Dalton Perspectives

Structural and Bonding Patterns in Tetrahedral and Pseudo-tetrahedral Transition-metal Complexes containing π-Donor Ligands

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The competition between ligands for energetically accessible metal orbitals underscores not only the ground-state metal–ligand bond parameters in a complex but is also responsible for its intrinsic reactivity, influencing among other things bond polarities and ease of displacement of ligands from the metal centre. *cis*/*trans* Influence and *cis*/*trans* effect are terms commonly used to describe the competition between ligands in square-planar and octahedral co-ordination complexes where mutually *cis*- and *trans*-ligand alignments occur.[1] Such terms are not appropriate for describing the competition between ligands in co-ordination environments where the orbitals are no longer directed along, or perpendicular to, the metal–ligand axes. A good example is the tetrahedral geometry whose traditional representation within a cube (with the x, y and z axes emerging from the centres of the faces) is shown in Fig. 1. Competitive effects are, therefore, not so readily assessed for such species and it is often necessary to resort to quantum chemical calculations. However, the tetrahedral geometry holds particular attractions for the study of competitive ligand π bonding due to the ability of metals in this co-ordination geometry to accommodate up to four multiply bonded groups all of which necessarily engage in competition for the available p and d metal orbitals capable of π bonding.[2]

In this perspective we shall examine a series of tetrahedral and pseudo-tetrahedral compounds containing ligands of differing π-bond capacities with a view to evaluating the consequences of π competition on the bonding and orientation of ancillary groups. We shall include within the definition of tetrahedral molecules complexes containing polyene or polyenyl ligands which are considered to occupy a single co-ordination site. Extended Hückel calculations by Hoffmann and co-workers[3,4] on half-sandwich carbonyl complexes of the type [M(cp)(CO)$_2$L] and [M(cp)(CO)(NO)L] (cp = cyclopentadienyl) and on bis(cyclopentadienyl) metal complexes[5] first laid the foundations for an understanding of the factors influencing the preferred orientations of ligands (L) such as carbene, alkene, alkyne and allyl with respect to the ancillary cyclopentadienyl ligands in these pseudo-tetrahedral environments. During the past 15 years or so since these studies, there have been many more complexes synthesised that display related orientation preferences of ancillary 'single-faced' π ligands, not only with cyclopentadienyl co-ligands but also with relatively hard π-basic groups such as 'oxo' and 'imido'. It is the objective of this perspective to draw together these seemingly quite different yet in many respects structurally related systems, to assess the influence of different π-bonded ligands on the structural patterns observed and to develop a simple unified approach to predicting ligand orientations and relative π-bond strengths in these tetrahedral and pseudo-tetrahedral environments.

Triad Representation of 'Tetrahedral' Molecules

To assist the analysis, a simple triad representation of a tetrahedral molecule will be used. If we consider a tetrahedral molecule containing the four ligands A, B, C and D and view the molecule along the A–M axis, then the three ligands B, C and D present a triad which is conveniently represented using the triangle notation below (right).

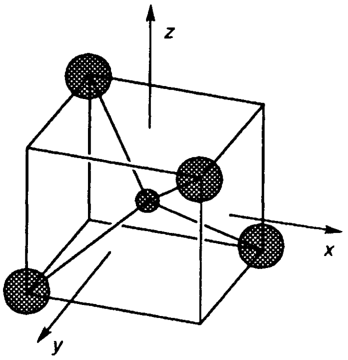
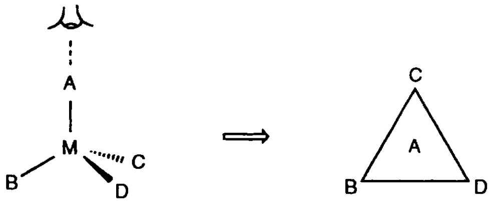
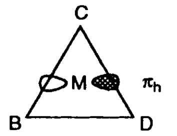
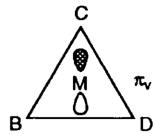


Fig. 1 Relationship of ligand positions with respect to x, y, z axes in a tetrahedral complex



Here, the metal lies above the the plane defined by B, C and D and directly beneath the ligand A which lies at the centre of the triangle along the normal to the BCD plane. If A is capable of π bonding to the metal, it could interact with either (or both) of





the π-symmetry orbitals (π$_h$ or π$_v$) in the diagrams above which illustrate the MBCD pyramid as viewed from A. Note that π$_h$ and π$_v$ are represented as p-type orbitals lying parallel to the BCD plane, but they could equally be forward-projecting lobes of dπ orbitals or, as is more likely the case, hybrids of both p and d orbitals. This representation captures the essence of molecular orbital (MO) calculations, in which Hoffmann and co-workers[3,4] aligned the z axis along the A–M vector and where C is cp and B, D are carbonyl or nitrosyl ligands.

Note that the metal orbitals have been shown aligned (for convenience) with respect to the M–C axis, but it is evident that the orbitals could also be orientated with respect to either the M–B or M–D axis. Since the π-bonding ligands are in competition for the available metal dπ-symmetry orbitals in a tetrahedral environment, the orientation of the available π-symmetry orbitals for ligand A will in effect depend on which of ligands B, C or D dominates the π bonding.

Ligand Types

Before proceeding further, we first need to consider the electronic and orbital characteristics of the various types of ligands. Table 1 shows the frontier orbital symmetries of a variety of fragments, classified as σ, π or δ according to their potential for bonding to the metal; the π-symmetry orbitals are assigned h or v subscripts depending on whether they align with the 'horizontal' or 'vertical' metal π orbitals in the diagrams in the previous section.

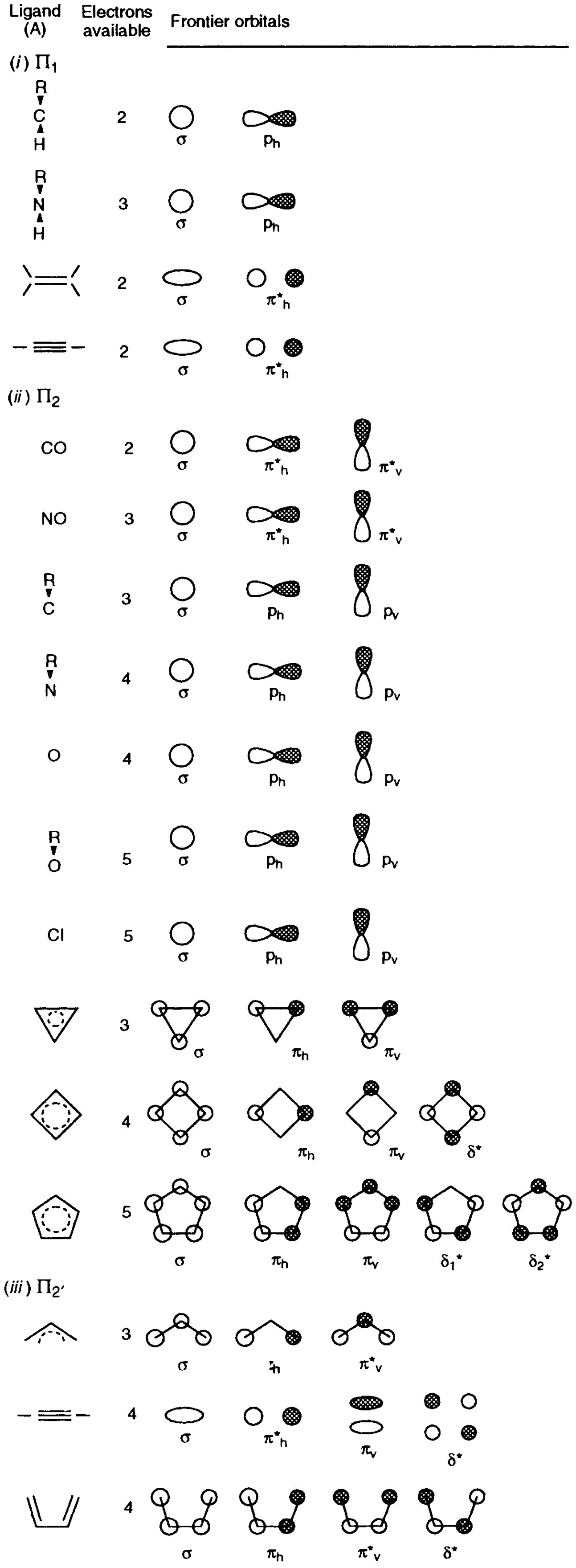
The ligands are grouped according to the number of π-symmetry orbitals available for bonding to the metal: (*i*) Π_1-type ligands; these have only one π-symmetry orbital and therefore can form at most a double bond to the metal consisting of a σ and π interaction (1σ, 1π). Such ligands have, on occasion, been referred to as 'single-faced' π ligands; and (*ii*) Π_2-type ligands; these possess two π-symmetry orbitals and thereby can form two equivalent π bonds potentially giving rise to a triple bond to the metal (1σ, 2π). It is helpful to make a distinction between ligands with degenerate π levels and those with π orbitals differing in energy, since for the latter one of the π orbitals becomes energetically more accessible to the metal. These latter ligands with non-degenerate π orbitals we shall denote as $\Pi_{2'}$.

