



Comprehensive Organometallic Chemistry III

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1.01

Classification of Organotransition Metal Compounds

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1.01.1 Introduction

The ability to evaluate whether a particular organotransition metal compound is likely to be inert or highly reactive is of considerable significance with respect to understanding, and predicting, the chemistry of a specific system. While experienced practitioners of organometallic chemistry may have a good sense as to what type of reactivity would be

expected for a specific organometallic compound, it is often difficult for non-specialists to assimilate this knowledge in an expeditious manner. In this regard, the only guide that is generally invoked is the “18-electron rule”. Despite its name, however, the “18-electron rule” is *not* a rule, and many chemists are aware of examples that deviate from it. One of the purposes of this article, therefore, is to place the applicability of the “18-electron rule” in context by evaluating the distribution of organotransition metal compounds as a function of electron count. By necessity, this requires knowledge of the procedure and pitfalls pertaining to electron counting. In addition to evaluating organometallic compounds according to their electron count, the distribution of compounds is also analyzed according to Green’s “Covalent Bond Classification (CBC) Method”¹ which provides a more useful means to evaluate the stability of a molecule than merely applying the “18-electron rule”.

1.01.2 Electron Counting Procedures and Valence Shell Electron Count in Transition Metal Complexes

The stability (loosely defined as “ability to be isolated”)² of an organotransition metal compound is dictated by a number of factors which include (i) the valence electron count, (ii) the coordination number, (iii) the d^n configuration and (iv) the valence (*cf* oxidation number) of the transition metal. Of these, the valence electron count (or, more simply, the “electron count”) is often the first to be evaluated, in large part because of the so-called “18-electron rule”.^{3,4} While the applicability of the “18-electron rule” will be discussed later, the usefulness of the electron count is that it provides a first order evaluation as to whether the complex is likely to contain (i) empty metal based orbitals (<18 electrons) or (ii) occupied metal-ligand antibonding orbitals (>18 electrons). This notion is often rationalized by consideration of the molecular orbital diagram of simple octahedral complexes employing σ -only interactions, *e.g.* $\text{Mo}(\text{PMe}_3)_6$, as illustrated in Figure 1. In terms of a molecular orbital analysis, the electron count corresponds to the number of electrons that occupy metal based orbitals and consideration of Figure 1 indicates that an 18-electron count results in full occupation of all bonding and nonbonding orbitals, with no occupation of metal-ligand

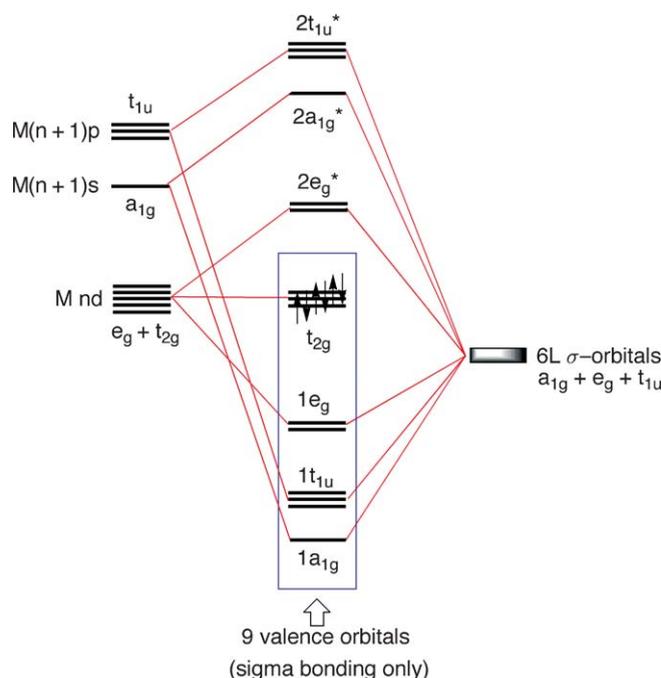


Figure 1 Molecular orbital diagram for an octahedral complex with σ -only interactions. Population of the molecular orbitals by 18-electrons results in occupation of six bonding and three nonbonding orbitals, with no occupation of antibonding orbitals. As such, it provides a simple rationalization for the concept of the 18-electron rule: a 20-electron complex with occupied antibonding orbitals would be expected to be unstable and dissociate a ligand to transform to an 18-electron complex, while a 16-electron complex would be able to bind an additional ligand and transform to an 18-electron complex. However, the nature of the molecular orbital diagram depends critically on the molecular structure (for example, see Figure 2) and so this explanation is necessarily over simplistic.

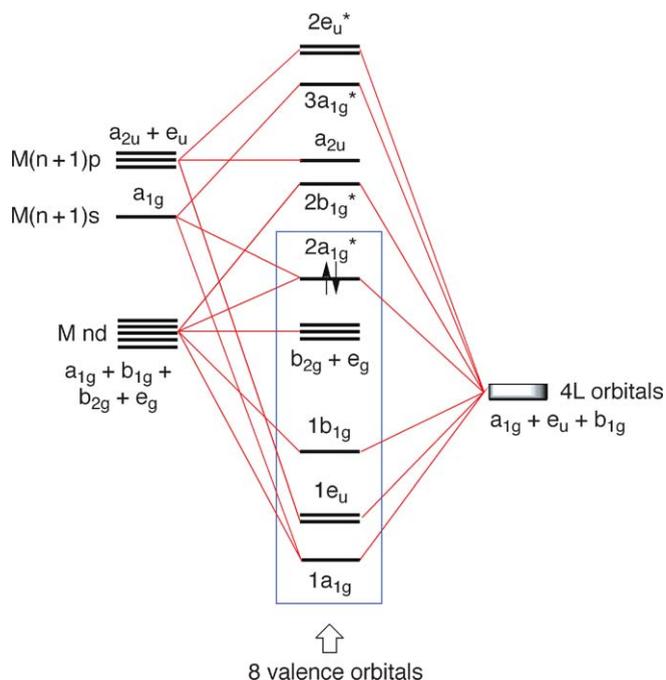


Figure 2 Molecular orbital diagram for a square planar complex with σ -only interactions. The MO diagram is closely related to that for an octahedral complex but with two important (and obvious) differences: (i) the ligand orbitals contribute only four bonding orbitals in the square planar structure, whereas six are contributed in the octahedral structure, and (ii) whereas the $d_{x^2-y^2}$ and d_{z^2} orbitals in an octahedral complex are degenerate and interact equally with the ligand orbitals, only the $d_{x^2-y^2}$ interacts strongly in a square planar geometry. Thus, only one of the d orbitals becomes strongly antibonding. An 18-electron configuration would require the occupation of the strongly antibonding orbital and, as such, a 16-electron configuration becomes favored for a square planar complex.

antibonding orbitals. The 18-electron count, in essence, may therefore be viewed to be a result of the transition metal using its nine valence orbitals, *i.e.* nd, $(n+1)s$, and $(n+1)p$,⁵ in such a manner that only bonding and nonbonding orbitals are occupied; as such, it is a counterpart to the Lewis-Langmuir “octet rule”.⁶ However, the molecular orbital diagram for a transition metal complex is highly dependent on its structure (see, for example, Figures 2 and 3), a consequence of which is that simple electron counting cannot always be used to indicate whether antibonding orbitals are occupied, or nonbonding orbitals are unoccupied.

For example, the molecular orbital diagram for a square planar complex (Figure 2) indicates that an 18-electron configuration results in the occupation of *two* metal-ligand antibonding orbitals derived from the $d_{x^2-y^2}$ and d_{z^2} orbitals. Thus, rather than an 18-electron configuration, a 14-electron count is required to achieve the situation in which all bonding and nonbonding orbitals are occupied and all antibonding orbitals are unoccupied. However, while the metal based $d_{x^2-y^2}$ orbital becomes strongly antibonding because its lobes point directly at the ligands, the d_{z^2} orbital becomes only slightly antibonding because its taurus does not overlap significantly with the ligand orbitals. As such, occupation of the d_{z^2} antibonding orbital is not prohibitive and square planar organotransition metal compounds such as $(R_3P)_2PtR_2$ are commonly characterized by a 16-electron count. Thus, an 18-electron configuration should, by no means, be considered an essential requirement for the existence of a stable organotransition metal compound. As will be discussed in more detail in Section 1.01.4.6.1, different metals favor different electron counts and, for this reason, the determination of the electron count of the metal in an organotransition metal compound remains an important component of evaluating its stability, even though the “18-electron rule” is not universally valid. In view of the importance of the electron count, the procedures used to determine these values are described below.

