Covalent d-Block Organometallics: Teaching Lewis Structures and sd/sd$^2$ Hybridization Gives Students Additional Explanations and Powerful Predictive Tools

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ABSTRACT

Despite tremendous efforts by instructors and textbook authors, students find it difficult to develop useful chemical intuitions about preferred structures, structural trends, and properties of even the most common d-block element organometallic species, that is d$^6$, d$^8$, and d$^{10}$ systems. A full molecular orbital analysis of a transition metal species is not always feasible or desirable, and crystal field theory, while generally useful, is often too simplistic and limited. It would be helpful to give students of organometallic chemistry an additional toolkit that helps them to understand d-block compounds, in particular highly covalent ones. It is well known in the research literature in organometallic chemistry that hybridization arguments involving s and d orbitals (such as sd and sd$^2$ hybridization for d$^8$ and d$^6$ systems, respectively) provides useful insight. However, this knowledge is much underused in undergraduate teaching and not taught in undergraduate textbooks. The purpose of this article is to make descriptions of bonding that are based on s,d-hybridized orbitals more accessible in a way that is directly useful for undergraduate teaching. Geometries of unusual low-coordinate structures can be successfully predicted. An in-depth physical explanation for the trans-influence, the weakening of a bond due to a strong bond trans to it, is provided. A clear explanation is given for why the cis isomer normally more stable than the trans isomer in square-planar d$^8$ complexes of the type MR$_2$L$_2$ (R = alkyl/aryl, L = relatively weakly bonded neutral ligand). Similarly, the relative stability of fac versus mer isomers in octahedral d$^6$ complexes of the type MR$_3$L$_3$ is explained. Relevant to catalysis, the method explains why strongly donating ligands do not always facilitate oxidative addition and why 12-electron and 14-electron Pd(0) species are thermodynamically much more accessible than one might expect. The method capitalizes on 1st year knowledge such as the ability to write Lewis structures and to use hybridization arguments. It also ties into the upper-year experience, including graduate school, where covalent d-block complexes may be encountered in research and where the hybridization schemes described here naturally emerge from using the NBO formalism. It is discussed where the method might fit into the inorganic curriculum.

KEYWORDS

Second-Year Undergraduate, Upper-Division Undergraduate, Graduate Education / Research, Inorganic Chemistry, Covalent Bonding, Organometallics, Transition Elements, Valence Bond Theory, Lewis Structures, Analogies/Transfer
INTRODUCTION

The organometallic chemistry of the d-elements is a difficult topic for students, even if they have successfully mastered the fundamentals of coordination chemistry, such as common geometries, d-electron counting, and crystal field theory. There is the complexity arising from π-bonded ligands such as 1,3-butadiene, cyclopentadienyl, etc., an area that is well covered by contemporary textbooks. Another difficulty, the topic of this article, resides with “simple” σ-donor ligands such as alkyls or hydrides. A metal-bound alkyl, formally considered to be an alkyl anion, is deceptively similar to ammonia/an amine. For example, CH₃⁻ is isoelectronic to NH₃. However, carbon is much less electronegative than nitrogen, and the metal-carbon bond is more covalent than the metal-nitrogen bond. In particular for the late transition metals of the 2nd and 3rd d-element row, such as Pd, Pt, Rh, Ir, metal alkyl bonds (and also metal-hydride bonds) are highly covalent.¹ Crystal field theory is unable to describe covalency, and deriving a full MO diagram for a transition metal complex, while adequate, is rather tedious. The purpose of this article is to provide the teacher/instructor with a simple method that can be taught in one hour that makes properties of covalent d-element compounds intuitive, in particular those very common ones with a d⁸ or d⁶ (low spin) or d¹⁰ configuration. Apart from first-year knowledge (specifically the ability to draw Lewis structures), the prerequisites assumed are only two: first, a basic familiarity with d-element chemistry to the extent that the d-electron count for a metal in a molecule can be derived, and, second, having attended one or two lectures on MO theory: knowing σ and σ* orbitals (for example, from H₂) and MO schemes for simple diatomics (O₂ and dihalogens X₂). If a student is able to draw pictures of all MOs in a diatomic molecule and is able to predict which ones are filled and which ones are empty, for example for I₂ (the example that will be used here), the student will have enough preparation to benefit from the method. No advanced MO theory (such as group theory or the ligand group orbital approach) is required. The method is based on a valence bond (VB) treatment (localized orbitals) and hybridization arguments involving s and d orbitals but uses some conceptual MO theory. This knowledge is available in the organometallic research literature and in graduate-level textbooks² but is much underused in undergraduate teaching and not taught in undergraduate textbooks. The method allows useful back-of-an-envelope predictions for highly covalent
organometallics. Geometries of unusual low-coordinate structures can be successfully predicted. An in-depth physical explanation for the trans-influence, the weakening of a bond due to a strong bond trans to it, is provided. A clear explanation arises for why the cis isomer normally more stable than the trans isomer in square-planar d^8 complexes of the type MR_2L_2 (R = alkyl/aryl, L = relatively weakly bonded neutral ligand) and why the fac isomer is more stable than the mer isomer in octahedral d^6 complexes of the type MR_3L_3. Applications to catalysis, the question of why strongly donating ligands not always thermodynamically favor oxidative addition, will be discussed. The approach capitalizes on students’ knowledge of basic organic chemistry (such as taught in their first organic chemistry course or even, at many places, in first year). In doing so, it removes part of the strangeness of organometallic chemistry. Consider Figure 1. The questions on the left-hand side^3 (organic) are straightforwardly tackled with the use of Lewis structures and hybridization arguments. Very similar methods will be used here for the problems on the right-hand side^4 (organometallic) of Figure 1.
Figure 1. Can we employ the methods we use to understand organic molecules (left) also to understand organometallic molecules (right)?
For clarity, a comment is in order on how the three distinct concepts “Lewis structure”, “VSEPR” (Valence Shell Electron Pair Repulsion), and “hybridization/VB theory” are linked. Lewis structures are an empirically supported organizing tool, not quantum mechanical – in fact, they are older than quantum mechanics. VSEPR may be used as quasi-classical (not explicitly quantum mechanical) geometry prediction method, based on domains that repel each other, and in most implementations it uses a Lewis structure as input. While it is possible to use VSEPR without Lewis structures, the electron counting algorithm used closely resembles what would be needed for a Lewis structure. While Lewis structures are not quantum mechanical per se, they can also serve as an excellent starting point for a valence bond description, which is a powerful quantum mechanical method and requires the concept of orbital hybridization. The fact that a Lewis structure, familiar to the pre-quantum era chemist, can be turned into a guess wavefunction for VB theory was a major factor in the success of VB theory. The predictive power of a carefully made hybridization argument is so strong that organic chemistry students to this day need to be able to predict approximate hybridizations in relevant orbitals of organic compounds. This point was reinforced in a 2019 article: chemistry students who were too reliant on VSEPR struggled in organic chemistry, a problem successfully alleviated by introducing them to orbital-based methods through MO calculations and derived (NBO) hybridization schemes. It is argued here that the method of proceeding from Lewis structures to hybridization schemes can also be very valuable in the teaching of organometallic chemistry. Figure 2 illustrates how back-of-an-envelope, qualitative VB theory (enabled by Lewis structures) solves the organic problems in Figure 1. It is important to remember relative orbital energies. From $E(2s) < E(2p)$ follows that $E(sp) < E(sp^2) < E(sp^3)$. For bond strengths (bond dissociation energies) to carbon, it follows that $BDE(sp) > BDE(sp^2) > BDE(sp^3)$. Therefore, the methyl cation (Figure 1, A) is clearly flat (Figure 2, A), in order to maximize s-character in the CH bonds. This allows the empty orbital to be the high lying p-orbital, with no energetic penalty (because it is empty). Conversely, in the methyl anion, because a p-orbital is relatively high in energy, it is not a good place to put a lone pair, so mixing in more s-character (pyramidalized structure) is preferred. This is already clear from an orbital energy standpoint, before pair-pair repulsion (VSEPR) is taken into account, which further strengthens the case for the pyramidal carbanion. While VSEPR alone would have also produced the correct answers for $\text{CH}_3^+ / \text{CH}_3^-$, VSEPR is of no help for the next problems.
(B and C). If the 2-phenyl-substituted ethyl cation (Figure 1 and Figure 2, B, structure I) were isomerized into the \textit{para}-ethyl substituted phenyl cation (structure II), three CH bonds that are sp$^2$ would be traded for three weaker sp$^3$ bonds, so clearly the cation with the p-hole is more stable than the isomeric cation with the sp$^2$-hole.$^{10}$ Regarding the organic problem in Figure 1, C, problems related to reactivity of individual bonds or groups in a molecule can be addressed by drawing the most important resonance structures (see Figure 2, C), which demonstrates how an electron-withdrawing substituent can lead to a positive partial charge on the \textit{para}-carbon of the arene. Why can’t we completely analogously address the organometallic problems (Figure 2, organometallic column)? It turns out that we can, but first we will have a look at typical undergraduate textbook explanations for the organometallic problems.
Figure 2. Valid Lewis structures enable hybridization arguments and aid chemical intuition. Why are we hesitant to use them for organometallic complexes? (Solutions to the organometallic problems will be shown in Figure 10 below)
CURRENT STATE OF UNDERGRADUATE LEVEL EXPLANATIONS

