

Electron Deficient Molecules

Examples of molecules with three centre two electron bonds
and their representation within the covalent bond classification

☺ The front of Balliol College today



Professor Christopher
Longuet-Higgins.

When he was an undergraduate (18 years old) in Balliol he published a paper with his Tutor Mr Bell FRS in Nature in 1945. The title was...

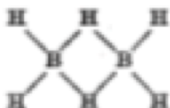
Structure of Boron Hydrides

LETTERS TO THE EDITORS

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Structure of Boron Hydrides

As recently shown¹, the interpretation of polyatomic structures does not require the hypothesis of resonance among several idealized valence-bond structures, a speculative application of the quantum-mechanical conception of resonance, which is in disagreement with numerous facts. They are accounted for by the principles of the classical (atomic and electronic) structural theories. The boron hydrides have been represented as resonance hybrids involving structures with one-electron linkages. Longuet-Higgins and Bell², in a most interesting and important discussion, have given convincing evidence that the introduction of the unique and theoretically unlikely one electron linkage between two unequal atoms is unnecessary, and that the boron hydrides should be represented by the bridge formulae of type



containing hydrogen bonds³.

Since hydrogen bonds are generally formed between atoms with unshared electrons and hydrogen atoms belonging to strongly polar linkages, whereas no unshared electrons are available at the B atom and the B—H linkage may be only slightly polar, Longuet-Higgins and Bell prefer to distinguish the linkages in the boron hydrides from other hydrogen bonds as resonance links. This implies a stabilization due to resonance involving no electron linkages. It is assumed that electrons belong to the orbitals of more than two atoms, that is, are non-localized.

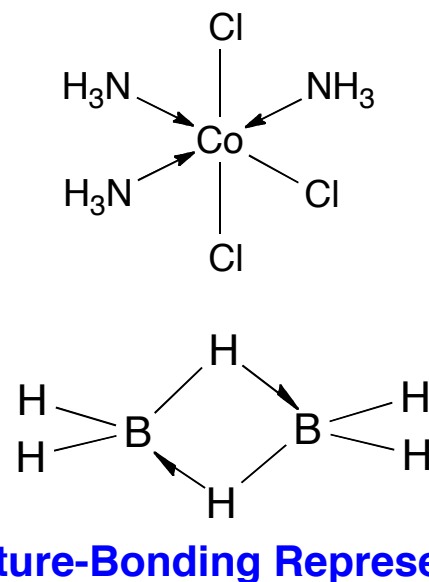
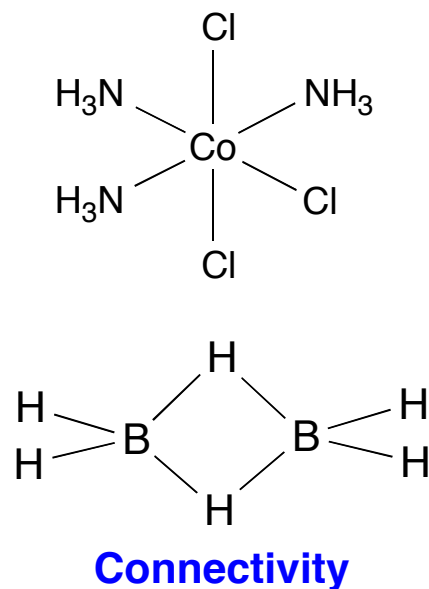


From PDF of
Original Paper
Nature, 1945,
155, 328

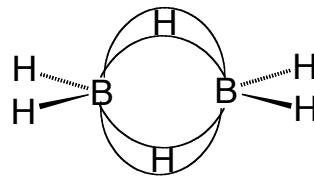
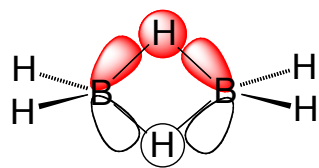
Supported by
IR and Raman
Data.

The Representation of Covalent Molecules

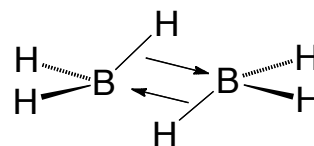
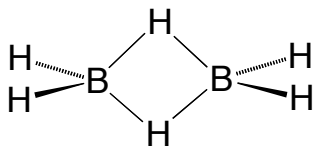
- Most organic compounds can be represented by using a black line to represent 2c-2e bonds.
- In contrast, many inorganic compounds cannot be represented so simply because the bonding must often be described in terms of dative interactions or 3c-2e interactions.
- In many situations, black lines are often just used to indicate connectivity and molecular shape, rather than the nature of the bonding and its electronic structure.
- Electronic structure can, however, be indicated by the appropriate use of arrows and formal charges. Such structures are described as **structure-bonding (SB) representations** and are very useful for identifying the MLXZ class and correct electron count of a molecule and are the basis of the Covalent Bond Classification method.



Representations of B₂H₆

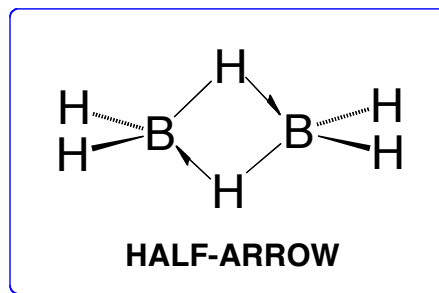


Orbital



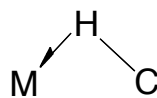
Historic

The use of the **half-arrow** distinguishes this as a 3c-2e bond

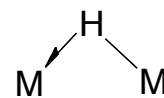


Preferred

Common examples of μ -X bonds in coordination compounds



agostic



bridging hydride

For electron counting purposes the half arrow represents donation of two electrons to a central atom. The two electrons of the 3c-2e bond are seen by both boron atoms. Hence each boron has an electron count of 8.

