Chemical Applications of Charge Density

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Chemical applications of charge density

1. VSEPR rules and the Laplacian
2. Hydrogen bonding
3. Metal-metal bonding
VSEPR (Valence Shell Electron Repulsion) rules are used to teach the elements of structure for main group compounds.

Simple theory based on a few elementary concepts:
1. Electrons in the valence shell around central atom are paired (Lewis structures)
2. Electrostatic repulsion between pairs leads to structures with the maximal distance between them
3. Repulsions for single bonds follow order: lone-pair lone pair > lone-pair bond pair > bond pair bond pair
4. Multiple bonds have stronger repulsion than single bonds
5. Bond pair repulsion decreases with increasing electronegativity of ligand
6. Explains why $\text{H}_2\text{O}$ is bent, $\text{NH}_3$ is pyramidal but $\text{BF}_3$ is planar, $\text{ClF}_3$ is T-shaped ...

### VSEPR rules and the Laplacian

<table>
<thead>
<tr>
<th>Steric No.</th>
<th>Basic Geometry 0 lone pair</th>
<th>1 lone pair</th>
<th>2 lone pairs</th>
<th>3 lone pairs</th>
<th>4 lone pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$180^\circ$ Linear</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$120^\circ$ Trigonal Planar</td>
<td>$&lt; 120^\circ$ Bent or Angular</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>4</td>
<td>$109^\circ$ Tetrahedral</td>
<td>$&lt; 109^\circ$ Trigonal Pyramid</td>
<td>$&lt; 109^\circ$ Bent or Angular</td>
<td></td>
<td></td>
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<tr>
<td>5</td>
<td>$90^\circ$ Trigonal Bipyramid</td>
<td>$&lt; 90^\circ$ Sawhorse or Seesaw</td>
<td>$&lt; 90^\circ$ T-shape</td>
<td>$180^\circ$ Linear</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$90^\circ$ Octahedral</td>
<td>$&lt; 90^\circ$ Square Pyramid</td>
<td>$&lt; 90^\circ$ Square Planar</td>
<td>$&lt; 90^\circ$ T-shape</td>
<td>$180^\circ$ Linear</td>
</tr>
</tbody>
</table>

VSEPR rules and the Laplacian

Laplacian “emphasises” local charge concentration

Laplacian recovers the shell structure of the atom (here a free S atom \(-^3\text{P}\)). This is completely invisible in the density $\rho$. Shows alternate shells of charge \textit{concentrations} and charge \textit{depletions}. Here we are concerned with the Valence Shell Charge Concentration (VSCC). Units of Laplacian in experimental CD studies usually given as $e\,\text{Å}^{-5}$.

VSEPR rules and the Laplacian

Plots of $L \equiv -\nabla^2 \rho$ for the SCl$_2$ molecule
(a) in molecular plane
(b) close-up of VSCC of S atom
(c) plot in the plane perpendicular to (a)

Critical points are marked by dots

**VSEPR rules and the Laplacian**

Plots of $L \equiv -\nabla^2 \rho$ for the T-shaped molecule $\text{ClF}_3$

(a) in molecular plane
(b) plot in the plane perpendicular to (a)

5 charge concentrations - 3 bond pairs and 2 lone pairs

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The Lennard-Jones Function: A Quantitative Description of the Spatial Correlation of Electrons As Determined by the Exclusion Principle - provides a physical basis for electron pairing through the operation of the Pauli exclusion principle - the conditional probability function for same spin electron is called the LJ function in honour of Lennard-Jones.

Is BF$_3$ ionic?

Arguments:
1. Bader atomic charges indicate high ionic character.
2. F-F “non-bonded” distances are remarkably constant, in line with observed structure being dominated by ligand-ligand repulsions.

Counter arguments:
1. While the B-F bond is undoubtedly highly polar, an ionic model can only account for ~ 60% of bond energy.
2. The F atom is strongly polarised, indicating significant covalent character.
3. It is a gas.