Fig. 2 shows the principal s and p (or σ and π) ligand orbitals for each ligand type with accompanying energy level diagrams to emphasise the similarities and differences within, and between, categories. Thus, for the Π_1 ligands, the singlet carbene has a vacant p orbital and so is able to accept π-electron density from the metal, while the amido ligand has three electrons distributed between its two available orbitals and so will act as a net π donor to the metal. Simple energy level diagrams can be derived for the cyclic Π_2 ligands, C_nH_n, by standing the ring on an apex. It can be seen that the π levels are degenerate* in each case and therefore directly comparable with CR, NR and OR. By contrast, it can be seen that the π levels for $\Pi_{2'}$ ligands are non-degenerate.

We shall probe the orientation effects imposed on Π_1 ligands due to the competition between Π_2 (and/or $\Pi_{2'}$) ligands as a 'measure' of competitive π-bonding effects. First, it is necessary to have an idea of the relative π-donor strengths of the Π_2 ligands; these are generally found to correlate with the nuclear charge (or electronegativity) of the main group atom (Table 2).[2] The group to the left within a given row is thus expected to form the stronger π bonds and the strength of π interaction will decrease along the diagonal from top left to bottom right.

Thus, a relative ordering of π-bonding strengths for these ligands of second row elements can be derived: RC > N > RN > O > OR > F. This ordering is supported by the trend in CO stretching frequencies observed for a limited series of octahedral complexes in which the multiply bonded group lies *trans* to the carbonyl ligand.[2] For the complexes $[W(O)Cl_2(CO)(PMePh_2)_2]$,[6] $[W(NBu^t)Cl_2(CO)(PMePh_2)_2]$[7] and $[W(CBu^t)Cl(CO)_2(Ph_2PCH_2CH_2PPh_2)]$,[8] ν(CO) decreases in the order O > RN > RC indicating that the RC unit releases a greater amount of electron density onto the metal centre which

Table 1 Classification of ligands by the number and type of their frontier orbitals (the electrons available correspond to the neutral ligand fragment)



Ligand (A)	Electrons available	Frontier orbitals				
(*i*) Π_1						
$R\rightarrow C\leftarrow H$	2	σ	p_h			
$R\rightarrow N\leftarrow H$	3	σ	p_h			
	2	σ	π^*_h			
–≡–	2	σ	π^*_h			
(*ii*) Π_2						
CO	2	σ	π^*_h	π^*_v		
NO	3	σ	π^*_h	π^*_v		
$R\rightarrow C$	3	σ	p_h	p_v		
$R\rightarrow N$	4	σ	p_h	p_v		
O	4	σ	p_h	p_v		
$R\rightarrow O$	5	σ	p_h	p_v		
Cl	5	σ	p_h	p_v		
	3	σ	π_h	π_v		
	4	σ	π_h	π_v	δ^*	
	5	σ	π_h	π_v	δ_1^*	δ_2^*
(*iii*) $\Pi_{2'}$						
	3	σ	π_h	π^*_v		
–≡–	4	σ	π^*_h	π_v	δ^*	
	4	σ	π_h	π^*_v	δ^*	

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* It should be noted that a Jahn–Teller distortion would remove the degeneracy for an isolated fragment. The view shown in Fig. 2 is adopted to assist comparisons between the different ligand types and for the purpose of electron 'book-keeping'.

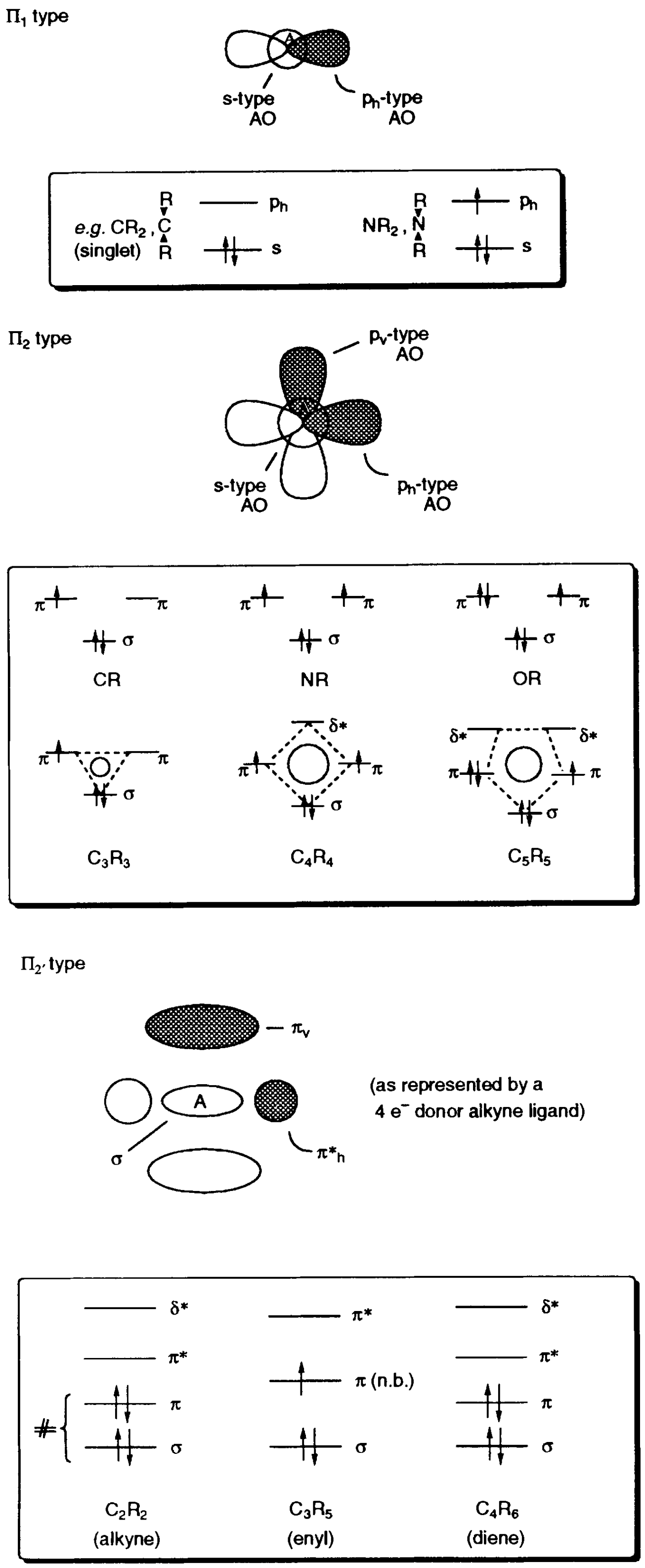

Fig. 2 Frontier orbital degeneracies of some representative ligands. The two orbitals indicated by # are the degenerate pair of filled alkyne C–C π-bonding molecular orbitals, but are shown as non-degenerate because of their different orientations with respect to the metal–ligand axis; n.b. = non-bonding

is then off-loaded into the π* acceptor orbital of the CO ligand resulting in a reduced CO stretching frequency.