1.01.2.1 Procedures for Determining the Electron Count

While the electron count for molecules such as $Mo(PMe_3)_6$ or $(R_3P)_2PtR_2$ is explicitly indicated by the respective molecular orbital diagrams (Figures 1 & 2), evaluation of the electron count for most molecules does not require one

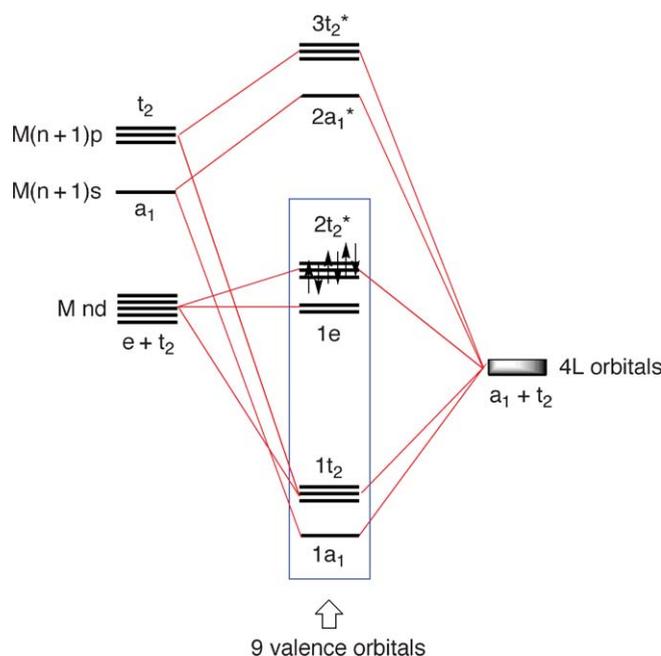


Figure 3 Molecular orbital diagram for a tetrahedral complex with σ -only interactions. The population of all bonding and nonbonding MO's of a tetrahedral complex results in a 12-electron, rather than 18-electron, configuration. An 18-electron configuration for a tetrahedral geometry requires the population of an antibonding t_2^* set. However, since the t_2^* set is only weakly antibonding because the d-orbitals do not point directly at the ligands, its occupation is not prohibitive and the 18-electron rule is applicable to many tetrahedral organometallic compounds.

to construct a molecular orbital diagram for the molecule of interest. Rather, the determination of the electron count of a metal in a compound merely requires knowledge of how many electrons the ligand array contributes to the valence shell of the metal.

There are two procedures for determining the electron count of an atom in a molecule which, *by necessity*, give the same value if applied correctly. The two electron counting procedures involve either (i) a neutral ligand formalism or (ii) an oxidation number formalism.^{7,8} The essential difference between the two methods is that the neutral ligand formalism deconstructs the molecule such that *all* ligands are neutral, whereas the oxidation number formalism deconstructs the molecule such that the pair(s) of bonding electrons are transferred to one partner (typically, but not always, the most electronegative), with the exception of homonuclear element–element bonds which are cleaved homolytically.⁷

An essential component of establishing the electron count for a metal in a molecule is identifying the number of electrons that each ligand contributes to the bonding and the electron donor numbers for a selection of common ligands according to the two formalisms are summarized in [Table 1](#).

1.01.2.1.1 Procedure for electron counting using the neutral ligand formalism

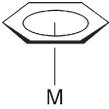
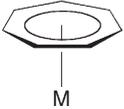
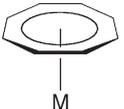
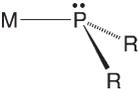
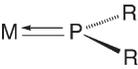
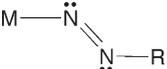
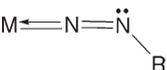
Employing the neutral ligand method, the electron count is the sum of (i) the number of valence electrons of the neutral metal ([Table 2](#)) and (ii) the number of electrons donated by all of the ligands in their neutral form; for cationic and anionic species, the sum is modified appropriately to take account of the charge on the molecule ([Figure 4](#)). The neutral form of some ligands may appear confusing at first glance, especially if it exists as a zwitterion. For example, consider the neutral form of the $[\text{PhB}(\text{CH}_2\text{PR}_2)_3]$ ligand in $\{[\text{PhB}(\text{CH}_2\text{PR}_2)_3]\text{M}\}$ derivatives ([Figure 5](#)). Since boron is attached to four groups it must bear a negative formal charge. To preserve electrical neutrality, one of the phosphorus atoms must bear a formal positive charge, with the result that the phosphorus can only contribute one electron to the metal ([Figure 5](#)). As such, $[\text{PhB}(\text{CH}_2\text{PR}_2)_3]$ corresponds to a five electron donor, with both neutral phosphorus atoms contributing two electrons each, and the positively charged phosphorus contributing one electron. It is evident that this results in the same electron count that would be obtained if $\{[\text{PhB}(\text{CH}_2\text{PR}_2)_3]\text{M}\}$ were to be viewed as an “ion-pair” with three phosphorus lone pairs of anionic $[\text{PhB}(\text{CH}_2\text{PR}_2)_3]^-$ being donated to a cationic metal center.

Table 1 Number of electrons provided by various ligands. Note that, for the oxidation number formalism, the sum of the number of electrons donated and the charge is equal to the number of electrons donated according to the neutral ligand formalism

| <i>Ligand</i> | <i>Metal-Ligand interaction</i> | <i>No. of electrons donated (neutral ligand formalism)</i> | <i>No. of electrons donated & charge (closed-shell formalism)</i> |
|---|---------------------------------|--|---|
| H | M—H | 1 | 2 (−1) |
| R | M—R | 1 | 2 (−1) |
| CR ₂ (Schrock alkylidene) | | 2 | 4 (−2) |
| CR(X) (Fischer carbene) | | 2 | 2 (0) |
| CR | M≡C—R | 3 | 6 (−3) |
| η^2 -C ₂ H ₄ | | 2 | 2 (0) |
| η^3 -C ₃ H ₅ | | 3 | 4 (−1) |
| η^3 -C ₄ H ₆ | | 4 | 4 |
| η^3 -C ₃ H ₃ | | 3 | 2 (+1) |
| η^4 -C ₄ H ₄ | | 4 | 6 (−2) ^a 4 (0) ^a |
| η^5 -C ₅ H ₅ | | 5 | 6 (−1) |

(Continued)

Table 1 (Continued)

| Ligand | Metal-Ligand interaction | No. of electrons donated (neutral ligand formalism) | No. of electrons donated & charge (closed-shell formalism) |
|--------------------------------|---|---|--|
| $\eta^6\text{-C}_6\text{H}_6$ |  | 6 | 6 (0) |
| $\eta^7\text{-C}_7\text{H}_7$ |  | 7 | 6 (+1) ^b 8 (-1) ^b 10 (-3) ^b |
| $\eta^8\text{-C}_8\text{H}_8$ |  | 8 | 10 (-2) ^c |
| CO | $\text{M} \leftarrow \text{CO}$ | 2 | 2 (0) |
| PR ₃ | $\text{M} \leftarrow \text{PR}_3$ | 2 | 2 (0) |
| NO (bent) | $\text{M} - \ddot{\text{N}}\text{O}$ | 1 | 2 (-1) |
| NO (linear) | $\text{M} \leftarrow \text{NO}$ | 3 | 2 (+1) |
| PR ₂ (pyramidal) |  | 1 | 2 (-1) |
| PR ₂ (planar) |  | 3 | 2 (+1) |
| N ₂ R (doubly bent) |  | 1 | 2 (-1) |
| N ₂ R (singly bent) |  | 3 | 2 (+1) |

^aThe closed shell form of square cyclobutadiene is a dianion. However, some articles assign a non-closed shell charge of zero to the cyclobutadiene ligand (see, for example: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, University Science Books: Mill Valley, California, 1987).

^bThe cycloheptatrienyl ligand has variously been assigned charges of +1, -1, and -3. See the text for a discussion of the merit of these values.

^cThe closed shell form of planar cyclooctatetraene is a dianion; the neutral form of cyclooctatetraene is not planar.

