4744 *Organometallics* **2006,** *25,* 4744−4747

A Simple Description of the Bonding in Transition-Metal Borane Complexes

Sir: It is well-known that a covalent bond between two atoms may belong to one of two classes, which are distinguished according to the number of electrons that each atom contributes to the two-center−two-electron bond. If each atom contributes one electron, the interaction corresponds to a normal covalent bond, whereas if one atom contributes both electrons, the interaction corresponds to a dative covalent or coordinate bond (Figure 1). As described in detail by Haaland, the distinction between these types of bonding situations is significant.[1] While dative σ bonding is a common feature of the transition metals, it is normally a Lewis base ligand (L) that provides the pair of electrons for the M←L bond in the vast majority of complexes, with there being relatively few well-defined complexes where the ligand is a Lewis acid (Z). In principle, one would expect that trivalent BX_3 derivatives should be capable of serving as Lewis acid ligands to an electron-rich transition metal, in a manner akin to that observed for main-group metals, as exemplified by $Cp^*Ga \rightarrow B(C_6F_5)_3$.[2] Indeed, the reactivity of transition-metal compounds towards BR_3 derivatives has long been investigated, but many of these studies have been called into question because of the lack of structural verification.[3] It is, therefore, significant that a variety of transition-metal complexes that feature M→B dative bonds have been recently structurally characterized.[4−6] In each case, the key to isolating these complexes is to use multidentate boranes which employ the chelate effect to stabilize the complex. For example, an extensive class of complexes with M→B dative bonds is provided by "metallaboratranes" ([κ^4-B(mim^R)$_3$]M) derived from tris(2-mercapto-1-R-imidazolyl)borane,[4,5] in which the M→B bond is supplemented by three M←S dative interactions.

However, as the variety of metal borane complexes has increased, divergent descriptions of the metal center in closely related compounds have started to emerge. In part, the different descriptions for these complexes are a consequence of the fact that complexes which feature σ Lewis acid ligands are sufficiently rare that it is not yet commonplace for chemists to recognize immediately the electronic impact of coordinating this class of ligand to a metal center. For example, with respect to the assignment of oxidation numbers, some view the BX_3 ligand as a neutral ligand,[7] while others view it as a dianion, $[BX_3]^{2-}$.[8−10] The ambiguity is a result of there being several

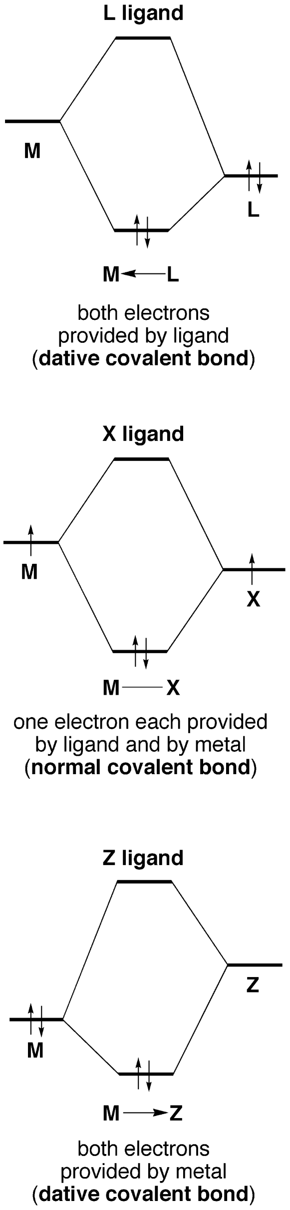

Figure 1. The three fundamental types of two-center−two-electron interactions, as classified by the number of electrons that the ligand contributes.

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(7) See, for example: Crossley, I. R.; Hill, A. F. *Organometallics* **2004**, *23*, 5656−5658.

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(9) Also see the comments in the Acknowledgments section of ref 7, which indicate that a reviewer favors the dianion $[BX_3]^{2-}$ formalism for oxidation number assignments.

