

Complementary spherical electron density model and its implications for the 18 electron rule

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Abstract

The Complementary Spherical Electron Density Model developed by Mingos and Hawes in 1985 is reviewed and its implications to 18 electron complexes and co-ordinatively unsaturated complexes are developed. These conclusions are particularly germane in view of the recent proposal by Landis that transition metal complexes are governed by a 12 rather than an 18 electron rule, Hall's recent OSRAM model and the availability of additional structural data.

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1. Introduction

This 40th Anniversary Issue of the Journal coincides with my involvement with the subject since I went to University in 1962 and in 1964–1965 I took my first course in organometallic chemistry (given by Jeff Leigh and Michael Green) and chose to write an extended essay on theoretical aspects of organometallic chemistry. Therefore I remember reading the first issues of the Journal and being excited by the wonderful structures of iron cluster compounds which were emerging from the Union Carbide Laboratories in Belgium [1]. I still have that essay and it is not one of which I am particularly proud. It represented my first attempt at typing and it is full of typographical errors and erasures, however it does provide me with a suitable reference point for assessing and reflecting on what has happened to the theoretical basis of the subject in the intervening years. The choice of essay proved to be prophetic in some respects because although I initially chose to do a PhD in synthetic chemistry the majority of fellow chemists

will associate me with my contributions to theoretical organometallic chemistry and more specifically, with the Polyhedral Skeletal Electron Pair Theory [2]. This together with the 18 electron rule has provided a crude conceptual framework for rationalising the ever increasing number of compounds which were isolated and structurally shown to have surprising and interesting geometries. Therefore, this Special Issue provides me with an opportunity for reflecting on what really underlines these concepts and to what extent they give us really valuable information.

My 1965 essay highlighted, not unexpectedly, the following fundamental concepts and methodologies:

18 Electron rule which of course represents an extension of the Lewis Octet Rule to organometallic transition metal compounds. The 18-electron rule is often erroneously [3] attributed to Sidgwick [4,5]. Sidgwick's classic book *The Electronic Theory of Valency* published in 1927 does not discuss the 18-electron rule with the detail implied by present textbooks. Sidgwick focused attention on the effective atomic number concept, but did not make any statement about the stability of organometallic compounds. Professor Ged Parkin [5] has brought to my attention that it was probably Langmuir [6] who actually

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first stated that that certain transition metal complexes, and specifically $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Mo}(\text{CO})_6$, possess an 18-electron valence configuration although he did not make a predictive general statement about stability. Later, Reiff [7] and Sidgwick and Bailey [8] separately described the application of this concept to rationalize the stability and structure of other nitrosyl and carbonyl complexes.

Pauling's electroneutrality principle [9] recognised that in low oxidation state compounds there must be a mechanism to redistribute charge from the metal back to the ligand. Within the valence bond formalism this was achieved by multiple bond formation. Pauling recognised that this principle was particularly important for rationalising the occurrence of metal carbonyls of the later transition metals.

The Dewar bonding model combined Pauling's electroneutrality principle and elementary symmetry concepts in order to account for the geometries of metal–alkene complexes. The historical development of this model has been discussed by me in some detail elsewhere [10].

Symmetry based molecular orbital analysis. At a time when even simple electronic calculators were not generally available it is not surprising that it was necessary to develop symmetry based molecular orbital concepts to account for the occurrence of metal sandwich compounds [11]. These qualitative analyses drew heavily on the knowledge of the π -systems of unsaturated organic molecules developed by Dewar and Longuet-Higgins [12] and culminated in the successful prediction and isolation of stable cyclo-butadiene complexes of iron and nickel [13].

In the intervening 40 years the widespread availability of high speed computers has revolutionised the ability of organometallic chemists to tackle theoretical problems [14] and it is not uncommon for synthetic chemists to report simultaneously the synthesis, structure and bonding analysis of a compound in one paper. The development of user friendly packages capable of performing molecular orbital calculations on complex molecules containing heavy metal atoms has been made possible by the Density Functional Methodology [15]. Although these studies have analysed specific problems, there have been fewer attempts at using the methodology to probe the fundamental concepts. These Density Functional calculations have largely superseded earlier extended Hückel calculations used extensively in the 1970's and 1980's by Hoffmann and his school [16]. These more sophisticated calculations can certainly provide much more accurate total energies and are routinely used to confirm the geometries of molecules using energy minimisation methods, but are less transparent and less amenable to generalised interpretation [17].

In addition to these improved computational methods the last four decades has seen the development of

conceptual models. The Polyhedral Skeletal Electron Pair Theory [2], the Zintl [18] and Isolobal Concepts [19] have done much to provide a crude theoretical framework for cluster compounds of the main group and transition metals. They have provided an effective bridge between main group and transition metal chemistry [20] and Fehlner has proposed the portmanteau "Inorganometallic Chemistry" to describe this interdisciplinary area. The extension of molecular orbital methods to infinite structures has also led to important connections between molecular and solid state chemistry [21].

The theoretical connection between main group and transition metal clusters depended on recognising that these two classes of compounds shared a common set of unavailable molecular orbitals, which had a predominance of s and p orbital character and were strongly metal–metal antibonding. Their antibonding character and their hybridisation towards the centre of the cluster seals their unavailability for metal–ligand bond formation. Therefore, the number of these unavailable molecular orbitals determines the limiting number of orbitals, which can be occupied by electrons which are formally donated by the ligands and the metal. In this review we shall demonstrate that this methodology also has relevance to mononuclear complexes and can lead to an interesting reformulation of the 18 electron rule. The development of the Polyhedral Skeletal Electron Pair Theory also led to the recognition that certain classes of polyhedra had a set of non-bonding orbitals which were dictated by the cluster topology and which could result in classes of clusters with the same geometry but alternative electron counts. Group theory has been used to identify the number and symmetries of these non-bonding molecular orbitals [22]. This principle also has a counterpart in mononuclear organometallic compounds [22] and these ideas will be developed further in this review.

The adoption of the adjectives *available* and *unavailable* rather than the more commonly used *bonding* and *antibonding* may seem initially to be unnecessary and imprecise and certainly needs some justification. The distinction between bonding and antibonding is particularly useful when the basis set of orbitals contributing to a molecular orbital have the same energy. In such molecules the relative energies of the molecular orbitals are determined exclusively by the number of nodes associated with each molecular orbital. The π -molecular orbitals of a hydrocarbon polyene provide a good illustration of this generalisation. When the contributing atomic orbitals have very different energies then of course the calculated energy of a specific molecular orbital depends not only on the extent of overlap between the orbitals but also on the relative orbital character of those atomic orbitals with different energies. For example, for a transition metal where the $(n + 1)p$ orbitals are separated

from the other valence orbitals by large promotion energies then a molecular orbital which has a high percentage of p orbital character contributed by the central metal atom may not be strongly antibonding but nonetheless could have a calculated energy which places it very high lying relative to the other occupied molecular orbitals. This orbital although not antibonding in the formal sense may not interact with the lone pair orbital of an additional ligand as a result of the high percentage of p orbital character. Therefore, the term unavailable rather than antibonding more precisely describes its ability to participate in bonding. Furthermore, the $(n + 1)p$ orbitals of a transition metal atom are so different from the nd and $(n + 1)s$ orbitals that a small increase in the amount of p orbital character can change the energy of the molecular orbital dramatically. When the relative energies of two complexes are being compared the relative bonding and antibonding contributions of the orbitals to the frontier molecular orbitals may not differ greatly and the energies of the frontier orbitals may be determined primarily by the contributions made by the $(n + 1)p$ orbitals. The Polyhedral Skeletal Electron Pair analogies between main group and transition metal cluster compounds were almost impossible to delineate when attention was focussed completely on the occupied orbitals. The locations of bridging and terminal carbonyls added many ill-defined interactions and only by identifying sets of common unavailable orbitals did the connection become clear. For cluster compounds orbitals were identified as unavailable if they had a high percentage of p orbital character, were antibonding between the metals and were hybridised towards the centre of the cluster by s–p mixing. Unavailable orbitals in the context of a mononuclear complex similarly have some or all of the following characteristics: a high percentage of p orbital character, strongly metal–ligand antibonding, hybridised in a non-ligand direction. This paper illustrates the advantages of concentrating on the unavailable orbitals in mononuclear complexes.

2. An alternative description of the 18 electron rule

The descriptions of the 18 electron rule in the majority of inorganic and organometallic textbooks provide an excellent introduction to how the total electron count in a complex or cluster may be calculated, but little understanding of why it works and what one is expected to do if it does not work. In fact the statements made can border on the misleading, for example “The 18 electron rule is a way to help us decide whether a given d-block transition metal organometallic complex is stable” [23]. Besides the obvious undergraduate caveats concerning the distinction between kinetic inertness and thermodynamic stability such a generalisation fails to

recognise that the ability to isolate a compound requires a deeper analysis of the bonding in the compound. To take some very trivial examples: N_2 and BF and CO_2 and NO_2^+ conform to the effective atomic number rule but their ease of isolation and reactivities could not be more different. The inorganic chemists’ view of the 18 electron rule reminds me of their corresponding view of the Woodward Hoffman Rules for pericyclic organic reactions. They tend to focus on the “allowed” and “forbidden” nature of the reactions rather than the more important consideration from the synthetic organic chemists’ point of view namely the way in which the stereochemistry of the product is influenced by whether the ring opening occurs in conrotatory or disrotatory manner. The allowed or forbiddenness of a reaction depends on the size of the activation barriers which are notoriously difficult to estimate on the basis of symmetry based qualitative arguments, whereas the stereochemistry depends on the much smaller difference between the two possible reaction pathways and in these circumstances symmetry considerations may prevail and provide an accurate prediction of the preferred pathway. The really useful information with regard to geometry and reactivity lies in recognising the electronic consequences of the frontier molecular orbitals.

