12th Oxford School on Neutron Scattering

St. Anne's College, University of Oxford

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Chemical Applications of Neutron Scattering

Part 1

Elastic Scattering and Structural Studies

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Part 1

Chemical Applications of Neutron Scattering

- **Coherent and Incoherent Scattering Cross-Sections** *(again!!).*
- **Structure Factors and Thermal Motion (ADP's).**
- **Single Crystal Neutron Diffraction: constant λ and TOF.**
- **Data Reduction: absorption, extinction……**
- **Applications:**

  Hydrogen Bonding and Weak interactions

  T dependence of ADP's and TLS correction

  Coordination Chemistry of Hydrogen.

- **The need for other techniques.**

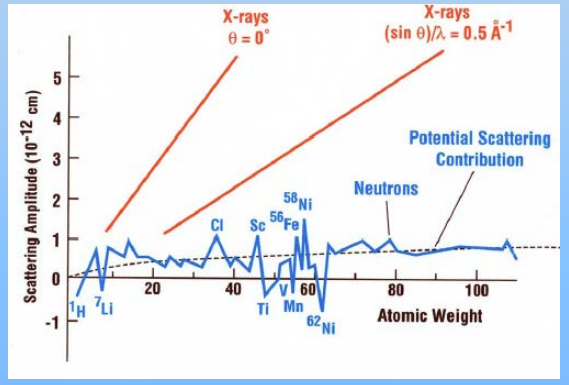
Neutron Properties

- **@ 293.6 K for a "neutron gas":**

  E = 25 meV, $\mathbf{v} \approx 2.2$ km s^{-1}, $\nu \approx 200$ cm $^{-1} \approx 6 \times 10^{12}$ Hz, $\lambda = h/m\mathrm{v} \approx 1.8$ Å

- **Zero Electric Charge:** ***Negligible absorption, scattering from the bulk.***

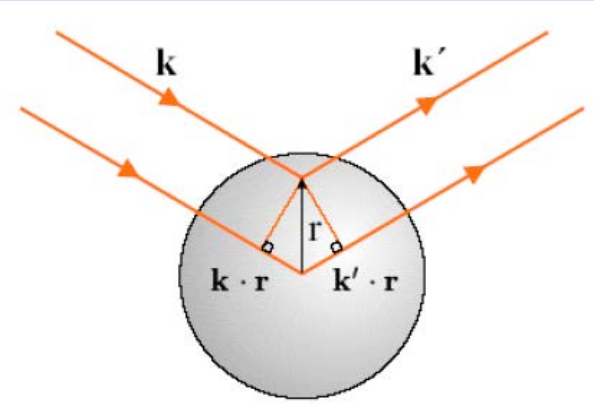
- **Neutron Scattering is a Nuclear Process:**



- **De Broglie Wavelength is Comparable with Interatomic Distances:** ***Bragg Scattering.***

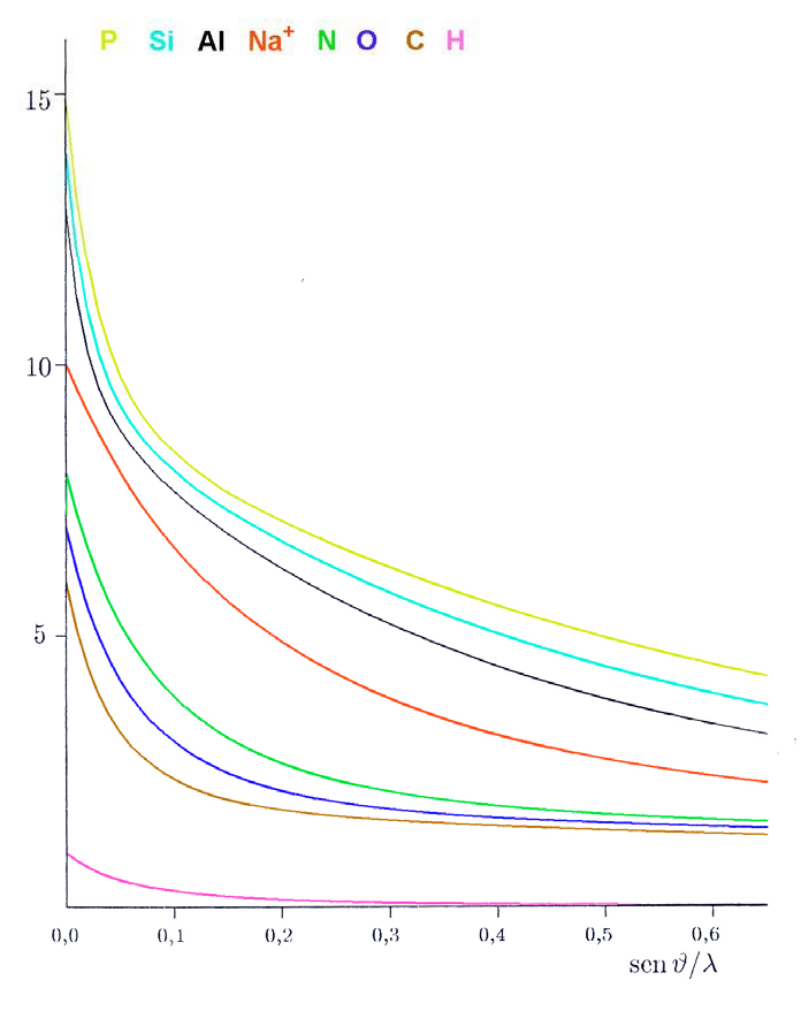
- **The Energy of Thermal Neutrons is Comparable with the Energy of Molecular and Lattice Vibrations (Phonons):** ***Inelastic Coherent & Incoherent Scattering Can Probe Lattice and Molecular Vibrations***

Atomic Scattering Factors for X-rays

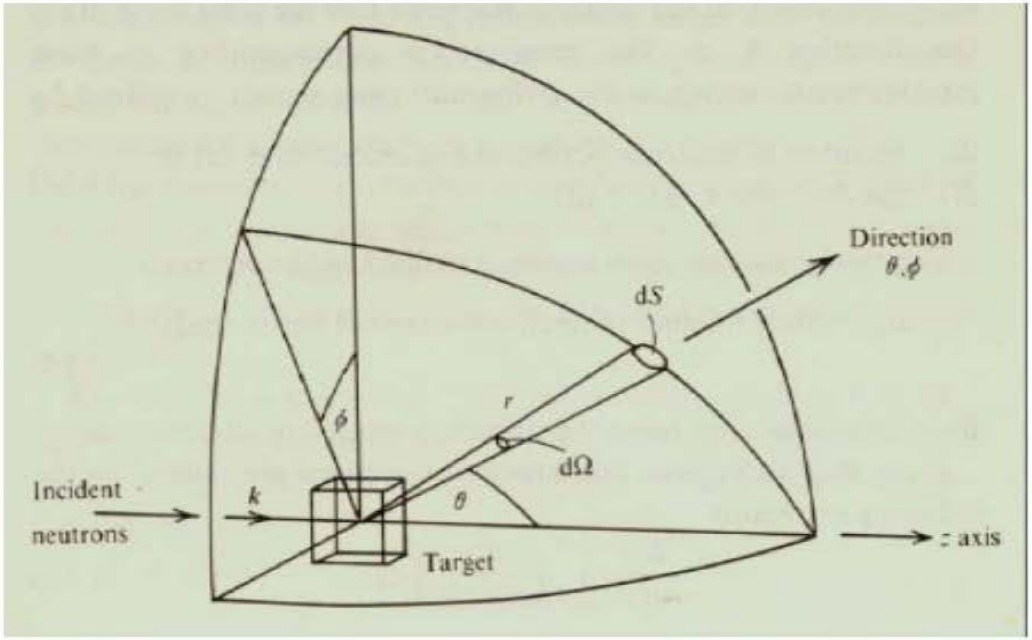


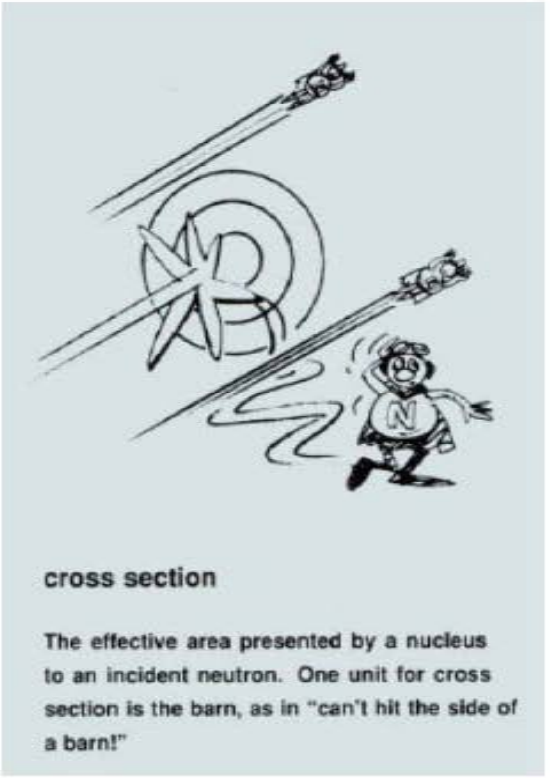
$$f(\mathbf{S}) = \int \rho(\mathbf{r}) \exp 2\pi i(\mathbf{S}\bullet\mathbf{r}) d\mathbf{r}$$

$$f(S) = 4\pi \int_0^\infty r^2 \rho(r) \frac{\sin 2\pi(Sr)}{2\pi(Sr)} dr$$



Cross Sections





Φ = number of incident neutrons per cm^2 per second

σ = total number of neutrons scattered per second / Φ

$$\frac{d\sigma}{d\Omega} = \frac{\text{number of neutrons scattered per second into } d\Omega}{\Phi\, d\Omega}$$

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\text{number of neutrons scattered per second into } d\Omega \text{ \& } dE}{\Phi\, d\Omega\, dE}$$

σ measured in barns:
1 barn = 10^{-24} cm^2

Attenuation = $\exp(-N\sigma t)$
N = # of atoms/unit volume
t = thickness

From R. Pynn . **Neutron Scattering: a Primer**. *Los Alamos Science (1990)*
(www.mrl.ucsb.edu/~pynn)

COHERENT and INCOHERENT NEUTRON SCATTERING

"$\mathbf{b_R}$" varies from **isotope to isotope**

$$\frac{d\sigma}{d\Omega} = \left| \sum_{\mathbf{R}} b_{\mathbf{R}} \exp\left(i\mathbf{Q}.\mathbf{R}\right) \right|^2 = \sum_{\mathbf{R}} \sum_{\mathbf{R'}} b_{\mathbf{R}} b_{\mathbf{R'}} \exp\left[i\mathbf{Q}.(\mathbf{R}-\mathbf{R'})\right] =$$

$$= \sum_{R} b_R^2 + \sum_{\mathbf{R,R'}}{}' b_{\mathbf{R}} b_{\mathbf{R'}} \exp\left[i\mathbf{Q}.(\mathbf{R}-\mathbf{R'})\right]$$

$$\sum_{\mathrm{R}} b_{\mathrm{R}}{}^2 = N \left\langle b_{\mathrm{R}}^2 \right\rangle$$

assuming no correlation $\langle b_R b_{R'} \rangle = \langle b_R \rangle \langle b_{R'} \rangle = \langle b_R \rangle^2$

$$\sum_{RR'}{}' b_R b_{R'} \exp\left[i\mathbf{Q}.(\mathbf{R}-\mathbf{R'})\right] =$$

$$= N \left\langle b_R \right\rangle^2 \sum_{RR'}{}' \exp\left[i\mathbf{Q}.(\mathbf{R}-\mathbf{R'})\right] = -N \left\langle b_R \right\rangle^2 + N \left\langle b_R \right\rangle^2 \sum_{R} \sum_{R'} \exp\left[i\mathbf{Q}.(\mathbf{R}-\mathbf{R'})\right]$$

$$\frac{d\sigma}{d\Omega} = N\left(\left\langle b^2 \right\rangle - \left\langle b \right\rangle^2\right) + N \left\langle b_R \right\rangle^2 \left| \sum_{R} \exp\left(i\mathbf{Q}.\mathbf{R}\right) \right|^2$$

$N\left(\left\langle b^2 \right\rangle - \left\langle b \right\rangle^2\right) = N \left\langle \left(b - \left\langle b \right\rangle\right)^2 \right\rangle$ Incoherent Scattering Cross Section

Neutron Scattering Cross Sections

COHERENT CROSS SECTIONS

$$\sigma_{coh} = 4\pi \langle b \rangle^2$$

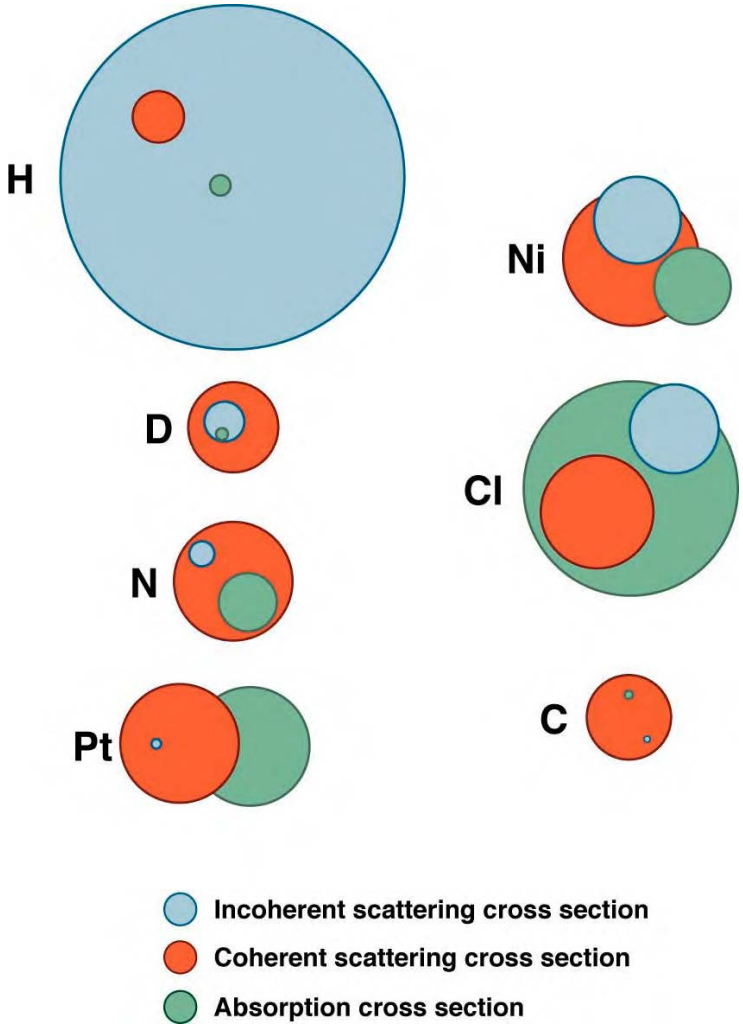
Coherent Scattering depends on the correlation between the positions of the same nucleus at different times and the positions of different nuclei at different times.
STRUCTURAL INFORMATION.

INCOHERENT CROSS SECTIONS

$$\sigma_{incoh} = 4\pi \left(\langle b^2 \rangle - \langle b \rangle^2 \right)$$

Incoherent Scattering arises from the random distribution of different isotopes with different scattering lengths. Incoherent Scattering depends on the correlation between the positions of the same nucleus at different times.
SPECTROSCOPY

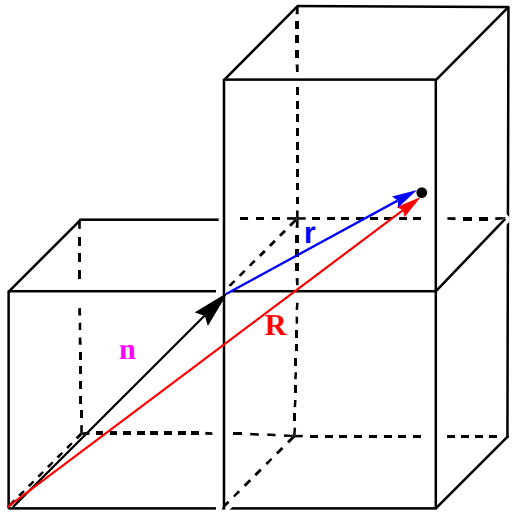
Neutron Incoherent Cross-Sections



Bragg Scattering in Crystals

$$\mathbf{R} = \mathbf{n} + \mathbf{r}$$

R ≡ *atomic position*
n ≡ *lattice vector* ≡ $n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$
$\mathbf{r}_{(xyz)}$ ≡ *atomic position in the unit cell*



$$|\mathbf{Q}| = \frac{4\pi \sin\vartheta}{\lambda}$$

$$|\mathbf{k}| = \frac{2\pi}{\lambda}$$

$$I = \left(\frac{d\sigma}{d\Omega}\right) = \left|\sum_{\mathbf{R}} b_R e^{i\mathbf{Q}.\mathbf{R}}\right|^2 == \left|\sum_{\mathbf{n}} \exp i(\mathbf{Q}.\mathbf{n}) \sum_{\mathbf{r}} b_r \exp i(\mathbf{Q}.\mathbf{r})\right|^2 = \left|\sum_{\mathbf{n}} \exp i(\mathbf{Q}.\mathbf{n})\right|^2 \left|\sum_{\mathbf{r}} b_r \exp i(\mathbf{Q}.\mathbf{r})\right|^2$$

Bragg Scattering in Crystals

$$\left|\sum_{\mathbf{n}} \exp i(\mathbf{Q}.\mathbf{n})\right|^2 = \frac{\sin^2 hN_1\pi}{\sin^2 h\pi}\frac{\sin^2 kN_2\pi}{\sin^2 k\pi}\frac{\sin^2 lN_3\pi}{\sin^2 l\pi}$$

if **Q** = **H**

$$I = \left(\frac{d\sigma}{d\Omega}\right) = N_1 N_2 N_3 \frac{(2\pi)^3}{V_{cell}} \sum_{\mathbf{H}} \delta(\mathbf{Q}-\mathbf{H})\left|F_{\mathbf{H}}\right|^2$$

$$F_{\mathbf{H}} = \sum_{\mathbf{r}} b_r^{coh} \exp i(\mathbf{H}\cdot\mathbf{r})$$

$F_{\mathbf{H}}$ ≡ **Structure Factor**

In Crystallography:

$$F_{hkl} = \sum_j b_j^{coh} \exp 2\pi i(\mathbf{S}\cdot\mathbf{r}_j) = \sum_j b_j^{coh} \exp 2\pi i(hx_j + ky_j + lz_j)$$

$$|\mathbf{S}| = \frac{2\pi \sin\vartheta}{\lambda}$$

$$\mathbf{S} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^*$$

$$\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$$

Bragg Scattering in Crystals

and finally **atoms do "move"….**

$$F_{\mathbf{H}} = \sum_{\mathbf{r}} b_r \exp i(\mathbf{H}\cdot\mathbf{r})\; T_r(\mathbf{H})$$

where "$T_r(H)$" is the **temperature factor** of atom "**r**".

for an ***harmonic crystal***

$$T_{\mathbf{r}}(\mathbf{H}) = \exp(-2\pi\langle\mathbf{H}.\mathbf{r})\rangle^2)$$

The Temperature Factor and the P.D.F. (Probability Density Function)

$$T(\mathbf{Q}) = \exp\{-\tfrac{1}{2}[\langle(\mathbf{Q}\cdot\mathbf{u})^2\rangle]\}$$

*p.d.f. of an atom ($p_\kappa(\mathbf{u})$) is the probability of finding an atom in the volume element d^3u when it is displaced by **u** from its rest position.*

If $\rho_0(\mathbf{u})$ ≡ scattering density

$$\rho_\kappa(\mathbf{u}) = \rho_0(\mathbf{u}) * p_\kappa(\mathbf{u})$$

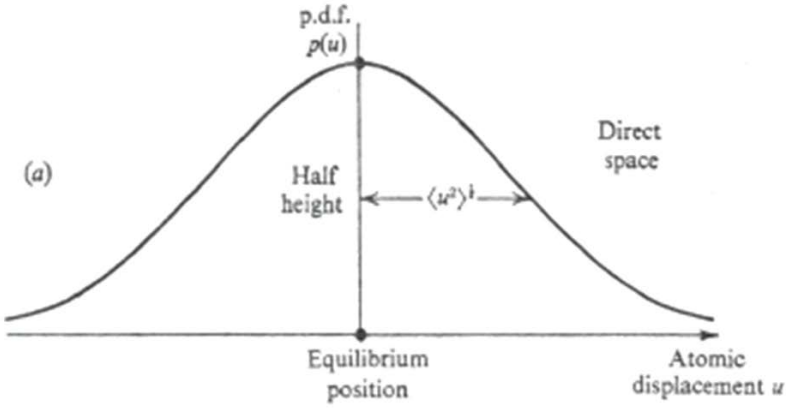
$$\text{F.T.}\,(\rho_\kappa(\mathbf{u})) = \text{FT}(\rho_{0,\kappa}(\mathbf{u})) \times \text{FT}(p_\kappa(\mathbf{u}))$$

$$T(\mathbf{Q}) = \int p_\kappa(\mathbf{u}) \exp i(\mathbf{Q}\cdot\mathbf{u})\, d^3\mathbf{u}$$

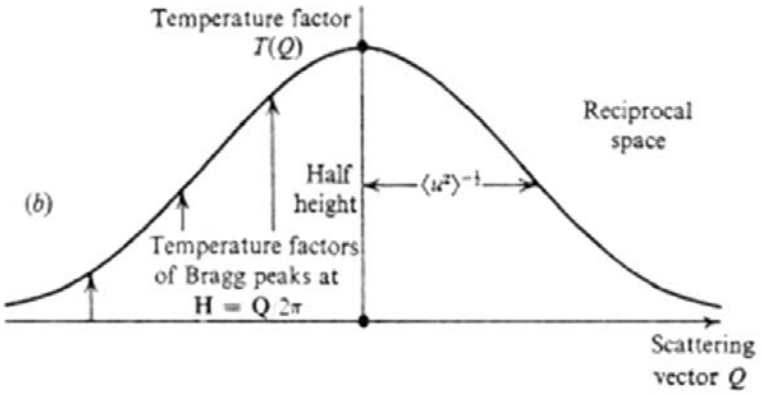
$$p_\kappa(\mathbf{u}) = (2\pi^3)^{-1}\int T(\mathbf{Q}) \exp -i(\mathbf{Q}\cdot\mathbf{u})\, d^3\mathbf{Q}$$

p.d.f. for a SHO is gaussian

$$p(u) = \left(2\pi\langle u^2\rangle\right)^{3/2} \exp\left(-\frac{u^2}{2\langle u^2\rangle}\right)$$



Probability Density Function



Temperature factor for an isotropically vibrating atom.

