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Impact of the Coordination of Multiple Lewis Acid Functions on the Electronic Structure and v^n Configuration of a Metal Center

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Abstract: The covalent bond classification (CBC) method represents a molecule as $ML_lX_xZ_z$ by evaluating the total number of L, X and Z functions interacting with M. The CBC method is a simplistic approach that is based on the notion that the bonding of a ligating atom (or group of atoms) can be expressed in terms of the number of electrons it contributes to a 2-electron bond. In many cases, the bonding in a molecule of interest can be described in terms of a 2-center 2-electron bonding model and the $ML_lX_xZ_z$ classification can be derived straightforwardly by considering each ligand independently. However, the bonding within a molecule cannot always be described satisfactorily by using a 2-center 2-electron model and, in such situations, the $ML_lX_xZ_z$ classification requires a more detailed consideration than one in which each ligand is treated in an independent manner. The purpose of this article is to provide examples of how the $ML_lX_xZ_z$ classification is obtained in the presence of multicenter bonding interactions. Specific emphasis is given to the treatment of multiple π-acceptor ligands and the impact on the v^n configuration, *i.e.* the number of formally nonbonding electrons on an element of interest.

INTRODUCTION

The use of Lewis-type structures, in which bonding pairs of electrons are depicted by lines between atoms, and nonbonding valence electrons (v^n) are represented by dots localized on the appropriate atoms, has had considerable impact on the development of chemistry. In particular, when utilized with simple electron counting procedures (*e.g.* the octet[1,2] and 18-electron[2a,3] rules), these representations of molecules *(i)* provide a very convenient rudimentary means to establish whether or not a molecule is chemically reasonable, and *(ii)* offer insight into the structure of the molecule (*e.g.* VSEPR theory) and its magnetic properties.

An extension of simple Lewis structure representations is provided by the Covalent Bond Classification (CBC) method introduced by Green,[4] in which the pair of bonding electrons between two atoms are formally differentiated according to how many electrons each atom contributes to the 2-center 2-electron (2c-2e) bond. Specifically, ligands attached to an element of interest (M) are characterized as L, X or Z, according to whether the neutral ligand contributes respectively two, one or no electrons, as illustrated in Figure 1 and Table 1. Using this approach, and after taking into account the overall charge by employing simple rules (Table 2), which are described in detail elsewhere,4 a molecule can be classified as $ML_lX_xZ_z$ by evaluating the total number of L, X and Z functions interacting with M (Table 1). By identifying the different types ligand functions that are attached to the element, the $ML_lX_xZ_z$ description provides a classification that is more detailed than one that simply focuses on oxidation state,[5] in which case the molecule is simply characterized by a single number.

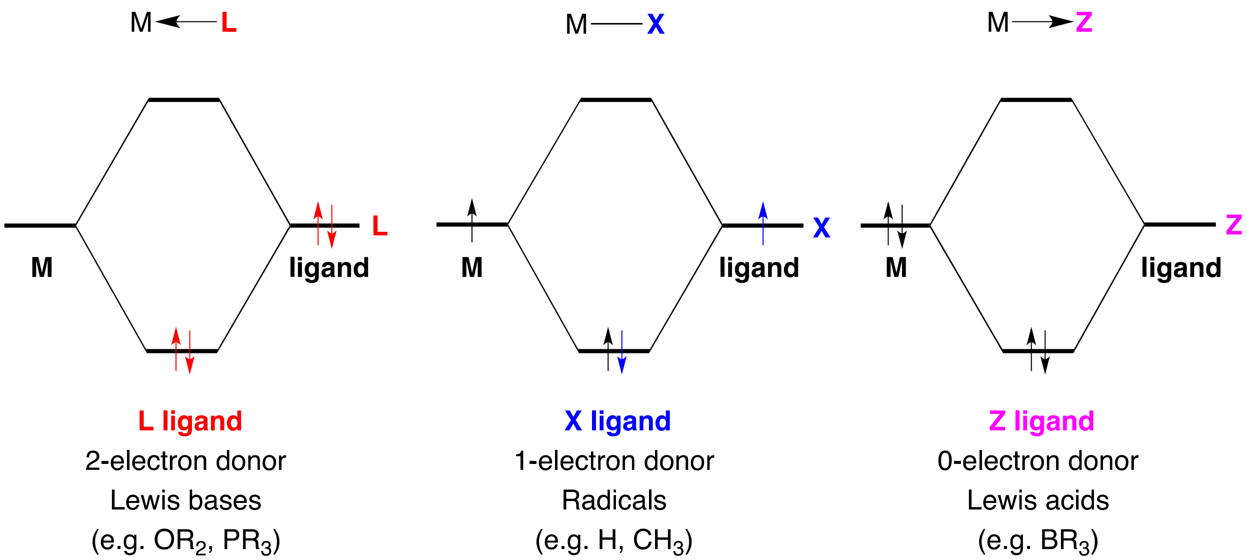


Figure 1. The Covalent Bond Classification (CBC) of L, X, and Z ligands, in which the ligands are classified in their neutral forms. L-type ligands (2-electron donors) are identified as Lewis bases, X-type ligands (1-electron donors) as radicals, and Z-type ligands (0-electron donors) as Lewis acids.

Table 1. Definitions pertaining to the CBC method and the equivalent neutral class.

Symbol	Definition
L	2–electron donor function
l	number of L functions
X	1–electron donor function
x	number of X functions
Z	0–electron donor function
z	number of Z functions
m	number of valence electrons on neutral M atom
VN	valence number VN = $x + 2z$
LBN	ligand bond number LBN = $l + x + z$
EN	electron number (or electron count) EN = $m + 2l + x$
v^n	number of electrons in formally nonbonding M orbitals[a] $n = m - x - 2z = m -$ VN

(a) v^n corresponds to d^n for transition metal compounds.

Table 2. Rules for converting $[\mathrm{ML}_l\mathrm{X}_x\mathrm{Z}_z]^\mathrm{Q}$ to the equivalent neutral class.

Condition	Rule
cation	$L^+ \rightarrow X$ and, if no L ligand is present, $X^+ \rightarrow Z$
anion	$Z^- \rightarrow X$, $X^- \rightarrow L$ and, if no Z or X ligand is present, $L^- \rightarrow LX$
L & Z combination	$LZ \rightarrow X_2$

The CBC method is a simplistic approach that is most easily applied when the bonding in a molecule of interest can be adequately expressed in terms of a 2c-2e bonding model. Since many compounds can in fact be described in this way, the CBC method provides a useful general means of relating different molecules to each other. However, for situations in which the bonding cannot be described satisfactorily by using a 2c-2e model, the $\mathrm{ML}_l\mathrm{X}_x\mathrm{Z}_z$ classification is not simply derived by treating each ligand independently but requires a more detailed consideration. This aspect of the CBC method for compounds that feature multicenter bonding interactions does not, however, appear to be well recognized.**[6]** The purpose of this article is, therefore, to elucidate how the $\mathrm{ML}_l\mathrm{X}_x\mathrm{Z}_z$ classification is derived for such compounds, with particular emphasis being given to compounds that contain π-acceptor ligands.

DISCUSSION

The electron count, v^n configuration and valence number are attributes that are frequently used to highlight a particular aspect of a molecule. For this reason it is important to have clarity with respect to their meaning and use, and the CBC method provides an approach to derive these values from the $\mathrm{ML}_l\mathrm{X}_x\mathrm{Z}_z$ classification (Table 1). This article focuses in particular on the impact of multiple π-acceptor ligands on the v^n configuration and valence state of a metal in a compound.

1. Impact of Coordination of L, X and Z Ligands on the v^n Configuration

As discussed above, the nonbonding valence electrons associated with the v^n configuration are typically included as dots in structure-bonding representations.4[c] The depiction of these nonbonding electrons is of chemical relevance because it provides a means to identify whether the atom can form additional bonds. A simple illustration is provided by the fact that the lone pair of electrons on nitrogen in NH_3 enables it to bind to the boron atom of BH_3 (Figure 2). However, while the inclusion of nonbonding electrons is common for main group elements, it is currently rarely adopted for transition metals, even though it was practiced in the past[7] and still does find some utility.[8] Excluding the nonbonding electrons from the representations for transition metals is not an indication of their chemical insignificance, but is a consequence of *(i)* the structures becoming unnecessarily cumbersome and *(ii)* VSEPR being of little utility for these elements. Hence, instead of including the electrons as dots, the number of electrons that have not been used in forming bonds is simply indicated by stating the d^n configuration.

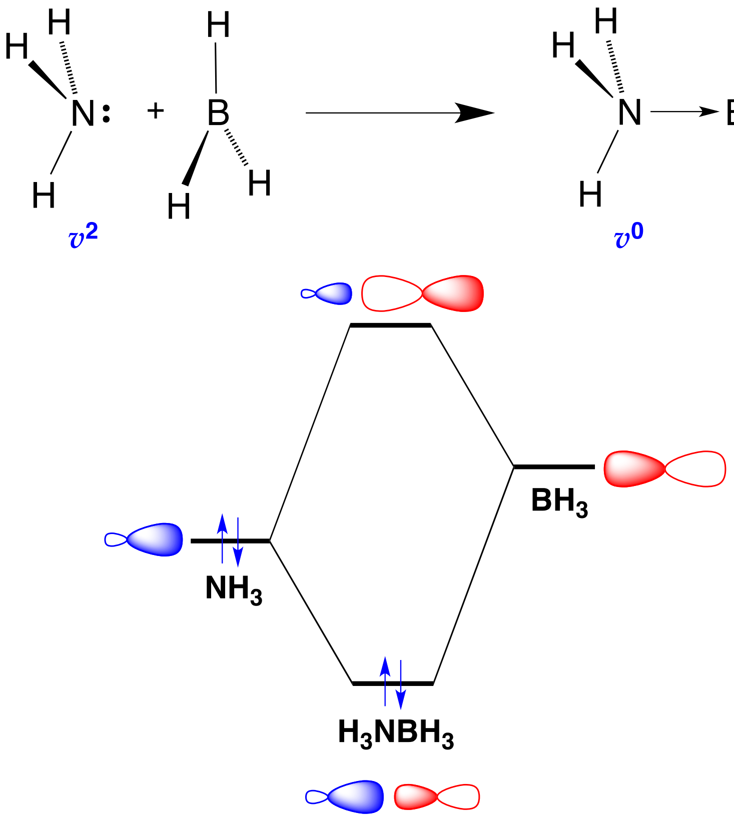
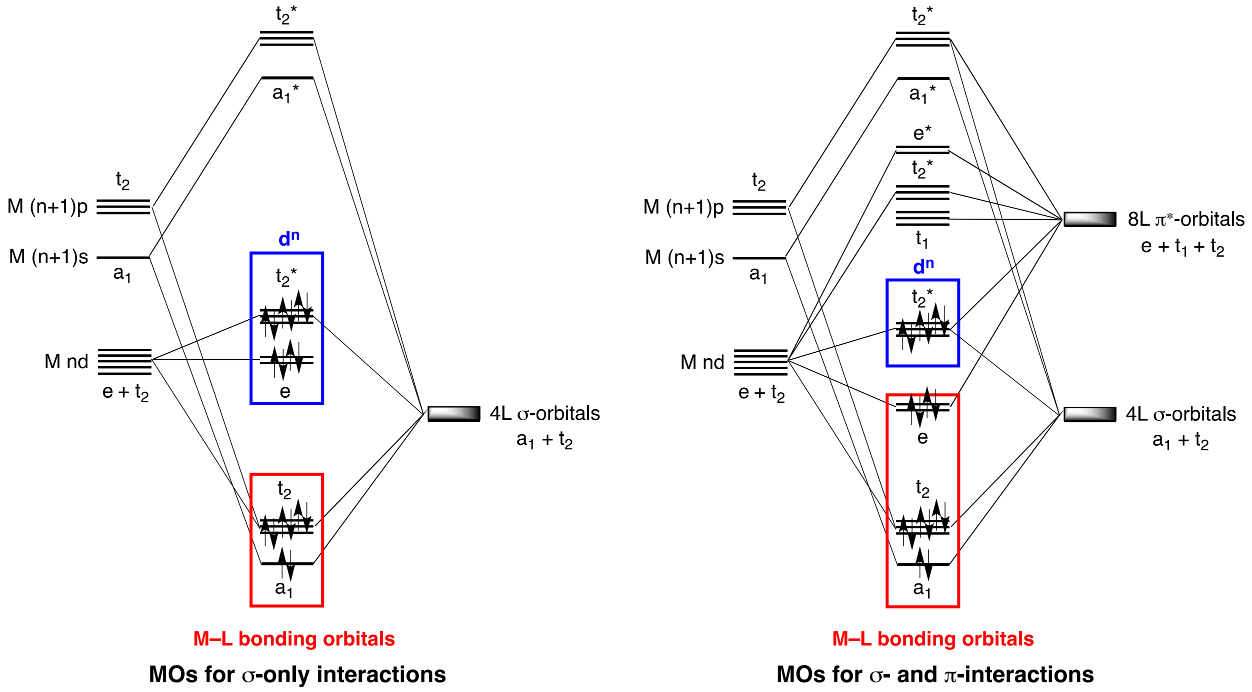


Figure 2. The nitrogen atom of NH_3 with a lone pair of electrons has a v^2 configuration but coordination by a Lewis acid, such as BH_3, results in it being reduced to v^0 since the electrons become a component of the $H_3N{\rightarrow}BH_3$ dative bond.

The assignment of the d^n configuration for a transition metal cation $[M]^Q$ in the gas phase is straightforwardly calculated by the expression $m - Q$, where m is the number of valence electrons associated with the neutral M atom, *i.e.* its Periodic Table group number.[9] With respect to covalent molecules, the d^n configuration corresponds to the number of electrons in *d*-based molecular orbitals that are formally localized on the metal after bond formation, *i.e.* those that are not components of metal-ligand bonding orbitals.[10,11] For example, the orbitals that determine the d^n configurations for tetrahedral and octahedral compounds with σ-only interactions are illustrated in Figure 3 and Figure 4 (left hand side). Thus, in addition to the orbitals that are rigorously nonbonding by virtue of symmetry requirements, metal-ligand antibonding orbitals that have *d*-character are also included in the d^n configuration because these typically possess more metal character than do the bonding orbitals, and also are available for subsequent bonding. The reason why the antibonding orbitals have a significant *d*-orbital component is that the ligating atoms are typically more electronegative than the metal, which results in the occupied bonding orbitals being associated more with the ligands, with the antibonding orbitals being associated more with the metal.



M–L bonding orbitals

MOs for σ-only interactions

M–L bonding orbitals

MOs for σ- and π-interactions

Figure 3. Qualitative molecular orbital diagram for a tetrahedral complex featuring *(i)* σ-only interactions (left) and *(ii)* σ- and π-interactions for ligands with two π^* acceptor orbitals (right), with emphasis on interactions involving the *d* orbitals. The electron count is for an 18-electron configuration and the bonding orbitals are highlighted in the red boxes while the orbitals associated with the d^n configuration are highlighted in the blue boxes. Note that the nonbonding e set of orbitals in the σ-only situation are stabilized in the presence of π-acceptor ligands and, if this interaction is deemed significant, *i.e.* it is an important component of the bonding that merits discussion, the orbitals are classified as bonding. Although the t_2 set of ligand π^* orbitals may also interact the M–L σ^* antibonding orbitals, this stabilizing interaction is not expected to be dominant because of the π *versus* σ-nature of the interaction.