Table 2 Number of valence electrons associated with the neutral transition metal atoms (i.e. the group valence). Note that the number of valence electrons is independent of their distribution within the nd and $(n+1)s$ levels

| Group 3 <i>Sc, Y, La</i> | Group 4 <i>Ti, Zr, Hf</i> | Group 5 <i>V, Nb, Ta</i> | Group 6 <i>Cr, Mo, W</i> | Group 7 <i>Mn, Tc, Re</i> | Group 8 <i>Fe, Ru, Os</i> | Group 9 <i>Co, Rh, Ir</i> | Group 10 <i>Ni, Pd, Pt</i> |
|-----------------------------|------------------------------|-----------------------------|-----------------------------|------------------------------|------------------------------|------------------------------|-------------------------------|
| 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |

neutral ligand method

Electron count = no. of M electrons + no. of ligand electrons – charge

oxidation number method

Electron count = no. of M^{n+} electrons + no. of (ligand) $^{\pm q}$ electrons

Figure 4 Procedures for determining the electron count by the neutral ligand formalism and the oxidation number formalism.

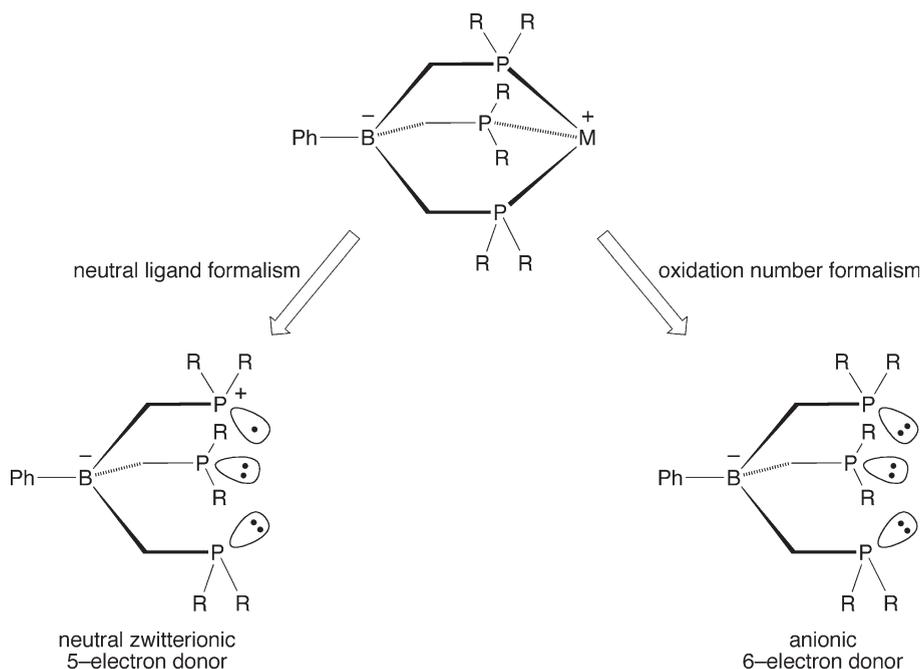


Figure 5 Electron count for the $[\text{PhB}(\text{CH}_2\text{PR}_2)_3]$ ligand according to the neutral ligand and oxidation number formalisms. The neutral form of the ligand is a zwitterion with a negative formal charge on boron and a positive formal charge on phosphorus. As a result of the positive charge, one of the phosphorus atoms is only a single electron donor, such that the neutral ligand is a 5-electron donor to M. With respect to the oxidation number formalism, the anionic form of the ligand serves as a 6-electron donor to cationic M^+ .

1.01.2.1.2 Procedure for electron counting using the oxidation number formalism

Electron counting using the oxidation number formalism is often referred to as either the ionic method or the closed shell method.^{9,10} However, it should be recognized that neither of these terms are particularly appropriate because (i) ligands such as CO are considered to be *neutral* in this formalism and (ii) certain ligands do not have a closed shell¹¹ with the assigned charge. Most notably, the bent nitrosyl ligand is assigned a charge of -1 , but the species NO^- is *not* a closed shell molecule since it is isoelectronic with O_2 and has a triplet ground state.

Using the oxidation number formalism, the electron count is the sum of (i) the number of valence electrons corresponding to the metal in its M^{n+} oxidation state (for cationic and anionic species, the charge is included in the oxidation state of the metal) and (ii) the number of electrons donated by all of the ligands in their assigned form

($L^{\pm q}$), as summarized in Figure 4. A requisite for using this method of electron counting is, therefore, the determination of oxidation number.

The oxidation number of a transition metal is determined by consideration of the charges associated with each ligand. However, while this is normally a trivial exercise when dealing with coordination compounds, problems arise when evaluating certain classes of organometallic (and related) compounds because the charge assigned to a ligand may be ambiguous. The first problem that arises is concerned with the precise rule that should be used to assign the charge on a ligand. In this regard, there are two methods that are frequently used: (i) the charge on the ligand is derived by transferring each shared pair of electrons to the more electronegative atom,⁷ and (ii) the ligand is removed in a closed shell configuration⁸ (for both of these methods, bonds between the same element are broken homolytically so that each atom receives one electron). In many cases, the application of these results has the same outcome and there is no ambiguity. For example, consider a M–Cl bond. Chlorine is more electronegative than the transition metals and, as such, the chlorine would be removed as Cl^- following rule (i). Application of rule (ii) requires the chlorine to be removed in a closed shell form, *i.e.* Cl^- . Thus, rules (i) and (ii) have the same outcome in this case; however, for more complex situations of the type that are frequently encountered in organometallic chemistry, the outcomes are *not* necessarily the same.

A simple illustration of a situation for which the application of the two rules has different outcomes is provided by $(\eta^5-C_5H_5)Ti(\eta^7-C_7H_7)$. Application of rule (i) would require both carbocyclic rings to be removed as anions because carbon is more electronegative than titanium, *i.e.* $[C_5H_5]^-$ and $[C_7H_7]^-$, and thus titanium would be assigned an oxidation number of +2. A totally different outcome, however, results if rule (ii) is applied because although $[C_5H_5]^-$ is a 6 π -electron aromatic closed shell species, the C_7 -symmetric $[C_7H_7]^-$ anion is *not closed shell*. The most commonly encountered closed shell form of the cycloheptatrienyl ligand is the 6 π -electron aromatic tropylium cation $[C_7H_7]^+$ and, on this basis, titanium would be assigned an oxidation number of zero. However, there is an additional problem because there exists another closed shell form of the cycloheptatrienyl ligand, which is the 10 π -electron aromatic trianion, $[C_7H_7]^{3-}$. If one were to select this form of the cycloheptatrienyl ligand, titanium would be assigned an oxidation number of +4. Thus, depending upon whether one were to classify the cycloheptatrienyl ligand as either a cation $[C_7H_7]^+$ (closed shell aromatic 6 π -electron configuration),^{12,13} a monoanion, $[C_7H_7]^-$ (open shell),¹⁴ or a trianion $[C_7H_7]^{3-}$ (closed shell aromatic 10 π -electron configuration),¹⁵ each of which have been presented in the literature, the oxidation number of titanium in $(\eta^5-C_5H_5)Ti(\eta^7-C_7H_7)$ may be assigned values of either 0, +2 or +4! Since the actual bonding in the molecule is invariant to the oxidation number, the large variation of oxidation number indicates that, by comparison to simple coordination compounds, the oxidation number is of limited utility in organometallic compounds. Indeed, a recent IUPAC article entitled *Nomenclature of Organometallic Compounds of the Transition Metals* concludes that it is inappropriate to assign oxidation numbers with respect to the nomenclature of organometallic compounds, *viz*: “As oxidation numbers cannot be assigned unambiguously to many organometallic compounds, no formal oxidation numbers will be attributed to the central atoms in the following section on organometallic nomenclature.”¹⁶

Problems in the assignment of oxidation numbers are by no means restricted to the cycloheptatrienyl ligand. For example, the simple “hydride” ligand exists in two closed shell forms, *i.e.* H^+ and H^- , but it is invariably viewed as H^- for the purpose of assigning oxidation numbers in transition metal compounds - despite the fact that certain metals (*e.g.* Pt) have a greater Pauling electronegativity than that of hydrogen!¹⁷ A similar dichotomy is observed for Lewis acid ligands such as AlR_3 , which may be treated as either neutral AlR_3 or as dianionic $[AlR_3]^{2-}$, depending upon whether the electron pair is transferred to the aluminum or to the transition metal. Aluminum has a Pauling electronegativity (1.61) that is in between the values for the transition metals (1.22–2.54),¹⁷ and thus the charge formally assigned to an AlR_3 ligand (0 or –2) could, in principle, vary for two otherwise closely related compounds if the oxidation number were to be determined by rule (i).