Existing undergraduate texts do not treat the problems of structure prediction for organometallic species, relative stability of isomers, and trans-influence as connected. No undergraduate textbook addresses structures for 12-electron complexes (PtMe$_2$ or IrMe$_3$), a topic that may be superficially considered exotic but is in fact deeply connected to the other problems discussed below. For the problems of relative stability of isomers, properties of bonds, and trans-influence, there is no unifying framework visible. For example, the Weller/Overton/Rourke/Armstrong, 7th ed, an excellent textbook in many ways, provides the following explanation for the trans-influence:

The trans influence is the extent to which the ligand T weakens the bond trans to itself in the ground state of the complex. The trans influence correlates with the $\sigma$-donor ability of the ligand T because, broadly speaking, ligands trans to each other use the same orbitals on the ligand for bonding. Thus if one ligand is a strong $\sigma$ donor, then the ligand trans to it cannot donate electrons to the metal so well, and thus has a weaker interaction with the metal.

Everything said is correct, but the explanation falls short of being fully satisfactory, because no attempt is made at explaining which exact orbitals are involved in bonding to the metal. If this were elaborated, the student would be able to see directly that two ligands trans to one another have to use the same orbital at the metal. The same textbook discusses both cis/trans isomerism (square planar case) and fac/mer isomerism (octahedral case) as possible geometries but does not address the relative stabilities in square-planar MR$_2$L$_2$ systems or in the technologically important (OLED emitters) Ir'C$_3$N$_3$' systems. This is not meant as a criticism of a particular textbook but as an example for what is seen in all undergraduate textbooks. While all current inorganic chemistry undergraduate textbooks give a good overview of crystal field theory, crystal field theory is too crude a simplification to be of use here. Current undergraduate texts cover molecular orbital (MO) theory in detail, as the go-to high-end treatment, but MO theory is not applied to problems of the type shown in Figure 1, A-C (right). A further, serious issue is that students who have learned to write valid Lewis structures for organic and main-group inorganic compounds have effectively been taught to unlearn Lewis structures for everything that contains a transition metal. No single undergraduate textbook shows how to draw Lewis structures or transition
metal compounds. Thus, a valuable theoretical framework, capable of unifying large parts of chemistry, is being sold short. A rationale for this neglect may be offered in a justification to the extent that bonding in transition metal complexes is often ionic, and that Lewis-structures assuming covalency are very rarely helpful. There is some truth in this, insofar as many Werner complexes, such as Cr(acac)$_3$, for example or metal chlorides, indeed show pronouncedly ionic character in the metal-ligand bonds. Organometallic complexes, however, in particular those of the 4d and 5d elements, contain much more electronegative metals$^1$ and much less electronegative ligands (carbon-based ligands), and the resulting high degree of covalency makes a treatment using Lewis-structures and VB theory very powerful, as has been shown in the literature, and as will be laid out below. Much of the chemistry described here can be found in the research literature, in particular the extensive work by Landis and Weinhold (and some others).$^2,12$ Briefly (for details, see the literature referenced), they arrive at the theoretical descriptions that will be used here in the following way: a high-quality quantum chemistry method (ab initio or DFT) is used to compute the wavefunction of the molecule in question, using canonical molecular orbitals (MOs) for the actual computations. The resulting multi-electron wavefunction obtained in the form of canonical MOs need not be used directly in the form in which it was computed. It can be re-written in many different ways, and generally many such transformations (re-writings) of the wavefunction into a different form do not change the values of the molecular properties (observables) predicted or the accuracy of the predictions. It is particularly useful to transform the MO-based wavefunction into one based on Natural Bond Orbitals (NBOs).$^{12a}$ While MOs have the advantage that they are adapted to the symmetry of the molecule, they are typically delocalized over the molecule, making them unwieldy. NBOs, in contrast, are no longer symmetry-adapted but they are strongly localized, often on one atom (a lone pair) or between two atoms (a bonding pair). Sometimes NBOs cannot be uniquely localized on one or two atoms but rather describe, for example, a three-center-four-electron (3c-4e bond), but the familiar molecules with localized bonds, such as methane and ammonia, do indeed contain localized bonds, since transformation into an NBO-based wavefunction leads to a localized description without loss of accuracy. For example, an MO computation on methane will generate four bonding MOs, a low-lying fully symmetrical one where the 2s-orbital on carbon and the 1s orbitals on all four hydrogens are in phase, plus a set of three degenerate orbitals, where each orbital in the set contains a carbon p-orbital
(pₓ, pᵧ, or pₚ) and s-orbitals on more than one hydrogen atom. However, unleashing the NBO transformation onto this wavefunction turns it, essentially losslessly, into an NBO wavefunction that is as good as the MO-based wavefunction at describing the properties of methane, but the orbitals used (NBOs) are localized. In fact, the valence shell NBOs are the four localized σ-bonds, loved by every organic chemist, each formed from overlap of exactly one hydrogen s-orbital and exactly one carbon-based sp³ hybrid! It turns out that highly covalent 12-electron transition metal complexes are described by localized bonds involving hybrid orbitals as cleanly and accurately as methane is. The above method, starting from high-level MO computations and NBO formalism, is the way the modern research community has arrived at the correct hybrid orbitals that describe covalent transition metal complexes. However, this current article introduces hybrid orbitals at metals in a slightly different way, specifically for undergraduate teaching. In addition to familiarity with basic, qualitative VB theory for organic molecules, only a small additional assumption related to relative sizes and energies of s and d orbitals at the metal is needed. With this input, the correct hybridizations for highly covalent systems can be derived with pen and paper, and from this exercise follows practically useful insight.
LEWIS STRUCTURE, HYBRIDIZATION, GEOMETRY

A main group problem as a warm-up exercise: \( \text{NH}_3 \) and \( \text{PH}_3 \)

Before using Lewis structures and qualitative VB theory on transition metal complexes, it is useful to first refresh students’ memory by presenting an easy main group example and then to challenge them by presenting a more difficult main group example. Predicting the structure of \( \text{NH}_3 \) is an easy exercise for college students, and already high school students are expected to be able to do this (Figure 3, top).

\[
\begin{align*}
\text{NH}_3 & \quad \text{PH}_3 \\
\text{Lewis Structure} & \quad \text{sp}^3 \\
\end{align*}
\]

\[
\begin{align*}
2p & \quad \text{hybridization} \\
2s & \quad \text{in bonds} \\
4 \times \text{sp}^3 & \quad \text{lone pair} \\
\end{align*}
\]