An alternative method of counting electrons for metal dimers and cluster with bridging hydrides or alkyls

The “half-electron” method apportions the one electron originating from a bridging hydride or alkyl ligand equally to both metals. The metal-metal bond order is predicted using the formula, with a view to the metals obeying the 18 electron rule.

$$\text{Number of } M - M \text{ bonds} = \frac{18m - N}{2}$$

Where m is the number of metal atoms and N is the **total** number of valence electrons

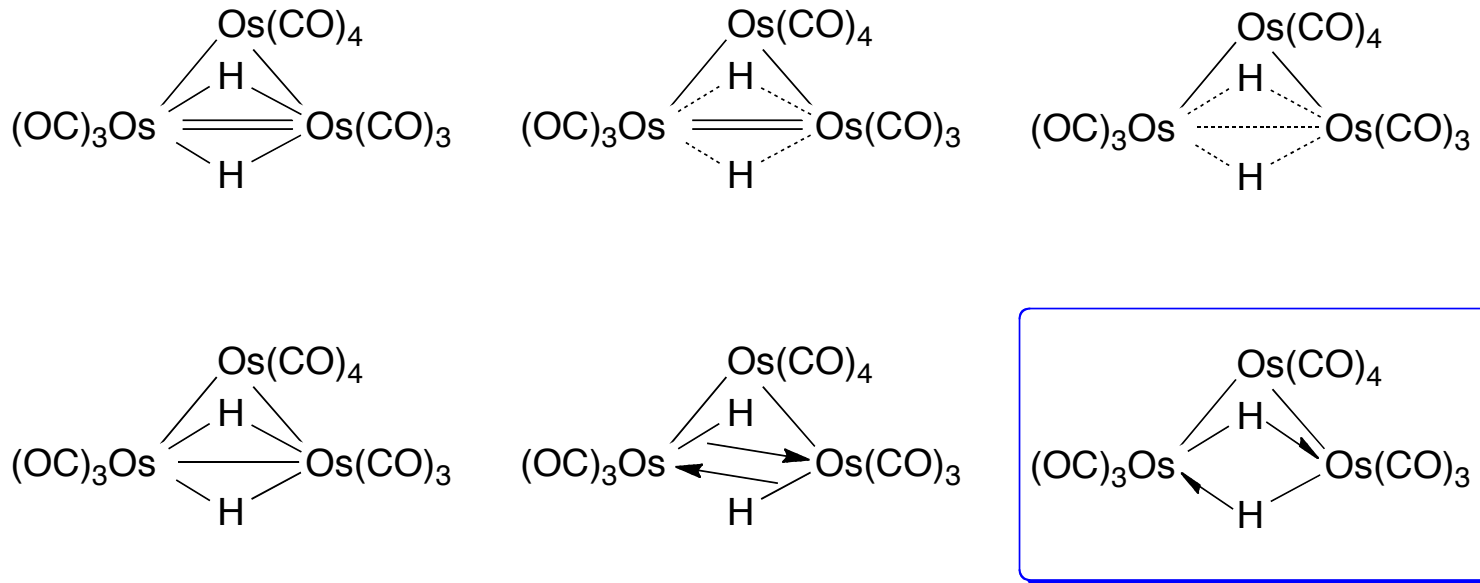
The problem with this method is that the application of the formula requires no knowledge of the structure and, for example, does not distinguish between terminal and bridging hydrogen ligands.

Also the predictions contradict the results of modern theoretical methods.

Occurrence and Representation of μ -X Bonds

Determination of correct bond order in transition metal compounds with bridging hydrogen ligands.

- Bond order ambiguities are common in the literature.
- $\text{Os}_3(\text{CO})_{10}\text{H}_2$ has been represented in the literature with a variety of bonding descriptions, varying from a $\text{Os}=\text{Os}$ double bond to no bond.

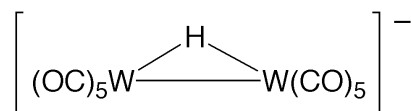


Os has 18 electron class of ML_4X_2 and NO Os-Os Bond

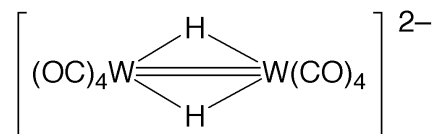
Direct M–M and 3–Center–2–Electron M–H–M Bonding Interactions

- Whereas the "half-electron" method assigns a M~M bond order that does not properly take into account the 3–center–2–electron nature of the interaction, the "half-arrow" method enables one to discuss the M~M bonding interaction in terms of both (i) **a direct M–M bond** and (ii) **a 3c–2e M–H–M bond**.
- Many other compounds may have their M~M bonding interactions described in such terms:

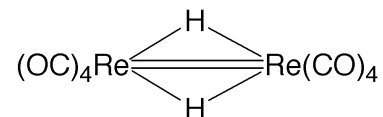
"Half-Electron" Method



1 M–M bond

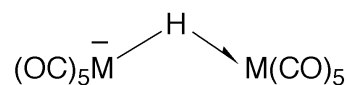


2 M–M bonds

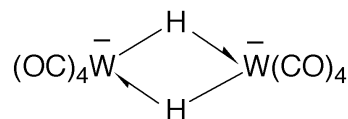


2 M–M bonds

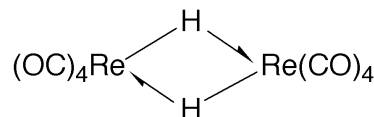
"Half-Arrow" Method



1 3c–2e M–H–M bond
0 M–M bond



2 3c–2e M–H–M bonds
0 M–M bond

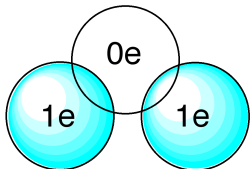
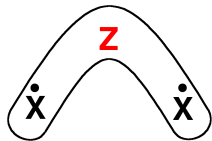
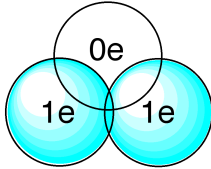
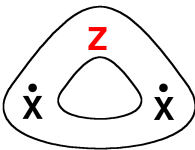
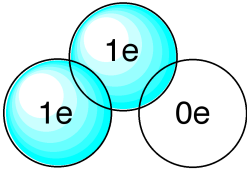
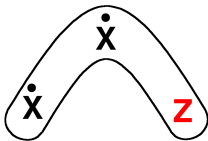
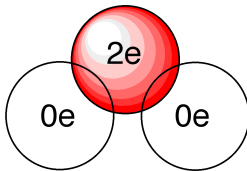
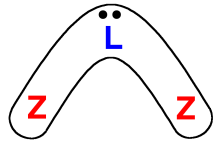
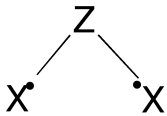
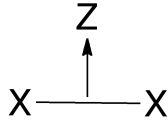
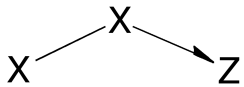
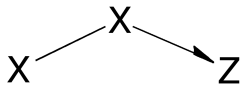
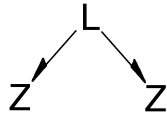


2 3c–2e M–H–M bonds
0 M–M bond

MO theory always agrees with the predictions of bond order using the half-arrow method.

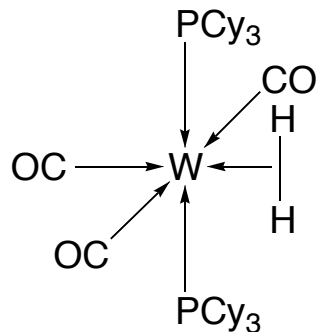
Classification of Three Centre-two Electron (3c-2e) Bonds by Electron Occupancy of the Orbital of the Bridging Atom

Four classes: $\mu\text{-Z}$ open, $\mu\text{-Z}$ closed, $\mu\text{-X}$, $\mu\text{-L}$

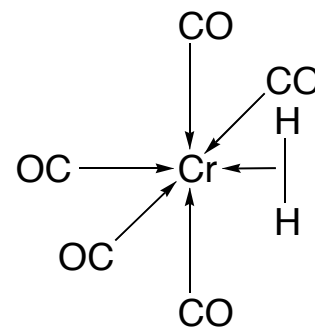
Short name	$\mu^{\circ}\text{-Z}$	$\mu^{\text{c}}\text{-Z}$	$\mu\text{-X}$	$\mu\text{-L}$
Open or closed	open	closed	open	open
Alternative orbital representations	 	 	 	 
Representation in structure-bonding figure			 or 	
Full name	$\text{X}-\mu^{\circ}\text{-Z}-\text{X}$	$\text{X}-\mu^{\text{c}}\text{-Z}-\text{X}$	$\text{X}'-\mu\text{-X}-\text{Z}$	$\text{Z}-\mu\text{-L}-\text{Z}$

Occurrence of Closed μ^c -Z Bonds in Coordination Chemistry

- Compounds with **closed** μ^c -Z bonds are most commonly encountered in transition metal dihydrogen compounds, which were first discovered by Kubas in 1984.

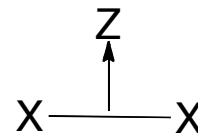
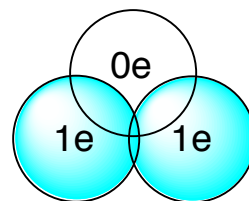
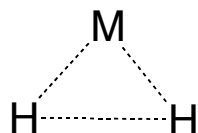


Kubas et al
JACS **1984**, *106*, 451

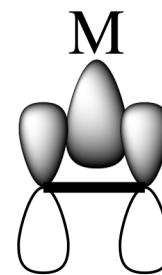
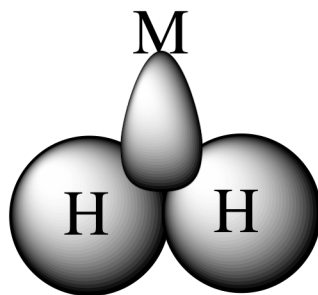
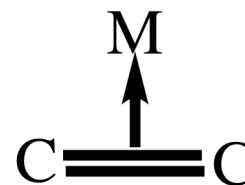
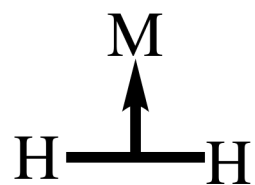


Upmacis et al
JCS Chem. Comm. **1985**, 27

- Dihydrogen compounds can be considered to possess **closed** μ^c -Z interactions because all three orbitals overlap.



Two μ - Z closed bonds



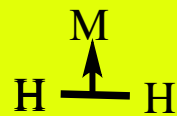
μ -Z^{cσ}

μ -Z^{cπ}

μ - Z closed, sigma

μ - Z closed, pi

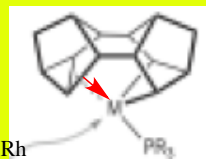
Examples of μ -Z^c (closed) bonds in transition metal compounds



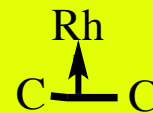
Dihydrogen
compounds



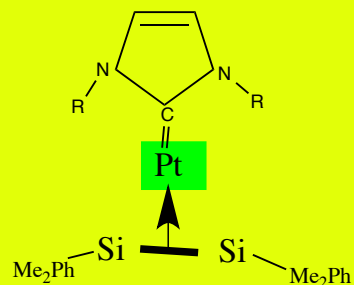
Olefin Compounds



Has a sigma C-C bond
[Rh(PR₃)(BinoreS)] complexes



A.B.Dhaokin, A.S. Weller JOMC,
730 (2013) 90 - 94

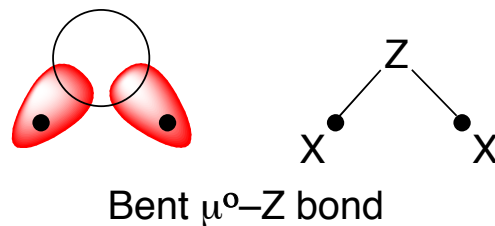


Pt[NHC(Dip)₂]- $(\text{SiMe}_2\text{Ph})_2$
(NHC = ; Dip = 2,6-diiso-propylphenyl)

