Characterization of Organometallic Compounds

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Main characterization methods:
• Xray diffraction ⇒ (static) structure ⇒ bonding
• NMR ⇒ structure en dynamic behaviour
• EA ⇒ assessment of purity
• (calculations)

Less frequently used:
• IR
• MS
• EPR

Not used much:
• GC
• LC
X-ray diffraction

- Need well-defined single crystal(s)
  - preferably about 0.1-0.2 mm in each dimension
  - may be cut from a larger crystal
  - needles and leaflets are a problem
  - tricks for handling highly air-sensitive compounds
- A measurement takes about a day
  - on a modern diffractometer
- Solution and refinement take a few hours
  - some details may require special attention
- Some compounds will never yield a good crystal structure!
X-ray diffraction

• X-ray diffraction actually measures electron density
  – positions of heavy atoms easy to find
  – H atoms often not found at all
  – if H atoms *are* found, bond lengths will not be accurate
  – it may be hard to distinguish between C/N/O, or e.g. Rh/Ag

• X-ray diffraction measures an average *in space* and *in time*
  – in case of disorder, you will see a superposition of molecules
  – hard to distinguish between dynamic and static disorder
  – what is the time-scale of X-ray diffraction?

• X-ray diffraction says nothing about purity of a sample!
  – it only says something about the one crystal you measured
  – "crystal picking"

• Don't always "believe" published X-ray structures, stay critical
Too weird to be true?

Electrochemical Preparation of Platinum Icocyaneide Clusters Containing Chelating Diphosphines. An Unprecedented Trinuclear Platinum Complex Involving a Coordinatively Unsaturated Metal Center, 

\[
[{\text{Pt}}(\text{diphosphine})(\text{isocyanide})_{2}\text{Pt}](\text{PF}_6)_2
\]


*Organometallics* **1994**, *13*, 1374
Indeed!

Clusters \([\text{Pt(diphosphine)(isocyanide)}\text{Pt}]^{2+}\) Recharacterized as \([\text{Pt(diphosphine)(isocyanide)}\text{Hg}]^{2+}\)

Tanase, T.; Yamamoto, Y.; Puddephatt, R.J.

*Organometallics* **1996**, 15, 1502
NMR spectroscopy

NMR of organometallic Compounds:
• The organic groups (alkyl/aryl)
• The other ligands
• The metal
• Coupling with heteronuclei
• Fluxionality (dynamical behaviour)
The organic groups (alkyl/aryl)

Alkyl groups
- at main group metals:
  - shift to high field (compared to a H or CH₃ substituent):
    - 0-4 ppm in ¹H, 0-15 ppm in ¹³C
  - the metal is a σ-donor!
  - how much? Look at difference in electronegativity!
- at transition metals:
  - larger high-field shift for metals with a partially filled d shell

Aryl groups
- usually low-field shift of ortho H, ipso and ortho C

Hydrides
- extreme high-field shift (up to 100 ppm) for metals with a partially filled d shell
• Non-"4n+2" systems usually become more aromatic, as if they had obtained the charge required by "4n+2":

• Arenes become less aromatic and sometimes more localized
The other ligands

- Olefins shift to higher field (metallacyclopropane character!)

<table>
<thead>
<tr>
<th></th>
<th>free ethene</th>
<th>coordinated ethene</th>
<th>cyclopropane</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{H})</td>
<td>5.2</td>
<td>1-3</td>
<td>0.2</td>
</tr>
<tr>
<td>(^{13}\text{C})</td>
<td>122</td>
<td>40-90</td>
<td>-3</td>
</tr>
</tbody>
</table>

*approximate* bond lengths:

- \(^1\text{H}\): 1.34 Å
- \(^{13}\text{C}\): 1.41 Å
- Bond length: 1.50 Å
The other ligands

- Terminal CO ligands
  $^{13}\text{C}$ 170-240 ppm
The metal

- Many metal nuclei have (an isotope with) non-zero spin
  - Metal NMR?
  - Coupling
  - Line broadening
- Metal NMR is often doable but not often useful
Expected pattern for $^1$H and $^{13}$C signals for an M-CH$_3$ group:

- M is NMR-inactive
- M has $S = 1/2$
- M has $S = 3/2$
- M has 30% $S = 1/2$, rest NMR-inactive
Fluxionality
(dynamical behaviour)

- The NMR time scale is ≈ seconds, we look at differences in peak positions of the order of Hz to hundreds of Hz.
- If nuclei move much more slowly, we see separate peaks.
- If nuclei move much faster, we see averaged peaks.
- In the intermediate region we see "coalescence".
- From the changes in the NMR spectrum you can extract both qualitative and quantitative information about the movement (reaction).
Fluxionality  
(dynamical behaviour)

High temperature  
Fast exchange  
"fast-exchange limit"

Coalescence

Low temperature  
Slow exchange  
"slow-exchange limit"

\[ k_{coal} = \frac{\pi}{\sqrt{2}} \Delta \delta \]
\[ \Delta G^\dagger = RT_{coal} \left[ 22.96 + \ln \frac{T_{coal}}{\Delta \delta} \right] \]
**Fluxionality**
*(dynamical behaviour)*

Figure 2. Temperature dependent $^{29}$Si NMR spectra of hexakis-(fluorodimethylsilyl)benzene in toluene-$d_6$. 