

The relevance of the complementary spherical electron density model to organometallic intermediates involved in homogeneous catalysis

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Abstract

The implications of the Complementary Spherical Electron Density Model, originally developed by Mingos and Hawes in 1985 and amplified in 2004, to co-ordinatively unsaturated intermediates in homogenous catalytic processes are discussed. The geometric consequences of the model for 16 and 14 electron complexes are particularly important and are supported by numerous recent X-ray crystallographic investigations. The character of the important frontier orbitals have been explored using density functional calculations. © 2006 Elsevier B.V. All rights reserved.

Keywords: Complementary spherical electron density model; 18 electron rule; Homogenous catalysis; 16 and 14 electron intermediates

1. Introduction

The historical development of the 18 Electron Rule in relation to organometallic transition metal compounds has been discussed at some length in a previous paper [1] and will not be repeated here. Its implications to homogenous catalytic processes were first articulated fully by Tolman in 1972 [2]. In his review he not only emphasised the wide applicability of the 18 electron rule in organometallic complexes, but also proposed the important generalisation that “The great majority of steps in a catalytic cycle involve 18 to 16 electron transformations”. This paradigm has stood the test of time and remains commonly quoted in undergraduate textbooks, although it is recognised that it is more generally applicable to catalytic processes involving the later transition metals. Moreover, in recent years the development of a wider range of ligands with varying steric requirements and electron donating characteristics and improved spectroscopic and crystallographic techniques have resulted in the isolation of an increased number of possible intermediates in catalytic processes with 14 elec-

tron configurations. Previously such complexes had only been generated and studied in low temperature inert gas matrices [3].

Whilst the Tolman paradigm clearly has many strengths it remains distant from a viable starting point for a detailed and intelligent discussion of its stereochemical consequences. The effective atomic number rule has the severe limitation that it does not carry information regarding the geometry of the complex and the characteristics of the frontier orbitals in possible intermediates with fewer electrons. The Complementary Spherical Electron Density Model [1,4] aims to compensate for this deficiency by giving a simple account of the geometries and frontier orbitals of 18, 16 and 14 electron complexes.

1.1. Conclusions of the Spherical Electron Density Model

According to the Complementary Spherical Electron Density Model the attainment of the 18 electron rule in transition metal compounds is closely associated with the occurrence of a set of complementary ligand and central metal atom orbitals which together emulate the occupied orbitals of an inert gas atom, both in terms of the angular momenta of the orbitals occupied and their high ionisation energies.

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A detailed analysis of the spherical harmonic descriptions of the LCAOs and the complementary metal orbitals has been given by Hawes and Mingos [1,4] and their results are only briefly summarised in Fig. 1.

18 electron complexes have a spherical arrangement of ligands and the ligand and metal orbitals form a complementary and complete set of orbitals which mimic the angular momentum properties of an inert gas atom. The filled metal orbitals have a high percentage of d orbital character, point away from the metal–ligand vectors and are stereochemically inactive. The filled and metal localised orbitals determine the site preferences and preferred conformations of π -acceptor ligands.

If L is a good π -acceptor ligand then these metal localised d orbitals are stabilised additionally and the 18 electron spherical shell of electron density is reinforced. The π -acceptor ligands will occupy positions and orientations which maximise the interactions between the empty π -orbitals of the ligand and the filled metal d orbitals. In complexes with strong π -donor ligands some or all of these d localised orbitals become unavailable but are replaced by orbitals with matching orbital characteristics on the ligands and the 18 electron rule is maintained, as long as the π -donor ligands do not contribute symmetry combinations which do not match the d set [4,5].

Since the lone pairs on the metal occupy orbitals which are complementary to the ligand LCAOs it follows that the most available electron density in the frontier orbitals is located along directions which lie between the ligands. Consequently protonation and electrophilic attack are in general favoured in these directions (see Fig. 2). When one of the ligands in the complex functions as a π -donor or acceptor in one preferred plane then the ligand will take up an orientation which maximises the interaction between

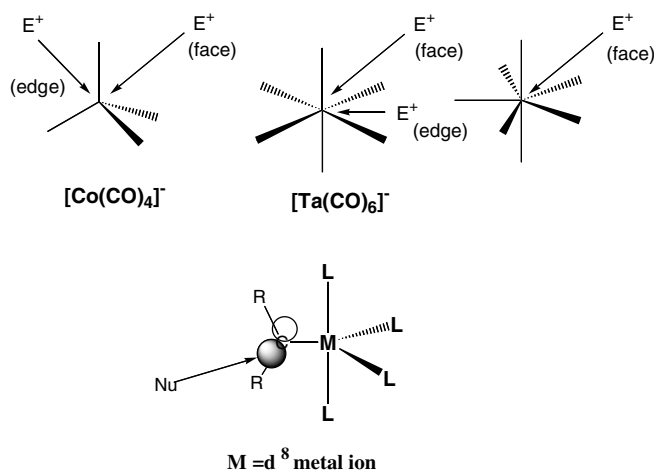


Fig. 2. Examples of electrophilic attack in 18 electron transition metal complexes utilising electron density located away from the ligand direction and nucleophilic attack in a carbene complex where in-plane attack is preferred [6].

the filled d orbital and the π -acceptor orbital of the ligand. For example the carbene complex illustrated in Fig. 2 has the carbene RCR plane orientated preferentially orthogonal to the trigonal plane, thereby permitting nucleophilic attack in the direction shown in Fig. 2. In contrast an alkene would prefer to lie within the trigonal plane.

In this paper we discuss some specific density functional calculations which provide some additional insight into the frontier orbitals of these 16 electron intermediates. Calculations, which are fully described in the Appendix, based on the rhenium and tungsten hydrides $[\text{ReH}_m]^{x+}$ and $[\text{WH}_m]^{x+}$, were used to model the systems. They confirm the symmetry and nodal properties of the frontier orbitals and specifically the nature of the out-pointing hybrid orbital proposed by the Complementary Spherical Electron Density Model.