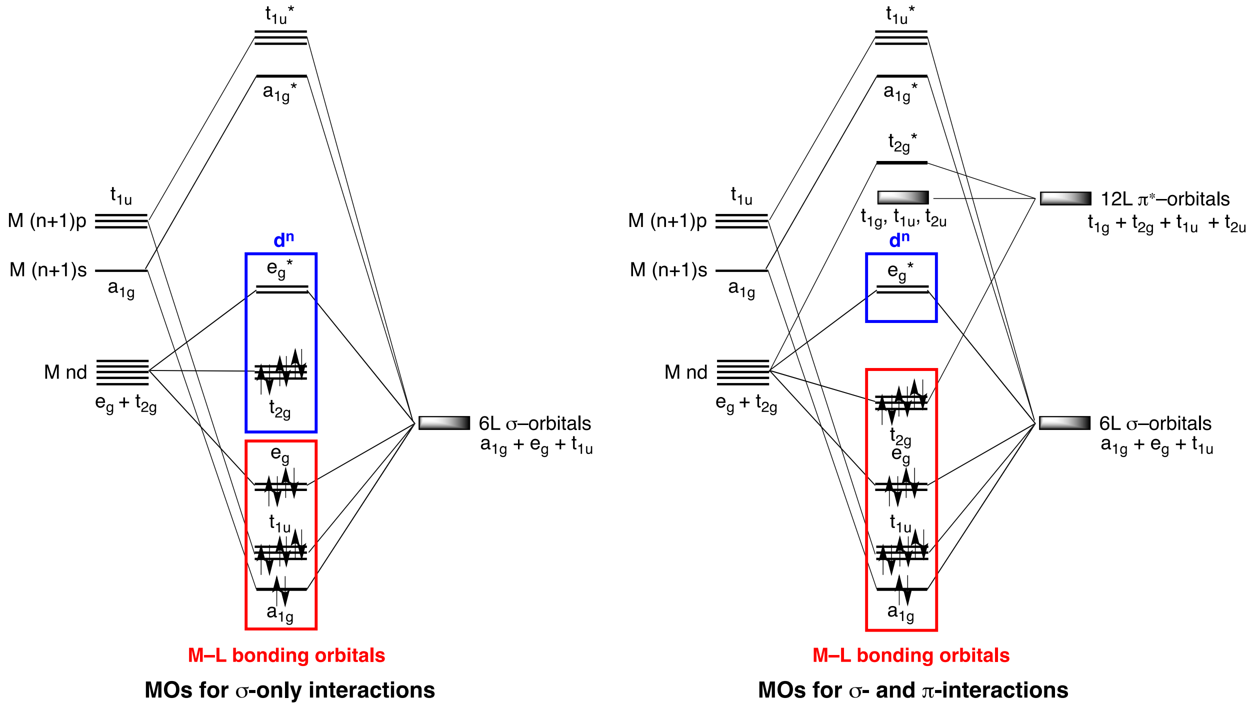


Figure 4. Qualitative molecular orbital diagram for an octahedral complex featuring σ-only interactions (left) and σ- and π-interactions for ligands with two π* acceptor orbitals (right), with emphasis on interactions involving the *d* orbitals. The electron count is for an 18-electron configuration and the bonding orbitals are highlighted in the red boxes while the orbitals associated with the d^n configuration are highlighted in the blue boxes. Note that the nonbonding t_{2g} set of orbitals in the σ-only situation are stabilized in the presence of π-acceptor ligands and, if this interaction is deemed significant, *i.e.* it is an important component of the bonding that merits discussion, the orbitals are classified as bonding.

Since it refers to the number of valence electrons that are not involved in bonding, the d^n configuration is naturally related to the valence number (VN) of the atom *via* the expression $n = m - \mathrm{VN}$, where m is the number of valence electrons associated with the neutral M atom.[4] The d^n configuration can also be determined by using oxidation states (OS), *i.e.* $n = m - \mathrm{OS}$.[5,10] In many cases, the valence and oxidation states are the same, and so the two equations often predict identical d^n values. However, due to the variety of different ways to define and assign oxidation states,[5,12-14] the predicted d^n configurations may vary for these different approaches.[15]

In addition to the above commonly employed simple expressions, namely $n = m - \mathrm{VN}$ and $n = m - \mathrm{OS}$, d^n configurations can also be computed *via* sophisticated calculations to determine the occupancies of the orbitals that have *d*-character. The d^n configuration so obtained is typically interpreted as being associated with the so-called physical or spectroscopic oxidation state.13-**16** In some cases, these orbitals may possess significant metal-ligand bonding character and, on such occasions, the derived d^n configuration would differ from the number of electrons that occupy nonbonding/antibonding orbitals. *As a result of these different approaches for assigning a* d^n *configuration, it is prudent for authors to indicate the method that is being employed and specify how the derived* d^n *configuration is to be interpreted.*

While metal-ligand bonding orbitals are typically considered to have more ligand character than metal character, this traditional view of bonding in transition metal compounds has been recently reevaluated. Most notably, Lancaster**[17]** and Hoffmann *et al***[18]** have emphasized situations in which the order is reversed, such that the bonding orbital possesses more metal character than does the antibonding orbital.**[19]** This situation is referred to as an "inverted ligand field" (Figure 5). Although this occurrence is certainly unusual for instances involving σ-bonding, it is common for ligands that have π-acid functions (which are typically π^* antibonding orbitals, *e.g.* CO) that provide a means to supplement the bonding; in such cases the bonding orbital has more metal character and the antibonding orbital has more ligand character (Figure 3 and Figure 4, right hand side).**[20]**

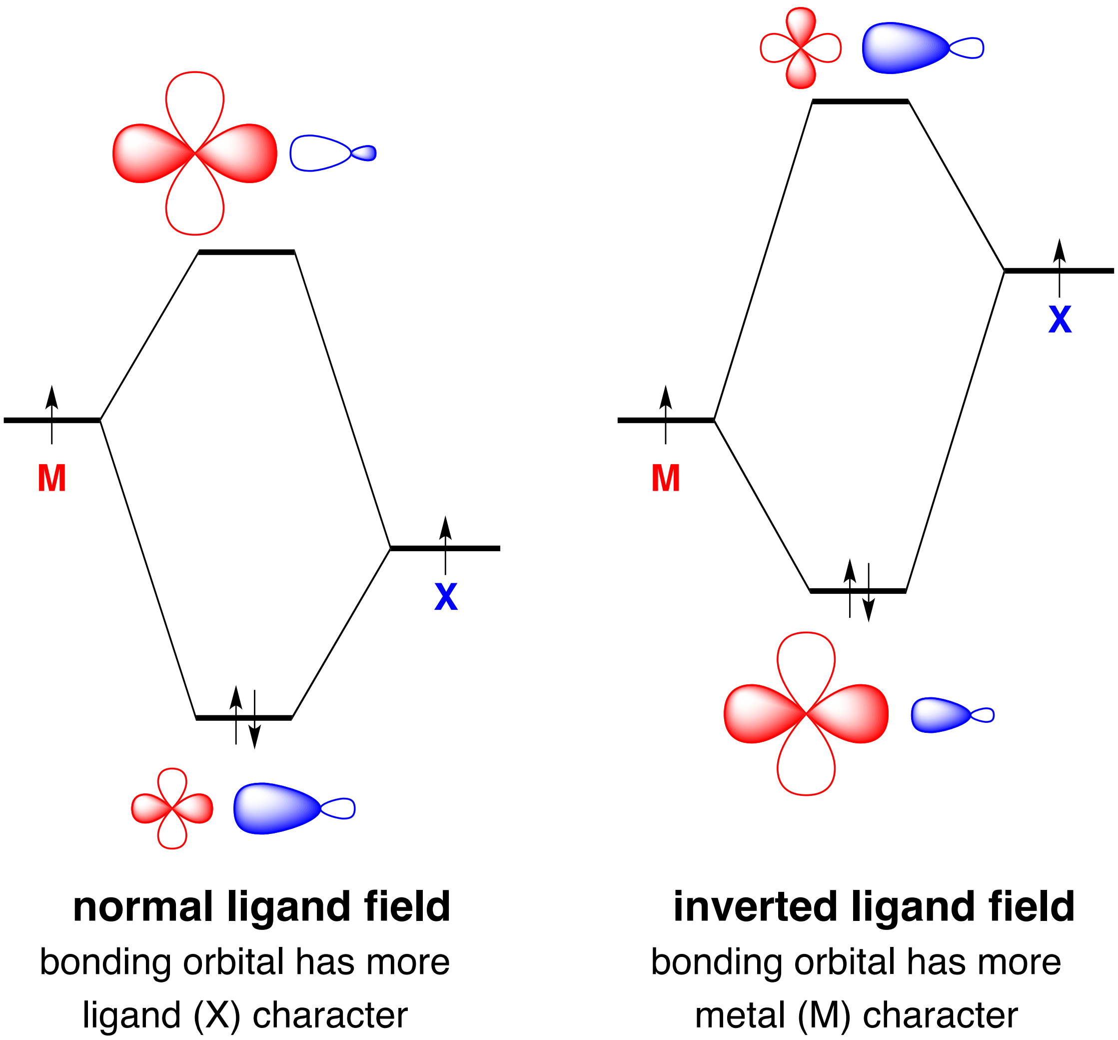


Figure 5. Normal (left) and inverted (right) ligand fields. The bonding orbital for a normal ligand field possesses more ligand character because the ligand orbital is lower in energy than that of the metal, whereas the bonding orbital for an inverted ligand field possesses more metal character.

The majority of ligands that are encountered possess L or X functions and the impact of their coordination to another atom is well known and normally causes little confusion. Thus, coordination of an L function has no impact on v^n while coordination of an X function necessarily reduces it to v^{n-1} (Figure 1). In contrast, Lewis acids are not as commonly featured as ligands and the impact of their coordination is less appreciated. Nevertheless, it should be evident from the definition of a Z ligand that its coordination must reduce v^n to v^{n-2} because the coordinating atom has to provide both electrons to form the 2c-2e bond. A well-known example is provided by the aforementioned coordination of the Lewis acid BH_3 to NH_3. The nitrogen atom of NH_3 has a lone pair of electrons, *i.e.* a v^2 configuration, but adopts a v^0 configuration upon coordination of BH_3 to form $H_3N \rightarrow BH_3$; specifically, the lone pair no longer exists because it has been used to form the N→B dative covalent bond (Figure 2).

Correspondingly, with respect to transition metals, coordination of a Lewis acid to a metal center with a d^n configuration reduces it to d^{n-2}.[21] More generally, for a given $ML_lX_xZ_z$ classification, the d^n configuration for transition metal complex is given by $n = m - (x + 2z)$. The origin of this expression is straightforward: each X ligand requires M to contribute one electron to the M–X bond, while each Z ligand requires M to contribute two electrons to the M→Z bond.

2. Coordination of Ligands with Polyfunctional Atoms

The simplest application of the CBC method pertains to situations in which each coordinating atom is monofunctional, such that the bonding can be represented as a simple 2c-2e bond. In some cases, however, as introduced above for π-acid ligands, the coordinating atom may be polyfunctional. For such situations, further consideration is required to identify the most appropriate classification of the ligand. As an illustration, a single oxygen atom can coordinate to an element by either a single, double or triple bond, depending upon the requirements of the attached element. Examples of these different interactions are provided by amine oxides ($R_3N^+–O^-$), ketones ($R_2C=O$) and certain transition metal oxo compounds ($L_nM^- \equiv O^+$),[22] in which the oxygen atom is respectively classified as Z, X_2, or LX_2 (Figure 6).[23]

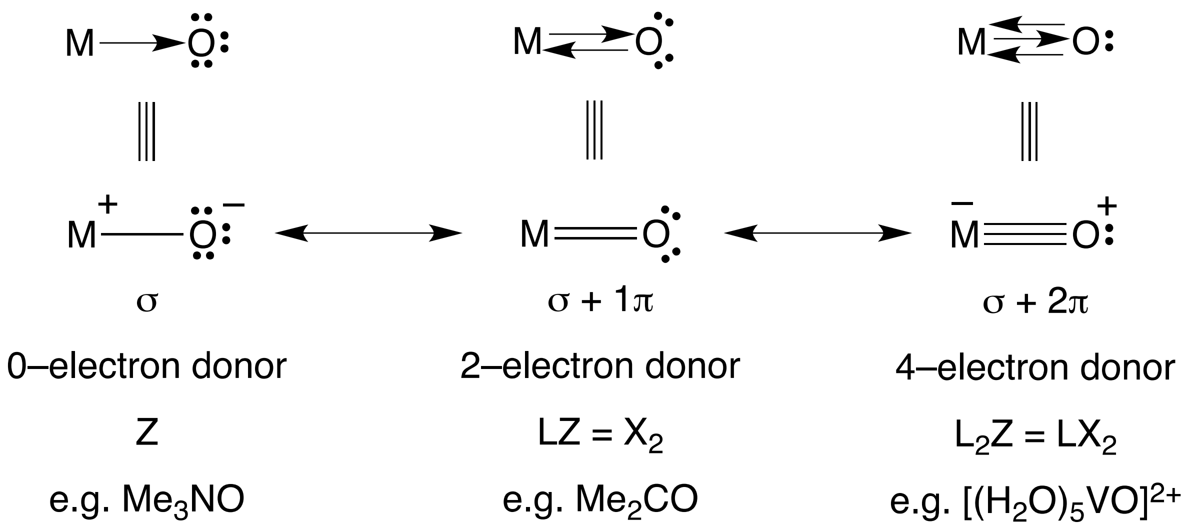


Figure 6. CBC description of oxo compounds. The oxygen can bind via either a single, double or triple bonds depending upon the nature of the atom to which it is attached.

Determination of the most appropriate assignment for an oxo ligand requires one to consider the nature of the element to which it is attached and, for the above examples, simple bonding considerations allow one to assign the best classification (Figure 6). For example, the nitrogen atom of Me_3N has an octet configuration and so the oxygen must serve as a Z ligand in order to preserve the configuration in Me_3NO. Likewise, the central carbon atom of Me_2C has a sextet configuration and so must form a double bond to oxygen in order to achieve an octet configuration upon formation of Me_2CO.