Based on this analogy I would argue that establishing that a complex obeys the 18 electron rule may provide a satisfying initial thrill because it confirms one can still add-up reliably, but in itself provides very little theoretical or chemical insight and no insight if it fails.

Firstly it is important to try and establish those areas where the 18 electron rule is likely to apply. Such a discussion is particularly relevant given Landis’ recent proposal [24] that the unavailability of the np valence orbitals in transition metal atoms makes it more appropriate to consider that transition metals are limited to sd^n ($n = 1–5$) hybridisation and therefore transition metal complexes should be considered in terms of a 12 electron rule (see also [25]). Complexes with more than 12 are better described as hypervalent and therefore analogous to BrF_5 , XeF_4 and SF_6 in main group chemistry. Frenking and Hall [17,26,27] have given a detailed analysis of why such arguments may be flawed, but nonetheless any generalised 18 electron rule should ideally incorporate complexes with fewer than 18 valence electrons.

There are two very significant differences in the relative energetics and radial distribution functions of the valence orbitals of main group and transition metals which are essential to an understanding of the underlying electronic basis of the 8 and 18 electron rule.

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: $(n + 1)s \sim nd \ll (n + 1)p$. As Hall has pointed out [27] the promotion energies separating the d and p

Table 1
Comparison of r_{\max} and r_{covalent} for the Group 14 elements (pm)

Element	r_{covalent}	r_{\max} (ns)	r_{\max} (np)
C	77	65	64
Si	117	95	115
Ge	122	95	119
Sn	140	110	137
Pb	144	107	140

orbitals are much larger in the former case than the latter and therefore it is not so justifiable to exclude the p orbitals completely in the latter. The most probable orbital radii of group 14 and group 6 elements summarised in Tables 1 and 2 result in the following significant differences [28]:

The 2s and 2p valence orbitals of carbon have very similar r_{\max} values and therefore they overlap almost equally well with the valence orbitals of atoms bonded to carbon. These comparable radii are ideal for effective s–p hybridisation although of course the different orbital energies prevent the formation of the idealised hybrids as originally proposed by Pauling. For the heavier group 14 elements the ns orbital becomes progressively more contracted relative to the np orbital and corresponds closely to the covalent radius of the element (r_{cov}). Consequently these orbitals hybridise less effectively than the second row elements. It follows that sp^3 hybridisation and the associated formation of compounds with 8 valence electrons will be more prominent for the second row elements than the heavier elements. For the heavier elements accepted wisdom suggests that the nd valence orbitals lie at too high energies and are too diffuse to make a significant contribution to bonding. Consequently it is not appropriate to describe compounds such as PF_5 , SF_6 and IF_7 as sp^3d , sp^3d^2 and sp^3d^3 hybridised, respectively, and instead the valence shell is restricted to sp^3 [28]. The molecules are described as hypervalent (i.e., they have in excess of 8 valence electrons) and some or all of the bonds are based on three-centre four-electron interactions [28]. Such compounds are particularly prevalent when the ligands are highly electronegative and capable of forming multiple bonds, e.g., F, O and N. The Complementary Spherical Electron Density Model, developed some years ago by myself and Hawes, suggests that in hypervalent compounds there are $(4 - n)\text{D}^\sigma$ functions localised on the

Table 2
Comparison of r_{\max} and r_{metallic} for the Group 6 transition elements (pm)

Element	r_{metallic}	r_{\max} (nd)	r_{\max} ($n + 1$)s
Cr	129	46	161
Mo	140	74	168
W	141	79	147

ligands which have the symmetry properties of the d orbitals but do not have a significant contribution from the d orbitals of the central atom [29].

For the Group 6 transition metals the nd valence orbitals, which have similar energies to the $(n + 1)s$ valence orbitals, have much smaller radii than the $(n + 1)s$ valence orbitals. The orbital radii of the latter correspond much closer to the metallic radii of the metals (see Table 2). From this data and a knowledge that the $(n + 1)p$ valence orbitals are much higher lying than nd and $(n + 1)s$ it is not surprising that Landis et al. [24] have found it plausible to suggest that the transition metals may favour sd^5 hybridisation rather than sp^3d^5 , which corresponds to a 12 rather than 18 electron rule. Indeed they have used this approximation to develop a very useful force field for molecular mechanics calculations of organometallic and co-ordination compounds.

In my view, the differences in radial distribution functions when taken together with the differences in orbital energies have the following important consequences. Effective d,s,p hybridisation will only occur when the ligands around the metal approach the metal sufficiently closely that they overlap effectively with both the nd and $(n + 1)s$ valence orbitals. There are two conditions for this to occur:

1. The ligand forms strong multiple bonds with the metal atom and therefore the metal ligand distance is significantly shorter than the sum of the covalent radii.
2. The ligand is a very small and has a low electronegativity, e.g., hydride.

It follows that most effective hybridisation will occur with ligands such as CO, NO, O and N capable of multiple bond formation and hydrogen or related ligands with low electronegativities. There are, of course, additional steric constraints which affect whether the 18 electron rule is achieved [30].

The extent of d–p hybridisation is also influenced by the total charge of the complex and the position of the metal in the Periodic Table. Specifically, the d–p promotion energy is smaller in negatively charged metal complexes and the relativistic effects associated with the heavier transition metals lead to a better match in radii of the s, p and d orbitals and more effective hybridisation.

3. 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 the high ionisation energies. Since for any $[ML_n]$ complex with $n > 4$ the ligand linear combinations generate a complete set of p functions $P_x^\sigma, P_y^\sigma, P_z^\sigma$. they will be represented in the complete set of wave functions for the whole molecule. Although, the extent of metal *vs* ligand involvement will depend only on the extent of overlap between metal and ligand orbitals and their relative energies. Specifically, if the ligand shell in ML_n provides $S^\sigma, P_x^\sigma, P_y^\sigma, P_z^\sigma, (n-4)D^\sigma \dots$ linear combinations then the metal contributes $(5-n+4)$ filled d orbitals with complementary angular momentum properties. Taken together they represent a complete shell in angular momentum terms, i.e., in an octahedral complex if the $(n-4)D^\sigma$ linear combinations corresponded to D_{z^2} ($l=0$) and $D_{x^2-y^2}$ ($l=2c$), e_g , then the corresponding filled metal d orbitals are d_{xz} ($l=1c$) d_{yz} ($l=1s$), d_{xy} ($l=2s$) (t_{2g}) (c and s represent the cosine and sine forms of the wave functions in their real rather than imaginary forms) [28,29].

In an octahedral complex the occupation of all orbitals except the 6 unavailable orbitals results in an 18 electron completed shell configuration as follows:

- (a) *Metal–ligand σ -bonding molecular orbitals (6)*. $S^\sigma, P_x^\sigma, P_y^\sigma, P_z^\sigma, D_{z^2}, D_{x^2-y^2}$ These molecular orbitals are localised mainly on the ligands but have a contribution from the matching s, p_x, p_y, p_z, d_{z^2} and $d_{x^2-y^2}$ orbitals
- (b) *Non-bonding metal localised molecular orbitals (3)*. d_{xz} ($l=1c$) d_{yz} ($l=1s$), d_{xy} ($l=2s$) These orbitals are stabilised by π -acceptor ligands and destabilised by π -donor ligands.

- (c) *Metal–ligand unavailable molecular orbitals (6)*. $S^{\sigma*}, P_x^{\sigma*}, P_y^{\sigma*}, P_z^{\sigma*}, D_{z^2}^*, D_{x^2-y^2}^*$ These molecular orbitals are antibonding and localised mainly on the metal but have a contribution from the matching ligand orbitals.

In an octahedral complex (a) and (b) represent available and (c) the unavailable molecular orbitals: unavailable because they are either strongly antibonding, $S^{\sigma*}$ and $P^{\sigma*}$ or have a high percentage of p orbital character. The total angular momenta of the orbitals associated with (a) and (b) adds up to zero, because of the complementary nature of the orbitals involved. Thus they correspond to a pseudo-spherical shell of electron density.

It is noteworthy that by switching attention to the unavailable molecular orbitals the question of the precise contribution of the p orbitals is circumvented. However small their contribution, the p orbitals are going to be classified as unavailable because of the large promotion energies required to access them [27].

The spherical polyhedra generate the available molecular orbitals – $S^\sigma, P_x^\sigma, P_y^\sigma, P_z^\sigma, (n-4)D^\sigma$ shown in Fig. 1: The unavailable molecular orbitals are the antibonding combinations of these linear combinations with the matching metal orbitals and their number is equal to the number of ligands:

- Tetrahedron (4)
 Trigonal bipyramid or square pyramid (5)
 Octahedron (6)
 Pentagonal bipyramid, capped octahedron, capped trigonal prism (7)
 Dodecahedron, square antiprism (8)
 Tricapped trigonal prism or capped square antiprism (9).

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 orbitals	■
Filled metal dp hybrids	■
Empty metal orbitals	■

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

Of course as the number of ligands increases the number of polyhedra which emulate a spherical shape increases in number and the energies separating them decreases.

A detailed analysis of the spherical harmonic descriptions of the LCAO's and the complementary metal orbitals has been given by Hawes and Mingos [29] and their results are summarised in Fig. 1. For co-ordination numbers 9–6 the complementary d orbitals have exclusively d orbital character if the spherical co-ordination polyhedra are utilised (see Fig. 1 for specific descriptions of the orbitals). The orbital energy ordering $(n+1)s \sim nd \ll (n+1)p$ dictates that it is essential to maximise the s and d orbital character in occupied orbitals and maximise the p orbital character in unoccupied orbitals and these spherical polyhedra satisfy this requirement even if L is a simple σ -donating ligand.