Coord. No.	Geometry	S	P ₀ z	P _{1c} x	P _{1s} y	D ₀ z ²	D _{1c} xz	D _{1s} yz	D _{2c} x ² -y ²	D _{2s} xy	Total electrons
2	Linear	■	■								14
3	Trigonal planar	■	■	■	■				■	■	16
4	Tetrahedral	■	■	■	■	■	■	■	■	■	18
5	Trigonal Bipyramid	■	■	■	■	■	■	■	■	■	18
5	Square Pyramid	■	■	■	■	■	■	■	■	■	18
6	Octahedron	■	■	■	■	■	■	■	■	■	18
6	Trigonal prism	■	■	■	■	■	■	■	■	■	18
7	Pentagonal bipyramid	■	■	■	■	■	■	■	■	■	18
7	Capped trigonal prism	■	■	■	■	■	■	■	■	■	18
7	Capped octahedron	■	■	■	■	■	■	■	■	■	18
8	Dodecahedron	■	■	■	■	■	■	■	■	■	18
8	Square antiprism	■	■	■	■	■	■	■	■	■	18
9	Tricapped trigonal prism	■	■	■	■	■	■	■	■	■	18

Ligand LCAO's	■
Filled metal d orbitals	■
Filled metal dp hybrids	■
Empty metal orbitals	■

Fig. 1. Description of 18 electron complexes according to the Complementary Spherical Electron Density Model.

2. Results and discussion

2.1. 16 electron complexes

According to the Tolman paradigm 16 electron species are crucial for understanding the transformations of organometallic species involved in homogeneous catalysis, however it fails to take the further step of providing some indication of their preferred geometries and most importantly the nature of the LUMO and HOMO in such complexes. The Complementary Spherical Electron Density Model [1,4] provides an important insight into Tolman's 16 electron paradigm by drawing attention to the relative energies of the valence orbitals of a transition metal atom. For the heavier main group elements the relative energies of the valence orbitals are: $ns < np \ll nd$. Whereas for the transition metals the relative energies are: $(n+1)s \sim nd \ll (n+1)p$. It follows that to create an electron pair hole in a 18 electron complex it is energetically most favourable to have it associated with a maximum amount of p orbital character and thereby retaining the maximum amount of d and s character in the occupied orbitals [1,4].

In a 16 electron complex the generation of a pure p orbital which is orthogonal to the ligand plane is the best way energetically of ensuring the presence of a high lying and empty orbital, however this cannot be achieved for higher co-ordination numbers because of steric repulsions. The formation of a dsp hybrid with the maximum amount of p orbital character is the next best choice.

Linear and trigonal planar geometries provide the most effective ways of generating geometries with orthogonal p orbitals and this is why these geometries are favoured for d^{10} complexes. Fig. 3 illustrates how the adoption of a planar geometry leaves an unoccupied metal p orbital perpendicular to the plane. Four co-ordinate square-planar complexes, which are extremely widespread, provide the most prevalent example of this principle and there are of course numerous examples of such d^8 complexes d^{10} Palladium complexes are involved in the Heck and Stille reactions and many of the isolated intermediates have the trigonal planar, ML_3 , and linear ML_2 geometries illustrated in Fig. 3 [7].

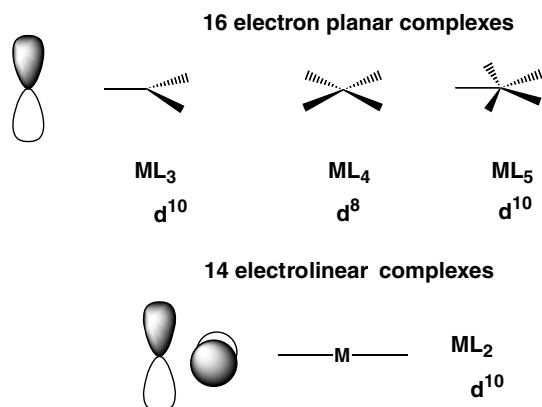


Fig. 3. Generation of an unavailable p_z orbital in planar complexes.

With higher coordination numbers it is increasingly difficult to fit all the ligands in one plane and empty hybrid orbitals with a high proportion of p character remain as the only viable lowest energy unoccupied orbitals. It follows that for a 16 electron ML_n complex ($n > 4$) the creation of a hybrid with maximum p orbital character is achieved by adopting a geometry derived from the preferred 18 electron co-ordination polyhedron for ML_{n+1} with the empty hybrid in the vacant position. The utilization of the same basic co-ordination polyhedron in 18 and 16 electron complexes has the added energetic advantage that the occupied frontier orbitals have a high proportion of the more stable d orbitals and point away from the ligands. We have previously described such co-ordination polyhedra, which are illustrated schematically in Fig. 4, as *nido* – by analogy with cluster structures [8] (see Fig. 4). Related co-ordination polyhedra with two and three vacant co-ordination sites with hybrids are similarly described as *arachno*- and *hypho*-.

The formation of a single hybrid with a high proportion of p orbital character requires the mixing of s , d_{z^2} and p_z orbitals and therefore places a restriction on the symmetry of the resultant 16 electron complex. Specifically mixing of these orbitals requires the absence of either a centre of symmetry or a mirror plane perpendicular to the direction of the hybrid. Therefore, 16 electron complexes of this type are required to belong to the point groups C_{nv} , or C_n or C_s [1]. Interestingly Hall's detailed molecular orbital analysis of transition metal hydrides has come to a similar conclusion in his Orbital Symmetry Ranked Method (OSRAM) [9].

The results of the DFT calculations on square-pyramidal $[WH_5]^+$ ion, **1a**, are shown in Fig. 5. It has frontier orbitals which will be recognisable to the majority of organometallic chemists and especially those who have utilised the *isolobal* concept [10]. The t_{2g} set of the parent octahedron is immediately recognisable and above it the out-pointing dsp hybrid with axial a_1 symmetry. In a 16 electron complex this is the out-pointing hybrid identified by the Complementary Spherical Electron Density model. It has 36% p orbital character whereas the lower lying three

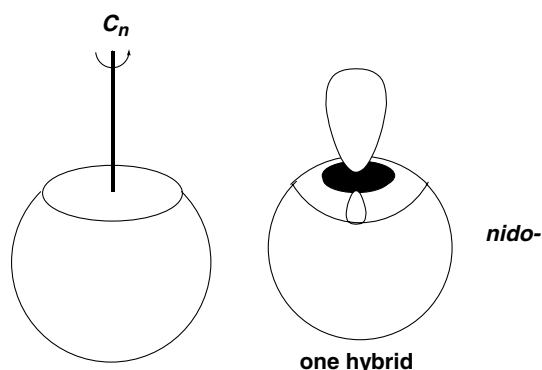


Fig. 4. Topology of *nido*-16 electron complexes. The out-pointing dsp hybrid emanating from the open face is also indicated.