**Rationale for orbitals used: s and p very similar in size**

\[
\begin{align*}
\text{PH}_3 & \quad \text{sp}^3 \\
\text{Lewis Structure} & \quad \text{hybridization} \\
3p & \quad \text{pure p} \\
3s & \quad \text{lone pair} \\
\end{align*}
\]

**Rationale for orbitals used: s smaller and contracted; p large**

Figure 3. Atomic orbital sizes and energies matter for a qualitatively correct VB description. While N-H bonding in ammonia involves hybrids that are essentially sp\(^3\), P-H bonding in phosphine involves much more p-character, with s-character enriched in the lone pair. Drawing the energy gap between s and p as larger (compared to \( \text{NH}_3 \)) works as a heuristic here to remind of the more contracted valence shell s orbital and leads to the correct structure prediction (avoidance of hybridization). It is not meant to represent the orbital energies of the free atom.\(^{13}\)
A valid Lewis structure is quickly arrived at, from the number of valence electrons of the constituent atoms, followed by formation of a maximum number of two-centre-two-electron (2c-2e) bonds. The 2s- and 2p-orbitals are quite similar in size, and sp\(^3\) hybridization, resulting in a tetrahedral structure of electron pairs, is tempting. It is not only tempting but also correct, since it minimizes repulsion between electron pairs. The prediction is closely matched by the experimental structure (bond angles in Figure 3).\(^{14}\) What is the structure of PH\(_3\), then? Most students get this wrong (in the author’s experience) when asked in a 3\(^{rd}\) year inorganic chemistry class. The tempting but wrong answer is “also sp\(^3\)-hybridized”. However, due to the radial node(s) that the higher p orbitals have (and also due to differential core screening of valence shell p versus s orbitals), the valence shell p orbitals become much larger than valence shell s orbitals for the heavier main group elements. The more contracted s is more prone to becoming a lone pair and the larger p is particularly suitable for making bonds.\(^{13}\) The result is a pressure to avoid hybridization. The lone pair, by virtue of being localized on one atom only, is not stabilized by bonding, so it should be placed in the most low-lying orbital available. This leads to lone pairs on heavy main group elements being rich in s-character (“pure s” in the most extreme simplification). As a consequence, the orbitals used for bonding are rich in p-character, “pure p” in a simple model that predicts 90° H-P-H angles for PH\(_3\). While “pure p” is an oversimplification, the experimental reality confirms the prediction, with angles (93.6°)\(^{15}\) that are much closer to 90° than to 109.5° (Figure 3, bottom). The point of this warm-up exercise is to stress the point that one cannot automatically always use the same hybridization mix for lone pairs and bonding pairs alike. Generally, lone pairs should be placed into the most low-lying orbitals if the orbitals in the valence shell of an element are of rather different size or energetically strongly separated. If this point is kept in mind, hybridizations and geometries for the organometallic problems that are of interest here follow as straightforwardly as for the PH\(_3\) example.
A d-Block problem: PtMe$_2$ and other 12e-MR$_2$

It is an interesting experience to ask a 3rd year inorganic chemistry class: “So, who can write down a valid Lewis structure for dimethylplatinum, PtMe$_2$?” In the authors’ over fifteen years of experience, no student (in a class of 40-60) has ever volunteered to present the right answer. Since students never write Lewis structures (showing all valence electrons) for transition metal complexes, an implicit assumption is that such an endeavor is taboo. However, answering this question is not intrinsically harder than answering the analogous question for NH$_3$ or PH$_3$. The answer (Figure 4, top left) is straightforwardly arrived at, by either using a Pt atom (“d$^{10}$”, 10 valence electrons) and two methyl radicals or, alternatively (using the convention that a metal-bonded alkyl is considered a carbanion), a Pt$^{2+}$ ion and two CH$_3^-$.

![Lewis Structure Diagram]

**Orbitals used (s and d energetically separated):**

- 6s
- 5d
- Use for the 4 lone pairs
- Hybridize s + d
- 2 x sd hybrid
- Oriented at 90°

**Figure 4.** The 12-electron transition metal compound PtMe$_2$ is not harder to describe than an 8-electron main group compound such as PH$_3$. Derivation of sd hybrids is shown explicitly. The small side lobes of the sd hybrids will be omitted, for simplicity, in the subsequent Figures.
But how will hybridization work out? To get this right, the additional and important input that “5d is significantly lower than 6s” (and generally for the transition metal valence shell that (n-1)d < ns) is then presented to class. This piece of information will enable the correct hybridization scheme, leading to a useful prediction of geometry. The lone pairs are placed in pure d-orbitals, with a rationale (lower energy) that is completely analogous to the argument used for the PH3 case. The orbitals Pt can then use for the bonds to two identical (methyl) groups are one s and one d. Making two identical sd hybrids is in order, and the shapes of the two sd hybrids and their relative orientation are easily derived by creating the two possible linear combinations: addition of s onto d with either + or – phase (The small side lobes of the sd hybrids will be omitted, for simplicity, in the subsequent Figures but are shown in Figure 4). The derivation suggests that the two sd hybrids are oriented at 90°, and it is predicted that the C-Pt-C bond angle in dimethylplatinum should be close to 90°. High-level quantum mechanics computations are in good agreement (102.9° computed for PtMe2, 86.5° for PtH2).2,12b

IrMe3 and other 12e-MR3

Using the same method, the structure of IrMe3 is correctly arrived at (Figure 5). It is useful to remember (and not so easily derived) that sd^2 hybrids are (apart from small and chemically irrelevant features close to the node) dumbbells and that each of them is oriented relative to the other two at 90°, just as the x, y, z Cartesian coordinates are oriented relative to each other. This wedge or corner-shaped geometry that results is the equilibrium geometry of IrMe3, as confirmed by high-quality computations on IrMe3 directly and by earlier computations on the very similar RhH3, where bond angles of narrower than tetrahedral (106.7°, IrMe3) and very close to 90° (94.4°, RhH3) were found.
Figure 5. The 12-electron transition metal compound IrMe$_3$ is normal-valent just as PtMe$_2$ (or PH$_3$). Shapes of sd$^2$ hybrids are not derived here – it is sufficient to remember that they are oriented at 90°. The small side lobes of the sd$^2$ hybrids are not shown.

The above examples are all “normal-valent” molecules: all valence electron pairs are either lone pairs or bonding pairs, and all bonding pairs are in 2-center-2-electron (2c-2e) bonds. PtMe$_2$ and IrMe$_3$ are very similar to those main group compounds that obey the octet rule, such as NH$_3$ or PH$_3$ or I$_2$. If a main group molecule were restricted to having only 2c-2e bonds, then the maximum number of electrons in the valence shell of its atoms would be 8 (except for hydrogen, where the number would be 2), because the valence shell is composed of three p-orbitals and one s-orbital. Similarly, if a transition metal
complex were only permitted to have 2c-2e bonds, then the maximum number of electrons in the valence shell of the metal would be 12, because the valence shell is composed of five d-orbitals and one s-orbital (3d/4s, 4d/5s, 5d/6s for first, second, third transition metal row, respectively). It is recognized now that main group compounds exceeding a valence electron count of 8 involve hypervalent bonding, i.e. not all bonds are 2c-2e bonds. Octet expansion could, in principle, occur while retaining the 2c-2e nature of bonds IF d-orbitals where significantly involved in bonding to main group elements (“sp$^3$d”, “sp$^3$d$^2$”...), but accurate computations show this not to be the case.$^{19}$ Modern methods show that d-orbitals, by virtue of their energetic inaccessibility, do not significantly contribute to bonding to main group elements. If wavefunctions for such molecules are computed and then localized (for example, with the NBO$^{12a}$ formalism), localization of electron pairs in lone pairs and 2c-2e bonds does not succeed but hypervalent bonds, such as three-centre-four-electron (3c-4e) bonds are needed, which is now generally acknowledged in undergraduate textbooks. However, the related fact that hypervalency is commonly encountered in bonding to transition metals is rarely addressed. Stressing this particular similarity provides a powerful unified view of main group and transition metal chemistry. Hypervalency is so common for transition metal compounds that normal-valent 12-electron complexes like Pt$R_2$ and Ir$R_3$, despite the simplicity of their electronic structure, are exceptionally hard to make. Unless very bulky R groups are used, attempt to make the 12-electrons species in solution will lead to strong coordination of the solvent, generating, for example, a 16-electron complex Pt$R_2$(solv)$_2$ or an 18-electron complex Ir$R_3$(solv)$_3$. In these hypervalent adducts, a strong tendency is seen to retain the 12-electron fragment as a transferable substructure, with very little (and predictable) change. Understanding this fact provides a powerful new way to analyze 16-electron d$^8$ and 18 electron d$^6$ complexes. The approach is straightforward but requires some basic understanding of 3c-4e bonds, which will be reviewed in the next section.
3C-4E BONDS
A main group example: when ligands approach dihalogen molecules end-on