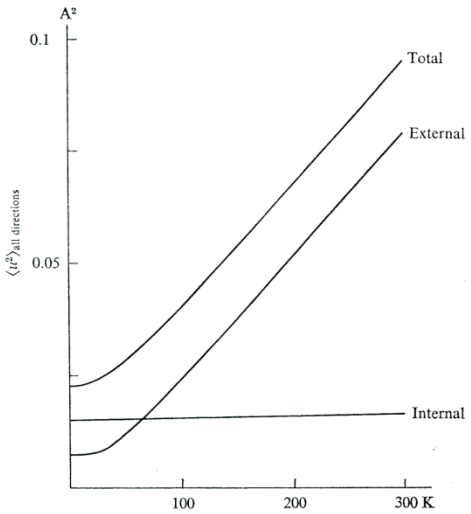
Both curves are Gaussians in the harmonic approximation

Temperature Factors and Atomic Vibrations

$$T_{\kappa}^{anis}(\mathbf{H}) = \exp\left\{-\left[2\pi \mathbf{H}^{\mathrm{T}}\mathbf{U}\mathbf{H}\right]\right\}$$

$$T_{\kappa}^{iso}(\mathbf{H}) = \exp\left\{-\left[2\pi \mathbf{H}^{\mathrm{T}}\mathbf{H}\left\langle u(\kappa)^2\right\rangle\right]\right\} = \exp\left(-\frac{4\pi^2 \sin^2\vartheta}{\lambda^2}\left\langle u(\kappa)^2\right\rangle\right) =$$

$$\exp\left(-B\frac{\sin^2\vartheta}{\lambda^2}\right)$$



$$\langle u_i^2\rangle = \frac{h}{8\pi^2\mu\nu}\coth\left(\frac{h\nu}{2kT}\right)$$

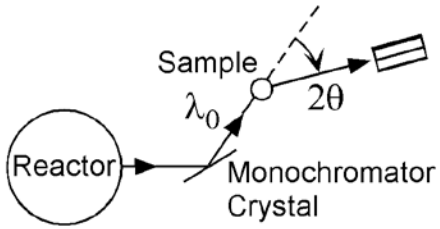
$$\mathbf{U} = \mathbf{t} + \mathbf{l} \wedge \mathbf{r}$$

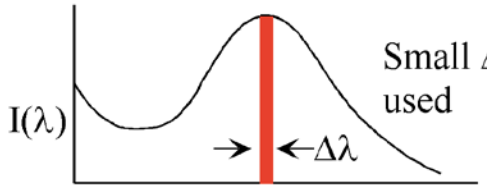
NEUTRON DIFFRACTION

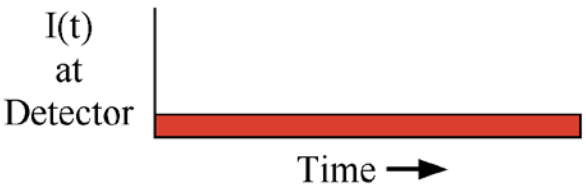
MEASURE F(d)

$$d = \frac{\lambda}{2\sin\theta}$$

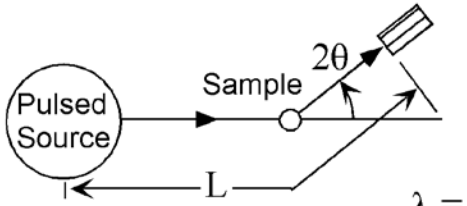
STEADY STATE TECHNIQUE



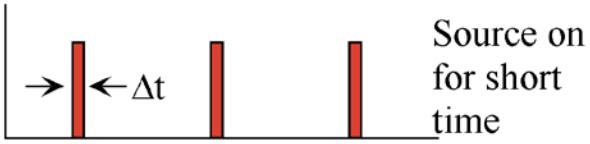


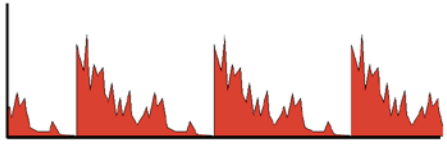


TIME OF FLIGHT TECHNIQUE

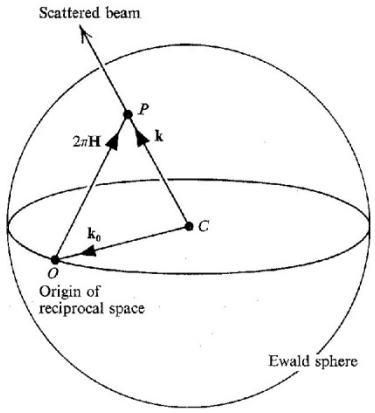


$\lambda = (h/m)\cdot(t/L)$

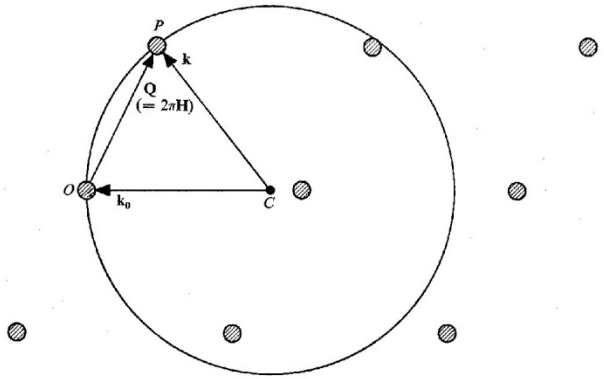


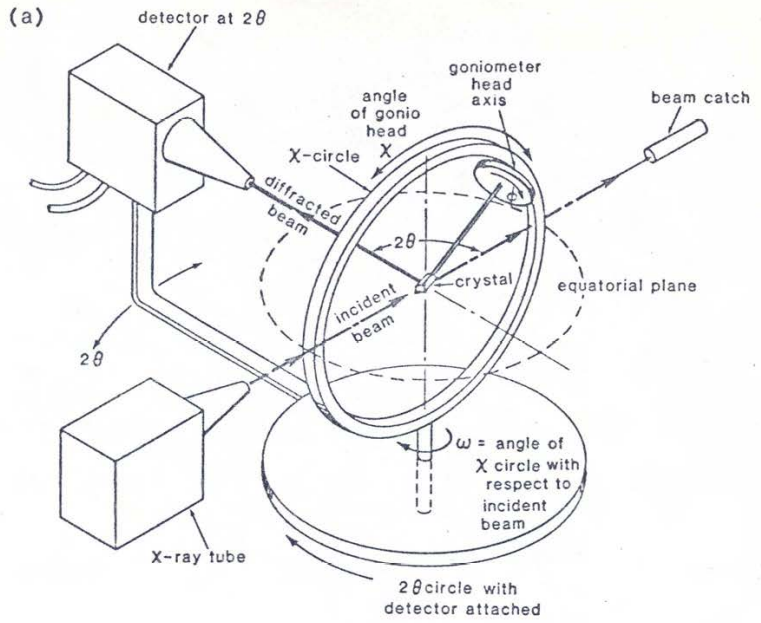


The Ewald Sphere



Ewald sphere of reflection. Bragg scattering takes place when the reciprocal-lattice point $2\pi\mathbf{H}$ lies on the sphere. The radius of the sphere is $2\pi/\lambda$.





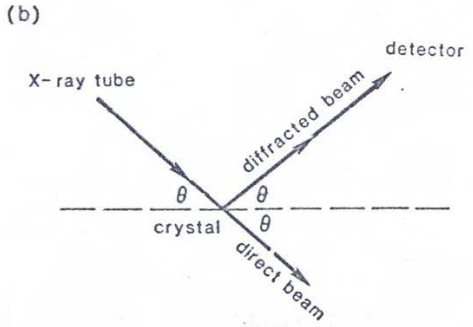
ϕ = spindle axis of goniometer head

2θ = angle between directions of incident and diffracted beams

= angle detector has to be rotated to intercept diffracted beam

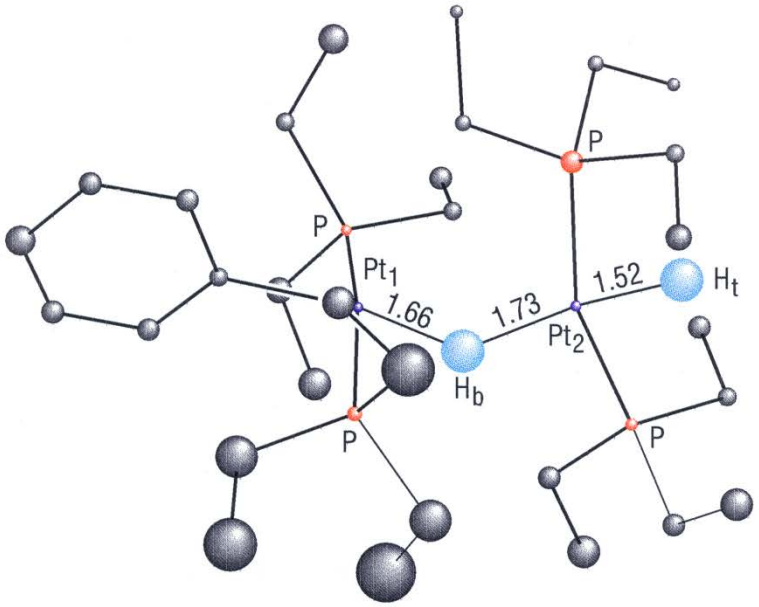
ω = angle between diffracted vector and plane of χ-circle

χ = angle between ϕ axis (gonio. head) and diffractometer axis (equatorial plane)



BNL Single *XXl* Diffractometer on H6

$[H_2Pt_2Ph(PEt_3)_4]^+[BPh_4]^-$
13K Neutron Diffraction Study



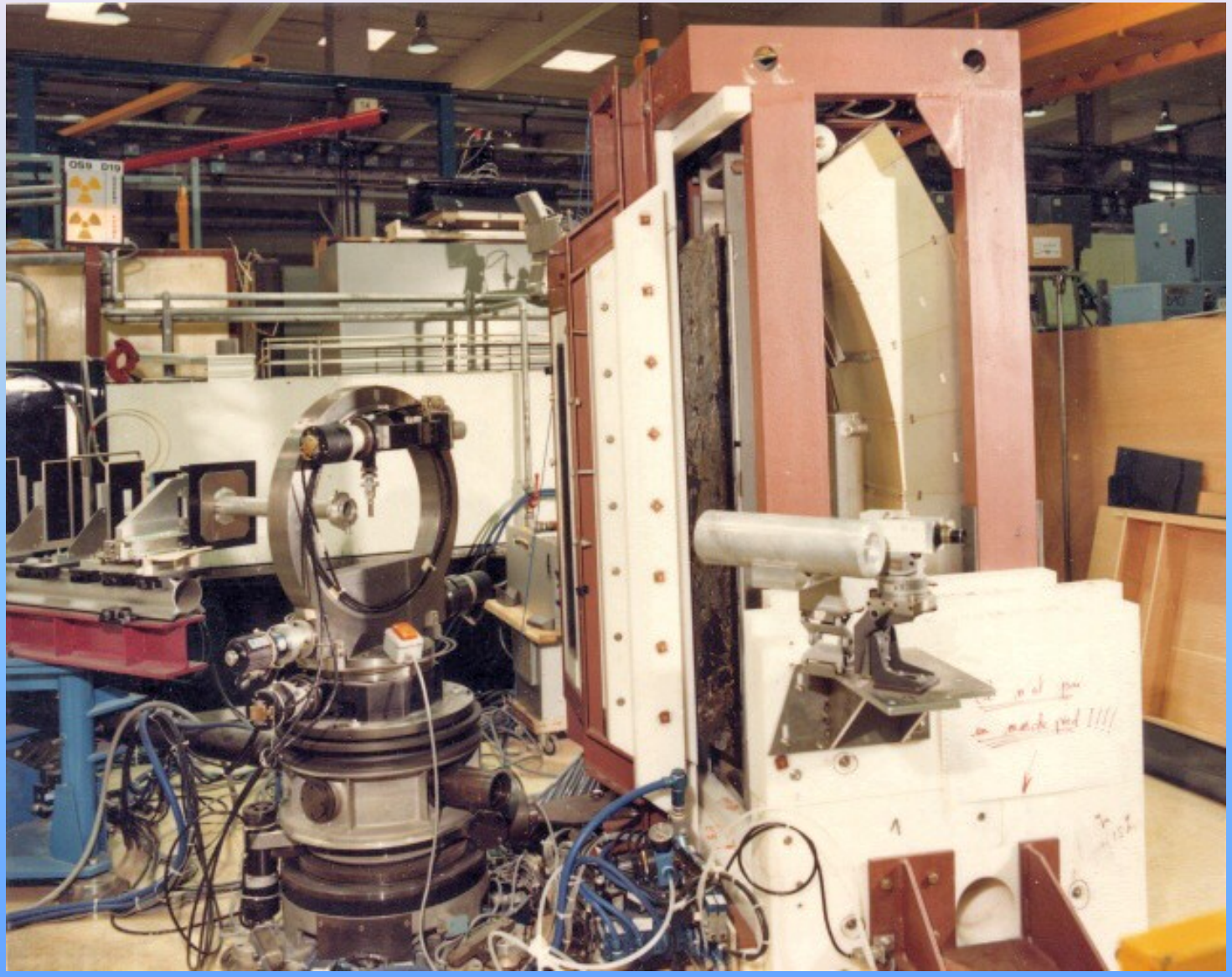
$Pt_1 \cdots Pt_2$ 3.05(1) Å

$\measuredangle Pt_1 - H_b - Pt_2$ 128(2)°

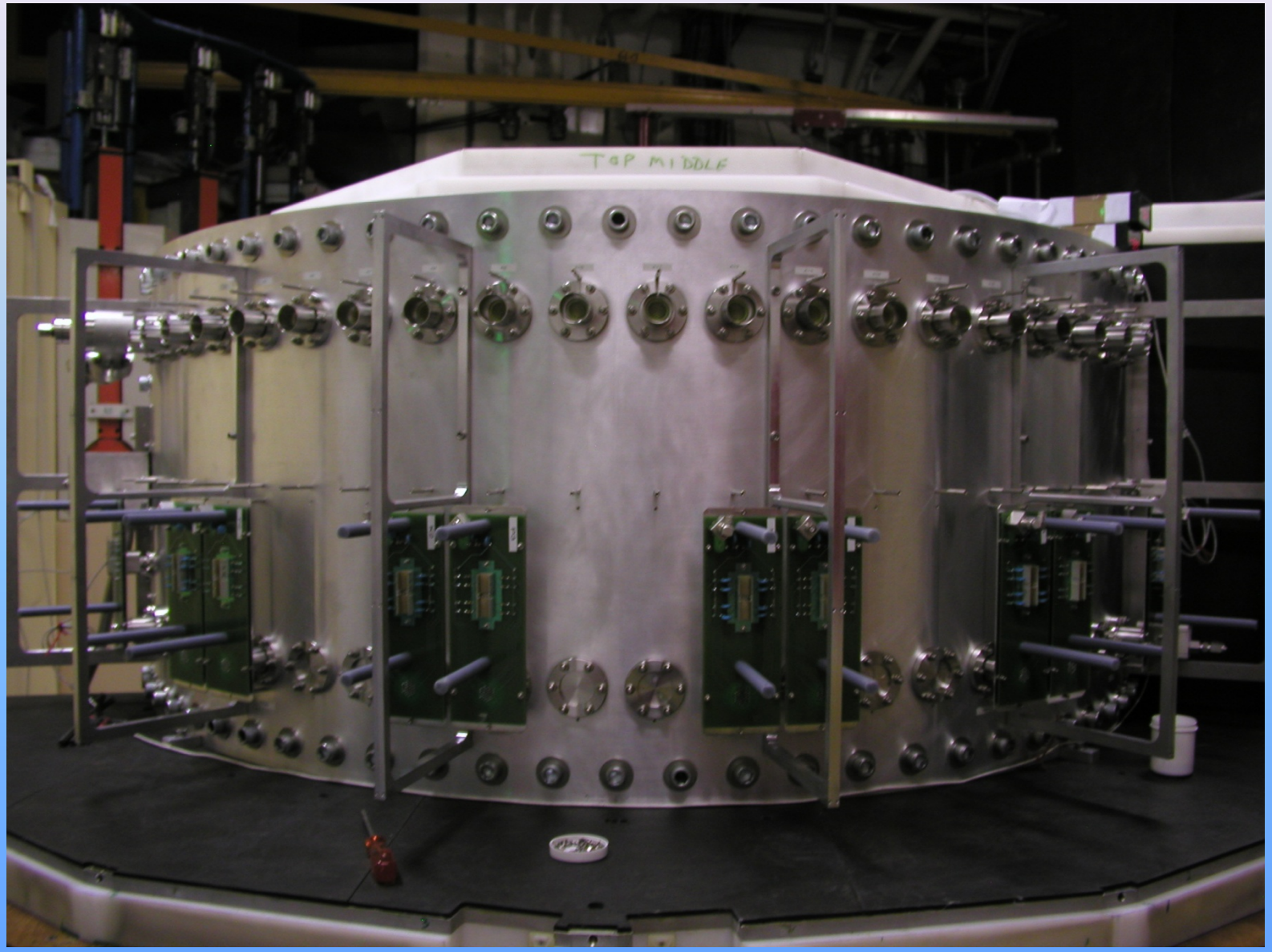
Ricci, Albinati and Koetzle (1995)

ADVANCES IN COORDINATION CHEMISTRY ARE LINKED TO ADVANCES IN INSTRUMENTATION

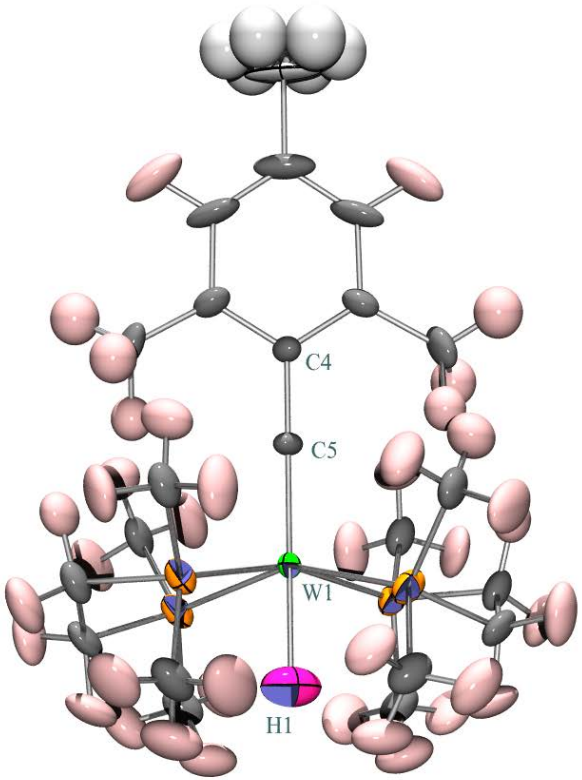
D19 “Old Banana Detector”



D19 New Detector 2007



trans - **W(C-Mesityl)(dmpe)$_2$H**



W – H1 1.84 (2) Å

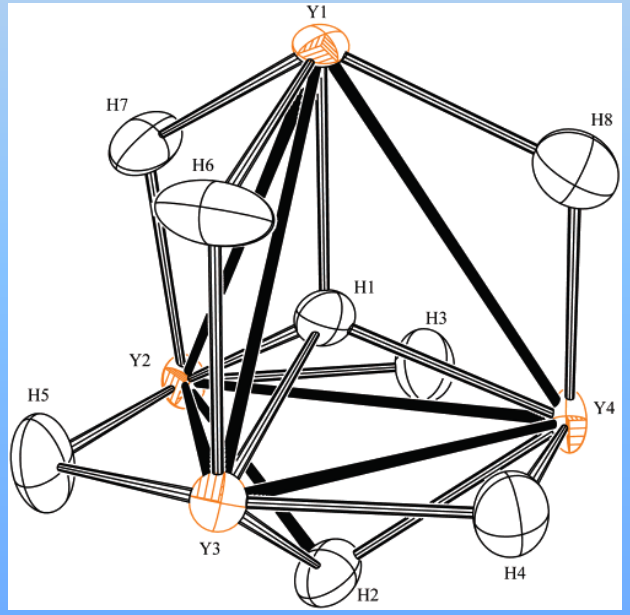
W – C5 1.868 (9)

C4 – C5 1.461 (8)