18 Electron ML_n complexes have the following frontier orbital occupations (indicated in yellow in Fig. 1):

Square-antiprism	$(d_z)^2$
Dodecahedron	$(d_{x^2-y^2})^2$
Capped octahedron	$(d_{x^2-y^2})^2 (d_{xy})^2$
Capped trigonal-prism	$(d_{x^2-y^2})^2 (d_{yz})^2$
Pentagonal-bipyramid	$(d_{xz})^2 (d_{yz})^2$
Octahedron	$(d_{xz})^2 (d_{yz})^2 (d_{xy})^2$

These complement the metal–ligand bonding molecular orbitals and together emulate a spherical shell of electron density in terms of the net zero angular momentum characteristics of the complementary and complete set of occupied orbitals.

If L is a good π -acceptor ligand then these metal localised 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. For example, in a pentagonal bipyramidal complex an axial π -acceptor ligand will preferentially occupy an axial site and thereby maximise its overlap and interaction with $(d_{xz})^2 (d_{yz})^2$. $[Mo(NO)(S_2CNMe_2)_3]$ provides a specific example of such a complex and is formally Mo(II) d^4 if NO is defined as NO^+ .

However, if the ligand(s) are strong π -donors then the effect is to destabilise the d-orbitals listed above. If the interactions are strong the result may very well be to destabilise some of the frontier orbitals and transform orbitals which were available in the ML_n complex into unavailable orbitals and thereby influence the optimal electron count. For example, if the axial ligand in a pentagonal bipyramidal is a strong π -donor, e.g., O or N, then the $(d_{xz})^2 (d_{yz})^2$ orbital pair is destabilised and joins the seven unavailable orbitals resulting

from the σ -interactions shown in Fig. 1 and the preferred frontier orbital occupations are $(d_{xz})^0 (d_{yz})^0$. These orbitals are rendered unavailable because they are the antibonding components of a strong π -interaction between ligand and metal orbitals. Therefore, strong π -donor ligands are capable of generating additional unavailable antibonding orbitals which have a high percentage of d orbital character, but in so doing generate complementary filled π -donor orbitals localised mainly on the ligands. If the electron pairs occupying these ligand orbitals are introduced into the electron count then the 18 electron count is maintained. For example, $[MoN(S_2CNMe_2)_3]$ has an 18 electron count if the nitrido-ligand is considered to be a 3 electron donor. The complex is formally Mo(VI) d^0 and this analysis, based on the unavailable orbitals, coincides with this formalism.

Therefore, the 18 electron rule when reframed in terms of the number of unavailable molecular orbitals may be used flexibly for complexes with π -acceptor and π -donor ligands. In those 18 electron complexes which have lower co-ordination numbers ($n=5$ and 4) the $18-2n$ electrons metal localised electrons cannot occupy exclusively orbitals with pure d orbital character and the point group symmetries indicate that in some of the frontier orbitals d–p mixing may occur. These orbitals are indicated in orange in Fig. 1. Even if the d–p mixing occurs to a small extent it may have significant energetic consequences because of the large promotion energies required to promote an electron from an nd to an $(n+1)p$ valence orbital.

Fig. 2 illustrates schematically a molecular orbital diagram for a tetrahedral ML_4 complex where initially the ligands are simple σ -donors. The σ -interactions create a set of matching $S^\sigma, P_x^\sigma, P_y^\sigma, P_z^\sigma$, bonding and antibonding molecular orbitals and the 4 antibonding components shown at the top of the figure are clearly strongly unavailable. The frontier orbitals have predominantly d orbital character and by symmetry split into the familiar t_2 and e sets. The latter, are non-bonding and localised exclusively on the metal, but the former may have variable admixtures of p orbital character, which will destabilise them relative to the e set. The extent of destabilisation will reflect the extent of d–p mixing and will influence whether these orbitals are designated as available or unavailable. If the d–p mixing is not extensive they are available and if both e and t_2 sets are occupied then an 18 electron configuration, d^{10} , is achieved.

If L is a good π -acceptor ligand then both e and t_2 orbitals have the appropriate symmetry to overlap with the ligand π^* -orbitals and such interactions will stabilise both e and t_2 and will encourage the complex to achieve an 18 electron configuration, i.e., the only unavailable orbitals are the strongly antibonding $S^{\sigma*}, P_x^{\sigma*}, P_y^{\sigma*}$,

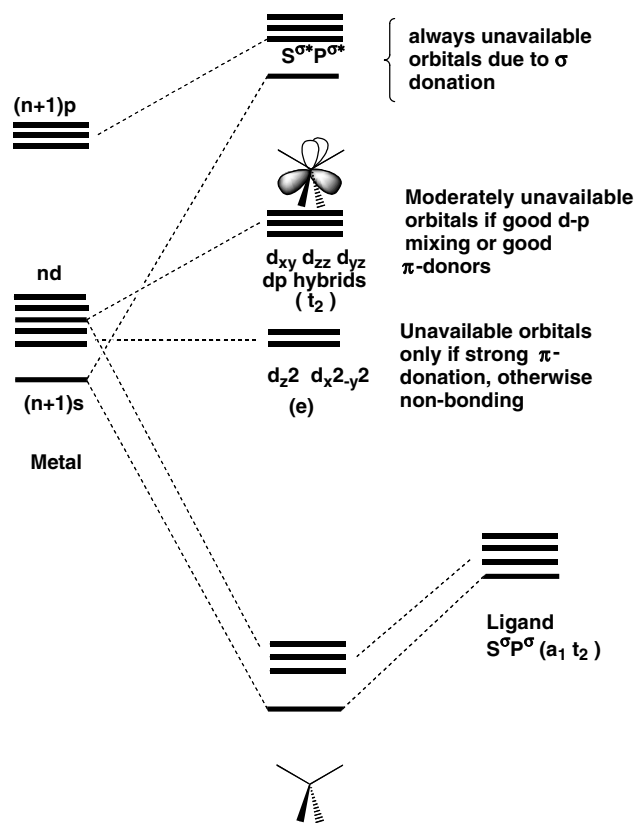


Fig. 2. Schematic representation of the molecular orbitals in a tetrahedral complexes emphasising the different classes of unavailable orbitals which can result in d^0 , d^4 and d^{10} closed shell and sub-shell configurations. This d–p hybridisation is discussed in more detail in [22].

$P_z^{\sigma*}$. These conclusions are summarised in Table 3. More generally, 18 electron 4 and 5 co-ordinate complexes are particularly favoured by π -acceptor ligands since they reduce the p orbital character in occupied hybrids by delocalising the orbitals onto the ligand. Complexes such as $Ni(CO)_4$, $Fe(CO)_5$ and related nitrosyl and isocyanide compounds provide specific examples. If the ligands are not such good π -acceptors then 16 and 14 electron complexes become favoured. For example tertri-

ary phosphine complexes of the platinum metals, particularly if the ligands have sterically demanding substituents, tend to form trigonal and linear $M(PR_3)_3$ and $M(PR_3)_2$ complexes.

In tetrahedral ML_4 complexes there are three dp hybrids (see Fig. 2) of t_2 symmetry and therefore if d–p mixing is effective then the number of unavailable orbitals may be increased to 7 from 4 by the addition of the t_2 set. Strong σ -donor ligands are particularly effective in promoting d–p hybridisation, e.g., H or R. Therefore, it is not surprising that 12 electron tetrahedral complexes such as OsR_4 , where R is a bulky aryl ligand, have been structurally characterised.

The t_2 set and the remaining d orbitals ($e(d_{z^2}, d_{x^2-y^2})$) are also capable of interacting with the π -donor orbitals if L is a π -donor and will become unavailable if the interaction is strong, i.e., the number of inaccessible orbitals may be raised to either 7 or 9. Consequently complexes with d^0 to d^4 electron configurations are likely to be favoured for tetrahedral complexes with π -donor ligands. These possibilities are summarised in the Table 3 in terms of the total number of valence orbitals in the valence shell. Besides the examples given in the Table there are also examples of MO_4^{x-} with d^0 – d^4 low spin configurations [28].

Drawing attention to the number of unavailable orbitals connects the complexes which have 18 valence electrons and those which have ligands where the number of σ - and π -donating orbitals exceeds the number of valence orbitals. For example, complexes which at first sight have 20 valence electrons, e.g., $[W(CO)(alkyne)_3]$, may readily be rationalised by assessing the number of unavailable molecular orbitals [33].

In ML_5 complexes there are 2 d–p hybrid orbitals in the d manifold (Fig. 1) and therefore in addition to the 18 electron closed shell configurations 14 electron possibilities exist with the appropriate ligands. An example with a 14-electron count is $[Ru(CO)(SAr)_4]$ ($Ar = 2,3,5,6$ -tetramethylphenyl). $Ru(CO)(SAr)_4$ adopts a trigonal bipyramidal structure with the CO ligand occupying one of the axial positions.[34] ML_3 complexes

Table 3
Unavailable and available orbitals in tetrahedral metal complexes, ML_4

No. of metal valence orbitals	No. of ligand orbitals	No. of unavailable orbitals	Total no. of available orbitals	Example
<i>π-acceptor ligands</i>				
9-s $p^3 d^5$	4 σ	4	9 + 4 – 4 = 9	$Ni(CO)_4$
<i>σ-donor ligands weaker π-acceptors</i>				
9-s $p^3 d^5$	4 σ	4	9 + 4 – 4 = 9	$Pt(PMe_3)_4$
<i>σ-donor ligands which result in good d–p mixing</i>				
9-s $p^3 d^5$	4 σ	4 + 3(t_2) = 7	6	$OsMes_4$, ReR_4^-
<i>Good π-donor ligands</i>				
9-s $p^3 d^5$	4 σ 4 σ (lone pair) + 8 π	4 + 3 + 2(e) = 9	16	OsO_4

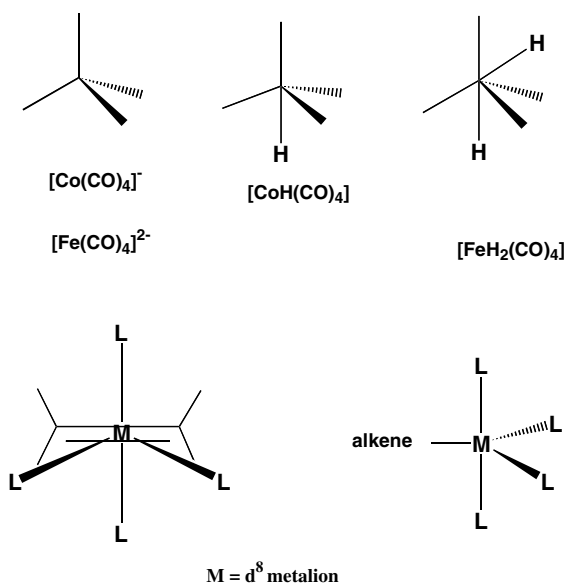


Fig. 3. Examples of protonation of transition metal complexes utilising electron density located away from the ligand direction and the maximisation of back donation when the d_{π} orbitals are non-degenerate.

have a similar pair of hybrids and give rise to similar possibilities.

