The Structure of Organometallic Polymers from Laboratory X-ray Powder Diffraction Data

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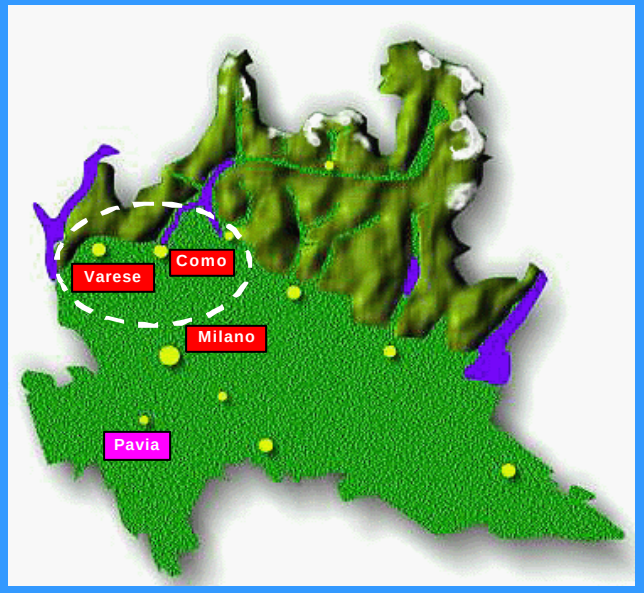
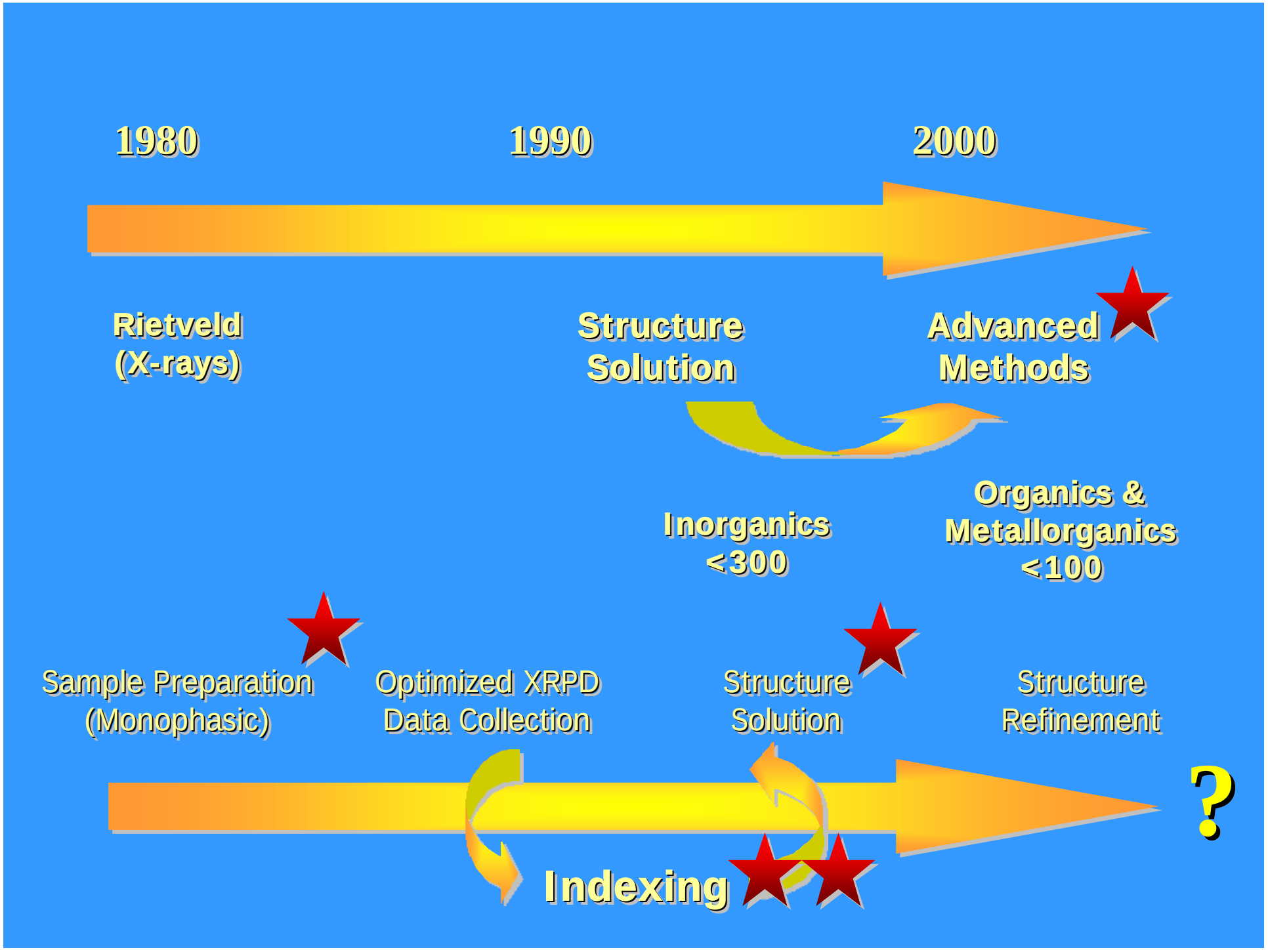



1980
1990
2000
Rietveld
(X-rays)
Structure
Solution
Advanced
Methods
Inorganics
<300
Organics &
Metallorganics
<100
Sample Preparation
(Monophasic)
Optimized XRPD
Data Collection
Structure
Solution
Structure
Refinement
Indexing
?