A related problem also results if rule (ii) is used to determine the oxidation number of complexes that possess Lewis acid ligands for which two closed shell forms exist. Thus, the AlR_3 ligand may be considered to be either neutral AlR_3 with a closed shell sextet (note that the term closed shell does *not* require an octet configuration)¹¹ or dianionic $[AlR_3]^{2-}$ with a closed shell octet. In these cases, some consideration needs to be given to determine the most appropriate closed shell form of the ligand. Two different criteria have been suggested. Firstly, it has been proposed that the closed shell form of the donor atom should generally have an octet configuration.¹⁸ When applied to an AlR_3 ligand, this rule would result in using $[AlR_3]^{2-}$ to determine oxidation numbers; the latter complex, however, is an unusual example of a species with aluminum in the +1 oxidation state and is unknown.¹⁹ An alternative suggestion, which is in keeping with the notion that the oxidation number of an atom was originally derived by removing the ligand in the form that it is *commonly encountered* in an uncoordinated state (*e.g.* Cl^- , NH_3 , and OH_2), is that, in ambiguous situations, the charge assigned to the ligand should correspond to its *stable* uncoordinated

form.²⁰ On this basis, it is more appropriate to assign the AlR_3 ligand a charge of zero, but this procedure is by no means adopted by all authors.

The above discussion emphasizes that one must be very careful to establish the criteria (which may by no means be explicitly stated) by which an author assigns oxidation numbers. The criterion generally employed in this article is that the ligand is assigned the charge which is associated with the ligand in its *stable* closed shell configuration, e.g. $[\text{C}_7\text{H}_7]^+$ rather than $[\text{C}_7\text{H}_7]^-$ or $[\text{C}_7\text{H}_7]^{3-}$, AlR_3 rather than $[\text{AlR}_3]^{2-}$, and C_2H_4 rather than $[\text{C}_2\text{H}_4]^{2-}$; in each case, the assigned charge corresponds to the species that is commonly encountered in the free state in chemical systems. The charges assigned to a variety of ligands are summarized in Table 1, from which it is evident that the oxidation number formalism treats ligands as negative (e.g. R^-), neutral (e.g. CO), or positive (e.g. $\eta^7\text{-C}_7\text{H}_7^+$), whereas they are always treated as neutral according to the neutral ligand formalism.

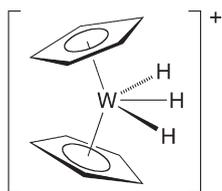
While the $\eta^7\text{-C}_7\text{H}_7$ ligand has been assigned different charges for the same coordination mode, several other ligands have been assigned different charges for different coordination modes. For example, with respect to the oxidation number formalism, the nitrosyl ligand is assigned a charge of +1 if the M-N-O bond is linear, and a charge of -1 if it is bent.²¹ The NO^+/NO^- classification for metal nitrosyls has, however, been severely criticized.²² For example, Enemark and Feltham have noted that “it is quite misleading to describe all linear complexes as derivatives of NO^+ and all bent complexes as derivatives of NO^- ” and that “assignment of oxidation states to the metal atom and NO is undesirable”.²³ Furthermore, Scheidt has succinctly stated that the NO^+/NO^- formalism leads to unusual oxidation assignments and that “this formalism has little or no heuristic value”,²⁴ while Richter-Addo and Legzdins emphasize that “assigning oxidation states to M-NO links is undesirable, since the formal oxidation states in $\text{Co}(\text{CO})_3\text{NO}$, $\text{Fe}(\text{CO})_2(\text{NO})_2$, $\text{Mn}(\text{CO})(\text{NO})_3$ and $\text{Cr}(\text{NO})_4$ have the unrealistic values of -1, -2, -3 and -4, respectively!”.²⁵ Finally, as noted above, another inconsistency with the assignment of oxidation numbers is that NO^- is *not* a closed shell species.

Two other ligands that are related to NO in the sense that the oxidation number formalism classifies them as either positive or negative depending upon the coordination geometry are the N_2R diazenido ligand²⁶ and the PR_2 phosphido ligand.²⁷ Thus, complexes with bent M-N-NR units are classified as derivatives of anionic $(\text{N}_2\text{R})^-$ ligands, while those with linear M-N-NR units are classified as derivatives of cationic $(\text{N}_2\text{R})^+$ ligands. Likewise, $[\text{MPR}_2]$ complexes that are pyramidal at phosphorus are classified as derivatives of anionic $(\text{PR}_2)^-$ ligands, while those that are planar at phosphorus are classified as derivatives of cationic $(\text{PR}_2)^+$ ligands.

As noted for the nitrosyl complexes, the classification of these ligands as cations renders some rather unusual oxidation number assignments. For example, the phosphido complexes $(\text{Cp}^{\text{R}})_2\text{M}(\text{PR}_2)_2$ ($\text{M} = \text{Zr}, \text{Hf}$)²⁸ which possess both planar and pyramidal PR_2 ligands would be classified as a $\text{Zr}(\text{II})$ and $\text{Hf}(\text{II})$ derivatives using the above oxidation number formalisms. However, in view of the fact that the organometallic chemistry of Zr and Hf is dominated by the +4 oxidation state, as exemplified by Cp_2MX_2 (e.g. $\text{X} = \text{Cl}, \text{Me}, \text{NMe}_2$),²⁹ the notion that $(\text{Cp}^{\text{R}})_2\text{M}(\text{PR}_2)_2$ should be classified as $\text{M}(\text{II})$ is most unusual. In this regard, the structurally characterized complex $(\text{Cp}^{\text{SiMe}_3})_2\text{Zr}(\text{PPh}_2)_2$ has been classified as possessing a $\text{Zr}(\text{IV})$ center,^{28b,29} with the authors thereby viewing both planar and pyramidal PPh_2 ligands as anionic $(\text{PPh}_2)^-$. In support of this suggestion, the reduction potential of $(\text{Cp}^{\text{R}})_2\text{ZrCl}_2$ ($\text{R} = \text{Me}_3\text{Si}$) (-1.59 V vs SCE) is similar to the quasi-reversible reduction potential for $(\text{Cp}^{\text{R}})_2\text{Zr}(\text{PPh}_2)_2$ (-1.72 V vs SCE)^{28b} and other $\text{Zr}(\text{IV})$ complexes.³⁰ It would, therefore, appear that the cationic $(\text{PR}_2)^+$ classification of planar phosphido ligands is of limited utility.

1.01.2.1.3 Examples of electron counting

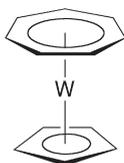
While both electron counting methods give the same answer for a given complex, the neutral ligand formalism is inherently simpler to apply since it eliminates the unnecessary step of first assigning oxidation numbers. Furthermore, for the set of cyclic $\eta^n\text{-C}_n\text{H}_n$ ligands, the number of electrons donated according to the neutral ligand method is equal to the number of carbon atoms (*i.e.* the value of n), whereas the number of electrons donated by the oxidation number method shows no direct relationship to the number of carbon atoms unless n is even. For example, the $\eta^7\text{-C}_7\text{H}_7$ cycloheptatrienyl ligand is considered to be a 7-electron donor using the neutral formalism but has been considered to be either a cationic 6-electron donor, a monoanionic 8-electron donor, or a trianionic 10-electron donor using the oxidation number formalisms. Likewise, regardless of the detailed nature of the bonding in carbene complexes $\{\text{M}[\text{C}(\text{R})\text{X}]\}$ (Section 1.01.4.3.2), the $[\text{C}(\text{R})\text{X}]$ ligand is always considered to contribute two electrons using the neutral ligand formalism, whereas it is viewed as a 4-electron dianionic ligand in Schrock alkylidenes and as a neutral 2-electron donor in Fischer carbenes. Thus, for the purpose of electron counting, the neutral ligand formalism provides the most direct method, as illustrated for some simple examples in Figure 6.