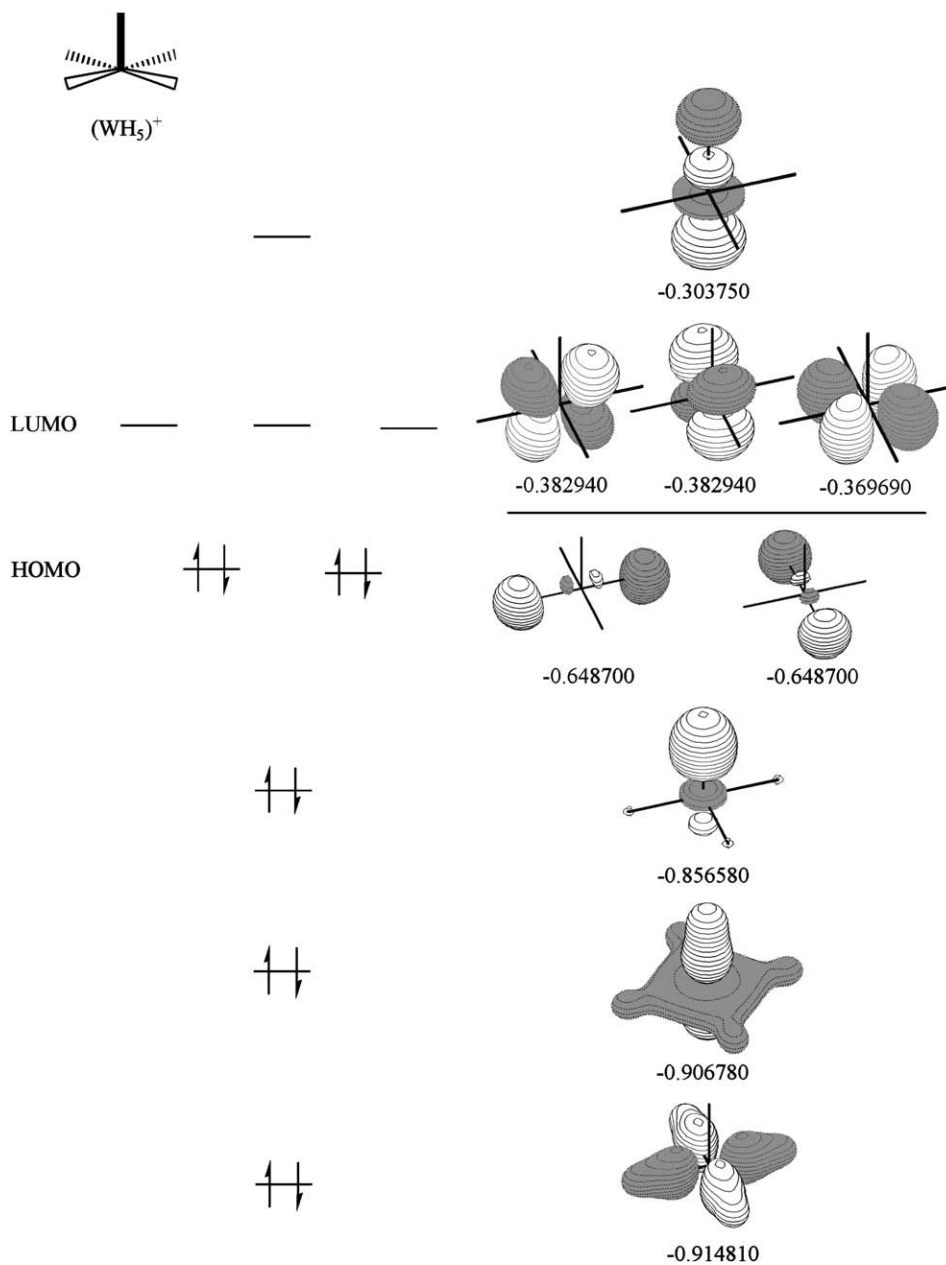
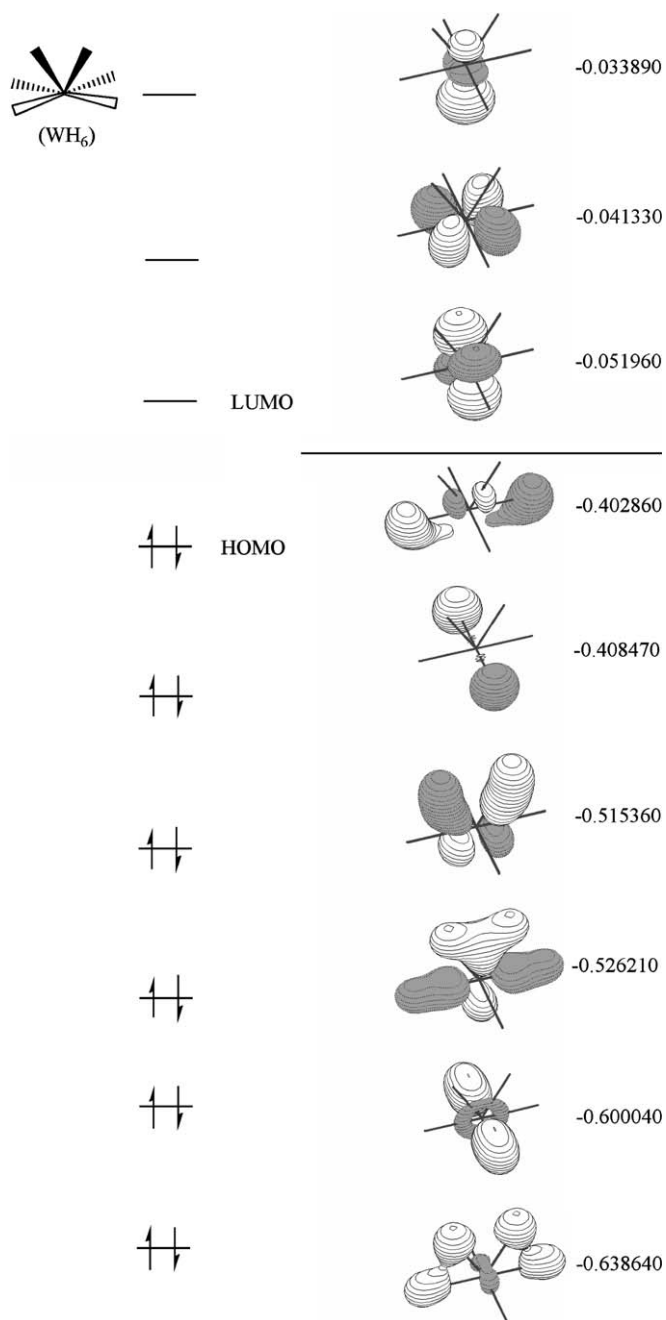


Fig. 5. Molecular orbitals in **1a** (energies in Hartrees).