Hydrogen bonds

Hydrogen bonds were first described (probably) by M. L. Huggins in 1919, but Linus Pauling (1931) was the first to coin the term hydrogen bond to describe the bonding in the [F-H...F⁻] anion.

<table>
<thead>
<tr>
<th>Strong</th>
<th>Moderate</th>
<th>Weak</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-H...A Bond lengths</td>
<td>mostly covalent</td>
<td>mostly electrostatic</td>
</tr>
<tr>
<td>H...A (Å)</td>
<td>D-H ≈ H...A</td>
<td>D-H &lt; H...A</td>
</tr>
<tr>
<td>D...A (Å)</td>
<td>1.2-1.5</td>
<td>1.5-2.2</td>
</tr>
<tr>
<td>Bond angles (°)</td>
<td>2.2-2.5</td>
<td>2.5-3.2</td>
</tr>
<tr>
<td>Bond energy (kcal mol⁻¹)</td>
<td>175-180</td>
<td>130-180</td>
</tr>
<tr>
<td></td>
<td>14-40</td>
<td>4-15</td>
</tr>
<tr>
<td>Examples</td>
<td>HF complexes</td>
<td>Acids</td>
</tr>
<tr>
<td></td>
<td>acid salts</td>
<td>Alcohols</td>
</tr>
<tr>
<td></td>
<td>proton sponges</td>
<td>Hydrates</td>
</tr>
<tr>
<td></td>
<td></td>
<td>All bio-molecules</td>
</tr>
</tbody>
</table>

Classification of H-bonds

## Hydrogen bonds

The five classes which all O–H⋯O bonds can be divided into:

<table>
<thead>
<tr>
<th>Class</th>
<th>Strength</th>
<th>Formula</th>
<th>Name</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Strong</td>
<td>[−O⋯H⋯O−]⁻</td>
<td>Negative Charge-Assisted H-Bonds</td>
<td>(−)CAHB</td>
</tr>
<tr>
<td>C</td>
<td>Strong</td>
<td>−O–H⋯O=⁻</td>
<td>Resonance-Assisted H-Bonds</td>
<td>RAHB</td>
</tr>
<tr>
<td>D</td>
<td>Moderate</td>
<td>R⋯O–H⋯O–H⋯R</td>
<td>Polarization-Assisted H-Bonds</td>
<td>PAHB</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Weak</td>
<td>−O–H⋯O&lt;⁻</td>
<td>Isolated H-Bonds</td>
<td>IHB</td>
</tr>
</tbody>
</table>

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*Strong H-bonds are often referred to as Low-Barrier H-Bonds (LBHB) [20].

*Sometimes called salt bridges [21].

*Where the two oxygens are connected by a π-conjugated system of variable length.

*Also called π-cooperative H-bond [21].

*Also called Induction-Assisted H-Bond (IAHB) [22], polarization-enhanced H-bond [21] or σ-cooperative H-bond [21].

*Non-charged, non-resonant, non-cooperative H-bonds.
Hydrogen bonds

It is generally agreed that weak H-bonds are primarily *electrostatic* in nature, while strong H-bonds have considerable covalent character.

How can we use charge density methods to shed light on this area?

- use topological properties to characterise bonds
- use charge densities to extract *interaction energies*

The values of $\rho(r)_{bcp}$ and $\nabla^2 \rho(r)_{bcp}$ provide *some* information, but recently other tools, such as the Source Function, have proved to provide interesting additional information.

Approximate potential and kinetic energy densities may be derived from $\rho(r)$ and $\nabla^2 \rho(r)$ using DFT type functionals - exact electrostatic energies may be computed.

Topological Definition of Hydrogen Bonding

Koch & Popelier have examined the characterisation of C-H...O bonds on the basis of charge density. The derived criteria have been used to induce the presence or absence of weak to moderate H-bonds in general.