| Neutral Ligand Method | | |
|----------------------------------|--------------|-------------|
| W | 6 | = 6 |
| $2(\eta^5\text{-C}_5\text{H}_5)$ | 2×5 | = 10 |
| 3H | 3×1 | = 3 |
| (+) charge | -1 | = <u>-1</u> |
| | | 18 |

| Oxidation Number Method | | |
|--------------------------------------|--------------------|------------|
| W^{VI} | $6 - 6^{\text{a}}$ | = 0 |
| $2(\eta^5\text{-C}_5\text{H}_5)^{-}$ | 2×6 | = 12 |
| 3H^{-} | 3×2 | = <u>6</u> |
| | | 18 |

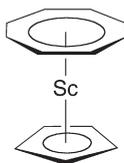
(a) oxidation number = $1 - (-2 - 3) = 6$



| Neutral Ligand Method | | |
|---------------------------------|--------------|------------|
| W | 6 | = 6 |
| $(\eta^5\text{-C}_5\text{H}_5)$ | 1×5 | = 5 |
| $(\eta^7\text{-C}_7\text{H}_7)$ | 1×7 | = <u>7</u> |
| | | 18 |

| Oxidation Number Method | | |
|-------------------------------------|--------------------|------------|
| W^0 | $6 - 0^{\text{a}}$ | = 6 |
| $(\eta^5\text{-C}_5\text{H}_5)^{-}$ | 1×6 | = 6 |
| $(\eta^7\text{-C}_7\text{H}_7)^{+}$ | 1×6 | = <u>6</u> |
| | | 18 |

(a) oxidation number = $0 - (1 - 1) = 0$



| Neutral Ligand Method | | |
|---------------------------------|--------------|------------|
| Sc | 3 | = 3 |
| $(\eta^5\text{-C}_5\text{H}_5)$ | 1×5 | = 5 |
| $(\eta^8\text{-C}_8\text{H}_8)$ | 1×8 | = <u>8</u> |
| | | 16 |

| Oxidation Number Method | | |
|--------------------------------------|--------------------|-------------|
| Sc^{III} | $3 - 3^{\text{a}}$ | = 0 |
| $(\eta^5\text{-C}_5\text{H}_5)^{-}$ | 1×6 | = 6 |
| $(\eta^8\text{-C}_8\text{H}_8)^{2-}$ | 1×10 | = <u>10</u> |
| | | 16 |

(a) oxidation number = $0 - (-1 - 2) = 3$

Figure 6 Comparison of the two procedures for determining the valence electron count. The advantage of the neutral ligand method is that it eliminates the unnecessary step of first determining the oxidation number of the metal (charge on molecule – Σ charge on ligands). Also, note that the number of electrons donated by a $(\eta^n\text{-C}_n\text{H}_n)$ ligand is simply equal to the value of n for the neutral ligand method, whereas this is not generally true for the oxidation number method.

In addition to its greater simplicity, other points to support the use of the neutral ligand formalism are that (i) it is the same method that is generally taught for determining the electron count in simple molecules such as CH_4 , NH_3 , and H_2O ,³¹ and (ii) historically, it is the same method that Sidgwick used in his discussion of the “effective atomic number” of an atom in a molecule.³² On the other hand, proponents of the oxidation number formalism favor it because the charge assigned to a ligand often corresponds to that of its uncoordinated state in chemical systems. However, as will be discussed in detail later, the charge on the metal suggested by this approach bears no relationship to reality and it does *not* accurately reflect the nature of the ligand *in the molecule*. The neutral ligand formalism will, therefore, be used exclusively throughout the remainder of this article for the purpose of electron counting.

1.01.2.1.4 A caveat for electron counting

The significance of electron counting is that it provides a simple means to establish how many electrons reside in molecular orbitals associated with the metal in a complex. Coupled with the basic knowledge of how a molecular orbital diagram depends on molecular symmetry (see, for example, Figures 1–3), the electron count provides a means to establish the extent to which metal–ligand bonding orbitals, nonbonding metal orbitals, and metal–ligand antibonding orbitals are occupied. For, example, the electron count of 18 for $\text{Mo}(\text{PMe}_3)_6$ indicates that a total of 9 bonding/nonbonding/antibonding orbitals associated with the metal are occupied, whereas the electron count of 16 for $\text{Pt}(\text{PR}_3)_2\text{R}_2$ indicates that a total of 8 bonding/nonbonding/antibonding orbitals associated with the metal are occupied. Examination of the respective molecular orbital diagrams in Figures 1 and 2 confirms this prediction.

However, it is important to note that simple electron counting does not always correctly predict the number of occupied bonding/nonbonding/antibonding orbitals associated with the metal in a molecular orbital diagram. A particularly notable example is provided by $\text{W}(\text{C}_2\text{R}_2)_3\text{CO}$, for which simple electron counting procedures, invoking the acetylene ligand as a 4-electron donor and the carbonyl ligand as a 2-electron donor, would predict a 20-electron count for the tungsten center. However, a molecular orbital analysis of this molecule indicates that one of the six $[(\text{C}_2\text{R}_2)_3]$ combination orbitals does not have the appropriate symmetry to interact with the metal and thus the electron count is 18, with the additional pair of electrons residing in a $[(\text{C}_2\text{R}_2)_3]$ ligand based a_2 orbital with no symmetry match amongst the metal s, p and d orbitals (Figure 7).³³

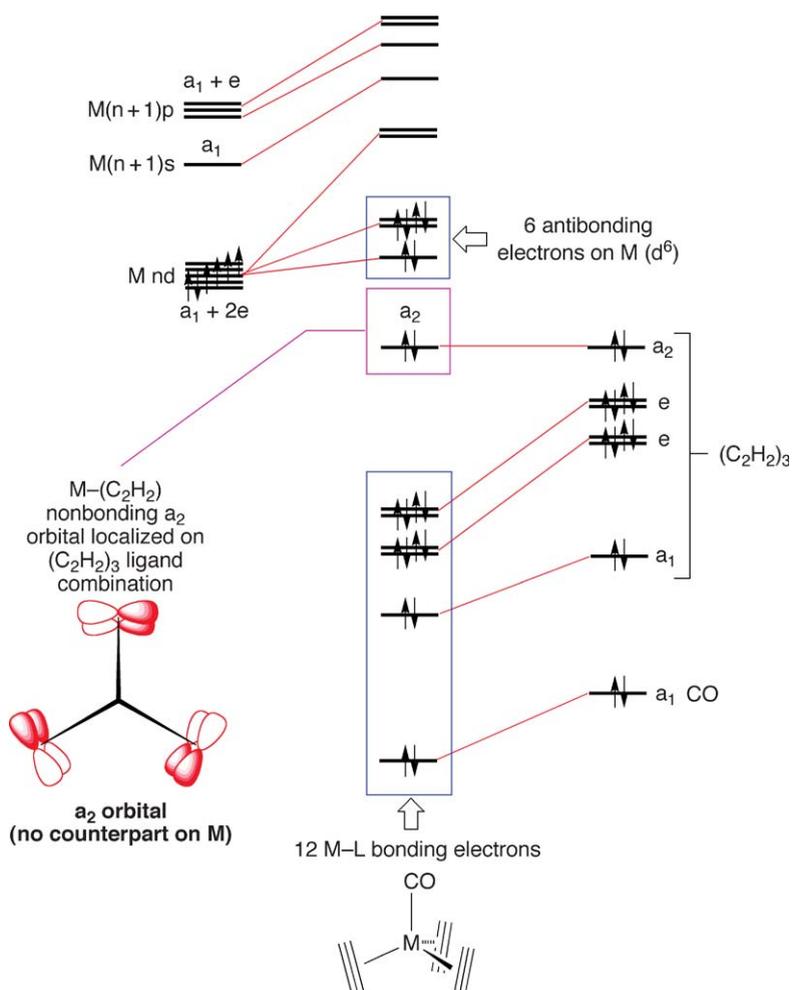


Figure 7 Molecular orbital diagram for $(\eta^2\text{-C}_2\text{H}_2)_3\text{M}(\text{CO})$ with C_{3v} symmetry. Three C_2H_2 ligands may donate 12 electrons, but 2 electrons reside in a $\text{M}(\text{C}_2\text{H}_2)$ nonbonding orbital. Thus, the three C_2H_2 ligands donate only 10 electrons to the metal center, such that $(\eta^2\text{-C}_2\text{H}_2)_3\text{M}(\text{CO})$ has an 18-electron configuration for $\text{M}=\text{W}$.