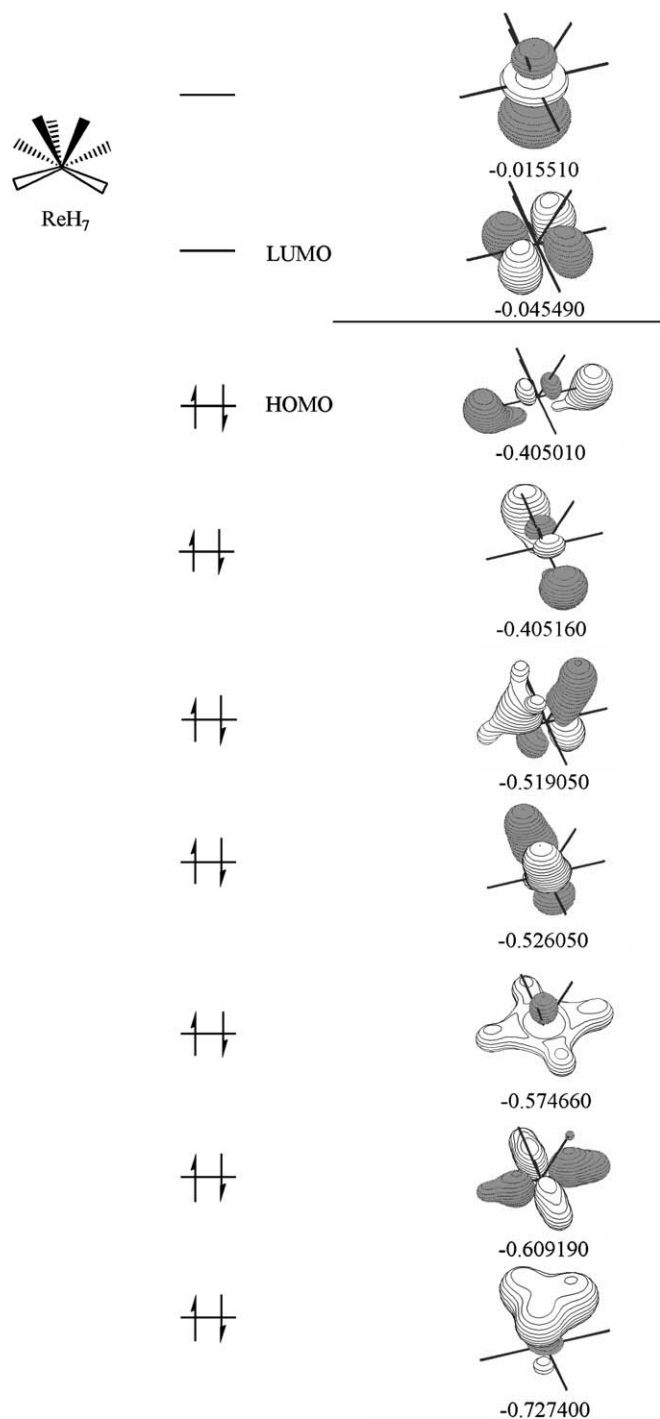
t_{2g} like orbitals have exclusively d character. This underlines the basic premise of the Complementary Spherical Electron Density Model that the occupied orbitals will maximise the d and s character and the virtual orbitals the p character. In the related $[\text{WH}_6]$, **1b**, four hydrides are retained in the equatorial plane, but the axial ligand has been replaced by two ligands with local C_{2v} symmetry, straddling the North Pole of the imaginary sphere (see Fig. 6). The effect of this is to replace the four frontier orbitals of $[\text{WH}_5]^+$ by three. The highest energy is again recognisable as the out-pointing hybrid with axial symmetry and having 48% p orbital character, and two out of the original three “ t_{2g} ” like orbitals – the in-plane d_{xy} and d_{xz} – the d_{yz} component having been used to form a bonding combina-

tion with the additional ligand in the region of the North Pole. In $[\text{ReH}_7]$, **1c**, the axial ligand of $[\text{WH}_5]$ has been replaced by three ligands on the polar region with local three fold symmetry, as shown in Fig. 7. The unoccupied orbitals are reduced to two and consist of the axial out-pointing dsp hybrid with 45% p orbital character and only the d_{xy} non-bonding orbital. These calculations therefore support the qualitative conclusions proposed earlier [1,4] and identify in the *nido*-co-ordination polyhedra an out-pointing hybrid with a significant degree of p orbital character and a residual number of the t_{2g} set depending on the number of ligands in the Northern hemisphere.

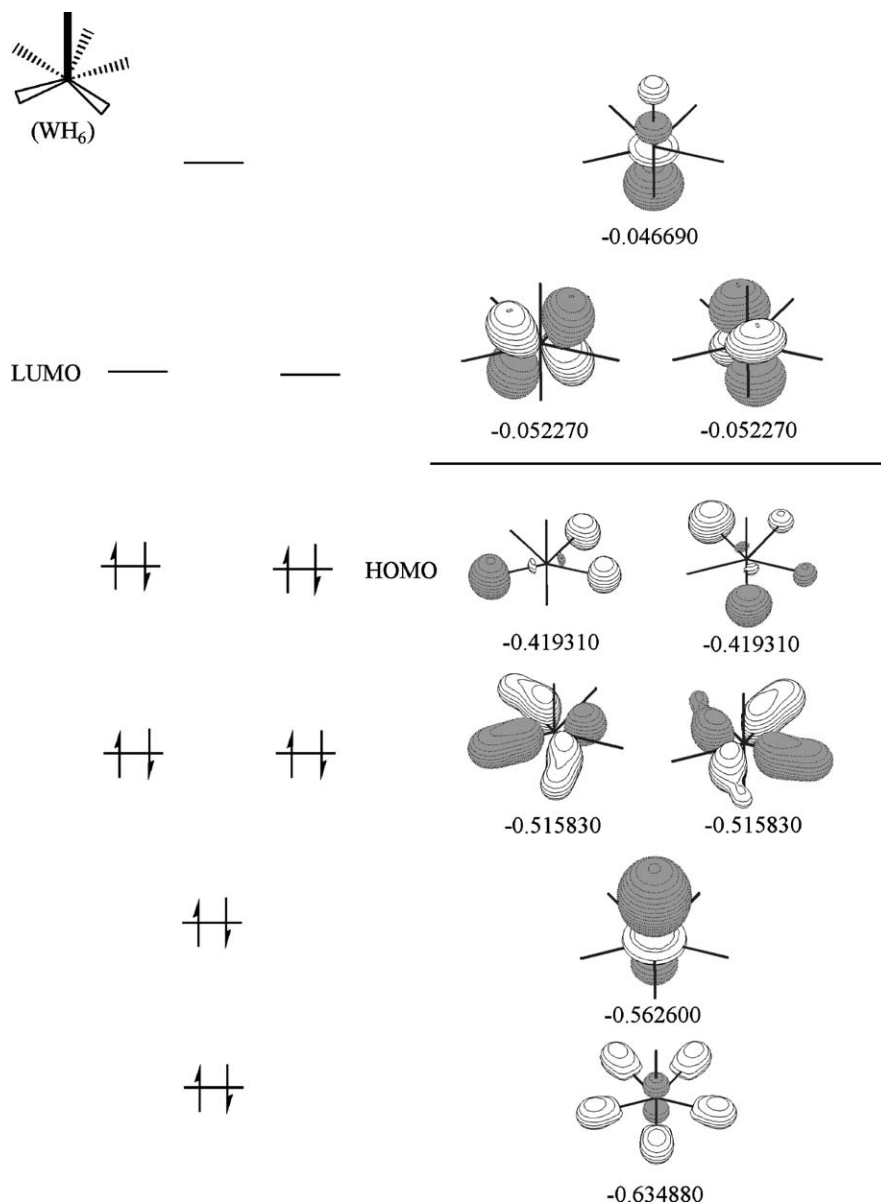
A related series of calculations on complexes with five ligands in the equatorial plane are illustrated in Figs. 8–10