Assuming familiarity with basic molecular orbital (MO) theory, the 3c-4e bond, a common instance of hypervalent bonding, makes sense. For the example of I₂, a MO treatment shows that the diiodine molecule is indeed electrophilic, due to its relatively low-lying σ-antibonding (σ*) orbital, which has large lobes on each end, trans to the I-I bond.

Introducing the 3c-4e bond: I₂ and iodide

I) Orbital interactions and MO diagram

Favorable filled/empty interaction on approach:

\[
\begin{align*}
\text{p lone pair} & \quad \text{σ*(I₂), empty} \\
\text{I-I B.O.} & = 1 \\
\text{prior to} & \\
\text{I’} & \text{approach}
\end{align*}
\]

The three AOs have re-mixed to form three new MOs:

- anti-bonding
- non-bonding
- bonding

II) Resonance description

\[
\begin{align*}
\text{I}^{-} & + \quad \text{I} \quad \text{I}^{-} \\
\text{(A)} & \\
\text{I}^{-} & + \quad \text{I} \quad \text{I}^{-} \\
\text{(B)} & \\
\text{1-I B.O.} & = \frac{1}{2} \\
\text{1-I B.O.} & = \frac{1}{2} \\
\text{Resonance structure A and B} & \text{ contribute equally in the symmetrical structure}
\end{align*}
\]

III) Experimental observation

\[
\begin{align*}
\text{I}^{-} & + \quad \text{I} \quad \text{I}^{-} \\
\text{2.715 Å} & \\
\text{180°} & \\
\text{2.917 Å} & \text{2.917 Å}
\end{align*}
\]

Figure 6. Hypervalent bonding (more specifically: 3c-4e bonding) in I₃⁻, formally derived from donation of a lone pair on I⁻ into the σ* of normal-valent I₂. I-I distances for free I₂,²⁰ and symmetrical I₃⁻ (decamethylferrocenium salt)²¹ are also shown, as well as heuristic bond orders (B.O.).
Figure 6 shows the filled-empty interaction for the initial attack of I⁻ on I₂. The elongation (weakening) of the I-I bond is easily seen from the nature of the orbital donated into: donation into an I-I anti-bonding (σ*) orbital weakens the I-I bond. It is not necessary to construct a full MO scheme to see this point. However, a MO scheme showing all the σ-MOs arising from the interaction of the p-lone pair on I⁻ with the existing bond of I₂ is also shown. The heuristic bond order for each I-I interaction I₃⁻ is 0.5: of the two filled MOs in the three-center-interaction, one is bonding, one is non-bonding. The bonding one stretches its “bonding power”, equivalent to one bond, over two I-I contacts, leaving each I-I contact with a bond order of 0.5. The resonance picture, likewise, leaves each I-I interaction with the unweighted average of one bond and no bond, that is one half bond. The experimental structure confirms the linearity of the molecule (as expected from the trans-attack) and the I-I bond weakening/elongation (2.715 Å → 2.917 Å). This is an example of a symmetrical 3c-4e bond. The iodine atom that initially came from free iodide is as strongly bonded to the central iodine as the other terminal I that was initially part of the I₂ molecule. It is important to realize that a much less donating nucleophile will weaken the initial I-I bond much less. To illustrate this point, an analogous discussion of the pyridine-I₂ adduct is shown (Figure 7). If a ligand binds to I₂ more weakly than I⁻ does, the ligand reduces the I-I bond order from 1.0 not quite by 0.5 units but by a lesser amount that is based on the exact weights of the resonance structures; knowing the exact bond order in the unsymmetrical case would require an actual computation and would not be solvable with pen and paper. Also, the full MO scheme for this unsymmetrical case (or just the σ-system, shown here for completeness; a student would not be able to derive this with pen and paper) would require a quantum-chemistry computation. Despite the more complicated nature of the full MO description, the qualitative argument still holds: the fact that the I-I bond is weakened is easily seen from inspecting the initial interaction. In a resonance description of a system where donation into the I-I bond is relatively weak, the I-I bonded canonical structure (A in Figure 7) will have a larger weight than the canonical structure that contains a full bond of I to the nucleophile but completely breaks the initial I-I bond (resonance structure B in Figure 7, II).
An unsymmetrical 3c-4e bond: I$_2$ and pyridine

\[
\text{π} \quad + \quad \text{I} \quad \longrightarrow \quad \text{π}
\]

I) Orbital interactions and MO diagram

Somewhat favorable
filled/empty
interaction on approach:

\[
\begin{align*}
\text{sp}^2 \quad \text{lone pair on} \\
\text{py}
\end{align*}
\]

\[
\sigma^{*}(I_2), \text{empty} \\
\sigma(I_2)
\]

\[
\text{I-I B.O.} = 1 \quad \text{prior to} \\
\text{I’ approach}
\]

\[
\begin{align*}
\text{N-I B.O.} & \quad > 0 \quad < 1 \\
\text{'non-bonding'} & \\
\text{bonding} &
\end{align*}
\]

The three AOs have re-mixed
to form three new MOs:

II) Resonance description

\[
\begin{align*}
\text{π} \quad + \quad \text{I} \quad \longrightarrow \quad \text{π}
\end{align*}
\]

\[
\begin{align*}
\text{I-I B.O.} & \quad > 0 \quad < 1 \\
\text{Resonance structure A and B} \\
\text{contribute unequally} \\
\text{(A has larger weight than B)}
\end{align*}
\]

III) Experimental observation

\[
\begin{align*}
\text{π} \quad + \quad \text{I} \quad \longrightarrow \quad \text{π}
\end{align*}
\]

\[
\begin{align*}
2.715 \text{ Å} \quad & \quad \longrightarrow \quad \text{π} \\
2.804 \text{ Å}
\end{align*}
\]

Figure 7. Hypervalent bonding (more specifically: 3c-4e bonding) in the I$_2$-pyridine-adduct. The experimental I-I bond length shows weakening compared to free I$_2$ but to a lesser extent than in I$_3$. \[\text{II} \]
3c-4e bonds: *trans* influence and *cis/trans* geometric preference for square-planar d\(^6\) MR\(_2\)L\(_2\)

The same way I\(_2\) can add an extra ligand *trans* to its I-I bond, PtMe\(_2\) can add an extra ligand *trans* to each of its two Pt-C bonds (Figure 8).