Given that the lone pairs on the metal occupy orbitals that are complementary to the ligand set it follows that the most available electron density is located along directions which lie between the ligands. It follows that protonation and electrophilic attack in general is favoured in these directions. The structures of metal carbonyl complexes which have been protonated or auroated (with AuPPh_3^+) show very clearly how these electrophilic ligands lie along a three fold axes of the parent carbonyl anions $[\text{M}(\text{CO})_4]^{x-}$ ($x = 1-3$). 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 a preferred orientation which maximises the interaction between the filled d orbital and the π -acceptor orbital of the ligand. For example the olefin complex illustrated in Fig. 3 has the olefin lying preferentially in the trigonal plane.

Rule 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 ligand directions and are

stereochemically inactive. The ligands must effectively overlap with the metal d and p orbitals to ensure the attainment of the 18 electron rule. The complementary set of filled and metal localised orbitals determine the site preferences and preferred conformations of π -acceptor ligands.

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.

3.1. 16 Electron complexes

There are two primary ways of creating an additional unavailable orbital with a high percentage of metal p orbital character. 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 unavailable orbital. If this cannot be achieved then the formation of a dsp hybrid with the maximum amount of p orbital character represents the next best choice.

Linear and planar geometries provide the most effective ways of generating geometries with orthogonal p orbitals and this is why these geometries are favoured for linear and trigonal-planar d^{10} complexes. Fig. 4 illustrates how the attainment of the geometry with the most favourable unavailable orbital may be made for a four co-ordinate complex. Four co-ordinate square-planar complexes provide the most prevalent example of this principle and there are of course numerous examples of d^8 square-planar complexes.

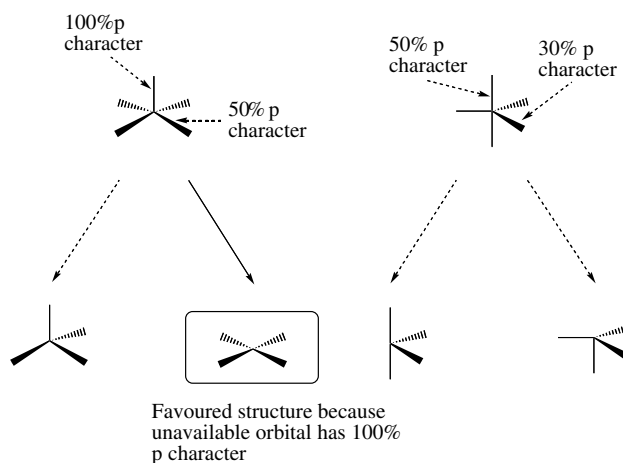


Fig. 4. Illustration of how the p orbital character is maximised in an ML_4 16 electron complex. Such complexes are favoured for metals with large d - p promotion energies.

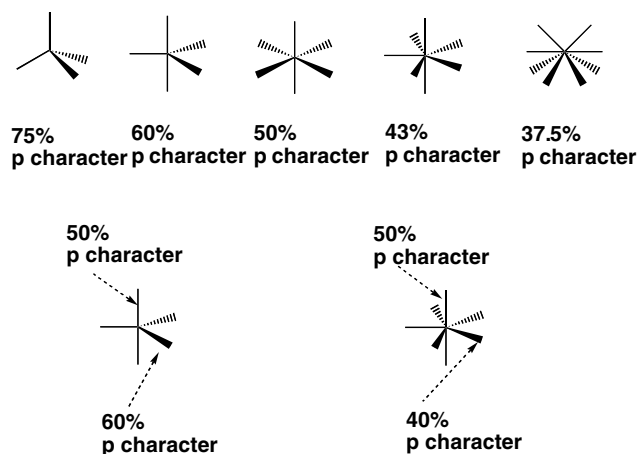


Fig. 5. Illustration of effect of co-ordination number on the average percentage p character in individual idealised hybrids and the differences between equatorial and axial hybrids. These hybridisation estimates do not take into account the differences in radial characteristics of the contributing orbitals [22].

Interestingly Hall's calculations [27] on 16 electron MH_5 complexes with low spin d^6 configurations suggest the planar D_{5h} geometry as a possibility despite the obvious steric crowding in the co-ordination plane.

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 alternative. In general one takes as the parent molecule the 18 electron compound and then introduces an empty hybrid orbital for each missing ligand. The fragment which remains is required to belong to a point group which enables d–p hybridisation to occur in order to maximise the participation of the metal's p orbital in the out-pointing hybrid.[29] For simple geometric reasons which are indicated in Fig. 5 the hybrid which maximises the p orbital character is that with the lowest co-ordination number. It is significant that the differences in p character decrease as the co-ordination number increases. It follows that for a 16 electron ML_n complex the creation of a hybrid with maximum p orbital character is achieved by adopting the co-ordination polyhedron for ML_{n+1} and locating the empty hybrid in the vacant position. We have previously described such co-ordination polyhedra as *nido*-by analogy with cluster structures [2]. Related co-ordination polyhedra with two and three vacant co-ordination sites with hybrids are described as *arachno*- and *hypho*- and they are also illustrated in Fig. 6. The utilization of the same co-ordination polyhedron in 18 and 16 electron complexes has the added energetic advantage that the occupied frontier orbitals have a high proportion

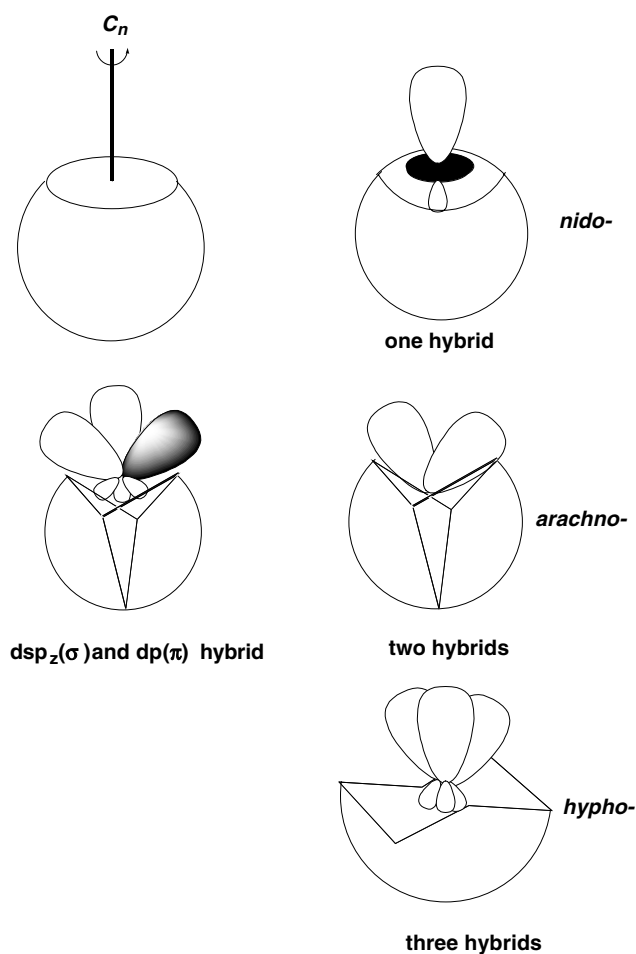


Fig. 6. Topology of *nido*-, *arachno*- and *hypho*-geometric shells. The out-pointing dsp hybrids emanating from the open face are also indicated.

of the more stable d orbitals and point away from the ligands.

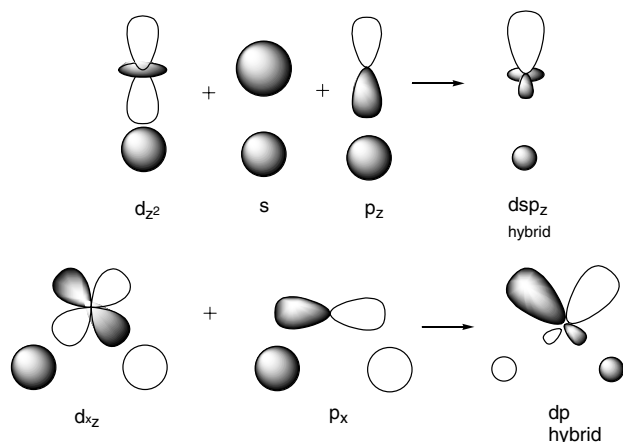
The formation of a single hybrid with a high proportion of p orbital character requires the mixing of s, d_{z^2} and p_z orbitals and therefore places a restriction on the symmetry of the resultant 16 electron complex. Specifically mixing of these orbitals requires the absence of either a centre of symmetry and 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 [22].