Fig. 6. Molecular orbitals in **1b**.

for **2a**, **2b** and **2c**. A similar pattern emerges – the pentagonal pyramidal $[\text{WH}_6]$ now has three frontier orbitals involving the out-pointing dsp hybrid orbital and the degenerate d_{xz}, d_{yz} pair of orbitals which are unoccupied in the d^0 W(VI) complex but are the highest occupied orbitals in a d^4 16 electron complex. In $[\text{ReH}_7]$ (Fig. 9) where there are two ligands in the North Polar region, with local C_{2v} symmetry then there are only two unoccupied frontier orbitals one with σ and one with π pseudo-symmetry. Finally in $[\text{ReH}_8]^-$ there is only out-pointing hybrid orbital with sigma symmetry and neither of the d_{xz}, d_{yz} pair of orbitals characteristic of a pentagonal pyramid.

Fig. 7. Molecular orbitals in **1c**.

The results of the calculations are summarised in Fig. 11. All the examples in the matrix have 16 electron configurations and *nido*-topologies. Those which are diagonally related also have the same number of ligands and therefore are alternatives as reactive intermediates in a specific reaction. Molecules lying along a row have increasing numbers of ligands in the polar region and those forming a column have increasing numbers of ligands on the equator. The calculations suggest that those

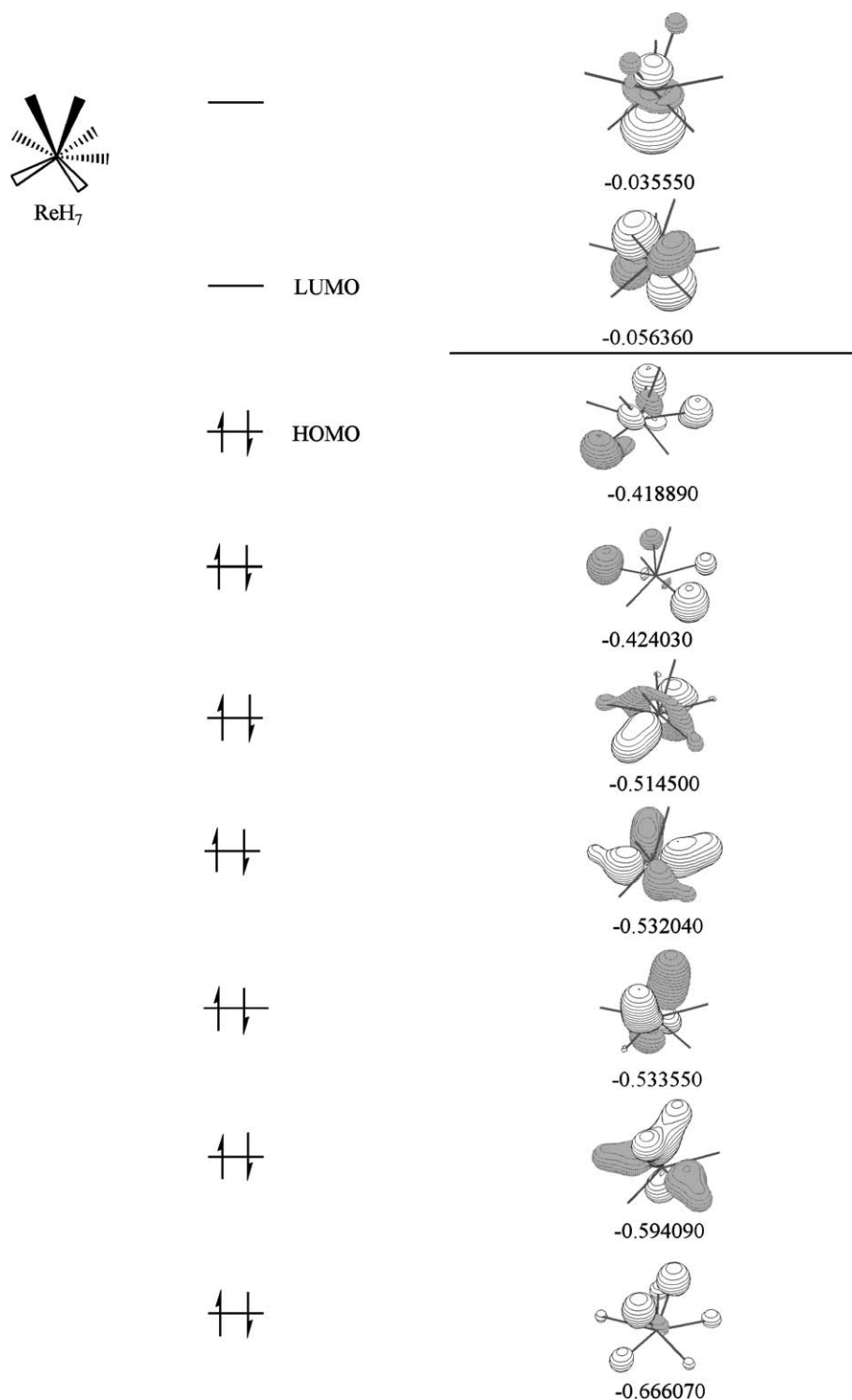
Fig. 8. Molecular orbitals in **2a**.

molecules with common topologies and the same number of ligands have similar energies. They share the following common features.