D19 @20K

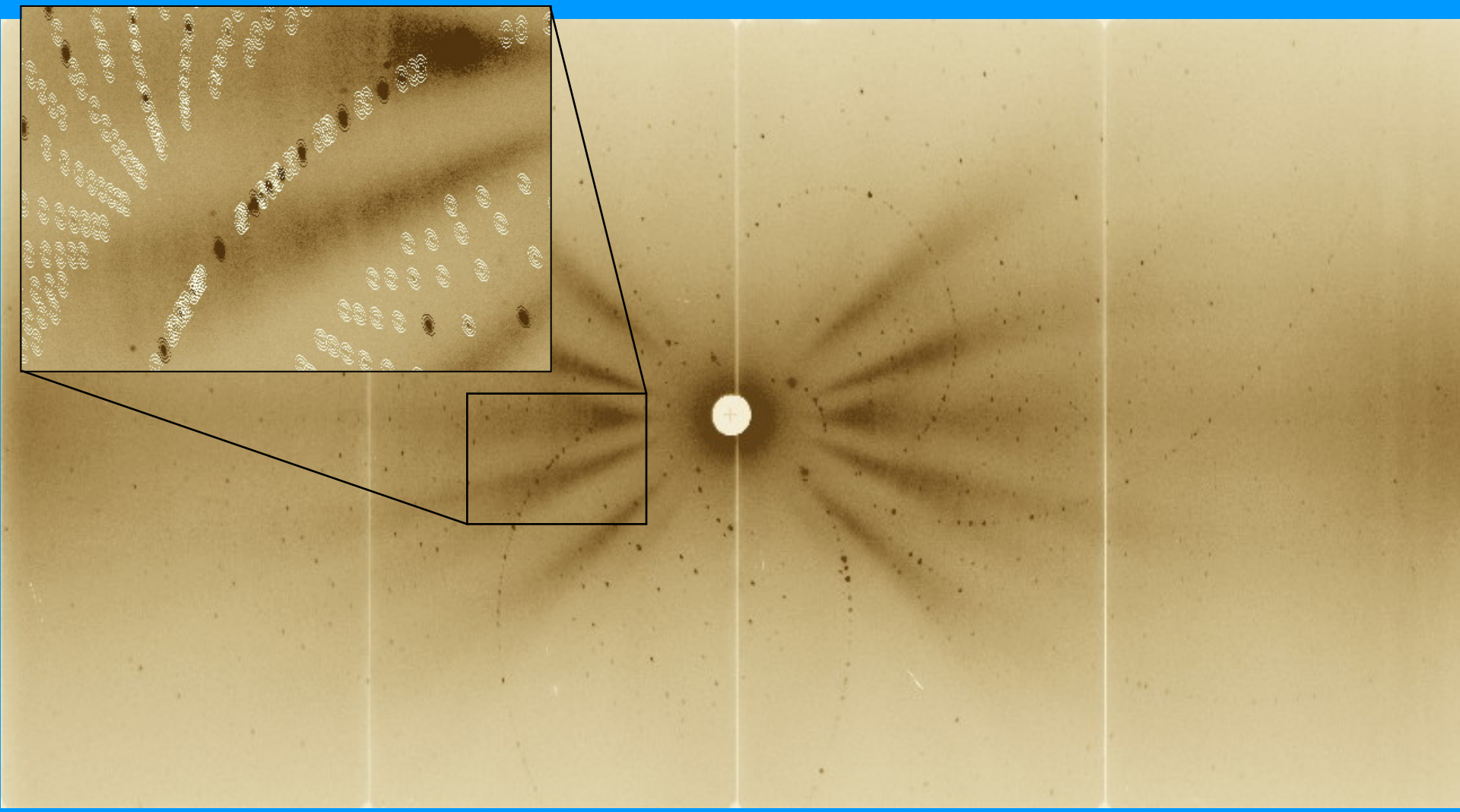
V = 2667 Å^3; C2/c

VIVALDI @ ILL



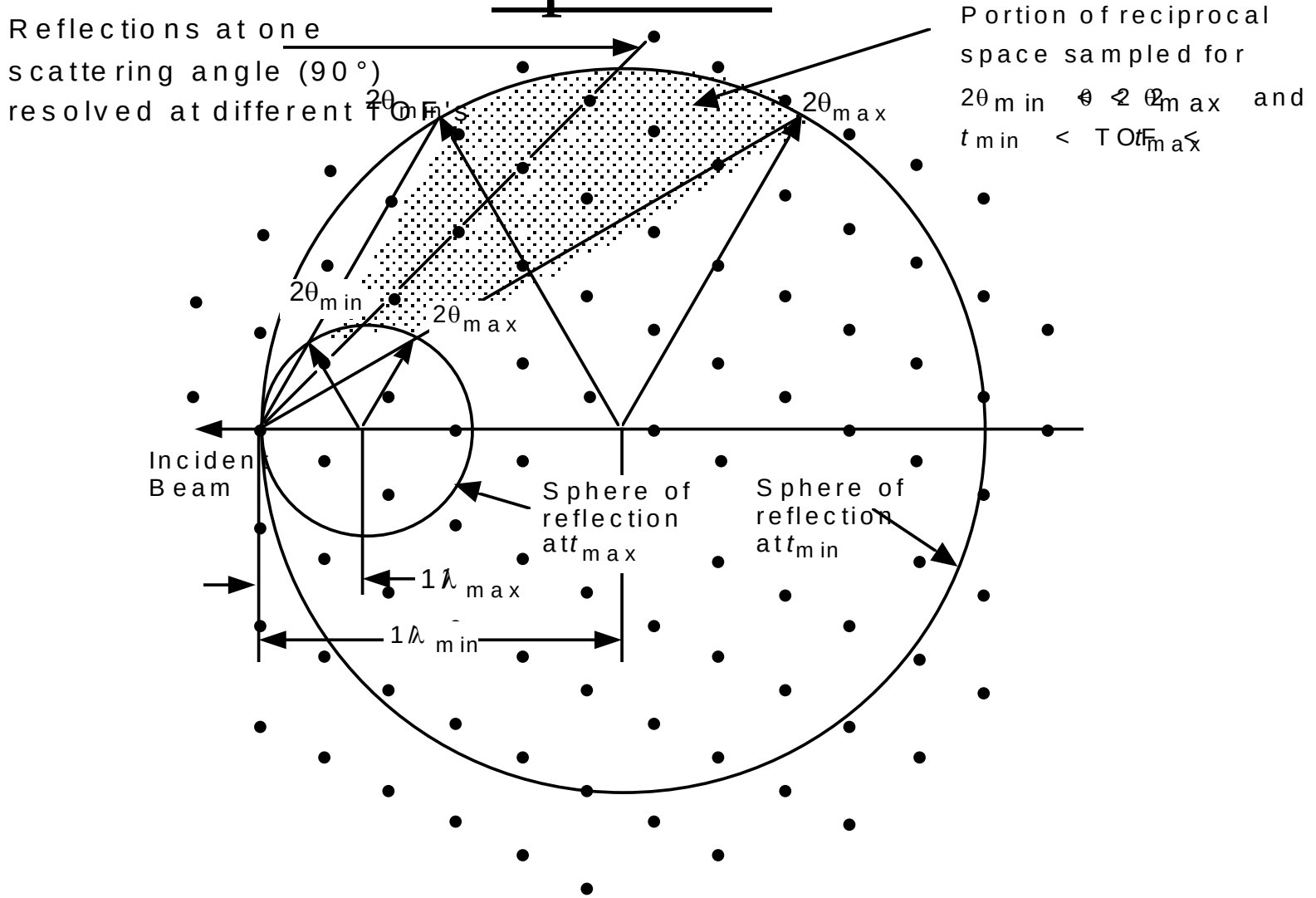
$[(C_5Me_4SiMe_3)YH_2]_4]$

VIVALDI

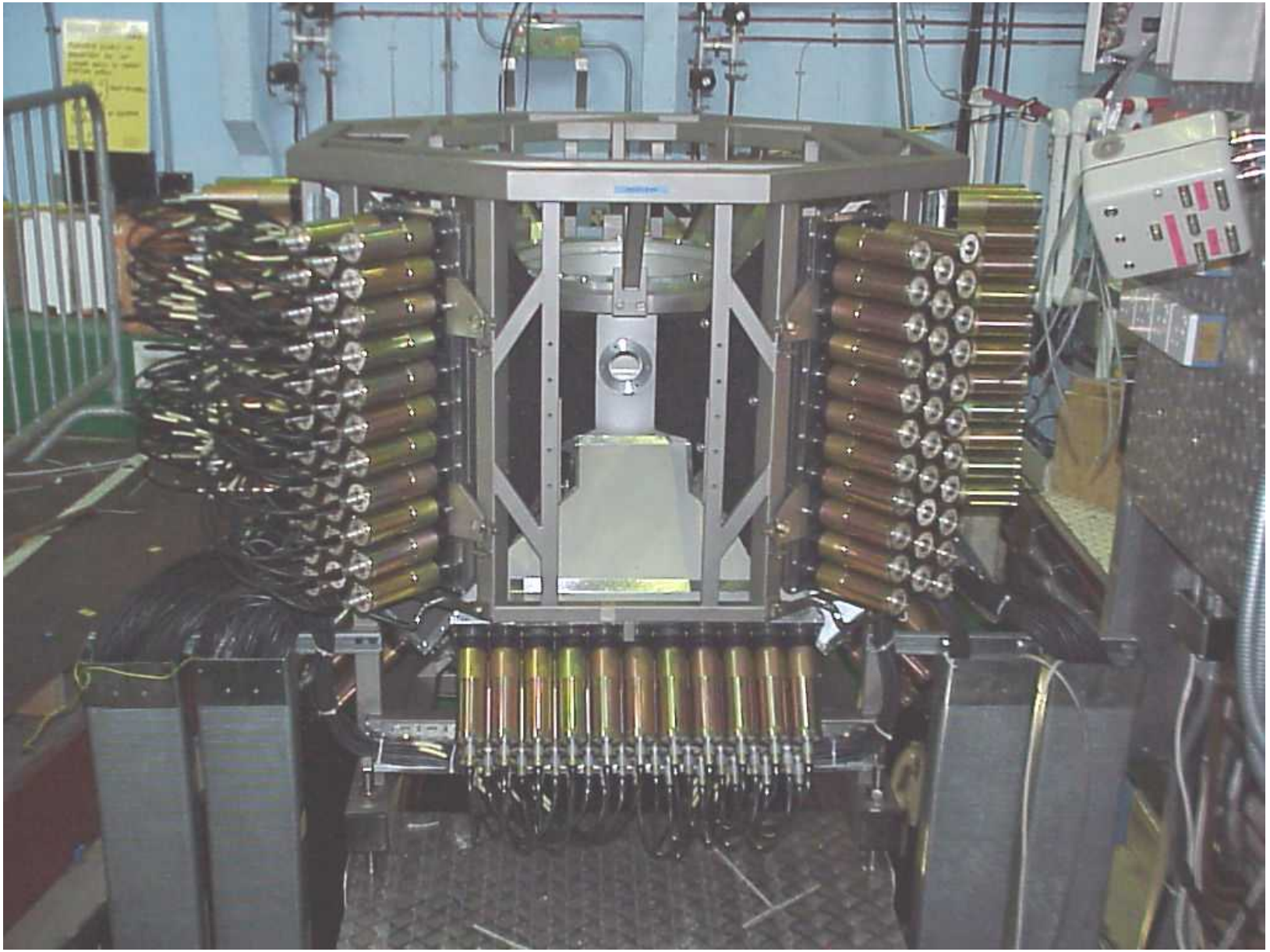


Typical neutron Laue pattern from $(C_5Me_4(SiMe_3)\text{-}Y)_4H_{11}[C_5Me_4(SiMe_3)*W]$, Stewart, Bau *et al.*

Ewald Spheres



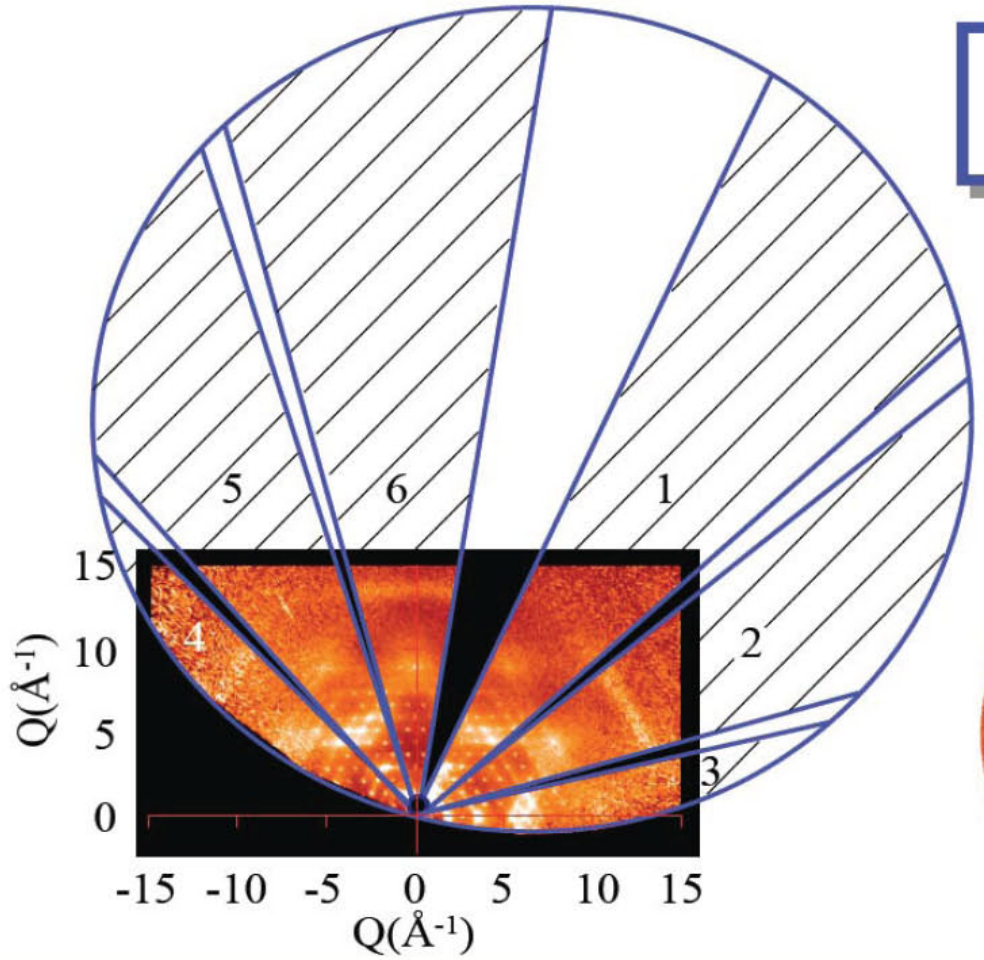
SXD - ISIS

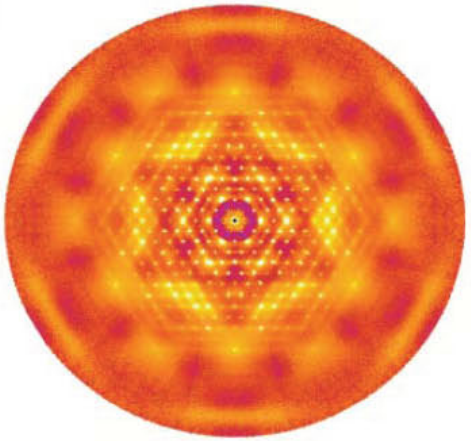


SXD in practice

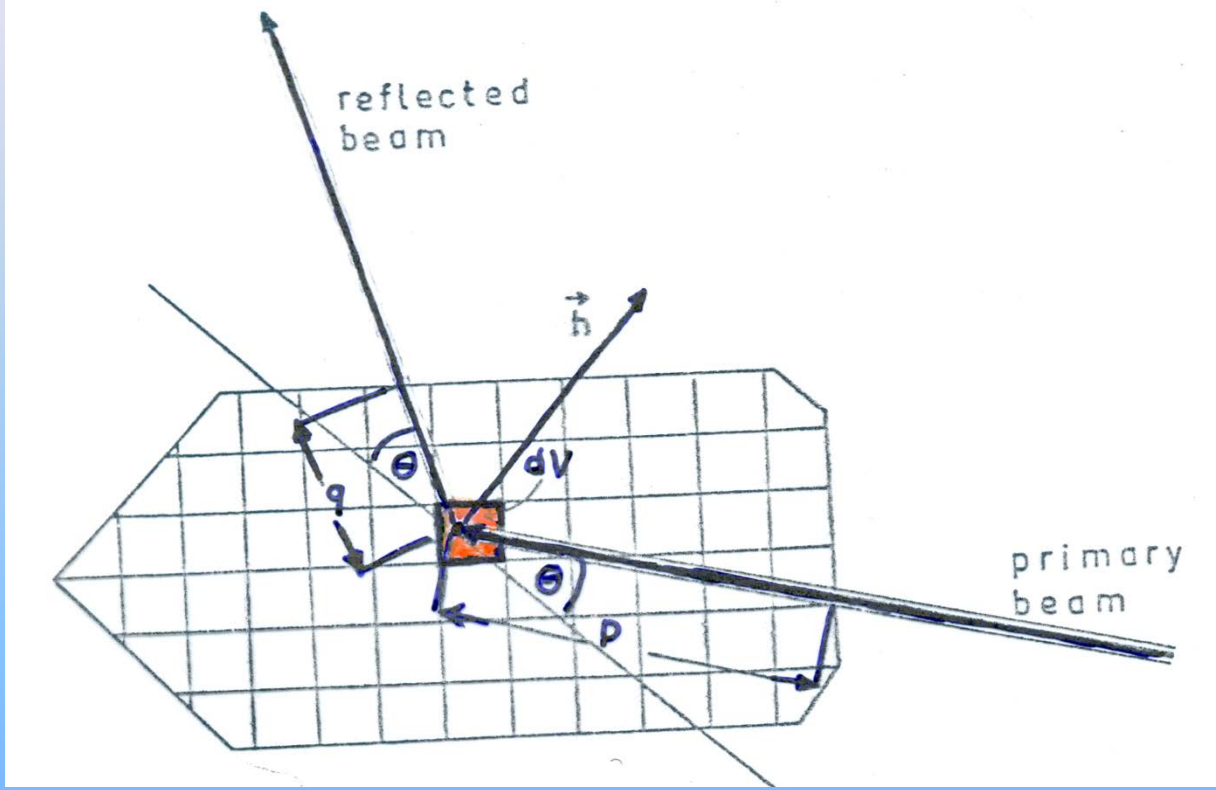
AN SXD DATA 'FRAME'

BENZIL on SXD 001 vertical, one crystal setting, six equatorial detectors.





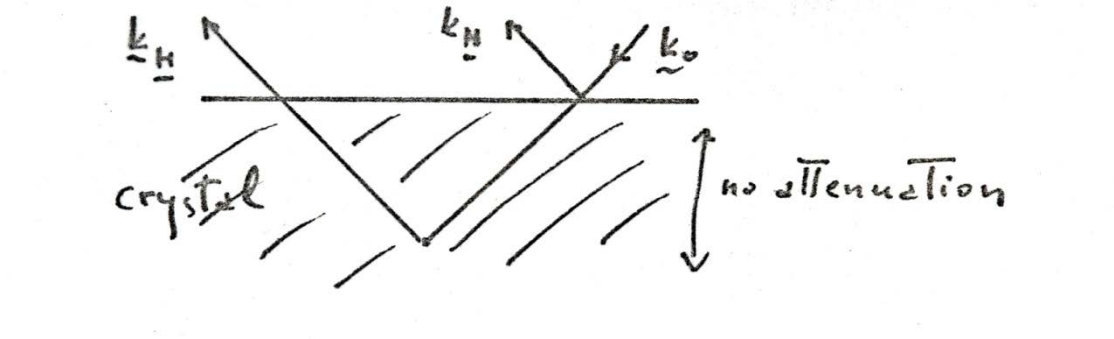
Absorption



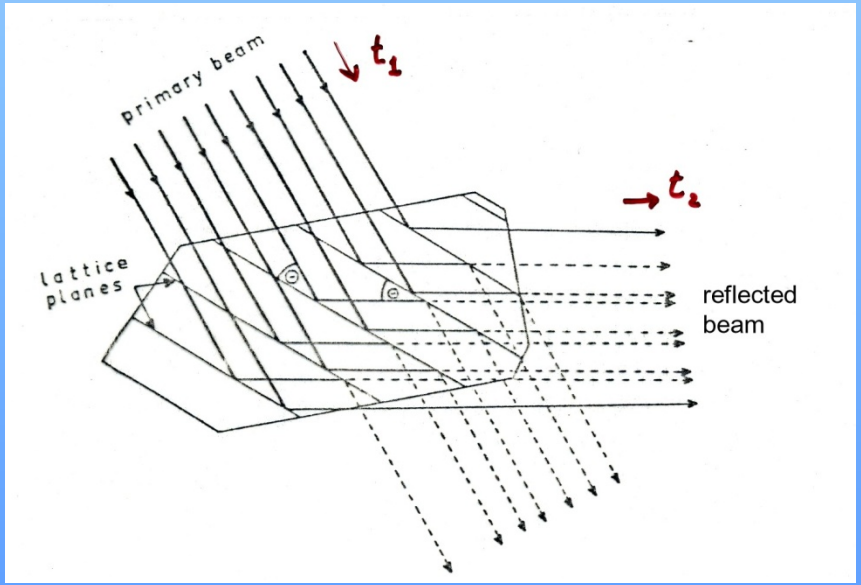
$$A = \frac{1}{V}\int_V e^{-\mu(p+q)}dV$$

Extinction I

- **Reduction of Intensity by scattering not by absorption**



- **Primary Extinction**: Weakening of Intensity by Multiple Reflections in the Crystal



Extinction I

Zachariasen 1967

1) Spherical Crystal
2) Ideal Perfect Crystal

$$\frac{\partial I_0}{\partial t_1} = -\sigma I_0 + \sigma I$$

$$\frac{\partial I}{\partial t_2} = -\sigma I + \sigma I_0$$

σ ≡ diffracting power

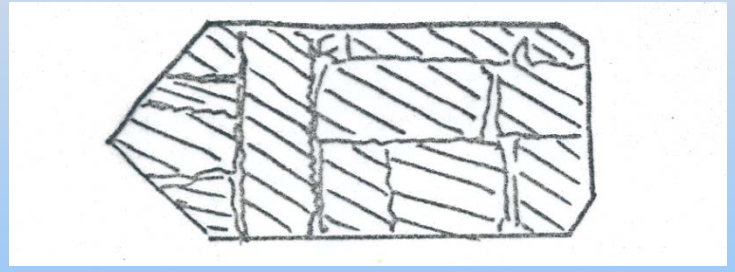
$$\text{Intensity reduction } \phi(\sigma) = \frac{1}{1+\sigma t}$$

Extinction II

- **Secondary Extinction**: **Weakening of the beam due to the shielding of the inner planes by the outer planes**
- **Most important for strong reflections at low sinθ/λ**

Mosaic Crystal

Zachariasen 1967



Zachariasen 1967

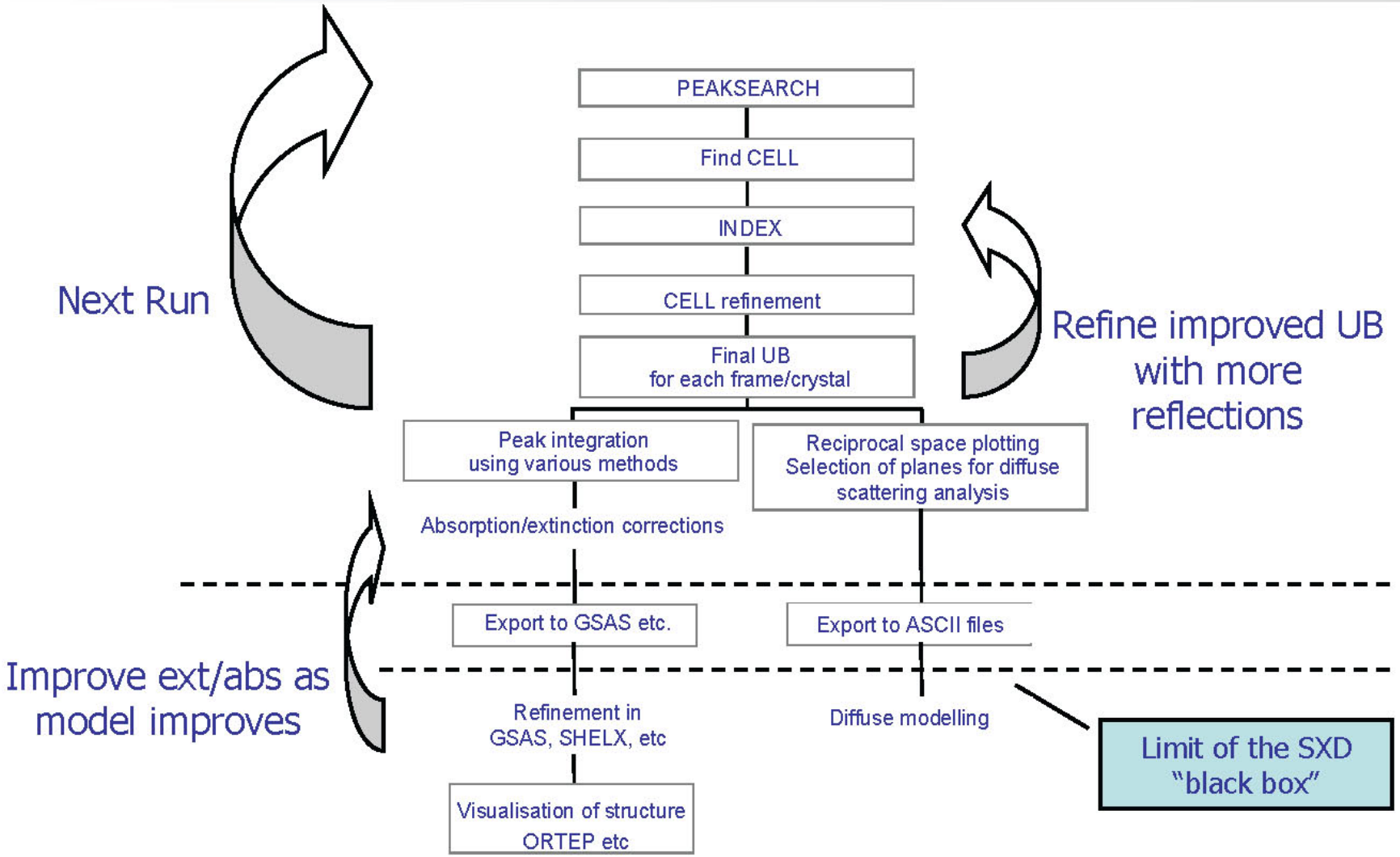
Type I
Depends mainly on *g*
(mosaic spread)

Type II
Depends mainly on *t*
(radius of mosaic blocks)

$$I = I_{obs}(1 + 2gI_{calc})$$

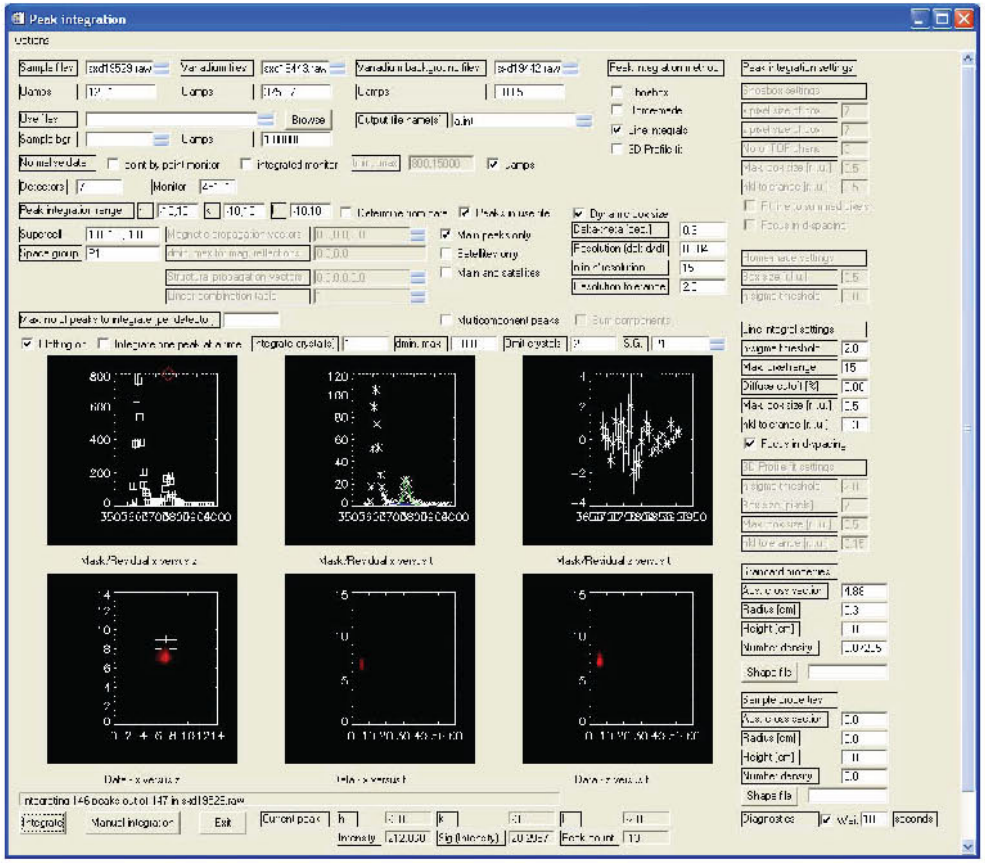
$$F_{crctd} = F_o\{k[1 + 0.001|F_c^2|\lambda^3/\sin 2\theta]^{-1/4}\}$$ (Shelxl)

SXD data processing

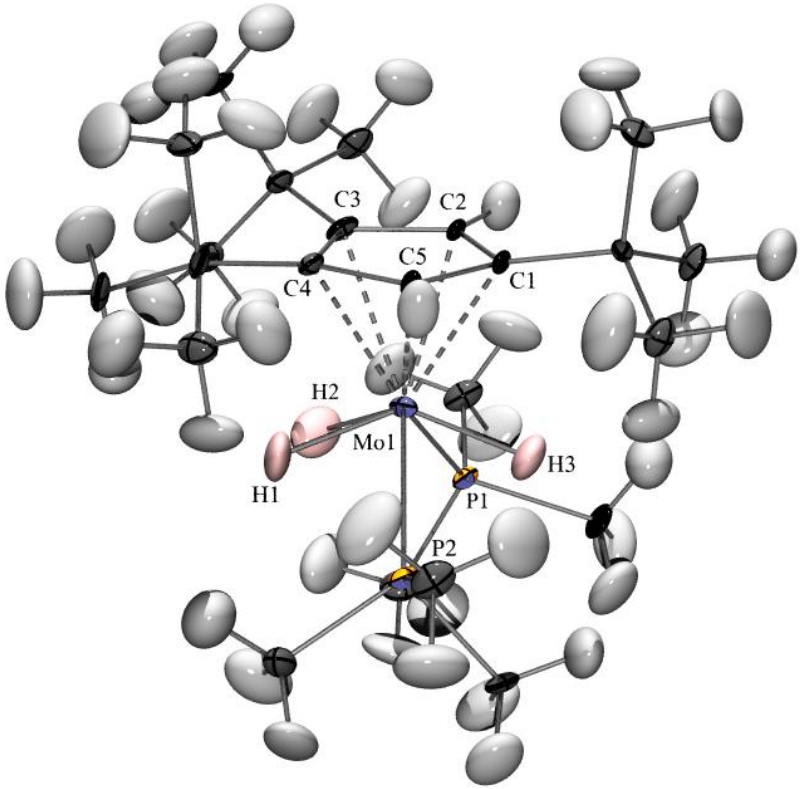


Peak integration

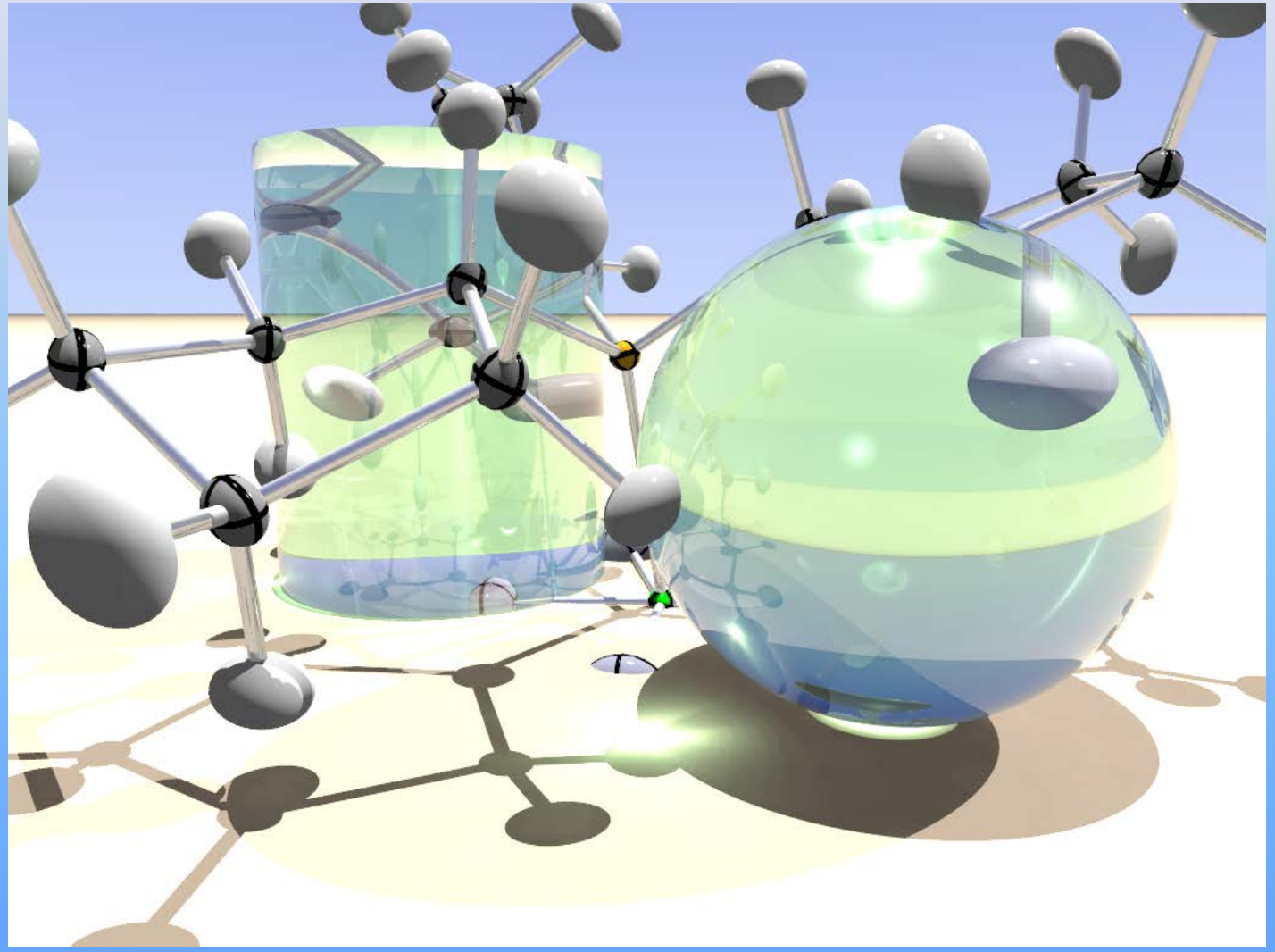
- Choice of three algorithms
  - Shoebox
  - Dynamic box
  - 3D Gauss ellipsoid
- Manual integration
- Information about resolution used
- Gives directly F^2
- Propagation vectors can be used