![Diagram of 3c-4e bonding in PtMe\(_2\)L\(_2\)](image)

Square-planar geometry
Pt-C bonds weakened

\[2 \text{LI} + \text{Pt-CH}_3 \rightarrow \text{Li} \text{Pt-CH}_3 \]

B.O.(Pt-C) = 1

**Figure 8.** 3c-4e bonding in PtMe\(_2\)L\(_2\)
Several important observations are made: a) since the geometry of PtMe$_2$ has a $90^\circ$ angle, and since the ligands L add *trans* to each Pt-C bond, the geometry that results for PtMe$_2$L$_2$ is *square planar*. It is a rather thrilling fact that this square-planar preference for four-coordinate d$^8$ complexes can be derived using a hybridization argument. Whoever has used crystal field theory before has now a second way to derive this important insight. b) if the two ligands L are not very donating, platinum will prefer the *cis* geometry of the two methyls, simply because it can then maximize covalent character in the two Pt-C bonds c) the more donating a ligand L is, the more the Pt-C bond *trans* to it will be weakened, since the added ligand’s lone pair is donating into a Pt-C $\sigma^*$ orbital. Seeing the *trans*-interactions in square-planar d$^8$ complexes as what they are, namely 3c-4e interactions, provides a clear explanation of the *trans*-influence. Note that a similar explanation cannot be obtained from the old (and incorrect) sp$^2$d hybridization scheme for square-planar d$^8$ complexes. The latter, incorrectly, gives platinum four hybrid orbitals to bind to four ligands, which would make two bonds *trans* to each other (each would be 2c-2e) rather independent from each other. Would a full MO diagram of a square-planar complex help correctly understand the *trans*-influence? An actual MO computation predicts the *trans*-influence indirectly through its numerical output.$^{23}$ It does not provide a straightforward, intuitive derivation. Qualitative MO diagrams for square-planar d$^8$ systems normally show all ligands as the same, under high symmetry ($D_{4h}$). Explaining the *trans*-influence through a full MO diagram would require a very advanced low-symmetry treatment. Thus, the method explained here, learning to see 3c-4e interactions where they exist, fills a real explanatory gap.

Everything said about platinum dimethyls applies to related d$^8$ complexes. A study on platinum diphenyls is referred to, where cis-PtPh$_2$(DMSO)$_2$ was found to be more stable than trans-PtPh$_2$(DMSO)$_2$ by 48 kJ/mol.$^{4B,1}$ Very similarly, to give an example from the first transition metal row, pyridine-coordinated nickel(II) dialkyls, R$_2$Ni(py)$_2$, prefer the *cis* over the *trans* geometry.$^{24}$ The T-shaped intermediate shown in Figure 8 is not just hypothetical. While it is difficult to make three-coordinate d$^8$ complexes (a fourth ligand often binds very easily), the examples that have been made indicate that a T-shaped geometry ($90^\circ$ and $180^\circ$ angles) is preferred over the trigonal ($120^\circ$ angles) alternative.$^{25}$
3c-4e bonds: *trans* influence and *fac/mer* geometric preference for octahedral d⁶ MR₃L₃

A completely analogous argument is made for IrR₃L₃, (Figure 9), where each of the three Ir-C bonds can accept an extra ligand *trans* to it. The resulting geometry is the familiar octahedral geometry but derived in an unfamiliar way. The benefits of the new derivation are the following insights: if the three ligands L are less donating than a carbanion, the d⁶ metal (such as iridium) will prefer the *fac* geometry of the three organic groups, to maximize covalent character in the Ir-C bonds.²⁶ The *mer*-geometry will be unfavorable: here two strongly donating methyls would have to fight for the same sd² hybrid instead of being able to maximize covalent character in bonding to their own sd² hybrid.

![Diagram of 3c-4e bonding in IrMe₃L₃](image)

Figure 9. 3c-4e bonding in IrMe₃L₃
The preference for \textit{fac} over \textit{mer} geometry for highly covalent $d^6$ systems can be pronounced, and this preference is, generally speaking, particularly strong when the remaining three ligands are weakly donating. For example, the trimethylplatinum(IV) unit ($\text{PtMe}_3^+$ is isoelectronic to $\text{IrMe}_3$) occurs virtually exclusively as the \textit{fac}-isomer in trimethylplatinum(IV) compounds. The Cambridge Crystallographic Database (CSD)\textsuperscript{27} (including updates until March 2020) contains 323 crystal structures containing the $\text{PtMe}_3$ substructure for platinum(IV), and all strictly \textit{trimethyl} structures for $\text{Pt(IV)}$ (315 structures) are \textit{fac} isomers with no single \textit{mer} example. If a fourth methyl is added (8 structures in the CSD), of course, two alkyls will be forced to be \textit{trans}.\textsuperscript{28} The trimethylplatinum(IV) unit is just one of many fragments in organometallic chemistry that have a strong preference for \textit{fac} geometry. To give another example, the $\text{Re(CO)}_3^+$ fragment, isoelectronic to $\text{IrMe}_3$ or $\text{PtMe}_3^+$, is exceptionally stable. It also has a strong preference for the \textit{fac} geometry; out of almost 4,000 structures in the CSD (3,972, not counting tetramethyls and pentamethyls), over 99 \% are \textit{fac}, with the few \textit{mer} examples requiring exceptionally donating ligands. The $\text{Re(CO)}_3^+$ unit is biocompatible and has found widespread use in bio-labeling, bioimaging and therapeutics.\textsuperscript{29} In cyclometalated iridium complexes of the type $\text{\{CN\}_3Ir}$, where a C,N-chelate ligand has a strongly donating, covalently bound carbanion end and a pronouncedly less donating nitrogen donor end, the \textit{fac} isomer will be more stable (typically by 30 kJ /mol) than the \textit{mer} isomer.\textsuperscript{40,2} The intermediates that occur when formally adding first one, then two additional ligands to a $d^6$ $R_3M$ fragment (before adding the third one) are very reasonable structural proposals for the rare cases of four-coordinate $d^6$ complexes (see-saw structure) and five-coordinate $d^6$ complexes (square pyramidal). For example, the first five-coordinate platinum(IV) alkyl complex ever discovered was square pyramidal,\textsuperscript{30} and subsequent structures have confirmed the prevalence of this geometry.\textsuperscript{31}

As a summary of some of the most important insights from analyzing $d^6$ complexes and $d^6$ complexes in the spirit of VB theory, the organometallic questions raised in Figures 1 and 2 are answered in Figure 10.
The list of potential insights does not end here. Selected insights will be discussed below, starting with the case of “pathological” structures that now appear quite simple.
SELECTED FURTHER APPLICATIONS OF THE METHOD

Pathological structures

The structure of trimesityliridium, IrMes₃, was reported in 1992. A reader of this article, identifying it as covalent 12-electron MR₃ compound, would recognize that it is a simple compound (all bonds are 2c-2e) and that its theoretical description is particularly easy. IrMes₃ is isoelectronic to IrMe₃, since the phenyl anion is an isoelectronic replacement for the methyl anion, and a mesityl is just a phenyl with methyl substituents in places that make it bulky. The prediction would be that the electronically preferred C-Ir-C bond angle should be close to 90° (sd² hybrids) but that the extreme bulk of the ortho-methyls, in particular inside the crowded IrC₃ wedge, will not tolerate a 90° angle but will force it to widen (Figure 11, A).

Figure 11. Three pathological structures are quite healthy, after all.
This is indeed observed, and the C-C bond angles are widened up from 90° to 107.5° (average of three angles for the experimental structure), for steric reasons, as a space-filling model shows. This description is straightforward for the modern reader familiar with hybridization in highly covalent d⁶ complexes. However, when this complex was discovered, it was described as “tetrahedral”, and the question of why the C-M-C angle is narrow (107.5° instead of 109.5°) was puzzled over. We know now that the observed bond angle is not a tetrahedral angle that is narrowed due to some strange effect, but is a 90° preferred angle that has been widened due to sterics. Very similar is the case of tris-norbornyl-bromo-nickel(IV). It, too, was in the initial report described as “tetrahedral”, and there was no good explanation for why the C-Ni-C angles involving three very bulky alkyls (norbornyls) are “narrowed” (that is compared to the ideal tetrahedral angle). The answer is that NiR₃⁺ is just another example of a 12-electron MR₃ complex that prefers 90° angles. The sterics of the bulky norbornyls widen the 90° bond angles to become 100° (Figure 11, B). Lastly, Yamamoto’s group reported the self-assembly of two unusual (C,O)²⁻ ligands around one palladium(IV) center, leading to the see-saw geometry shown in Figure 11, C. The structure makes complete sense, with the two carbanions binding at an almost ideal right angle with nothing trans to them, suggesting that these are 2c-2e bonds involving each their own sd² hybrid. The remaining sd² hybrid is utilized in a 3c-4e interaction with the two oxygen donors trans to each other.