1. A bond path and bcp between H and acceptor atom.
2. The value of $\rho(r)_{\text{bcp}}$ in the range $0.05 \rightarrow 0.2$ eÅ$^{-3}$
3. The value of the Laplacian is positive and “reasonable” $0.5 \rightarrow 3.3$ eÅ$^{-5}$
4. Mutual penetration of hydrogen and acceptor, $\Delta r = r^0 - r_{\text{bcp}}$ is positive for both. $r^0$ is "non-bonded" radius, experimentally taken as van der Waals radius. This is a necessary and sufficient condition.
7. Decrease of dipolar polarisation of H atom.
8. Decrease in atomic basis volume.

Criteria 5-8 difficult to apply in experimental studies, but first four criteria often used.

Topology of Hydrogen bonds

Espinosa et al have examined the topological properties of a large number of H-bonded compounds.

Two clear cut cases emerged in terms of $\rho(r)_{bcp}$ and $\nabla^2 \rho(r)_{bcp}$ for the D-H and the H...A interactions

- strong H-bonds - $\rho(r)_{bcp} \sim 1-1.3$ eÅ$^{-3}$  $\nabla^2 \rho(r)_{bcp}$ is negative $\sim -5-15$ eÅ$^{-5}$
- weak H-bonds - $\rho(r)_{bcp} \sim 0.5, 0.02$ eÅ$^{-3}$  $\nabla^2 \rho(r)_{bcp}$ is positive $\sim 0.5 - 5$ eÅ$^{-5}$

Clear correlations between these topological and geometrical parameters were found, the clearest being with $\lambda_3$ (curvature along bond path)

The Source Function

\[ \rho(\mathbf{r}) = -\left(\frac{1}{4\pi}\right) \int \frac{\nabla^2 \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' = \sum_\Omega \int_\Omega \text{LS}(\mathbf{r}, \mathbf{r}') \, d\mathbf{r}' \equiv \sum_\Omega S(\mathbf{r}, \Omega) \]

\[ \text{LS}(\mathbf{r}, \mathbf{r}') = \left(-\frac{1}{4\pi}\right)(|\mathbf{r} - \mathbf{r}'|)^{-1} \nabla^2 \rho(\mathbf{r}') \]

Local source

Green’s Function or influence function. It represents the effectiveness of how the cause \( \nabla^2 \rho(\mathbf{r}') \) gives rise to the effect \( \rho(\mathbf{r}) \)

\[ S(\mathbf{r}, \Omega) \quad \text{Source function from atom } \Omega \text{ to } \rho(\mathbf{r}) \]

Potentially available from experimental density
Does not require the presence of a bond critical point

Topology of Hydrogen bonds

Gatti has examined the nature of H-bonds, within the scheme of Gilli & Gilli using the Source Function. Posed the question - how do the balance of contributions to H-bonding (covalent vs electrostatic) change with the nature of the H-bond?

Calculations on water dimer at varying D-H...A distances
- atomic percentage contributions change dramatically along reaction profile
- at long D-H...A distances, source for H is very negative \( (i.e \) a sink)
- at long D-H...A distances all atoms make significant contributions - indicative of the importance of the delocalised electrostatic component
- at short D-H...A distances, the 3-centre nature of the H-bond is emphasised

Topology of Hydrogen Bonds

Gatti has examined the nature of H-bonds, within the scheme of Gilli & Gilli using the Source Function. Posed the question - how do the balance of contributions to H-bonding (covalent vs electrostatic) change with the nature of the H-bond?

1. H$_5$O$_2^+$ +CAHB
2. formic acid-formate complex -CAHB
3/4. malonaldehyde (C$_s$ equi and C$_{2v}$ t.s.) RAHB
5. water trimer PAHB
6. water dimer IHB

Clear that these different H-bonds have very different source contributions

Energetics of Hydrogen bonds

Espinosa *et al* have also shown strong correlations between approximate $G(r_{bcp})$ and $V(r_{bcp})$ (derived from Abramov functionals) and $D(H...O)$. HOWEVER, Spackman has shown that the promolecule density gives very similar results!