- They all have an out-pointing hybrid orbital with a significant amount of p orbital character (30–50%) pointing towards the South Pole and having σ -pseudo symmetry (a_1) in an axial point group, which in a 16 electron complex would be the LUMO.
- If one chooses diagonal partners which share a common formula, i.e. ML_5 , ML_6 or ML_7 the *nido*-structures vary in the number of frontier orbitals with π -pseudo symmetries. For example, two π -like orbitals for the pentagonal pyramidal ML_6 , one for that based on the square pyramid and none for that based on the trigonal bipyramid.

This gives the transition metal 16 electron fragments a degree of flexibility not accessible to a corresponding main group fragment. Specifically, if the fragment is presented to an axially symmetric good π -acceptor such as CO or NO^+ then other things being equal the pentagonal pyramidal fragment with two π -donor orbitals is preferred. Alternatively, an axially symmetric π -donor would favour the structure based on a trigonal pyramid with three additional ligands around the North Pole.

- A ligand with a single π -acceptor or donor orbitals, e.g. an alkene or a carbene, would find a suitable match with the middle example of the diagonal triplet.
- The frontier orbitals of the fragments also determine whether the fragment is capable of undergoing oxidative-addition reactions. Specifically the first two

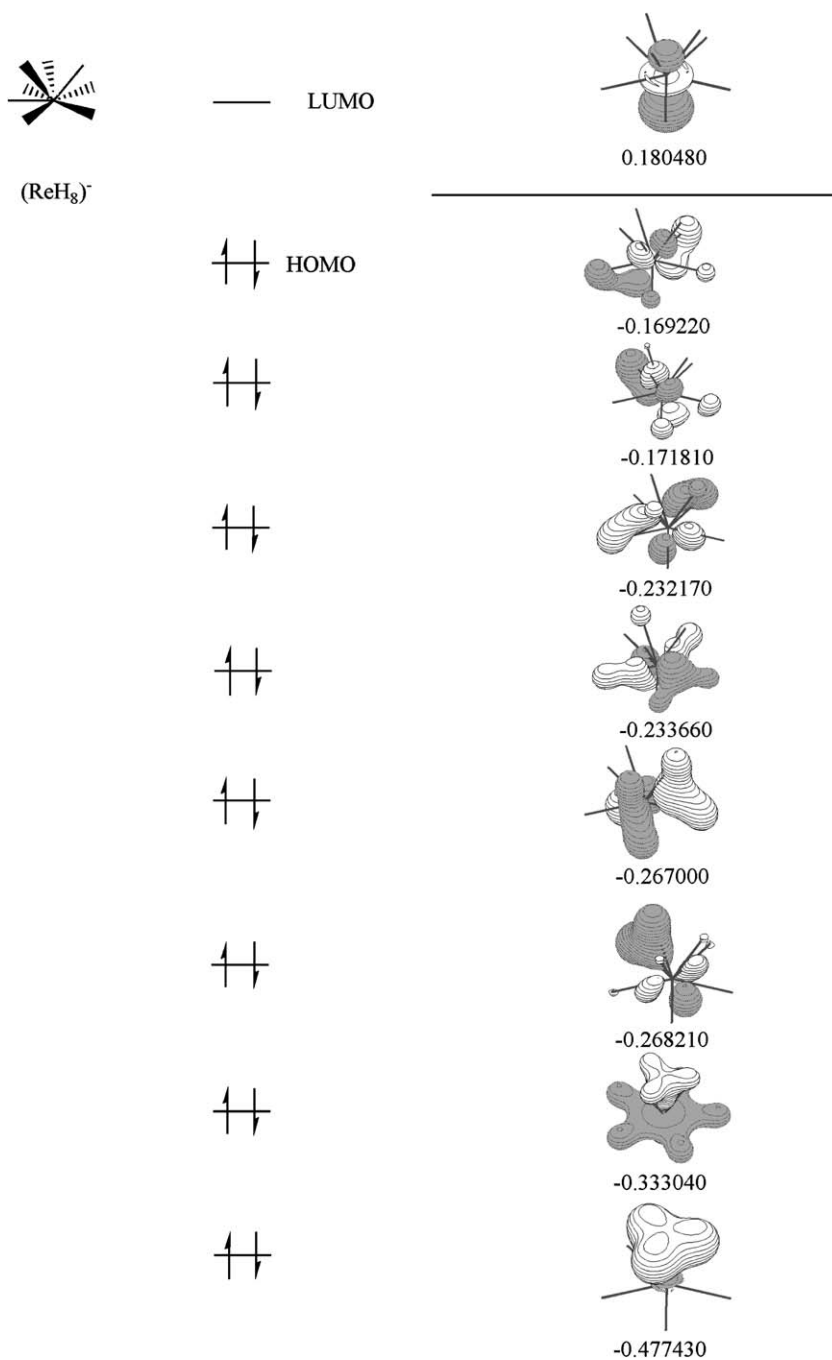
Fig. 9. Molecular orbitals in **2b**.

examples of the ML_6 triplet are more able to undergo oxidative addition than the third which does not have either a d_{xz} , or d_{yz} filled orbital necessary to initiate the electron transfer to the empty π^* orbitals of the ligand undergoing oxidative-addition.

(e) Similar considerations apply to whether the ligand coordinating to the vacant site undergoes restricted rotation.

Therefore, the transition metal 16 electron intermediates have a common *nido*-topology and a flexibility which enables them to fine-tune their electron donating and accepting properties according to the ligand which is offered to them.

Generally, in the absence of a ligand the fragment takes up the geometry which is based on the completed spherical geometry with one ligand missing. For example, $Mo(CO)_5$

Fig. 10. Molecular orbitals in **2c**.

[3] has a square pyramidal – *nido* – octahedral geometry and $\text{RuCl}_2(\text{PPh}_3)_3$ [11] has a closely related geometry (see Scheme 1). This makes such transition metal 16 electron fragments ideal for forming supplementary bonds with weak donor functions such as C–H bonds. There are now many examples of such complexes with an *agostic* C–H bond occupying the vacant co-ordination site and an example is illustrated in Scheme 1 [5,12].

