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Correspondence

An Unambiguous Electron-Counting Notation for Metallaboratranes

Sir: To bookkeep electrons in covalent compounds, chemists employ a range of formalisms—artificial constructs that may reflect to some useful extent real properties but are themselves imaginary. A chemical bond might therefore be considered in terms of the oxidation number (ON) or "state" (sic) or formal charge of constituent elements. The two formalisms do not have any existential meaning as such but, rather, are derived from alternative axioms that consider hypothetical states in which electrons are variously apportioned to the atoms involved. The former exaggerates ionicity by assigning the bonding electrons to the more electronegative element; the latter emphasizes covalency by dividing bonding electrons between constituent elements. As with canonical or valence bond forms, neither represent real situations; rather, chemists imagine that a consideration of both may facilitate the understanding of chemical phenomena. Within transition-metal chemistry, many properties of simple Werner-type complexes are usefully interpreted in terms of the metal ON and the d^n configuration that follows from the expression $n = \mathrm{ME} - \mathrm{ON}$ (ME = Ölander group number), *presupposing that there is no ambiguity in the assignment of ON*. In such complexes, simple ligands attract little debate regarding their contribution to ON assignments, and the derived d^n configuration is taken to reflect the number of electrons essentially, though even in such simple systems not exclusively, housed in metal−ligand nonbonding or antibonding orbitals comprised primarily of metal d orbitals.

Many ligands, however, display strong covalency in bonding to transition metals, in particular in the field of organotransition-metal chemistry, such that the axiom upon which ON is assigned becomes less definitive. One such case, of which there are many, involves the nitrosyl ligand. The apparent dichotomy in behavior of this simple diatomic ligand led to the familiar linear-NO^+ vs bent-NO^- classification with the attendant implications for ON assignment. In the case of a bent M−N−O geometry, a pair of electrons is notionally assigned exclusively to nitrogen (NO^-), while for a linear M−N−O arrangement this pair is assigned to the metal and an analogy between NO^+ and isoelectronic CO is entertained. The issue is, however, somewhat clouded by complexes in which the nitrosyl ligand displays intermediate *semibent* behavior. Furthermore, for later transition metals with high d occupancies, situations arise where the linear/nonlinear behavior is not predicted on the basis of simple 18-electron counting rules. Thus, for example, from an effective atomic number perspective, the complex $[RuCl(NO)_2(PPh_3)_2]^+$ would require two linear three-electron nitrosyl ligands (neutral formalism); however, in the solid state one is linear and the other bent, while in solution the two ligands exchange their roles on the ^{15}N NMR time scale.[1] Thus, although there is no debate as to the overall number of valence electrons available for binding NO, it is not always clear to what extent these should be assigned to the metal, the nitrogen, or both. A useful tool, therefore, in the development of ideas concerning the bonding of NO was the $(MNO)^n$ notation of Enemark and Feltham.[2] In this shorthand, n refers to the number of electrons associated with the metal d orbitals and the MNO group and corresponds to the d^n configuration that would be assigned on the basis of NO^+ coordination. Thus the isoelectronic 18-electron complexes $[Re(NO)(CO)_2(PPh_3)_2]$, $[OsCl(CO)(NO)(PPh_3)_2]$, and $[IrCl_2(NO)(PPh_3)_2]$ are all described as $(MNO)^8$ systems, although the nitrosyl progressively bends along the series.[2c]

Metallaboratranes are a recently new class of compound in which a metal−boron dative bond is housed within a cage or chelated structure, recalling Brown's azaboratrane, $N(CH_2CH_2O)_3B$.[3] The majority of such complexes have arisen from our investigations of the chemistry of poly(methimazolyl)borates (Chart 1; mt = methimazolyl),[4−14] however, very recently Bourissou has reported the first examples of nonmethimazolyl-based metallaboratranes that are derived from the preformed ambiphilic ligand $PhB(C_6H_4P^iPr_2)_2$, a result that is certain to inspire a significant broadening of the field.[15] Furthermore, Rabinovich[16] and more recently Parkin[17] have reported examples based on variously N-substituted (mt^R) derivatives of the $HB(mt)_3$ ligand. With charged or neutral 16- or 18-electron and 5- or 6-coordinate examples based on the metals Ru, Os, Rh, Ir, Pt and Co, it would appear that metallaboratranes constitute a potentially broad group of compounds for which one might seek to assign ON and d^n configurations to the metals concerned. There is no problem in assigning ON, given that the isolable boranes $HB(mt)_2$, $B(mt)_3$, and $PhB(C_6H_4P^iPr_2)_2$ are neutral