Effective d–p hybridisation is governed by the following matrix element derived from second order perturbation theory which depends on the ability of the d and p orbitals to overlap with the ligands orbitals (the appropriate linear combination being represented by L) and a minimum energy gap between the d and p orbitals ($E_{d_{z^2}} - E_{p_z}$) [31].

$$\frac{\langle d_{z^2}|L\rangle\langle p_z|L\rangle}{(E_{z^2} - E_L)(E_{d_{z^2}} - E_{p_z})}$$

E_i = Energy of orbital i
 L = LCAO of Ligand donor orbitals

$\langle d_{z^2}|L\rangle$ and $\langle p_z|L\rangle$ represent the overlap between the metal orbitals and the ligand LCAO's

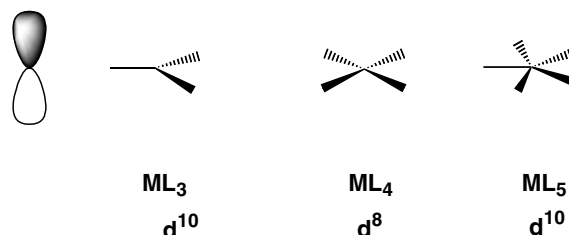


The formation of a hybrid in the z -direction and suitable for σ -bond formation requires p_z - d_{z^2} mixing, and the formation of hybrid with π -pseudo symmetry along the z -axis requires d_{xz} - p_x mixing. Neither is possible without the location of ligand orbitals in directions which enable them to overlap simultaneously with both orbitals being mixed, i.e., in the z -direction in the first example and angularly arranged ($L-M-L > 90^\circ$ and $< 180^\circ$) in the xz plane in the second example.

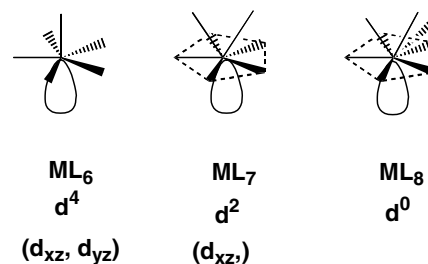
Interestingly Hall's detailed molecular orbital analysis of transition metal hydrides has come to a similar conclusion and they are summarised in Table 4, together with the point group symmetries of the optimised geometries. Indeed his Orbital Symmetry Ranked Method (OSRAM) also emphasises the importance of the symmetry aspects of the problem, since it analyses the irreducible representations of the metal's atomic orbitals and the ligand LCAO's in order to identify which LCAO's match up the with the spherical harmonics of the metal AO's [27].

Indeed his results indicate a specific pattern whereby the MH_6 complex is based on a pentagonal bipyramid with a missing axial vertex (see Fig. 7). It is significant that for the pentagonal-bipyramid the axial hybrid has more p orbital character than the equatorial hybrid as shown in Fig. 5. The related ML_7 and ML_8 16 electron complexes are based on related geometries with a pentagonal equatorial plane and successively more ligands occupying the space opposite the empty hybrid orbital and presumably maximising the dsp mixing. In the pentagonal pyramid, ML_6 , the metal $d_{xz}d_{yz}$ pair retain

16 electron planar complexes



16 electron pyramidal complexes



18 electron parent

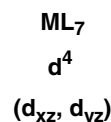


Fig. 7. Generation of an unavailable p_z orbital in planar complexes and *nido*-co-ordination polyhedra with an out-pointing (to the South) d - p hybrid. In the three 16 electron examples the pentagonal girdle is augmented by 1, 2 and 3 ligands in the Northern hemisphere.

Table 4

Symmetries of optimised geometries for 16 electron metal hydrido-complexes (see Fig. 7 also)

Complex	Metal electron configuration	Optimised point group	Comment
$[MH_8]$	d^0	$<C_{2v}$ or C_s	Five equatorial hydrogens and three more hydrogens on one side ($[OsH_8]$)
$[MH_7]$	d^2	C_{2v}	Five equatorial hydrogens and two more on one side $[OsH_7]^-$
$[MH_6]$	d^4	C_{5v}	Pentagonal pyramidal
$[MH_5]$	d^6	D_{5h}	D_{5h} has an empty p orbital vertical to the pentagonal plane

100% d character by being orthogonal to the ligands and thereby provide the maximum stabilisation for a d^4 complex. In ML_7 the pair of ligands hybridises d_{yz} with p_y and the d^2 pair is accommodated in d_{xz} , which retains 100% d character. In ML_8 the three ligands in the Northern hemisphere hybridise both $d_{xz}d_{yz}$ with p_x and p_y , creating two less available empty hybrid orbitals. Fig. 8 gives examples of how analogous *nido*-fragments may be constructed for other bipyramids.

Kubacek and Hoffmann analysis of the 16 electron complexes $ML_2'L_2''L_2'''$ where π -donor and acceptor ligands are in competition non-octahedral geometries are preferred because they maximise the instability of one component of the t_{2g} set. The argument therefore resembles those made above since it emphasises increasing the energy gap at the frontier level [35].

There is an alternative mechanism for creating unavailable dp hybrid orbitals in *nido*-co-ordination fragments which was not considered in the initial analysis [29], but which is now apparent. Fig. 6 suggests the formation of an out-pointing d_2sp_z (a_1) with σ -symmetry towards the missing vertex of the *closo*-polyhedron. However, an empty orbital of π -symmetry $d_{xz}p_x$ may be generated if the ligand arrangement is more appropriate for $d_{xz}p_x$ mixing than d_2sp_z mixing. A pentagonal

arrangement of ligands with two missing non-adjacent ligands satisfies this requirement. The resultant local geometry is Y-shaped and the resultant polyhedral fragment has the topology of a bi-dimpled sphere.

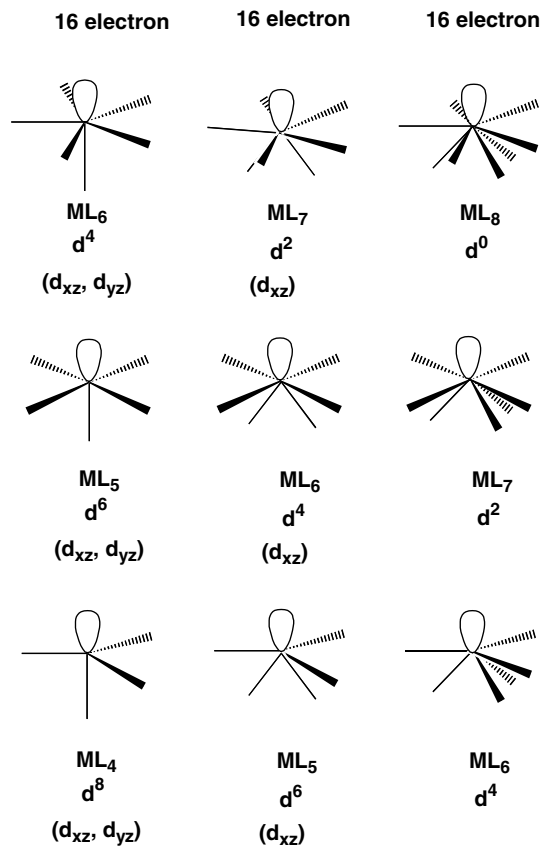
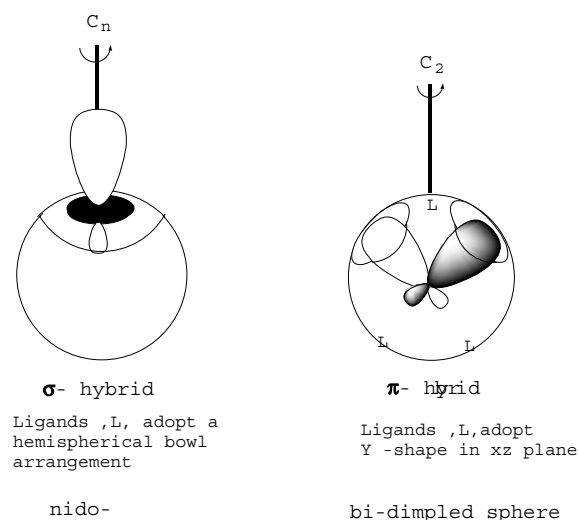
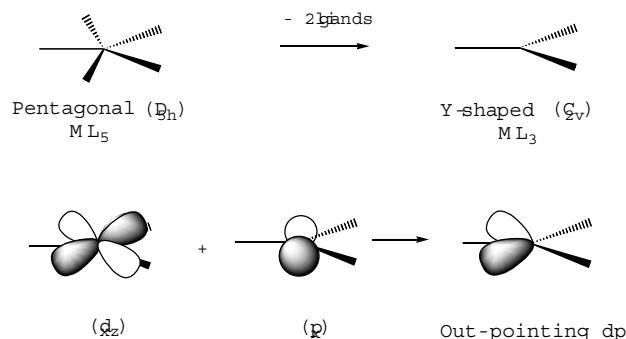


Fig. 8. Examples of *nido*- ML_n co-ordination polyhedra based on bipyramids with a missing vertex and the introduction of 1, 2 and 3 ligands in the lower polar region.



Therefore, for 16 electron ML_5 complexes two possibilities exist either a C_{4v} square pyramidal fragment based on a *nido*-octahedron (σ -out-pointing hybrid) or a pentagonal bipyramid with two missing equatorial vertices (a π -out pointing hybrid between the remaining Y-shaped equatorial ligands). $RuCl_2(PPh_3)_2$ is square-pyramidal and $IrHCl_2(P^tBu_2Ph)_2$ provides a specific example of a distorted trigonal-bipyramid with a Y shaped equatorial arrangement of ligands [26].

Rule 2

In 16 electron complexes effective d-p mixing results either in a nido-bowl like geometry or a bi-dimpled spherical topology with a ligand disposition that provides occupied orbitals with a maximum amount of d character and empty frontier orbitals where the d orbital character is minimised by d-p mixing. That d-p mixing requires the ligands simultaneously to overlap

with the *d* and *p* orbitals. Similar considerations apply to arachno- and hypho-co-ordination polyhedra. π -Hybridisation involving two *d* orbitals results in a topology which corresponds to a sphere with a hollowed longitudinal torus.