Similar arguments apply to the 14 electron intermediates, where *arachno*-geometries based on the completed spherical geometry with two missing vertices predicted by

the Complementary Spherical Electron Density Model [1]. Examples of such complexes, which have been recently characterised, and based on the *cis*-divacant octahedron are illustrated in Scheme 2. These structures, underline an important difference between main group and transition metal molecular geometries. In the former the empty orbitals are stereochemically active whereas in the latter it is the lone pairs that are stereochemically active. The stereochemical activity of the empty orbitals in transition metal complexes makes them ideal for incorporating weak supplementary co-ordinate bonds. For example, agostic bonds

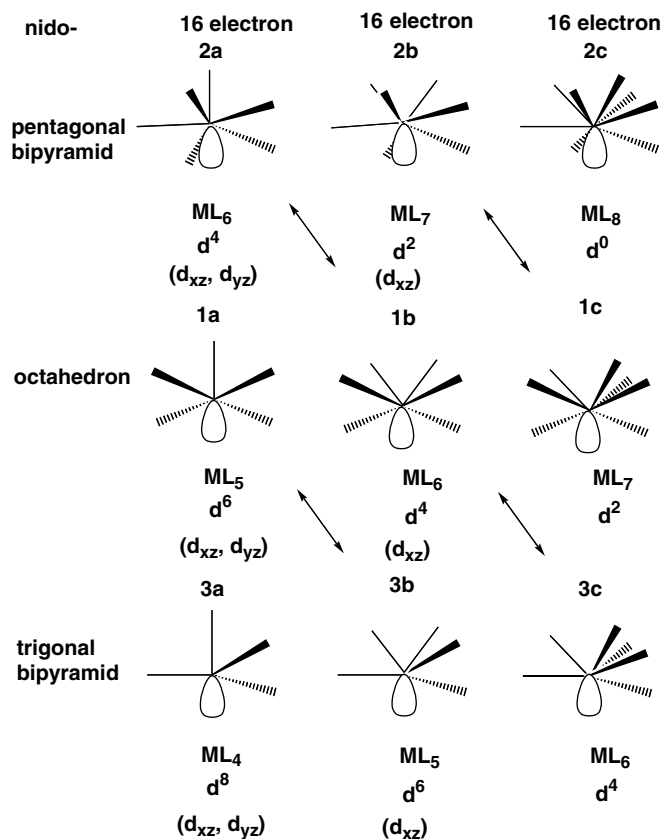
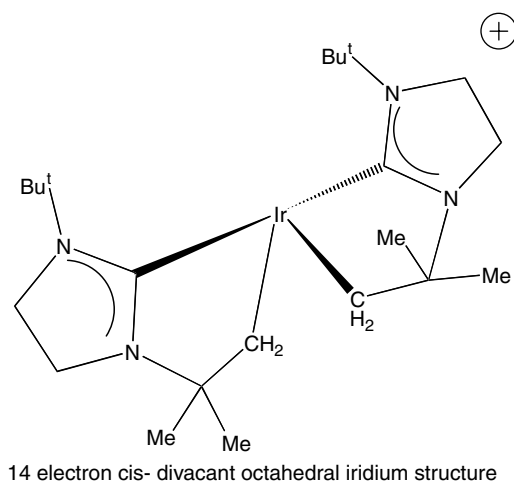
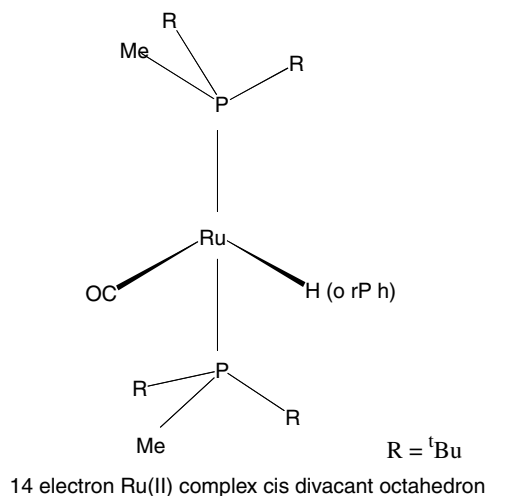
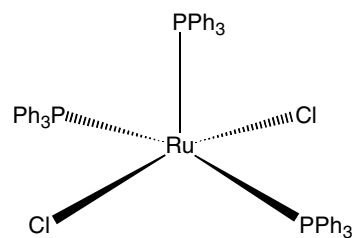


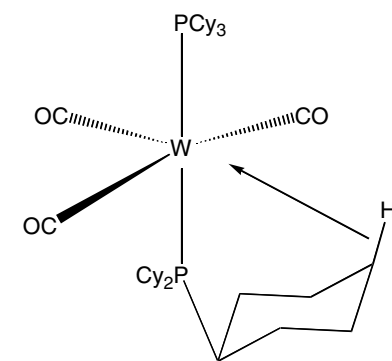
Fig. 11. Summary of the frontier orbitals of 16 electron nido-co-ordination fragments.

from organic pendant groups. Examples of such interactions are illustrated in Scheme 3 [13,14]. The parent 14 electron molecules do not have to undergo a reorganisation in order to form such supplementary bonds and this clearly has an energetic advantage particularly when weak supplementary bonds are being formed. The greater predominance of transition metal complexes with agostic interactions is clearly related to such considerations [15,16].

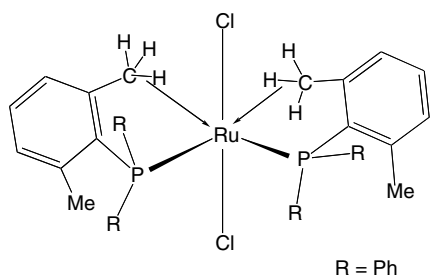


Scheme 2.

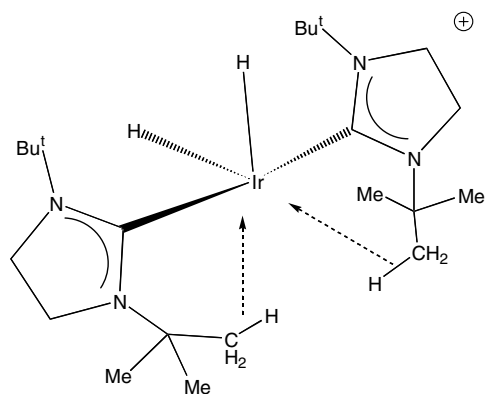
All the arguments developed above have assumed that the molecules have singlet ground states and need to be modified in the rare examples where the ground state is a triplet. It will be familiar to the reader that singlet and triple carbenes have very different geometries and



Scheme 1.



