November 18, 2003 - Lecture 20: Organometallic Chemistry I.

The chemistry of transition metal-carbon bond - structure and bonding

**CO complexes:**
- L→M σ donation, M→L π backdonation (π acid behavior)
- 18e rule can be readily applied to rationalize stoichiometry and overall molecular structure
- CO is a strong field ligand ⇒ large 10Dq ⇒ low spin (most cases closed shell singlet) complexes
- the π acid behavior stabilizes the low oxidation states
- structure of neutral CO complexes:
  - Groups 4-6: M(CO)\(_6\) \(O_h\) unstable for Group 4 (not enough e\(-\) to donate)
  - Group 7: \((OC)_5\)M-M(CO)\(_5\) \(D_{4d}\) d electron in \(e_g\) forms metal-metal σ-bond
  - Group 8: \((OC)_3\)M(M(CO)\(_3\)) \(D_{3h}\) to obey the 18e rule
  - Group 9: \((OC)_3\)M(μ(CO))\(_2\)M(CO)\(_3\) \(C_{2v}\) M-M bond and bridging CO ligands
  - \(M_4(CO)_{12}\) \(C_{3v}\) axial M(CO)\(_3\), equatorial [M(CO)\(_2\)(μ(CO))]\(_3\)
  - \((OC)_4\)M…M(CO)\(_4\)…M(CO)\(_4\) \(D_{3h}\) M-M-M bonding between \(xy, x^2-y^2\) orbitals
  - Group 10: M(CO)\(_4\) \(T_d\) \(d^{10}\) electron configuration

(Spectroscopy of CO complexes can be derived from isoelectronic neutral complexes)

**Spectroscopy of CO complexes (IR - vibrational):**
- CO stretching frequency (ν\(_{\text{CO}}\)) is characteristic to complex geometry, metal and ligand environment
- it is well isolated from other stretching modes ⇒ can be used as a "fingerprint"
- ν\(_{\text{CO}}\) energy range for
  - uncoordinated CO 2143 cm\(^{-1}\)
  - terminal CO 2100-1850 cm\(^{-1}\)
  - \(μ_2\) bridging 1860-1700 cm\(^{-1}\)
  - \(μ_3\) bridging below 1750 cm\(^{-1}\)

- ν\(_{\text{CO}}\) is indicative of the strength of the M→L backdonation:
  - \([\text{Ti(CO)}\(_6\)]^{2-}\) 1748 cm\(^{-1}\) \([\text{Cr(CO)}\(_6\)]^-\) 1984 cm\(^{-1}\)
  - \([\text{V(CO)}\(_6\)]^-\) 1858 cm\(^{-1}\) \([\text{Mn(CO)}\(_6\)]^{1+}\) 2094 cm\(^{-1}\)
  - \([\text{AgCO}]^{1+}\) 2204 cm\(^{-1}\)

- ν\(_{\text{CO}}\) is sensitive to the change in the ligand environment:
  - \(\text{Ir(PPh}_3)_2(\text{CO})\text{ClI}_2\) 2067 cm\(^{-1}\) \(\text{Ir(PPh}_3)_2(\text{CO})\text{ClBr}_2\) 2072 cm\(^{-1}\) \(\text{Ir(PPh}_3)_2(\text{CO})\text{Cl}_3\) 2075 cm\(^{-1}\)

- the number of ν\(_{\text{CO}}\) bands is characteristic of the geometry:
  - M(CO)\(_6\) \(O_h\) normal modes \(T_{1u}\) expected 1 ν\(_{\text{CO}}\)
  - C-O stretching has the same symmetry as M-C σ-bonds ⇒ the corresponding irreps. are \(A_{1g}, E_g, T_{1u}\) ⇒ to get IR absorption the molecular dipole needs to change (or IR active modes transforms as Cartesian coordinates, Raman active modes are totally symmetry)

<table>
<thead>
<tr>
<th>(\text{M(CO)}(_3)L)</th>
<th>(C_{4v})</th>
<th>(A_{1}+E)</th>
<th>2 ν(_{\text{CO}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{M(CO)}(_4)L_2(\text{t}))</td>
<td>(D_{4h})</td>
<td>(E_u) (no (z)!)</td>
<td>1 ν(_{\text{CO}})</td>
</tr>
<tr>
<td>(\text{M(CO)}(_4)L_2(\text{c}))</td>
<td>(C_{2v})</td>
<td>(A_{1}+B_1+B_2)</td>
<td>3 ν(_{\text{CO}})</td>
</tr>
<tr>
<td>(\text{M(CO)}(_5))</td>
<td>(D_{3h})</td>
<td>(A_2''+E')</td>
<td>2 ν(_{\text{CO}})</td>
</tr>
<tr>
<td>(\text{M(CO)}(_4))</td>
<td>(T_d)</td>
<td>(T_2)</td>
<td>1 ν(_{\text{CO}})</td>
</tr>
</tbody>
</table>
Phosphine, phosphite complexes:

- for electron counting - they considered as 2e⁻ donors (can substitute CO in complexes)
- real electron donor/acceptor properties are determined by the substituents on the P
  - class I: σ and π donors \( PR_3, \text{R}=\text{alkyl} \)  P lone pair, P-C σ-bonds
  - class II: σ donors \( PAr_3 \) P lone pair only
  - class III: σ donors/π acceptors \( P(OR)_3 \) P lone pair, P-O σ* 

(more electronegative substituents → less electron density in P-X bonds → lower P-X σ* → more backdonation
similar effect to LMCT energy change in UV/VIS as the optical electronegativity increases)

- steric interactions:
  - a measure of the bulkiness of the P-ligand is the Tolman cone angle
    \( PCy_3: 170° \quad PPh_3: 145° \quad PMe_3: 135° \quad P(OMe)_3: 107° \)

- agostic interaction between ligand H and the empty metal d orbital:
  - example: \( W(CO)_3(PCy_3)_2 \) IR shows more than one \( \nu_{CO} \) bands (\( M(CO)_3L_2(t) \) is \( D_{3h} \), normal mode \( E' \))
    \( ^1H \) NMR shows more than one type of H
  → octahedral coordination with a H from the Cy group coordinated to the metal