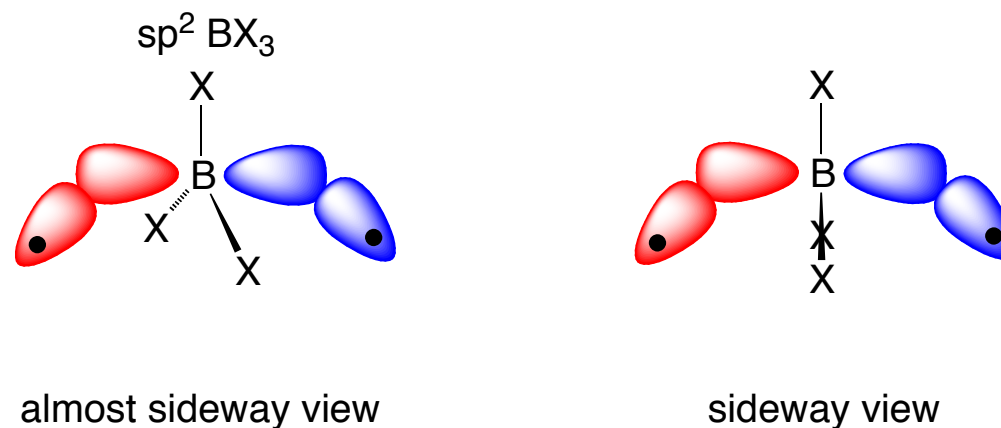
Berthon-Gelloz, G.; de Bruin, B.; Tinant, B.; Marko, I. E.
. *Angew. Chem., Int. Ed.* 2009, 48, 3161.

N.Takagi and S. Sakaki, *JACS*, 2012, 134, 11749.

Representation of Open μ^0 -Z 3c-2e Bond



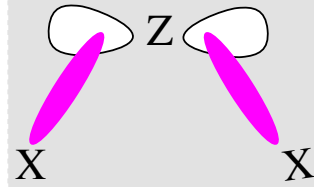
- The • — dot-line representation is used to indicate that it is a 3-centre-2-electron bond and not two 2-centre-2-electron bonds.



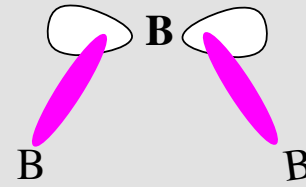
- Since Z does not contribute any electrons to the 3c-2e bond, the two X groups serve as an L donor to Z.

CBC mrepresentation of B_4H_9

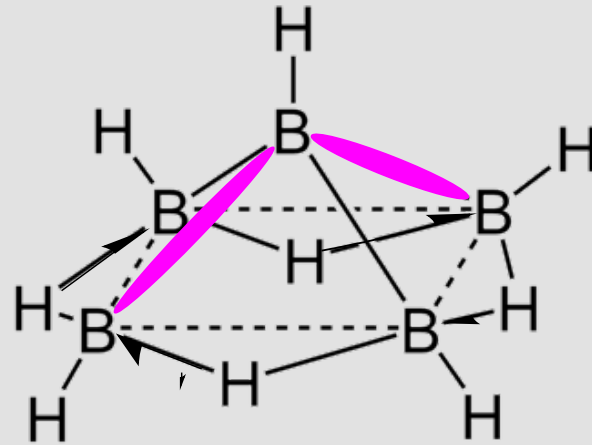
The $\mu-Z^\circ$ (open) bond in B_5H_9



General figure for
 $\mu-Z^\circ$ (open) bond



The $\mu-Z^\circ$ (open)
bond in B_5H_9

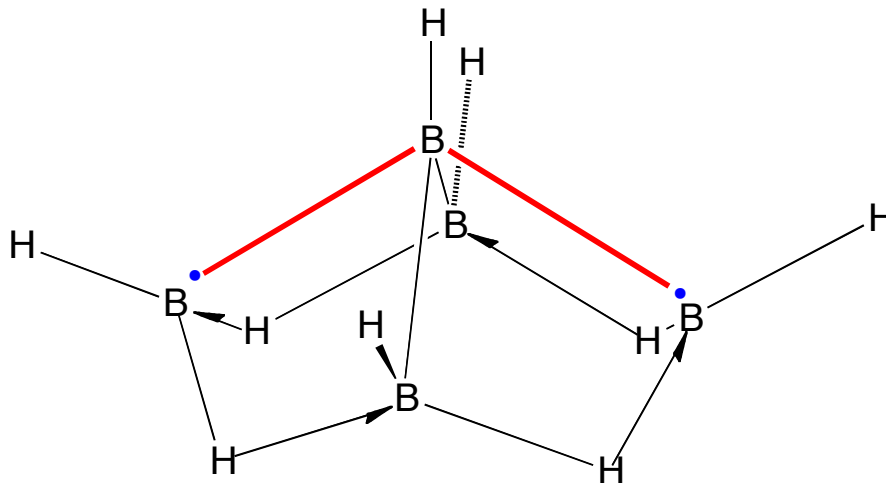


The $\mu-Z^\circ$ (open) bond in B_5H_9 .
All 4 basal B have tetrahedral
 BLX_3 class.