Coordination Compounds are not always Single Crystals

XRPD on conventional diffractometers allows fairly complex structural determinations

- » 20 mg of ‘pure’ monophasic compound
- asymmetric unit volumes < 800 $Å^3$
- Number of independent atoms < 40
- Synchrotron (eventually + neutron) PD experiments allow to tackle twice more complex problems

PD lacks of resolution but affords substantial structural information

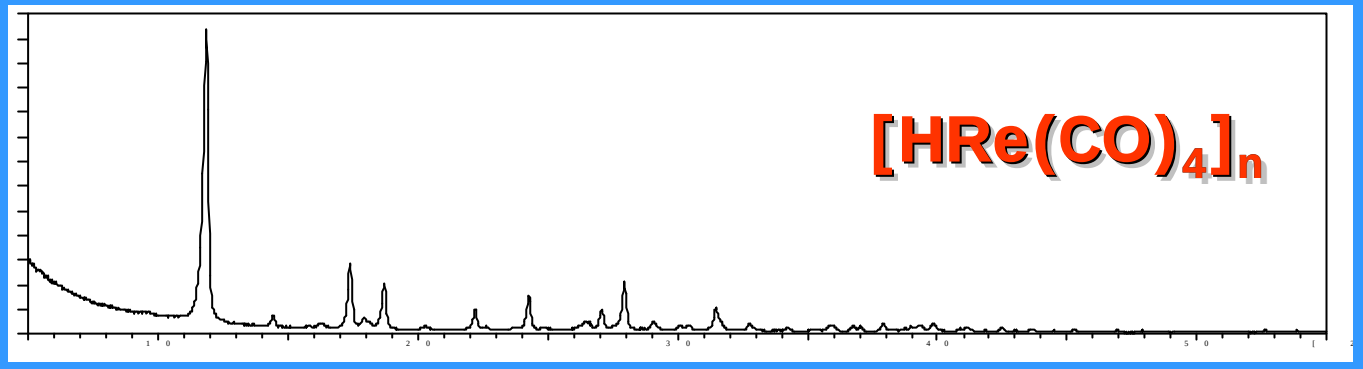
- connectivity pattern, molecular conformation and shape,
- crystal packing, details on 'heavy' atoms stereochemistry,
- rough bonding parameters,
- structural relationships between different phases,
- microstructure (stress, strain and faults)

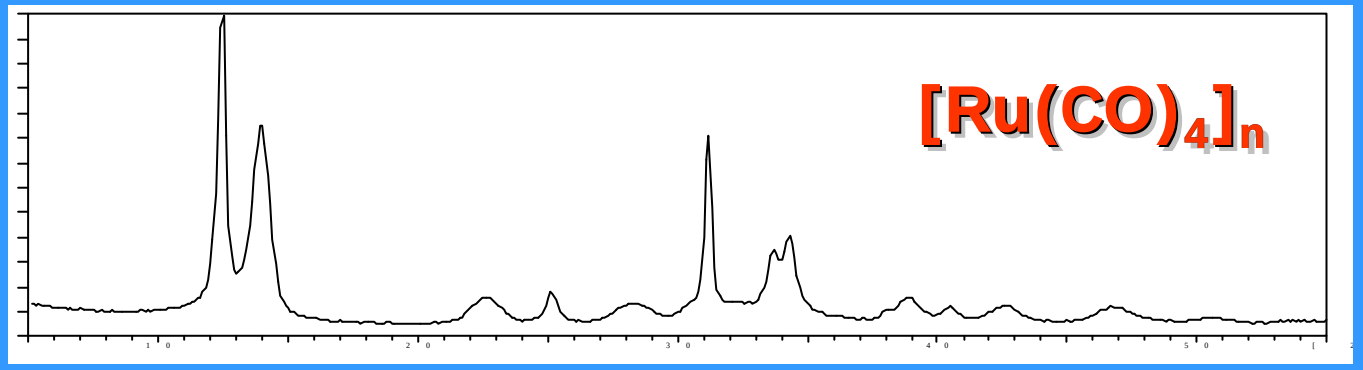
Single Crystal structural analyses are faster, simpler and more accurate than XRPD structural determinations

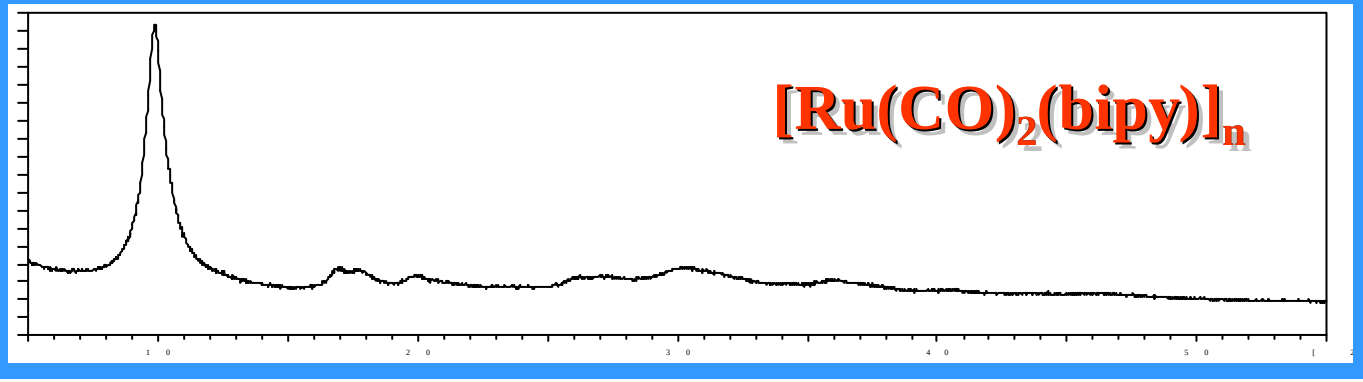
An XRPD study is worthwhile only when suitable Single Crystals lack

- Compounds which cannot be recrystallised
- Very small crystals
- Crystal aggregates
- Twins
- Metastable phases
- Solid-state reaction products