In other situations, however, the best description of a polyfunctional atom may require the use of calculations because the differences in the possible options for the ligand may not be definitive. For example, consider the coordination of a CY_2 carbene ligand to a metal center (Y = R, Ar or heteroatom substituent). A CY_2 moiety formally has a sextet configuration with a pair of nonbonding electrons, such that it can serve as both a σ-donor (L) and as a π-acceptor (Z). In all examples of [MCY_2] compounds the σ-component is essential, but the π-component is variable. Indeed, there are two extremes that are referred to as "Fischer carbenes", where there is little π-interaction, and "Schrock alkylidenes", where there is a significant π-component (Figure 7).**[24]** The

Fischer carbene CY_2 ligand is thus commonly identified as an L ligand, while the Schrock alkylidene ligand is classified as an LZ ligand, which is equivalent to X_2.24,[25] The equivalence of LZ and X_2 for Schrock alkylidenes is completely appropriate because the substituents on the carbene carbon atom are hydrogen atoms or alkyl groups and thus the *p* orbital on carbon is unoccupied in its singlet form (or singly occupied in its triplet form). In contrast, the substituents on Fischer carbenes are heteroatoms with lone pairs that can also interact with the carbon *p* orbital, thereby minimizing the ability of the carbene carbon to participate in a π-acceptor interaction with the metal. A similar situation obtains for the coordination of *N*-heterocyclic carbenes (NHCs)[26-28] and cyclic (alkyl)(amino)carbenes (cAACs)[29,30] to a metal center, where donation of electron density from the adjacent nitrogen atoms reduces the ability of the carbene carbon to participate in a π-acceptor interaction with a metal center. Thus, while Schrock alkylidenes are aptly represented as LZ = X_2 ligands, other CY_2 ligands are better represented as LZ′ where the secondary Z′ component remains unspecified until a further investigation of the molecule is performed.[31]

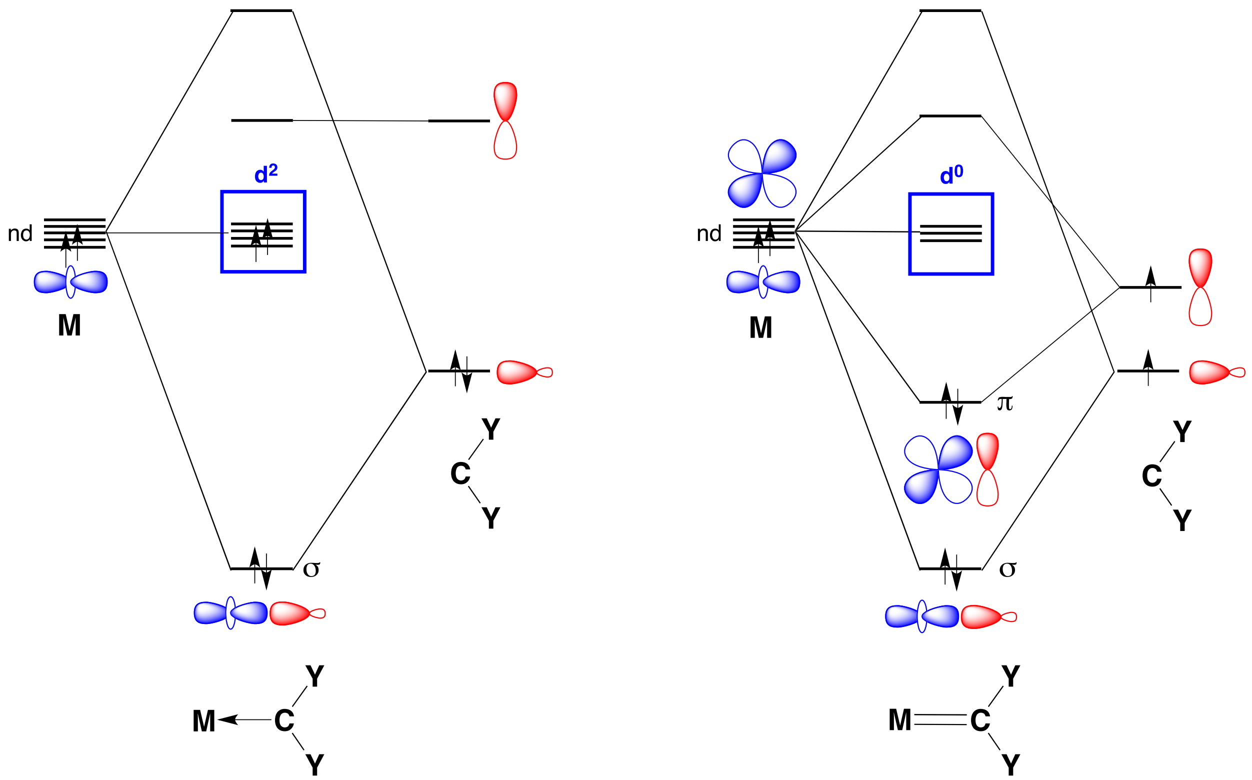


Figure 7. Qualitatative molecular orbital diagrams for extreme representations of coordination of a singlet (left) and triplet (right) CY$_2$ moiety to a metal center that is arbitrarily represented with a d^2 configuration. Coordination of a triplet CY$_2$ ligand results in a d^n configuration being reduced to d^{n-2}. Note that the high energy p-orbital on carbon in the singlet form (left) is involved a π-interaction with a lone pair on the adjacent heteroatom (not shown), which reduces its ability to serve as an acceptor orbital for the metal. Backbonding utilizing this orbital (a Z′ component) would formally correspond to a resonance structure in which there is no π-donation from the adjacent heteroatom.

Similar to the situation with Fischer carbenes and Schrock alkylidenes, the bonding of olefins to a metal center involves σ-donation (an L function) of the π-bonding electrons and π-backbonding (a Z function) into the C–C π*-orbital, *i.e.* the well-known Dewar–Chatt–Duncanson model.[32] If there is little backbonding, the molecule is typically referred to as an olefin adduct, whereas it is referred to as a metallacyclopropane if the backbonding is extensive. A generic olefin ligand, therefore, would be characterized as LZ′ but, for the purpose of providing a simple classification of molecules, unless there are clear reasons to do otherwise, it is acceptable to assign an olefin as an L donor since this is the primary interaction. It must, however, be recognized that that the derived classification would need consideration of the secondary Z′ component prior to attempting to utilize it to describe more details about the bonding. While backbonding interactions are most commonly of a π-nature, it should be noted that a variety of ligands possess δ-acid functions (*e.g.* cyclopentadienyl, benzene and cycloheptatrienyl), that also provide important secondary bonding interactions.[33,34,35]

Another common example of a polyfunctional group is provided by CO, which is well-known to serve as both a σ-donor and π-acceptor ligand: the σ-donor orbital is the carbon lone pair and the π-acceptor orbitals are the two C–O π*-antibonding orbitals. Thus, a metal–carbonyl interaction can be represented by the three resonance structures shown in Figure 8, which indicate that it can serve as an L, X_2 or X_2Z ligand, all of which correspond to a 2-electron donor, but differ with respect to both the M–C and C–O bond orders.

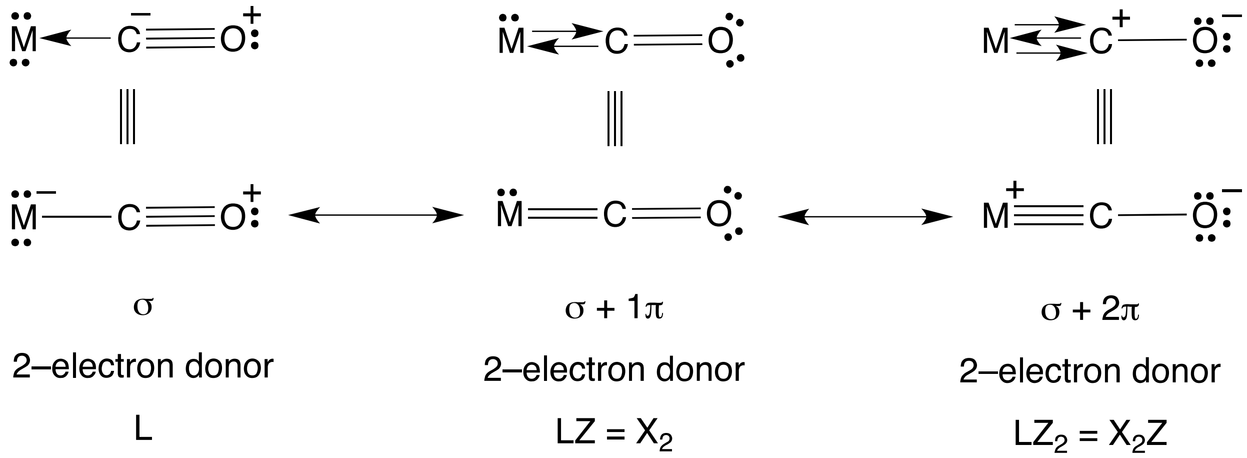


Figure 8. Resonance structures for coordination of CO to a metal center. In each case the CO serves as a 2-electron donor to the metal center but the M–C and C–O bond orders vary from 1 to 3.

While the two π*-orbitals in CO are degenerate, the ability of both of them to interact equally with the metal center depends on the symmetry of the molecule. For example, if the molecule were to exhibit C_{4v} symmetry with an axial CO ligand, both π*-

orbitals would interact equally with metal-based *d* orbitals; however, this would not be the situation if the molecule were only to possess C_{2v} symmetry. On this basis alone, it is evident that assigning the Z_z component of the interaction requires consideration of the symmetry of the molecule in question. Moreover, the magnitude of the backbonding interaction depends critically on the nature of the metal center and, in particular, the d^n configuration. It is, therefore, evident that the CO ligand cannot simply be classified universally as LZ_2. As such, similar to coordination of CY_2, it is appropriate to consider the CO ligand as LZ′, where the Z′ component remains unspecified until a further investigation of the molecule is performed. For the purposes of the simple classification of molecules, however, it is acceptable to assign a CO ligand as L because this is the primary interaction, as indicated by the fact that CO may bind to certain d^0 metal centers that are not capable of backbonding to a first approximation.[36,37]

NO is closely related to CO but, as a consequence of the additional electron, terminal NO ligands may coordinate in both linear and bent modes. As with CO, the linear coordination can be described by three principal resonance structures (Figure 9). An important difference, however, pertains to the nature of the π-interactions because, whereas the π* orbitals of CO are the LUMO, they are the singly occupied HOMO for NO. The π* orbitals of NO thus have both donor (X) and acceptor (Z) character and so their involvement in the bonding is much more essential than in carbonyl compounds (Figure 10).

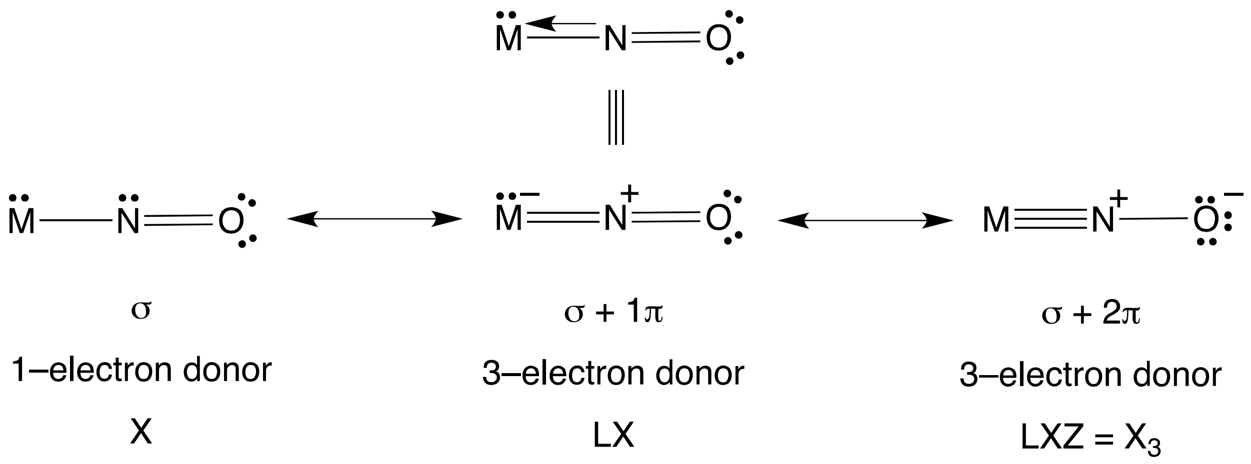


Figure 9. Resonance structures for coordination of a linear NO ligand to a metal center, which indicates that it can serve as an X, LX or X_3 ligand.

Although the simple Lewis-type representation of the NO molecule suggests that it could serve as an LX ligand, symmetry arguments indicate that, if π-interactions are operative, NO must serve as an LXZ ligand if it coordinates axially to a metal center that possesses a three-fold or four-fold axis of rotation. Formation of a diamagnetic compound would thus require the metal to contribute three electrons to the two bonding π-molecular orbitals, such that the interaction can be represented as $\mathrm{M{\equiv}\overset{+}{N}{-}\overset{-}{O}}$. Linear NO in such molecules thus acts as an X_3 ligand, which is in accord with the LXZ description after applying the LZ = X_2 transformation.[38]

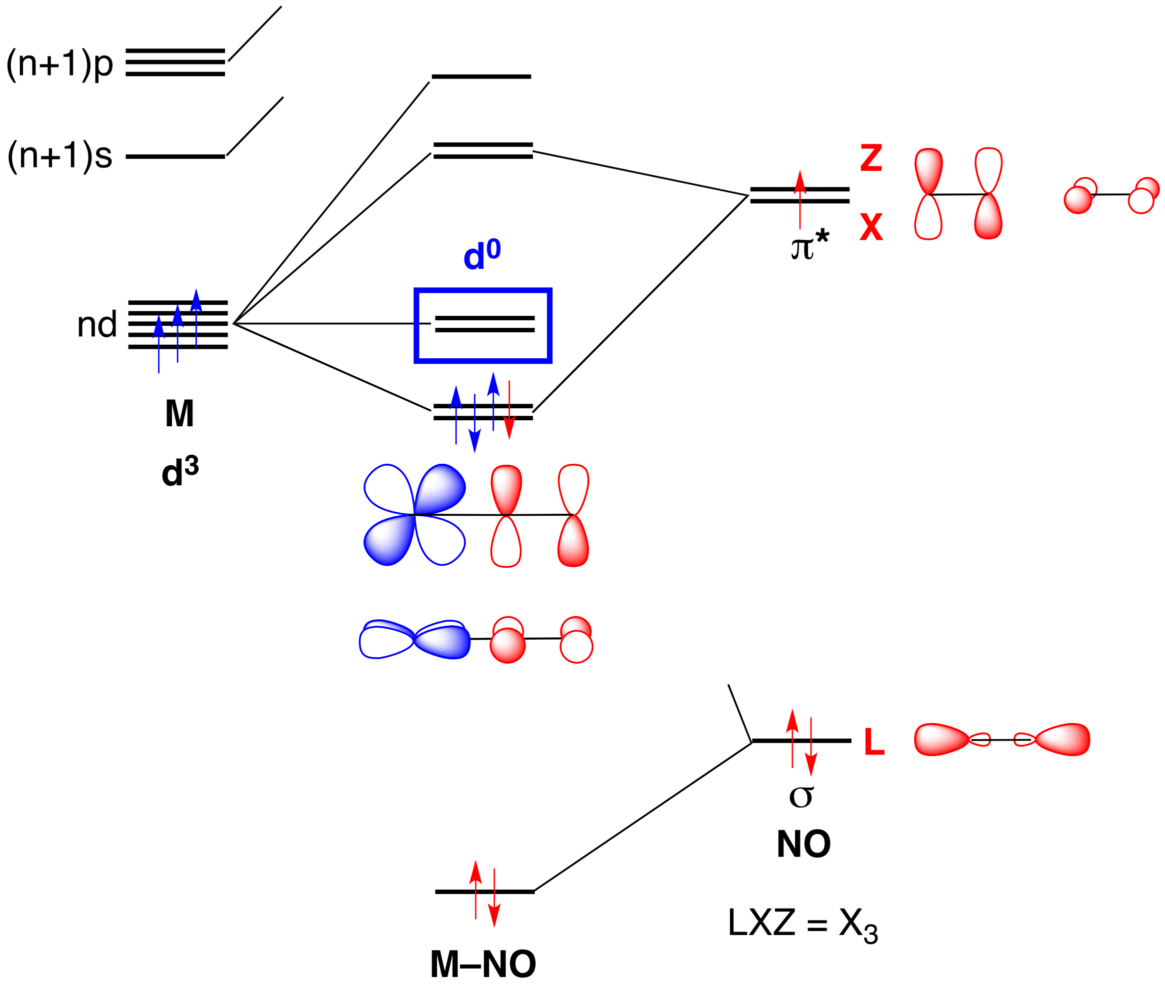


Figure 10. Qualitative partial molecular orbital diagram for coordination of a linear NO ligand to a d^3 metal center with C_3 or C_4 symmetry. The metal center contributes three electrons to the bonding orbitals such that it adopts a d^0 configuration and the NO serves as an X_3 ligand.