Table 2 The trend in π-donor capacity for some isoelectronic/isolobal species

Ligand electrons available	Isoelectronic species		
3	RC	N	
4		RN	O
5			RO	F

Decreasing π-donor capacity

Increasing electronegativity

Isonumerality

It is useful to compare ligand fragments that are capable of contributing equivalent numbers of electrons. Such species can be strictly isoelectronic (*e.g.* the charged fragments N^{3-}, O^{2-}; RN^{2-}, RO^- *etc.*) but this need not necessarily be so (*e.g.* RC, C_3R_3; RN, C_4R_4 *etc.*). Therefore, the term isonumeral is proposed to designate ligands capable of contributing the same number of electrons to the metal valence shell. For example, we consider an alkoxo unit, OR, to be a five-electron ligand to reflect the *maximum* number of electrons it can potentially denote to the metal, and in this respect it is isonumeral with the η^5-cyclopentadienyl ligand.† As far as the symmetries of their filled or half-filled frontier orbitals are concerned, the groups cp and OR may also be regarded as being pseudo-isolobal. It should, however, be noted that they are not strictly isolobal, since not only does the cp ligand use five atoms to bind to a metal compared with one for the alkoxo group, but it also has δ-symmetry orbitals available for back donation (Table 1). Nevertheless, here it is wished to emphasise the similarities between what, at first sight, appear to be quite different ligands, similarities which may provide useful insight into understanding the structural patterns and relationships between seemingly unrelated complexes. Thus, in the following sections, it will be useful to extend the strict isolobal concept to embrace a diverse range of related pseudo-isolobal ligand fragments. Indeed, it is helpful to extend the use of the term isonumeral to include metal–ligand fragments that have the same number of electrons in the metal valence shell even though the lobal characteristics of the ligands involved do not strictly allow them to be described as isolobal. For example, the isoelectronic series: Ti(OR), V(NR), Cr(NR) (below) may be extended to include the

$$\underset{(4)\ (5)}{\mathrm{Ti(OR)}} \xleftrightarrow[\sigma]{} \underset{(5)\ (4)}{\mathrm{V(NR)}} \xleftrightarrow[\sigma]{} \underset{(6)\ (3)}{\mathrm{Cr(CR)}} \xleftrightarrow[\sigma]{} \underset{(7)\ (2)}{\mathrm{Mn(CO)}}$$

isonumeral manganese carbonyl fragment, Mn(CO). This series of metal–ligand fragments clearly forms part of a much more extensive isonumeral/'isolobal' family which can be conveniently represented in the form of a matrix (Table 3) in which each entry gives the electron count for the metal–ligand fragment; the diagonals indicated then correspond to isonumeral series.

Note that on the basis of such arguments we are able to compare CO, a ligand usually responsible for stabilising low-oxidation-state metal complexes, with ligands such as CR, NR and OR which are more normally associated with stabilising high-oxidation-state metal environments. The key difference

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† The reader should bear in mind that for the purposes of electron 'book-keeping' in relation to the 18 electron rule, OR would normally be regarded as either a one- or three-electron ligand (applying a neutral counting formalism).

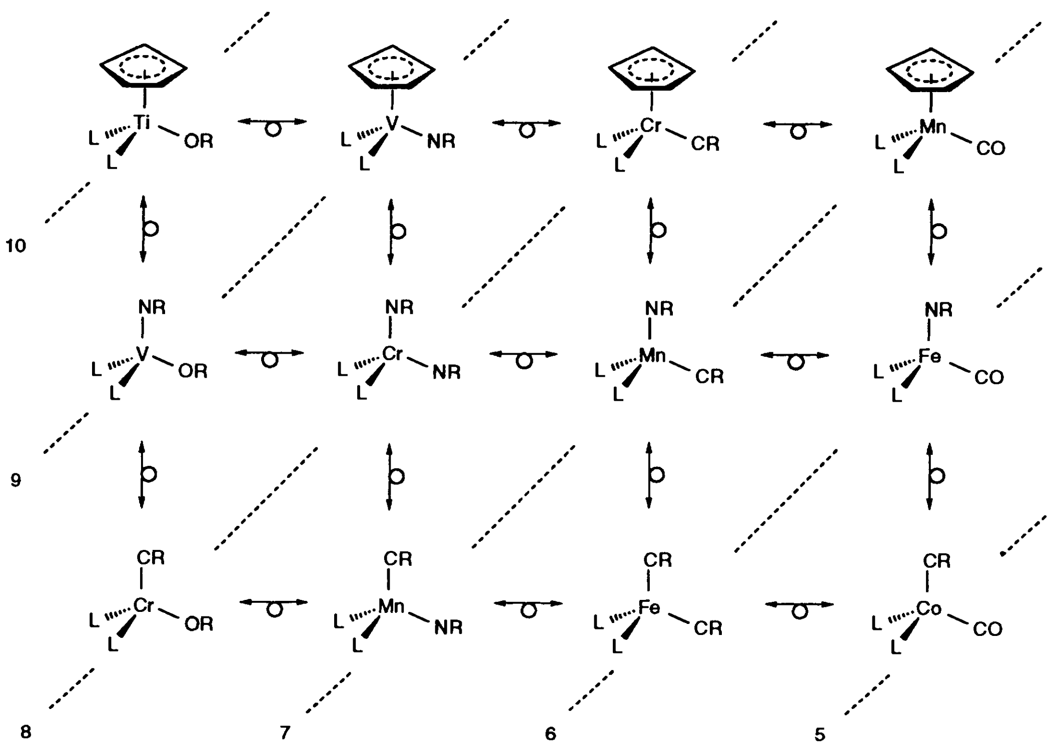


Fig. 3 Isonumeral/'isolobal' relationships for complexes [ML$_2$(L′)L″] showing variations in L′, L″ and M (total number of electrons supplied by L′ and L″ shown on diagonals). A single line between the metal and ligand is used as an indicator of connectivity and does not imply anything about bond order

Table 3 Electron counts for a selection of ML units

Ligand* \ M	Ti	V	Cr	Mn	Fe
CO, N$_2$ (2)	6	7	8	9	10
CR, NO (3)	7	8	9	10	11
NR (4)	8	9	10	11	12
cp, OR (5)	9	10	11	12	13

Isonumeral series of ML units/fragments

* Figures in parentheses refer to the number of available ligand electrons

Table 4 Some 'isoelectronic'/'isolobal' relationships

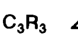
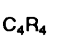
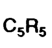
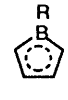
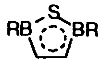
Ligand electrons available	'Isoelectronic' species			
3	RC	N	C$_3$R$_3$ 	C$_3$R$_5$ 
4	RN	O	C$_4$R$_4$ 	C$_4$R$_6$ 
5	RO	F	C$_5$R$_5$ 	
	Π$_2$			Π$_{2'}$

Table 5 Some cyclopentadienyl analogues

Ligand electrons available	'Isoelectronic' species		
3			
4			
5			

between CO and the others is that, although they all possess filled π orbitals, those of CO are strongly bonding between carbon and oxygen and therefore not available for dative π bonding to a metal, whereas the filled π orbitals of OR, *etc.* are lone pairs which are available to form O ⟶ M dative π bonds. By contrast, CO employs its empty π* anti-bonding orbitals for π back-bonding. Because such ligands use orbitals of similar symmetry yet lie at opposite ends of the π-acidity/basicity spectrum, they may be regarded as complementary.

The 'isolobal' and isonumeral analogy can, then, be readily extended to cyclic hydrocarbon Π$_2$ ligands (Table 4) and even taken a little further to encompass acyclic or cyclic Π$_{2'}$ ligands including a variety of heterocyclic ring systems, for example the bora- and phospha-cyclopentadienyl analogues shown in Table 5.

Exploiting these extensions of the conventional isoelectronic and isolobal definitions, it is possible to construct tables of pseudo-isolobal species which are useful in comparing familiar complexes with more distant relatives. Consider for example the series of complexes shown in Fig. 3 which may be considered to be derived from [MnL$_2$(cp)(CO)] (top right) by incremental increases in the combined ligand electron count as the transition series is crossed from right to left. A similar series can be derived for the cyclic hydrocarbons shown in Fig. 4. Some recent examples where such isonumeral and 'isolobal' relationships between cyclic hydrocarbons and imido groups occur will be highlighted in a later section.

Of particular relevance to the following sections of this study are the Π$_1$ ligands such as alkylidene (CHR), amido (NHR),

