limitations, is very similar to the situation involving the three alkyne ligands in C_{3v} (η^2-$RC_2CR)_3W(CO)$ discussed by the author approximately 35 years ago.[16] Each of the alkyne ligands in (η^2-$RC_2CR)_3W(CO)$ can individually donate four electrons to the central tungsten atom, namely two through a σ bond and the other two through a π bond. If all three alkyne ligands were to donate four electrons each to the tungsten atom in this matter, then (η^2-$RC_2CR)_3W(CO)$ would be a 20-electron complex. However, the tungsten atom only has two orbitals of suitable symmetry for π-bonding to the three alkyne ligands related by the C_3 axis, so that only two of the three alkyne ligands are four-electron donors and the third alkyne ligand is a two-electron donor. Therefore, the complex (η^2-$RC_2CR)_3W(CO)$ has the favored 18-electron configuration rather than a 20-electron configuration.

Acknowledgements

I am indebted to the National Science Foundation for partial support of this work under grant CHE-0209857.

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