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different procedures for assigning charges to ligands. For example, the charge on a ligand may be derived either by transferring each shared pair of electrons to the more electronegative atom[11] or by removing the ligand in a closed-shell configuration.[12,13] In many cases, the same ligand charge results no matter which set of rules one follows. However, in some cases the outcomes are different, as evidenced by the charges assigned to BX_3.[7−9]

Furthermore, additional problems may ensue regardless of which of the above methods one chooses to use to assign oxidation number. For example, boron has a Pauling electronegativity (2.0) that is in between the electronegativities of the transition metals, e.g. Co (1.8) and Rh (2.2);[14] thus, if one assumes that the pair of electrons is transferred to the more electronegative atom, the charge assigned to a BX_3 ligand (0 or −2) could vary for two otherwise closely related $M \rightarrow BX_3$ compounds. Analogous problems also exist if one chooses to assign a charge that corresponds to a closed-shell configuration, because BX_3 has two reasonable closed shell configurations, namely neutral BX_3 and dianionic $[BX_3]^{2-}$. The former has a sextet configuration and corresponds to the form in which BX_3 molecules are typically encountered in the free state, whereas the latter has an octet configuration but corresponds to an unusual example (albeit precedented)[15] of boron in the +1 oxidation state; thus, an author needs to establish which factor they consider determining in the assignment of the closed-shell charge of a borane ligand.

In view of the above discussion, it is therefore understandable that some authors could favor assigning a charge of 0, and others a charge of −2, to BX_3 ligands. Since the oxidation number is frequently used to determine the d^n configuration[16] of a metal center,[17] it is evident that the ambiguity in oxidation number causes a corresponding ambiguity in d^n configuration. However, whereas oxidation numbers depend on how one chooses to deconstruct the molecule, the d^n configuration is a function of the *molecule* and must be *independent* of how one decides to deconstruct it. As such, a system of evaluating molecules that results in different d^n configurations for the same molecule according to the preference of an author is unsatisfactory.

To circumvent this problem in $M \rightarrow BX_3$ chemistry, it has recently been proposed that the discussion should move away from the topic of d^n configuration and that the molecule should instead be described by the notation $(M \rightarrow B)^n$; within this notation, n corresponds to the d^n configuration of the metal *prior* to coordination of the neutral BX_3 ligand.[18] The notion behind introducing this description is associated with the Enemark−Feltham notation for metal nitrosyls, a concept that was created to reconcile problems arising from oxidation number assignments of bent (NO^-) and linear (NO^+) nitrosyl complexes. The NO^+ formalism, in particular, results in very unusual oxidation number assignments, and Richter-Addo and Legzdins have emphasized that "assigning oxidation states to M−NO links is undesirable, since 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!".[19] Enemark and Feltham have also noted that "it is quite misleading to describe all linear complexes as derivatives of NO^+ and all bent complexes as derivatives of NO^-".[20] For this reason, Enemark and Feltham proposed that metal nitrosyl compounds should instead be defined in terms of a $\{M(NO)_x\}^n$ classification, where n is the total number of electrons associated with the metal d and NO π^* orbitals; this is equivalent to the d^n configuration obtained assuming that the nitrosyl is classified as NO^+. Thus, regardless of whether a nitrosyl ligand is linear or bent, it is classified by the *same* $\{M(NO)_x\}^n$ description.

While it is true that there is a common problem with assigning d^n configurations for metal nitrosyl and metal borane complexes because of unusual oxidation number assignments, a flaw in the analogy results from the fact that there are *two* distinct metal nitrosyl coordination mode extremes (linear and bent) but only *one* coordination mode for a metal borane complex. Thus, whereas linear and bent nitrosyl compounds correspond to totally different electronic structures resulting from different numbers of orbital interactions,[21] there is only one electronic description for a metal borane complex which involves σ overlap between a single orbital on M and a single orbital on B, as illustrated in Figure 2. Despite this description of a metal−borane bond, it has been suggested that there are two bonding extremes that are represented as $M \rightarrow B$ and $M^+{-}B^-$, which respectively correspond to d^n and d^{n-2} configurations for the metal.[22] However, the two descriptions $M \rightarrow B$ and $M^+{-}B^-$ correspond to *exactly the same bonding situation* and are merely different *representations* of a dative bond (Figure 2). Specifically, notations of the type $D \rightarrow A$ and $D^+{-}A^-$ to describe a dative bond between a donor and acceptor have existed for almost 80 years[23−25] and are used interchangeably *without* implying any difference in bonding.[26] Since $M \rightarrow B$ and $M^+{-}B^-$ have the same

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(10) For other aspects of problems in oxidation number assignments, see: (a) Steinborn, D. *J. Chem. Educ.* **2004**, *81*, 1148−1154. (b) Holder, D. A.; Johnson, B. G.; Karol, P. J. *J. Chem. Educ.* **2002**, *79*, 465−467.