The triply bonded description of a linear metal nitrosyl interaction was first proposed for complexes of the type $[M(NO)(CN)_5]^{n-}$ in 1966 by Gray,[39] who subsequently emphasized the analogy between the triple bonding motif in metal nitrido and metal nitrosyl compounds.[40] The analogy between the electronic structure of nitrido and nitrosyl complexes has also been noted by Wieghardt[41] and Mingos,[42] while Cummins has described $(RR'N)_3CrNO$ as possessing an incipient Cr≡N triple bond.[43,44] However, while C_3 and C_4-symmetric linear metal nitrosyls may exhibit a M≡□□□triple bond, this type of interaction is not required if the molecule has lower symmetry, in which case it could potentially serve as an LX ligand, such that one of the π* NO antibonding orbitals remains unoccupied.

The linear X_3 mode of the nitrosyl ligand indicates that coordination of NO reduces a d^n configuration to d^{n-3} with respect to the occupancy of the *d*-based molecular orbitals that are not metal-ligand bonding (Figure 10). As noted above, d^n configurations may also be derived from oxidation state assignments and, in this regard, a linear nitrosyl ligand is usually classified as a cation (NO^+), while a bent nitrosyl ligand is classified as an anion ($NO^–$).[45,46,47] The cationic description of a ligand, however, is certainly unusual, such that Richter-Addo and Legzdins stated that "… the formal oxidation states in $Co(CO)_3NO$, $Fe(CO)_2(NO)_2$, $Mn(CO)(NO)_3$ and $Cr(NO)_4$ have the unrealistic values of –1, –2, –3 and –4, respectively!"45 Enemark and Feltham have likewise stated that "assignment of oxidation states to the metal atom and NO is undesirable",46 and so rather than focus on d^n configurations they introduced the $\{MNO\}^n$ notation, where *n* is the total number of electrons associated with the metal d orbitals and NO π*–orbitals;46 in essence, the introduction of the $\{MNO\}^n$ parameter provides a means to circumvent arguments concerned with the ambiguity in interpretation of the d^n configuration.

In support of the above X_3 description of a linear nitrosyl, the need for a metal to contribute three electrons to the bonding is indicated by the fact that there are no stable nitrosyl compounds in which neutral NO coordinates to a metal center with fewer than three *d* electrons, *i.e.* a $d^{<3}$ configuration. Alternatively, using the Enemark-Feltham notation, this can be restated as there being no metal nitrosyl compound that is classified as $\{MNO\}^{<4}$.46 In contrast, CO is known to coordinate to d^0 metal centers, albeit weakly.36,37 This simple observation clearly indicates the essentiality of π-backbonding in metal nitrosyl compounds.[48] Furthermore, computations also indicate that π-backbonding in nitrosyl compounds is significantly stronger than in carbonyl compounds, as illustrated by the calculated W–NO bond length in $[W(CO)_5(NO)]^+$ (1.891 Å) being considerably shorter than the W–CO bond lengths (2.107 Å and 2.178 Å)[49] by values that are much greater than the difference in covalent radii of carbon and nitrogen (0.06 Å).[50]

3. Coordination of Multiple π-Function Ligands

Due to the symmetry properties of π-function ligands, the coordination of multiple ligands does not necessarily have a cumulative effect with respect to the $ML_lX_xZ_z$ classification,4[c,]44 a situation that does not appear to be widely appreciated.6 For example, while a single NO ligand can serve as an X_3 donor, this description is not possible for coordination of two NO ligands because there is an insufficient number of *d* orbitals of appropriate symmetry to enable the formation of two M≡□□ triple bonds. As an illustration, consider the partial MO diagram for a *trans*-$M(NO)_2$ moiety that focuses on the π-interactions (Figure 11).[51]

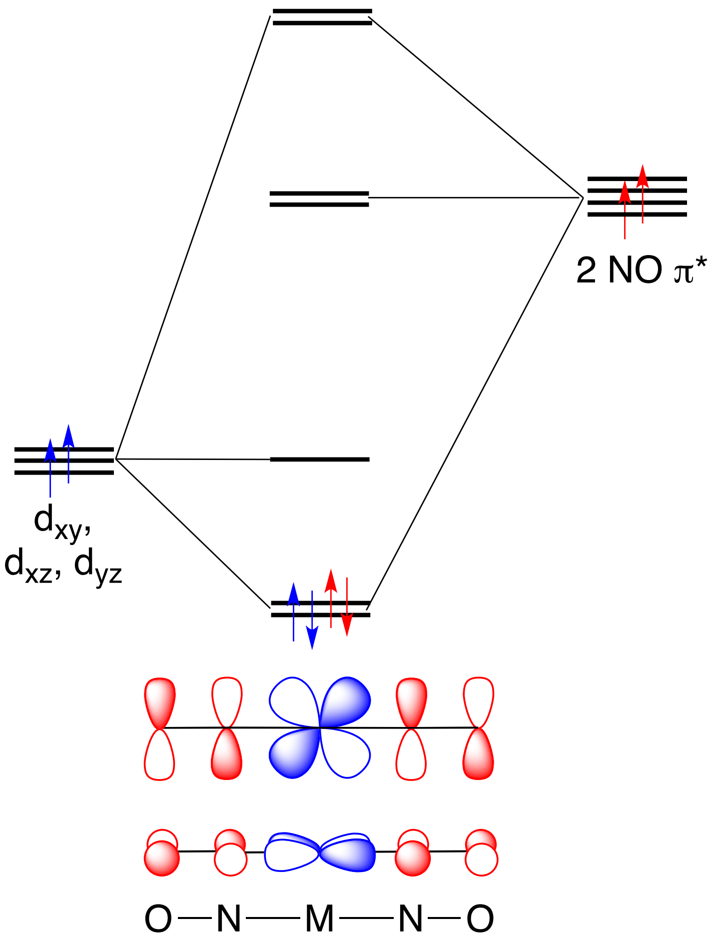


Figure 11. Partial MO diagram for a *trans* dinitrosyl compound focusing on the π–interactions in an octahedral environment. Two sets of NO π* orbitals interact with the same metal d orbitals, such that the metal is only required to contribute *two* electrons to the bonding orbitals, and two sets of NO π* orbitals remain nonbonding. Coupled with the two ON→M dative covalent interactions (not shown), each nitrosyl may be classified as an LX ligand.

In this case, the two NO ligands interact with the same pair of *d* orbitals, thereby resulting in two 3c-2e π-bonds, rather than 2c-2e π-bonds. Since each NO ligand possesses a single electron in the π* orbitals, it is evident that the metal only needs to contribute *two* electrons to form these 3c-2e π-bonds. The pair of NO ligands thereby acts as an $[X_2]$ combination with respect to the π-bond component, such that each NO behaves overall as an LX ligand. Much more common than *trans* dinitrosyl compounds are *cis* complexes, because this geometry maximizes π-bonding since it allows access to a third *d* orbital, as illustrated in Figure 12.42[a] Thus, in order to coordinate the two nitrosyl ligands, the metal center is required to contribute *four* electrons to the three M–NO π-bonding orbitals; as such, each NO ligand may be regarded overall as an LX_2 ligand.

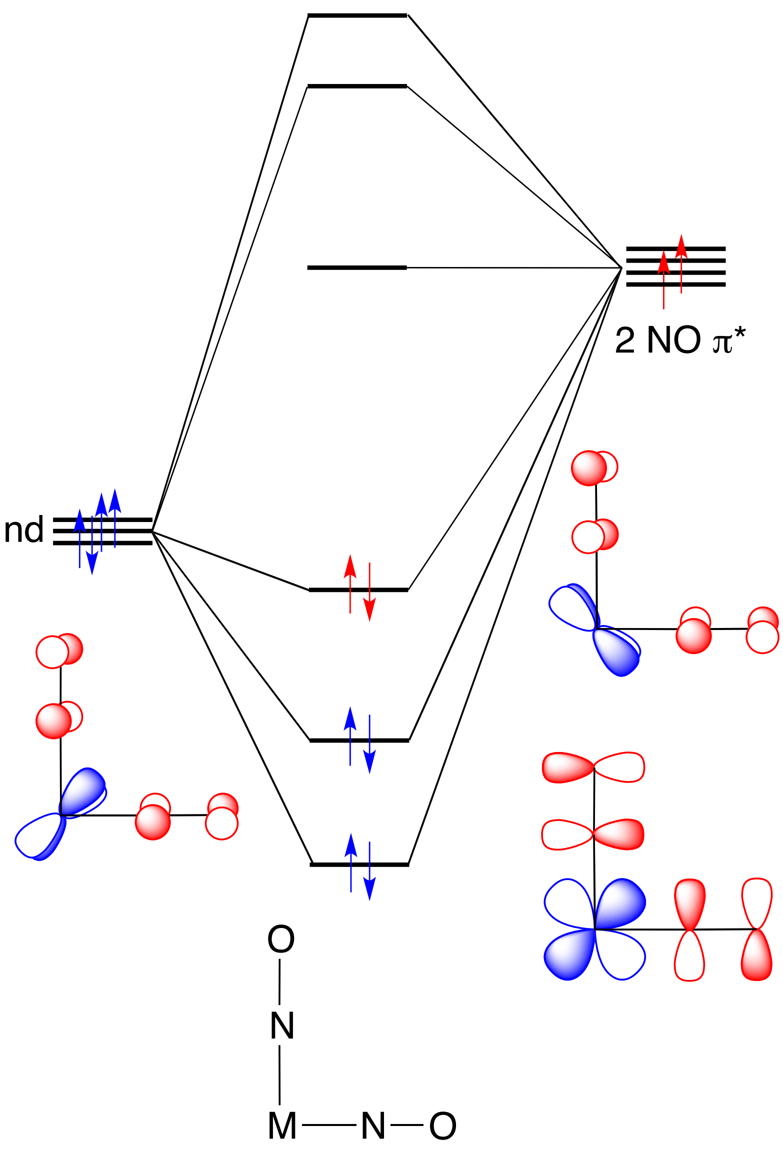


Figure 12. Partial MO diagram for a *cis* dinitrosyl compound focusing on the π–interactions in an octahedral environment. Three sets of NO π* orbitals interact with three metal d orbitals to form three bonding orbitals, such that one set of NO π* orbitals remains nonbonding. Since the two NO ligands provide two electrons for the three bonding molecular orbitals, the metal center is required to contribute four electrons. Coupled with the two ON→M dative covalent interactions (not shown), each nitrosyl may be classified as an LX_2 ligand.

Trinitrosyl metal complexes with linear nitrosyl ligands are not common[52] and there are few tetranitrosyl examples, but one is provided by $Cr(NO)_4$. The impact of incorporating π-interactions into the tetrahedral σ-only bonding scheme of $M(NO)_4$ is illustrated in Figure 13. Of particular note, the nonbonding e set of *d* orbitals interacts with the corresponding set of NO π^* orbitals (which belong to e, t_1 and t_2 representations) to yield bonding and antibonding orbitals but, in contrast to the aforementioned examples, the metal does not need to provide any electrons for the bonding e set of molecular orbitals because the four NO ligand π^* orbitals are occupied by four electrons; as such, the π-interaction is effectively an $[L_2]$ combination. Therefore, together with the σ-interactions, the four NO ligands serve overall as an $[L_6]$ combination.

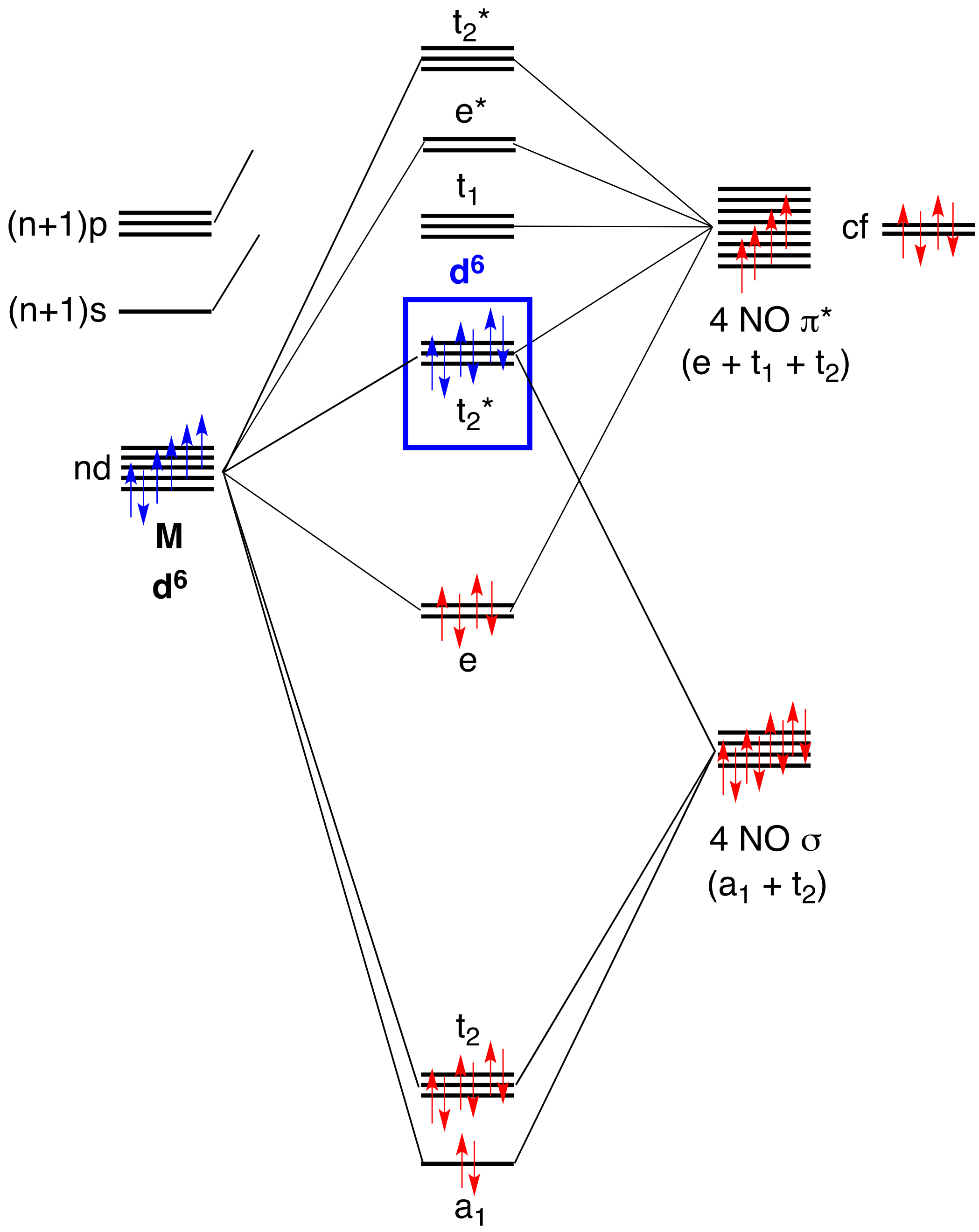


Figure 13. Qualitative molecular orbital diagram for $M(NO)_4$ for a Group 6 metal. π-Backbonding interactions result in the e set being classified as bonding orbitals, rather than nonbonding as observed in a σ-only framework. Since the NO π* orbital combination possesses four electrons, the metal does not need to provide any electrons to occupy the e set, thereby allowing six electrons to occupy the d-based t_2* orbitals, and hence a d^6 configuration.