Carbonylic Polymers







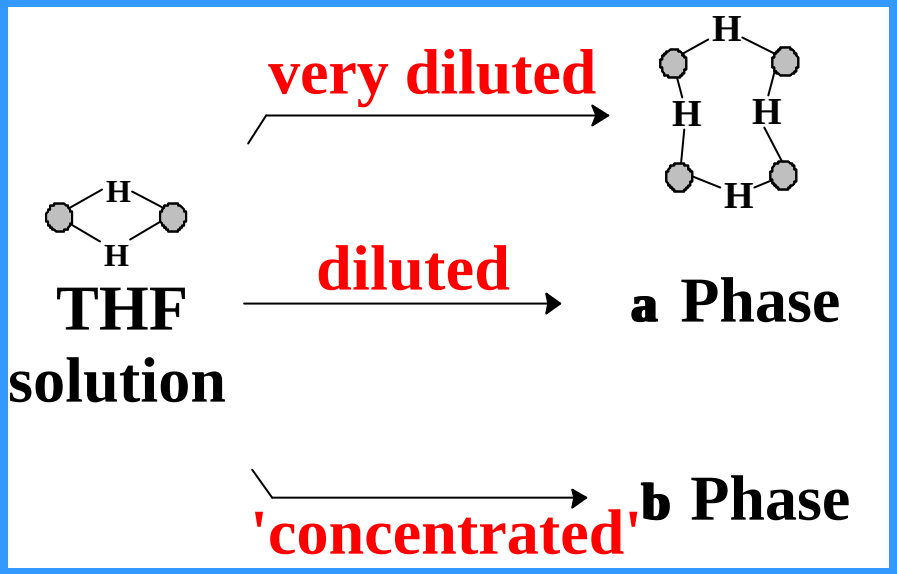
FWHM,°

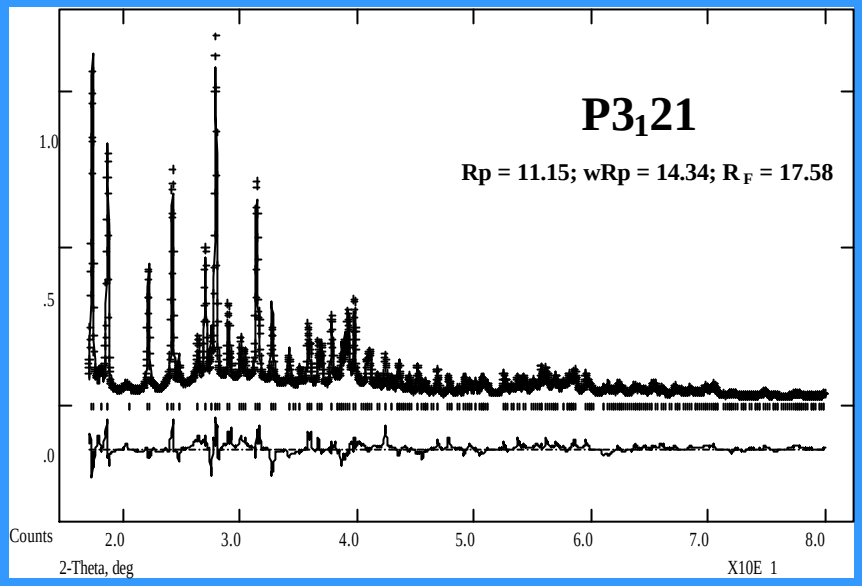
0.15

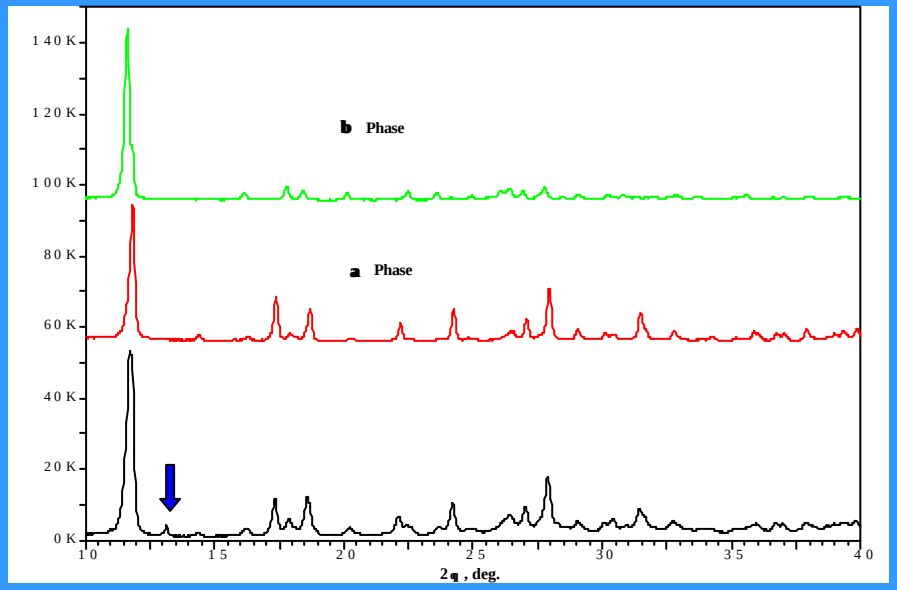
0.30 to 1.20

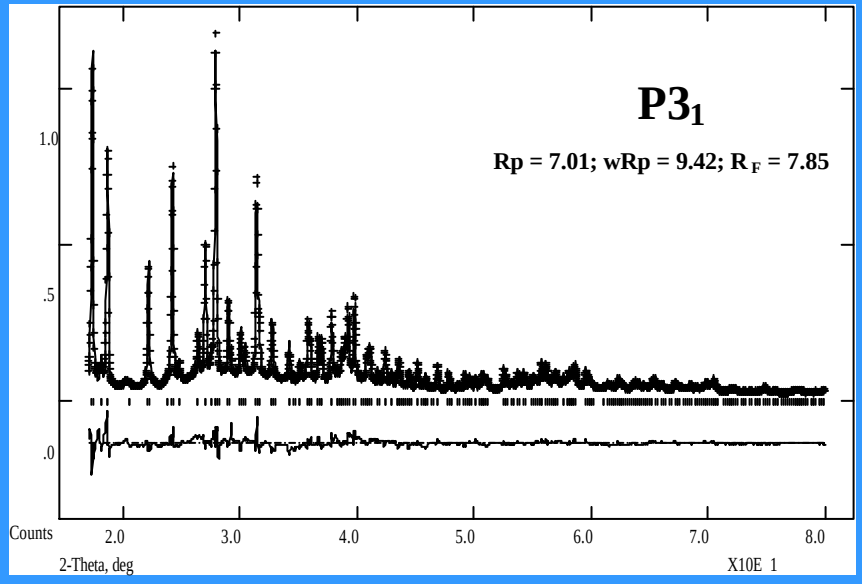
1.50

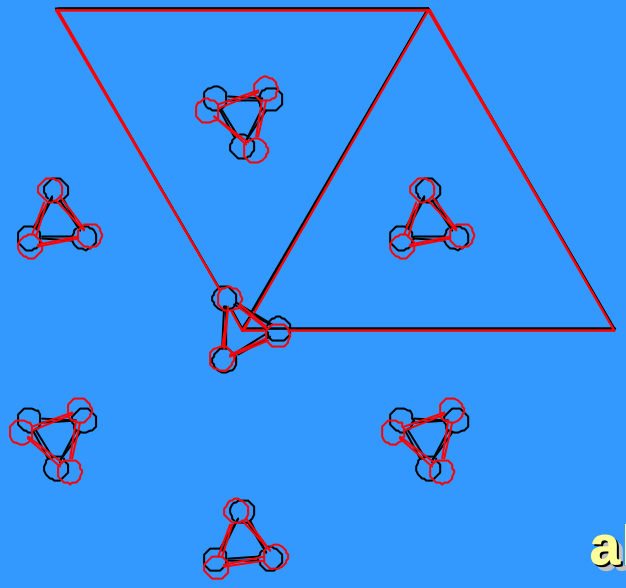
$Re_2(\mu\text{-}H)_2(CO)_8$ decomposes in THF affording a solid mixture







