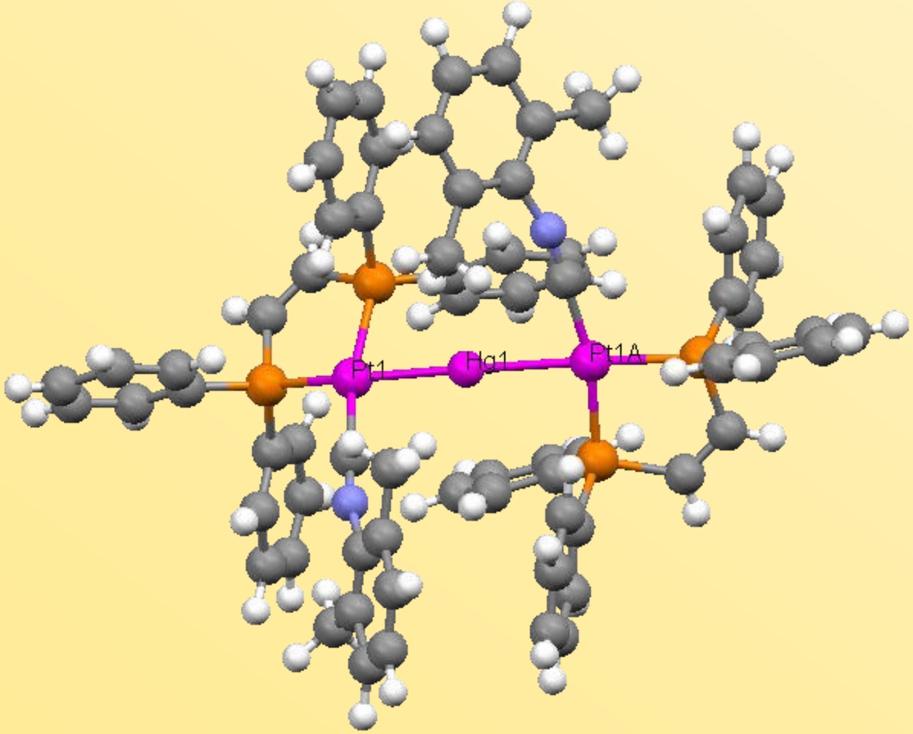
Characterization of Organometallic Compounds



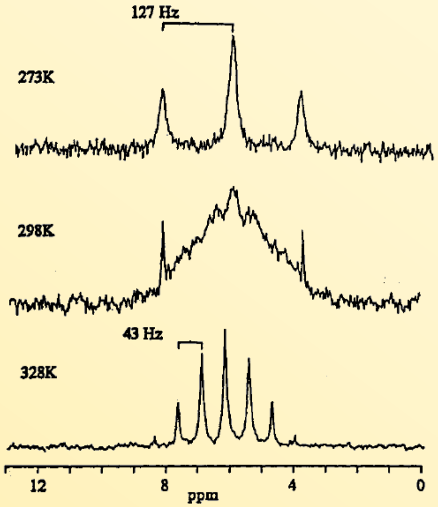


Figure 2. Temperature dependent ^{29}Si NMR spectra of hexakis-(fluorodimethylsilyl)benzene in toluene-d_8.

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Characterization of organometallics

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 !