The $\mu-Z^\circ$ (open) bond acts as a
L'-ligand to the central boron,
so that B also has the class BLX_3

Example of Open μ^0 -Z 3c-2e Bond

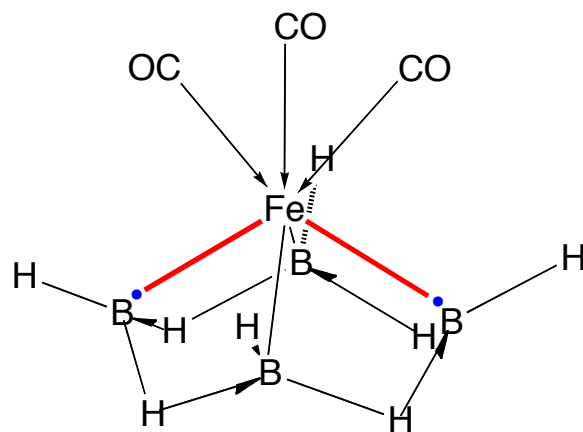
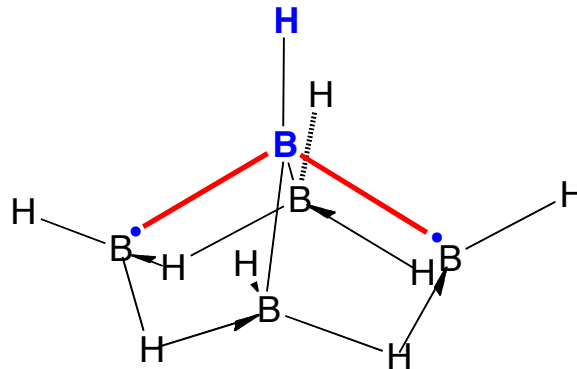
- **Open** μ^0 -Z bonds have been recognized only recently.
- A clear example of a compound that features a μ^0 -Z bond is B_5H_9 .



- The notation proposed for the μ^0 -Z bond is the dot-line.
- The presence of the **dot** signifies that this is a 3c-2e bond rather than two 2c-2e X-X bonds.

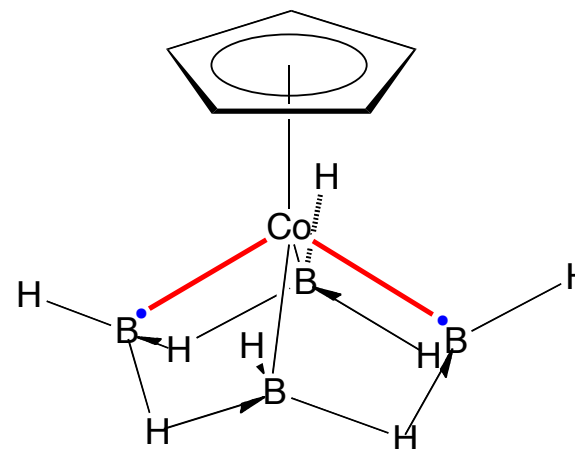
Other Examples of Open μ^0 -Z 3c-2e Bonds

- The axia **B-H** moiety of B_5H_9 may be replaced by metal fragments to give $[M](B_4H_8)$ derivatives that feature μ^0 -Z bonds.



Grimes
JACS **1977**, *99*, 5646
 ML_4X_2

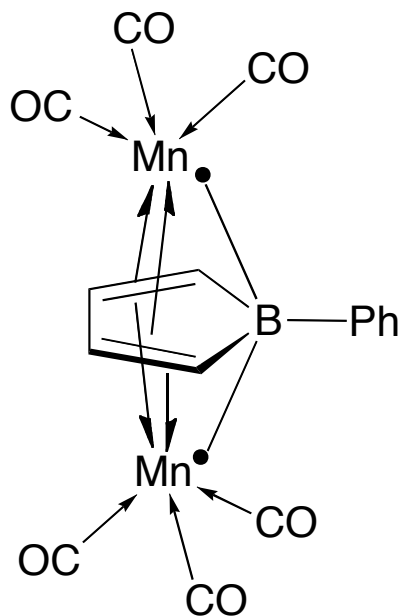
Class of iron
 $FeL_4X/2 = 18$



Greenwood
JCS Chem. Comm. **1974**, 718
 ML_3X_3

Class of Cobalt
 $CoL_3X_3 = 18$

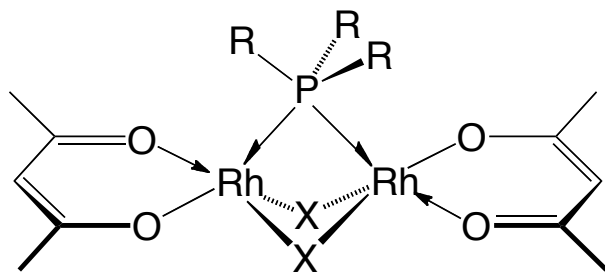
Bridging Boroles: Another Example of a μ^0 -Z Interaction



