Quantum Chemical Explorations of Stereochemistry in Organometallic Reactions

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What is Computational Chemistry?

- A branch of chemistry that can explore many varieties of systems by modeling them in computer programs that:
  - invoke the principles of quantum theory (to optimize geometries and calculate heats of formation, here);
  - or, apply empirical data to large systems (as in the constraint of all $C_{sp3}-H_{1s}$ bond lengths in a protein).

- Primary research consideration: Better accuracy depends on more time and computing power.
Methods:
Gaussian and Spartan programs

► From quantum chemistry to quantities: Taking theory and developing programs to probe molecules
  ▪ Basis set: very roughly, the set of AOs to be combined and depicted as MOs, including core orbitals as well as valence orbitals
    ► I input Cartesian coordinates (x,y,z) and atomic numbers (Z), and I specify a basis set (e.g.: 3-21G) using computer-understood notation
  ▪ Method: the way quantum theory is represented mathematically within the calculation to include or omit different concepts and levels of accuracy
    ► Semi-empirical (PM3): based partially on experimental data like heats of formation, ionization energies and atomization energies
    ► Ab initio (e.g.: Hartree Fock (HF), B3LYP, MP2, MPY, QCI and CCSD): entirely theoretical
      ▪ HF: Each electron interacts with all others at once, not with every other one individually.
        ► Does not treat electron correlation, overestimating the electron’s energy
Classical and Quantum Mechanics Basics
For Geometry Optimizations

Probing the molecule’s vibrational frequencies:

**Hooke’s Law:** \( F = -kx \)

Integration of Hooke’s Law:
Simple Harmonic Oscillator

\[
E = 2kx^2
\]

**For \( \text{H}_2 \):**

1) \( F = \frac{1}{4\pi\epsilon_0}(q_1q_2/r^2) \)

2) \( E = (n + \frac{1}{2})\hbar\nu \)

\( x \) represents any one variable among many (For all molecules there exist \( 3n \) degrees of freedom: 3 translational, 3 rotational and \( 3n-6 \) vibrational for nonlinear molecules)
The Imaginary Frequency

- Given: \( V = \frac{1}{2\pi} \sqrt{k/\mu} \)

- When Gaussian reports an imaginary (negative frequency):
  - \( k < 0 \) →
  - \( \frac{d^2}{dx^2}[E(x)] < 0 \) →
  - concave downward Energy function →
  - unstable equilibrium
  - each extreme indicates an energy well
    with respect to the given variable
Advanced Inorganic lab meets Computational Chemistry


- This summer: Computation-based treatment of the system from start to finish, that is, from Mo(CO)₆ to the final product.
**Current Study: Mo(CO)$_6$ to Mo(CO)$_3$(C$_6$H$_5$N)$_3$**

- **Objective:**
  - Optimize geometries of starting material, product and all intermediates;
  - Elucidate reaction mechanism and TS$^\dagger$ structures;
  - Determine enthalpies of formation and overall enthalpy of reaction.

- **Input information:**
  - Methods: HF, B3LYP (both ab initio)
  - Basis functions: 3-21G, 6-31G(d) and Lanl2dz
  - 3 in 3-21G communicates that each core AO be represented by 3 Gaussian functions
    - $g(\alpha,\mathbf{r})=c x^n y^m z^l e^{-\alpha \mathbf{r}^2}$
  - 21 in 3-21G communicates
    - With its two digits that each valence AO will be represented by two basis functions,
    - One of which will be the sum of two Gaussian functions, the other of which is a Gaussian itself
  - Charge=0; Multiplicity=1

* Associations exist between pyridines and Mo.
B3LYP and HF Results: Optimized Geometries and Heats of Reaction

\[ \Delta_{\text{Rxn}} H^\circ (g) = +34.4 \text{ kcal/mol (HF)} \]
\[ +36.0 \text{ kcal/mol (B3LYP)} \]

\[ \Delta_{\text{Rxn}} H^\circ (g) = -29.4 \text{ kcal/mol (HF)} \]
\[ -25.7 \text{ kcal/mol (B3LYP)} \]

\[ \Delta_{\text{Rxn}} H^\circ (g) = +5.0 \text{ kcal/mol (HF)} \]
\[ +10.3 \text{ kcal/mol (B3LYP)} \]

B3LYP: Shorter bond lengths, greater endothermicity and lesser exothermicity
$\Delta_{\text{Rxn}}H^\circ_{(g)}$ for Mo(CO)$_6 \rightarrow \text{fac-Mo(CO)$_3$(pyr)$_3$}$:

$\Delta_{\text{Rxn}}H^\circ_{(g)}$ =
+5.5 kcal/mol (HF)
+12.2 kcal/mol (B3LYP)

Mo(CO)$_6 \rightarrow \text{fac-Mo(CO)$_3$(pyr)$_3$}$

$\Delta_{\text{Rxn}}H^\circ_{(g)}$ =
+19.7 kcal/mol (HF)
+(22.5 + ?) (B3LYP)
+4.7 kcal/mol (from NIST $\Delta_f H^\circ_{(g)}$ values)

*Current B3LYP calculation is approaching this conformer

Experimentally determined structure (X-ray crystallography)
Determining the Reaction Pathway

► Finding the lowest-energy transition states or intermediates
► Using enthalpies of reaction to argue the reaction mechanism:
  - Dissociation (S$_N$1-like) or Dissociative Interchange (S$_N$2-like)?

Does a transition state exist along the dissociative path for the removal of a carbonyl ligand? Or, is the energy required for dissociation simply
\[ \Delta H^\circ \text{(Products)} - \Delta H^\circ \text{(Reactants)} \] (ignoring entropy)?

No/Yes.

Do transition states exist for seven-ligand complexes between the 18-electron species?

Yes.

What, then, is the reaction pathway?

Compare energies (HF):

\[
\text{Mo(CO)}_6 \rightarrow \text{Mo(CO)}_5 + \text{CO} \\
\Delta_{\text{Rxn}} H^\circ = +34.4 \text{ kcal/mol}
\]

\[
\text{Mo(CO)}_6 + \text{pyr} \rightarrow [\text{Mo(CO)}_5 \text{(CO)(pyr)}]^+ \\
\Delta_{\text{Rxn}} H^\circ = E_a = +18.8 \text{ kcal/mol}
\]

The energy differences (D versus DI) for the three sets of reactions:

15.6, 13.1 and 10.4 kcal/mol

Therefore, the reaction proceeds via **Dissociative Interchange**
In the Future…

- Fully characterize each step of the synthesis:
  - Optimize geometries,
  - Calculate enthalpies of reaction, and
  - Determine TS\textsuperscript{‡} structures and reaction pathways

- Reveal nature of the *syn-anti* isomerization in final product;
  The predicted scheme follows:
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