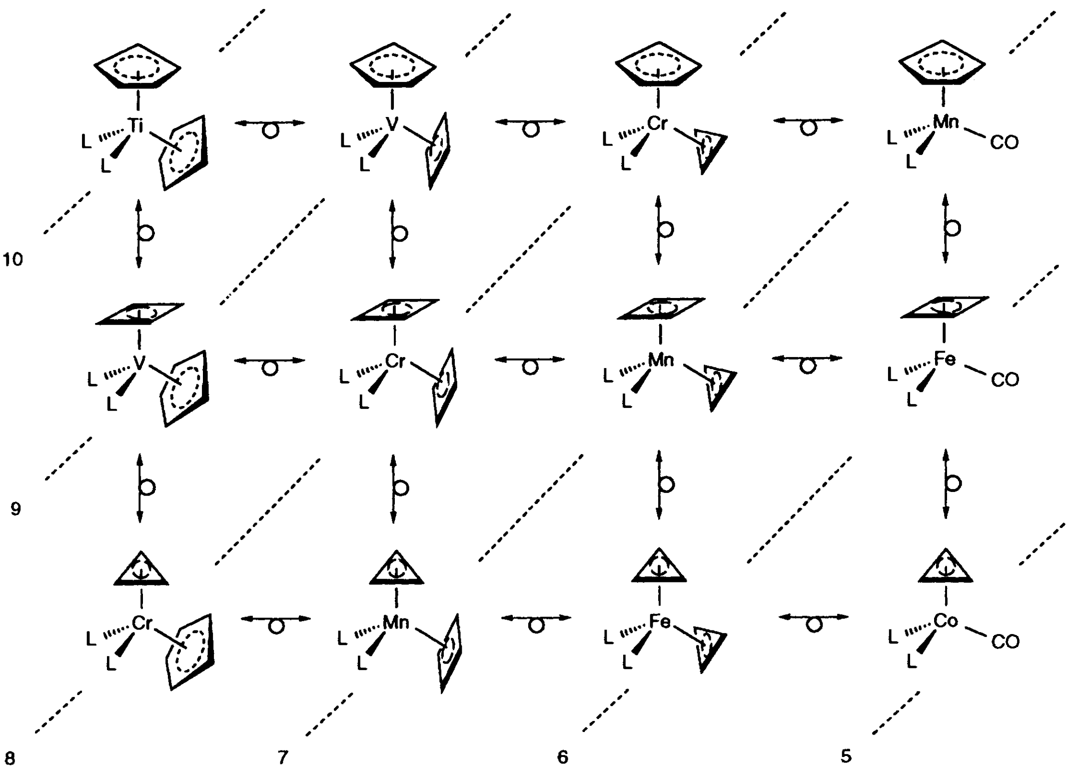


Fig. 4 Isonumeral/'isolobal' relationships for complexes $[ML_2(L')L'']$ showing variations in L', L″ amd M focusing primarily on C_nH_n ligands (total number of electrons supplied by L' and L″ shown on diagonals)

alkene (C_2R_4) and the 'two-electron' alkyne ligand (C_2R_2), which have available only one π orbital for interaction with a metal centre and so an orientational preference should be observed depending upon which of the metal π_h or π_v orbitals is the most accessible. In the following sections, we shall examine the effect of first one of the three ligands in the triad dominating the π-donor bonding and then the situation where two ligands possess approximately equal π-donor bond strengths.

Complexes possessing a Single Dominant Π_2-Donor Ligand

The bonding in a pseudo-tetrahedral complex containing a strong Π_2-donor ligand is, in general, found to be dominated by the π-donor group. This can be understood from an orbital viewpoint by considering the d orbital splitting diagram for a tetrahedral species derived (unconventionally) with the *z* axis aligned along the Π_2-ligand–metal axis[9] (Fig. 5). Here, instead of the usual 'three over two' pattern, the degeneracy of the upper triplet is split into an e and a_1 set. There are now two sets of doubly degenerate orbitals, the upper set allowing π interactions with the π donor to be maximised while the lower e set aligns orthogonal to the M–Π_2-ligand bond thereby minimising interactions with the Π_2 ligand. Since we are now viewing the molecule side-on to the M–A axis, it is apparent that d_{xy} effectively corresponds to π_h viewed from A while both d_{xz} and dz^2 can form π interactions with A in the vertical plane (π_v). Note that d_{xz} is already engaged in π bonding with the 'axial' Π_2 ligand and that the d_{z^2} orbital is σ bonding with respect to the Π_2 ligand whilst also being capable of forming a π interaction with A of the type illustrated in Fig. 6. This provides a simple illustration of the competition for ligand–metal π bonds in a 'tetrahedral' geometry.

Let us now take a look at some examples. First, consider the four-co-ordinate imido–alkylidene complexes $[M(NC_6H_3Pr^i_2\text{-}2,6)(CHBu^t)(OBu^t)_2]$ (M = Mo or W) and $[Mo(NBu^t)(CHBu^t)\{OCH(CF_3)_2\}_2]$ synthesised by Schrock[10] and Osborn[11] and their co-workers respectively; a triad representation of

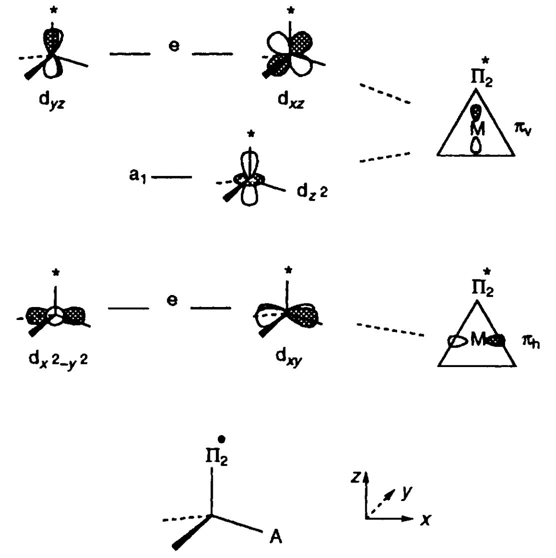


Fig. 5 The d orbital splitting diagram for a tetrahedral complex possessing a single dominant Π_2-donor ligand (derived with the *z* axis aligned in the direction of the Π_2 ligand)

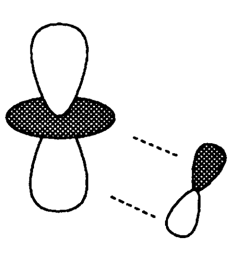
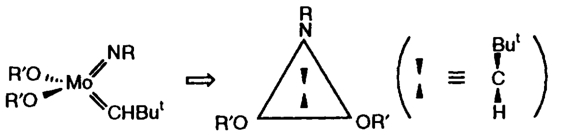
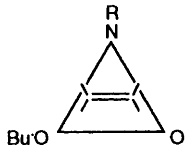


Fig. 6 The 'side-on' π interaction between a d_{z^2}-type metal orbital and a π-symmetry ligand orbital

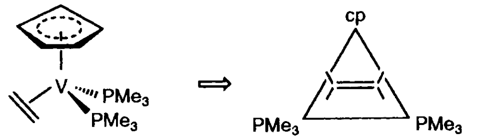
these molecules is shown below alongside the more conventional view. The imido ligand and the two alkoxides are both Π_2 ligands, *i.e.* capable of forming two π interactions in addition to a σ bond to the metal.



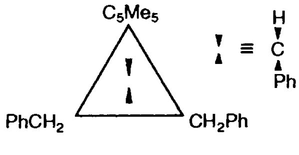
The orientation of the alkylidene substituents established by X-ray crystallography[10] is indicated by the wedge shaped lines and shows alignment in the M–N–C(alkylidene) plane. For steric reasons the *tert*-butyl substituent lies *syn* to the imido group and so effectively points to the strongest Π_2 ligand in the triad. A related alkene complex, $[M(NR)(C_2R_4)(OBu^t)_2]$, not to our knowledge synthesised to date, would be anticipated to have the alkene orientation depicted below that allows its π-acceptor orbital to align with π_h.

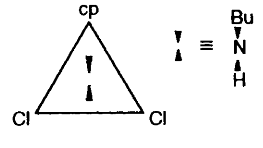


A similar situation is found in cyclopentadienyl metal complexes, an example being the vanadium complex $[V(cp)(PMe_3)_2(C_2H_4)]$ synthesised by Teuben and co-workers.[12] The cyclopentadienyl ligand, considered to occupy a single coordination site in the tetrahedron, bonds to the metal using a combination of one σ and two π-donor interactions, the same as for the imido group in the previous example. Since the PMe_3 ligands cannot function as π donors, the cyclopentadienyl ligand dominates in this pseudo-tetrahedral d^4 complex, a point the alkene ligand helpfully 'underlines' by its orientation viewed in the triad below.

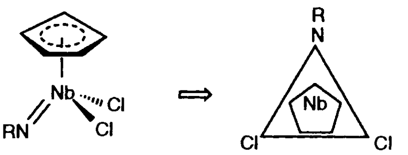


The dominance of the cyclopentadienyl ligand is also apparent in the complexes $[Ta(C_5Me_5)(CHPh)(CH_2Ph)_2]$[13] and $[Ti(cp)Cl_2(NHBu^t)]$[14] in which the planes of the alkylidene and amido substituents align with the metal–ring centroid vector, effectively pointing to the cyclopentadienyl ligand as the dominant π-bonding ligand. If the π system in the ligand is extended, *e.g.* in $[Ti(cp)Cl_2(=N=CBu^t_2)]$,[15] the preferred orientation of the substituents changes by a 90° twist, as expected for alignment of the nitrogen p orbital with π_h.