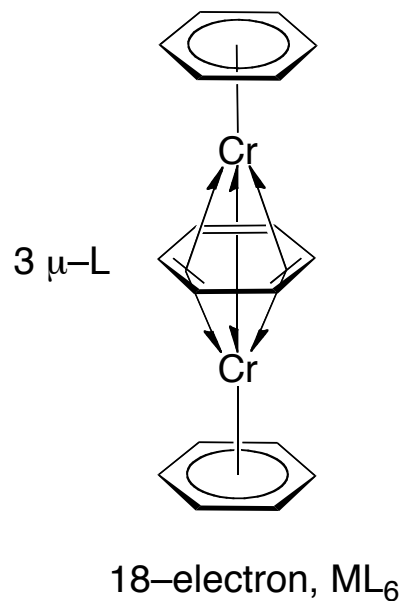
Class
ML₅X
18 e

Herberich
Angew. Chem. Int. Ed.
1983, 22, 996

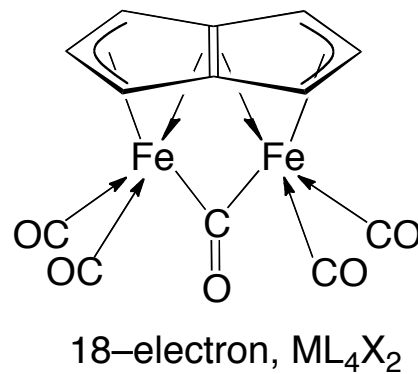
Examples of Compounds with μ -L Bonds



X = CPh₂; R = Me, Et, Buⁿ
16-electron, ML₂X₃



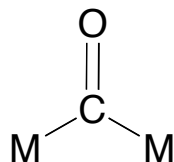
18-electron, ML₆



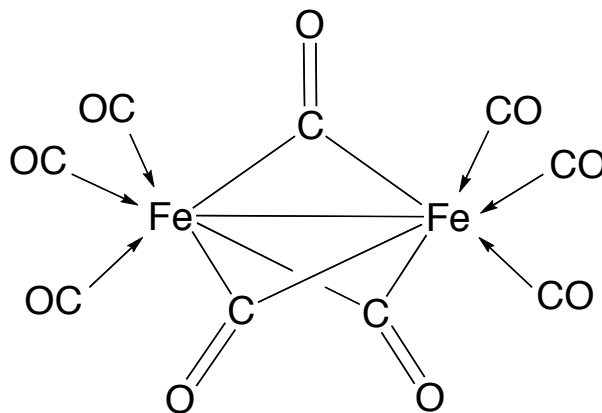
18-electron, ML₄X₂

Symmetrically Bridging Carbonyl Compounds

- Symmetrically bridging carbonyl compounds are invariably represented as "ketone" derivatives.

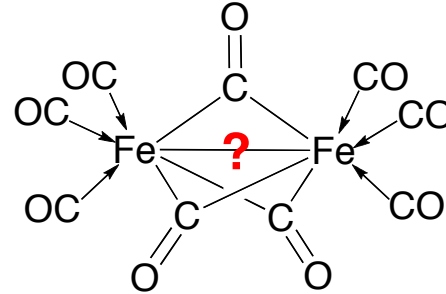


- $\text{Fe}_2(\text{CO})_9$ was the first polynuclear metal carbonyl to be characterized by X-ray diffraction, thereby confirming the presence of bent carbonyl ligands.



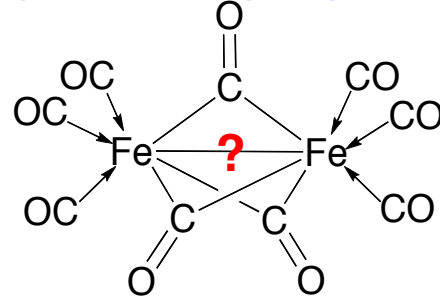
- $\text{Fe}_2(\text{CO})_9$ is invariably drawn with an Fe–Fe bond to achieve an 18-electron configuration, and Brateman stated that “**This bond is real, not formal**”

Bonding in $\text{Fe}_2(\text{CO})_9$

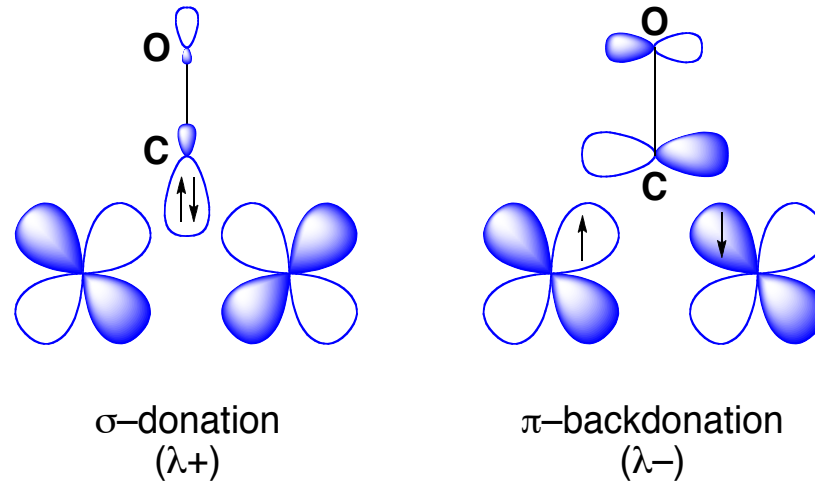


- However, in the 1970s, Hoffmann pointed out that the $\text{Fe}\cdots\text{Fe}$ interaction in $\text{Fe}_2(\text{CO})_9$ is actually **antibonding** and **repulsive**.
- Numerous subsequent calculations support Hoffmann's analysis.
- Heijeser: "... along the Fe-Fe bond axis there is a negative density difference";
- Bauschlicher: "No evidence is found for a direct Fe-Fe bond. The Fe's are held together by three center Fe-CO-Fe bonds."
- Rosa: "... the two $\text{Fe}(\text{CO})_3$ fragments are not kept together by direct Fe-Fe bonding but by the presence of the bridging carbonyls."
- Ponec: "... the bonding interactions between the metal atoms do not have the character of a direct Fe-Fe bond anticipated on the basis of 18-electron rule."
- **So why do organometallic chemists and text books continue to represent the molecule with an Fe–Fe bond?**