Although the variable nature of the linear NO ligand, as summarized in Table 3, may seem unusual, there is actually much precedent for this type of situation where a combination of multiple identical ligands is not simply a sum of the individual ligands. For example, while many terminal metal oxo species possess a $\overset{-}{\mathrm{M}}\equiv\overset{+}{\mathrm{O}}$ triple bond,[53,54] a *trans*-$M(O)_2$ moiety is better described as possessing double bonds because the two oxo ligands compete for the same *d*-orbitals in a manner akin to that of the two nitrosyl ligands; the interactions are, however, more accurately described as comprising two 2 σ bonds and two 3c–2e π-bonds. In contrast to the double bonds for a *trans*-$M(O)_2$ moiety, the M≈O bond order in a *cis*-$M(O)_2$ entity is increased to 2.5 because the symmetry allows an extra d-orbital to become available. Likewise, consideration of a tetrahedral metal oxo compound indicates that the maximum M≈O bond order is 2.25 for a d^0 metal center.[55,56] The impact of the multicenter *versus* two-center nature of these π-interactions is indicated by the observation that the M–O bond lengths of monooxo compounds are on average shorter than those of related dioxo and trioxo compounds.[57]

Table 3. Classification of $(NO)_n$ combinations assuming that π-interactions are significant.

composition	**geometry**	**classification of $(NO)_n$ combination**
$M(NO)_2$ (trans)	octahedral	L_2X_2
$M(NO)_2$ (cis)	octahedral	$L_2ZX_2 = LX_4$
$M(NO)_4$	tetrahedral	L_6

A closely related situation occurs with respect to the electron count of transition metal compounds that contain multiple polyfunctional L donor groups. A simple example is provided by $W(C_2R_2)_3CO$, which would possess a 20-electron configuration if each acetylene ligand were to be considered as a 4–electron L_2 donor, with the carbonyl ligand being a 2–electron L donor. However, a molecular orbital analysis indicates that of the six possible combinations of π-orbitals of the $[(C_2R_2)_3]$ fragment, one of them does not have the appropriate symmetry to interact with the metal center. Specifically, the a_2 orbital has no symmetry match with the metal s, p and d orbitals and so it remains nonbonding such that the electron count is reduced to 18.[58] Other examples where molecular orbital considerations dictate that a ligand based orbital must remain nonbonding, thereby preserving the 18-electron rule, are provided by Cp_3MX,[59] $Os(NAr)_3$,55,[60] $(RN)_3MoL$,[61] $M(BH_4)_4$[62] and [η^8–pentalene]$_2$M (M = Ti, Zr, Hf).[63,64]

The situations described above, in which the impact of a given ligand (such as oxo, alkyne, cyclopentadienyl and imido) on a metal center varies with the number of ligands, are features that are completely independent of the CBC method. As such, it must be emphasized that it is not surprising that similar manifestations would emerge when using the CBC method. Thus, in the present case, while a single nitrosyl ligand may be classified as an X_3 ligand, polynitrosyl moieties, $[M(NO)_n]$, should ***not*** be classified as MX_{3n}, and consideration of the orbital interactions is required to provide a more appropriate description of the molecule. Although this issue has been previously discussed,4[c,]44 it does not appear to be well known.6 As such, it needs to be emphasized that simply classifying $[M(NO)_n]$ as MX_{3n}6 will inevitably result in incorrect interpretations with respect the electronic nature of a molecule.

Anionic molecules with metals that possess negative oxidation states are certainly interesting species from a variety of perspectives and metal carbonyl anions, $[M(CO)_l]^{Q-}$, are one such class of molecules, as highlighted by Ellis.[65] With respect to the bonding in these compounds, there is a close correspondence with nitrosyl complexes because the carbon monoxide anion, CO^-, is isoelectronic with NO; as such, π-bonding becomes an essential component of the bonding because the π^* orbital in CO^- is now occupied. In essence, the bonding representation shifts from $M\leftarrow CO$ to $M=C=O$ and $\overset{+}{M}\equiv C-\overset{-}{O}$ as backbonding increases (Figure 8). The importance of these resonance structures has been discussed by Beck.[66]

Rather than viewing metal carbonyl anions as derivatives of $(CO)^-$, a more common approach for discussing the bonding in $[M(CO)_l]^{Q-}$ is to consider that the molecule is hypothetically derived by coordination of CO to an anionic metal center. By so doing, the electron density on an already negative metal center would be increased. However, effective π-backbonding serves to ensure that the electron density is transferred from the metal to oxygen. In this regard, a simple illustration of how π-backbonding is influenced by the charge on the molecule is provided by calculations on octahedral $[M(CO)_6]^Q$ complexes, which show that the contribution of the t_{2g} orbitals (*i.e.* the rigorously nonbonding orbital assuming only σ-interactions) to the bonding increases from 4.2% in cationic $[Ir(CO)_6]^{3+}$ to 76.6% in anionic $[Hf(CO)_6]^{2-}$.**67** Thus, the t_{2g} orbitals transform from being classified as largely nonbonding in $[Ir(CO)_6]^{3+}$ to bonding in $[Hf(CO)_6]^{2-}$. This progression is necessarily accompanied by a decrease in the d^n configuration using the definition that this quantity refers to electrons in *d*-based molecular orbitals that are not considered to be bonding.

An excellent experimental illustration of how the charge on the molecule influences the nature of the bonding in binary metal carbonyl compounds, $[M(CO)_n]^Q$, is provided by ν_{CO} IR spectroscopic data, as compiled by Wolczanski.**68** For example, ν_{CO} for the series of isostructural octahedral complexes, $[M(CO)_6]^Q$, decreases in the sequence $[Fe(CO)_6]^{2+}$ (2197 – 2204 cm^{-1}),**69** > $[Mn(CO)_6]^+$ (2096 cm^{-1}) > $Cr(CO)_6$ (2000 cm^{-1}) > $[V(CO)_6]^-$ (1859 cm^{-1}) > $[Ti(CO)_6]^{2-}$ (1748 cm^{-1}).68,**70** This progressive change is clear evidence of enhanced backbonding and a shift towards a contribution from the $M^+{\equiv}C{-}O^-$ resonance structure as the negative charge on the molecule increases.

Other experimental evidence for an increase in M–C bonding as the charge on the molecule is increases is provided by Peters' report of the series of complexes $[(SiP^{iPr}{}_3)Fe(CO)]^Q$ (Q = +1, 0, –1), in which the Fe–CO bond length progressively decreases as the charge becomes more negative, namely $[(SiP^{iPr}{}_3)Fe(CO)]^+$ (1.842 Å), $[(SiP^{iPr}{}_3)Fe(CO)]$ (1.769 Å) and $[(SiP^{iPr}{}_3)Fe(CO)]^-$ (1.732) Å.**71** In accord with a shift towards the $M^+{\equiv}C{-}O^-$ resonance structure as the charge on the molecule becomes more negative, it is noteworthy that the monoanion, $[(SiP^{iPr}{}_3)Fe(CO)]^-$, may be alkylated to form $(SiP^{iPr}{}_3)Fe{\equiv}COSiMe_3$.71 The latter molecule is classified as a carbyne,71 and thus the alkylation reaction reflects a Lewis structure for $[(SiP^{iPr}_3)Fe(CO)]^-$ with a negative charge localized on the oxygen rather than on the metal. Closely related to CO are isocyanide (CNR) ligands and similar effects are also observed upon formation of anionic derivatives.**[72]** For example, Figueroa has reported that $[Cp^*Co(CNAr^{Tripp2})]^{2-}$ has a very short Co–C bond length (1.670 Å) that is consistent with a Co≡C triple bond.**[73]**

Within the CBC method, charged molecules of the type $[ML_lX_xZ_z]^Q$ are transformed to the equivalent neutral class (Table 2);4 for binary carbonyl anions, $[M(CO)_l]^{Q-}$, the simplest transformation is $L^- \rightarrow LX$, which would convert $[M(CO)_l]^{Q-}$ to a classification of $[ML_{l-Q}X_Q]$. However, as discussed for NO above, the appropriate classification requires the symmetry of the molecule to be considered. For example, $[Fe(CO)_4]^{2-}$ would be classified as the 18-electron molecule ML_4X_2, as illustrated by the qualitative molecular orbital diagram (Figure 14). Thus, the neutral metal atom contributes two of its electrons to the e set of bonding orbitals,**[74]** such that the iron center possesses a d^6 configuration. In essence, in the presence of strong π-backbonding, a tetrahedral array of four CO ligands is a $[L_4Z_2]$ complement. Thus, $[Fe(CO)_4]^{2-}$ is classified as $[ML_4Z_2]^{2-}$, which becomes ML_4X_2 upon transforming to the equivalent neutral class (Table 2). Similar analyses can be performed for other metal carbonyl anions and the classification of multiple carbonyl ligand combinations, assuming that π-backbonding is a significant contribution, is summarized in Table 4. Thus, if π-backbonding is considered to be significant in $[Co(CO)_4]^-$, the molecule would be classified as $[ML_4Z_2]^-$ which transforms to ML_3X_3, with a d^6 configuration, and not the d^8 configuration that has been inferred by not taking into account the symmetry requirements of multiple π-acceptor ligands.6

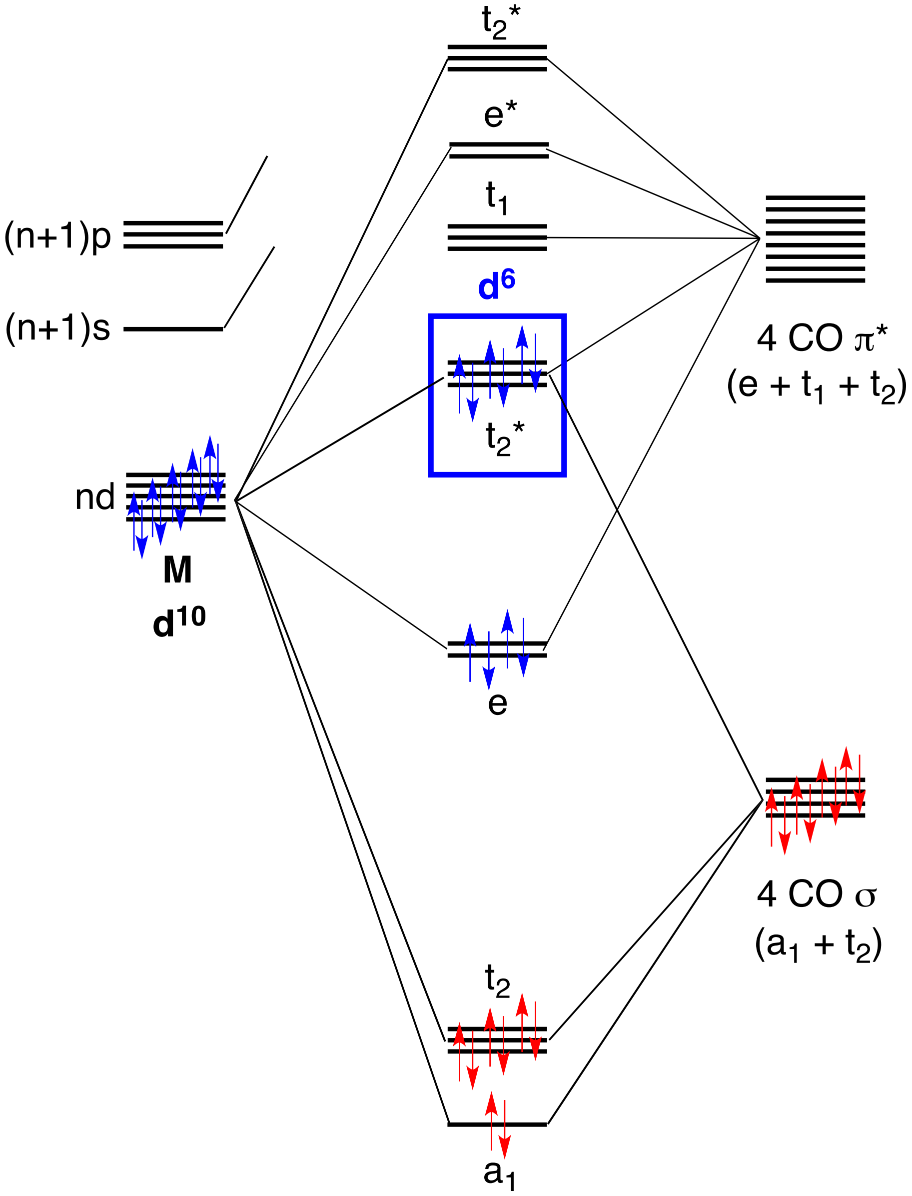


Figure 14. Qualitative molecular orbital diagram for $[M(CO)_4]^Q$ compounds with an 18–electron configuration, in which backbonding is considered to be significant *e.g.* $[Fe(CO)_4]^{2-}$. Note that the occupied e-set of bonding orbitals are not included in the formally nonbonding d^n configuration if there is significant backbonding**.**

Table 4. Classification of $(CO)_n$ combinations assuming that π-interactions are significant.

composition	**geometry**	**classification of $(CO)_n$ combination**
$M(CO)_4$	tetrahedral	$L_4Z_2 = L_2X_4$
$M(CO)_5$	trigonal bipyramidal	$L_5Z_2 = L_3X_4$
$M(CO)_6$	octahedral	$L_6Z_3 = L_3X_6$

It has been suggested that the ML_4X_2 CBC description of $[Fe(CO)_4]^{2-}$ as possessing a d^6 configuration is not in accord with its diamagnetic nature because d^6 tetrahedral compounds are expected to be paramagnetic.6,[75] However, this notion appears to be based on a σ-only molecular orbital diagram that does not take into account the fact that the presence of ligands with π-acceptor orbitals reduces the d^n configuration if the interaction is significant. If the bonding e set of orbitals were to be included in the above d^n configuration (*i.e.* neglecting the bonding character), the molecule would be characterized as "d^{10}", a situation that corresponds closely to the reason for the introduction of the Enemark-Feltham notation for metal nitrosyls, which is not surprising in view of the aforementioned isoelectronic relationship between NO and $(CO)^-$.