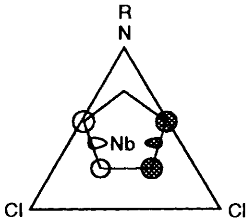




An interesting situation arises when the strongly π-donating NR unit is in competition with a strong polyenyl π donor such as the cyclopentadienyl ligand. A series of half-sandwich niobium,[16] molybdenum[17] and rhenium[18] compounds of general formula $[M(cp)(NR)Cl_2]$ shows a significant ring-slippage along with an orientation preference for the C_5R_5 ring such that one of the ring carbons eclipses the M–NR bond (the ring is orientated so as to 'point' to the NR group). This is illustrated below for $[Nb(cp)(NR)Cl_2]$ using the triad notation viewed down the ring centroid–metal axis.



The ring-slippage has been attributed in general terms to the strong *trans* influence of the imido ligand leading to a weakening of the two metal–carbon bonds *trans* to the NR group and a consequent adjustment towards an allyl–ene cp bonding situation.[16–18] However, the ring distortion also follows from our previous observations for a 'single dominant' NR π-donor ligand. For the two π-type interactions of the cyclopentadienyl group, it is expected that the interaction perpendicular to the M–N bond (**I**), *i.e.* with π_h, will be stronger than with the metal π-symmetry orbital (π_v) nearly parallel to the M–N bond (**II**). Consequently, the filled cp π-level in **II** will remain largely ligand centred and give rise to the allyl–ene distortion.



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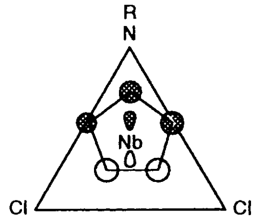
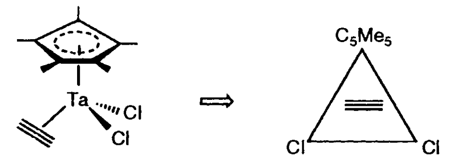
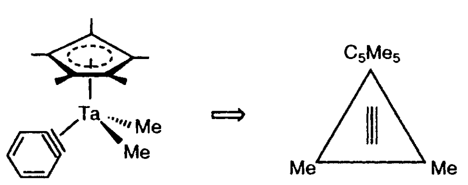
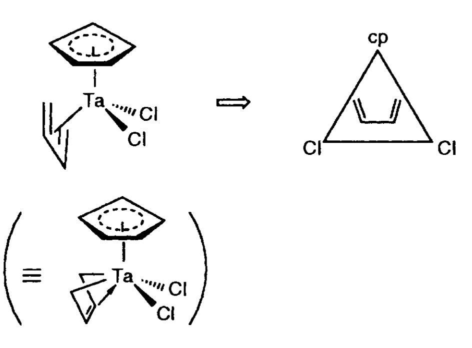


II

Orientation effects are also often seen for $\Pi_{2'}$ ligands in competition with strong Π_2 donors. The strongest π interaction is again expected to be with π_h, but the orientation of the $\Pi_{2'}$ ligand is less easily predicted since their frontier π-symmetry orbitals are non-degenerate (see Fig. 2) and either of the π interactions could dominate. Just which will dominate will depend on a number of factors including (*i*) the energies of the

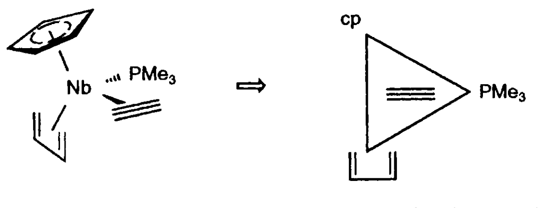






ligand π and π* levels relative to π_h and π_v of the metal fragment and (*ii*) the directional properties of the ligand π orbitals (with respect to the metal). For the four-electron acetylene and benzyne complexes $[Ta(C_5Me_5)(PhC{\equiv}CPh)Cl_2]$[19] and $[Ta(C_5Me_5)(C_6H_4)Me_2]$,[20] the orientation of the diphenylacetylene is the same as that expected for a Π_1 ligand, indicating that the π bonding may be dominated by alignment of the π*-acceptor orbital with π_h. However, steric factors have also been suggested to play a role since the less bulky benzyne ligand is found to align in a perpendicular orientation. The alignment of the butadiene ligand in $[Ta(cp)(C_4H_8)Cl_2]$[21a] is consistent with the butadiene π-donor orbital interacting with π_h, the π* acceptor orbital then aligning with π_v.

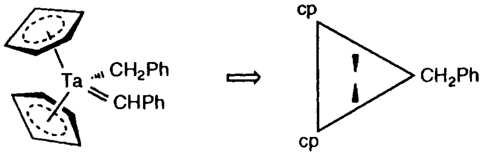
A useful illustration of how the π-bonding capacities of Π_2 and Π_2' ligands can be compared in a complex is provided by the example, $[Nb(cp)(\eta^4\text{-}C_4H_6)(\eta^2\text{-}PhC{\equiv}CMe)(PMe_3)]$[21b] which, in addition to possessing a Π_2 cp ligand, has two different $\Pi_{2'}$ ligand systems, the butadiene and alkyne groups. Without knowing anything about the detailed MO description of the complex, the orientation of the alkyne (see the triad representation below) indicates that the π-donor bonding is dominated by the cp and butadiene ligands, a point reinforced by low-frequency ^{13}C NMR shifts for the acetylenic carbons which reflect little or no donation of electron density from the orthogonal π system of the alkyne.

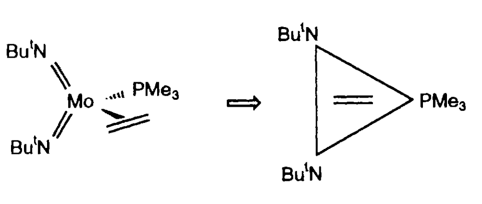


To summarise, in this section we have seen that in complexes containing one strong Π_2-donor ligand, the orientations of Π_1 co-ligands such as C_2R_4, CHR and NHR reflect the presence of that ligand: C_2R_4 or C_2R_2 identify the strong π donor by 'underlining' it, while the substituents on ligands such as CHR and NHR point towards it.

Complexes possessing Two Dominant Π_2-donor Ligands

When a complex already contains two strong Π_2-donor ligands, a third Π_1 ligand will be expected to orientate so as to avoid competition with the two π-donor groups. For example, the benzylidene ligand in $[Ta(cp)_2(CHPh)(CH_2Ph)]$[22] aligns one lobe of its p orbital towards the σ-bonded CH_2Ph ligand with the other bisecting the two cp groups (the orientation of the triad shown below is chosen here to match the conventional representation of the molecule). This is, of course, the well established bent metallocene geometry, for which the electronic constraints are well documented both through their extensive derivative chemistry[23] and through detailed quantum chemical calculations.[5,24]





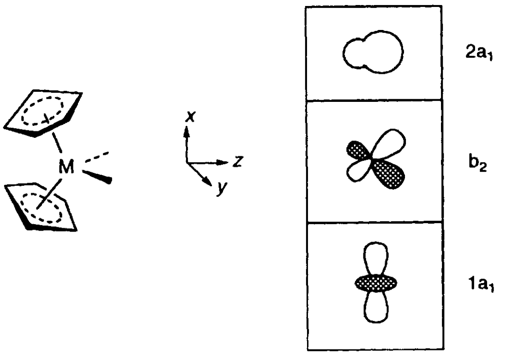
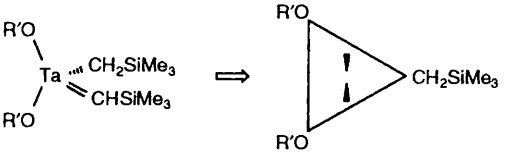


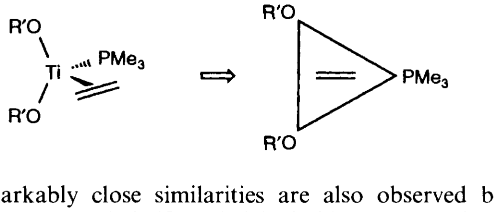
Fig. 7 The shapes of the frontier orbitals of the bent-metallocene fragment, $M(cp)_2$ (projecting in the *yz* plane)

For a bent-metallocene fragment, $M(cp)_2$, the ancillary ligands interact with the three low lying orbitals which project in the *yz* plane (Fig. 7), the so-called 'equatorial binding plane' or 'binding wedge' of the metallocene fragment. The orientations of Π_1 ligands will then be dominated by interactions of their p or π-symmetry orbitals with metal π-symmetry combinations in this plane.