Do electron-rich ligands make oxidative addition thermodynamically more favorable?

The analysis so far has provided a clear rationale for the trans-influence, a way to understand why having two strong bonds trans to each other is energetically unfavourable. This has very important implications for catalysis. While it is generally true that making a ligand on a metal complex more electron-donating will normally make oxidative addition of a substrate to that metal complex thermodynamically more favorable, this expected effect could be counteracted by an opposing effect (that may actually dominate) if the oxidative addition reaction happens to place two strong ligands trans to each other. Figure 12, A, shows a famous example where a more electron rich spectator ligand will favor oxidative addition only if the newly added groups are not forced to have strong donors trans to them (in ‘PCP’Ir) and not if the newly added groups are forced to have strong donors trans to them (in
When differently substituted (different Y) \( {('PCP')Ir} \) complexes are made and reacted with \( \text{H}_2 \), the equilibrium will be shifted from \( \text{Ir}^{	ext{i}} \) to \( \text{Ir}^{	ext{iii}} \) if Y is more electron-rich. In stark contrast, when differently substituted (different Y) \( {('PCP')Ir(CO)} \) complexes are made and reacted with \( \text{H}_2 \), the equilibrium will be shifted in the opposite direction, from \( \text{Ir}^{	ext{i}} \) to \( \text{Ir}^{	ext{iii}} \) if Y is more electron-rich. Related to the second case is another example, shown in Figure 12, B, the oxidative addition of methane to \( \text{(R_3P)_2PtCl}_2 \). Here, the methyl and the hydride that are added to the platinum have strong donor ligands \( \text{trans} \), and making the phosphine more electron-rich (\( \text{PMe}_3 \) instead of \( \text{PH}_3 \)) does not render oxidative addition more favorable (in a thermodynamic/equilibrium sense) but makes it energetically more uphill.

\[ \]
A) Ir$^I$ versus Ir$^{III}$ pincer:

Donating substituents $Y$ *push equilibrium towards oxidative addition*...

in (‘PCP’)Ir, where there is nothing *trans* to newly added groups:

![Diagram of oxidative addition](image)

Donating substituents $Y$ *push equilibrium towards reductive elimination*...

in (‘PCP’)Ir(CO), which has strong donors *trans* to newly added groups:

![Diagram of reductive elimination](image)

B) Pt$^{II}$ versus Pt$^{IV}$ in methane oxidative addition:

Donating phosphines *push equilibrium towards reductive elimination*...

in trans-Pt(PR$_3$)$_2$Cl$_2$, which has strong donors *trans* to newly added groups:

![Diagram of oxidative addition](image)

Figure 12. If oxidative addition places two strongly donating ligands *trans* to each other, then making other spectator ligands more electron-rich will likely not make oxidative addition thermodynamically more favored. Donating substituents in (‘PCP’)Ir(CO) achieve the opposite of what they achieve in (‘PCP’)Ir.
Extension to $d^{10}$ systems

The method described here is not primarily concerned with sd and sd$^2$ hybridization *per se*. Rather, sd and sd$^2$ hybridization have simply resulted from applying the suggested method to $d^8$ and $d^6$ systems, respectively. The suggested method simply involves using known orbital energies for bonded transition metal systems$^{16}$ and taking them as a governing principle: $(n-1)d < ns < np$ ($n = 4$ for Sc, Ti, V, ...; $n = 5$ for Y, Zr, Nb, ... $n = 6$ for Lu, Hf, Ta...). Two rules were implicitly applied:

(I): Disregard involvement of np, because these orbitals are too high in energy.

(II): When the decision is made where to put lone pairs, take $(n-1)d < ns$ as a rule, which means that the lone pairs are put into the d orbitals, to the maximum extent possible.

The remaining orbitals, used in bonding, can end up being hybrids (as is the case for $d^8$ and $d^6$) or not, as will be the case for $d^{10}$. It is hoped that this qualitative VB method captures the essence of what a high-level computation (typically done using canonical MOs) followed by localizing orbitals (often now done with NBO) does. While nobody expects a “back of an envelope” method to yield a description that is as accurate as what a supercomputer (or a few hours of compute time on a PC) would yield, the qualitative agreement is remarkably good. Predictions made with the simple VB method qualitatively hold up against high-level computations (and against experiment) for many $d^6$ and $d^8$ systems, as discussed in multiple places above.

The method also extends quite well to $d^{10}$ systems, such as Ni(0), Pd(0), Pt(0), Cu(I), Ag(I), Au(I), Zn(II), Cd(II), Hg(II). First, it should be mentioned that the separation between ns and np (rule I) is larger for the second and third transition metal row compared to the first transition metal row, so completely neglecting valence shell p-orbitals at the metal is very much justified for Cd$^{2+}$ and Hg$^{2+}$ but is a cruder approximation for Zn$^{2+}$. Still, bonding to Zn$^{2+}$ is essentially hypervalent, and qualitatively correct predictions can often be obtained from a simplified hypervalent picture where the only acceptor orbital at Zn$^{2+}$ is 4s.$^{39}$ For the third transition metal row system Au$^+$, the realization that the acceptor orbital on Au(I) is essentially an s-orbital (6s) has led to the exceptionally useful gold-hydrogen analogies,
inspiring a large amount of chemistry that is new but can be understood through analogies.\(^4\) Focusing on the catalytically relevant second transition metal row example of Pd(0), shown in Figure 13, the hypervalent picture (no p-orbital involvement at Pd) is also strongly supported by high-level computations. The only normal-valent structure is Pd(0) with one ligand, a 12-electron complex. Rule (II) comes into play, and all five lone pairs are in d-orbitals (Figure 13, A).

**Figure 13.** Pd(0) accepts electron pairs with its 5s orbital. Pd(0) with one ligand contains a 2c-2e bond (A). When more ligands are added, bonding becomes hypervalent (B).
The donor ligand creates a Lewis acid-base adduct by donating with its lone pair into the $5s$ orbital of Pd, forming a $2c$-$2e$ bond. However, the resulting $\sigma^*$ is sterically and electronically very accessible, and a number of additional donor ligands can donate into the same $s$-orbital on Pd, creating, in order, $3c$-$4e$, $4c$-$6e$, $5c$-$8e$ interactions (Figure 13, B). Every added ligand will be bound more weakly than the previous ligands (this would need group theory or the ligand group orbital approach to derive). This is a “law of diminishing returns,” and there is no special significance attached to the 18-electron rule which would ask for four ligands on Pd(0) – in fact, many stable three-coordinate Pd(0) complexes have been synthesized, and two-coordinate Pd(0) complexes are easily enough accessible to play a key part in catalytic cycles. High quality computations confirm that $p$-orbitals at Pd are not involved and that the simple picture shown in Figure 13 is essentially correct, except for added energetic contributions from back-donation (metal-to-ligand) and dispersion (van-der-Waals) interactions, which are captured in high-quality computations, but not in the simple picture.