Regarding the CBC classification of a d^6 configuration for $[Fe(CO)_4]^{2-}$, it is pertinent to note that this description is in accord with Wolczanski's view of this molecule. Specifically, Wolczanski has emphasized that the formal oxidation state of Fe(–II) for $[Fe(CO)_4]^{2-}$ is "not a reality" and favors an Fe(II) description.68,[76,77] Supporting this suggestion, the Bader charge of Fe in $[Fe(CO)_4]^{2-}$ (+1.02) is very similar to that in the Fe(II) counterpart, $[Fe(CO)_6]^{2+}$ (+1.37);[78,79] the difference in charge on the iron certainly does not reflect the +4 units difference in oxidation states of these two molecules, although it must be recognized that the actual charge and oxidation state may bear no relation.22,[80] As noted above, any incipient negative charge that is placed on the metal in $[Fe(CO)_4]^{2-}$ is removed by strong backbonding with the carbonyl ligands, thereby reducing the d^n count such that it resembles the Fe(II) species, $[Fe(CO)_6]^{2+}$. In this regard, it is relevant that $[Fe(CO)_4]^{2-}$ and $[Fe(CO)_6]^{2+}$ possess the same CBC description, namely ML_4X_2. The two molecular species differ, however, in that π-backbonding is a critical component for $[Fe(CO)_4]^{2-}$ but is of much less significance for $[Fe(CO)_6]^{2+}$.

In addition to coordination of multiple π-acid ligands to transition metals, examples are also known for main group metals, although they are less commonly encountered. Nevertheless, the bonding principles enunciated above also apply to main group compounds, with the distinction that the metal donor orbitals are *p*-orbitals rather than *d*-orbitals. Examples of such compounds are provided by the beryllium and zinc complexes,[**81**] $(cAAC^{Ar})_2Be$[**82**] and $(cAAC^{Ar})_2Zn$[**83**] (Figure 15), which feature cyclic (alkyl)(amino)carbene ligands that possesses both σ-donor and π-acceptor character.30 Interestingly, despite the overall similarity of $(cAAC^{Ar})_2Be$ and $(cAAC^{Ar})_2Zn$, the molecules were described in significantly different ways.

The zinc compound was the first to be reported and was described as a "singlet biradicaloid", in which the bonding involved each cAAC ligand coordinating *via* a normal covalent σ-bond in the triplet state, with the unpaired electrons on each carbon forming a 3c-2e linear π-bond using the vacant *p*-orbital on Zn. In contrast to this description in which the zinc is divalent by virtue of the two σ-bonds, the beryllium counterpart was subsequently described as a "zero-valent" compound with two singlet carbenes donating two pair of electrons to beryllium. The lone pair of electrons on beryllium is, nevertheless, involved in a 3c-2e linear π-bond with the two vacant *p*-orbitals on the carbon atoms. In view of this 3c-2e interaction, it is evident that the beryllium no longer possesses a lone pair of electrons and hence should not be classified as zerovalent.

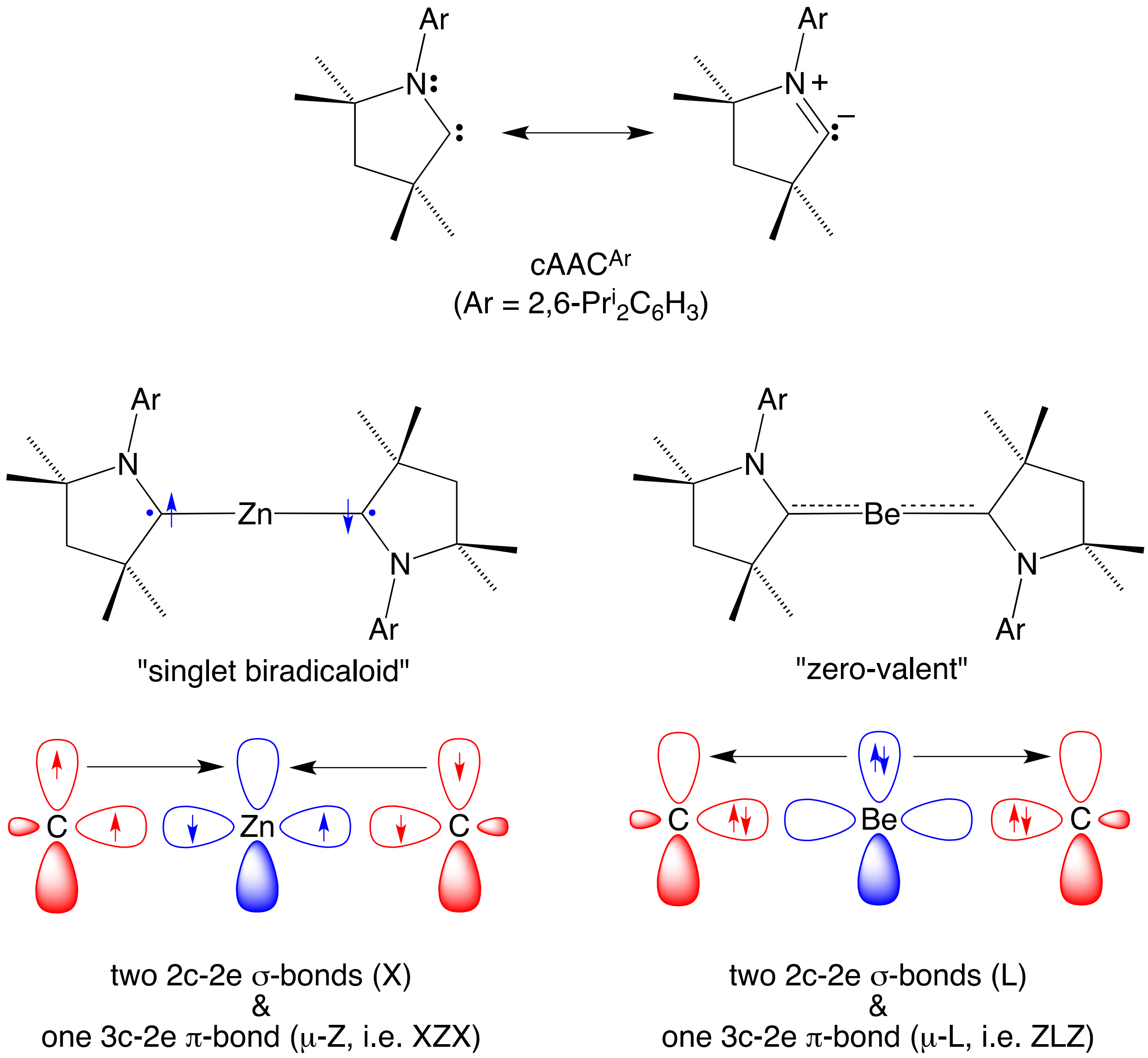


Figure 15. Representations of $(cAAC^{Ar})_2Zn$ and $(cAAC^{Ar})_2Be$ as described in the literature and their proposed bonding scheme. The zinc compound is described as "singlet biradicaloid", in which each $cAAC^{Ar}$ ligand coordinates *via* a normal covalent σ-bond in the triplet state, with the unpaired electrons on each carbon forming a 3c-2e linear π-bond using the vacant *p*-orbital on Zn. In contrast, the beryllium compound is described as "zero-valent" in which each singlet carbene donates a pair of electrons to beryllium. The lone pair of electrons on beryllium is, nevertheless, involved in a 3c-2e linear π-bond with the two vacant *p*-orbitals on the carbon atoms. Despite these apparently very different descriptions, there is no difference with respect to the CBC approach (see **Figure 16**).

Despite these very different descriptions for two similar main group metal compounds, $(cAAC^{Ar})_2Be$ and $(cAAC^{Ar})_2Zn$, no rationale was provided as to why these compounds should be represented with very different bonding patterns. Intriguingly, a closely related zinc complex, namely $(BICAAC)_2Zn$, has been described as both a "singlet biradicaloid" and as "zero valent";**[84]** it is not evident how both of these terms can be applied to the same molecule. $(BICAAC)_2Zn$ is also reported to be stable to water, which would be most unusual for a *bona fide* zerovalent zinc compound. The zerovalent designation for beryllium is also highly unusual for compounds of this element. Classifying a metal center in $(cAAC^{Ar})_2M$ as zerovalent is only appropriate if the $cAAC^{Ar}$ ligand serves as a σ-L donor, with negligible π-interactions, such that the metal effectively retains its nonbonding lone pair. If π-interactions with the *p* orbitals on the carbon are considered to participate significantly in the bonding, the metal centers in the molecules are more appropriately classified as divalent. Since the bonding of both $(cAAC^{Ar})_2Be$ and $(cAAC^{Ar})_2Zn$ is proposed to involve participation of the carbon *p* orbitals,82,83 both molecules may be classified as divalent compounds. In this regard, it is pertinent that Landis has also addressed the zerovalent description of some transition metal $(cAAC)_2M$ compounds.**[85]**

From the perspective of the CBC method, both $(cAAC^{Ar})_2Be$ and $(cAAC^{Ar})_2Zn$ have the same classification, namely MLX_2 (Figure 16 and Figure 17). For example, viewing the $cAAC^{Ar}$ ligand as a singlet, the bonding in "zerovalent" $(cAAC^{Ar})_2M$ is represented in terms of an L interaction involving σ-donation from each carbon lone pair, supplemented by a Z interaction involving 3c-2e π-donation of the lone pair in the metal *p* orbital to both empty *p* orbitals on carbon (*i.e.* a ZLZ 3c-2e interaction).**[86]** The metal center is thus classified as ML_2Z, which is equivalent to MLX_2 using the relationship that $LZ = X_2$. Thus, as with metal carbonyl and nitrosyl compounds, the $ML_lX_xZ_z$ description of $(cAAC^{Ar})_2M$ is not simply the sum of the contribution of two individual ligands that would be either ML_2 or MX_4 depending on the magnitude of the π-interactions.

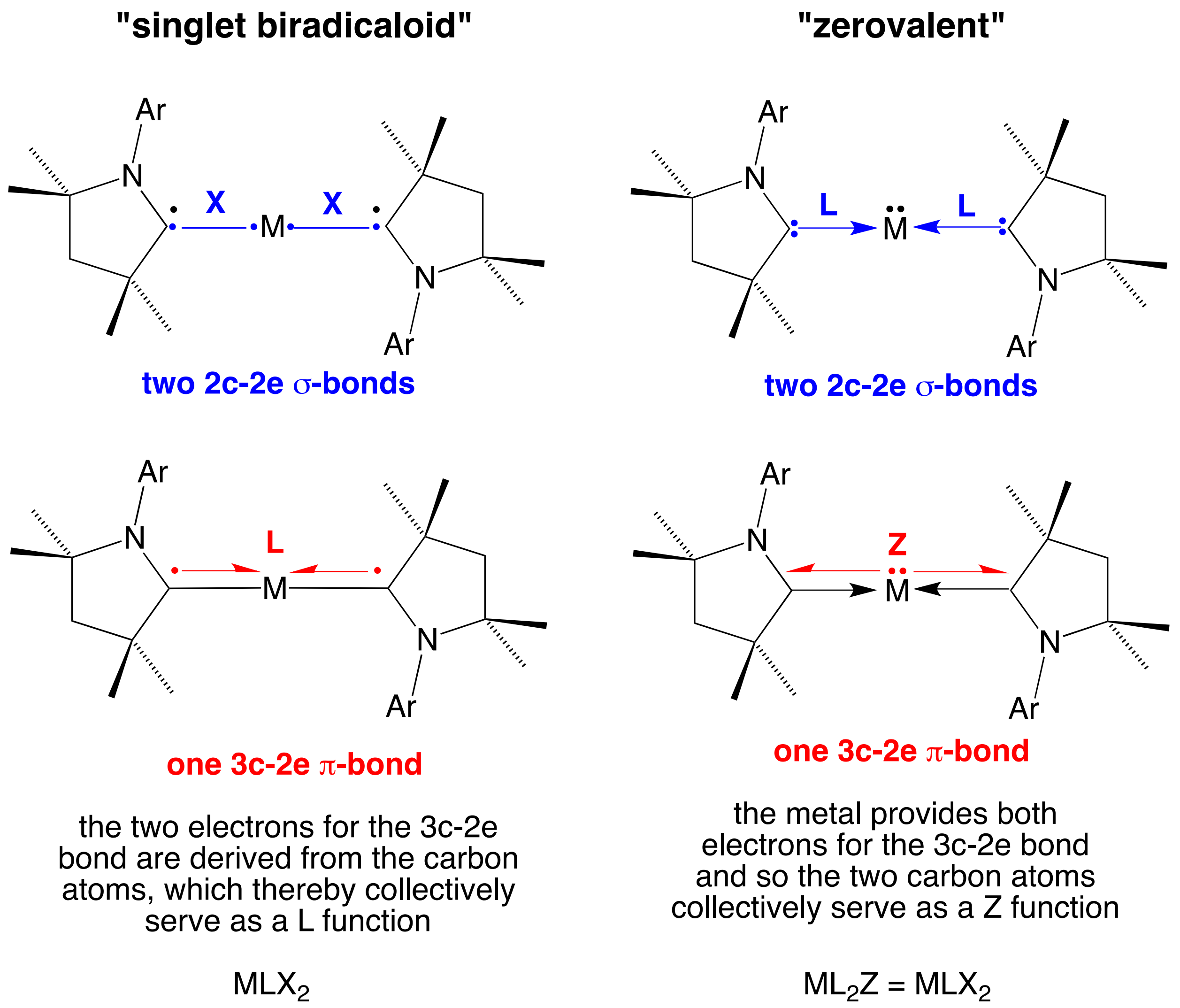
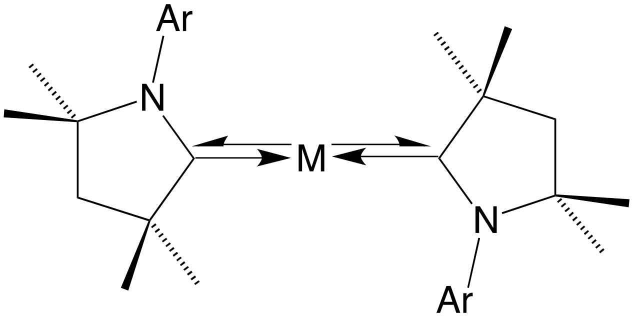


Figure 16. Demonstration that the "singlet biradicaloid" and "zerovalent" descriptions of $(cAAC^{Ar})_2M$ are equivalent according to the CBC method. For each description, the upper figure illustrates the two 2c-2e σ-bonds, while the bottom figure illustrates the 3c-2e π-bond.