Analogous situations arise for Cp_3MX ,³⁴ $\text{Os}(\text{NAr})_3$,³⁵ $(\text{RN})_3\text{MoL}$,³⁶ $\text{M}(\text{BH}_4)_4$ ³⁷ and $[\eta^8\text{-pentalene}]_2\text{M}$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$),^{38,39} in each case, the electron count is reduced from 20 to 18 because a specific ligand orbital combination has no symmetry match with a metal based s, p or d orbital.⁴⁰ It is, therefore, evident that electron count can only be viewed as a *guide* – albeit a very useful guide – to indicate the nature of the occupied and unoccupied orbitals, and hence stability of a compound.

1.01.2.2 Ligands with Variable Electron Donor Number and Coordination Number

Many ligands have the ability to coordinate with variable hapticity and consequently variable electron donor number. For example, the cyclopentadienyl ligand commonly coordinates *via* η^5 -, η^3 - and η^1 -modes,⁴¹ for which the electron donor numbers are 5, 3, and 1, respectively (Figure 8).⁴² Likewise, benzene may coordinate *via* η^6 -, η^4 - and η^2 -modes, for which the electron donor numbers are 6, 4, and 2, respectively. Acyclic ligands that exhibit variable coordination modes are also known. For example, allyl coordinates in both η^3 - and η^1 -modes, serving as a 3-electron donor and a 1-electron donor ligand, respectively. Other examples of ligands that exhibit variable electron donor and coordination numbers are listed in Table 3.

1.01.2.3 Ligands with Variable Electron Donor Number without Change in Coordination Number

In addition to ligands such as cyclopentadienyl and benzene that donate variable numbers of electrons due to differences in hapticity, there are also ligands that may donate variable numbers of electrons while *maintaining the*

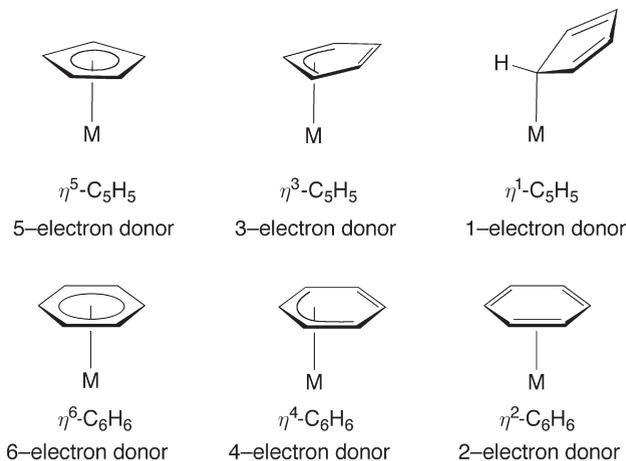


Figure 8 Variable electron donor numbers resulting from different coordination modes for cyclopentadienyl and benzene ligands.

Table 3 Examples of ligands that exhibit variable electron donor number associated with a change in coordination number

| Ligand & coordination mode | Electron donor number |
|---------------------------------|-----------------------|
| $\eta^5\text{-C}_5\text{H}_5$ | 5 |
| $\eta^3\text{-C}_5\text{H}_5$ | 3 |
| $\eta^2\text{-C}_5\text{H}_5$ | 3 |
| $\eta^1\text{-C}_5\text{H}_5$ | 1 |
| $\eta^6\text{-C}_6\text{H}_6$ | 6 |
| $\eta^4\text{-C}_6\text{H}_6$ | 4 |
| $\eta^2\text{-C}_6\text{H}_6$ | 2 |
| $\eta^3\text{-C}_3\text{H}_5$ | 3 |
| $\eta^1\text{-C}_3\text{H}_5$ | 1 |
| $\kappa^2\text{-O}_2\text{CMe}$ | 3 |
| $\kappa^1\text{-O}_2\text{CMe}$ | 1 |

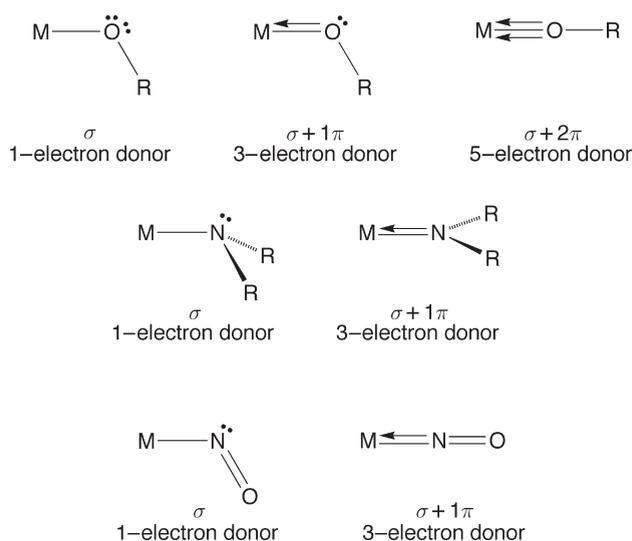
Table 4 Examples of ligands that exhibit a variable electron donor number while maintaining the same coordination number

| Ligand & coordination mode | Electron donor number |
|-------------------------------|-----------------------|
| OR (bent) | 1 or 3 |
| OR (linear) | 5 |
| NO (bent) | 1 |
| NO (linear) | 3 |
| NR ₂ (pyramidal) | 1 |
| NR ₂ (planar) | 3 |
| NR (bent) | 2 |
| NR (linear) | 4 |
| C ₂ R ₂ | 2 or 4 |
| E (E = O, S, Se, Te) | 0, 2, or 4 |

same coordination number to the metal (Table 4). In each case, the electron donor number of the ligand is dictated by the electronic requirements of the metal center. For example, an alkoxide (OR) ligand is a neutral 1-electron σ -donor but may also function as neutral 3-electron and 5-electron donor ligands (Figure 9). The nitrosyl (NO) ligand is closely related to the alkoxide ligand and coordinates to a metal center as either a neutral 1-electron donor and as a neutral 3-electron donor if the lone pair on nitrogen donates to the metal center. The 1-electron donor interaction is characterized by a bent M–N–O geometry, while the 3-electron donor interaction requires a linear geometry. The amide (NR₂) ligand also serves as a 1-electron and 3-electron donor ligand, corresponding to pyramidal and planar geometries, respectively, at nitrogen.

The imido ligand (NR) is an example of a multiply bonded group that may coordinate as either a neutral 2-electron donor and as a 4-electron donor. While nitrogen-to-metal lone pair donation and the formation of a $\bar{M} \equiv \overset{+}{N}R$ triple bond requires a linear M–N–R unit, it must be emphasized that the converse is not true. Thus, it is possible for steric interactions to enforce a linear geometry, in which case the lone pair resides in a p-orbital on the nitrogen.⁴³

A subtle example of variable electron donor properties is provided by alkynes which may be either 2- or 4-electron donors, with negligible change in coordination properties (Figure 10).⁴⁴ Thus, in addition to the C–C π -bond in the [MC₂] plane ($\pi_{||}$) serving as a 2-electron σ -donor in a similar manner to that in metal–olefin complexes, the perpendicular π -bond of the alkyne (π_{\perp}) may also serve as donor, but in a π rather than σ sense. Thus, alkynes may be classified as 2-electron (σ) or 4-electron ($\sigma + \pi$) donors. To facilitate electron counting, these interactions may be represented with single and double arrows, respectively.

**Figure 9** Variable electron donor numbers for ligands with the same coordination number (for clarity, the backbonding component is not illustrated for the nitrosyl ligand; see Section 1.01.4.3.2).

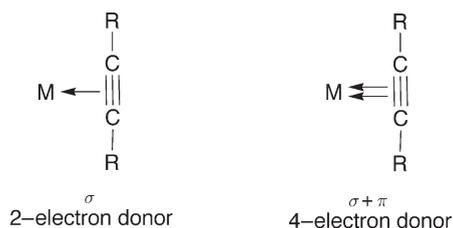


Figure 10 Variable electron donor numbers for ligands with the same coordination mode.

