November 4, 2004 - Lecture 17: Organometallic Chemistry II.

Olefin complexes:
- first olefin complex (1827) - Zeise's salt K[PtCl₃(C₂H₄)], (first OM compound 1760 - ((H₃C)₂As)₂O)
- VB: π-complex Mⁿ⁺·H₂C=CH₂, but better if metallacyclopropane Mⁿ⁺²⁺·H₂C⁻¹⁺⁻CH₂ loss of planarity
- MO: σ-donor (from a π-orbital) for monoolefin and π-donor for oligoolefin complexes + π-acceptor (π acid behavior) - Dewar-Chatt-Duncanson donation/backdonation
- formation of olefin complexes influenced by σ-acceptor (high EA) and π-donor (low PE) nature of the metal

<table>
<thead>
<tr>
<th>Atom/Ion</th>
<th>Ni(0)</th>
<th>Pd(0)</th>
<th>Pt(0)</th>
<th>Rh(I)</th>
<th>Ir(I)</th>
<th>Pd(II)</th>
<th>Pt(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nd¹⁰ → nd¹⁰ (n+1)s¹</td>
<td>1.20</td>
<td>1.30</td>
<td>2.40</td>
<td>7.31</td>
<td>7.95</td>
<td>18.56</td>
<td>19.42</td>
</tr>
<tr>
<td>nd¹⁰ → nd⁹ (n+1)p¹</td>
<td>1.72</td>
<td>4.23</td>
<td>3.28</td>
<td>1.60</td>
<td>2.40</td>
<td>3.05</td>
<td>3.39</td>
</tr>
</tbody>
</table>

- electron donation (charge 0)/count vs. coordination (use 18e rule to construct complexes)
  - 2 e⁻  η²-ethylene  (PtCl₃(C₂H₄))¹⁻
  - 4 e⁻  η³-allyl (1-): ((C₃H₅)PdCl)₂
  - η⁴-butadiene  (C₄H₆)Fe(CO)₃
  - η⁴-cyclopentadiene  (C₅H₆)₂Mo(CO)₂
  - 6 e⁻  η⁵-cyclopentadienylidene (1-): Cp₂Fe(D₅d); Cp₂Ru(D₅h)
  - η⁶-benzene  (C₆H₆)₂Cr
  - 6,4 e⁻  cyclooctatetraene  (η⁶ cot)Cr(CO)₃
  - (η⁴ cot)CoCp
  - (η⁴,η⁴ cot)Fe₂(CO)₆

Alkyl complexes
- VB: charge -1, 2e⁻-donor - considered as carbanions - in reactivity homolytical M-C cleavage
  (Co-corrin B12 - bioorganometallic chemistry)
- MO: σ-donor only
  - isolobal analogy between H₃C⁻ (7e⁻ in sp³ hybrid) and (OC)₃Mn⁻ (7e⁻ on metal d orbitals in dsp³ hybrid)
  - related aryl, acyl ligands: weak π-acid character (π* is higher than in CO) - increased M-C(COR) B.O.
  - agostic interaction between β-H and vacant metal d orbital
    - β-H elimination gives olefin + hydride complex
      - reverse process - polymerization of olefins - chain propagation via metallohydridocyclobutane (TS)
      - chain termination via β-H elimination
      - no hydride in catalysis ⇒ carbene/alkylidene complex (1,3 H-shift)
      - chain propagation via metallocyclobutane (Intermediate)
      - chain termination via 'back biting'

Alkylidene and carbene complexes
- VB structure M=C< but different how it binds to transition metals
  - carbene charge 0  2e⁻-donor  σ-donor, π-acceptor (using a singlet carbene description)
  - alkylidene charge -2  4e⁻-donor  σ,π-donor
- Fischer-type carbene complexes (OC)₃W=C(OMe)Ph  electrophilic C (δ⁺)
  - M: low oxidation state, late transition metal d⁶-d¹⁰ - π backdonation is dominant
    (carbene carbon accepts e⁻ from the metal to minimize the effect of charge separation)
- Schrock-type alkylidene complexes CpTaCl(CH₂CMeₑ)(=CHCMe₃)  nucleophilic C (δ⁻)
  - M: high oxidation state, early transition metal d⁰-d⁵ - π donation is dominant
    (carbene carbon has enough e⁻ to stabilize metals with stripped d-manifold)
• Selected carbene complexes with great importance in olefin metathesis reactions)
  Classical (ill-defined) carbenes: W/MoCl₄(=CHR)
  Osborn/Bassett carbenes: W/MoCl₄(OR)ₓ(=CHR)
  Schrock carbenes: Mo(=NAr)(OAr)₂(=CHR)
  Grubbs carbenes: RuCl₂(PR₃)₂(=CHR)
  Hermann-Grubbs carbenes: RuCl₂(PR₃)(N-diaryl-imidazole-ylidene)(=CHR)

• vinylidene complexes
  M=C=CR₁R₂ two perpendicular π systems, VSEPR consideration for equatorial ligands vs. π bonds vs. CR₁R₂ arrangement

Alkylidyne and carbyne complexes
• VB structure: M≡C- but different how it binds to transition metals
  carbyne charge +1 2e⁻-donor (σ-donor, two perpendicular π-acceptor)
  alkylidyne charge -3 6e⁻-donor (σ,π-donor)

• from Fischer carbene - electrophilic BX₃ removes OMe
  (OC)₅W=C(OMe)Ph → X(OC)₄W(≡CPh)

• from Schrock alkylidene - intramolecular αH abstraction
  CpTaCl(CH₂CMe₃)(=CHCMe₃) → CpTaCl(PMe₃)₂(≡CHCMe₃)

Alkyl/alkylidene/alkylidyne complex for comparing single, double and triple M-C bonds

W(≡C-t-Bu)(=CH-t-Bu)(CH₂-t-Bu)(dmpe)
W≡C 1.79Å; W=C 1.94Å; W-C 2.26Å  W≡C-C 175.4°; W=C< 150.5°; W-C− 124.6°

Dihydrogen complexes (with great relevance to bioinorganic chemistry: hydrogenases)
• MO: DCD donation/backdonation: σ-donor and π-acceptor (to σ* orbital)
• VB: alternative bonding picture - dihydride: Mⁿ⁺ w/ 2 H⁻
• equilibrium between η₂-H₂ and 2H⁻: dependent on the magnitude of backdonation (tuning phosphine)
  example W(CO)₃(P(iPr)₃)₂(H₂) - 85% H₂ vs. 15% 2H⁻
  (final paper: how the %-s were determined)