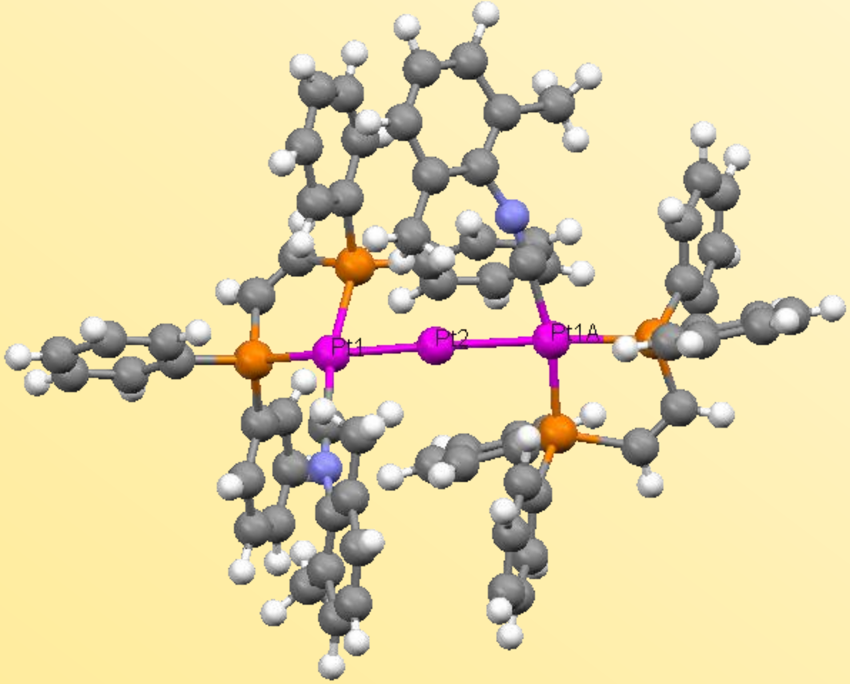
X-ray diffraction

- 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 Icocyanide Clusters Containing Chelating Diphosphines. An Unprecedented Trinuclear Platinum Complex Involving a Coordinatively Unsaturated Metal Center, $[\{Pt(diphosphine)(isocyanide)\}_2Pt](PF_6)_2$

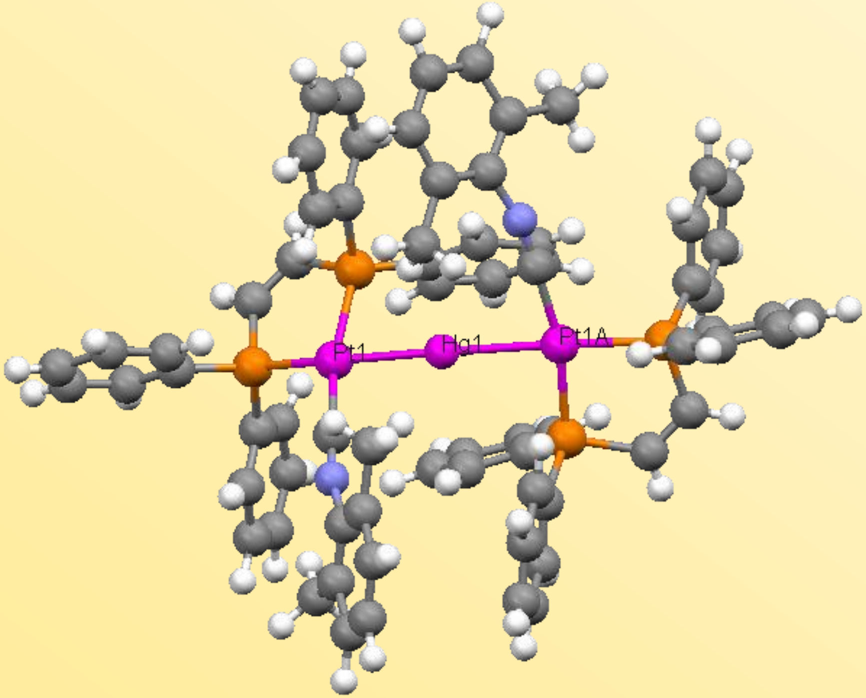
Tanase, T.; Ukaji, H.; Kudo, Y.; Ohno, M.; Kobayashi, K.; Yamamoto, Y.
Organometallics **1994**, *13*, 1374



Indeed !

Clusters [{Pt(diphosphine)(isocyanide)}$_2$Pt]$^{2+}$ Recharacterized as [{Pt(diphosphine)(isocyanide)}$_2$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

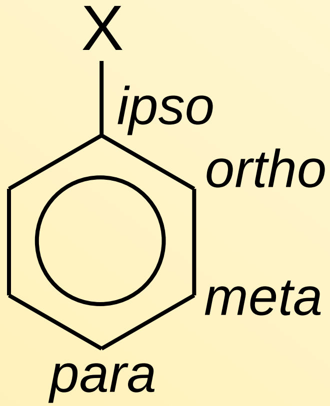
- at main group metals:
  - shift to high field (compared to a H or CH_3 substituent): 0-4 ppm in ^1H, 0-15 ppm in ^{13}C
  - the metal is a σ-donor!
  - how much? Look at difference in electronegativity!
- at transition metals:
  - larger high-field shift for metals with a partially filled *d* shell