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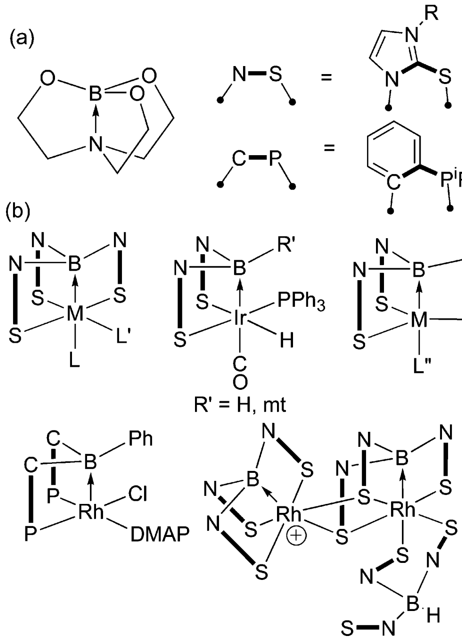
10.1021/om0602512 CCC: $33.50

Chart 1. (a) Azaboratrane and (b) Metallaboratranes[a,4−17]



[a] Abbreviations: MLL′ = $Ru(CO)(PPh_3)$, $Os(CO)(PPh_3)$, $RhCl(PPh_3)$, $Rh(cod)^+$, $Rh(PMe_3)_2{}^+$, $Rh(S_2CNMe_2)$, $RhH(PPh_3)$, $Rh(PPh_3)(CNC_6H_2Me_3)^+$, $PtH(PPh_3)^+$, PtI_2; M′L″ = $Pt(PPh_3)$, $Co(PPh_3)^+$; DMAP = 4-(dimethylamino)pyridine.

molecules and make no net contribution to the metal ON. Thus, by common convention the d^n configuration is given by n = ME − ON. However, an alternative convention for deriving "n" has been suggested by Green in his Covalent Bond Classification (CBC) system,[18] wherein n = ME − VN such that VN is the valence number (as distinct from the ON). While not widely applied, this version of d^n may differ for less routine ligands because the axioms upon which Green bases VN are distinct from those for ON. Specifically, in the case of a Lewis acid interacting with a transition metal, or indeed an amine, for the purposes of deriving d^n (or v^n for main-group elements) the electron pair in the dative bond, however weak or strong, is considered to be completely confiscated by the Lewis acid. Accordingly, d^n and v^n are reduced by two units relative to the more common ON convention, where this pair of electrons is awarded to the more electronegative element. Thus, within the CBC system the borane adducts $[Re(BH_3)(CO)_5]^-$ and $H_3N\rightarrow BH_3$ would be designated as having trivalent d^4 Re[19] and pentavalent v^0 N. Although the CBC d^n configuration may appear counterintuitive, given that boron is less electronegative than all of the platinum-group metals, among which metallaboratranes emerged, clearly neither method is more or less "correct" in its d^n assignments; they are simply distinct quantities that are corollaries arising from disparate dictums.

It is in the axiomatic variation between conventional and CBC d^n assignments for Lewis acid adducts that we perceive an analogy with the NO^-/NO^+ dichotomy—distinctions arise from the attribution of the electron pair to either the Lewis acid or metal in the former and to the nitrogen or metal in the latter. These are, of course, artificial distinctions that simply arise from incongruent axioms. The reality will fall somewhere between these hypothetical extremes; it will vary from case to case, and the subtleties of specific cases will only be quantified by computational studies. Just as the $(MNO)^n$ notation proved expedient in nitrosyl chemistry, we suggest that a similar $(\mathit{M}\rightarrow \mathit{B})^n$ notation would remove ambiguity in describing metallaboratranes or indeed all such Lewis acid adducts of transition metal complexes. Since their inception, we have taken to appending $(\mathit{M}\rightarrow \mathit{B})$ to the line formula of our metallaboratranes to highlight the bond of interest, following the tradition often encountered in denoting compounds with metal−metal multiple bonds, e.g., $[W_2(O^tBu)_6](\mathit{W}\equiv \mathit{W})$. We therefore suggest that to this be added a superscript number[20] that denotes the total number of electrons associated with metal d orbitals and the M→B group (Table 1). This is not meant to indicate the d^n configuration as such (though it equates to this within the ON convention). Rather, it should be taken to indicate that a pair of electrons is associated *to some unspecified extent* with the metal−boron dative interaction. In principle, this shorthand might be easily extended to other Lewis acids to which transition metals form dative bonds.