Less obvious is the 'metallocene-like' orientation preference for the ethylene ligand in the bis(imido) complex $[Mo(NBu^t)_2(C_2H_4)(PMe_3)]$.[25] An explanation is provided by the similarities in the symmetry properties of the frontier orbitals of the cyclopentadienyl and imido fragments, both of which bind to a metal *via* a combination of 1σ and 2π donor interactions as outlined in Table 1. Some of the implications for the binding of such '1σ,2π' ligands to metal centres have been discussed by Schrock and co-workers[26] and used to explain the orientation preference of the η^2-acetone ligand in $[W(NC_6H_3Pr^i{}_2\text{-}2,6)_2(\eta^2\text{-}O{=}CMe_2)(PMe_2Ph)]$.[26a]

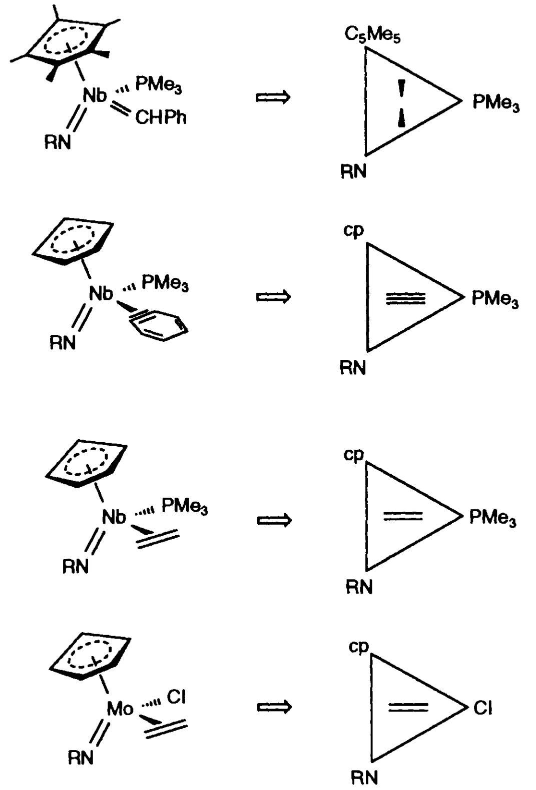
Bent metallocene-like orientations are also seen in the bis(phenoxide) complexes $[Ta(OC_6H_3Bu^t{}_2\text{-}2,6)_2(CHSiMe_3)(CH_2SiMe_3)_2]$[27] and $[Ti(OC_6H_3Ph_2\text{-}2,6)_2(C_2H_4)(PMe_3)]$[28] described by Rothwell and co-workers. Here, the two phenoxide ligands (OR'), which like cp and NR bond through σ + 2π interactions, dominate the bonding leading to metallocene-like orientations of the alkylidene and ethylene group respectively.





Remarkably close similarities are also observed between metallocenes and half-sandwich imido systems based on niobium[29] and molybdenum.[17] For example, the alignment and bond parameters associated with the benzyne ligand in the η^2-benzyne derivative[29b] below mirror in virtually all respects the zirconocene derivative $[Zr(cp)_2(\eta^2\text{-}C_6H_4)(PMe_3)]$ described by Buchwald *et al*,[30] while the benzylidene complex[29b] may be regarded as a direct analogue of $[Zr(cp)_2({=}CHCH_2Bu^t)(PMe_3)]$ reported by Schwartz and co-workers.[31]

Indeed, calculations on the half-sandwich niobium systems support the presence of metallocene-like frontier orbitals for the Nb(cp)(NR) fragment[16b] and reinforce the close relationship evident between M(cp)$_2$, M(cp)(NR) and [M(NR)$_2$] fragments,[16,26a,29] the more general implications of which are discussed in the following section.

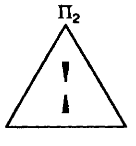


Similar reasoning accounts for the orientation of the acetylene ligand in the half-sandwich oxo complex [Mo(cp)(O)(CF$_3$C≡CCF$_3$)(SC$_6$F$_5$)].[33] Here, an 18 electron count is achieved with the acetylene acting as a two-electron (Π_1) ligand and the acetylene is directed towards the SC$_6$F$_5$ group showing that the cyclopentadienyl and oxo ligands dominate the π-donor bonding.

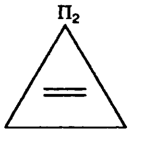
However, when the oxo ligand is replaced by carbonyl, the cp and SC$_6$F$_5$ ligands now dominate the π-donor bonding and the acetylene responds like a compass needle, reorientating towards the CO ligand.[33] Thus, here the Π_1 acetylene may be used as an indicator of relative ligand π-donor strength. Analogous orientation effects are also seen in the tungsten complexes [W(cp)(O)(PhC≡CPh)Ph][34] and [W(cp)(O)(PhC≡CH)(CH$_2$CO$_2$Et)],[35] where the acetylene aligns with the Ph and CH$_2$CO$_2$Et groups respectively, and even in heterobimetallic systems such as [(cp)(O)(PhC≡CPh)MoRu(CO)$_2$(cp)][36] where the molybdenum-bound acetylene aligns with the Mo–Ru bond.

We can conclude from the examples discussed in this and the previous section that ligands capable of forming two strong π bonds tend to dominate the bonding in tetrahedral and pseudo-tetrahedral environments allowing ligands capable of forming only one π interaction to be exploited as sensors to identify the dominant π-bonding groups. In the absence of overriding steric influences, the following simple rules hold.

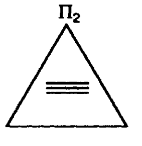
1. For tetrahedral or pseudo-tetrahedral species containing a single dominant Π_2 donor, if a triad notation is employed, the substituents of an ancillary carbene (or alkylidene) ligand will point to the strongest π donor [1(*i*)], while an alkene or alkyne will doubly or triply underline it [1(*ii*) and 1(*iii*)].



1(*i*)

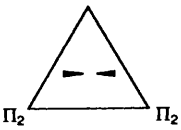


1(*ii*)

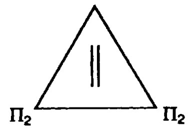


1(*iii*)

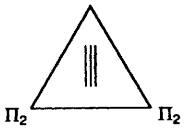
2. For complexes containing two strong Π_2-donor ligands, the alkene and alkyne groups point to the weakest π donor [2(*ii*) and 2(*iii*)], the alkylidene substituents underline it [2(*i*)].



2(*i*)



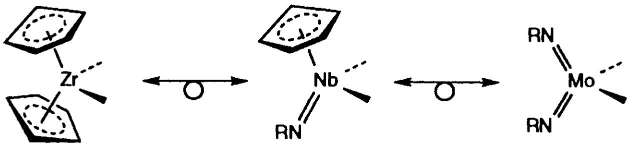
2(*ii*)



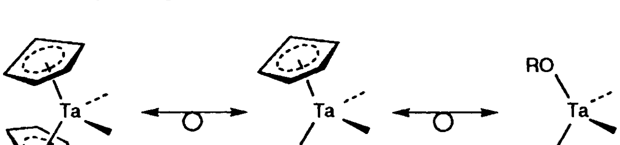
2(*iii*)

Relationships Between Tetrahedral Complexes containing Strong Π-donor Ligands

The examples outlined in the previous section have highlighted the close relationships between complexes possessing donor ligands with similar frontier orbital symmetries. For example, the bonding between metals and CR, NR, OR or cp groups is dominated by a combination of one σ- and two π-interactions (Table 1). The cp group of course also has two δ-symmetry acceptor orbitals available for back-donation but provided these back δ-bonding interactions are weak, they will have minimal impact on the metal–ligand bonding. Since the NR ligand carries a formal 2– charge compared with the singly charged cp group, an 'isolobal' series with identical d electron counts transcends three groups of the transition series, illustrated for Zr, Nb and Mo below. This may be particularly useful for identifying new systems, which by comparison with the well established chemistry of zirconocenes, may offer potential as new catalysts or stoichiometric reagents in organic synthesis. Such a relationship may be extended to other metallocenes (see Fig. 8) and thus provides a useful basis on which to predict or interpret the derivative chemistry of new imido complexes of other transition metals. It may also be used to account for the stability of late-transition-metal imido derivatives such as [Ir(C$_5$Me$_5$)(NBu^t)][45] and [Os(C$_6$Me$_6$)(NBu^t)][46] whose mononuclear 'pogo-stick' structures were perhaps at first a little surprising. However, when the analogy between NR and cp ligands is considered, these complexes can be seen to be closely related to osmocene and [Re(C$_6$H$_6$)(C$_5$H$_5$)] respectively. Recent photoelectron spectroscopic studies by Green and co-workers[47] support this analysis.