Aryl groups

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

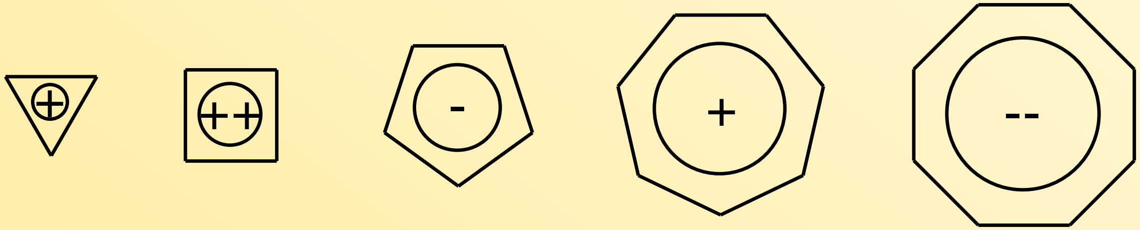
Hydrides

- extreme high-field shift (up to 100 ppm) for metals with a ***partially filled*** *d* shell

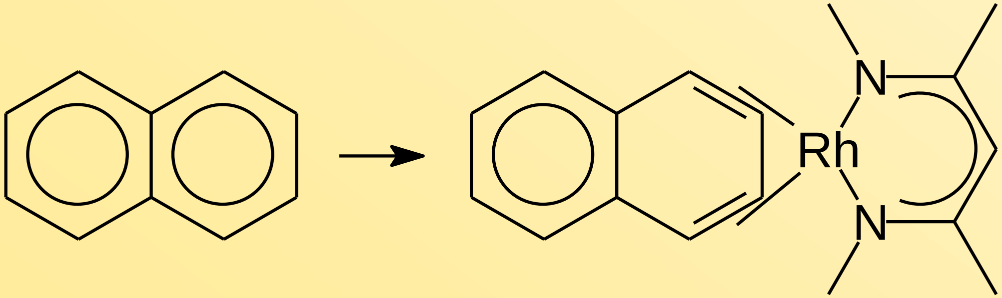


The other ligands

- Non-"***4n+2***" systems usually become more aromatic, as if they had obtained the charge required by "***4n+2***":



- Arenes become <u>less aromatic</u> and sometimes <u>more localized</u>

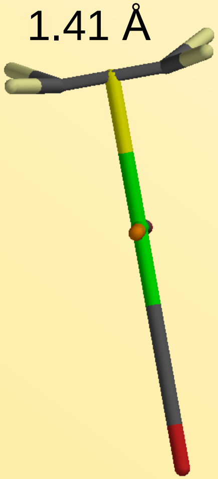


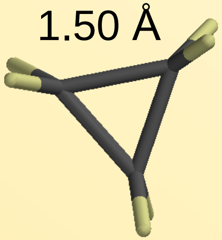
The other ligands

- Olefins shift to higher field (metallacyclopropane character!)

	free ethene	coordinated ethene	cyclopropane
^{1}H	5.2	1-3	0.2
^{13}C	122	40-90	-3

approximate bond lengths:





The other ligands

- Terminal CO ligands

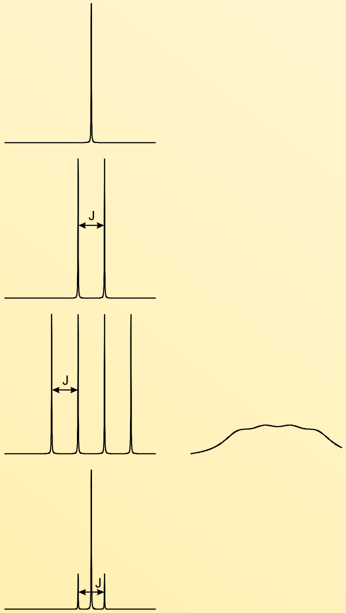
  ^{13}C 170-240 ppm

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*

Coupling to heteronuclei (metal and others)

Expected pattern for ^{1}H and ^{13}C signals for an M-CH$_3$ group:



M is NMR-inactive

M has $S = 1/2$

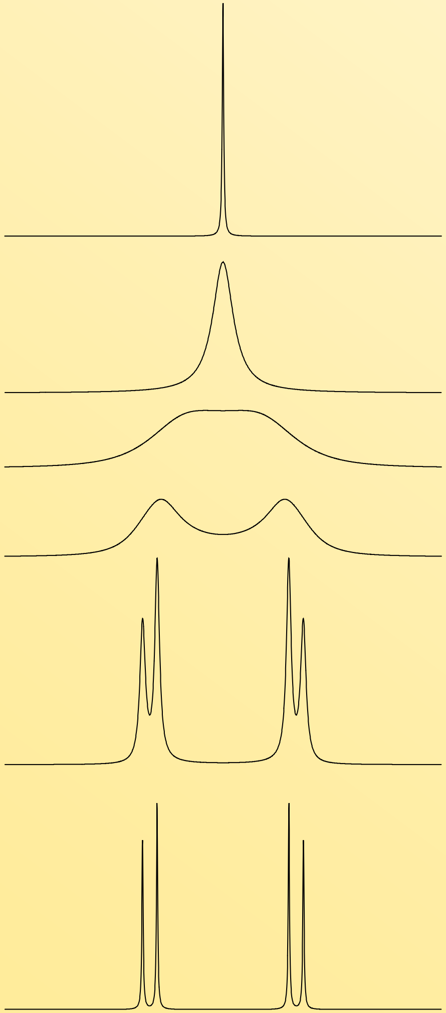
M has $S = 3/2$

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"

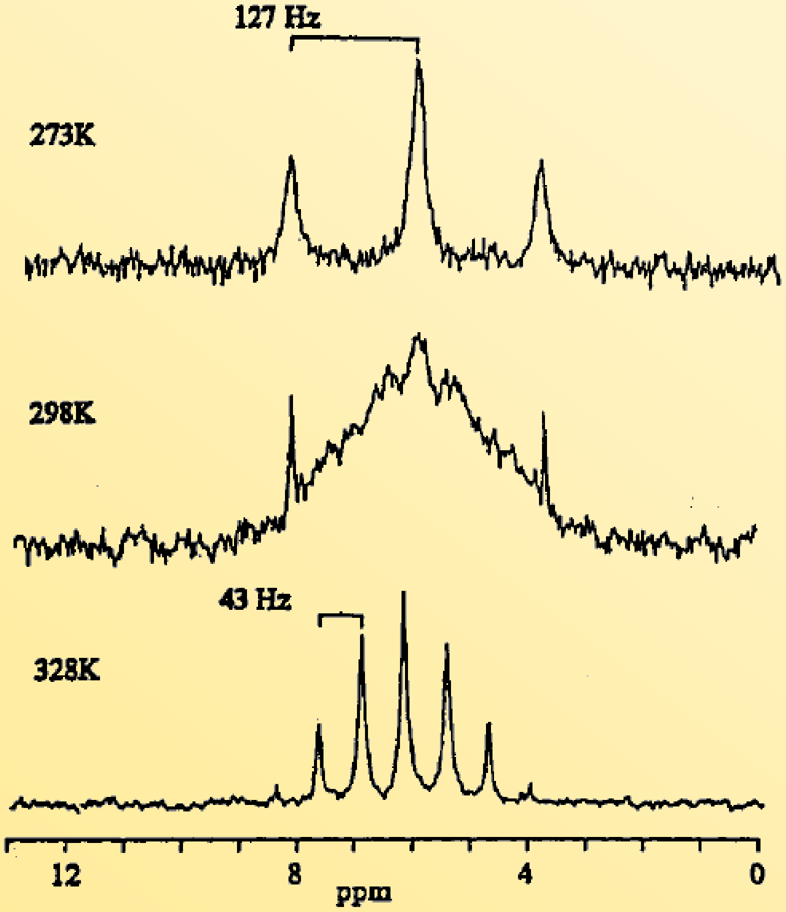
Coalescence

$$k_{coal} = \frac{\pi}{\sqrt{2}} \Delta\delta$$

$$\Delta G^{\ddagger} = RT_{coal}\left[22.96 + \ln \frac{T_{coal}}{\Delta\delta}\right]$$

Low temperature
Slow exchange
"slow-exchange limit"

Fluxionality (dynamical behaviour)



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