Table 1. $(\mathit{M}\rightarrow \mathit{B})^n$ and $(\mathit{M}\rightarrow \mathit{Z})^n$ Designations for Selected Metallaboratranes and Related Compounds[a]

complex	d^n	
	ME − ON	ME − VN
$[Os(CO)L\{B(mt)_3\}](\mathit{Os}\rightarrow \mathit{B})^{8}$	d^8	d^6
$[Ru(CO)_2\{B(mt)_3\}](\mathit{Ru}\rightarrow \mathit{B})^{8}$	d^8	d^6
$[IrH(CO)L\{HB(mt)_2\}](\mathit{Ir}\rightarrow \mathit{B})^{8}$	d^8	d^6
$[RhClL\{B(mt)_3\}](\mathit{Rh}\rightarrow \mathit{B})^{8}$	d^8	d^6
$[PtI_2\{B(mt)_3\}]\ (\mathit{Pt}\rightarrow \mathit{B})^{8}$	d^8	d^6
$[PtL\{B(mt)_3\}](\mathit{Pt}\rightarrow \mathit{B})^{10}$	d^{10}	d^8
$[CoL\{B(mt^{tBu})_3\}]^+(\mathit{Co}\rightarrow \mathit{B})^{8}$	d^8	d^6
$[RhCl(DMAP)\{PhB(C_6H_4P^iPr_2)_2\}](\mathit{Rh}\rightarrow \mathit{B})^{8}$	d^8	d^6
$Na[Re(CO)_5(BH_3)](\mathit{Re}\rightarrow \mathit{B})^{8}$	d^8	d^4
$[IrH_2(PMe_3)(C_5Me_5)(AlPh_3)](\mathit{Ir}\rightarrow \mathit{Al})^{6}$	d^6	d^4
$Na[Fe(AlPh_3)(CO)_2(C_5H_5)](\mathit{Fe}\rightarrow \mathit{Al})^{8}$	d^8	d^4
$[OsW(CO)_{10}(PMe_3)](\mathit{Os}\rightarrow \mathit{W})^{8}$ (Os)	d^8	d^6
$[Co(HgCl_2)(CO)_2(C_5H_5)](\mathit{Co}\rightarrow \mathit{Hg})^{8}$ (Co)	d^8	d^6
$[Mo(CO)(NO)L(C_5H_5)(HgCl_2)](\mathit{Mo}\rightarrow \mathit{Hg})^{6}$ (Mo)	d^6	d^2
$[IrCl(CO)L_2(SO_2)](\mathit{Ir}\rightarrow \mathit{S})^{8}$	d^8	d^6
$[Ta\{CH_2B(C_6F_5)_2\}(CO)(C_5H_5)_2](\mathit{Ta}\rightarrow \mathit{B})^{2}$	d^2	d^0
$[Rh_2(\mu\text{-}BCat)H_3(dippe)_2](\mathit{Rh}\rightarrow \mathit{B})^{8}$	d^8	d^6
$[Pt_2(\mu\text{-}BCat)(BCat)(dppm)_2(PPh_3)](\mathit{Pt}\rightarrow \mathit{B})^{9}$	d^9	d^6
$[FePd(\mu\text{-}BCl_2)(CO)_2(PCy_3)(C_5H_5)](\mathit{Pd}\rightarrow \mathit{B})^{10}$ (Pd)	d^{10}	d^8

[a] Abbreviations: L = PPh_3, ME = Ölander group number, ON = oxidation number, VN = CBC valency number, DMAP = 4-(dimethylamino)pyridine, Cat = catecholato (1,2-$C_6H_4O_2$), dppm = bis(diphenylphosphino)methane, dippe = 1,2-bis(diisopropylphosphino)ethane.

The purpose of introducing this notation is to preempt possible confusion that may arise from exponents of the ON vs CBC conventions using the same words to speak a different language when assigning d^n configurations. Although only two metallaboratranes have been the subjects of computational studies, the results are sufficiently distinct to presage a gradation of M→B dative interactions. Thus, Bourissou has found that the MO description of his rhodaboratrane $[RhCl(DMAP)\{BPh(C_6H_4P^iPr_2)_2\}](\mathit{Rh}\rightarrow \mathit{B})^{8}$ essentially conforms to the generally accepted view of a dative or coordinate bond: i.e., only limited transfer of electron density to the Lewis acid. Thus the two-center, two-electron Rh→B interaction is described as involving a major contribution from the d_{z^2}(Rh) orbital to the HOMO with little distortion due to its interaction with a vacant boron orbital. In a natural bond order analysis, the NLMO was found to comprise ca. 80% d_{z^2} and major delocalization tails (17%) from the vacant