(11) Pauling, L. *J. Chem. Soc.* **1948**, 1461−1467.

(12) (a) Lewis, J.; Nyholm, R. S. *Sci. Prog. (London)* **1964**, *52*, 557−580. (b) Nyholm, R. S. *Pure Appl. Chem.* **1968**, *17*, 1−19.

(13) For both of these methods, an exception is that bonds between the same element are broken homolytically.

(14) Pauling, L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 93.

(15) For example, $[BH_3]^{2-}$ has been spectroscopically identified as a product of the reduction of B_2H_6 with alkali-metal naphthalides. See: Godfroid, R. A.; Hill, T. G.; Onak, T. P.; Shore, S. G. *J. Am. Chem. Soc.* **1994**, *121*, 12107−12108.

(16) The d^n configuration is the number of electrons that are housed in metal d orbitals that are either primarily nonbonding or have metal−ligand antibonding character. See ref 12b and: Jean, Y. *Molecular Orbitals of Transition Metal Complexes*; Oxford University Press: New York, 2005; pp 12, 31.

(17) (a) *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: New York, 1994; Vol. 2, p 961. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley: New York, 2005; p 43. (c) Mingos, D. M. P. *Essential Trends in Inorganic Chemistry*; Oxford University Press: New York, 1998; p 299.

(18) Hill, A. F. *Organometallics* **2006**, *25*, 4741−4743.

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

(20) (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; Vol. 12, pp 155−215. (c) Westcott, B. L.; Enemark, J. H. In *Inorganic Electronic Structure and Spectroscopy*; Lever, A. B. P., Solomon, E. I., Eds.; Wiley: New York, 1999; Vol. II (Applications and Case Studies), Chapter 7, pp 403−450.

(21) A linear metal nitrosyl is described by *three* orbital interactions between the metal and NO (one σ and two π), whereas a bent metal nitrosyl is described by *two* orbital interactions between the metal and NO (one σ and one π).

(22) See the graphical abstract of ref 18. **Note added in proof:** The graphical abstract of ref 18 has been modified following acceptance of this article. The original graphical abstract used the $M^+{-}BX_3^-$ description, whereas the current version uses the representation $M^{2+}{\leftarrow}BX_3^{2-}$. By analogy with Figure 2, however, it is evident that $M \rightarrow BX_3$, $M^+{-}BX_3^-$, and $M^{2+}{\leftarrow}BX_3^{2-}$ correspond to equivalent descriptions of a covalent metal−borane interaction involving the occupation of a single M−B σ bond by a pair of electrons.

(23) See, for example: (a) Sidgwick, N. V. *The Electronic Theory of Valency*; Clarendon Press: Oxford, U.K., 1927. (b) Sidgwick, N. V.; Bailey, P. R. *Proc. R. Soc. (London)* **1934**, *144*, 521−537.

(24) Parkin, G. *J. Chem. Educ.* **2006**, *83*, 791−799.

(25) Also note that these two representations are *not* resonance structures because they correspond to the *same* electron distribution.