Chalcogenido ligands (O, S, Se and Te), and especially the most commonly encountered oxo and sulfido ligands, provide an even more subtle means to provide different electron donor properties with negligible variation in coordination properties.⁴⁵ Specifically, metal-chalcogenido interactions may be considered to be a composite of three resonance structures, with formal single [$\overset{+}{M}-\overset{-}{E}$], double [$M=\overset{-}{E}$], and triple [$\overset{-}{M}\equiv\overset{+}{E}$] bonds, corresponding to 0-electron, 2-electron, and 4-electron donors, respectively.⁴⁵

1.01.2.4 Bridging Ligands

An essential component of electron counting requires representing the molecule in a form that conveys the number of electrons a ligand donates to a metal center. However, certain bridging ligands cause problems with respect to determining the electron count in polynuclear organometallic compounds. Specifically, whereas the contribution of many bridging ligands to the electron count may be readily inferred by a simple valence bond description of the bonding, as illustrated by Cl, carbonyl, and alkylidene ligands, bridging hydride and alkyl ligands frequently cause problems because the 3-center-2-electron interaction is often not represented properly for electron counting purposes. In this regard, a large variety of bonding representations for bridging hydride ligands have been presented in the literature (Figure 11), but most of these are not particularly helpful from the perspective of electron counting. Thus, while a dashed line could be used to indicate the existence of a 3-center-2-electron interaction, it is not immediately obvious how this representation enables the electron count to be determined.

Bridging hydride and alkyl compounds bear a close analogy to other molecules that possess 3-center-2-electron bonds, such as transition metal dihydrogen complexes [$M(\eta^2-H_2)$] and alkane σ -complexes [$M(\eta^2-RH)$]. For the

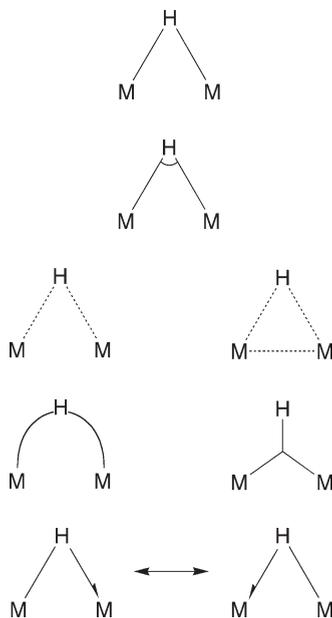


Figure 11 Representations of 3-center-2-electron M–H–M interactions presented in the literature.

purposes of electron counting, the 3-center-2-electron bond in a transition metal dihydrogen complex $[M(\eta^2-H_2)]$ can be described as a sharing of the pair of electrons in the H–H σ -bond with the metal, and thus a dihydrogen ligand contributes a pair of electrons to the electron count of M. The situation is exactly the same with a bridging hydride complex $[M(\mu-H)M]$, as illustrated for simplicity by diborane, the archetype of 3-center-2-electron bonding. In essence, the two B–H–B interactions may be viewed as involving donation of the σ -bond electron density of the B–H bond of one BH_3 fragment into an empty orbital on boron of the other fragment (Figure 12). In this way, one clearly sees how the electronic unsaturation of the boron atom in BH_3 is removed and an octet configuration is attained.

Green has introduced a modified representation for the 3-center-2-electron bonding interaction in which a “half arrow” is drawn from the bridging hydrogen atom rather than a “full arrow” from the midpoint of the M–H bond (Figure 13);^{1,46} note that the “straight half arrow” is not to be confused with the “curly half arrow” that is used in describing organic reaction mechanisms. Despite the different form of the representation, the “half arrow” notation is intended to convey exactly the same information as that involving an arrow from the center of the bond, and thus the representation $M-H-M'$ depicts that the pair of electrons associated with the M–H sigma bond is donated into a vacant orbital on M' . The principal advantage of the “half arrow” notation is that it is less cumbersome for molecules with multiple bridging groups. This notation is also very similar to that using a “full arrow” from an atom to represent interactions involving bridging ligands that possess a lone pair, such as chloride. The important distinction between the “half arrow” and “full arrow” representations is that the former implies donation of a *bond* pair into a vacant orbital (such that the bonding involves one 3-center-2-electron bond), while the latter implies that a *lone pair* is available for donation into a vacant orbital (such that the bonding may involve two 2-center-2-electron bonds).

The “half arrow” notation is not restricted to M–H–M interactions, but applies equally well to other complexes that exhibit 3-center-2-electron bonds, such as those involving coordination of (i) C–H and B–H bonds, *e.g.* agostic alkyl complexes⁴⁷ and borohydride derivatives,⁴⁸ and (ii) M–C bonds, *e.g.* symmetrically bridging methyl ligands.

In contrast to the above electron counting method for M–H–M and related 3-center-2-electron interactions, an alternative method merely apportions the electron associated with the hydride ligand equally to both metals,^{49,50} and the bond order is determined by application of the formula $m = (18n - N)/2$ where m is the number of 2-center-2-electron M–M bonds, n is the number of M atoms, and N is the total electron count. Employing the neutral ligand electron counting procedure, this method has the outcome that a bridging hydrogen atom or alkyl radical contributes half of an electron to the electron count at each metal center of a dinuclear complex. An important consequence of the difference between these two electron counting procedures is that they result in different M–M bond orders in order to achieve a specific electron count, as illustrated by the selection of compounds in Figure 14. Computations on a variety of dinuclear $[M(\mu-H)M]$ complexes, however, indicate that the most appropriate description of the bonding is that obtained by application of the “half arrow” method rather than that assuming a bridging hydrogen atom contributes half of an electron to the electron count at each metal center. For example, a molecular orbital analysis of the bonding in $[CpMo(\mu-O_2CH)]_2(\mu-PH_2)(\mu-H)$ indicates that the direct Mo–Mo interaction is a single bond, in accord with that predicted using the “half arrow” method, whereas the “half electron” method would predict a Mo=Mo double bond.⁵¹ The extent of metal-metal bonding in a complex may also be evaluated in terms of the Complementary Spherical Electron Density Model which seeks to minimize the number of “unavailable” orbitals.⁴

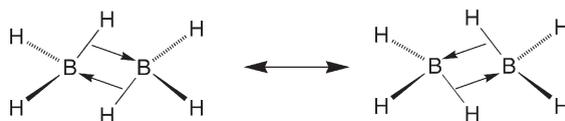


Figure 12 Representations of the 3-center-2-electron B–H–B interaction in diborane which emphasizes the octet configuration of boron.

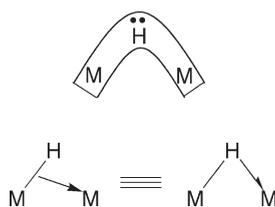


Figure 13 The “half-arrow” representation of a 3-center-2-electron M–H–M interaction, which may be viewed as donation of a pair of electrons associated of the M–H sigma bond into a vacant orbital on the other M.

Other examples which illustrate that the “half electron” method for counting bridging hydride and alkyl ligands is flawed are provided by $[\text{Cp}_2\text{ZrH}_2]_2$ and $[\text{CpReH}_3]_2$. Thus, for the zirconocene dimer, $[\text{Cp}_2\text{Zr}(\text{H})]_2(\mu\text{-H})_2$, the “half-electron” method predicts a $\text{Zr}=\text{Zr}$ double bond whereas the “half-arrow” method indicates that each Zr center can attain an 18-electron configuration without forming two 2-center-2-electron $\text{Zr}\text{-Zr}$ bonds (Figure 14). Since the Zr center of mononuclear Cp_2ZrH_2 is d^0 , and therefore incapable of forming a 2-center-2-electron $\text{Zr}\text{-Zr}$ bond, it is evident that the “half electron” description of the bonding results in an untenable description of the $\text{Zr}\text{-Zr}$ interaction. With respect to $[\text{CpReH}_3]_2$, three isomers that differ according to whether there are (i) no bridging hydrogens, $[\text{CpReH}_3]_2$, (ii) two bridging hydrogens, $[\text{CpReH}_2]_2(\mu\text{-H})_2$ and (iii) four bridging hydrogens, $[\text{CpReH}]_2(\mu\text{-H})_4$ have been considered.⁵² The “half-electron” method predicts the existence of a $\text{Re}\equiv\text{Re}$ triple bond for each of these isomers, regardless of how many hydrogen atoms bridge the two metals. The notion that the $\text{Re}\text{-Re}$ bond order would not vary with the number of bridging hydrogen atoms is counterintuitive and, indeed, calculations indicate that the $\text{Re}\text{-Re}$ bond order is actually reduced as the hydride ligands bridge,⁵² a result that is consistent with the “half-arrow” counting method.