Rule 3

The empty hybrid orbitals are stereochemically active and if formed by σ -hybridisation point towards the missing ligand(s) and create two vacancies in the same plane

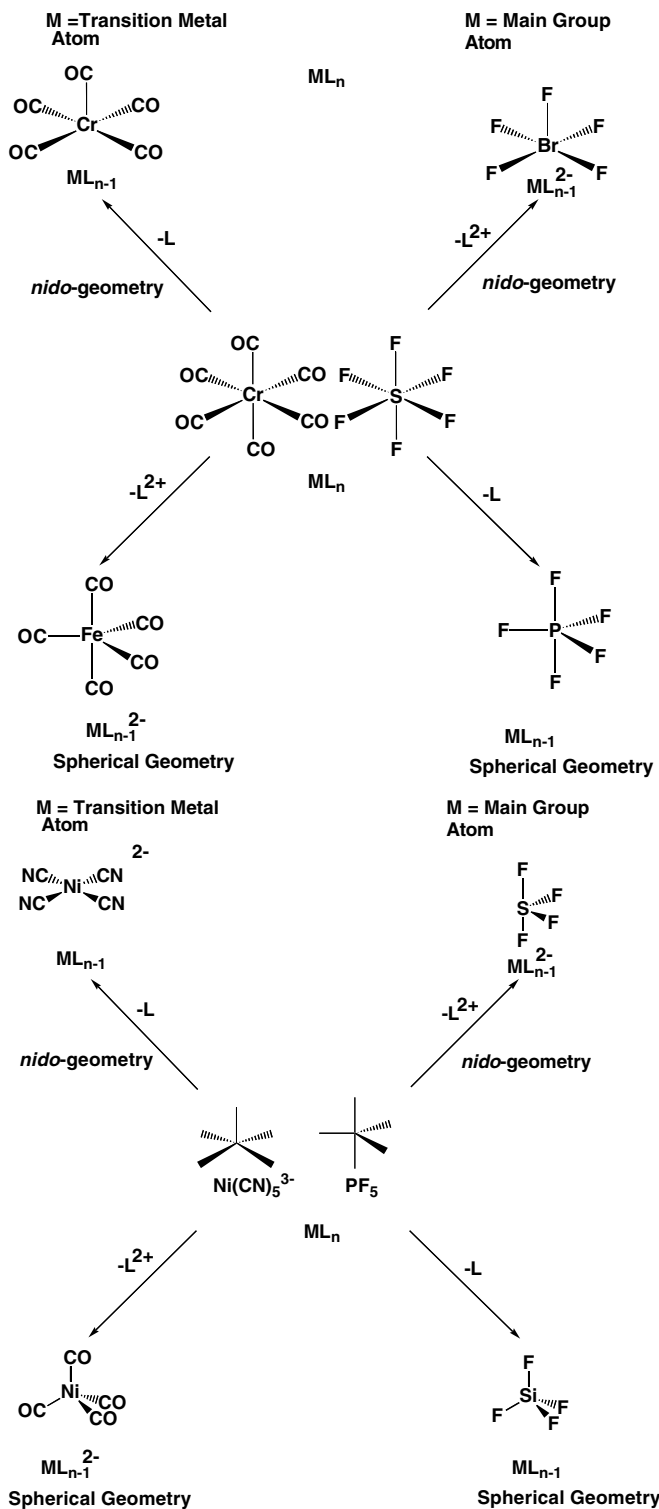


Fig. 9. Examples of geometrically related main group and transition metal compounds. The complementary nature of the geometries arises because in the former lone pairs are stereochemically active whereas in the latter empty hybrid orbitals are stereochemically active.

by π -hybridisation, as shown below. The ligands in the coordination sphere of *nido*-, *arachno*-, and *hypho-co-ordination* polyhedra move towards the site occupied by the empty hybrid orbital.

Landis [24] has suggested that many main group and transition metal compounds share common geometries because they are hypervalent [27]. Detailed calculations on PdH_3^- [27] and ClH_3 suggest that the bonding patterns are not common to both molecules and only the latter is accurately described as hypervalent. Furthermore, the Complementary Spherical Electron Density Model has previously shown that these two classes of complexes share common geometries because in main group compounds lone pairs are stereochemically active whereas in transition metal compounds empty hybrid orbitals are stereochemically active. This structural relationship first published in 1985 [29] is illustrated in Fig. 9 and serves to underline these relationships. Although the empty orbitals are stereochemically active the other ligands in the transition metal complex bend towards the vacancy if the molecule does not have a horizontal plane of symmetry. This contrasts with the situation in main group chemistry where the ligands distort away from the lone pair.

These unavailable orbitals clearly have a role in indicating the stereochemistries of the complexes with 16 electrons but are also important in defining how transition states which they represent may be stabilised preferentially. Therefore, they define a 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

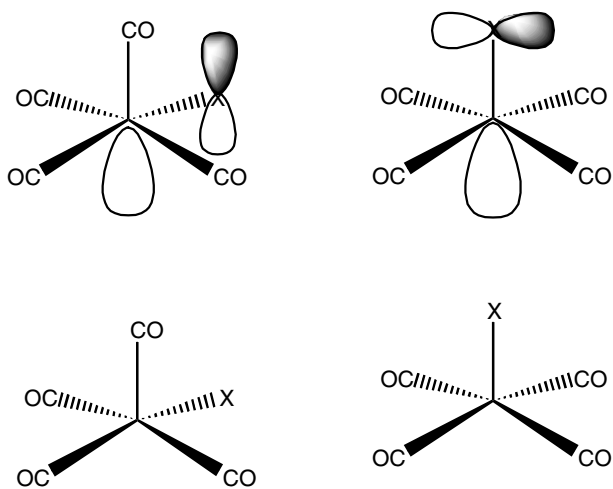


Fig. 10. Stabilisation of the empty orbital in square-pyramidal 16 electron complexes.

in the substitution of $\text{M}(\text{CO})_5\text{X}$ complexes [32]. Similar considerations apply to the other *nido*-co-ordination polyhedra and it is possible to define π -donor and agostic interactions which stabilise the 16 electron complex or intermediate (see Fig. 10).

More generally it is obvious that identifying the empty orbital in 16 electron complexes provides useful information concerning the location and orientation of π -donors which are capable of stabilising the empty orbital.

3.2. 14 Electron complexes

In 14 electron complexes there are two unavailable orbitals with the maximum amount of p orbital character to be generated and the most obvious way is to utilise *arachno*-polyhedral fragments as illustrated in Fig. 6. The removal of two adjacent vertices from the parent structure generally limits the symmetry of the remaining shell to C_{nv} or C_n . In terms of the symmetry elements of these point groups the relevant unavailable orbitals comprise of an out-pointing $d_{z^2}sp_2$ (a_1) with σ -symmetry and a $d_{xz}p_x$ out pointing hybrid (b_2 symmetry). Some examples of 14 electron complexes displaying *arachno*-geometries are illustrated in Fig. 11.

Interestingly, within Hall's detailed analysis of hydrides [27] the most stable 16 electron complexes generally belong to the point groups C_{nv} and the calculated minimum energy geometries are in agreement with the geometries proposed by the complementary spherical electron density model.

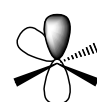
The alternative mechanism for creating unavailable dp hybrid orbitals with π -symmetry is also observed in *arachno*- and *hypho*-co-ordination fragments. In d^8 ML_3 complexes the T-shape and Y-shaped planar geometries provide two alternative ways of generating in plane dp hybrids, one of σ -pseudo symmetry in the former case and one of π -pseudo symmetry in the latter. In Hall's calculations [27] this possibility is apparent and for example for d^8 ML_3 complexes the alternative geometries are T-shaped for PdH_3^- and Y-shaped for AgH_3 . For 14 electron MH_5 complexes a C_{3v} geometry is generally pre-

Examples of 14 electron molecules



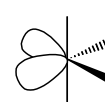
$\text{Pd}(\text{PCy}_3)_2$

Linear



$\text{Rh}(\text{PPh}_3)_3^+$

T-shaped (C_{2v})



$\text{Mo}(\text{CO})_4$

saw-horse (C_{2v})

Fig. 11. Examples of 14 electron complexes based on *arachno*-fragments. In the first two examples the unavailable orbitals include one and two pure p orbitals, respectively, the remainder are hybrids.

ferred and can be associated with the formation of a degenerate pair of dp hybrids with π -symmetry. The topology of such co-ordination shell is based on a sphere with a hollowed out latitudinal area, which extends right around the sphere. Fig. 12 provides an illustration of this possibility for a range of co-ordination numbers.

3.3. 12 Electron complexes

Referring back to Fig. 6 it is apparent that 12 electron complexes have three vacancies in their co-ordination polyhedron and adopt *hypho*-polyhedra. The utilisation of three equivalent hybrids in the C_{nv} point groups permits involves an out-pointing d_zsp_z (a_1) with σ -symmetry and a pair of $d_{xz}p_x$, $d_{yz}p_y$ out pointing hybrid with π -e symmetry. The d^0 $M(\text{CO})_3$ and $\text{Rh}(\text{mesityl})_3$ complexes provide specific examples of the application of this principle. For lower co-ordination numbers it is impossible to have axial symmetry and for example d^8 ML_2 complexes have an angular geometry which uses two out-pointing hybrids in the plane and an empty p_z orbital perpendicular to the plane. d^4 MH_4 complexes may either utilise a C_{4v} geometry with a_1 and e out-pointing orbitals or take up the T_d geometry described above and utilise the

frontier orbitals illustrated in Fig. 2. As the co-ordination number increases then the amount of p orbital character in the hybrid orbital decreases and the number of alternative parent structures increases. So for d^0 ML_6 a D_{3h} structure based on a trigonal-prism could be viewed as a *hypho*-triccapped-trigonal-prism and this geometry is observed in a wide range of d^0 complexes particularly with bidentate sulfur based ligands. The three in plane hybrids would have predominantly s, d_{xy} , $d_{x^2-y^2}/p_x$, p_y character, but no p_z character. It could also form the basis of accounting for the C_3 geometry observed in WMe_6 – the additional distortion from D_{3h} to C_{3v} being rationalised by d– p_z mixing of the frontier orbitals [24,27].