Bonding in Bridging Carbonyls



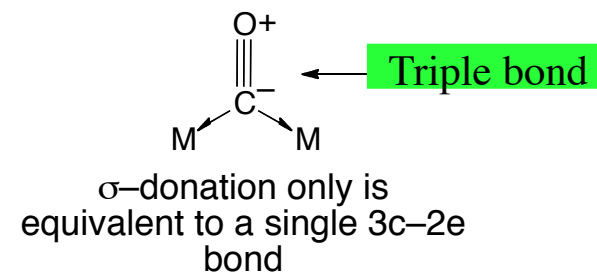
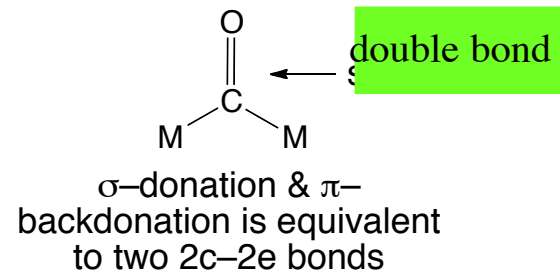
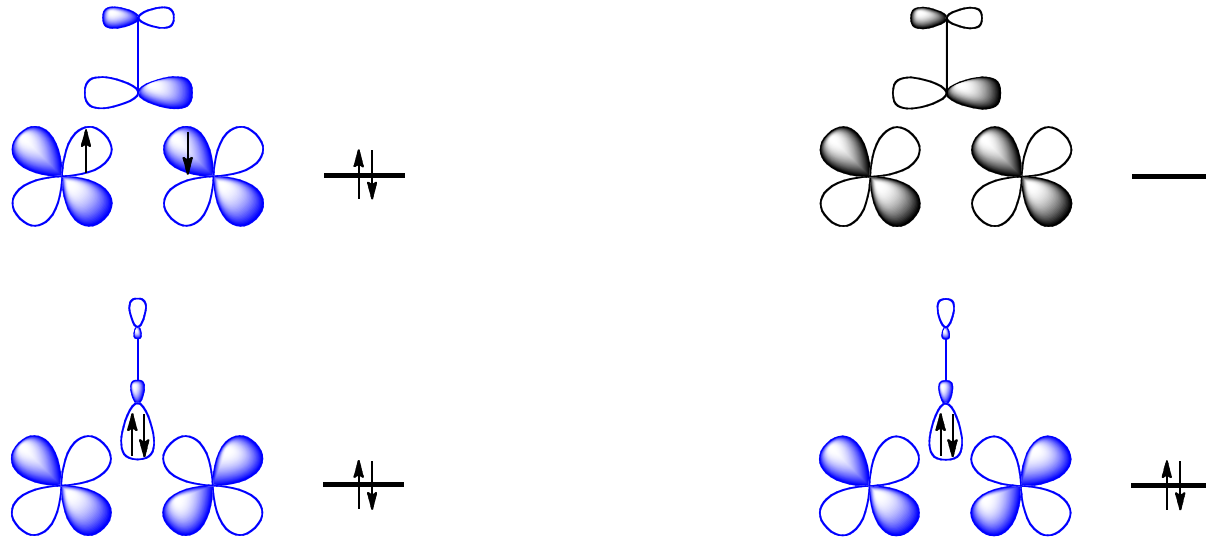
- An indisputable feature of many calculations is that the bonding of a symmetrically bridging carbonyl ligand can be expressed in terms of two 3-center molecular orbitals.



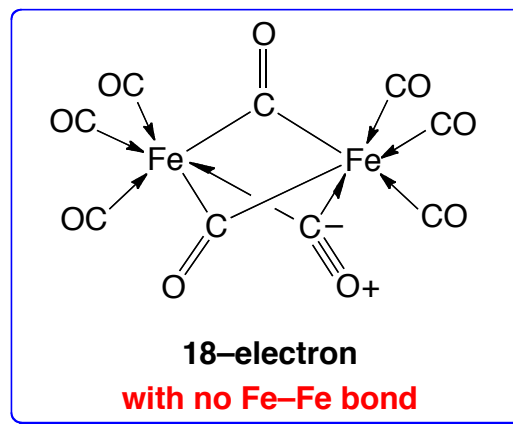
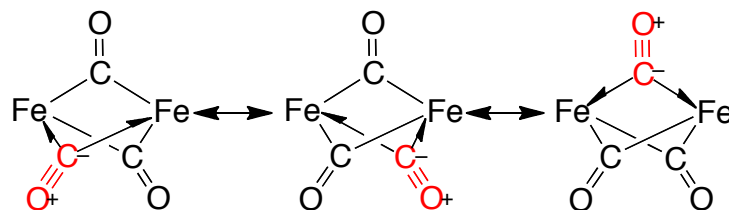
- Representing a bridging carbonyl as a "ketone" derivative, i.e. two 2c-2e bonds, requires both of these molecular orbitals to be occupied.

Bonding in Bridging Carbonyls

- If there is no backbonding, the bonding must be represented as a 3c-2e interaction.



- The three bridging CO ligands participate in **three donor interactions**, but only **two backbonding** interactions.
- Therefore, **one** of the CO ligands can only be represented as a 3c-2e bond.



Cite this: *Chem. Commun.*, 2012, **48**, 11481–11503

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FEATURE ARTICLE

The occurrence and representation of three-centre two-electron bonds in covalent inorganic compounds

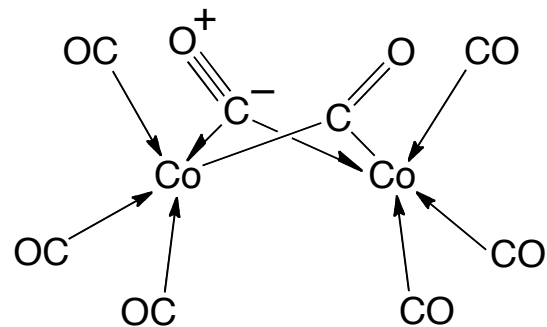
Jennifer C. Green,^a Malcolm L. H. Green^{*a} and Gerard Parkin^{*b}

Received 23rd July 2012, Accepted 12th September 2012

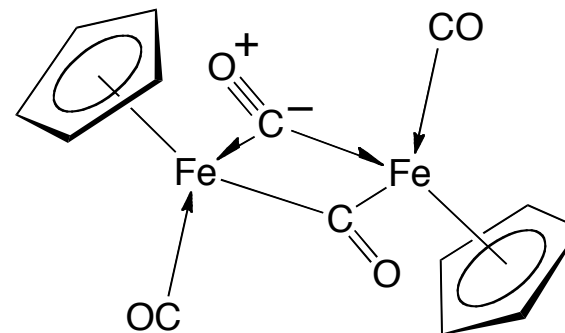
DOI: 10.1039/c2cc35304k

Bonding in Bridging Carbonyls

- 3c-2e "non-ketonic" bonding also rationalizes the absence of M–M bonds in other carbonyl compounds.