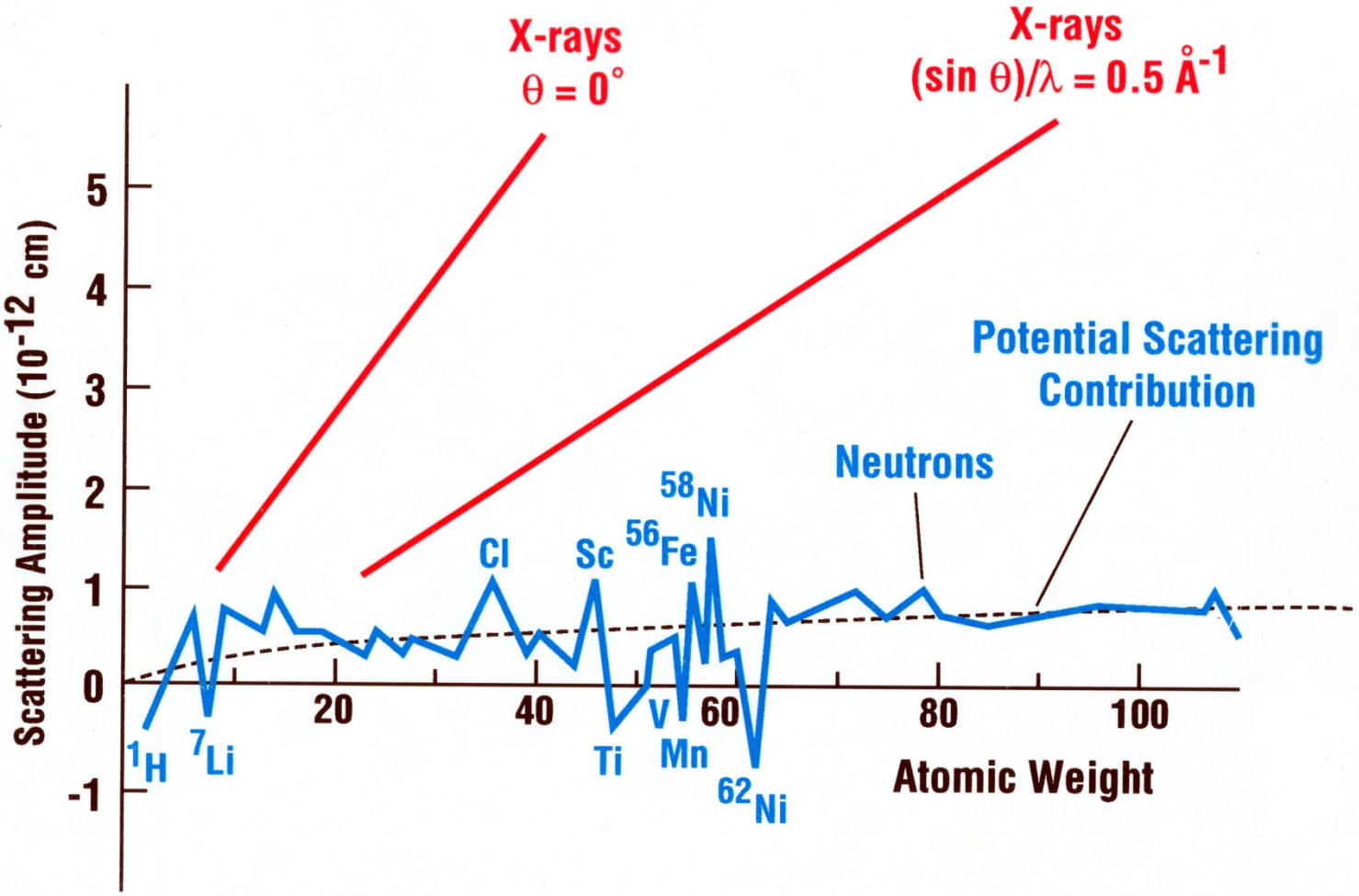


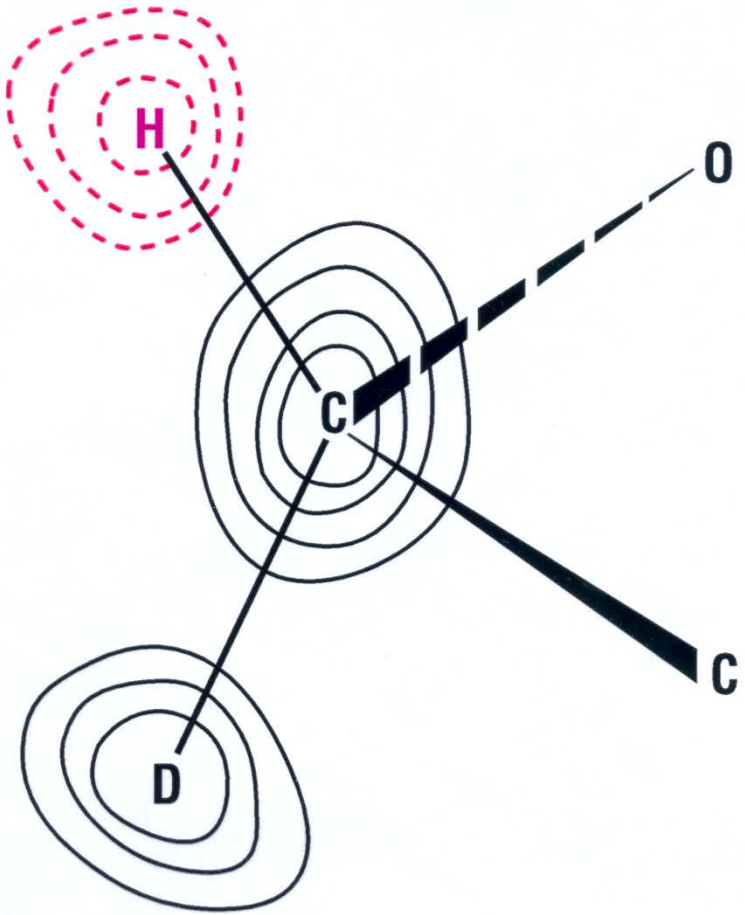
(cp*)Mo(H)$_3$L$_2$ SXD Data



Applications

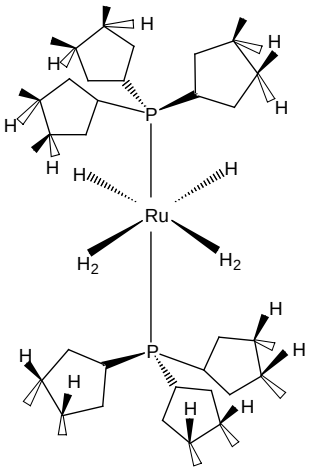



X-rays
θ = 0°
X-rays
(sin θ)/λ = 0.5 Å-1
Potential Scattering
Contribution
Neutrons
Scattering Amplitude (10-12 cm)
5
4
3
2
1
0
-1
20
40
60
80
100
Atomic Weight
1H
7Li
Cl
Sc
Ti
V
56Fe
Mn
58Ni
62Ni



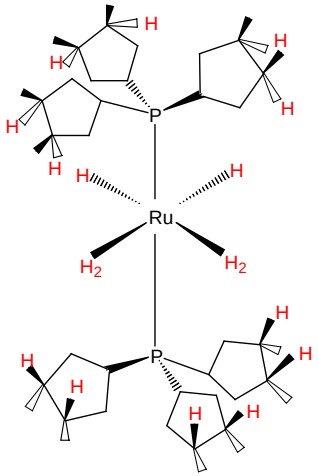
+ neopentyl-1-*d* alcohol (S)
(yeast alcohol dehydrogenase)

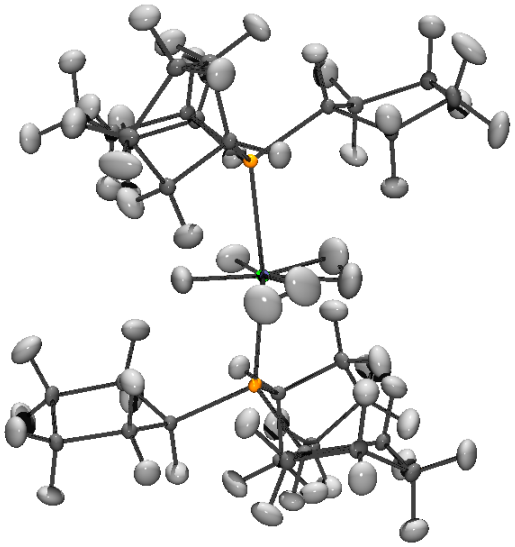
H – D Selective Exchange

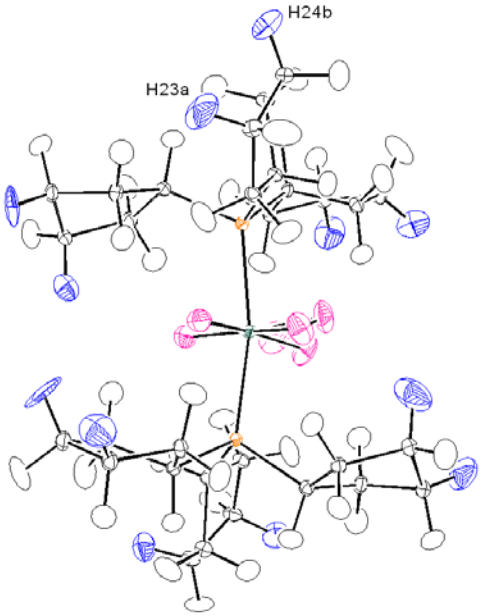


H_2 / D_2

DX

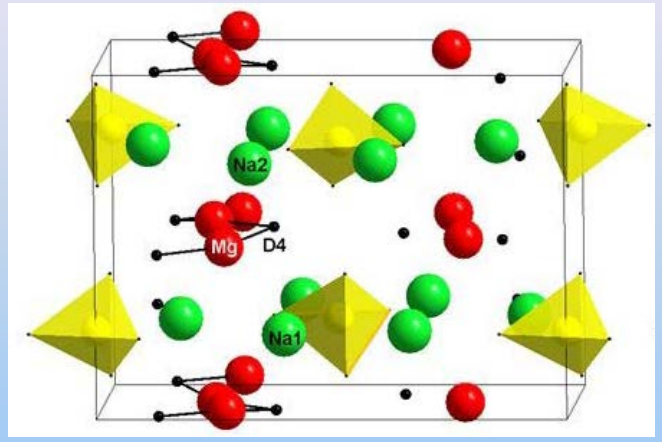




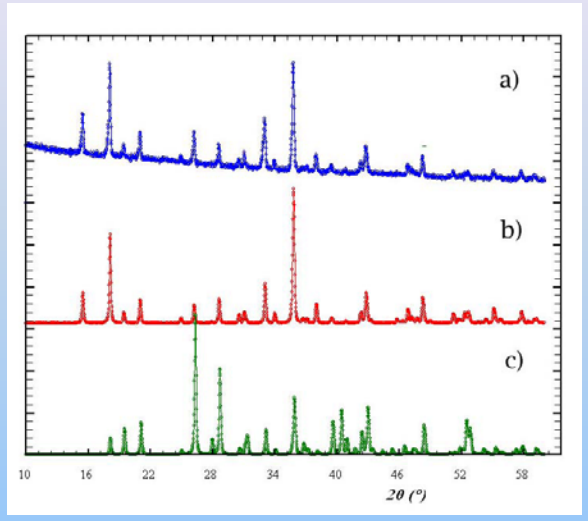


S.o.f.'s D_2/H_2 or H > 0.9 CD/CH = 0.7

The Structure of $Na_2Mg_2NiH_6$

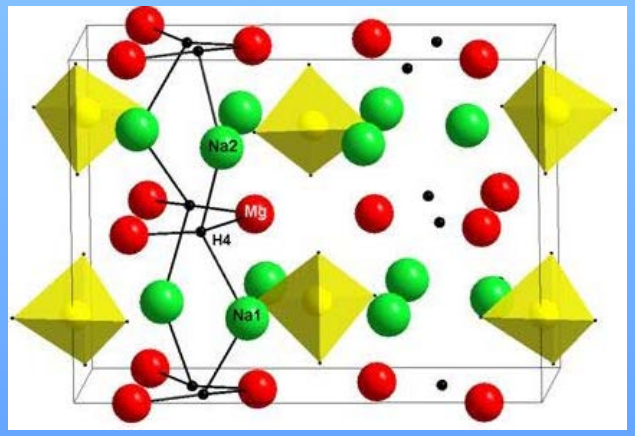


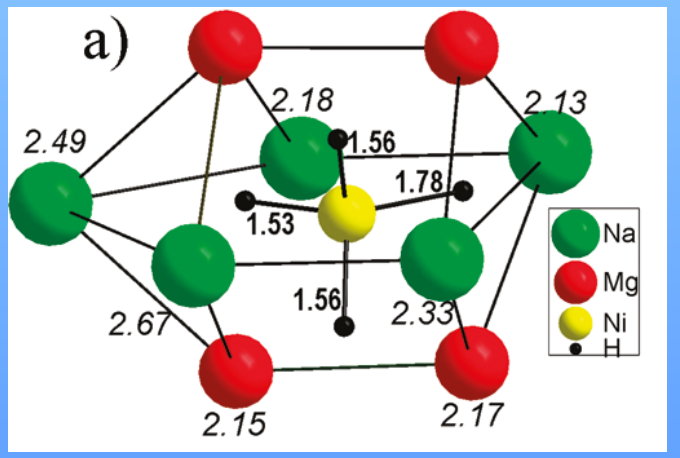
Na – Mg 2.66 Å
Na – H ~ 3.3 Å
Mg – H > 2.72 Å



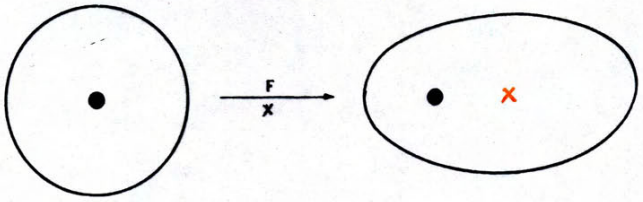
b_{coh} (Mg) = 5.375(4)
b_{coh}(D) = 6.674(6)

a) exp. XRD pattern b) correct model c) Mg/D



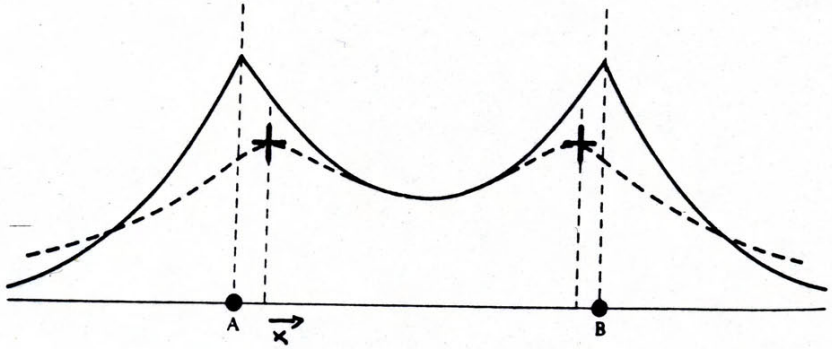


K. Yvon & al. Inorg Chem. 48, 5052 (2009)



$\bar{x}$ = shift from the nucleus . F ≡ electric field

$$\bar{x} = \frac{q F}{e} \qquad \bar{x} = 4.5\, q_0^3 / R^2 \qquad \left\{ \begin{array}{l} \bar{x} = 0.03 \text{ Å} \\ R = 5.0 \text{ Å} \end{array} \right.$$



Charge density along the axis for vibrating and non-vibrating H_2^+.
The crosses denote 'apparent' positions of the nuclei.

for each electron:

$$\chi = (\phi_A + \phi_B) / \sqrt{2(1+S)}$$

$$\rho = \chi^2 = \phi_A^2 + \phi_B^2 - \frac{S}{1+S}(\phi_A^2 + \phi_B^2) + \frac{2}{1+S}\phi_A \phi_B$$

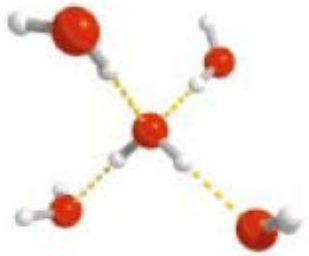
$$\bar{x} = \int x \rho \, d\tau$$

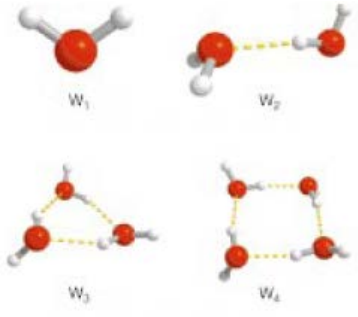
X-ray vs. Neutron Diffraction

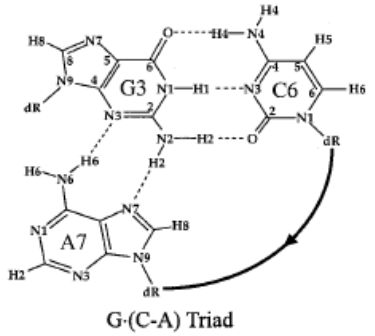
Systematic Differences in Observed Bond Separations

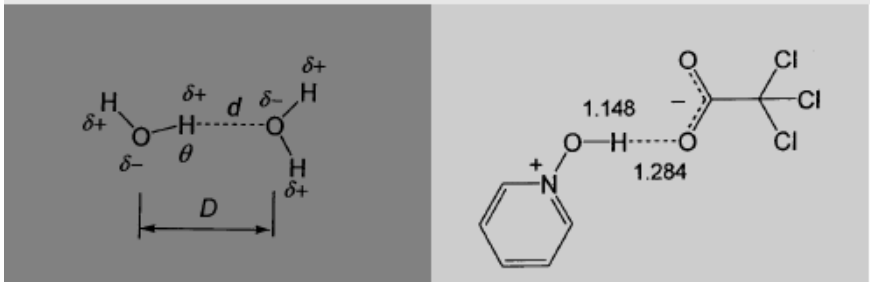
C – H	– 0.096 (7) Å	
O – H	– 0.155 (10) Å	
C = C	– 0.005 (1) Å	
C = C	– 0.008 (2) Å	*(benzenoid)*
C – OH	0.005 (1) Å	
C – O	0.008 (2) Å	

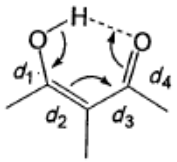
A Few Types of Hydrogen-Bonds

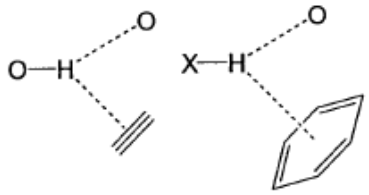


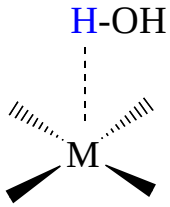


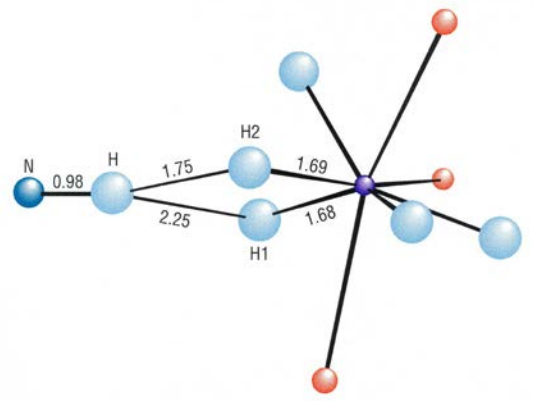




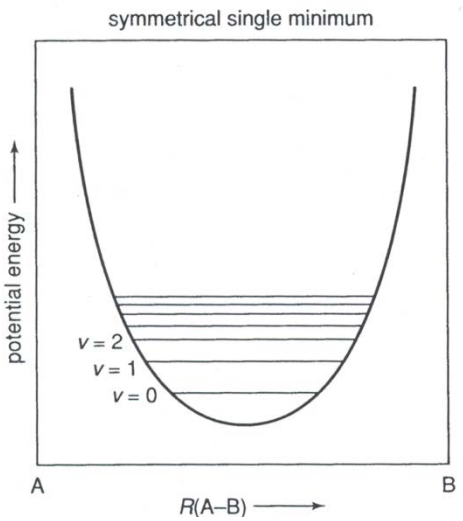


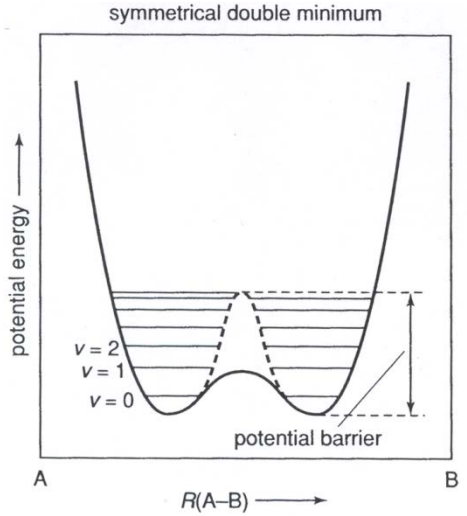


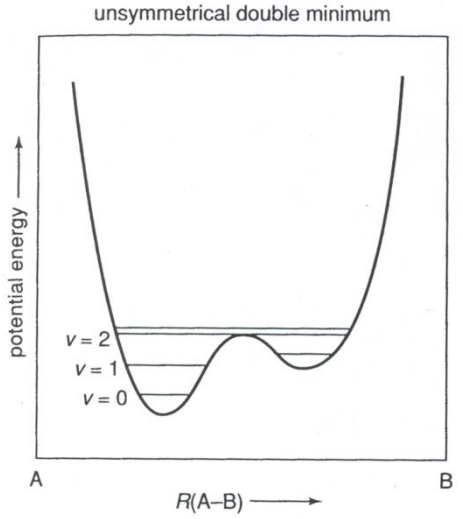


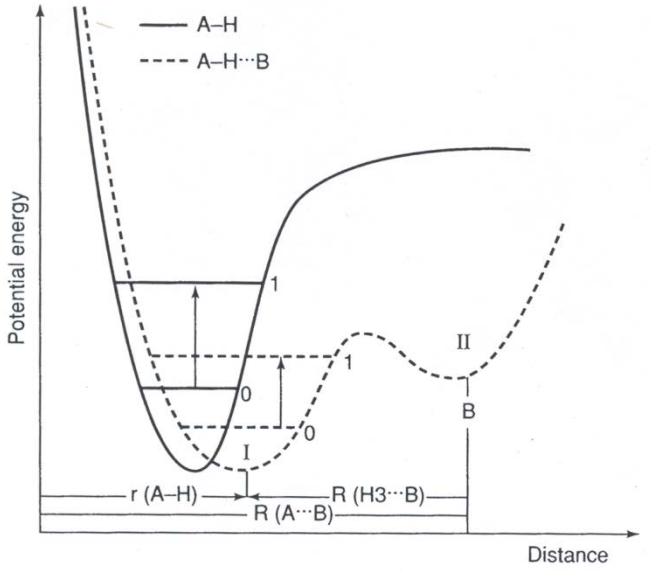


Potential Energy Landscapes for Hydrogen Bonds

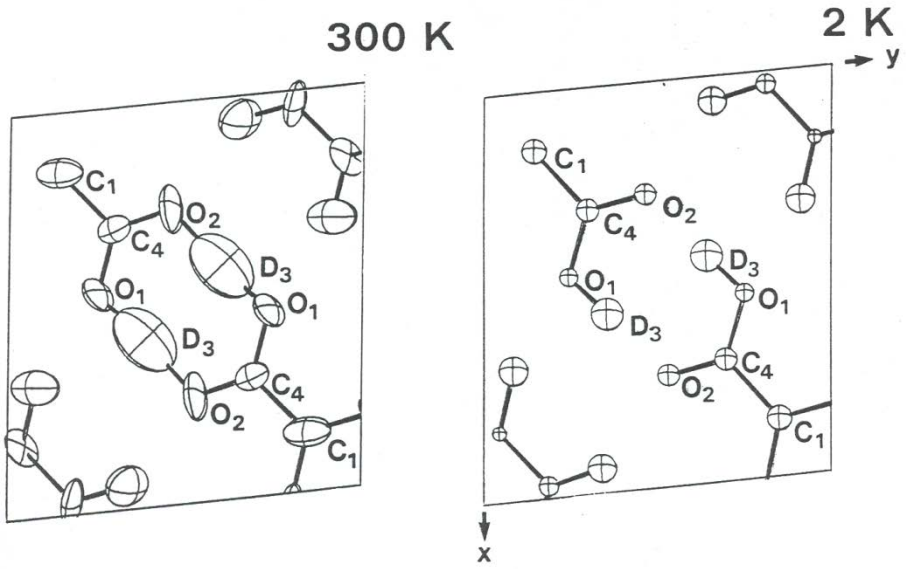


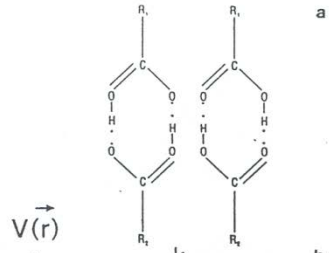


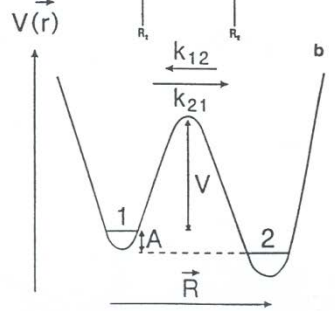




Proton Transfer in Terephtalic Acid







B.H. Meier & al., *Chem. Phys. Lett.* 108, 522 (1984)