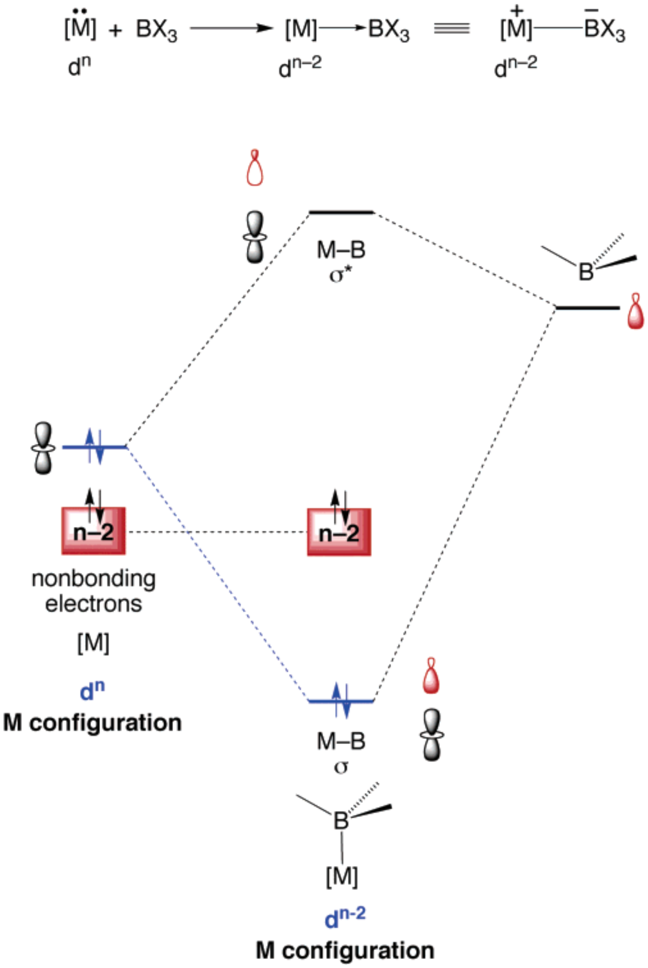

Figure 2. Basic molecular orbital diagram for coordination of a BX_3 ligand to a d^n transition-metal center. The formation of the metal−boron bond requires that a pair of electrons must be supplied by the metal, and so the metal center in the adduct adopts a d^{n-2} configuration. The interaction may be represented as either M→B or M^+−B^-, which are alternative representations of a dative bond and are *not* resonance structures of each other.

meaning, it is evident that they must also correspond to the same d^n configuration for a given molecule. Thus, the notion that M→B corresponds to a d^n configuration and M^+−B^- to a d^{n-2} configuration is inappropriate. As a consequence, the value of the proposed $(M{\rightarrow}B)^n$ notation is diminished.

Since a M→B bond corresponds to a single two-center−two-electron interaction, it is a simple issue to identify how coordination of BX_3 to a metal center influences the d^n configuration of the metal. Thus, as illustrated by the qualitative molecular orbital diagram of Figure 2, the interaction between a filled metal-based orbital and the empty orbital on boron results in the transfer of a pair of electrons from the metal to a M−B *bonding* orbital. As such, a metal center that originally possessed a d^n configuration becomes d^{n-2} upon coordination to BX_3, a view that is supported by calculations.[27] It is important to emphasize, however, that this is not a new concept. For example, in 1927, while discussing the concept of dative bonding, Sidgwick noted that the valence of the donor atom increases by 2 upon coordination by an acceptor.[23a] Furthermore, and of more specific relevance to the present article, King stated in 1967 that coordination of a Lewis acid (e.g. BH_3) to a metal center oxidizes it by 2 units.[28,29] Both of these statements are in accord with the d^n configuration being reduced to d^{n-2} upon coordination of a Lewis acid. A particularly lucid example of this notion is provided by coordination of the simplest Lewis acid, namely H^+; thus, it is well established that protonation of a d^n metal center results in a metal hydride with a d^{n-2} configuration. It is, therefore, evident that coordination of BX_3 to a metal center would have the same impact on the d^n configuration.

The above discussion indicates that ambiguities in oxidation number assignment complicate determination of the d^n configuration. Oxidation number ambiguities are by no means limited to metal borane compounds, and problems resulting from misinterpretation of oxidation numbers are increasing, such that the oxidation number formalism is becoming of limited utility in organometallic chemistry. Indeed, a recent IUPAC article states: "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."[30] Problems resulting from the inappropriate application of oxidation number assignments are surmounted by the application of Green's covalent bond classification (CBC) method for classifying covalent compounds.[31] The principal advantage of this method is that it was specifically designed for covalent molecules; therefore, it does not suffer from any limitations or problems resulting from the rules imposed by the various definitions of oxidation number.

The CBC method is based on the notion that there are three elementary types of metal−ligand interactions that may be classified according to the number of electrons the ligand contributes to the two-center−two-electron bond. The different types of ligands are represented by the symbols L, X, and Z, which correspond respectively to two-electron, one-electron, and zero-electron *neutral* ligands (Figure 1).[31,32] An L-function ligand is a Lewis base which interacts with a metal center via a dative covalent bond in which both electrons are donated by the L ligand (e.g. PR_3); an X-function ligand is one which interacts with a metal center via a normal two-electron covalent bond (e.g. R); and a Z-function ligand is a Lewis acid (e.g. BX_3). A given ligand may have one or more of the above functions, and a molecule is classified as $[ML_lX_xZ_z]$ according to the type and number of various ligand functions.[31] A principal distinction between the CBC method and a classification based on oxidation numbers is that the former evaluates the nature of the metal *within the molecule*, whereas the oxidation number formalism merely assigns a charge to *an isolated atom* after the ligands have been removed. Since the CBC method focuses