Adopting the alternative perspective in which the $cAAC^{Ar}$ ligand is viewed as a triplet and $(cAAC^{Ar})_2M$ is described as a "singlet biradicaloid", each M–C σ-bond corresponds to an X interaction, while the electrons in the two carbon *p*-orbitals provide both electrons for the 3c-2e π-bond; the metal does not contribute any electrons such that the overall combination corresponds to an L interaction. Thus, the metal center is also classified as MLX_2 for this description of the bonding.

The fact that the two bonding representations give rise to the same CBC description is not surprising because they correspond to the same molecular orbital pattern. Specifically, the molecular orbitals of a molecule are independent of how one chooses to deconstruct the molecule in a hypothetical manner. For example, the molecular orbitals of WCl_6 are independent of whether one decides to construct the molecule as *(i)* W and six Cl atoms or *(ii)* W^{6+} and six Cl^{-} ligands. Thus, if interactions with both the *sp*^{2} and *p* orbitals of the cAAC ligand are deemed significant, it is evident that bonding within the C–M–C moiety of $(cAAC^{Ar})_2M$ may be described by two C–M–C σ-bonding orbitals and one C–M–C π-bonding orbital. The metal contributes two electrons to these bonding orbitals and hence is divalent, as illustrated in Figure 18.



$ML_2Z = MLX_2$

Figure 17. CBC representation of $(cAAC^{Ar})_2M$. The 3c-2e π-interaction is represented with two "half-arrows" which indicate that the pair of electrons is donated to both carbon atoms.

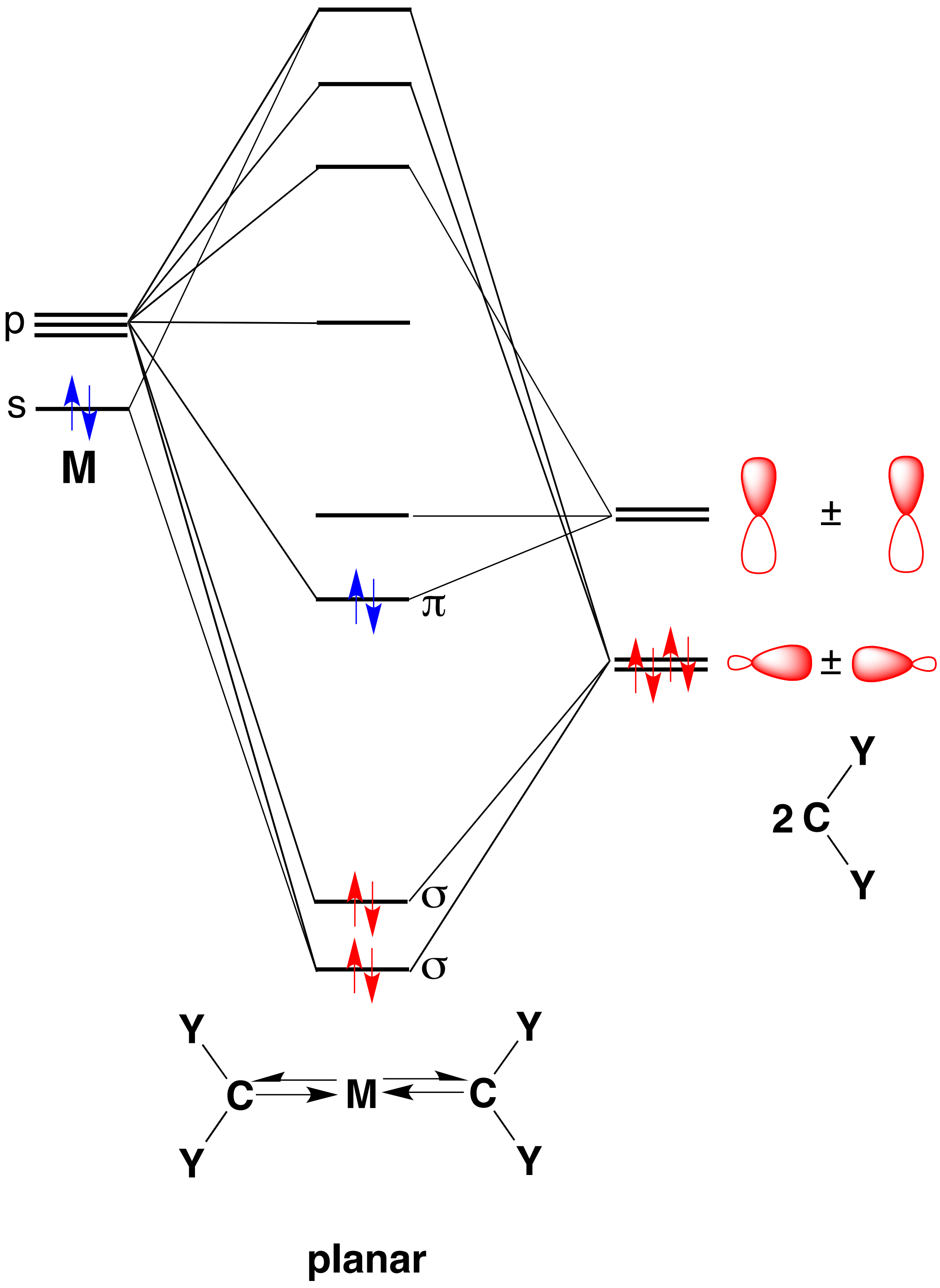


Figure 18. Qualitative molecular orbital diagram for coordination of two [CY_2] moieties to a main group metal in a planar (non orthogonal) arrangement. The interactions result in two σ-bonding orbitals and one π-bonding orbital. The metal contributes two electrons to these bonding orbitals and so is divalent.

SUMMARY

The CBC method enables a covalent molecule to be classified as $ML_lX_xZ_z$, which indicates the number and types of ligand functions (L, Z and Z) that surround an element of interest (M). In addition to providing a classification, the $ML_lX_xZ_z$ description also contains information that relates to electron count, v^n configuration and valence. As such, the $ML_lX_xZ_z$ description embodies more information than a simple number that corresponds to oxidation state.

By comparison to L and X functions, ligands that coordinate to a metal by using a Z function as their primary interaction (*i.e.* Lewis acids) are not as common, such that their impact on the v^n configuration and valence is not as well recognized as those for L and X donor ligands. Furthermore, the majority of Z interactions that are encountered are of either π- or δ-character, and hence of a secondary nature, such that the Z component is often not included in deriving the primary CBC classification of a molecule; nevertheless, it is useful to indicate the presence of these interactions by using the Z' notation to represent an undetermined component.

However, although π- and δ-interactions may often be considered to be of a secondary nature to the overall bonding, there are situations in which they may be a critical component of the bonding and, in such cases, the Z component should be explicitly included. Specific examples in which it is important to consider including a Z π-component are metal nitrosyls, metal carbonyl anions, and metal carbenes/alkylidenes. Inclusion of the Z component, however, requires due attention be given to the symmetry requirements of the π-interactions, and this is of particular importance when there are multiple π-acceptor ligands present in the molecule.[4c,44] Failure to take these symmetry requirements into account will result in the incorrect classification of a molecule, as illustrated by $W(CO)_6$ and $Cr(NO)_4$ having been represented as MX_{12},[6] which is an implausible classification for these elements.

Acknowledgments

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REFERENCES

(1) (a) Lewis, G. N. *Valence and The Structure of Atoms and Molecules* The Chemical Catalog Company, 1923.

(b) Lewis, G. N. *J. Chem. Phys.* **1933**, *1,* 17-28.

(2) (a) Langmuir, I. *Science* **1921**, *54*, 59-67.

(b) Langmuir, I. *Proc. Natl. Acad. Sci. U. S. A.* **1919**, *5*, 252-259.

(3) (a) Mingos, D. M. P. *J. Organomet. Chem.* **2004**, *689*, 4420-4436.

(b) Jensen, W. B. *J. Chem. Educ.* **2005**, *82,* 28-28.

(c) Rasmussen, S. C. *ChemTexts* **2015,** *1*, 10.

(4) (a) Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127-148.

(b) Green, M. L. H. in *Molybdenum: An Outline of its Chemistry and Uses*, Braithwaite, E. R.; Haber, J. (Eds.), Chapter 2, Elsevier, Amsterdam, 1994.

(c) Parkin, G. *Comprehensive Organometallic Chemistry III*, Volume 1, Chapter 1; Crabtree, R. H. and Mingos, D. M. P. (Eds), Elsevier, Oxford, 2007.

(d) Green, M. L. H.; Parkin, G. *J. Chem. Educ.* **2014**, *91*, 807-816.

(e) Green, J. C.; Green, M. L. H.; Parkin, G. *Chem. Comm.* **2012**, *48*, 11481-11503.

(f) Green, M. L. H.; Parkin, G. *Dalton Trans.* **2016**, *45*, 18784-18795.

(5) (a) Karen, P.; McArdle, P.; Takats, J. *Pure Appl. Chem.* **2014**, *86*, 1017-1081.

(b) Karen, P.; McArdle, P.; Takats, J. *Pure Appl. Chem.* **2016**, *88*, 831-839.

(6) Norman, N. C.; Pringle, P. G. *Dalton Trans.* **2021**, DOI: 10.1039/d0dt03914d..

(7) See, for example: Pauling, L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(8) Weinhold, F.; Landis, C. R. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: Cambridge U.K., 2005.

(9) Note that this d^n description is only strictly appropriate for positively charged species where the xd orbitals are sufficiently lower in energy than the $(x + 1)s$ orbital such that the latter is not occupied. See:

(a) "Atomic Energy Levels as Derived From the Analyses of Optical Spectra, Vol I" C. E. Moore, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.)* (1971).

(b) "Atomic Energy Levels as Derived From the Analyses of Optical Spectra, Vol II" C. E. Moore, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.)* (1971).

(10) Jean, Y. *Molecular Orbitals of Transition Metal Complexes*, Oxford University Press, New York (2005).

(11) (a) Nyholm, R. S. *J. Inorg. Nucl. Chem.* **1958**, *8*, 401-422.

(b) Nyholm, R. S. *Pure Appl. Chem.* **1968**, *17*, 1-19.

(12) For example, Jørgensen has described *(i)* "formal oxidation numbers" that are written with superscript Roman numerals, *e.g.* Cr^{II}, *(ii)* "spectroscopic oxidation states", that are derived from observed excited levels and are written with the Roman numerals on line and in parentheses, *e.g.* Cr(III), *(iii)* "conditional oxidation states" that are derived by consideration of the occupation of partly filled shell with the smallest average radius and are written with the Roman numerals on line and in square brackets, *e.g.* Ti[II] (interestingly, for this definition, the configurations $[Ar]3d^2$ for Ti^{+2}, $[Ar]3d^24s$ for Ti^+ and $[Ar]3d^24s^2$ for Ti^0, all correspond to Ti[II]), *(iv)* "quanticule oxidation states", *e.g.* N{III} in NH_3 and N{V} in NH_4^+, and *(v)* "distributed quanticule oxidation states", which is closely related to the concept of formal charges. See:

(a) Jørgensen, C. K. *Oxidation Numbers and Oxidation States*; Springer: Heidelberg, Germany, 1969.

(b) Jørgensen, C. K. *Struct. Bond.* **1966**, *1*, 234-248.

(13) Wieghardt has introduced the term "physical oxidation state" as being synonymous with Jørgensen's "spectroscopic oxidation state". See: Chaudhuri, P.; Verani, C. N.; Bill, E.; Bothe, E.; Weyhermuller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2001**, *123*, 2213–2223.

(14) (a) Postils, V.; Delgado-Alonso, C.; Luis, J. M.; Salvador, P. *Angew. Chem. Int. Edit.* **2018**, *57*, 10525-10529.

(b) Gimferrer, M.; Van der Mynsbrugge, J.; Bell, A. T.; Salvador, P.; Head-Gordon, M. *Inorg. Chem.* **2020**, *59*, 15410-15420.

(15) In addition, the presence of element-element bonds will also result in different d^n configurations using the expressions $n = m - \mathrm{VN}$ and $n = m - \mathrm{OS}$ because the latter does not take into account the electrons that are needed to form the element-element bond.

(16) See, for example:

(a) Ashley, D. C.; Baik, M. H. *ACS Catal.* **2016**, *6*, 7202-7216.

(b) Štekláč, M.; Breza, M. *Polyhedron* **2021**, *201*, 115172.

(c) Jørgensen, C. K. *Coord. Chem. Rev.* **1966**, *1*, 164-178.

(17) (a) Walroth, R. C.; Lukens, J. T.; MacMillan, S. N.; Finkelstein, K. D.; Lancaster, K. M. *J. Am. Chem. Soc.* **2016**, *138*, 1922−1931.

(b) DiMucci, I. M.; Lukens, J. T.; Chatterjee, S.; Carsch, K. M.; Titus, C. J.; Lee, S. J.; Nordlund, D.; Betley, T. A.; MacMillan, S. N.; Lancaster, K. M. *J. Am. Chem. Soc.* **2019**, *141*, 18508-18520.

(18) Hoffmann, R.; Alvarez, S.; Mealli, C.; Falceto, A.; Cahill, T. J.; Zeng, T.; Manca, G. *Chem. Rev.* **2016**, *116*, 8173-8192.

(19) For other examples, see:

(a) Ruccolo, S.; Rauch, M.; Parkin, G. *Chem. Sci.* **2017**, *8*, 4465-4474.

(b) Steen, J. S.; Knizia, G.; Klein, J. *Angew. Chem. Int. Edit.* **2019**, *58*, 13133-13139.

(20) Cooper, G.; Sze, K. H.; Brion, C. E. *J. Am. Chem. Soc.* **1989**, *111*, 5051-5058.

(21) Parkin, G. *Organometallics* **2006**, *25*, 4744-4747.

(22) It must be emphasized that the positive charge on oxygen in the triply bonded form is the formal charge and is not intended to reflect the actual charge. See, for example: Parkin, G. *J. Chem. Educ.* **2006**, *83*, 791-799.

(23) Lewis structures that feature dianionic O^{2-} are not included because the CBC method is concerned with compounds that feature covalent bonds.

(24) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 6th ed., Wiley, Hoboken, 2014, Chapter 11.

(25) Note that the X_2 notation is equivalent to the carbene being viewed as a triplet, while the L notation is equivalent to it being viewed as a singlet.

(26) (a) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39-91.

(b) Jahnke, M. C.; Hahn, F. E. in *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools, 2nd edition*, Diez-Gonzalez, S., Ed. Royal Soc Chemistry: Cambridge, 2017; Vol. 27, pp 1-45.

(c) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361-363.

(d) Arduengo, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530-5534.

(27) (a) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485-496.

(b) Dröge, T.; Glorius, F. *Angew. Chem. Int. Edit.* **2010**, *49*, 6940-6952.