Energetics of Hydrogen bonds

The question then arises - “are the experimental data providing anything more than noise about a trendline determined by the promolecule electron distribution”?

Conclusion: “experimental electron densities in weak interactions are indeed systematically different from those of a promolecule”

Atomic Energies in QTAIM

There are two forms of the kinetic energy expression:

- Gradient kinetic energy:
  \[ G(r) = \frac{\hbar^2}{2m} N \int d^3 \tau \nabla \Psi^* \cdot \nabla \Psi \]

- Schrödinger kinetic energy:
  \[ K(r) = \frac{\hbar^2}{4m} N \int d^3 \tau \left[ \Psi \nabla^2 \Psi^* + \Psi^* \nabla^2 \Psi \right] \]

\[ K(r) = G(r) - \frac{\hbar}{4m} \nabla^2 \rho(r) \]

These two forms are identical if the Laplacian vanishes, as it does when integrating over an atomic basin. Then \( E(\Omega) = -G(\Omega) = 1/2 \ V(\Omega) \)

Exact expressions for \( G(r) \) are NOT available directly from experimental data

\[ G(r) = (3/10)(3\pi^2)^{2/3} \rho(r)^{5/3} + (1/6) \nabla^2 \rho(r) \]

Abramov approximation for \( G(r) \) at bcp (ONLY valid for regions where \( \nabla^2 \rho < 0 \), i.e. closed-shell interactions).

\[ V(r) = (1/4) \ \nabla^2 \rho(r) - 2G(r) \] - Virial relationship

Mallinson et al have reported several experimental charge density studies on proton sponges which exhibit a range of H-bonded interactions - from very strong N-H..N to very weak Cπ..Cπ interactions. They studies reveal a continuous transition from weak H-bonding to covalent bonding.

\[ \text{Figure 11. Morse type dependence of } \nabla^2 \rho_b [\text{eÅ}^{-2}] \text{ on interpenetration parameters } (\Delta r_D + \Delta r_A) [\text{Å}]. \]

\[ \nabla^2 \rho_b = 3.5(6) \times 3.4(1.5)(1 - \exp[2.5(4) - (1.164) - (\Delta r_D + \Delta r_A)])^2. \]

\text{R} = 0.87 \text{ for } N = 63 \text{ data points.}

P. R. Mallinson et al (1003) J. Am. Chem. Soc. 125, 4259
de Vries et al. have studied the intermolecular interaction energies in urea crystals, using the multipole model refined against theoretical data. They conclude that “it is not possible to extract the effect of intermolecular interactions from diffraction data with the current multipolar refinement techniques”

A Note of Caution

“... for H...O interactions, critical point densities \( \rho_{bcp} \) and their distance dependence are closely similar to those calculated for the overlap of the unperturbed atomic charge densities (the promolecule electron density) so that great care in the interpretation of experimental and theoretical intermolecular charge densities is called for.”


Review chapters on AIM concepts and H-bonding in books:
Topological studies on metal-metal bonds

Metal-metal bonding is an important aspect of organometallic chemistry.

Undergraduate treatment - **18 electron rule.** Very useful in explaining short(ish) metal-metal distances, but ignores the effects of bridging ligands.

Numerous theoretical studies based on orbital interpretations conclude there is only (at best) a weak direct M-M interaction in bridged bonds.

Fe$_2$(CO)$_9$  Fe-Fe = 2.523 Å

Short M-M distance √
Diamagnetic √
Required by 18-e rule √

But what does CD say?