LIMITATIONS OF THE CURRENT ANALYSIS INVOLVING SD- AND SD$^2$ HYBRIDIZATION

A key limitation that students should be made aware of is that the simplified method as described here is only applicable to highly covalent compounds. In other words, VB/hybridization arguments will be much more difficult for compounds where the bonding is mostly ionic. Since elements of the 2nd and 3rd transition metal row are significantly more electronegative than elements of the first transition metal row, in fact approaching the electronegativity of carbon, the methods should work very well for closed-shell (no unpaired electrons; bonding MOs filled, anti-bonding MOs empty) organometallic compounds of the more electronegative 2nd and 3rd row elements, such as Pd, Pt, Rh, Ir, Ru, and Os. For example, it is important to understand, as was explained here, that tris-cyclometalated iridium(III) (and also rhodium(III)) complexes, for a large number of cyclometalated C,N-ligands, have an electronic preference for the fac isomer. However, it would be untrue to assume that the same should be true for all cases of fac/mer isomerism, for all metals. In fact, for electropositive metals and for cases where the two donors in one chelate are fairly similar in donor strength, a statistical distribution favoring the mer-isomer is typically observed. Further, it would be incorrect to assume that all highly covalent metal alkyls (or
hydrides) that are described via $s^nd^{m}$ hybrids at the metal involve 90° (and 180°) angles. This article has concentrated on $sd$ hybrids and $sd^2$ hybrids (with some treatment of $d^{10}$ systems, where, to an approximation, only $s$ is involved in bonding). Higher $s^nd^{m}$ hybrids have complicated shapes and angles. For example, given the method described in this article, one would be able to successfully (and correctly) predict that tungsten hexamethyl ($WMe_6$) is $sd^5$-hybridized at tungsten. However, a geometry prediction would be beyond the scope of this article, since the angles involved in $sd^5$ hybrids are very unusual and no angle involved here is 90° or 180°. Indeed, $WMe_6$ is not octahedral but can assume various unusual structures that are energetically quite similar.\textsuperscript{2,44} Still, the value of understanding $sd$ hybrids and $sd^2$ hybrids relies not only in that they are simple cases. They are also particularly important cases, since they describe bonding in covalent $d^6$ systems and $d^8$ systems, which are very common, in particular in catalytic cycles.

**A SUGGESTED PLACE FOR S,D-HYBRIDIZATION IN THE INORGANIC CURRICULUM**

In the author's own experience, teaching the new method ($s,d$-hybridization in covalent bonding) provided a good fit for an in-depth course taught for 3rd year students which the author teaches at the Mississauga Campus of the University of Toronto, an optional course that directly follows a 2nd year foundation course (also taught by the author). However, how well (and where) the material fits for other instructors will depend on the details of their inorganic curriculum. The inorganic curriculum in North America is not very uniform, and a 2015 analysis of responses from instructors who were ACS (American Chemical Society) members revealed that the diversity in the curriculum can be organized using cluster analysis. The foundational courses fall into one of four categories: \textit{Descriptive Chemistry; Fundamentals & Selected Topics; Foundation Survey: Fundamentals; Foundation Survey: Comprehensive}.\textsuperscript{45} The in-depth courses fall each into one of three categories: \textit{In-Depth Survey: Core, In-Depth Survey: Comprehensive,} and \textit{Advanced Inorganic: Selected Topics}.\textsuperscript{46} Considering the topics taught by the author in 2nd and 3rd year (syllabus excerpts shown in the Supporting Information), his 2nd year course can be classified as \textit{Foundation Survey: Fundamentals}, and his 3rd year course as \textit{In-depth Survey: Comprehensive}. The
The author decided to teach in the foundational (2nd year) course sufficient MO theory to allow understanding of three-center-four-electron (3c-4e) bonds in small molecules such as I$_3^-$ and ICl$_3$. Following a short review of quantum mechanical principles (two 1-hour lectures), the treatment of VB theory and MO theory took two lectures. The 3c-2e bond was introduced using the H$_3^+$ example, followed by the more conventional example of diborane. The 3c-4e bond was then introduced using first I$_3^-$ and later ICl$_3$, in a dedicated lecture discussing hypervalent interhalogen compounds. The theoretical treatment was accompanied by a lab where the students synthesize dimeric ICl$_3$ (I$_2$Cl$_6$), a hypervalent main group compound. Building on an elementary understanding of MO theory (two lectures), the discussion of hypervalent bonding took one lecture hour only, and the lecture slides provided closely resemble Figures 6 and 7 in this paper. In this foundational course, although hypervalent bonding was explicitly discussed for main group compounds (using MO arguments and also resonance structures in a VB description) the electronic structure of d-element complexes was discussed on a crystal field theory level. Without doubt, crystal field theory is the most useful model (simplified theory) there is for the electronic structure d-element compounds, and there is no replacement. The method that forms the topic of this paper, hybridization involving s and d orbitals, is more specialized. It was introduced at the beginning of the 3rd year (in-depth) course, using exactly one lecture hour. The topic was introduced with a qualitative VB treatment of the differences between NH$_3$ and PH$_3$ (10 minutes), with slides that closely resemble Figure 3. The same VB method was then applied to PtMe$_2$ and IrMe$_3$ (20 minutes), shown here in Figures 4, 5. Now why do platinum(II) dialkyls prefer to be four-coordinate and square-planar and why do iridium(III) dialkyls prefer to be six-coordinate and octahedral? The answer is very similar to the answer for the question “why does I$_2$ bind another iodide to make I$_2$2?” The answer is in all cases: “because an energetically accessible $\sigma^*$ orbital is available, with a large lobe trans to the existing $\sigma$-bond. At this point, an understanding of hypervalent compounds is needed (from main group chemistry; Figures 6 and 7), but students have this knowledge already from the prerequisite foundational course. Just a very quick refresher pointing to I$_3^-$ was needed (5 min.) in the 3rd year course. The remaining 15 min. of class time, in the 3rd year course, were used to show how the normal valent fragments PtMe$_2$ and IrMe$_3$ bind extra ligands (here Figures 8 and 9), with the d$^{10}$ example (Figure 13 here) also shown. This one hour spent in the 3rd year class on sd/sd$^2$/d$^{10}$ was always found to be extremely well-spent: electronic
concepts such as electronic preference for cis versus trans (d⁸) and fac versus mer isomerism (d⁶) in highly covalent compounds, as well as the pervasive trans influence, appear, in subsequent lectures on organometallic topics, not as difficult special problems but are clear from the beginning, in a unified way. In this course, students are not required to read the original literature, but interested students are referred to the graduate-level book by Landis and Weinhold. Later in the course, an introduction into catalytic cycles will be given, and having the proper theory right from the beginning provides a good basis for the understanding of palladium(0) complexes with different coordination numbers (d¹⁰ example). Further, this approach prevents students from becoming overwhelmed by the complexity of organometallic chemistry and by the feeling that chemistry is hopelessly compartmentalized. Everyone in class is familiar with drawing valid Lewis structures, showing all valence electrons, for small main group compounds. Doing the same for transition metal complexes relieves the unfounded but common fear that bonding in organometallic complexes may be difficult beyond comprehension. The 2015 survey of in-depth courses has noted a consistent trend, across all three types of in-depth courses, to increase content in organometallic chemistry and to increase content related to covalent bonding and MO theory. Providing a new way to understand covalent bonding in organometallic complexes is definitely consistent with the larger trend.

The isolobal analogies by Hoffmann are also discussed early in the 3rd year course. The topic of sd/sd² hybridization is taught before the isolobal analogies, to avoid a possible misconception: methane and 18-electron-ML₆ complexes are both very stable closed-shell systems, and setting them as (to a very rough approximation) equivalent, that is ‘isolobal’, provides a fantastic starting point for further exploration, such as the insight that 16-electron-ML₅ complexes are electrophiles much as carbocations are: after all, 16-electron-ML₅ is isolobal to CH₃⁺. This powerful analogy, however, does not imply that the bonding in 18-electron-ML₆ complexes and in methane is the same. Despite bonds being hypervalent in 18-electron-ML₆ complexes and being normal-valent (2c-2e) in methane and other alkanes, the two types of compounds can still be isolobal, because they are both very stable closed-shell systems (all bonding MOs are filled and all antibonding MOs are empty). To make this point clear, some hypervalent antimony chemistry is introduced. SbF₆⁻ is also hypervalent in nature but nevertheless isolobal to CH₄, and the prediction that SbF₅ should be isolobal to CH₃⁺ is powerfully confirmed by its reactivity.
Of the subject matter discussed in this article, the following topics were found to be more suitable for graduate classes: "pathological structures" (Figure 11 here) and the question of when (and when not) electron-rich ligands will favor oxidative addition (Figure 12 and corresponding discussion in the text). Many students taking a graduate course at the University of Toronto are already performing NBO analysis on the compounds explored in their own research, and they appreciate the link that is made between high-level computations and back-of-an-envelope qualitative VB theory.