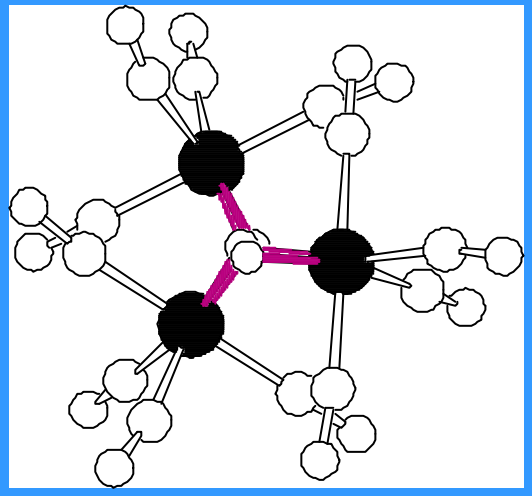


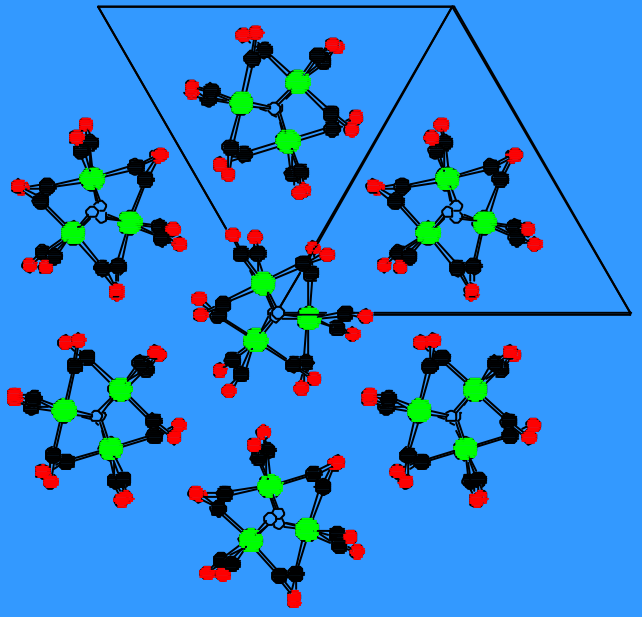


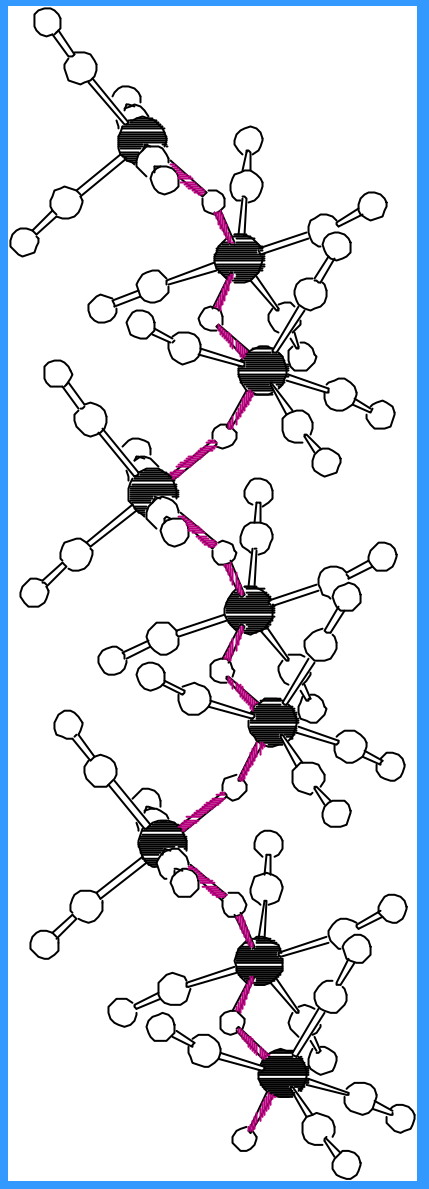
a-$[HRe(CO)_4]_n$

side view

along [001] (top view)







c

$[HRe(CO)_4]_n$

Organometallic Analogues of Cycloalkanes

C-C bond = Re (H) Re bond (2 e^-) 3.2 - 3.4 Å

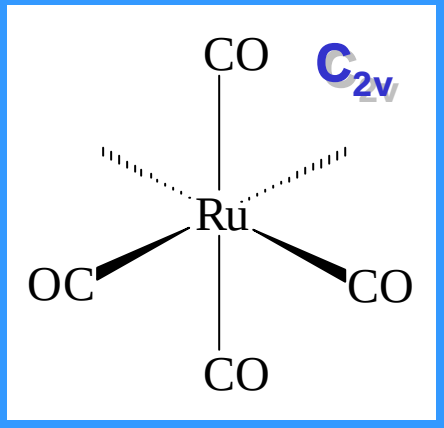
C=C bond = Re $(H)_2$ Re bond (4 e^-) 2.86 Å

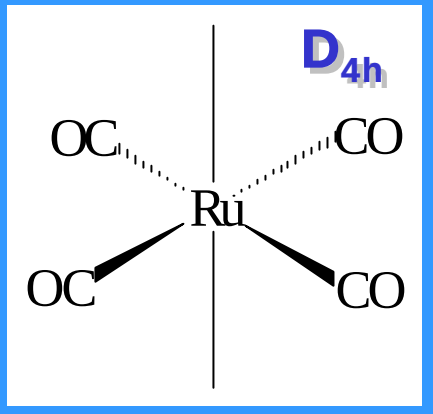
Nuclearity	$C_nH_{2n} = [CH_2]_n$	$[HRe(CO)_4]_n$	Reference
2	Ethylene	$H_2Re_2(CO)_8$	Our work, J.Am.Chem.Soc., 1990, *Single Crystals*
3	Cyclopropane	$H_3Re_3(CO)_{12}$	
4	Cyclobutane	$H_4Re_4(CO)_{16}$	
5	Cyclopentane	$H_5Re_5(CO)_{20}$	M. Bergamo et al., Angew.Chem., 2002 *Single Crystal*
6	Cyclohexane	$H_6Re_6(CO)_{24}$	Our work, Angew.Chem., 2002 *Powder Diffraction*
¥	Polyethylene	Poly-$[HRe(CO)_4]$	