Similarly charged cp and OR (or SR) ligands lead to an



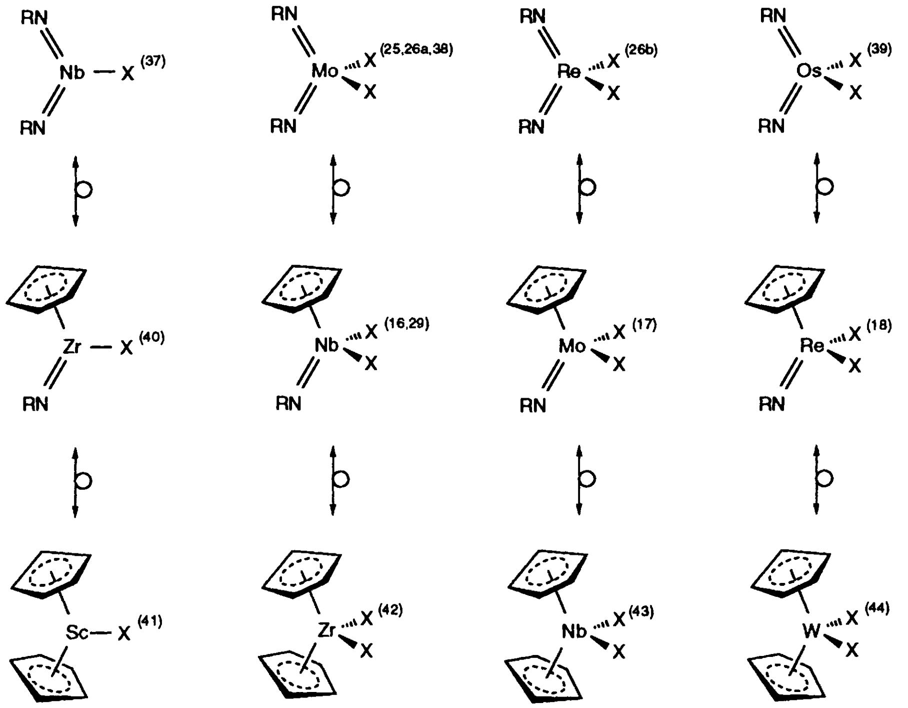


Fig. 8 Relationships between complexes containing $M(cp)_2$, $M(cp)(NR)$ and $M(NR)_2$ fragments (the metals are chosen to highlight systems whose chemistry is currently under development; X is used here to designate a one-electron ligand such as halide or alkyl; in some cases additional two-electron bases may also be attached to the metal centre). Literature references are indicated in parentheses

'isolobal' and isonumeral relationship for complexes of the same metal (illustrated for tantalum).

What other donor ligand combinations might be anticipated to give rise to similar 'isolobal' relationships? First, consider an acetylene ligand which, when acting as a four-electron donor, also binds to a metal using a combination of one σ and two π interactions. Although one of the π interactions is formally derived from a π* acceptor orbital, extensive back-donation from an electropositive metal centre will lead to considerable charge density on the acetylene carbons and make the dianion description $[C_2R_2]^{2-}$ appropriate. The relationship of the bound acetylene to an $[NR]^{2-}$ unit is then apparent. Thus, it might be anticipated that $[Ta(C_5Me_5)(PhC{\equiv}CPh)Cl_2]$ would display characteristics comparable with $[Ta(C_5Me_5)(NR)Cl_2]$ provided that the intrinsic reactivity of the acetylene ligand could be moderated. Relationships then become evident between bis(acetylene) derivatives and complexes possessing combinations of cp, NR and RC≡CR units (Fig. 9). Williams and Schrock[48] have recently described a series of such compounds for rhenium. However, the development of an extensive isolobal chemistry based on acetylene ligands seems unlikely due to their inherent insertion/coupling reactivity at metal centres. More promising are isolobal derivatives based on more robust ligand systems, witness the extensive metallocarborane chemistry based on the analogy with the cp group. A ligand perhaps deserving of attention in early-transition-metal systems is the cyclobutadiene group, which Longuet-Higgins and Orgel[49] noted in the 1950s is ideally suited to forming strong covalent interactions with transition metals. The C_4R_4 group is a four-electron donor with orbital characteristics analogous to the imido group, yet the chemistry of early-transition-metal cyclobutadiene complexes remains largely unexplored.

Such an analogy may be readily extended to heteroatom-containing ring systems such as the six-electron borabenzene anion $[RBC_5H_5]^-$ or the dianionic borollides $[RBC_4H_4]^{2-}$ described by Herberich[50] and Siebert[51] (and the three-dimensional variations on these provided by icosohedral fragments, $[C_2B_9H_{11}]^{2-}$ *etc.*, that interact with metals through C_2B_3 or CB_4 pentagonal faces); these would be expected to form derivatives analogous to established cp and imido systems, and additionally the reduced symmetry of the heterocyclic ring is expected to result in orientation preferences when in competition with strong π-donor groups. Similar orientation effects may be anticipated for other 'non-symmetrical' hetero-atom-containing ring systems such as phosphacyclopentadienyl derivatives containing C_3P_2, C_4P rings, . . . *etc.* of the type described by Mathey *et al.*[52] and Nixon.[53]

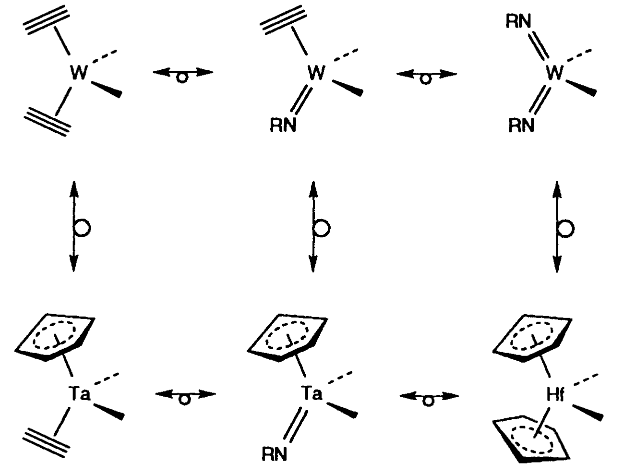


Fig. 9 Relationships between fragments containing combinations of Cp, NR and C_2R_2 ligands

There are also now many examples of complexes containing *three* strongly donating Π_2 or $\Pi_{2'}$ ligands. In this situation, due to the severe competition for the available dπ-metal orbitals, the full complement of ligand π electrons is not usually donated to the metal. This is most clearly evident in three-fold symmetry complexes such as $[Os(NR')_3]$,[39] $[M(NR')_3X]$ (M = Mn,[54] Tc[32] or Re[26c]), $[W(NR'_3)L]$[55] (R' = $C_6H_3Pr^i_2$-2,6) and acetylene derivatives such as $[Re(RC{\equiv}CR)_3X]$[56] and $[W(RC{\equiv}CR)_3L]$.[57] These would be formally 20-electron species if each imido or acetylene residue is considered to donate four electrons. However, such three-fold symmetric complexes characteristically possess an occupied ligand-based non-bonding MO which effectively reduces the electron count to 18. The relationship between these complexes and other $M(\Pi_2)_3(\Pi_{2'})_{3-n}$ (n = 0–3) species is also then apparent, for example the fragments $[Ta(C_5Me_5)_2(NR)]^+$,[58] $[Zr(C_5H_5)_2(NR)]$,[59] $[W(C_5Me_5)(O)_2]$,[60] $[Re(O)(RC{\equiv}CR)_2]^+$ [9] and $[W(C_5Me_5)(NR)_2]^+$ [61] tend to behave as 16-electron species and in general are often accompanied by exceptional reactivity. Wigley and co-workers[61] have termed such compounds 'π-loaded'.

Low-valent Systems

Although the analysis presented so far has largely focused on high-valent complexes where π-donor interactions are of overriding significance, the first detailed MO studies of the factors influencing the orientations of Π_1 ligands were carried out by Hoffmann and co-workers[3,4] on pseudo-tetrahedral low-valent systems of the type $[M(cp)(CO)_2(L)]$ and $[M(cp)(CO)(NO)(L)]$ (where L is a single-faced π ligand such as carbene, alkene, alkyne or allyl). For the non-symmetrical nitrosyl case, the orientation preference of the carbene ligand in, for example, $[Cr(cp)(CO)(NO)({=}CPh_2)]$[62] has been interpreted in terms of the relative π acidities of the CO and NO^+ groups.

How does this description compare with the treatment we have adopted for the high-valent metal–π-donor ligand systems described in the previous sections? Qualitatively, we would expect very little difference: the MO descriptions of the fragments $M(cp)(CO)_2$ and $M(cp)(CO)(NO)$ also apply to high-valent transition-metal systems, since irrespective of whether the ligands are π donors or π acceptors (*e.g.* NR, Cl, *vs.* CO *etc.*) they bind to the metal using similar combinations of σ and π-symmetry orbitals (Table 1). It is only the relative energies of the orbitals and the localisation of the electrons ultimately in ligand- or metal-centred molecular orbitals that distinguish the high- and low-valent situations.