(c) Hock, S. J.; Schaper, L.-A.; Hermann, W. A.; Kuhn, F. E. *Chem. Soc. Rev.* **2013**, *42,* 5073-5089.

(28) Sau, S. C.; Hota, P. K.; Mandal, S. K.; Soleilhavoup, M.; Bertrand, G. *Chem. Soc. Rev.* **2020**, *49*, 1233-1252.

(29) (a) Soleilhavoup, M.; Bertrand, G. *Acc. Chem. Res.* **2015**, *48*, 256-266.

(b) Lavallo, V.; Canac, Y.; Prasang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Edit.* **2005**, *44*, 5705-5709.

(c) Jazzar, R.; Soleilhavoup, M.; Bertrand, G. *Chem. Rev.* **2020**, *120*, 4141-4168.

(d) Melaimi, M.; Jazzar, R.; Soleilhavoup, M.; Bertrand, G. *Angew. Chem. Int. Edit.* **2017**, *56*, 10046-10068.

(30) Mondal, K. C.; Roy, S.; Maity, B.; Koley, D.; Roesky, H. W. *Inorg. Chem.* **2016**, *55*, 163-169.

(31) The Z′ component for a Fischer carbene is associated with a situation in which the high energy p-orbital illustrated in Figure 7 (left hand side) becomes available. Since this p-orbital is also involved in a π-interaction with the adjacent heteroatom, the Z′ component formally corresponds to a resonance structure in which there is no π-donation from the adjacent heteroatom.

(32) Mingos, D. M. P. *J. Organomet. Chem.* **2001**, *635*, 1-8.

(33) *Orbital Interactions in Chemistry*, Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. Wiley, Hoboken, New Jersey (2013).

(34) (a) Green, M. L. H.; Ng, D. K. P. *Chem. Rev.* **1995**, *95*, 439-473.

(b) Green, J. C.; Kaltsoyannis, N.; Sze, K. H.; Macdonald, M. *J. Am. Chem. Soc.* **1994**, *116*, 1994-2004.

(35) (a) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149-155.

(b) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499-525.

(c) Zhu, G.; Janak, K. E.; Figueroa, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2006**, *128*, 5452-5461.

(d) Byers, B. P.; Hall, M. B. *Organometallics* **1987**, *6*, 2319-2325.

(36) Lupinetti, A. J.; Strauss, S. H.; Frenking, G. *Prog. Inorg. Chem.* **2001**, *49*, 1-112.

(37) (a) Howard, W. A.; Trnka, T. M.; Parkin, G. *Organometallics* **1995**, *14*, 4037-4039.

(b) Howard, W. A.; Parkin, G.; Rheingold, A. L. *Polyhedron* **1995**, *14*, 25-44.

(38) Alternatively, if there were to be no π-overlap, a variety of other bonding situations could be considered, depending upon the occupancy of the π* orbitals associated with NO in the molecule. For example, NO would be regarded as an X ligand if the π* orbitals are doubly occupied, or as an L ligand if the π* orbitals are singly occupied.

(39) Manoharan, P. T.; Gray, H. B. *Inorg. Chem.* **1966**, *5*, 823-839.

(40) (a) Hummel, P.; Gray, H. B. *Coord. Chem. Rev.* **2007**, *251*, 554-556.
(b) Hummel, P.; Winkler, J. R.; Gray, H. B. *Theor. Chem. Acc.* **2008**, *119*, 35-38.

(41) Bendix, J.; Meyer, K.; Weyhermüller, T.; Bill, E.; Metzler-Nolte, N.; Wieghardt, K. *Inorg. Chem.* **1998**, *37*, 1767-1775.

(42) (a) Mingos, D. M. P. *Struct. Bond.* **2014**, *153*, 1-44.
(b) Mingos, D. M. P. *Struct. Bond.* **2014**, *154*, 1-51.

(43) Odom, A. L.; Cummins, C. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6613-6614.

(44) For other examples that support the M≡□□□triple bond description of a linear nitrosyl interaction in a high symmetry situation, see: Landry, V. K.; Pang, K. L.; Quan, S. M.; Parkin, G. *Dalton Trans.* **2007**, 820-824.

(45) Richter-Addo, G. B.; Legzdins, G. B. *Metal Nitrosyls*, Oxford University Press, New York, 1992.

(46) (a) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339-406.
(b) Feltham, R. D.; Enemark, J. H. In *Topics in Inorganic and Organic Stereochemistry*; Wiley: New York, **1981**, *12*, 155-215.
(c) Westcott, B. L.; Enemark, J. H. in *Inorganic Electronic Structure and Spectroscopy*; *Inorganic Electronic Structure and Spectroscopy, Volume II: Applications and Case Studies*, Lever, A. B. P.; Solomon, E. I.; Eds, Chapter 7, pp 403-450, 1999

(47) For reviews of metal nitrosyl compounds, see:
(a) Hayton, T. W.; Legzdins, P.; Sharp, W. B. *Chem. Rev.* **2002**, *102*, 935-991.
(b) McCleverty, J. A. *Chem. Rev.* **2004**, *104*, 403-418.
(c) Machura, B. *Coord. Chem. Rev.* **2005**, *249*, 2277-2307.
(d) Scheidt, W. R.; Ellison, M. K. *Acc. Chem. Res.* **1999**, *32*, 350-350.
(e) Mingos, D. M. P.; Sherman, D. J. *Adv. Inorg. Chem.* **1989**, *34*, 293-377.

(48) Ampssler, T.; Monsch, G.; Popp, J.; Riggenmann, T.; Salvador, P.; Schroder, D.; Klufers, P. *Angew. Chem. Int. Edit.* **2020**, *59*, 12381-12386.

(49) Ehlers, A. W.; Dapprich, S.; Vyboishchikov, S. F.; Frenking, G. *Organometallics* **1996**, *15*, 105-117.

(50) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832–2838.

(51) For examples of *trans* metal dinitrosyl compounds, see:

(a) Cavichiolo, L. J.; Hörner, M.; Crespan, E. D.; Vaz, M. G. F.; Evans, D. J.; Nunes, F. S. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1613-1618.

(b) Göldner, M.; Geniffke, B.; Franken, A.; Murray, K. S.; Homborg, H. *Z. Anorg. Allg. Chem.* **2001**, *627*, 935-947.

(52) For example, see:

(a) Bohnenberger, J.; Krossing, I. *Angew. Chem. Int. Edit.* **2020**, *59*, 5581-5585

(b) Hess, J. L.; Hsieh, C.-H.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **2011**, *50*, 8541-8552.

(c) Hsieh, C.-H.; Pulukkody, R.; Darensbourg, M. Y. *Chem. Commun.* **2013**, *49*, 9326-9328.

(53) *Metal-Ligand Multiple Bonds*, Nugent, W. A.; Mayer, J. M.; Wiley, New York (1988).

(54) Winkler, JR.; Gray, H. B. "Electronic structures of oxo-metal ions"*Struct. Bond.* **2012**, *142*, 17-28.

(55) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149-167.

(56) In addition to these examples involving either π-acceptor or π-donor ligands, situations involving both types of ligands have been discussed. See, for example: Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. "Metal dπ-ligand π conflicts in octahedral oxo, carbyne, and carbonyl-complexes" *J. Am. Chem. Soc.* **1987**, *109*, 5203-5208.

(57) (a) Nugent, W. A.; Mayer, J. M. *Metal-ligand multiple bonds*, Wiley: New York, 1988.

(b) Mayer, J. M. "Metal-oxygen multiple bond lengths: A statistical study" *Inorg. Chem.* **1988**, *27*, 3899-3903.

(58) (a) Tate, D. P.; Augl, J. M.; Ritchey, W. M.; Ross, B. L.; Grasselli, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 3261-3265.

(b) King, R. B. *Inorg. Chem.* **1968**, *7*, 1044-1046.

(c) Laine, R. M.; Moriarty, R. E.; Bau, R. *J. Am. Chem. Soc.* **1972**, *94*, 1402-1403.

(59) (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729-1742.

(b) Jacobsen, H.; Berke, H.; Brackemeyer, T.; Eisenblätter, T.; Erker, G.; Fröhlich, R.; Meyer, O.; Bergander, K. *Helv. Chim. Acta* **1998**, *81*, 1692-1709.

(c) Lukens, W. W., Jr.; Andersen, R. A. *Organometallics* **1995**, *14*, 3435-3439.

(d) Palmer, E. J.; Bursten, B. E. *Polyhedron* **2005**, *25*, 575-584.

(e) Strittmatter, R. J; Bursten, B. E. *J. Am. Chem. Soc.* **1991**, *113*, 552-559.

(f) Bursten, B. E.; Rhodes, L. F.; Strittmatter, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 2758-2766.

(g) Bursten, B. E.; Strittmatter, R. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1069-1085.

(60) (a) Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H.; Davis, W. M. *Inorg. Chem.* **1991**, *30*, 3595-3604.

(b) Anhaus, J. T.; Kee, T. P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642-1643.

(61) Morrison, D. L.; Wigley, D. E. *Inorg. Chem.* **1995**, *34*, 2610-2616.

(62) Davison, A.; Wreford, S. S. *Inorg. Chem.* **1975**, *14*, 703.

(63) Jonas, K.; Korb, P.; Kollbach, G.; Gabor, B.; Mynott, R.; Angermund, K.; Heinemann, O.; Krüger, C. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1714-1718.

(64) (a) Costuas, K.; Saillard, J.-Y. *Chem. Commun.* **1998**, 2047-2048.

(b) King, R. B. *Appl. Organomet. Chem.* **2003**, *17*, 393-397.

(c) Gleiter, R.; Bethke, S.; Okubo, J.; Jonas, K. *Organometallics* **2001**, *20*, 4274-4278.

(65) (a) Ellis, J. E. *Inorg. Chem.* **2006**, *45*, 3167-3186.

(b) Ellis, J. E. *Organometallics* **2003**, *22*, 3322−3338.

(c) Ellis, J. E. *Polyhedron* **1989**, *8*, 1611-1614.

(66) Beck, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 168–169.

(67) Frenking, G. *J. Organomet. Chem.* **2001**, *635*, 9-23.

(68) Wolczanski, P. T. *Organometallics* **2017**, *36*, 622-631.

(69) Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. W.; Aubke, F. "Homoleptic, σ-bonded octahedral superelectrophilic metal carbonyl cations of iron(II), ruthenium(II), and osmium(II). Part 2: Syntheses and characterizations of $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os)" *Inorg. Chem.* **2005**, *44*, 4206-4214.

(70) Ellis, J. E.; Chi, K.-M. "Synthesis, isolation, and characterization of $[K(cryptand\ 2.2.2)]_2[Hf(CO)_6]$, the first substance to contain hafnium in a negative oxidation state. Structural characterization of [K(cryptand 2.2.2)]2[M(CO)6]•Pyridine (M = Ti, Zr, and Hf)" *J. Am. Chem. Soc.* **1990**, *112*, 6022-6025.

(71) Lee, Y.; Peters, J. C. *J. Am. Chem. Soc.* **2011**, *133*, 4438-4446.

(72) Weber, L. *Angew. Chem. Int. Edit.* **1998**, *37*, 1515-1517.

(73) Mokhtarzadeh, C. C.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *J. Am. Chem. Soc.* **2018**, *140*, 8100-8104.

(74) Correspondingly, the dianionic metal contributes four electrons to the bonding orbitals.

(75) For examples of paramagnetic d^6 metal complexes that feature only σ-donor ligands, see: Hawrelak, E. J.; Bernskoetter, W. H.; Lobkovsky, E.; Yee, G. T.; Bill, E.; Chirik, P. J. *Inorg. Chem.* **2005**, *44*, 3103-3111.

(76) It should be noted that Wolczanski's approach assigns a reference state of +2 for iron compounds.

(77) Furthermore, Jensen has stated that the oxidation state of Mn in $[Mn(CO)_4]^{3-}$ is better assigned as V rather than –III. See: Jensen, W. B. *J. Chem. Educ.* **2011**, *88*, 1599-1600.

(78) Koch, D.; Golub, P.; Manzhos, S. "Stability of charges in titanium compounds and charge transfer to oxygen in titanium dioxide" *J. Phys: Conf. Ser.* **2018**, *1136*, 012017.

(79) Furthermore, the NBO charge on the iron in $[Fe(CO)_4]^{2-}$ (–0.436) is also similar to that in the Fe(II) counterpart, $[Fe(CO)_6]^{2+}$ (–0.520). See reference 68.

(80) (a) Koch, D.; Chaker, M.; Ihara, M.; Manzhos, S. *Molecules* **2021**, *26*, 5541.
(b) Aullón, G.; Alvarez, S. "Oxidation states, atomic charges and orbital populations in transition metal complexes" *Theor. Chem. Acc.* **2009**, *123*, 67-73.

(81) With respect to the description of zinc as a main group metal, it is pertinent to note that IUPAC has defined a transition element as "An element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell",[a] neither of which apply to zinc. This aspect of zinc has been discussed in detail by Jensen[b] and also mentioned in many other articles.[c-j]
(a) IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. https://doi.org/10.1351/goldbook.
(b) Jensen, W. B. *J. Chem. Educ.* **2003**, *80*, 952-961.
(c) Constable, E. C. *Dalton Trans.* **2019**, *48*, 9408-9421.
(d) Cao, C. S.; Vernon, R. E.; Schwarz, W. H. E.; Li, J. *Front. Chem.* **2021**, *8*, 813. (10.3389/fchem.2020.00813).
(e) Schlöder, T.; Kaupp, M.; Riedel, S. *J. Am. Chem. Soc.* **2012**, *134*, 11977−11979.

(f) Riedel, S.; Kaupp, M. *Coord. Chem. Rev.* **2009**, *253*, 606-624.

(g) Jensen, W. B. *J. Chem. Educ.* **2008**, *85*, 1491-1492 .

(h) Jensen, W. B. *J. Chem. Educ.* **2008**, *85*, 1182-1183 .

(i) Valentine, A. J. S.; Talapin, D. V.; Mazziotti, D. A. *J. Phys. Chem. A* **2017**, *121*, 3142-3147.

(j) Tsui, B. T. H.; Morris, R. H. *Inorg. Chem.* **2021**, *60*, 13920-13928.

(82) Arrowsmith, M.; Braunschweig, H.; Celik, M. A.; Dellermann, T.; Dewhurst, R. D.; Ewing, W. C.; Hammond, K.; Kramer, T.; Krummenacher, I.; Mies, J.; Radacki, K.; Schuster, J. K. *Nat. Chem.* **2016**, *8*, 890-894.

(83) Singh, A. P.; Samuel, P. P.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Sidhu, N. S.; Dittrich, B. *J. Am. Chem. Soc.* **2013**, *135*, 7324-7329.

(84) Rajendran, N. M.; Gautam, N.; Sarkar, P.; Ahmed, J.; Das, A.; Das, S.; Pati, S. K.; Mandal, S. K. *Chem. Commun.* **2021**, *57*, 5282-5285.

(85) Landis, C. R.; Hughes, R. P.; Weinhold, F. *Organometallics* **2015**, *34*, 3442-3449.

(86) For a detailed discussion concerned with classification of compounds that contain 3c-2e interactions, see reference 4e.