Metal-metal bonding without bridging ligands

$\text{Mn}_2(\text{CO})_{10}$

100 K, Nonius KappaCCD
$I2/a$

Spherical atom refinement
$R(F) = 0.021$  \( wR(F^2) = 0.061 \)

GOF 1.11 $\Delta \rho$ 0.62 → -0.81

7052 data  101 parameters

XD refinement
$R(F) = 0.014$  \( wR(F^2) = 0.016 \)

GOF 2.16 $\Delta \rho$ 0.27 → -0.20

6532 data  296 parameters

Mn-Mn bond
Mn1-Mn1a  2.9031(2) Å  
2.9042(8)

$\rho(r_{bcp})$ 0.144(3)e Å$^{-3}$
0.190(4)  0.192

$\nabla^2 \rho(r_{bcp})$ 0.720(3) e Å$^{-5}$
0.815(8)  0.124

Metal-metal bonding without bridging ligands

\[ \text{Mn}_2(\text{CO})_{10} \]

\[ \text{100 K, Nonius KappaCCD} \]

\[ \text{I2/a} \]

Spherical atom refinement

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Mn1-Mn1a 2.9031(2) Å

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\( \rho(r_{bcp}) \)

0.144(3)e Å\(^{-3}\)

0.190(4) 0.192

\( \nabla^2 \rho(r_{bcp}) \)

0.720(3) e Å\(^{-5}\)

0.815(8) 0.124

\( \delta(Mn-Mn) \)

0.29


Source function for $\text{Mn}_2(\text{CO})_{10}$

Contributions to the source function at the Mn-Mn bcp from (a) Mn atoms (b) CO$_{eq}$ and (c) CO$_{ax}$. Blue curve = real system, red curve to two non-interacting Mn(CO)$_5$ groups.

Metal-metal bonding with carbonyl bridges

Evolution of metal-metal bonding in \([\text{FeCo(CO)}_8]\) anion

Conclusion - metal-metal bonding disappears early on in the profile, with initial formation of ring structure


Source function for Co$_2$(CO)$_8$

Source function shows that the basic picture is similar for the two isomers, the all-terminal $D_{3d}$ which has a bcp, and the $C_{2v}$ isomer which does not.

In the unbridged case, the Co atoms act as a sink at the bcp.

In the bridged case, they act (very marginally) as a source.

Due to differing behaviour of the Laplacian near the reference point (an order of magnitude more positive in the $C_{2v}$ isomer).

$\text{LS}(r, r') = -\left(\frac{1}{4\pi}\right) \cdot \frac{\nabla^2 \rho(r')}{|r - r'|}$

Reinhold *et al* interpret the minimum in the total energy density $H$ as indicative of a “bent” Co-Co bond.

The presence of such an interaction is also indicated from an orbital study.


Metal-metal bonding with hydride bridges

Experimental study on [Cr₂(μ-H)(CO)₁₀]⁻

“we note that the M-H-M systems have undisputedly many subtler features associated with even smaller energy gradients that therefore hamper an easier rationalization of the bonding effects”

Metal-metal bonding with alkyldyne bridges

Co$_3$(µ$_3$-CX)(CO)$_9$ (X=H,Cl)

Metal-metal bonding with alkyldyne bridges

Metal-metal bonding with alkylidyne bridges

Atomic graph of alkylidyne carbon. Critical points in Laplacian $L \equiv -\nabla^2 \rho$

- $(3,-3)$ charge concentrations
- $(3,-1)$ saddle points
- $(3,+1)$ charge depletions

Isosurface of the Laplacian $L \equiv -\nabla^2 \rho$ at $+10$ eÅ$^{-5}$

$\text{Co}_3(\mu_3\text{-CX})(\text{CO})_9 \ (a=\text{H}, \ b=\text{Cl})$
Structural variability in $M_3(\mu-H)(\mu-CX)(CO)_{10}$


Charge density in Fe\textsubscript{3}(\mu-H)(\mu-COMe)(CO)\textsubscript{10}

Experimental data
100 K, Nonius KappaCCD
$P2_1/c$
Spherical atom refinement
$R(F) = 0.026 \quad wR(F^2) = 0.059$
GOF 1.04 $\Delta \rho 0.72 \rightarrow -0.90$
17177 data 243 parameters

XD refinement
$R(F) = 0.018 \quad wR(F^2) = 0.016$
GOF 1.53 $\Delta \rho 0.30 \rightarrow -0.30$
13970 data 701 parameters