With respect to the isomer with four bridging hydrogen atoms, $[\text{CpReH}]_2(\mu\text{-H})_4$, it is important to note that situations arise where the “half-arrow” method does *not* predict an 18-electron configuration for both metals in a dinuclear complex. Thus, molecules such as $[\text{CpReH}]_2(\mu\text{-H})_4$, $[\text{Cp}^*\text{Re}(\text{CO})_2]_2(\mu\text{-H})_2$, $\{[\text{MeC}(\text{CH}_2\text{AsPh}_2)_3\text{Co}]_2(\mu\text{-H})_3\}^+$, $[\text{Cp}^*\text{Ru}]_2(\mu\text{-H})_4$, and $[(\text{Et}_2\text{PPh})_2\text{Re}(\text{H})_2]_2(\mu\text{-H})_4$ each possess a 20-electron configuration, which indicates that

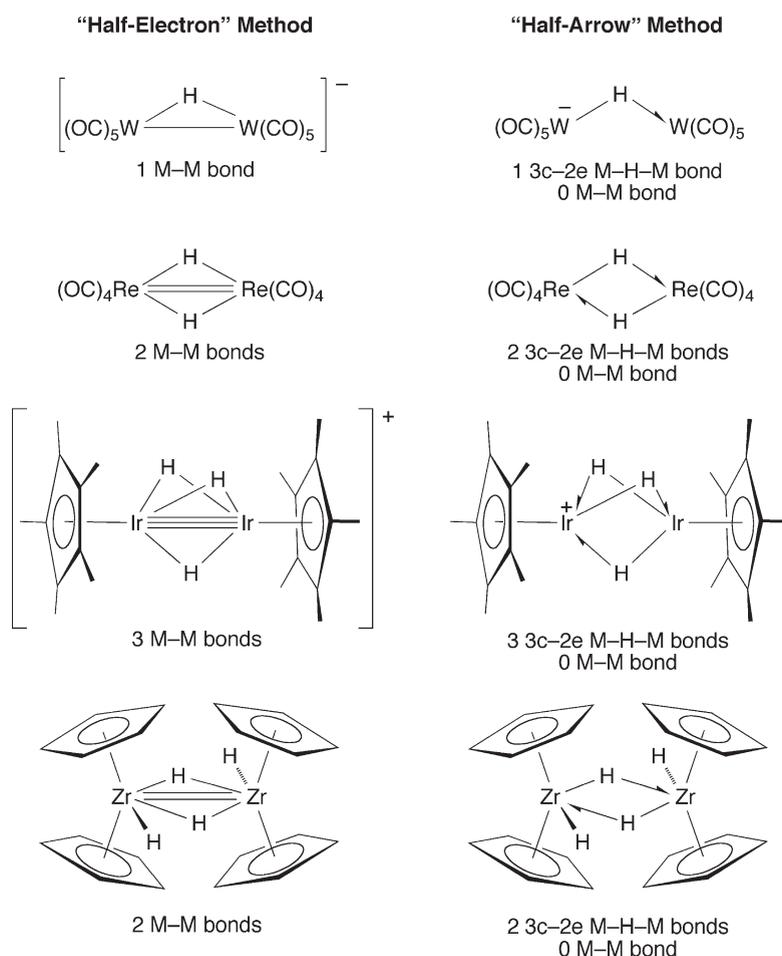


Figure 14 Different descriptions of the metal–metal bond orders in some dinuclear complexes with bridging hydride ligands according to the electron counting method. The “half-electron” method does not explicitly take into account the 3-center-2-electron nature of the $\text{M}\text{-H}\text{-M}$ interaction and thus results in a greater $\text{M}\text{-M}$ bond order than would be predicted theoretically. In contrast, the “half-arrow” method treats the 3-center-2-electron nature of the $\text{M}\text{-H}\text{-M}$ interactions explicitly and thereby predicts a $\text{M}\text{-M}$ bond order which is in accord with theory.

M–M antibonding orbital. The resulting interaction has been termed an “antibond”,⁵³ and may be depicted by using a crossed-dashed $M \cdots \times \cdots M$ representation in which the cross is intended to emphasize that the direct interaction is *antibonding*.⁵¹ Despite the presence of an “antibond”, the overall interaction between the two metal centers is favorable because of the stabilization resulting from the formation of the 3-center-2-electron bond.⁵⁴

1.01.3 Valence, Oxidation Numbers and Coordination Numbers in Organometallic Compounds

It is important to emphasize that assessing the viability of the existence of a molecule by only evaluating the electron count at a metal center has serious limitations. For example, although the hypothetical molecule “ $W(PMe_3)_2(CH_3)_8$ ” may be regarded as an 18-electron molecule, it has little chance of existing because the tungsten requires eight valence electrons to coordinate the eight methyl groups in a 2-center-2-electron bonding scheme, but tungsten only possesses six valence electrons. The formulation “ $W(PMe_3)_2(CH_3)_8$ ” is, therefore, clearly unreasonable unless 3-center-2-electron bonding is invoked. In addition to electronic considerations, steric considerations would suggest that the 10-coordinate tungsten complex “ $W(PMe_3)_2(CH_3)_8$ ” could be unstable; indeed, since a transition metal has only nine valence orbitals available, a metal center that is coordinated to 10 monodentate ligands is unusual. It is, therefore, evident that, in addition to the electronic count of the metal center, other criteria are required to discern whether a molecule possesses a reasonable structure. In this regard, formal charge, oxidation number, and valence are often used to address electronic properties, while coordination number generally provides an indication of steric saturation.

1.01.3.1 Valence, Oxidation Number and d^n Configuration

As indicated above, the nonexistence of a molecule such as “ $W(PMe_3)_2(CH_3)_8$ ” is implied by the fact that the valence of tungsten, *i.e.* the number of electrons that the atom uses in bonding, is greater than the group valence. At this point, it is pertinent to discuss explicitly this usage of the term “valence” because the concepts and definitions of valence have been refined considerably over the years. In this regard, the definition employed by Sidgwick remains the most useful for covalent molecules: the valence of an atom in a covalent molecule is simply the number of electrons that it has used in bonding.⁵⁵ In a molecular orbital sense, the valence corresponds to the number of electrons that a specific element contributes to molecular orbitals that have bonding character and is therefore equal to the difference between (*i*) the number of valence electrons in the free atom (*i.e.* the group valence) and (*ii*) the number of “nonbonding” electrons on the atom in the molecule.

$$\text{valence} = \text{no. electrons in valence shell of free atom} - \text{no. “nonbonding” electrons on atom in molecule} \quad (1)$$

Despite this simple and useful definition, it is unfortunate that valence has been taken to be synonymous with (*i*) oxidation number, (*ii*) number of bonds, and (*iii*) coordination number.^{55,56} The origin of this confusion is that, for certain simple molecules, the valence is often coincidentally equal to either the oxidation number, number of bonds or coordination number. For example, for neutral AH_n hydrides (*e.g.* CH_4 , NH_3 , and OH_2) the valence, magnitude of the oxidation number, number of bonds and coordination number each have the same value, n . This relationship, however, breaks down in many cases, as illustrated by $[NH_4]^+$, for which the nitrogen atom has used all five of its valence electrons and is pentavalent, but its oxidation number is -3 , the number of bonds is 4, and the coordination number is 4.

The most serious problems, however, arise when valence and oxidation number are confused. In many cases, the valence and oxidation number are identical, but there are many examples for which they deviate. For instance, the equivalence between valence and oxidation number breaks down when either (*i*) homonuclear element-element bonds are present, (*ii*) the ligands attached to the atom of interest are dissociated with opposite charges, *e.g.* H^+ and Cl^- , or (*iii*) the ligand is dissociated as a cation, *e.g.* H^+ , NO^+ and $(C_7H_7)^+$. Illustrative examples of these breakdowns are provided by consideration of some simple molecules. Thus, with respect to the issue of the neglect of homonuclear element-element bonds in the determination of oxidation number, the valence of the central carbon in CMe_4 is four, but the oxidation number is zero. Likewise, the valence of carbon in CH_2Cl_2 is also four, but the oxidation number is zero because, in terms of electronegativity differences, H is viewed as “ H^+ ” and Cl is viewed as “ Cl^- ” when attached to carbon. Finally, as noted above, the valence of nitrogen in $[NH_4]^+$ is five, but its oxidation number is -3 .