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[26] Thus, one form is not intended to imply more or less electron transfer than the other, but even if it did, it would not change the fact that the occupied orbital is a M−B *bonding* orbital and that the d^n configuration must therefore be reduced by 2 upon coordination. Likewise, the d^n configuration is not typically regarded to be a function of the degree of electron transfer (i.e. the relative electronegativity of a ligand) in a normal covalent bond.

[27] See, for example, ref 5c and: Aullón, G.; Alvarez, S. *Inorg. Chem.* **1996**, *35*, 3137−3144.

[28] King, R. B. *Adv. Chem. Ser.* **1967**, *No. 62*, 203−220.

[29] π and δ back-bonding interactions may also impact the d^n configuration (see, for example, ref 10a). However, whereas the σ interaction in $M{\rightarrow}BR_3$ is the *only* component to the bonding, π and δ back-bonding interactions (e.g. involving C_2H_4 and C_6H_6 ligands) are secondary components and, thus, their contribution is normally neglected in evaluating the formal d^n configuration.[12b] A complete understanding of the molecule would, nevertheless, require the roles played by the potential π and δ acceptor orbitals of the ligand to be evaluated.

[30] Salzer, A. *Pure Appl. Chem.* **1999**, *71*, 1557−1585.

[31] (a) Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127−148. (b) Parkin, G. *Comprehensive Organometallic Chemistry III*; Elsevier: Amsterdam, in press.

[32] For an early description of the L, X, and Z classification, see ref 28.

on the nature of the orbital interactions within the molecule, it is not subject to the idiosyncracies of oxidation number assignment and thereby provides a means to establish the d^n configuration of the metal in the *molecule*, as opposed to the oxidation number formalism, which yields the configuration for an isolated charged atom. In this regard, the d^n configuration for a given $[ML_lX_xZ_z]$ classification[33] is given by the expression $n = m - x - 2z$ (where m is the number of valence electrons in the neutral metal atom),[31] from which it is evident that coordination of a single Lewis acid function (Z) to a metal center reduces a d^n configuration to d^{n-2}.

In summary, the change in the d^n configuration of a metal center upon coordination of a BX_3 ligand may be readily inferred by noting that coordination of a Lewis acid requires the metal to use two of its nonbonding/antibonding electrons in forming the M→B bond. While a notation such as $(M{\rightarrow}B)^n$ notation may prevent arguments between those who are committed to classifying a borane ligand with a charge of either 0 or −2, the pedagogical value of this concept is not clear. For example, as an extension of this notation, what information is conveyed by representing the borane adduct of ammonia as $H_3NBH_3(N{\rightarrow}B)^2$? The formal d^n configuration is a longstanding and useful concept in transition-metal chemistry and can be maintained as such for compounds that feature σ Lewis acid ligands—assuming that it is recognized that coordination of a single σ Lewis acid reduces the d^n value to d^{n-2}.

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Note Added after ASAP Publication. In the version of this paper posted on the Web Aug 23, 2006, an incorrect citation was given in ref 33. The version of this reference that now appears is correct.

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(33) If the molecule bears a charge, the $[ML_lX_xZ_z]^{Q\pm}$ assignment is reduced to its "equivalent neutral class"[31] to enable comparisons between molecules of different charge. Care must be exercised when performing the transformation to ensure that the most appropriate CBC is assigned. For example, $[Re(CO)_5(BH_3)]^-$ has been assigned to the classification $[ML_4X_3]$,[18] but the molecule is more appropriately classified as $[ML_5X]$: i.e., an octahedral d^6 rhenium complex. The appropriate transformation for reduction of $[ML_5Z]^-$ to its equivalent neutral class is $Z^- \rightarrow X$.[31b] A simple illustration to show the validity of this assignment is provided by noting that $[Re(CO)_5(BH_3)]^-$ may be conceptually derived by coordination of H^- to the vacant orbital on boron in $Re(CO)_5(BH_2)$, which possesses a $[ML_5X]$ classification.

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