Thus, in accord with a π-donor approach, CO and NO could be considered to lie at the weak end of a π-donor scale. It then follows that the symmetrical dicarbonyl complexes $[Mn(cp)(CO)_2(L)]$ (L = Π_1 ligand, *e.g.* carbene, alkene, two-electron alkyne *etc.*) would be expected to show an alignment of their Π_1 ligands with respect to the single dominant π-donor, the cyclopentadienyl group. This is indeed the case as exemplified by **I** and **II** in Fig. 10. It can also be seen from **III** and **IV** that as the π system in the carbene ligand is extended, the preferred orientation of the substituents changes by a series of 90° twists consistent in each case with alignment of the p orbital of the metal-bound carbon with π_h.

For the mixed carbonyl–nitrosyl complex, $[Cr(cp)(CO)(NO)(CPh_2)]$, mentioned earlier and the related tertiary phosphine/phosphite rhenium derivatives $[Re(cp)(NO)(PPh_3)({=}CHPh)][PF_6]$[68] and $[Re(C_5Me_5)(NO)\{P(OPh)_3\}({=}CH_2)][PF_6]$[69] (Fig. 11) described by Gladysz and co-workers, the relative donor capacities of CO *versus* NO are seen to be important. If NO is considered as a neutral ligand (rather than as the nitrosonium ion), then it may be regarded as a better π donor than CO and the alignment of the carbene p orbital with the weaker π donors CO, PPh_3 and $P(OPh)_3$ can be ascribed to cp and NO dominating the π-donor bonding resulting in an orientation preference reminiscent of the type seen in bent metallocene derivatives.

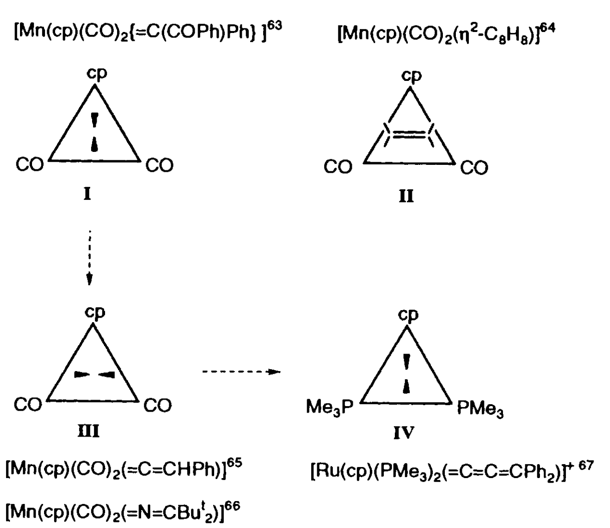


Fig. 10 Examples of low-valent complexes containing Π_1 ligands

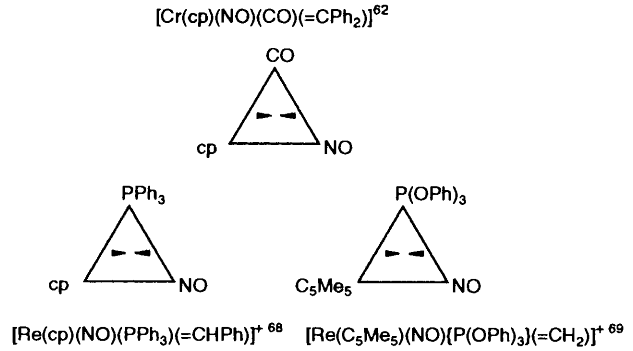
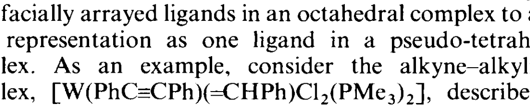


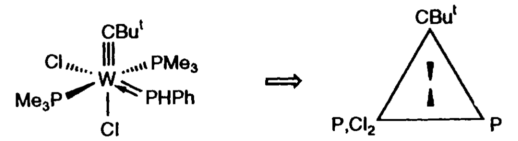
Fig. 11 Orientations of carbene ligands in low-valent complexes containing three different co-ligands

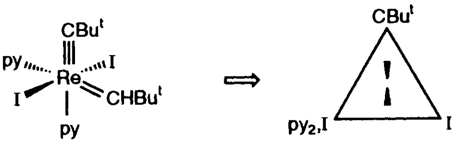
Other Co-ordination Geometries

Strong ligand orientation preferences are quite common for other co-ordination geometries, especially octahedral species, which are open to a more straightforward analysis since the alignment of the ligands along the co-ordinate axes allows a clear distinction between the d orbitals responsible for forming π bonds (the t_{2g} set) and σ bonds (the e_g set). However, it is worth noting that such complexes can also be viewed according to a triad analysis since the octahedral geometry can be reduced to a distorted tetrahedron by considering three facial ligands to occupy a single co-ordination site. This is, of course, precisely the assumption made for half-sandwich species, where the polyenyl ligand may be regarded as occupying three facial co-ordination sites in an octahedron or a single site in a pseudo-tetrahedron. By the same analogy, it is possible to group any three facially arrayed ligands in an octahedral complex to allow their representation as one ligand in a pseudo-tetrahedral complex. As an example, consider the alkyne–alkylidene complex, $[W(PhC{\equiv}CPh)({=}CHPh)Cl_2(PMe_3)_2]$, described by Mayr *et al.*[70] Grouping the facially orientated chloride and PMe_3 ligands (outlined) gives the triad representation shown to the right. The alternative face (to the rear of the molecule) would lead to the mirror image. It is found that the orientation of the alkylidene ligand is dominated by the alkyne for which there is good spectroscopic evidence for it acting as a four-electron ($\Pi_{2'}$) ligand.

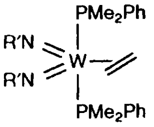


The complexes $[W({\equiv}CBu^t)(PHPh)Cl_2(PMe_3)_2]$[71] and $[Re({\equiv}CBu^t)({=}CHBu^t)I_2(py)_2]$[72] (py = pyridine) are examples in which phosphide and alkylidene orientations are dominated by the strongly π-bound (Π_2) terminal alkylidyne group.





Even for geometries that do not readily reduce to a tetrahedral form, the guidelines would still be expected to hold. Consider, for example, the trigonal-bipyramidal bis(imido)metal complex $[W(NC_6H_3Pr^i{}_2\text{-}2,6)_2(C_2H_4)(PMe_2Ph)_2]$,[26a] in which the imido and ethylene ligands occupy the equatorial sites of a trigonal bipyramid and the phosphines are positioned in the axial sites. Due to the C_{2v} symmetry of the complex, it is not possible to confirm by NMR spectroscopy whether the ethylene C=C axis aligns with the imido groups (**A**) or the two phosphines (**B**), see below. However, the guidelines for two dominant π-donor groups indicate that the C=C axis should bisect the N–Mo–N plane and orient towards the weakest π donors, in this case the phosphine ligands. This orientation has recently been confirmed in the structure of the molybdenum analogue.[73]



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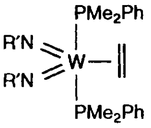

B

Conclusion

In this study, we have found it useful to classify ligands according to the number of electrons they have available for bonding to a metal, the symmetries of their frontier orbitals and their capacity to form multiple bonds to metals. Ligands capable of forming two strong π bonds to a metal are found to dominate the bonding in tetrahedral and pseudo-tetrahedral environments allowing ligands capable of forming only one π interaction to be exploited as sensors to identify the dominant π-bonding groups. These observations lead to some general guidelines that govern the preferred orientations of Π_1 ligands in the presence of strong Π_2 donor groups.

By comparing a series of complexes, it is thereby possible to derive a qualitative ordering of ligand π-bond strengths. For example, the imido group is seen to π bond more effectively than OR, cp and Cl, whereas cp π bonds more strongly than Cl and SR. All of these ligands of course dominate the solely σ-bonding groups such as PMe_3 and alkyl and π acceptors such as CO, CHR and alkenes.

Also it has been useful to extend the concept of isolobality to highlight relationships between complexes containing ligands of a similar class (Π_1, Π_2, $\Pi_{2'}$ *etc.*) and further to compare isonumeral metal–ligand fragments. It is not proposed that such relationships should be regarded as rigid, but rather that they can be used as an aid for understanding stoichiometry and structural patterns in new and seemingly unrelated systems, at the same time providing a useful basis for evaluating their likely reactions.

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