14 electron Ru(II) complex
with two weak agostic interactions
cis divacant octahedron



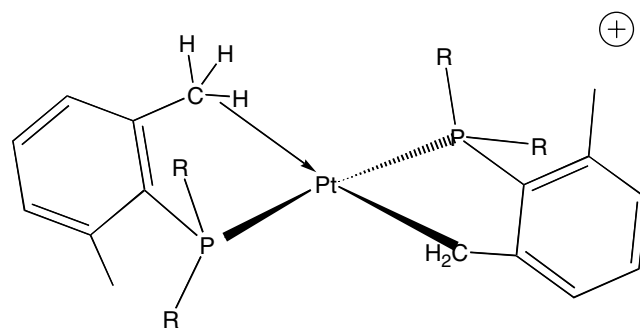
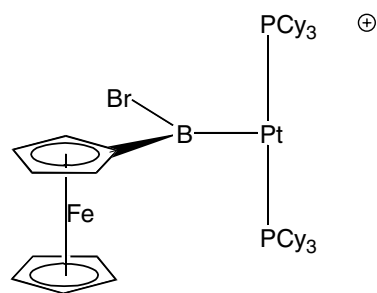
14 electron cis- divacant structure
with weak agostic interactions

Scheme 3.

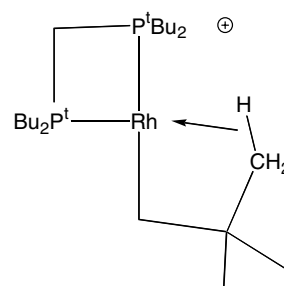
the latter has a linear geometry which enables the two unpaired electrons to occupy space as far apart as possible. Therefore, it is not too surprising that a 14 electron four co-ordinate triplet ruthenium complex would have a *trans*- rather than a *cis*-divacant structure based on an octahedron [17].

14 electron d^8 complexes adopt T-shaped geometries whereby the an empty p orbital perpendicular to the coordination sphere is augmented by a hybrid orbital with a high proportion of p orbital character in the plane. Examples, of such complexes with and without agostic supplementary interactions are illustrated in Scheme 4 [18–20].

The unavailable and occupied orbitals in 16 and 14 electron fragments clearly have a role in indicating the stereochemistries of reactions where they occur as intermediates or transition states and the model developed above illustrates how information concerning their frontier orbitals may be gleaned. For example, they can define a clear geometric preference when it comes to product formation. For example, the 16 electron d^6 transition state $\text{MX}(\text{CO})_4$ has an empty out-pointing hybrid orbital which may be stabilised preferentially by electron donation. A π -donor in the equatorial plane is much more able to stabilise this transition state than one axially located and therefore one has a plausible interpretation of the *cis*-directing effect in the substitution of $\text{M}(\text{CO})_5\text{X}$ complexes (see Fig. 12). Similar, considerations apply to the other *nido*-co-ordination polyhedra and it is possible to define π -donor and agostic



14 electron Pt(II) complex with agostic interaction



14 electron rhodium(I) complex with weak agostic interaction

Scheme 4.

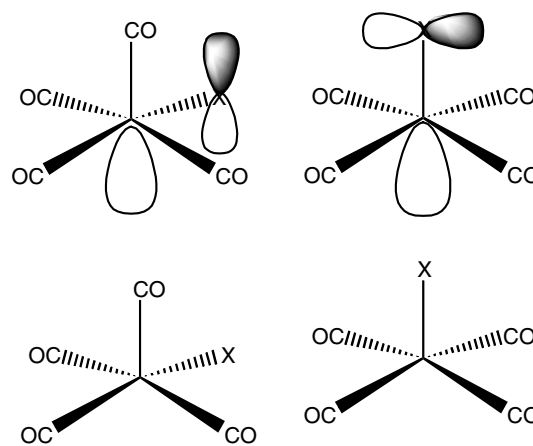


Fig. 12. Stabilisation of the empty orbital in square-pyramidal 16 electron complexes.

stic interactions which stabilise the 16 electron complex or intermediate.

3. Conclusions

In summary identifying the empty orbital(s) in 16 and 14 electron complexes provides useful information concerning the location and orientation of the frontier orbitals, which may control the stereochemistries and reactivities of the catalytic intermediates.

Acknowledgements

Professor Zhenyang Lin and his students are thanked most sincerely for their considerable help with the calculations. The Alexander von Humboldt Foundation is thanked for financial support.

Appendix A

Computational method: HF

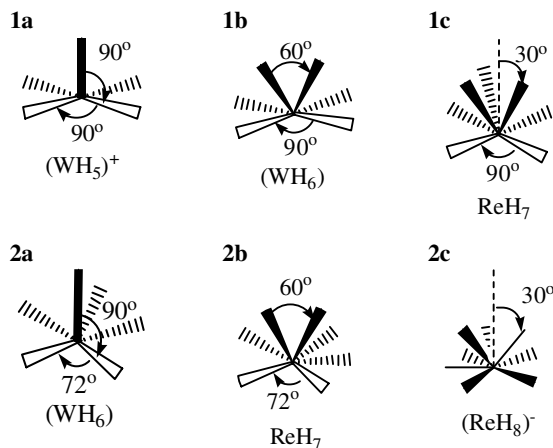
Basis set: lanl2dz (W and Re), 6-31G (hydrogen)

Structures

W–H bond length. 1.733 Å (from the structure of $\text{WH}_6(\text{PiPr}_2\text{Ph})_3$, see Inorg. Chem. 23 (1984) 4103).

Re–H bond length. 1.680 Å (from the structure of ReH_9^{2-}).

Remark. The reason for choosing different metals is to avoid calculating species that are highly charged. Calculations of highly charged species, which are also highly electron-deficient, give unreasonable results.



Basis sets

- The effective core potentials (ECPs) of Hay and Wadt with a double- ζ valence basis set (LanL2DZ) were used to describe W and Re: (a) W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284.
- The 6-31G basis set was used for H: (a) P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.

Program used

- All calculations were performed with the Gaussian 03 software package on Pentium IV PC computers: M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Vreven, Jr., K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, revision B05, Gaussian, Inc., Pittsburgh, PA, 2003.

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