Å
Fe1-Fe2 2.64603(16)
Fe1-Fe3 2.67669(17)
Fe2-Fe3 2.60037(15)
Fe1...C1 2.6762(4)
Fe2/Fe3-C1 1.86
$\Phi = 90.1(1)^\circ$
Charge density in Fe$_3$(μ-H)(μ-COMe)(CO)$_{10}$

Main features:
1. Ring cp for Fe(μ-H)(μ-CR)Fe
2. Bond cp’s for other two Fe-Fe interactions
3. Ring cp between Fe...C(alk)

ρ(r) (eÅ$^{-3}$) $\nabla^2\rho$ (eÅ$^{-5}$) $\varepsilon$
Fe-Fe (bcp) 0.24 0.30 0.40
Fe-Fe (rcp) 0.35 2.09 -
Fe...C (rcp) 0.22 1.31 -

Geometry Å
Fe1-Fe2 2.739
Fe1-Fe3 2.744
Fe2-Fe3 2.646
Fe1...C1 2.685
Fe2/Fe3-C1 1.86
Φ = 87.5°

Optimised B3LYP 6-311G (C/H/O) Wachters+f Fe
Charge density in $\text{Fe}_3(\mu\text{-H})(\mu\text{-COMe})(\text{CO})_{10}$

Main features:
1. Ring cp for Fe$(\mu\text{-H})(\mu\text{-CR})$Fe
2. Bond cp's for other two Fe-Fe interactions
3. Bond cp between Fe-C(alk)

<table>
<thead>
<tr>
<th>Bond Cp</th>
<th>$\rho(r)$ (eÅ$^{-3}$)</th>
<th>$\nabla^2 \rho$ (eÅ$^{-5}$)</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Fe (bcp)</td>
<td>0.23</td>
<td>0.46</td>
<td>0.85</td>
</tr>
<tr>
<td>Fe-Fe (rcp)</td>
<td>0.34</td>
<td>2.28</td>
<td>-</td>
</tr>
<tr>
<td>Fe-C (bcp)</td>
<td>0.23</td>
<td>1.48</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Geometry Å

- Fe1-Fe2: 2.741
- Fe1-Fe3: 2.752
- Fe2-Fe3: 2.650
- Fe1...C1: 2.653
- Fe2/Fe3-C1: 1.86

$\Phi = 85.9^\circ$

optimised B3LYP Ahlrichs TZV

Jyväskylä Summer School on Charge Density August 2007
Charge density in $\text{Fe}_3(\mu\text{-H})(\mu\text{-COMe})(\text{CO})_{10}$

**Main features:**
1. Ring cp for Fe$(\mu\text{-H})(\mu\text{-CR})\text{Fe}$
2. NO bond cp’s for other two Fe-Fe interactions
3. Bond cp between Fe...C

**Experimental multipole density**

<table>
<thead>
<tr>
<th></th>
<th>(\rho(r) \text{ (eÅ}^3)</th>
<th>(\nabla^2 \rho \text{ (eÅ}^5)</th>
<th>(\varepsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Fe (rcp)</td>
<td>0.24</td>
<td>1.44</td>
<td>-</td>
</tr>
<tr>
<td>Fe..C (bcp)</td>
<td>0.24</td>
<td>1.40</td>
<td>2.37</td>
</tr>
</tbody>
</table>
Multipole refinements with synthetic data

- **Gas phase wavefunction** B3LYP/6-331G
  - s.f. from 30 Å pseudo cubic unit cell
  - Refine elaborate XD multipole model

- **CRYSTAL03 periodic DFT wavefunction**
  - Project DFT density into s.f.
  - Refine XD multipole model

Fe...C(alkylidyne) bcp

Highly curved Fe-Fe bcp
Charge density in Fe$_3$(µ-H)(µ-COMe)(CO)$_{10}$

Isosurfaces of density $\rho$ in Fe$_3$(µ-H)(µ-COMe)(CO)$_{10}$ viewed normal to the Fe$_3$ plane
Fe₃(µ-H)(µ-COMe)(CO)₁₀