18–electron



18–electron

M. Benard, *J. Am. Chem. Soc.*, 1978, **100**, 7740

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E.D. Jdemmis, A.R. Pinhas and R. Hoffmann, *J. Am. Chem. Soc.*, 1980, **102**, 2576,

A.A. Low, K.L. Kunze, P.J. MacDougall and M.B. Hall, *Inorg. Chem.* **1991**, **30**, 1079–1086.

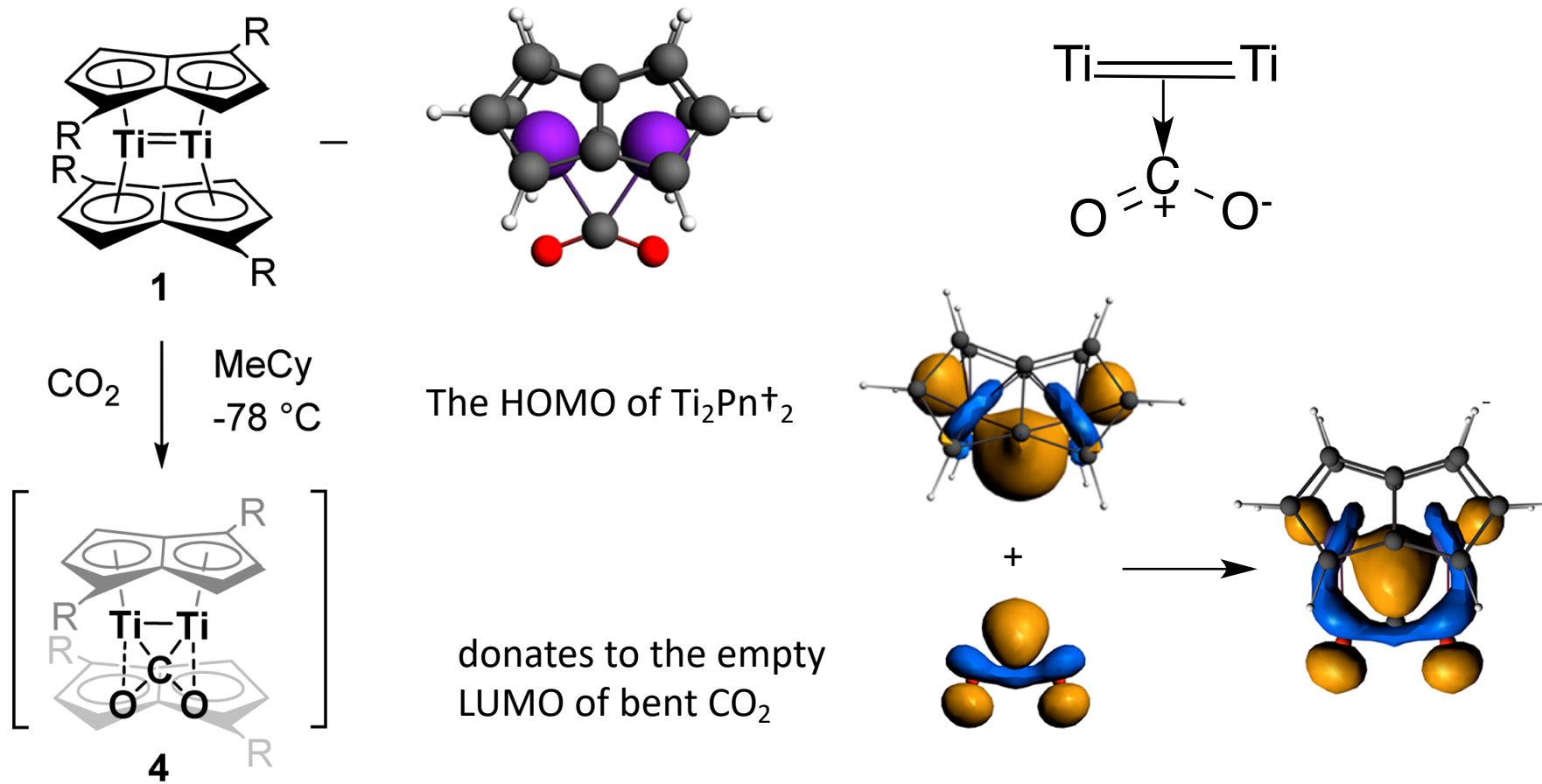
R. Ponec, G. Lendvay and J. Chaves, *J. Computational Chem.*, 2008, **29**, 1387 – 1398.

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Example of CO₂ acting as a μ Z ligand

Bis(pentalene)ditanium double-sandwich compound Ti₂Pn[†]₂ (Pn[†] = 1,4-{SiⁱPr₃}₂C₈H₄) reacts with CO₂ forming a complex with the CO₂ bridging the two Ti atoms



A. F. R. Kilpatrick, J. C. Green, and F. G. N. Cloke, *Organometallics*, 2015, 150705080046009.

A. F. R. Kilpatrick, J. C. Green, and F. G. N. Cloke, *Organometallics*, 2015, 150704080128001.

Summary

1. There are four different types of 3c-2e bonds: μ^0 -Z, μ^c -Z, μ -X and μ -L.
2. Structure-bonding (S-B) representations of a molecule that utilize the half-arrow or dot-line representation of the molecules which contain 3c-2e bonds indicate electron counts and bond orders that are much more in accord with theory than those predicted by other representations that focus on oxidation states and other methods of counting electrons.
3. SB representations that use the half-arrow and dot-line formalisms provide a simple and direct method for counting electrons and also determining the MLX class of any atom in a molecule.
4. Useful information pertaining to the CBC method may be found at:

“Application of the Covalent Bond Classification Method for the Teaching of Inorganic Chemistry.” Malcolm L. H. Green and Gerard Parkin *J. Chem. Educ.* **2014**, *91*, 807.

<http://www.covalentbondclass.org>