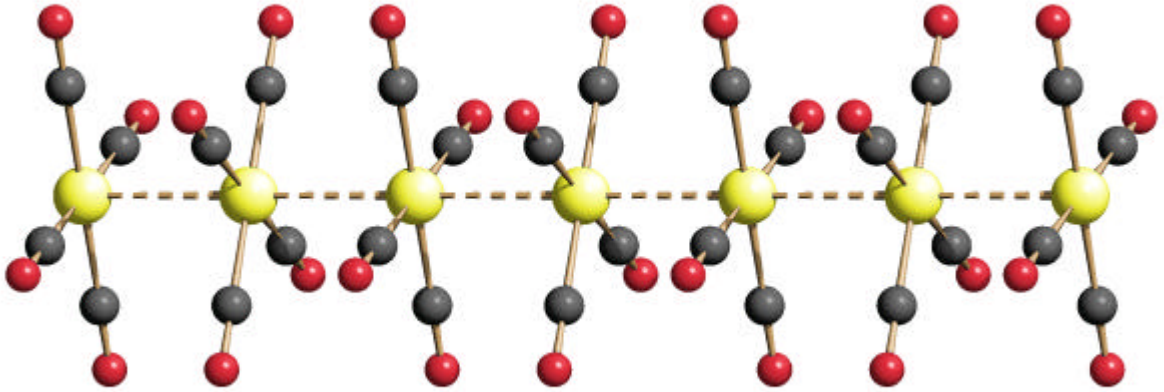
"... there appears to be only one possible example of a polymeric carbonyl, namely $[Ru(CO)_4]_n$..." F.A.Cotton & G.Wilkinson, Advanced Inorganic Chemistry, 5th Ed, p.1028

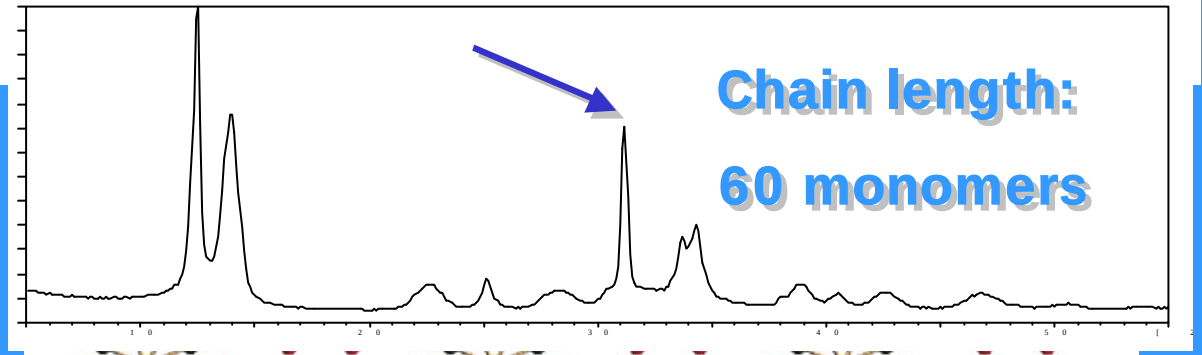
Photochemistry on $Ru_3(CO)_{12}$ in the presence of free CO

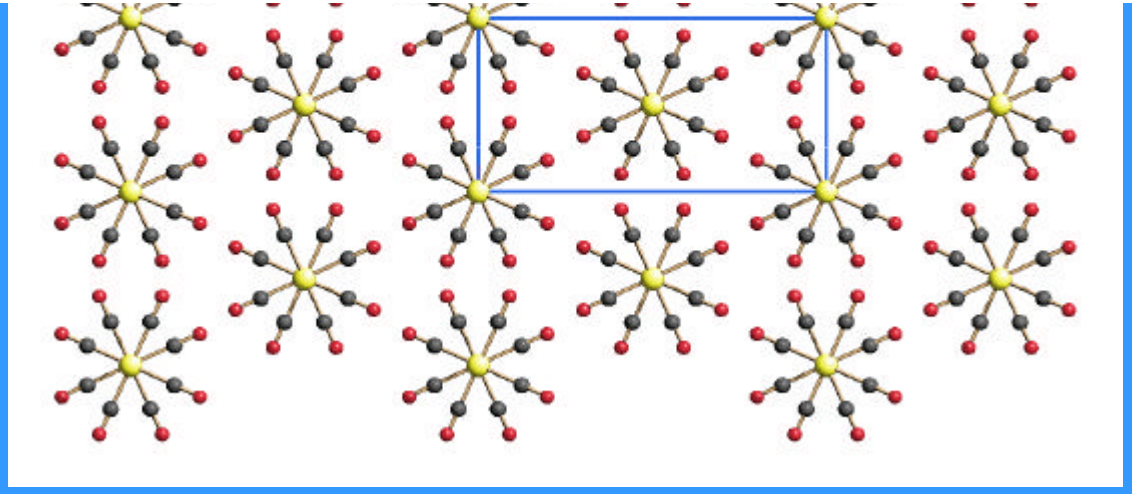
From IR spectral data, it was suggested to possess cis-C_{2v} monomers bound in a zig-zag fashion