Delocalisation indices

<table>
<thead>
<tr>
<th>Dist</th>
<th>δ(A-B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1-Fe2</td>
<td>0.40</td>
</tr>
<tr>
<td>Fe1-Fe3</td>
<td>0.38</td>
</tr>
<tr>
<td>Fe2-Fe3</td>
<td>0.21</td>
</tr>
<tr>
<td>Fe1-C15</td>
<td>0.19</td>
</tr>
<tr>
<td>Fe2-C15</td>
<td>0.91</td>
</tr>
<tr>
<td>Fe3-C15</td>
<td>0.93</td>
</tr>
<tr>
<td>Fe2-H27</td>
<td>0.45</td>
</tr>
<tr>
<td>Fe3-H27</td>
<td>0.44</td>
</tr>
<tr>
<td>Fe-C(O)</td>
<td>~1.0</td>
</tr>
<tr>
<td>Fe2-C18</td>
<td>0.13</td>
</tr>
<tr>
<td>Fe-O</td>
<td>~0.17</td>
</tr>
</tbody>
</table>

Optimised structure B3LYP - 6-311G* (C/H/O) Wachters+f Fe
Source Function in $\text{Fe}_3(\mu$-$\text{H})(\mu$-$\text{COMe})(\text{CO})_{10}$

Source % contributions at Fe-Fe bcp (theoretical) and Fe-Fe midpoint (expt)
Source Function in Fe$_3$(μ-H)(μ-COME)(CO)$_{10}$

Source % contributions at Fe...C$_{\text{alkylidyne}}$ rcp (theoretical) and bcp (expt)
Structural variability in $M_3(\mu-H)(\mu-CX)(CO)_{10}$

A - $X=\text{COMe}, M=\text{Ru}$
$\Phi = 94.9^\circ$
$\text{Ru}...\text{C} = 2.921\text{Å}$

B - $X=\text{Ph}, M=\text{Os}$
$\Phi = 78.2^\circ$
$\text{Os}...\text{C} = 2.585\text{Å}$

C - $X=\text{H}, M=\text{Os}$
$\Phi = 69.7^\circ$
$\text{Os}...\text{C} = 2.353\text{Å}$

D - $X=\text{Ph}, M=\text{Os}$
$\Phi = 66.6^\circ$
$\text{Os}...\text{C} = 2.286\text{Å}$


\[ \text{Fe}_3(\mu-\text{H})(\mu-\text{CH})(\text{CO})_{10} \]

**Geometry**

<table>
<thead>
<tr>
<th>Dist</th>
<th>Å</th>
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<tbody>
<tr>
<td>Fe1-Fe2</td>
<td>2.674</td>
</tr>
<tr>
<td>Fe1-Fe3</td>
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</tr>
<tr>
<td>Fe2-Fe3</td>
<td>2.669</td>
</tr>
<tr>
<td>Fe1-C1</td>
<td>2.146</td>
</tr>
<tr>
<td>Fe2-C1</td>
<td>1.877</td>
</tr>
<tr>
<td>Fe3-C1</td>
<td>1.877</td>
</tr>
<tr>
<td>Fe2-H2</td>
<td>1.686</td>
</tr>
<tr>
<td>Fe3-H2</td>
<td>1.686</td>
</tr>
<tr>
<td>C1-H1</td>
<td>1.090</td>
</tr>
<tr>
<td>Fe1-C2-O2</td>
<td>166.5°</td>
</tr>
<tr>
<td>Fe1-Fe2-Fe3-C1</td>
<td>65.8°</td>
</tr>
</tbody>
</table>

Optimised structure B3LYP - 6-311G* (C/H/O) Wachters+f Fe

\( \text{Fe}_3(\mu-\text{H})(\mu-\text{CH})(\text{CO})_{10} \)

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Optimised structure B3LYP - 6-311G* (C/H/O) Wachters+f Fe

Molecular graph and critical points (bps’s in red, ring cp in yellow)