KH_2PO_4 (KDP) – Ferroelectric Phase Transition

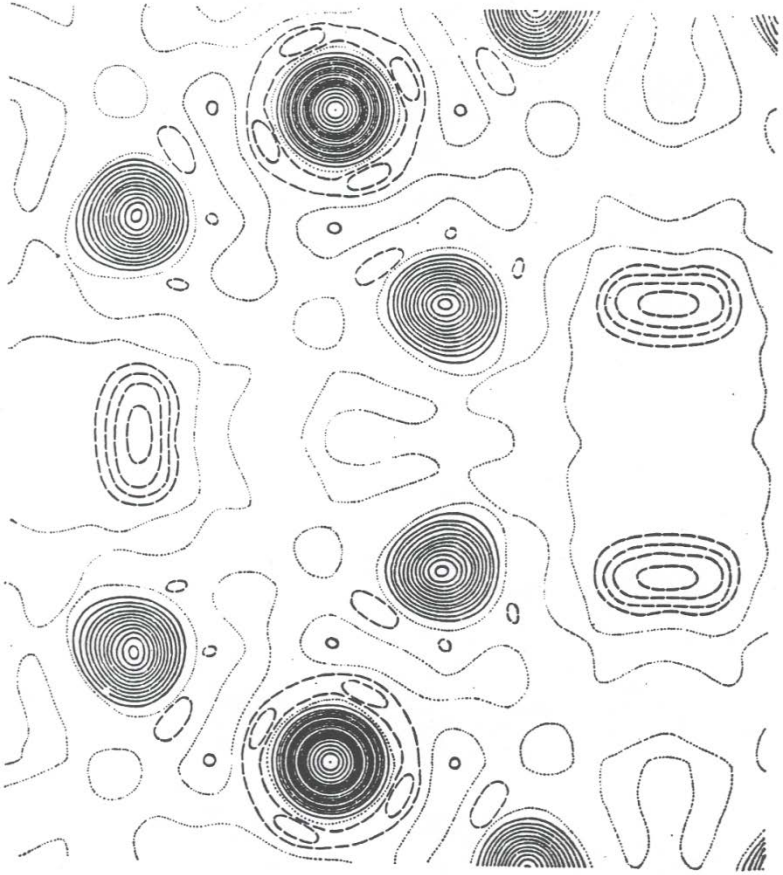
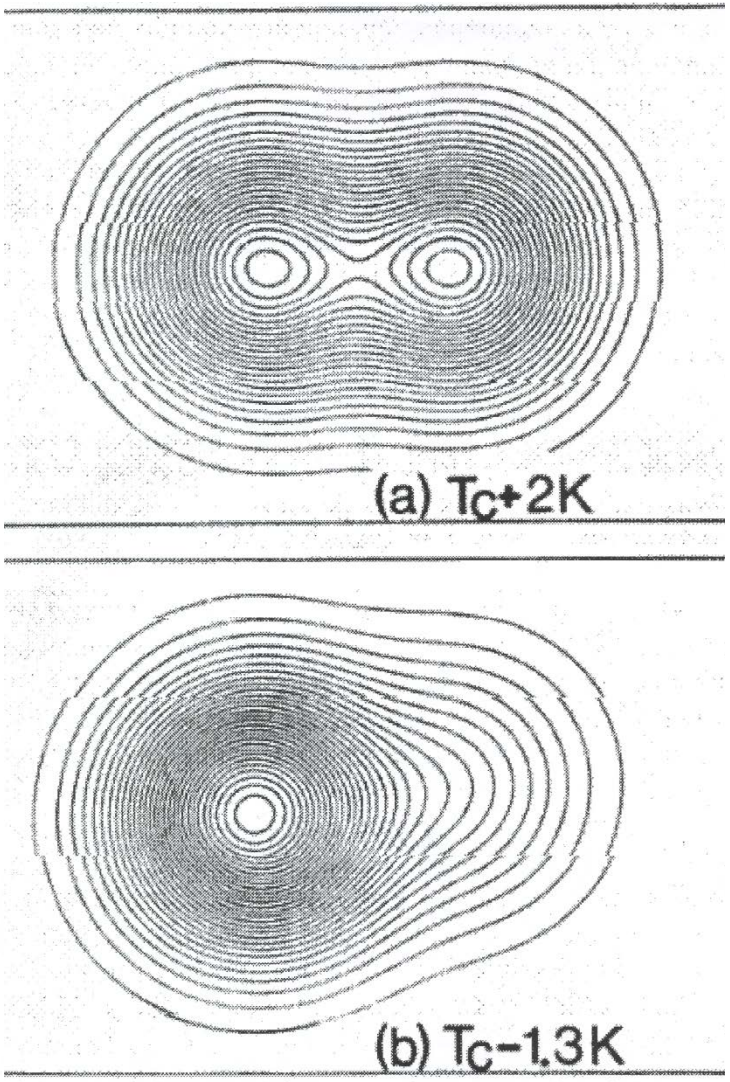
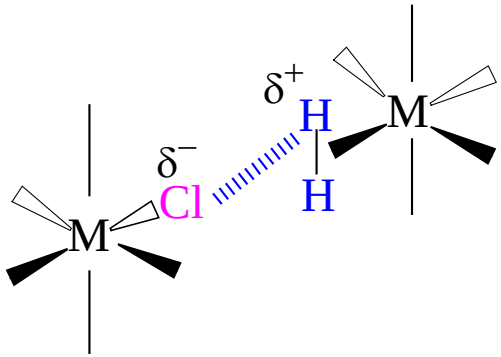


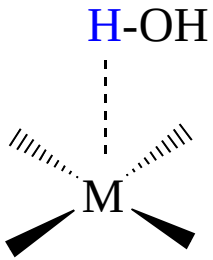
FIG. 107. A Fourier projection of the scattering density on the (001) plane of KH_2PO_4 at room temperature. Contours are at intervals of 50 units, with additional contours at −75, −125. Full lines are positive, broken lines are negative, and dotted lines are zero contours. The most intense peaks are superimposed K, P. The other positive peaks are O: the negative peaks H. (Bacon and Pease, 1953.)

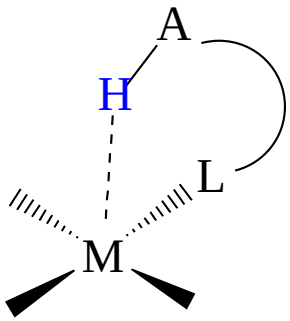


Non-Classical "Weak" Interactions

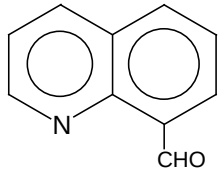
$L_n M—H^{\delta-} \cdots {}^{\delta+}H—A$

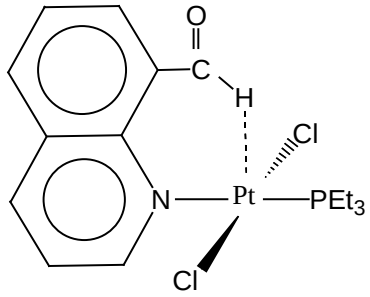






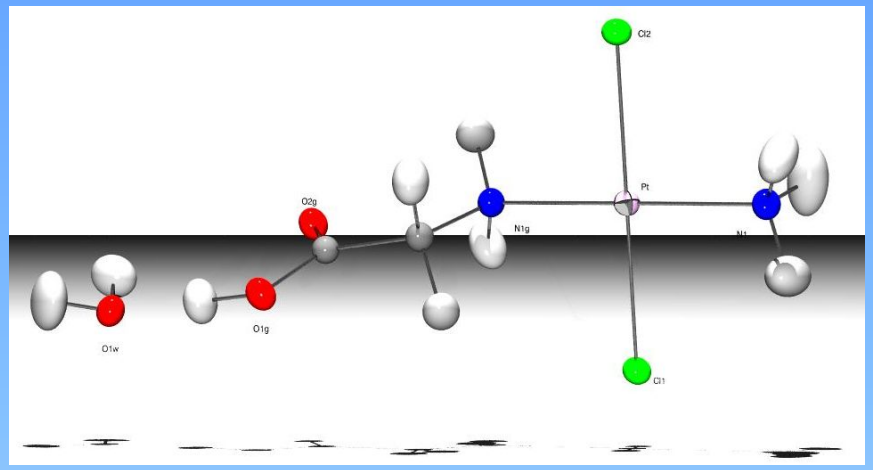
HA L =



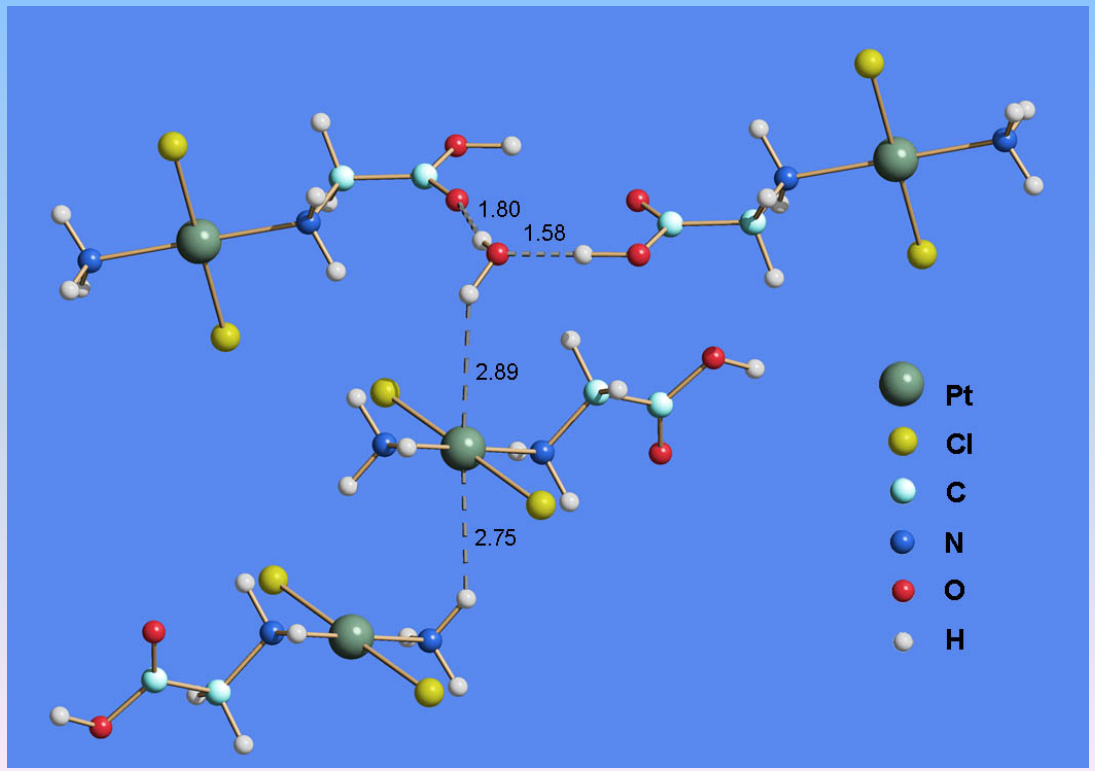


$d_{(M\cdots H)} \approx 2.5 - 2.9$ Å

$Pt(NH_3)(gly)Cl_2 \cdot (H_2O)$



1.30 x 0.50 x 0.50 mm



D19 @ 20K

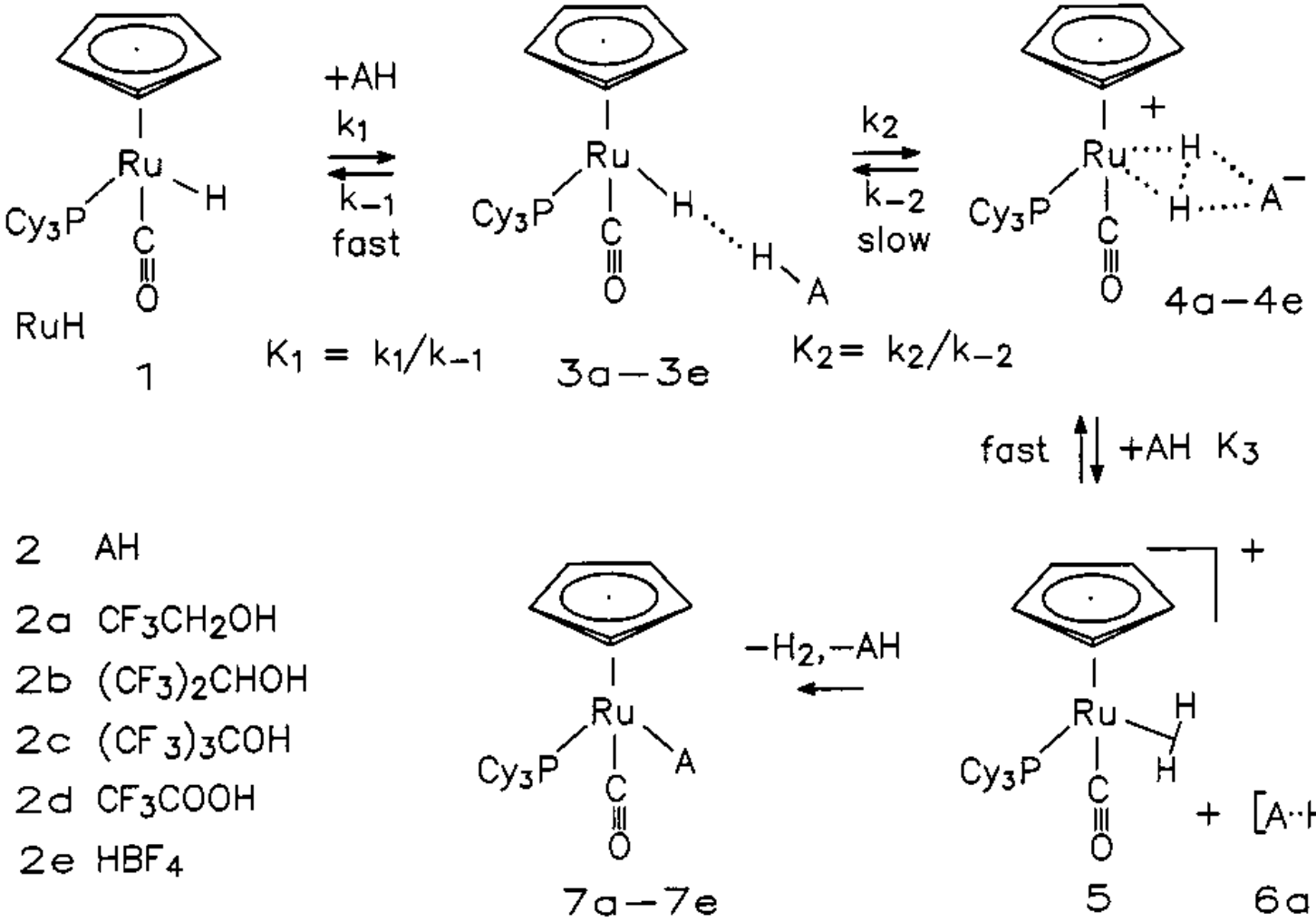
Pt – N1 2.040(2) Å

Pt – H1 2.89(1) Å

N – C 1.480(3) Å

Angew. Chem. Int. Ed. **2010**, *49*, 7440

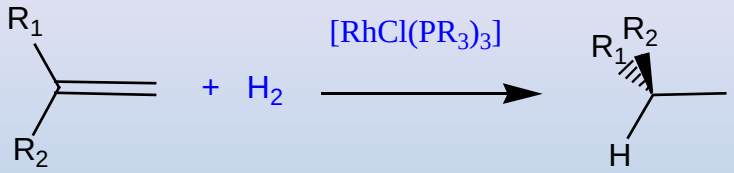
Proton Transfer to $CpRuH(CO)(PCy_3)$



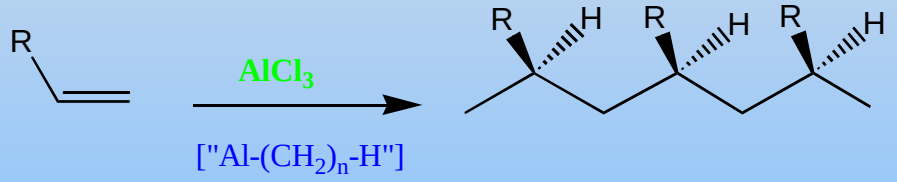
Shubina, Limbach & al. *Eur. J. Inorg. Chem*. (2001) 1753

Reactions Involving Hydrido-Complexes

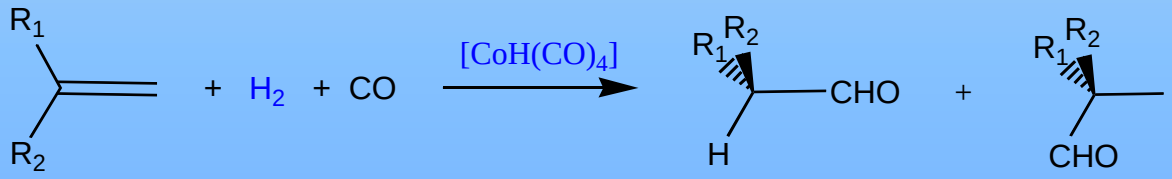
Homogeneous Hydrogenation



Olefin Polymerization



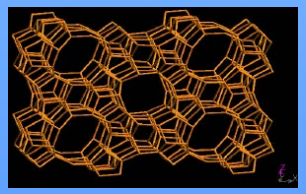
Olefin Hydroformilation



Materials for Hydrogen Storage

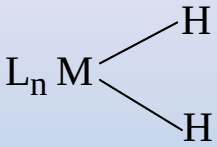
(new entry)

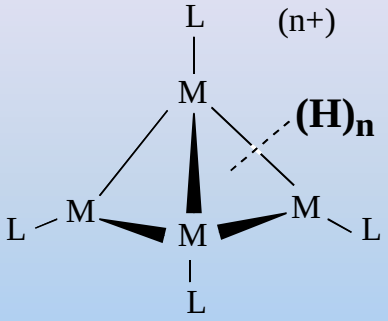
$$NaAlH_4 \overset{TiX_3}{\rightleftarrows} \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2$$



Types of Metal - Hydrogen Interactions.

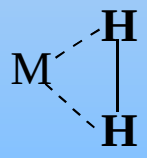
Classical Metal Hydrides:

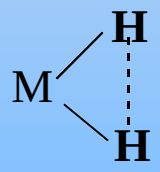




$L_n M—H_{(n)}—ML_n$

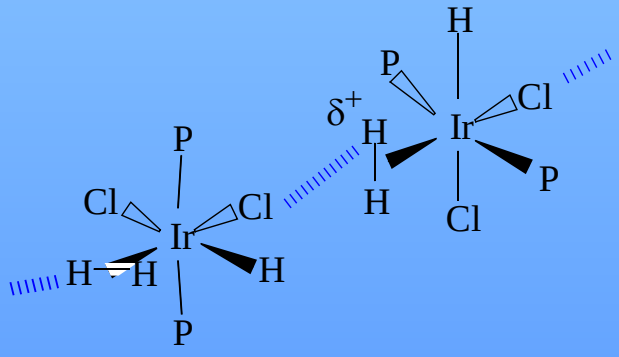
"Non-Classical" Metal Hydrides:





Non-Classical "Weak" Interactions:

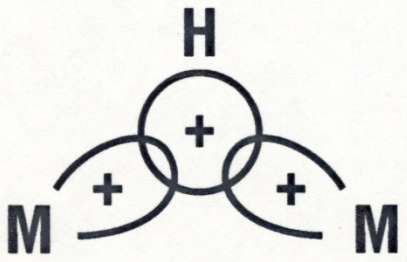
$L_n M—H^{\delta-} \cdots {}^{\delta+}H—X$



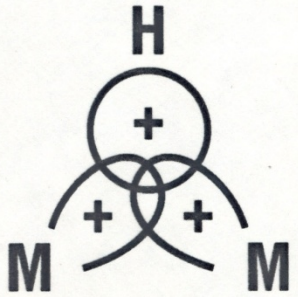
Structural Features of Complexes with Bridging Hydride Ligands

The M-H-M´ bond is bent to a greater or lesser extent depending on the extent of the direct M-M´ interaction.