Ru – Ru 2.94 Å

Staggered

$Ru(CO)_4$

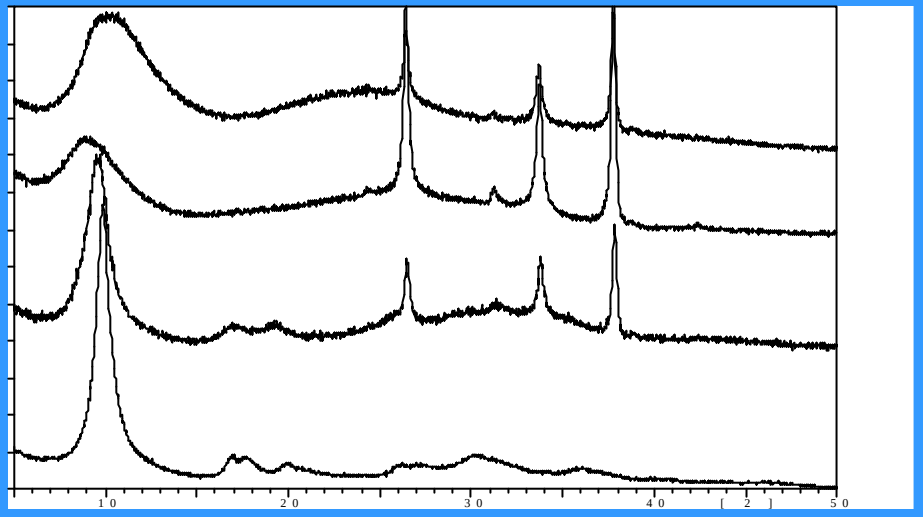
Orthorhombic

Pseudo hexagonal

Strain in ab

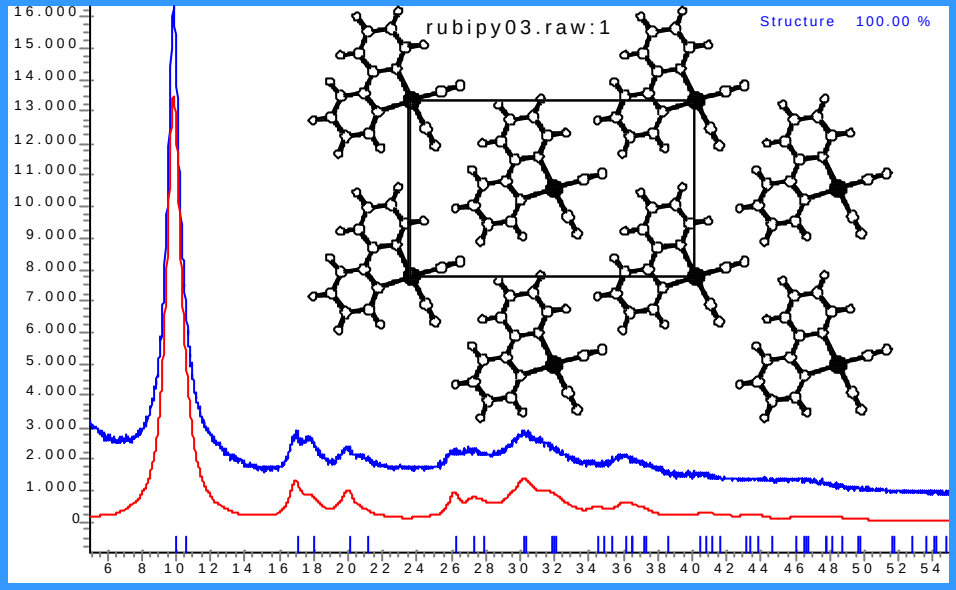
$$n\ [Ru^{II}(bipy)(CO)_2Cl_2] + 2n\ e^- \quad [Ru^0(bipy)(CO)_2]_n + 2n\ Cl^-$$

- 6,6'-dimethylbipy
- 4,4'-dimethylbipy
- 1,10-phenanthroline
- 2,2'-bipyridine (bipy)



- **Manual cell determination:**
  ***d**²** **ratios of *ca.* 1:3:4:7 + bump at d = 3 Å ; splitting; Orthorhombic Cmmm, 10.4 x 16.8 x 3.0 Å.**

- **Model building: C_{2v} $Ru(bipy)(CO)_2$; free z rotation; simulated annealing by TOPAS; R_p, 0.034; R_{wp}, 0.043**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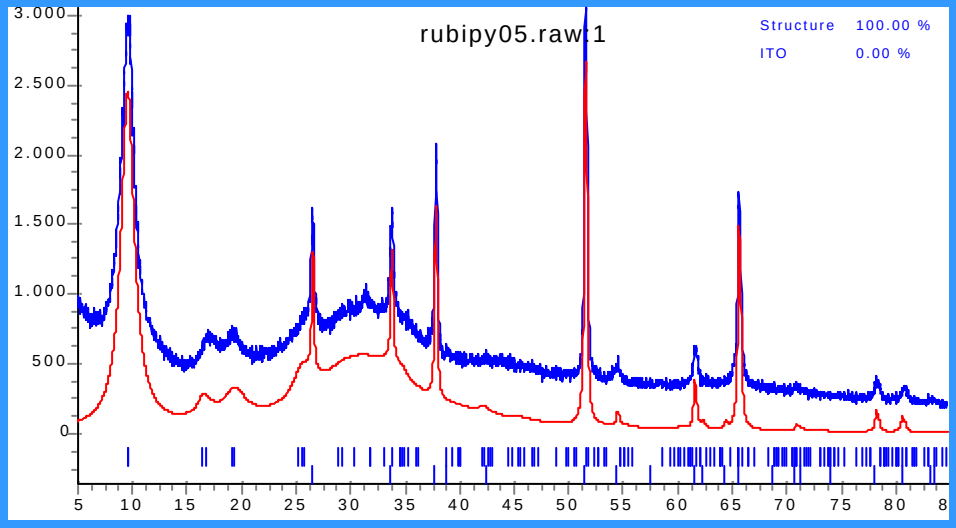
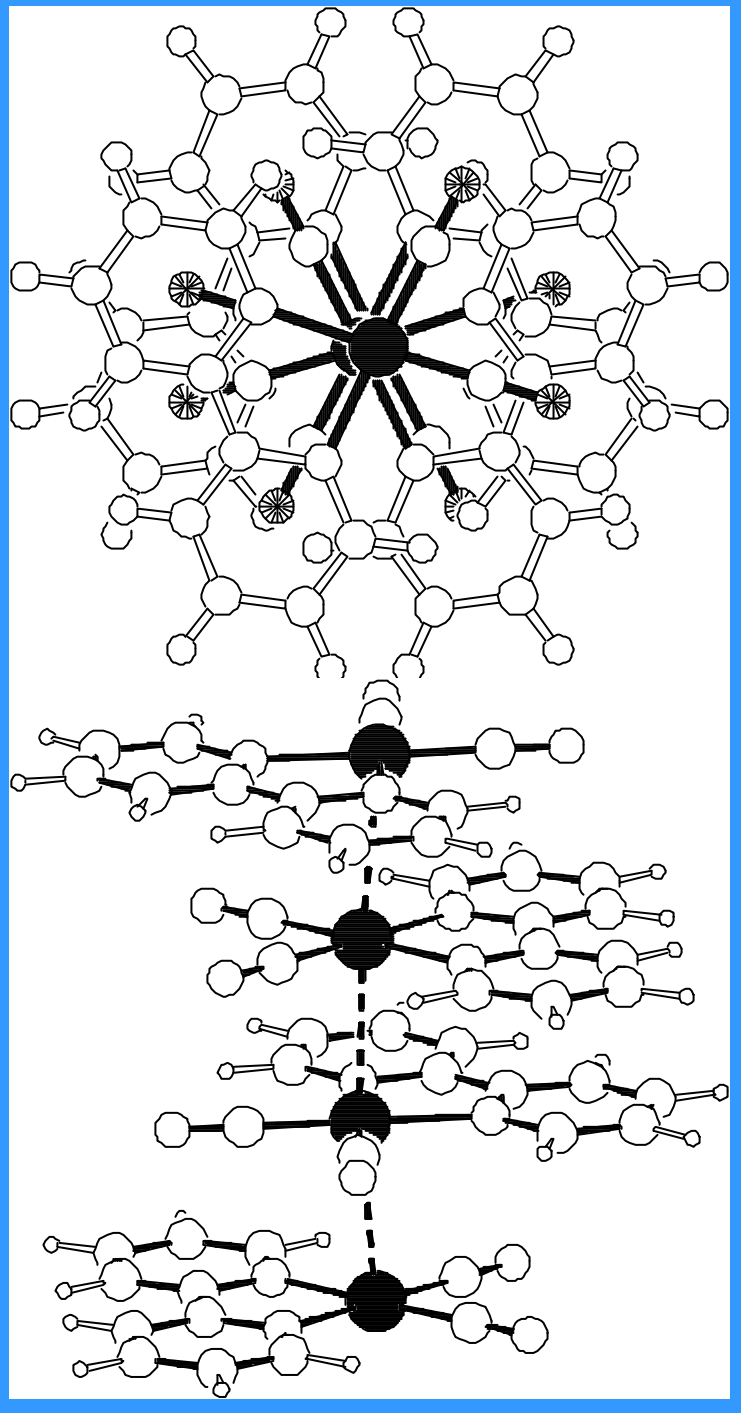
Structure 100.00 %
16.000
15.000
14.000
13.000
12.000
11.000
10.000
9.000
8.000
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0
6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54