**CONCLUSION**

The approach presented here remedies several misconceptions. The first misconception is that main group compounds and transition metal compounds need fundamentally completely different methods for description. When the author draws Lewis structures of 12-electron organometallics, students frequently comment "I did not know that this can be done". Another misconception is that VB theory is for beginners and that every advanced analysis has to use MO theory. The use of VB theory for transition metal chemistry has been making a comeback in the research community, mostly due to the success of the widely available NBO algorithms. Introducing undergraduates to successful localized bonding ideas is timely. Another misconception is that 18 electron d⁰ complexes are so extraordinarily stable that the 16 electron and 14 electron species must be prohibitively uphill. This misconception arises easily if the 18 electron rule is stated as a rule without clear explanation of how the relative abundance of 18 electron complexes (but also 16 electron complexes) arises. The misconception hinders full comprehension of palladium(0) catalysis, where 16 electron and 14 electron species are easily accessible. MO theory is not always the most efficient way to clear up misconceptions. Sometimes, as is also the case for the trans-influence, a reasonably accurate, quantum-chemically defensible, localized bonding approach is better, which needs a 21st century understanding of hybridization. A few years ago, an instructor wondered whether the concept of hybridization should be retired, in particular in the teaching of general and organic chemistry. The answer, found in many letters and articles sent in response, was a resounding "no". To the many arguments that have been made in favor of using localized hybrid orbitals, this current article has added several ones that are specific to transition metal chemistry. The most
important fact to remember is that neither the delocalized (canonical) MO picture nor the localized bond picture is “more correct”. After all, these are just two different ways to write down the same multi-electron wavefunction. While both descriptions, if the underlying wavefunction is the same, produce the same values for all observables related to the molecule, the MO-based description is symmetry adapted, which makes it a more elegant basis for the study of perturbations (such as electronic excitations or ionizations). On the other hand, the localized picture provides fragments that are transferable and recognizable. Since expert intuition is based on recognition, it is an incredibly valuable skill being able to switch from the delocalized picture to a localized picture. Being able to swiftly switch toolkits is one of the greatest intellectual skills one can acquire. This point was famously made by Feynman, who (among other things) was revered for being able to solve “impossible” integrals. He explained his secret: he knew another less commonly taught technique, and he had learned to pull out the second toolkit for cases where the tools in the first one were blunt.

ASSOCIATED CONTENT
Supporting Information
Lecture schedules and learning outcomes for the 2nd year (foundational) course and the 3rd year (in-depth) course, lecture slides for the s,d hybridization lecture in the 3rd year course, selected problems for that course.

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1 Pauling’s electronegativity scale holds up very well for d-element chemistry. A study on d^{10} alkyls explains: “Traditional Pauling values are used […]. The popular Allred–Rochow scale ascribes quite unrealistic electronegativities to the heavier transition elements, presumably as a consequence of its inadequacies in the estimation of shielding parameters […] and Allen’s spectroscopic electronegativities are difficult to determine for d-block elements” (Smith, D. W. Electronegativity equilibration and organometallic thermochemistry: the strengths of carbon–carbon bonds in metal alkyls. *J. Organomet. Chem.* 1999, 585, 150-153). An earlier study on various d^n organometallics similarly preferred the Pauling scale: Labinger, J. A.; Bercaw, J. E. Metal-Hydride and Metal-Alkyl Bond Strengths: The Influence of Electronegativity Differences. *Organometallics* 1988, 7, 926-928. Using the Pauling scale, the platinum-carbon bond is predicted to be largely covalent (EN(C) = 2.5; EN(Pt)=2.2; similar values for Rh, Ir). In a 2018 computational model optimized for accurate prediction of bond polarities in d-element compounds, quantum chemistry-derived Mulliken electronegativities were used that closely mirrored Pauling’s scale (platinum and the other 2^nd and 3^rd row late transition elements were very similar in electronegativity to carbon): Kwon, S.; Naserifar, S.; Lee, H. M.; Goddard, W. A., III. Polarizable Charge Equilibration Model for Transition Metal Elements. *J. Phys. Chem. A* 2018, 122, 9350–9358.


8 Example: what is more acidic: acetylene or methane? The stability of the conjugate base is easily judged by considering the hybridization of the orbital that is occupied by the lone pair in the carbanion (lower energy if more s-character).


10 Considering the hole provides a shortcut compared to considering all bonds. The same way electrons ‘want’ to fill the bottom of an energy scheme, the same way holes, like bubbles in water, will rise to the top. The relative stability of the carbanions here would be the exact opposite of the relative stability of carbocations.


13 Modern computations agree that for the heavier main group elements, the sizes of valence shell s and p orbitals diverge in the direction of r_p >> r_s and that the central atom uses much more p-character in bonds and more s-character in the (relatively contracted) lone pair than the than the period 2 elements do. While the detailed analysis is highly non-trivial, the effect is real and uncontroversial. Surprisingly, the expectation that the s-p energetic gap also increases is not met in the case of the free atoms, but we are not interested in free atoms here (see also Ref 16). For advanced treatments: a) Kutzelnigg, W. Chemical Bonding in Higher Main Group Elements. Angew. Chem. Int. Ed. 1984, 23, 272-295. b) Wang, Z.-L.; Hu, H.-S.; von Szentpály, L.; Pyykkö, P.;


16 In transition metal *compounds*, it is always true for the valence orbitals used to describe the *bound* structure that (n-1)d is lower than ns (and also that np is even higher than ns), irrespective of what is true for the energetics of the *free metal atoms*: Schwarz, W. H. E. The Full Story of the Electron Configurations of the Transition Elements. *J. Chem. Educ.* **2010**, *87*, 444-448. This knowledge is used here as an input into the qualitative VB method described, and relative atomic orbital energies are consistently referring to the resulting bound structure and not to the free atom, even where a “neutral atom formalism” is used to put together a molecule.

17 If a convention is used where the metal is at the origin of the coordinate system and one Pt-C bond points in x-direction and the other Pt-C bond points in y-direction, the d-orbital employed in the two sd hybrids used for the two Pt-C bonds would be the dₓ²₋ᵧ² orbital. The remaining d-orbitals would be used as “pure d” lone pairs. While a detailed analysis shows that one of the d lone pairs has a small s-component mixed into it (Ref 2), this be safely neglected in an introductory treatment.


24 Cámpora, J.; del Mar Conejo, M.; Mereiter, K.; Palma, P.; Pérez, C.; Reyes, M. L.; Ruiz, C. Synthesis of dialkyl, diaryl and metallacyclic complexes of Ni and Pd containing pyridine, α-


26 If the three ligands L become as donating as a carbanion, the fac over mer preference will vanish.


34 Describing the structure as containing essentially free NiR₃⁺, in this current analysis, is justified by the observation of the very long Ni-Br bond (2.39 Å), which suggests that describing the bromide as non-bonded is a permissible approximation.

35 Not considering a very weakly coordinated solvent molecule, not shown here.


38 a) Original computational study: Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. Computational Study of Reductive Elimination Reactions to Form C-H Bonds from Platinum(II) and Platinum(IV) Centers with Strongly Coordinating Trimethylphosphine Ligands. *Organometallics* **2001**, *20*, 2669-


50 The “energy levels within a molecule”, which seem to be correct with MO theory but wrong with a localized description, do not represent an observable. In fact, there are no energy levels *within* a molecule. The only energy here that is an observable is the overall energy of the system (the molecule). That various spectroscopies seem to be observing energy levels within a molecule is an illusion and testament to the great power of a symmetry-adapted (MO) picture to provide an elegant description of how the system behaves under a perturbation. MO energies do such a great job that one might mistake them for being real.