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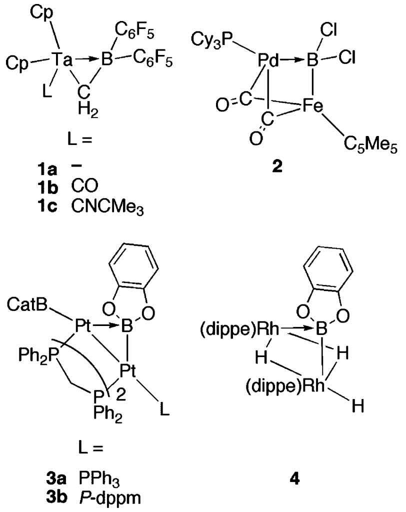
(18) Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127.

(19) A further axiom of the CBC model[18] is that, in arriving at the equivalent neutral class ML_lX_x, the charge of a complex is accommodated by the transformation (L^-) = X. Thus, $ML_5Z-[Re(CO)_5(BH_3)]^-$ transforms to $ReL_4XZ = ReL_4X_3$.

(20) We also suggest that this be italicized to avoid ambiguity when a line formula is followed by a citation: e.g., $[Os(CO)(PPh_3)\{B(mt)_3\}](\mathit{Os}\rightarrow \mathit{B})^{8}$.[6]

Chart 2. Nonclassical Examples of Metal→Boron Dative Interactions[a]



[a] Abbreviations: dppm = bis(diphenylphophino)methane; dippe = 1,2-bis(diisopropylphophino)ethane.

boron orbital.[15] Thus, for most intents and purposes, the electron pair may be considered primarily metal-based. In contrast, Parkin concludes that for the hypothetical iridaboratrane [IrCl(PH$_3$){B(C$_3$H$_3$N$_2$S)$_3$}], the 3c−4e $^{-}$Cl→Ir→B interaction involves contributions from d_{z^2} to the Cl−Ir−B bonding combination but not to the Cl−Ir−B nonbonding combination, for which the major iridium-based orbital is Ir p_z (10.4%) in combination with Cl p_z (48.4%) and B p_z (7.7%).[17] Further subtleties will no doubt emerge from computational studies of metallaboratranes, with many factors contributing to the Lewis basicity of a transition metal and, hence, the degree of resulting electron transfer from the metal to a Lewis acid.

The preceding discussion has concerned metallaboratranes in which the metal-boron dative bond is a two-center, two-electron bond of M−B σ symmetry. A number of other situations have, however, occurred in recent times where one valence bond representation involving an M→B interaction might be considered to contribute to the overall bonding picture (Chart 2). These are also included in Table 1 to illustrate how the $(M-B)^n$ notation might also be employed for these less straightforward cases. The first, [Ta{CH$_2$B(C$_6$F$_5$)$_2$}(L)(C$_5$H$_5$)$_2$] (**1**; L = CO, CNCMe$_3$), reported by Piers,[21] involves what might be described as borataalkene ligands but which could also be described as comprising a conventional Ta−C bond supplemented by a $(Ta\rightarrow B)^2$ interaction. Various examples of bridging boryl ligands also call for comment. Braunschweig's complex [FePd(μ-BCl$_2$)(CO)$_2$(C$_5$Me$_5$)(PCy$_3$)] (**2**) has an essentially tetrahedral geometry at boron.[22] However, three examples of "semi-bridging" boryls **3** and **4** have been structurally characterized by Norman and Marder in which the boron is best described by a canonical form involving essentially trigonal (σ-boryl) coordination to one metal buttressed by a σ-retrodative interaction from the second metal,[23,24] in a manner reminiscent of the bonding in semibridging carbonyl ligands.

In conclusion, the charm and utility of transition-metal chemistry lies in the manifold variations in the energies of the metal orbitals that may be achieved by altering the nature of coligands, charge, metal, and coordination number in complexes. It may therefore be anticipated that as the field of metallaboratranes develops, a spectrum of behavior for the M→B bond will emerge, involving different degrees of electron transfer from the metal to the Lewis acid. A cohesive notation for indicating the overall number of electrons associated with the metal and the M−B unit should therefore serve to preempt confusion that might arise from electron-counting formalisms based on contradictory dictums. It is hoped that adoption of the recommended $(M\rightarrow B)^n$ notation will obviate such a situation.

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