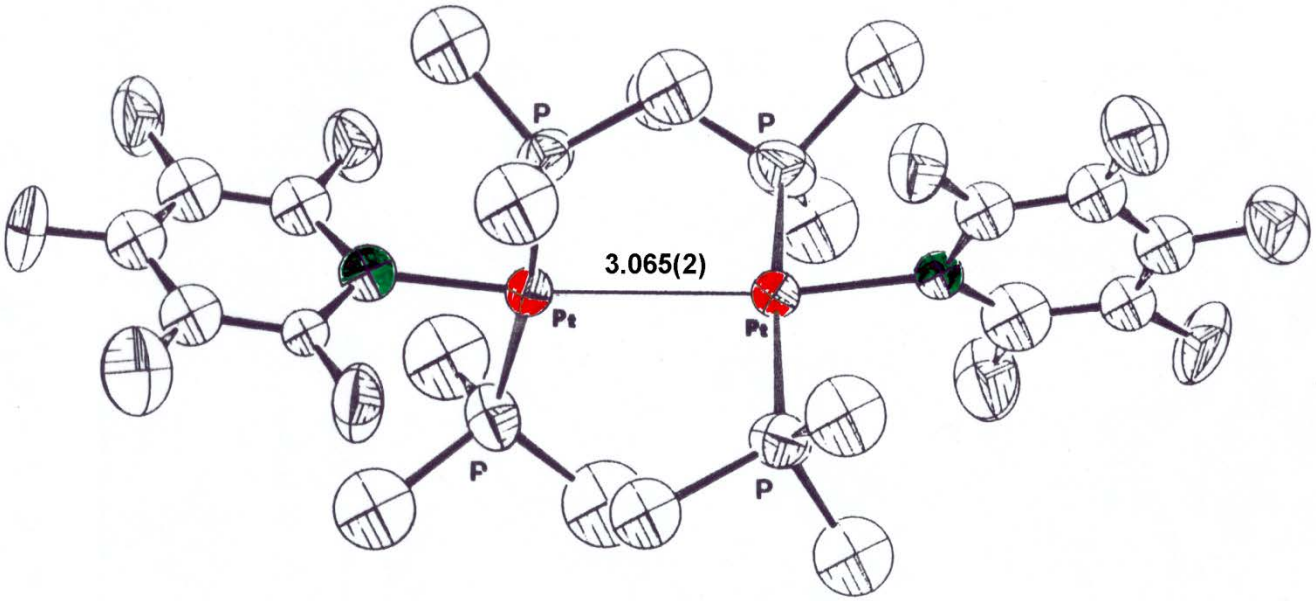
Weak M-M´ Interactions ("Open")



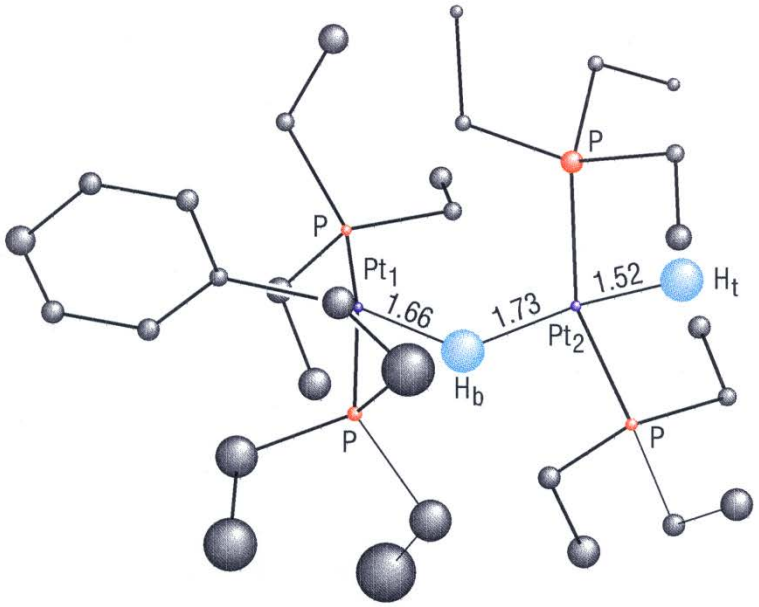
Strong M-M´ Interactions ("Closed")



X-ray Structure of $[(Cl_5C_6)(PMet_3)_2Pt\text{-}H\text{-}Pt(PMet_3)_2(C_6Cl_5)]^+$



$[H_2Pt_2Ph(PEt_3)_4]^+[BPh_4]^-$
13K Neutron Diffraction Study



$Pt_1 \cdots Pt_2$ 3.05(1) Å

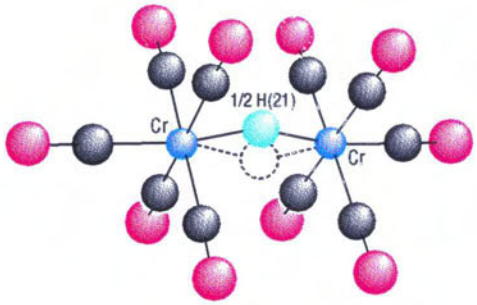
$\measuredangle Pt_1 - H_b - Pt_2$ 128(2)°

Ricci, Albinati and Koetzle (1995)

Structural Features of Complexes with Bridging Hydride Ligands

Weak M-M´ Interactions ("Open")

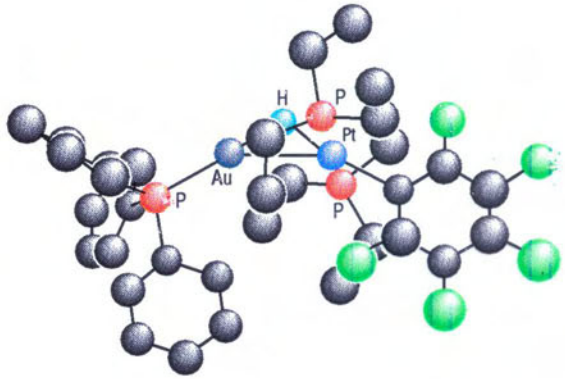
$[(CO)_5Cr(\mu\text{-}H)Cr(CO)_5]^-$



Cr-H-Cr = 145.2(3) - 158.9(6)°

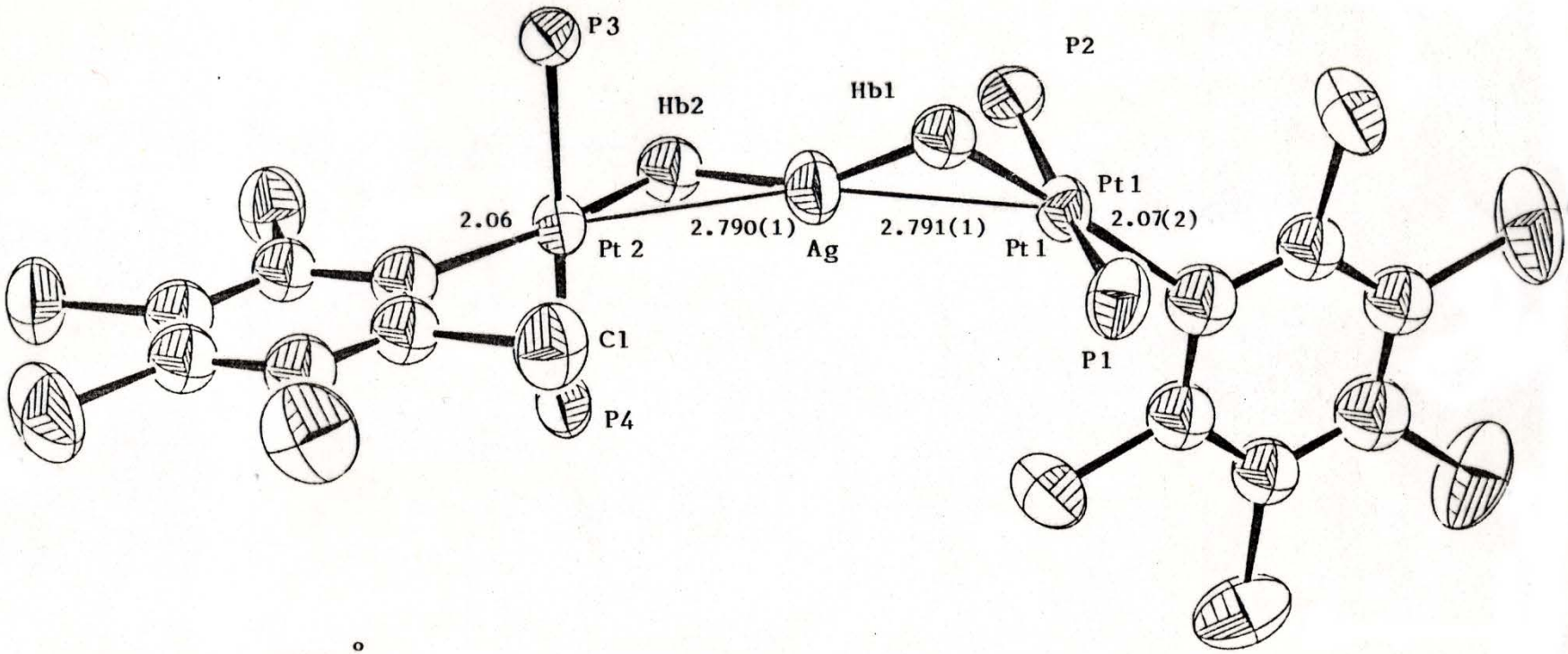
Weak M-M´ Interactions ("Closed")

$[(PPh_3)Au(\mu\text{-}H)Pt(C_6F_5)(PEt_3)_2]^-$



Au-H-Pt = 103(4)°

X-ray Structure of $[(Cl_5C_6)L_2Pt - H - Ag - H - Pt(C_6Cl_5)]^+$ (R.T. data)

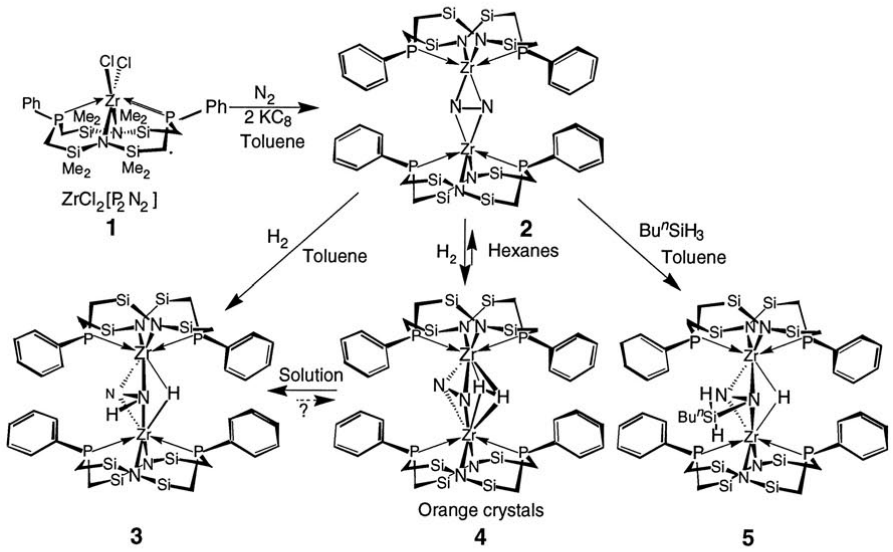


Pt1 – Hb1	1.70(8)	Å
Pt2 – Hb2	1.80(10)	
Ag – Hb1	1.79(11)	
Ag – Hb2	1.62(14)	
Pt1 – P1	2.311(5)	
Pt1 – P2	2.330(5)	
Pt2 – P3	2.334(6)	
Pt2 – P4	2.306(6)	

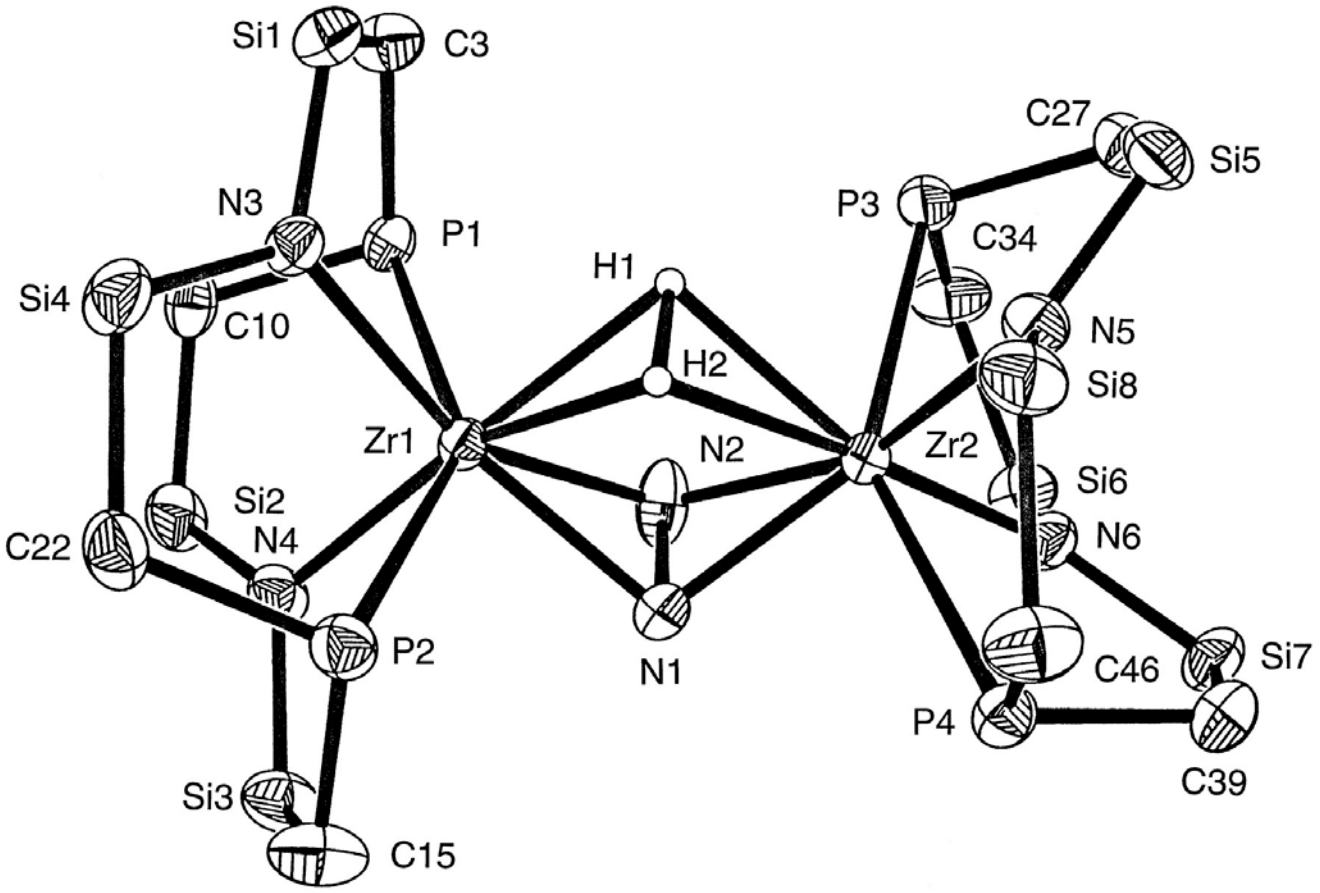
Pt1 – Ag – Pt2	166.04(4)	°
Ag – Pt – C_{av}	148.5 (7)	°

Pt – Hb – Ag	107 (1)	°
Hb1– Ag – Hb2	152 (2)	°

Scheme for the Preparation of N_2 and "H_2 "Complexes from $ZrCl_2[P_2N_2]$

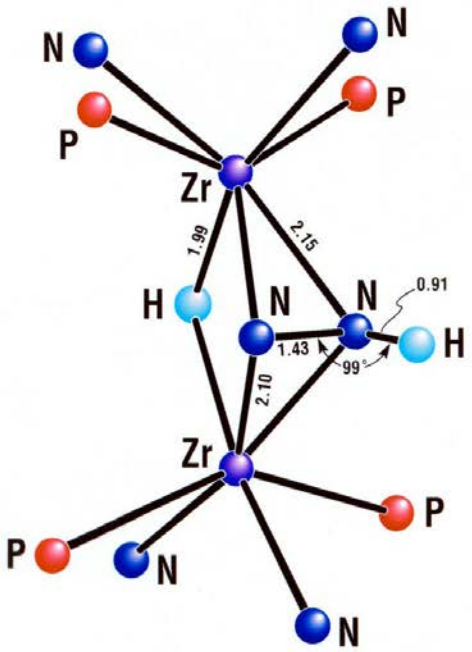


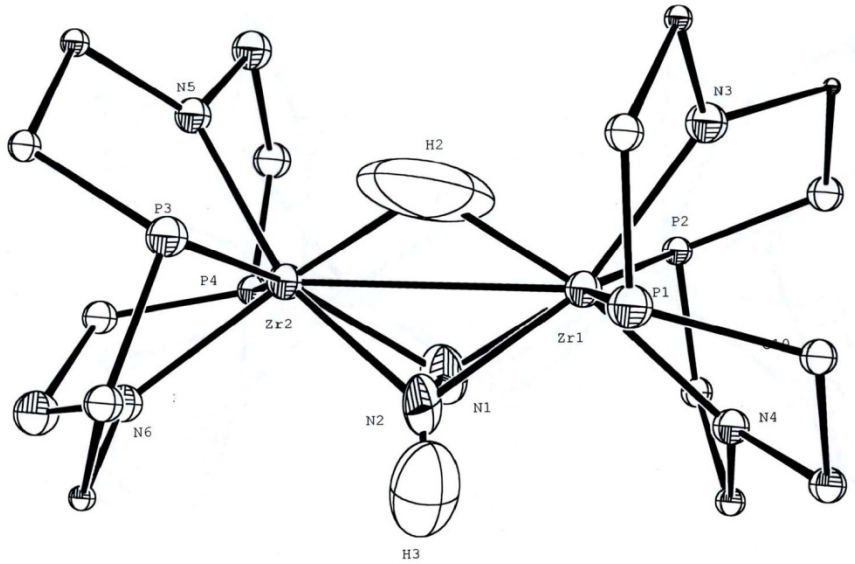
M.D. Fryzuk, V.G. Young & al. Science, **1997**, *275*, 1445


Si1
C3
N3
P1
Si4
C10
C22
Si2
N4
P2
Si3
C15
Zr1
H1
H2
N2
N1
C27
Si5
P3
C34
N5
Si8
Zr2
Si6
N6
C46
Si7
P4
C39

$[P_2N_2]Zr(\mu\text{-}N_2H)(\mu\text{-}H)Zr[P_2N_2]^*$

Neutron Structure at 25 K

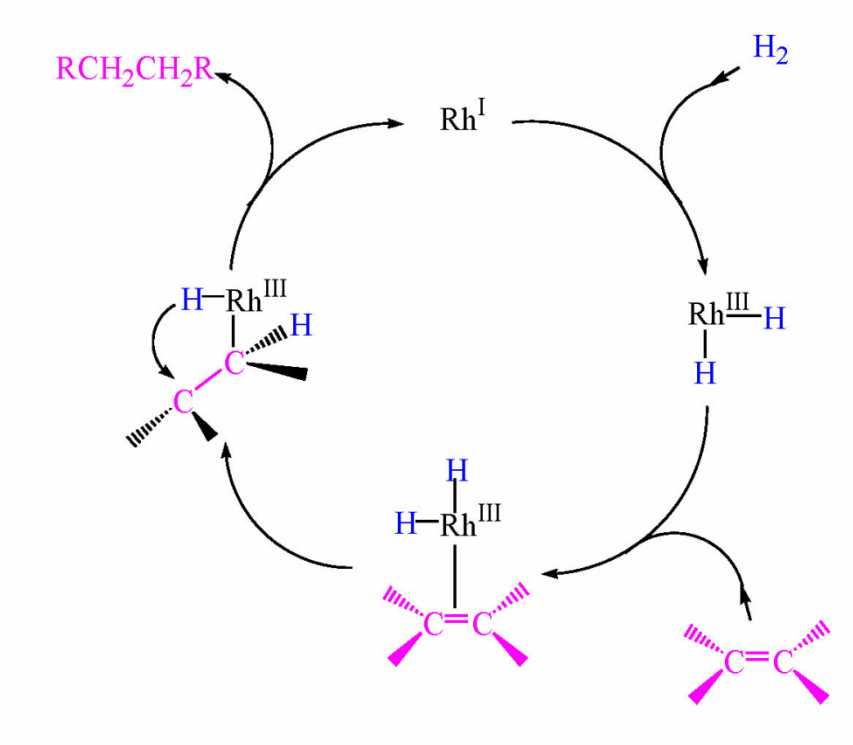




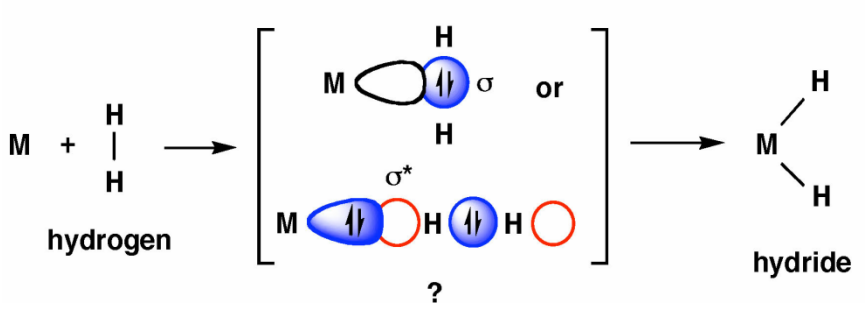
Albinati, Fryzuk, Klooster, Koetzle and Mason (1998)

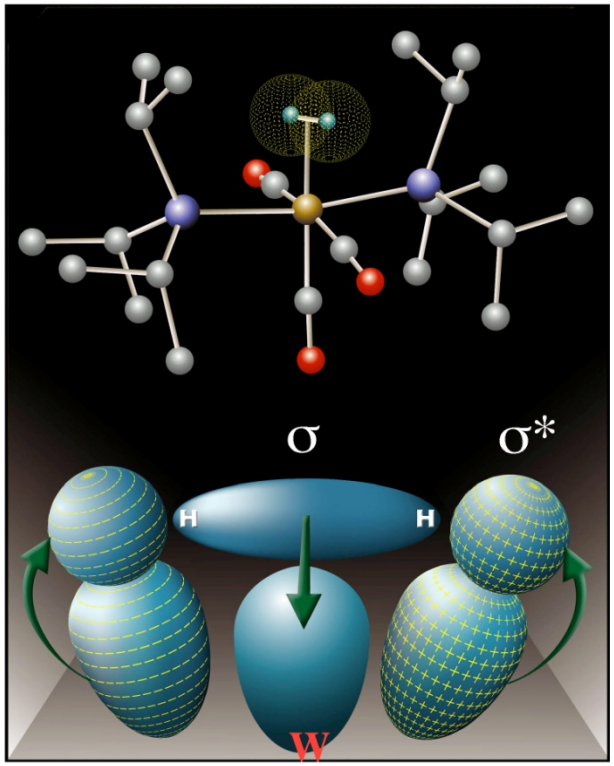
*$[P_2N_2]$ = $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$

Schematic Catalytic Cycle for Homogeneous Hydrogenation



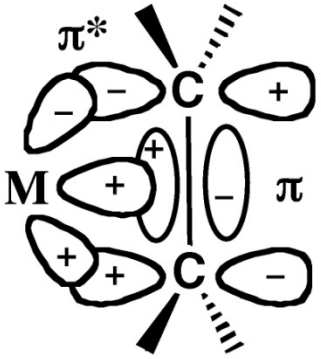
Metals break H-H bonds but HOW?





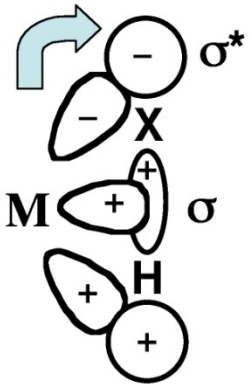
Bonding in $W(CO)_3(P^iPr_3)_2(H_2)$: ***donation of the bonding σ electrons in H_2*** **to a filled metal d orbital and backdonation to the antibonding orbital (σ*) of H_2**

backdonation is critical in stabilizing H_2 and other σ complexes



M–π bond

olefin complex

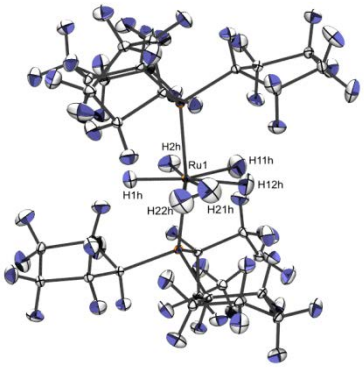


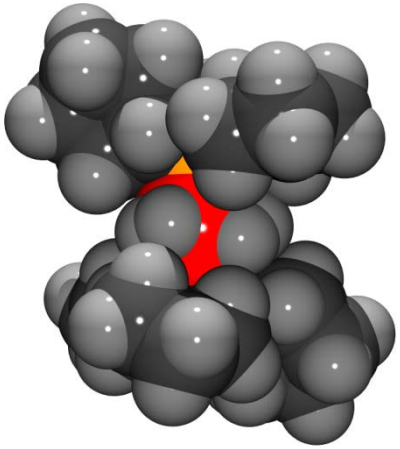
M–σ bond

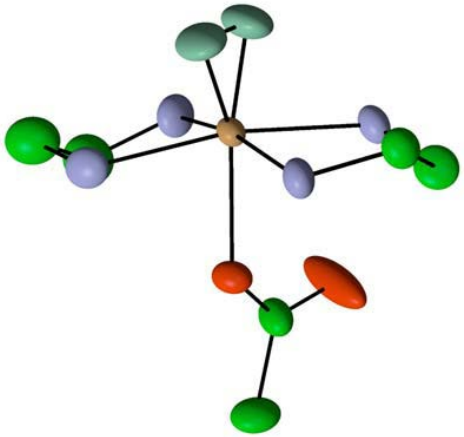
X = H, C, Si, etc

Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466.