4. Complexes where d–p mixing is less effective

The primary thesis developed above is that although the $(n+1)p$ orbitals of a transition metal atom are high lying they provide a crucial role in determining the geometries of a whole range of transition metal complexes where the d–p mixing is encouraged by short metal–ligand distances and good overlap between the ligand orbitals and the metal d and p orbitals. Specifically d–p hybrids are important in defining the number and location of unavailable orbitals. Although d–p mixing may not be extensive, on a soft potential energy surface it may prove very influential in discriminating between alternative geometries.

There are a large number of complexes with more sterically demanding ligands which do not form such

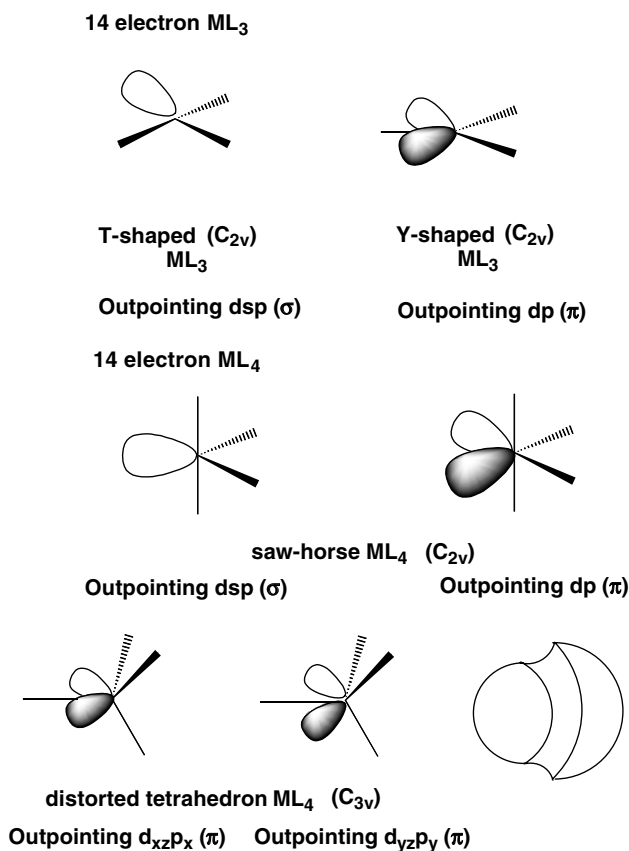


Fig. 12. Alternative ways of creating unavailable d–p hybrids in 14 electron complexes.

Table 5
Examples of octahedral complexes with partially filled d shells

Complex	d^n Occupying the t_{2g} set	Geometry
TiF_6^{2-}	d^0	Distorted octahedral
$\text{Ti}(\text{OH}_2)_6^{3+}$	d^1	Octahedral
OsF_6	d^2	Octahedral
IrF_6	d^3	Octahedral
PtF_6	d^4 low spin	Octahedral
$\text{Ru}(\text{NH}_3)_6^{3+}$	d^5 low spin	Octahedral
$\text{Co}(\text{NH}_3)_6^{3+}$	d^6 low spin	Octahedral

Shaded examples correspond to 18 electron complexes.

Table 6
Examples of 7-co-ordinate complexes with partially filled d shells

Complex	d^n Occupying the two non-bonding d orbitals	Geometry
ZrF_7^{3-}	d^0	Pentagonal bipyramidal
$\text{V}(\text{CN})_7^{4-}$	d^2	Pentagonal bipyramidal
$\text{OsH}_4(\text{PMe}_2\text{Ph})_3$	d^4	Pentagonal bipyramidal
$\text{MoBr}_4(\text{PMe}_2\text{Ph})_3$	d^2	Capped-octahedral
$\text{WBr}_3(\text{CO})_4$	d^4	Capped-octahedral
NbF_7^{3-}	d^0	Capped-trigonal-prism
$\text{Mo}(\text{CNBu}^t)_7^{2+}$	d^4	Capped-trigonal-prism

Table 7
Examples of 8-co-ordinate complexes with partially filled d shells

Complex	d ⁿ Occupying the single non-bonding d orbital	Geometry
MoH ₄ (PMe ₂ Ph) ₄	d ²	Dodecahedron
NbCl ₄ (diars) ₂	d ¹	Dodecahedron
ZrF ₈ ⁴⁻	d ⁰	Bicapped-trigonal-prism
W(CN) ₈ ⁴⁻	d ²	Square-antiprism

strong covalent bonds. These complexes frequently adopt a common spherical geometry which minimises the repulsions between the ligands and adopt the same shape for complexes for several d electron counts. In an ML_n (n = 6–8) the variable d electron counts arise from occupation of (9 – n) d orbitals which are localised primarily on the metal. Tables 5–7 provide specific examples of such complexes:

Rule 4

Complexes where the ligands do not induce effective d–p mixing may adopt spherical polyhedral geometries and have partially filled d shells as frontier orbitals.

5. Other ramification of unavailable orbitals

Focussing attention on the number of unavailable molecular orbitals has additional advantages, which cannot be explored fully here. A couple of examples will, however, suffice to indicate the possible scope of the methodology [2].

In hydrido-complexes the formation of a three-centre two-electron bond involving the bridging hydrogen shown in Fig. 13 creates two-unavailable orbitals – the non-bonding (or strictly speaking weakly metal–metal antibonding) and the antibonding molecular orbital. Therefore, in electron counting terms the presence of each bridge of this type results in two unavailable orbitals and of course each terminal metal–ligand bond results in one unavailable molecular orbital. The methodology may be illustrated by reference to B₂H₆, which has 12 valence electrons.

Total number of valence orbitals	=14 (2×4 for B = 6 for H)
No of unavailable terminal B–H Antibonding m.o.'s	=4
No. of unavailable B–H–B m.o.'s	=4 (2 for each bridge)
Total number of unavailable orbitals	=8
Total number of available m.o.'s	=6 which can accommodate 12 electrons

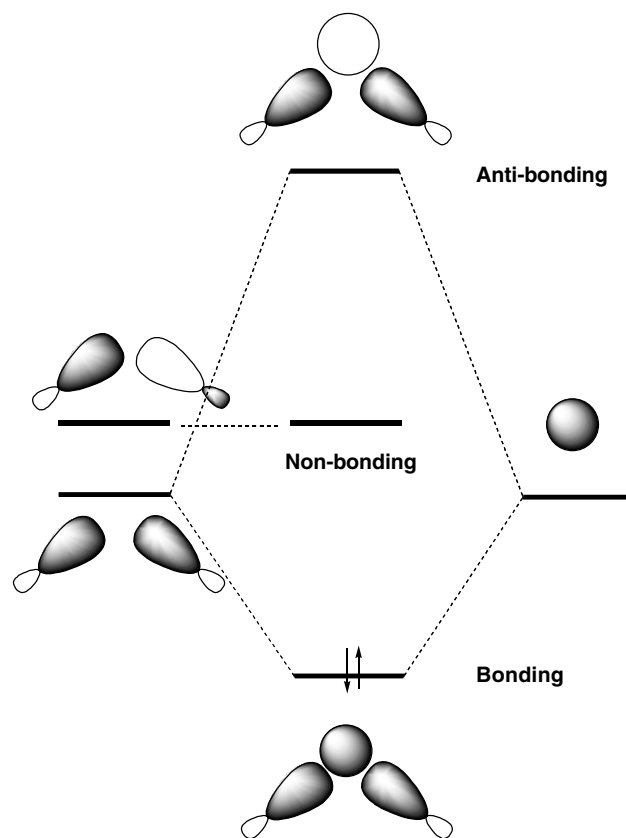


Fig. 13. A representation of three-centre bond in bridged hydrido complexes.

Fig. 14 provides some examples of the relevance of this principle to transition organometallic chemistry. The orbitals associated with the bridging hydrogens are added to the number of total available orbitals. The methodology may be extended to polynuclear hydrido-cluster compounds.

The description of the bonding in terms of the number of unavailable molecular orbitals introduces an additional degree of flexibility which can prove useful. For example, [(triphos)Co(μ-H)₃Co(triphos)]⁺ has an additional electron pair compared to the related iron complex shown in Fig. 14 and more detailed molecular orbital calculations have indicated that the additional electrons reside in an orbital of e' symmetry which is non-bonding with respect to the hydrogens but weakly antibonding with respect to the metals. This complex is therefore paramagnetic and has a slightly longer metal–metal bond.