rubipy05.raw:1
Structure 100.00 %
ITO 0.00 %
3.000
2.500
2.000
1.500
1.000
500
0
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80

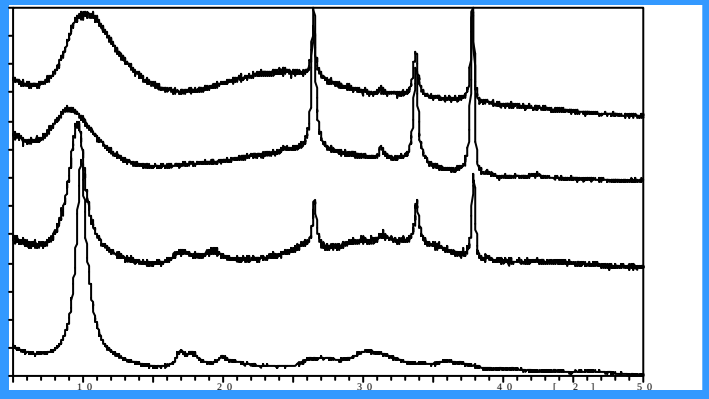


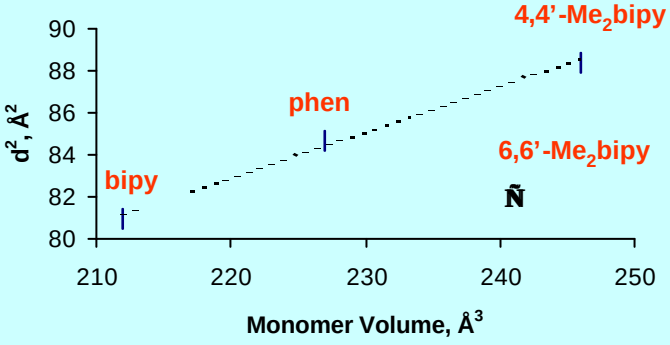
Correlation between molecular size and XRPD features

- Most prominent peak near $2\theta = 10°$ has hkl with l = 0
- Molecular volumes estimated by SMILE (D.Eufri, A.Sironi, *J.Mol.Graphics*, 1989, *7*, 165)
- For nearly equal spacings along z, d^2(peak at 10°) μ V_{mol}

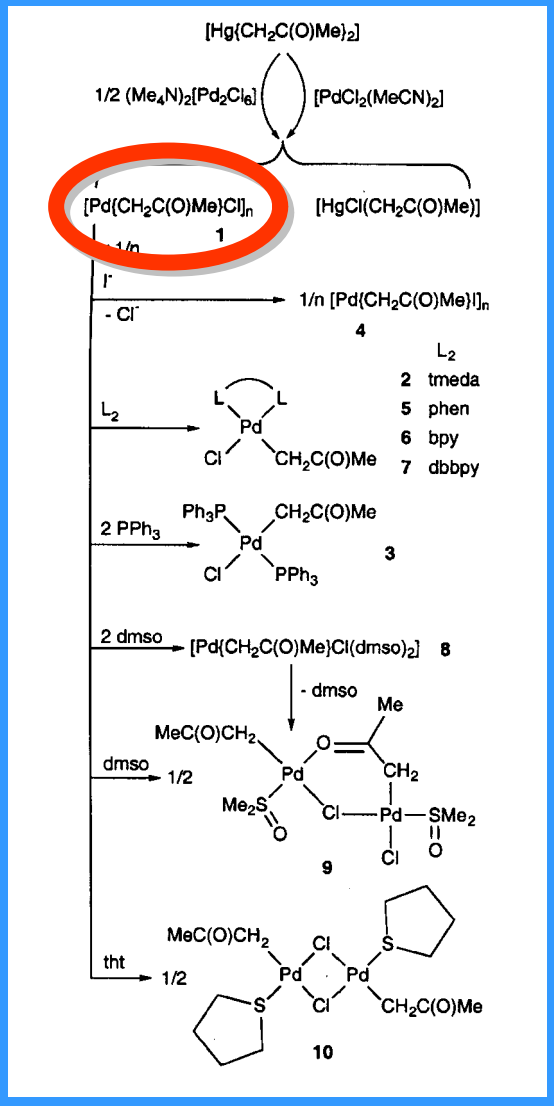
Electrochemically-generated $Ru(CO)_2(L)$ thin films

- 6,6'-dimethylbipy
- 4,4'-dimethylbipy
- 1,10-phenanthroline
- 2,2'-bipyridine (bipy)