H-H Distances (Å) from Single *XXl* Neutron Diffraction

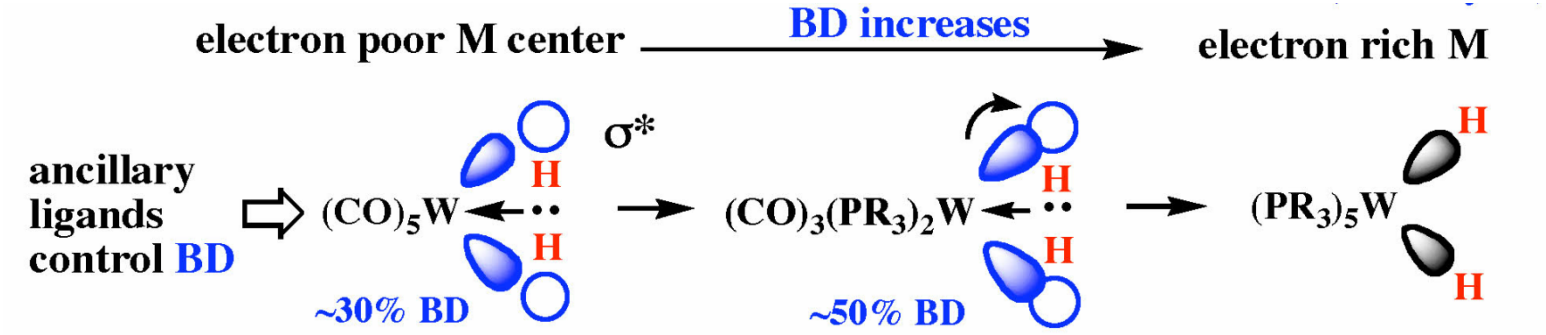


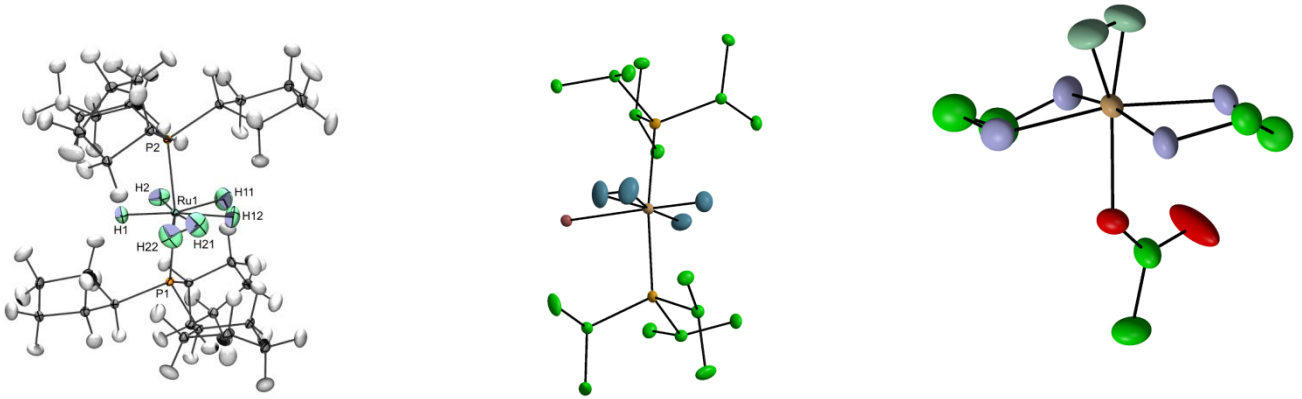


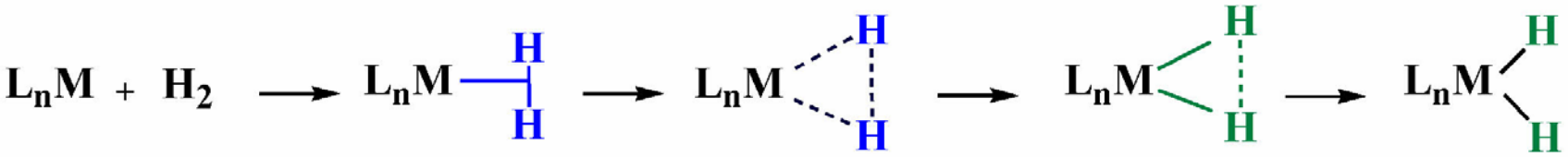


$[Ru(dppe)_2(H)(H_2)]^+$	0.82(3)	$[Os(en)_2I(H_2)]^+$	1.224(7)
$[Ru(cp^*)(dppm)_2(H_2)]^+$	1.08(3)	$[Os(en)_2(OAc)(H_2)]^+$	1.34(2)
$Ir(P^iPr_3)_3Cl_2(H)(H_2)$	1.11(3)	$[Os(PMe_2Ph)_3(H)_5]^+$	≥1.49(4)
$Ir(P^iPr_3)_2I(H)_2(H_2)$	0.856(9)	$Ir(P^iPr_3)_2Br(H)_2(H_2)$	0.819(8)

Backdonation is critical for the stability of M-H_2 Complexes



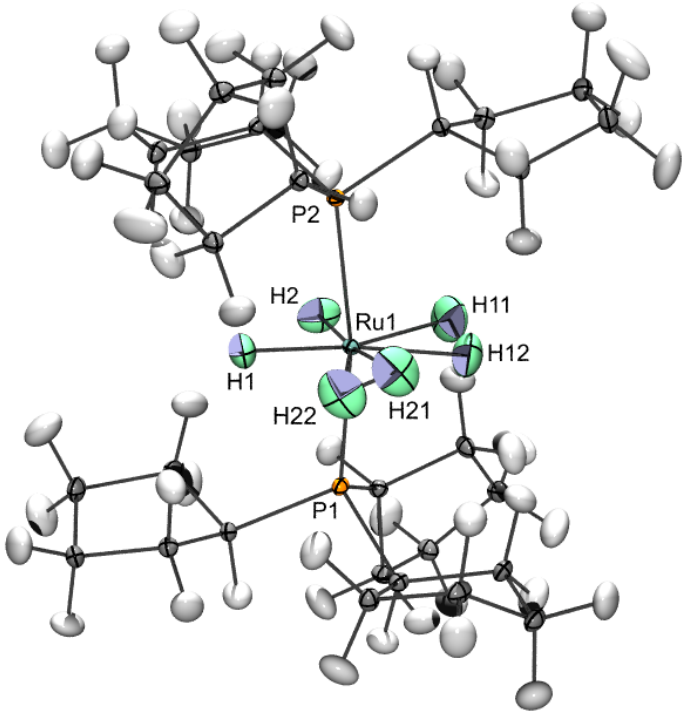




η^2 0.8 – 0.9Å *streched* 1.0 – 1.2Å *weak interactions* ≥ 1.3Å ≥1.7Å

The Structure of $RuH_2(H_2)_2((Cyp)_3)_2$

D19 @20K

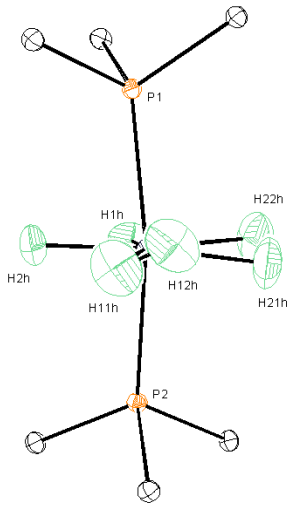


H – H	0.825(7)	0.835(7) Å
Ru - (H1)	1.730(5)	1.753(5) Å
Ru - (H2)	1.745(5)	1.764(5) Å
Ru - H	1.628(4)	1.625(4) Å

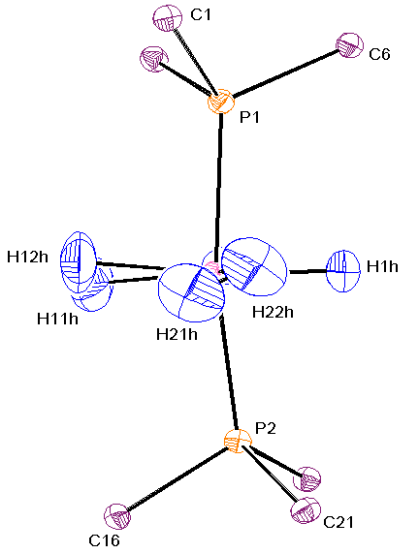
P - Ru - P 168.9(1)°

$Ru(H)_2(H_2)(P(cyp)_3)_2$: a Parametric Study on D19

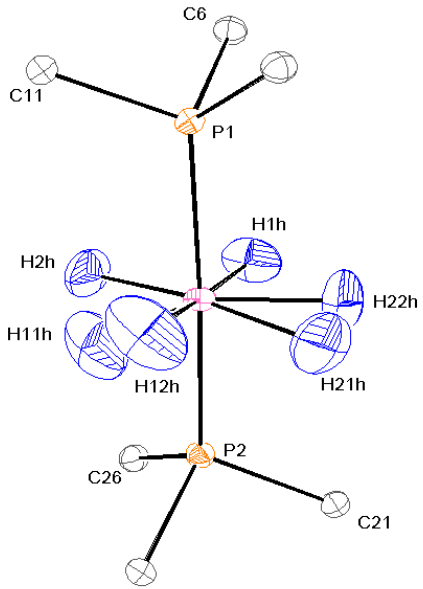
20K



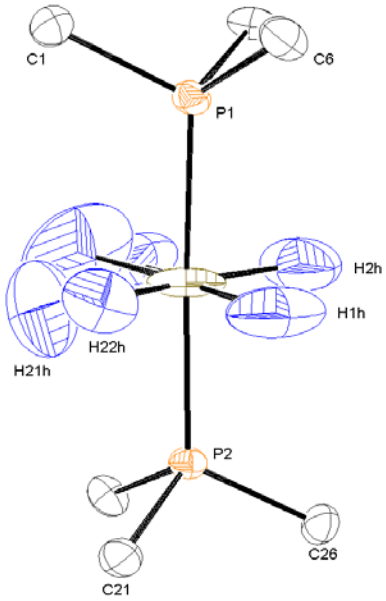
60K



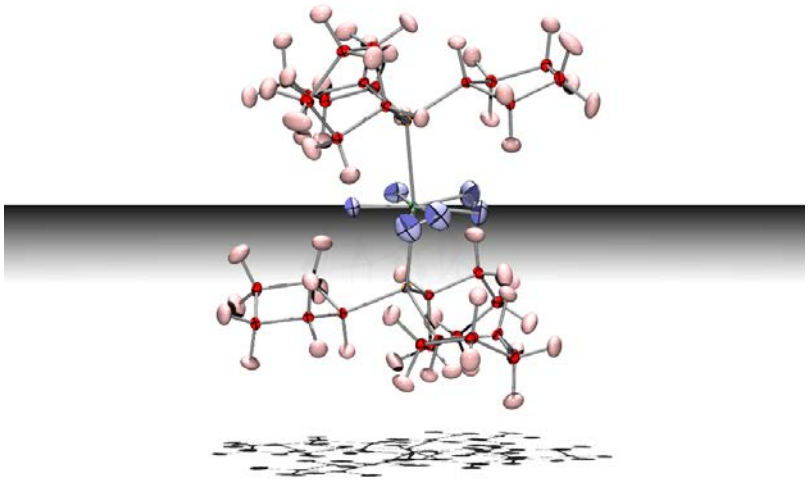
100K



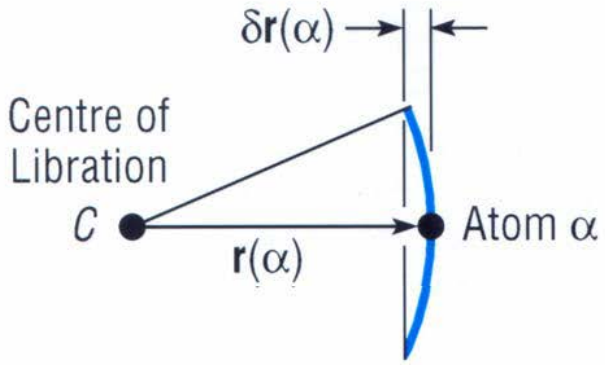
180K



$RuH_2(H_2)_2(P(Cyp)_3)_2$

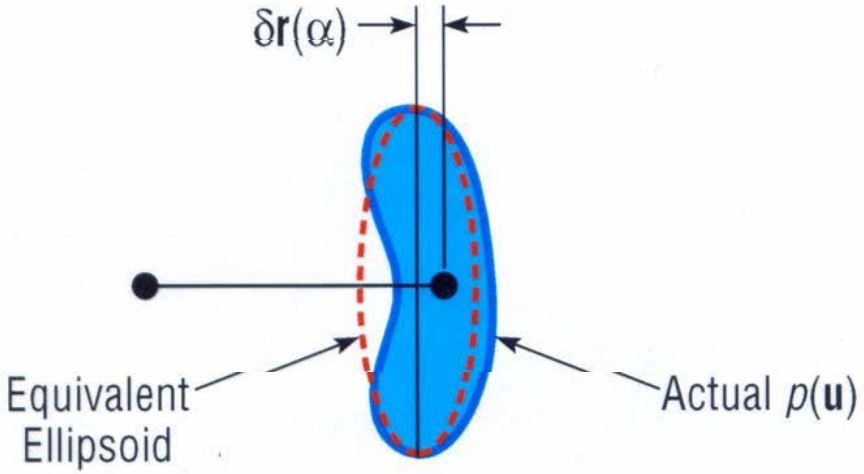


	20K	60K	100K	180K
H11 – H12	0.825(8)	0.796(8)	0.794(8)	0.73(5)
Ru – H1	1.628(4)	1.618(4)	1.626(4)	1.69(2)
Ru – P1	2.307(3)	2.309(3)	2.310(2)	2.325(8)
P1 – Ru – P2	168.9(1)	168.8(1)	168.72(9)	178.0(5)



P.D.F. from Libration

P.D.F. from Translation



Total P.D.F. from Translation and Vibration

Rigid Molecule – The TLS Model

time average

$$\mathbf{B}^{atom}(\kappa) = \left\langle \mathbf{u}(\kappa)\left(\mathbf{u}(\kappa)\right)^{T} \right\rangle$$

(3x1) matrix; u_i = inst.disp

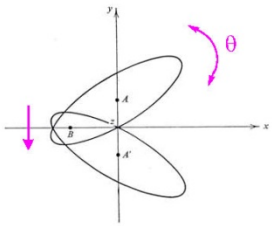
for a rigid molecule

$$\mathbf{B}^{mol}(\kappa) = \begin{pmatrix} \mathbf{T} & \mathbf{S} \\ (\mathbf{S}^{*})^{T} & \mathbf{L} \end{pmatrix}$$

$$\mathbf{T}(\kappa) = \left\langle \mathbf{u}(\kappa)\left(\mathbf{u}(\kappa)\right)^{T} \right\rangle$$

$$\mathbf{L}(\kappa) = \left\langle \boldsymbol{\theta}(\kappa)\left(\boldsymbol{\theta}(\kappa)\right)^{T} \right\rangle$$

$$\mathbf{S}(\kappa) = \left\langle \mathbf{u}(\kappa)\left(\boldsymbol{\theta}(\kappa)\right)^{T} \right\rangle$$



distance of atom κ from center of libration

$$\boxed{\delta\mathbf{r}(\kappa) = -\frac{1}{2}\left[\left(\mathrm{trace}\mathbf{L}\right)\mathbf{r}(\kappa) - \mathbf{L}\mathbf{r}(\kappa)\right]}$$

H - H Distances (Å) and TLS Correction

	Uncorrected	TLS	Solid State NMR
$Fe(PEtPh_2)_3(H)_2(H_2)$	0.82 (1)	1.05	
$[Fe(dppe)_2(H)(H_2)][BF_4]$	0.82 (2)	0.85	0.90
$[Os(dppe)_2(H)(H_2)][PF_6]$	0.79 (2)	0.96	0.99
$[Os(dppe)_2(Cl)(H_2)][PF_6]$	1.15 (3)	1.24	1.19
$[Os(en)_2(I)(H_2)]$	1.224 (7)	1.272	
$[Ru(cp^*)(dppm)_2(H_2)][BF_4]$	1.08 (3)	1.09	1.02

Zilm, K.W.; Millar, J.M. Adv. Magn. Opt. Reson. *1990*, ***15***, 163

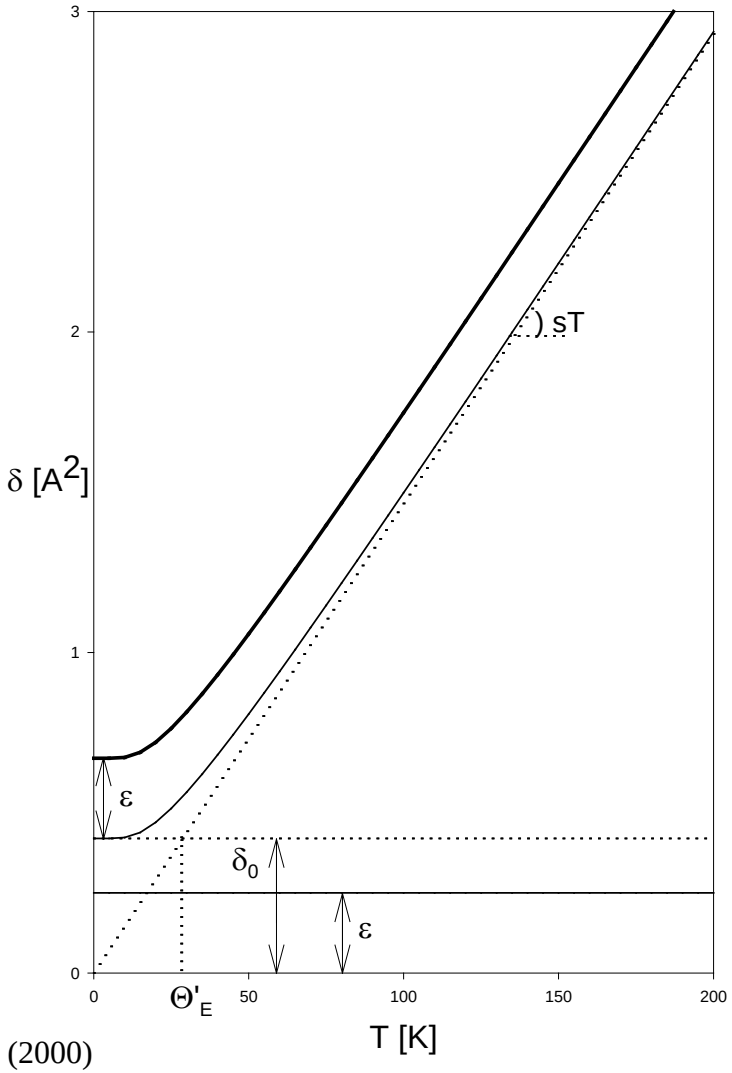
Molecular Motion from the Temperature Dependence of ADP's

$$\Sigma^{x}(T) = AgV\delta(1/\omega,T)V'g'A' + \varepsilon$$

ADPs, determined experimentally at several temperatures

Intramolecular, **high frequency vibrations and disorder** (ε) (~temperature independent)

Low frequency, **large-amplitude vibrations** (ω), e.g. librations, translations and deformations (**V**)



H.B. Bürgi, S. Capelli *Acta Cryst.* ***A56***, 403 (2000)

Molecular Motion from the Temperature Dependence of the ADPs

$$\sum^{X}(T) = \mathbf{AgV}\boldsymbol{\delta}(\omega^{-1},T)\mathbf{V}^{T}\mathbf{g}^{T}\mathbf{A}^{T} + \boldsymbol{\varepsilon}$$

Σ(T) observed atomic mean square displ. at multiple T

A transformation matrix from atomic to normal modes coords

V eigenvectors matrix

ε 3x3 upper triangular tensor
contribution to ADPs from high □□s small amplitude vibrations

δ(T) diagonal matrix of mean square normal modes displacements

For each normal mode j

$$\boldsymbol{\delta}(T) = \left(\frac{h}{2\omega_j}\right)\coth\left(\frac{h\omega_j}{2k_bT}\right)$$

Considering only T and L

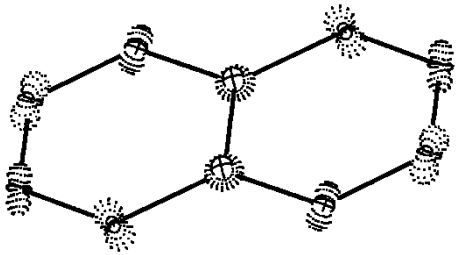
$$\sum^{X} = \mathbf{A}\begin{pmatrix}\mathbf{T} & \mathbf{S}\\ \mathbf{S}^{T} & \mathbf{L}\end{pmatrix}\mathbf{A}^{T} + \boldsymbol{\varepsilon}$$

Burgi & Capelli *Acta Cryst A*, 403 (2000)

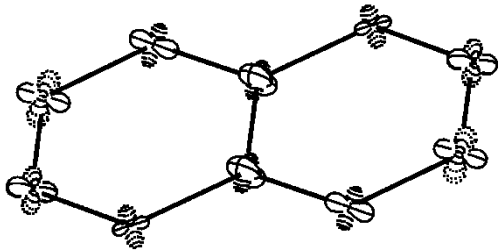
Naphthalene : ADP's and rms difference surfaces

X-ray (SR)

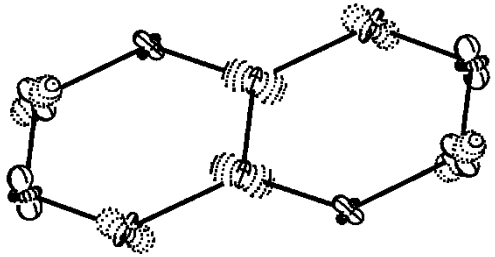
10 K



30 K

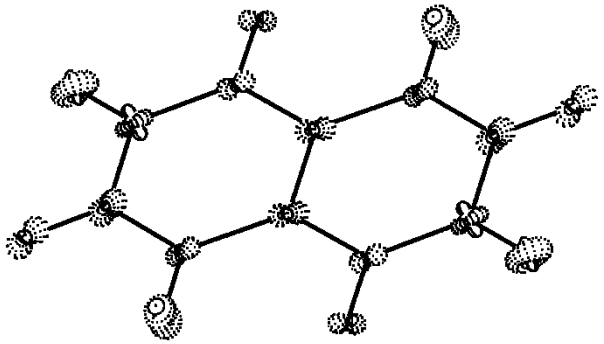


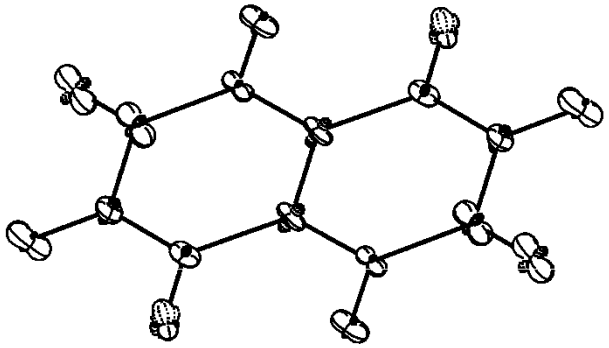
150 K

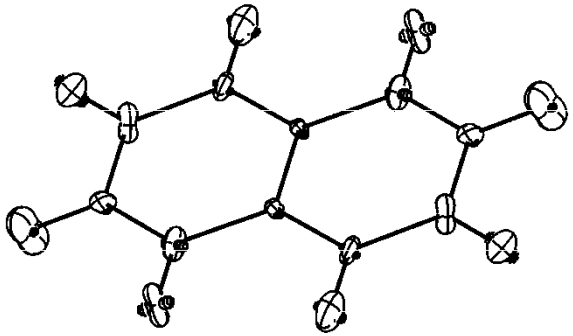


Neutron

5 K

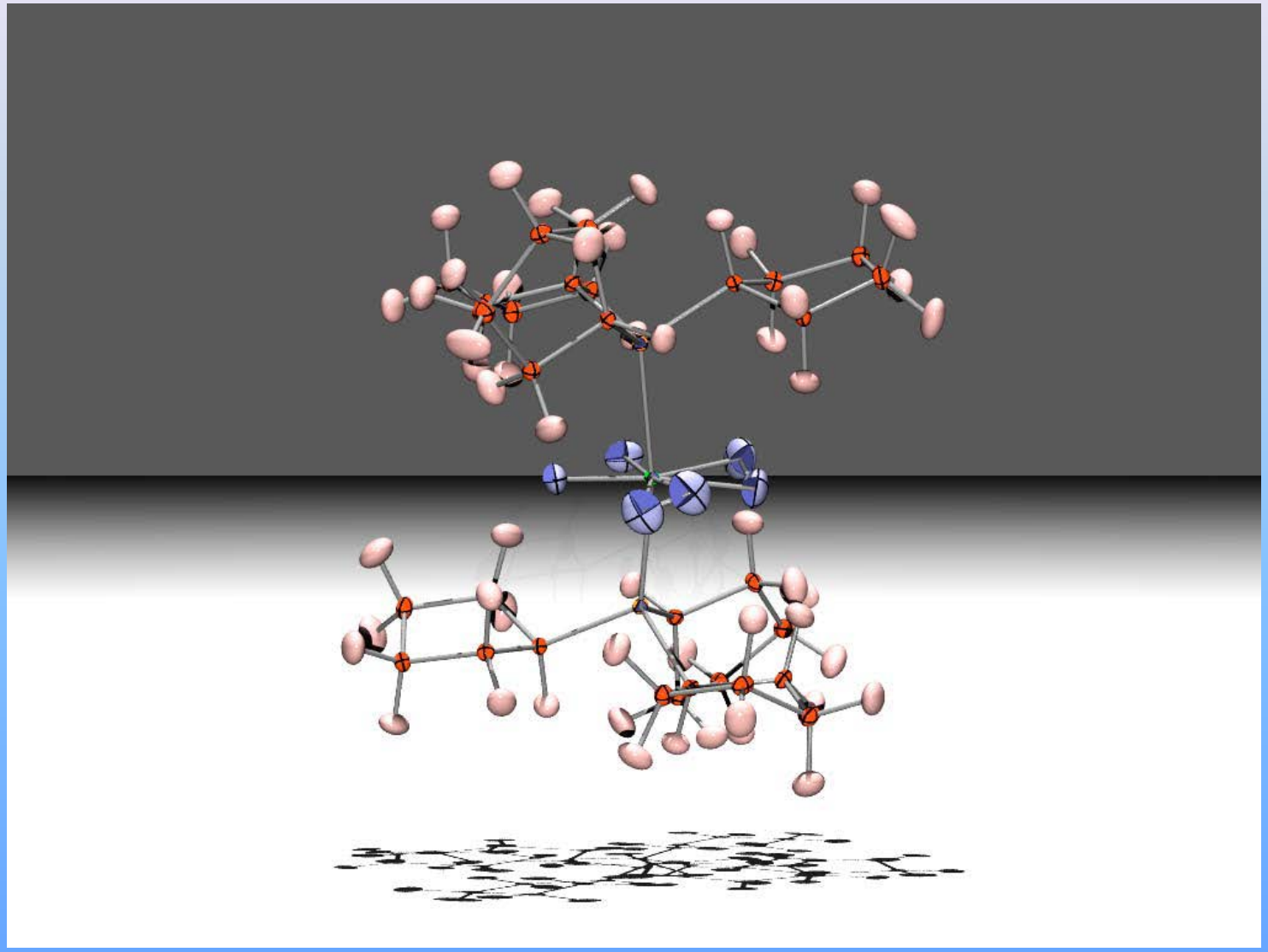






The Structure of $RuH_2(H_2)_2((Cyp)_3)_2$

D19 @20K



MODELS OF MOTION USED TO ANALYSE THE 20, 60 AND 100K NEUTRON DATA (with both THMA and ADP-analysis)

1) Rigid-body description:
the motion of the molecule as a whole is defined by 6 degrees of freedom :
$L_x, L_y, L_z, T_x, T_y, T_z$

➔ Serious problems in describing the out-of-plane displacements of the H atoms involved in the di-hydrogen groups

ε(H) ➔	**0.017(2)**	**0.001(1)**	**0.005(1)**
		0.019(2)	**-0.006(1)**
			0.058(2)

2) Rigid-body + internal rotations of the di-hydrogen groups:
8 degrees of freedom:
$L_x, L_y, L_z, T_x, T_y, T_z, U_1, U_2$

➔ Significant improvement in the description of the out-of-plane displacements in the di-hydrogen groups

ε(H) ➔	**0.018(2)**	**0.000(1)**	**0.000(1)**
		0.018(2)	**0.005(1)**
			0.028(2)

➔ **normal mode frequencies for di-hydrogen rotations: 104 and 170 cm^{-1}**

[Albinati A., Capelli S.C., Mason S.A., (**2010**) in preparation.]