The analysis of the frontier molecular orbitals in ML₃ and ML₄ complexes of course leads naturally to the *isobal* analogy which has been widely used in organometallic chemistry. The replacement of π-acceptor ligands by π-donor ligands introduces additional unavailable molecular orbitals which have to be taken

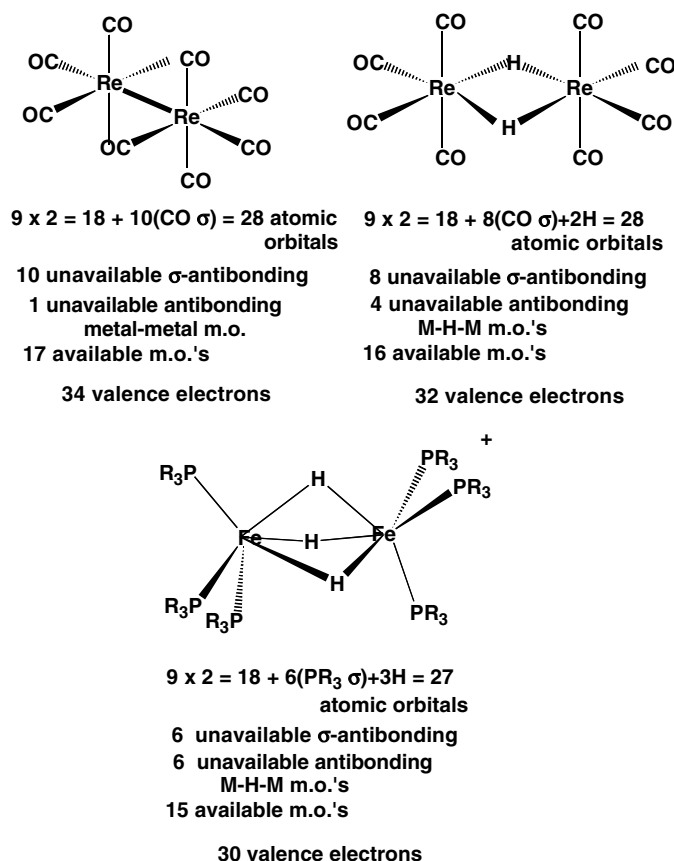


Fig. 14. Examples of how the unavailable orbitals may be used to account for the electron counts in bridged hydrido-complexes.

into account. For example, a $\text{Co}(\text{CO})_3$ fragment with C_{3v} symmetry has three electrons occupying a frontier set of hybrid orbitals as required for a *hypho*-fragment (see Fig. 6) and six electrons occupying an a_1 and e set of orbitals localised mainly on the metal. Replacement of the carbonyls by OR π -donor ligands makes the frontier orbitals unavailable and the frontier orbitals become the lower set of metal localised orbitals. Therefore, formally d^9 and d^3 metal ions give rise to analogous structures (see Fig. 15).

6. Summary

The review has demonstrated that the Complementary Spherical Electron Density Model may be utilised to account not only for molecules which conform to the 18 electron rule but also to complexes which diverge from it. In contrast to recent proposals the p valence orbitals of the metal atoms are not ignored but are shown to make a significant contribution to influencing the geometries of the great majority of transition metal complexes. Although we accept that the p orbitals are very high lying relative

to s and p they nonetheless make a small and crucial contribution particularly in complexes with fewer than 18 valence electrons. Complexes with 16, 14 and 12 valence electrons have to have by definition 1, 2 and 3 unavailable orbitals and filled frontier orbitals with a maximum amount of d orbital character. p-Orbital mixings provide the most effective way of making the unoccupied molecular orbitals less available energetically. The formation of a hybrid in the z-direction and suitable for σ -bond formation requires p_z - d_{z^2} mixing, and the formation of hybrid with π -pseudo symmetry along the z-axis requires d_{xz} - p_x mixing.

In cluster chemistry similar arguments [36] regarding the role of p orbitals were articulated and it was concluded that although the p orbitals did not contribute greatly to the metal-metal bond strengths they did provide an important role in defining the number of unavailable orbitals and therefore the preferred cluster geometry for a given electron count [2]. In many mononuclear transition metal complexes there is a relatively soft potential energy surface connecting alternative geometries and one specific geometry may be favoured because a small admixture of p character

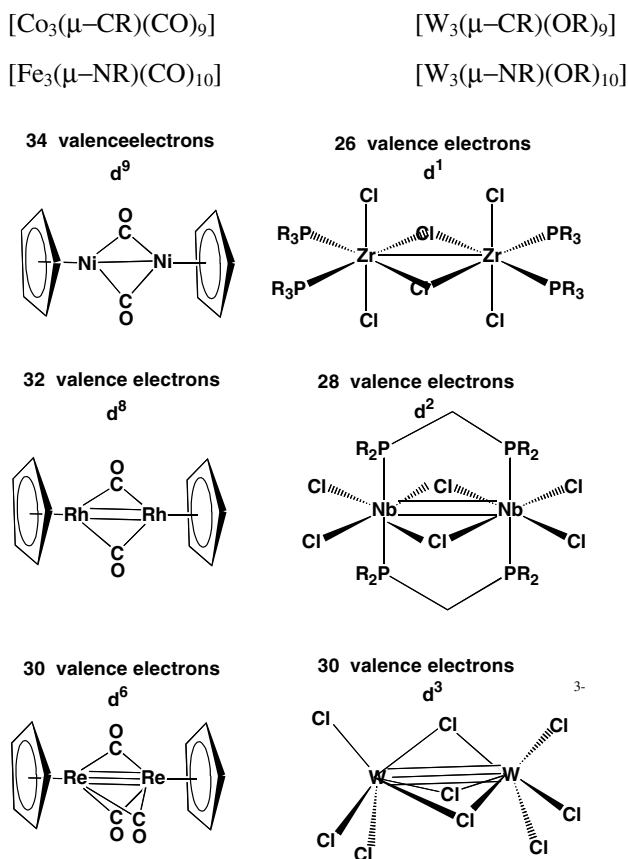


Fig. 15. Examples of metal–metal bonded complexes with π -acceptor and donor ligands.

raises the HOMO–LUMO gap and permits a greater localisation of d orbital character in the highest occupied orbitals.

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References

- [1] W. Hübel, W. Braye, *J. Organometal. Chem.* 3 (1965) 25; W. Hübel, W. Braye, *J. Organometal. Chem.* 3 (1965) 38.
- [2] D.M.P. Mingos, D.J. Wales, *Introduction to Cluster Chemistry*, Prentice Hall, New Jersey, USA, 1990.

- [3] Ch. Elschenbroich, A. Salzer, *Organometallics*, VCH, Weinheim, Germany, 1989.
- [4] N.V. Sidgwick, *The Electronic Theory of Valency*, Clarendon Press, Oxford, UK, 1927.
- [5] G. Parkin, Columbia University, New York, NY, personal communication.
- [6] I. Langmuir, *Science* 54 (1921) 59.
- [7] F. Reiff, *Z. Anorg. Allg. Chem.* 202 (1931) 375.
- [8] N.V. Sidgwick, R.W. Bailey, *Proc. R. Soc. (London) A* 144 (1934) 521.
- [9] L. Pauling, *Nature of the Chemical Bond*, third ed., Cornell University Press, Ithaca, NY, 1960.
- [10] D.M.P. Mingos, *J. Organometal. Chem.* 635 (2001) 1.
- [11] L.E. Orgel, *Introduction to Transition Metal Chemistry*, Methuen, London, 1962.
- [12] M.J.S. Dewar, *Theory of Organic Chemistry*, McGraw Hill, New York, USA, 1969.
- [13] A. Efraty, *Chem. Rev.* 77 (1977) 691.
- [14] E.R. Davidson (Ed.), *Computational Transition Metal Chemistry*, *Chem. Rev.* (100) (2000) 351–807.
- [15] P.D. Lyne, D.M.P. Mingos, T. Zeigler, A.J. Downs, *Inorg. Chem.* 32 (1993) 4785.
- [16] T.A. Albright, J.K. Burdett, M.-H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, USA, 1985.
- [17] G. Frenking, N. Fröhlich, *Chem. Rev.* 100 (2000) 717.
- [18] E. Zintl, *Z. Anorg. Chem.* 1 (1939) 52.
- [19] D.M.P. Mingos, M. Eliañ, M.M.L. Chen, R. Hoffmann, *Inorganic Chemistry* 15 (1976) 1148.
- [20] T.P. Fehlner, *Inorganometallic Chemistry*, Plenum Press, New York, NY, 1992.
- [21] R. Hoffmann, *Solids and Surfaces*, VCH, Weinheim, Germany, 1988.
- [22] D.M.P. Mingos, R.L. Johnston, *J. Chem. Soc. Dalton Trans.* (1987) 647, and 1445; Z. Lin, D.M.P. Mingos, *Struct. Bond.* 71 (1989) 1.
- [23] R.H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, third ed., Wiley-Interscience, New York, NY, 2001.
- [24] C.R. Landis, T. Cleveland, T.K. Firman, *J. Am. Chem. Soc.* 120 (1998) 2641, and references therein.
- [25] R.B. King, *Inorg. Chem.* 37 (1998) 3857.
- [26] D.M.P. Mingos, G. Frenking (Eds.), *J. Organometal. Chem.* 635 (2001) 1.
- [27] C.A. Bayse, D.M. Hall, *J. Am. Chem. Soc.* 121 (1999) 1348, and references therein.
- [28] D.M.P. Mingos, *Essential Trends in Inorganic Chemistry*, OUP, Oxford, UK, 1998.
- [29] D.M.P. Mingos, J.C. Hawes, *Struct. Bond.* 63 (1985) 1.
- [30] T.E. Müller, D.M.P. Mingos, *Trans. Metal. Chem.* 20 (1995) 553.
- [31] D.M.P. Mingos, in: F.G.A. Stone, R. West (Eds.), *Adv. Organometal. Chem.* 15 (1982) 1.
- [32] D.M.P. Mingos, in: G. Wilkinson, E.W. Abel, F.G.A. Stone (Eds.), *Comprehensive Organometallic Chemistry* 3 (1982) 1.
- [33] R.B. King, *Inorg. Chem.* 7 (1968) 1044.
- [34] M.M. Millar, T. O'Sullivan, N. de Vries, S.A. Koch, *J. Am. Chem. Soc.* 107 (1985) 3714.
- [35] P. Kubacek, R. Hoffmann, *J. Am. Chem. Soc.* 103 (1981) 4320.
- [36] R.G. Woolley, in: B.F.G. Johnson (Ed.), *Transition Metal Clusters*, Wiley and Sons, Chichester, UK, 1980, p. 607; R.G. Woolley, *Nouv. J. Chim.* 5 (1981) 441.