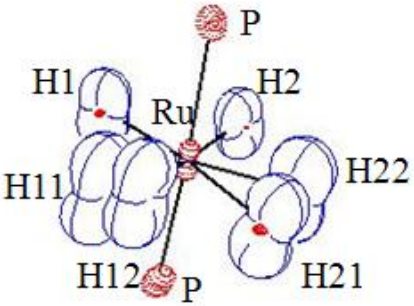
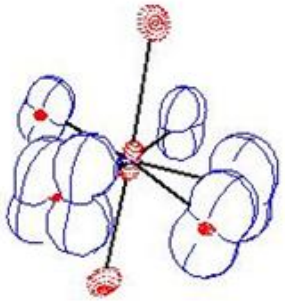
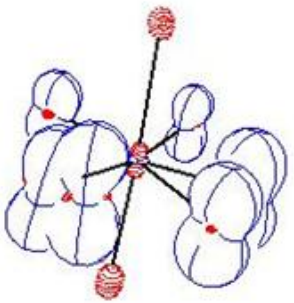
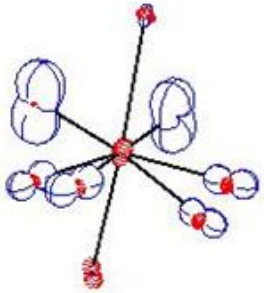
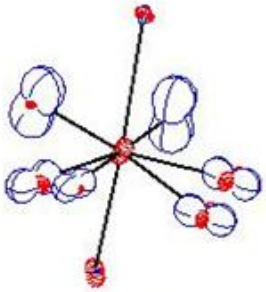
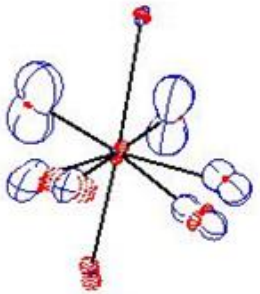
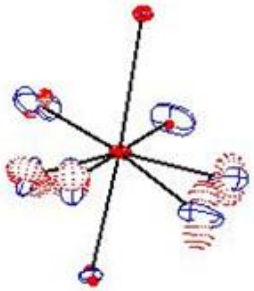
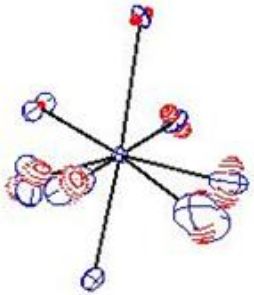
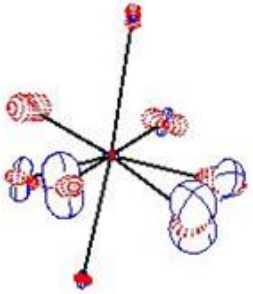
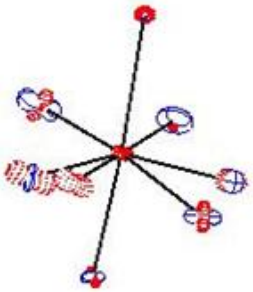
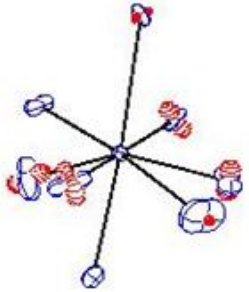
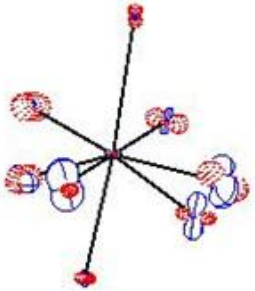
Models used for the ADP's analysis

Model	T (K)	R (%)	Goof	Obs	Par	Obs/Par ratio	Degrees of freedom
A	20 60 100	41 36 33	5.16 5.01 5.82	54	20	2.70	6 librations, 6 translations, 8 coupling terms
B	20 60 100	23 19 17	3.83 3.39 3.83	54	32	1.69	6 librations, 6 translations, 8 coupling terms + 6 components of the librations of the di-hydrogen groups
C	all	12	1.62	162	28	5.79	1 librational frequency, 3 translational frequencies, 24 components of the 4 temperature-independent ε-tensors
D	all	9	1.16	162	32	5.06	3 librational frequencies, 3 translational frequencies, 2 eigenvector components, 24 components of the 4 temperature-independent ε-tensors

Bond Distances (Å) Corrected for Libration

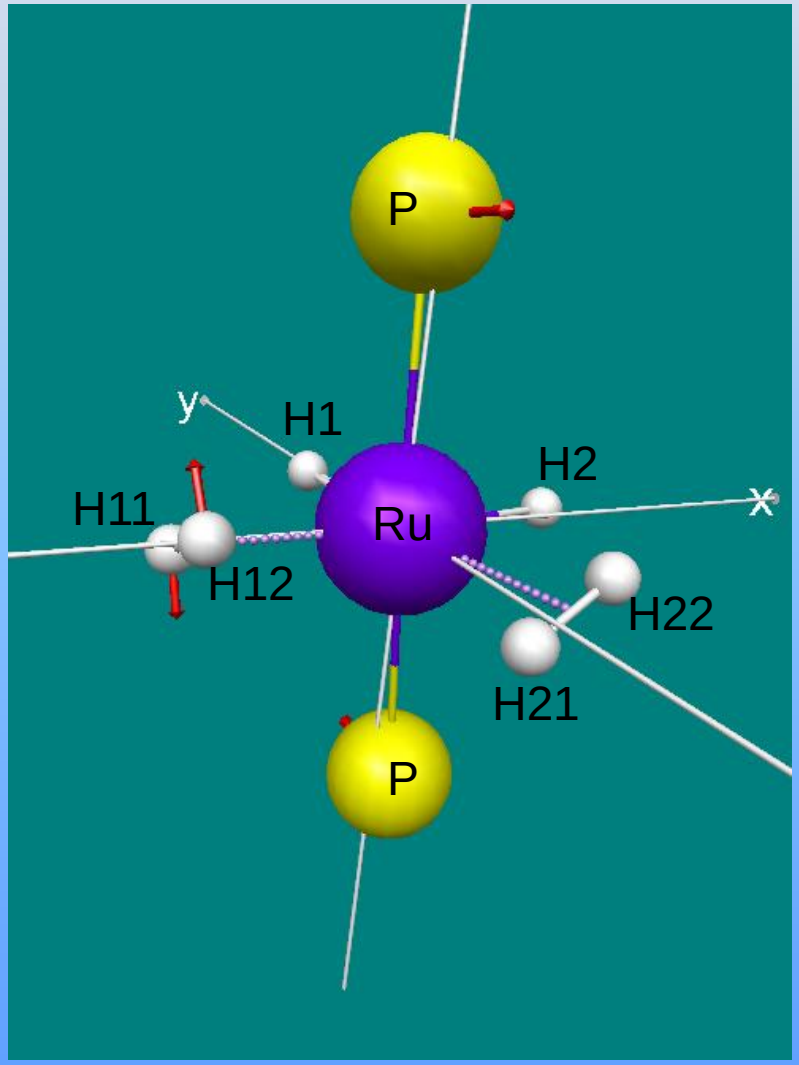
T	RU-H11		RU-H12		RU-H21		RU-H22	
(K)	TLS	ADP	TLS	ADP	TLS	ADP	TLS	ADP
20	1.7397	1.7475	1.7618	1.7709	1.7732	1.7819	1.7537	1.7610
60	1.7322	1.7412	1.7606	1.7710	1.7699	1.7786	1.7488	1.7562
100	1.7435	1.7540	1.7543	1.7682	1.7673	1.7755	1.7491	1.7580

T	H11-H12			H21-H22		
(K)	TLS	ADP	Exp	TLS	ADP	Exp
20	0.831	**0.899**	**0.825(8)**	0.840	**0.911**	**0.835(8)**
60	0.804	**0.887**	0.796(8)	0.826	**0.902**	0.820(8)
100	0.806	**0.916**	0.794(8)	0.820	**0.910**	0.812(8)

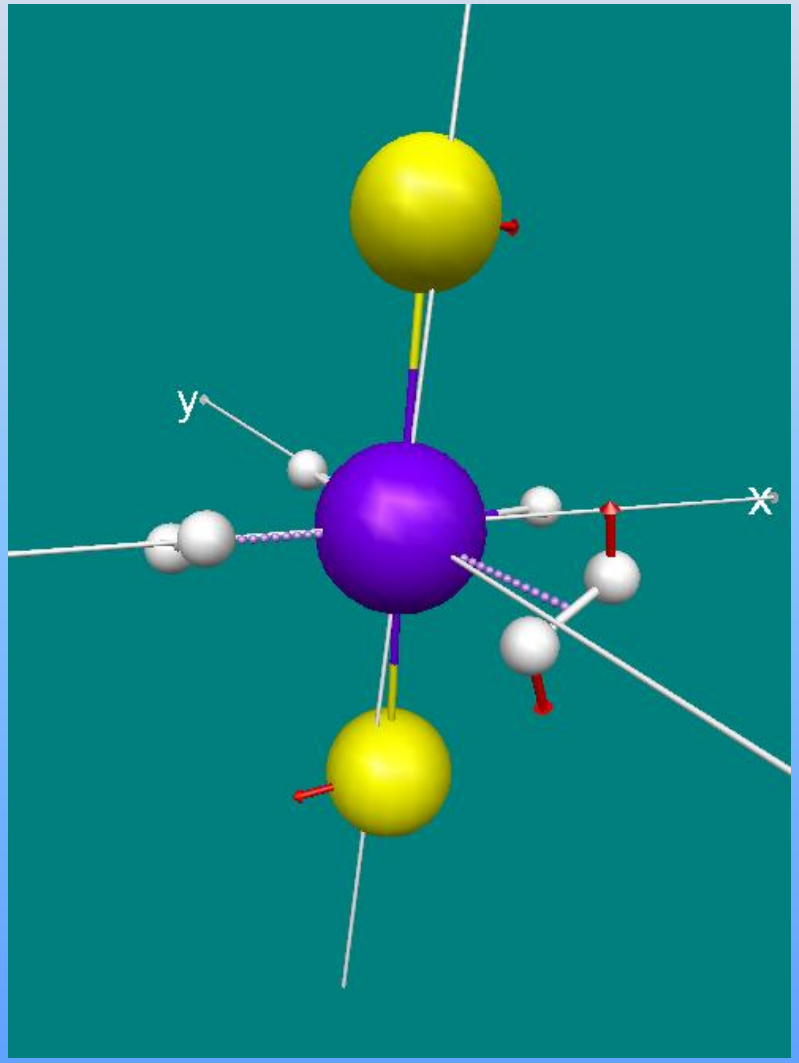
	20K	60K	100K
THMA: rigid-body model R_{20K} = 41% Goof = 5.16 R_{60K} = 36% Goof = 5.01 R_{100K} = 33% Goof = 5.82			
THMA: rigid-body model + H_2 librations R_{20K} = 23% Goof = 3.83 R_{60K} = 19% Goof = 3.39 R_{100K} = 17% Goof = 3.83			
ADP-analysis: rigid-body model R_{all_T} = 12% Goof = 1.62			
ADP-analysis: rigid-body model + H_2 librations R_{all_T} = 9% Goof = 1.16			

Dihydrogen Ligands:
Low Frequency Normal Modes

104.5 cm^{-1}



170.3 cm^{-1}

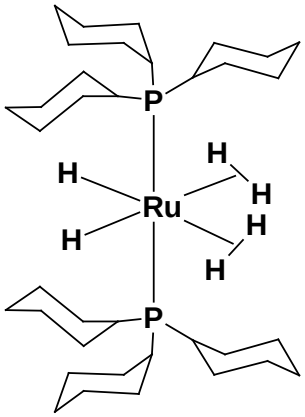


H-H Distances (Å) vs. J^{HD} (Hz)

	$d_{(H-H)}$	J^{HD}
$W(CO)_3(P^iPr_3)_2(H_2)$	0.82 (1)	34.0
$[Fe(dppe)_2(H)(H_2)]^+$	0.82 (2)	30.5
$[Ru(dppe)_2(H)(H_2)]^+$	0.82 (3)	32.0
$[Os(dppe)_2(H)(H_2)]^+$	0.79 (2)	25.5

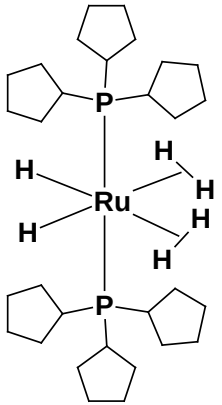
H / D Exchange in $Ru(H_2)(H)_2L$

From ^{1}H-NMR spectra in C_6D_6:



No significant H/D exchange after 24 h

$RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$



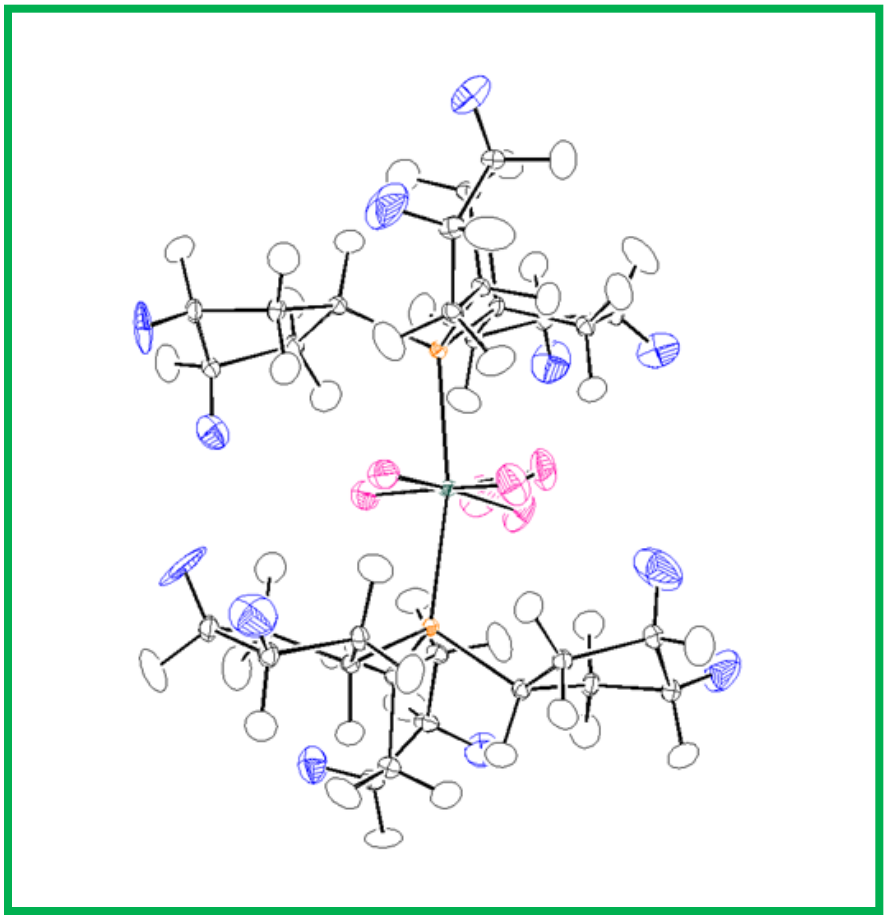
H/D exchange within 1h

$RuH_2(\eta^2\text{-}H_2)_2(PCyp_3)_2$

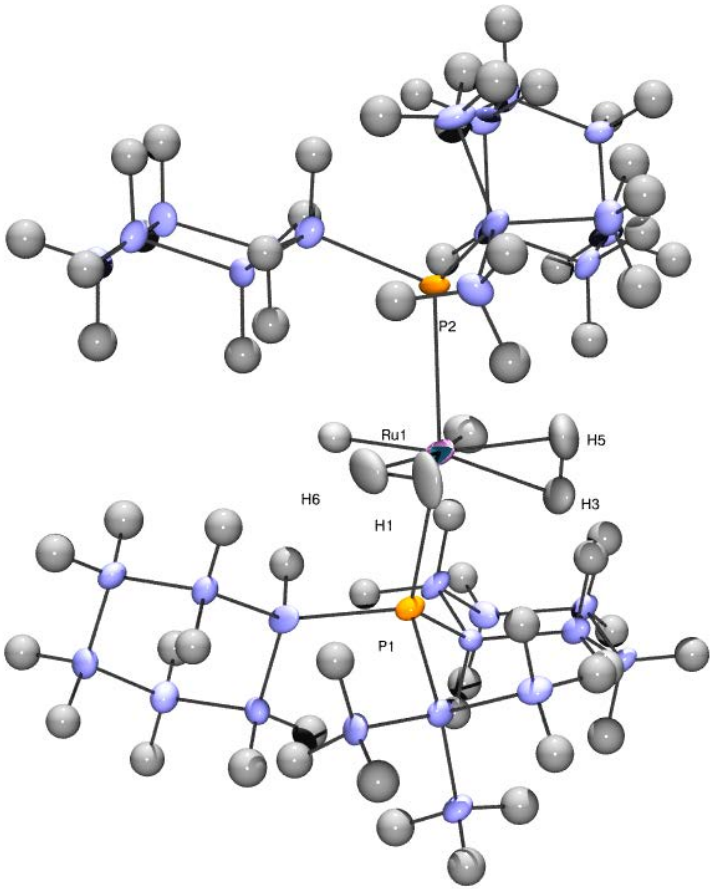
s.o.f.'s D_2/H_2 or H > 0.9

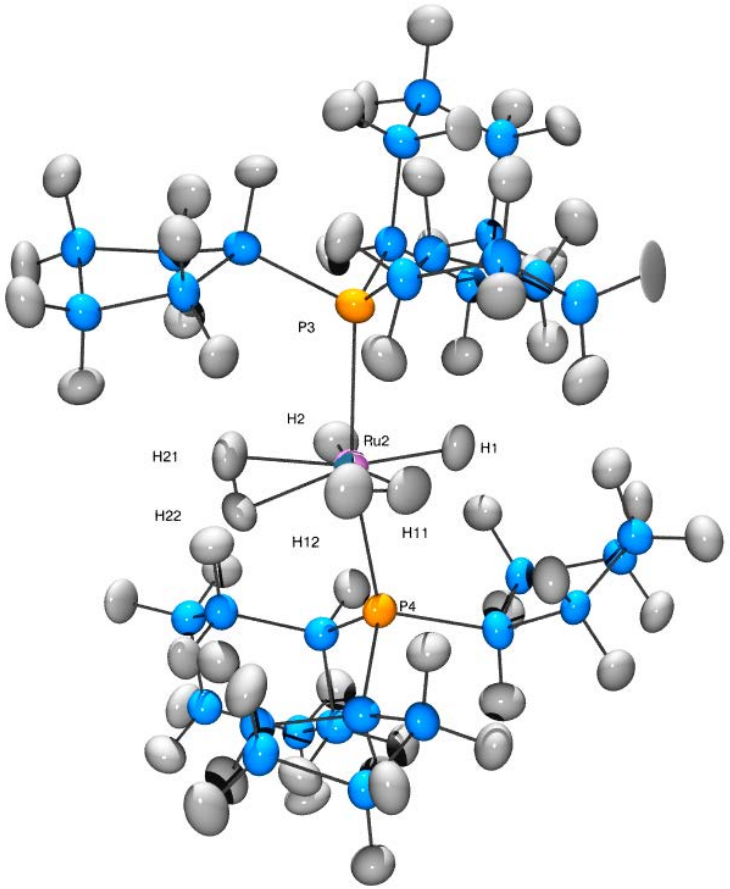
H = 0.9 ; CD / CH = 0.7

H – D Selective Exchange



$Ru(H_2)(H)_2L_2$





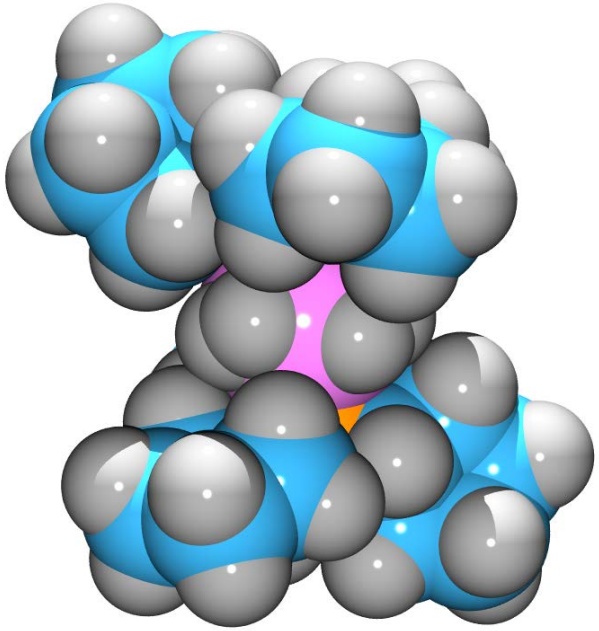
L = $P(cy)_2(^tBut)$

H–H 0.85(2) 0.84(2) Å

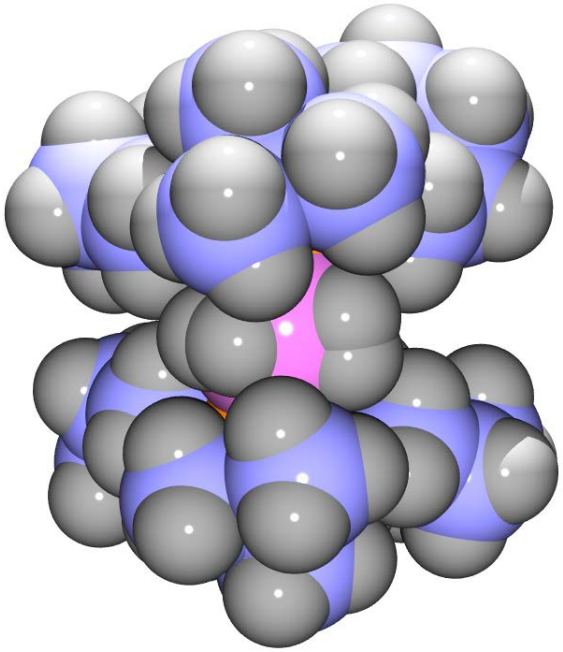
L = $P(cyp)_2(cy)$

H–H 0.82(2) 0.84(2) Å (av.)

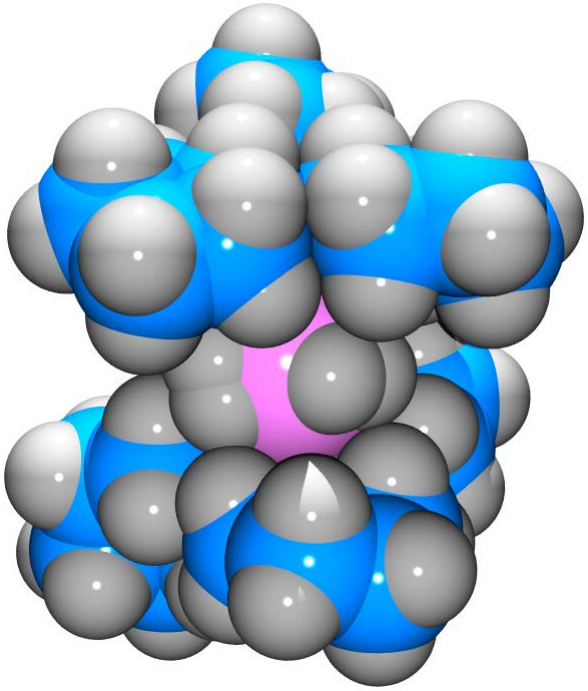
$Ru(H_2)(H)_2L_2$



$L = P(cyp)_3$



$L = P(cy)_2(^tBut)$



$L = P(cyp)_2(cy)$

We need more experimental data…….

....Part 2