Polymeric $[Pd(acetonyl)Cl]_n$



I⁻

Tmeda

Phen

Bipy

PPh_3

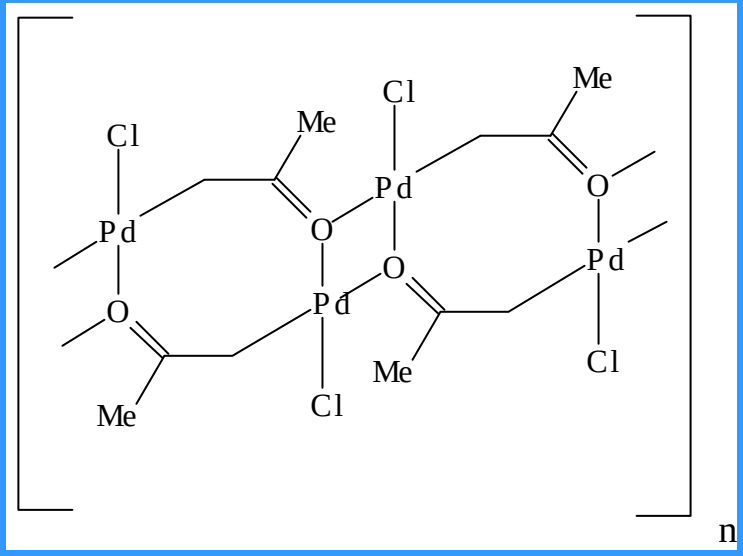
dmso

tht

"a key product for the synthesis of acetonylpalladium(II) complexes"

J.Vicente, et al.

***Organometallics* 2001, *20*, 2767**



- Indexing by TREOR-90 [M(11) = 15; F(11) = 37 (0.017,18)];
- Space Group Ibca, from systematic absences;
- Structure solution and refinement by simulated annealing and the Rietveld method, respectively, using TOPAS-R;
- C···C antibumping restraints and a rigid group for the acetonyl moiety were employed.
- Anisotropic peak broadening employed.

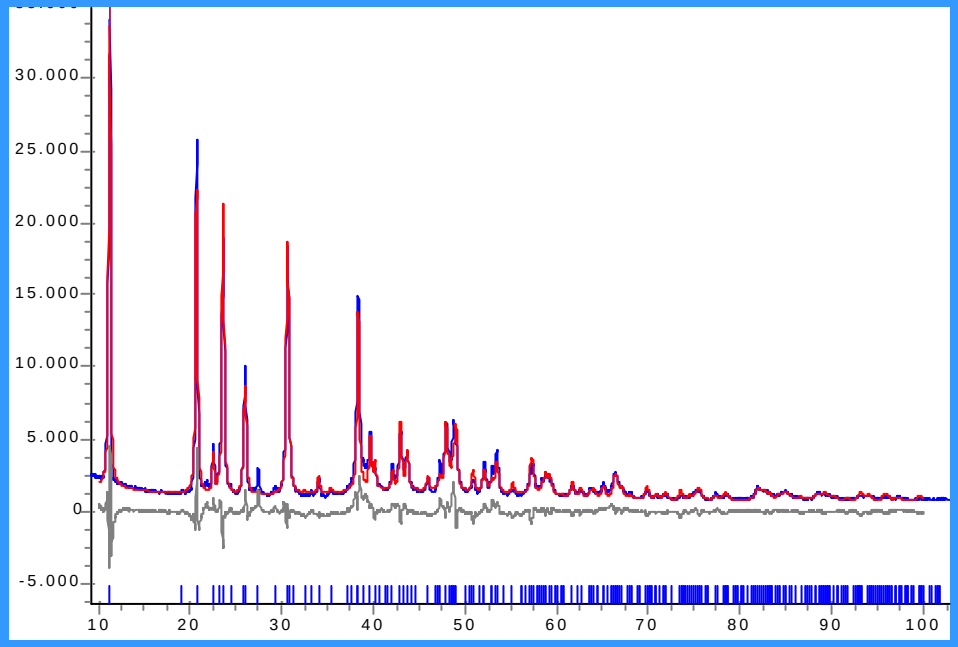
Rwp = 0.128

Rp = 0.096

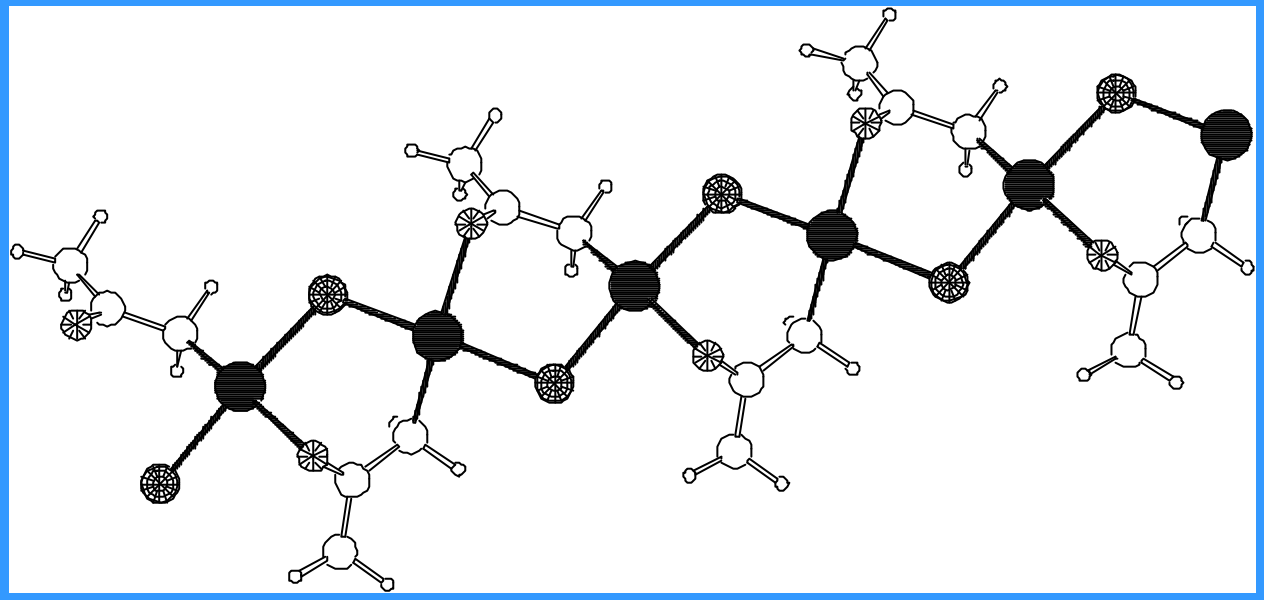
RBragg = 0.089

4500 data

$10 < 2\theta < 100^{\circ}$ range



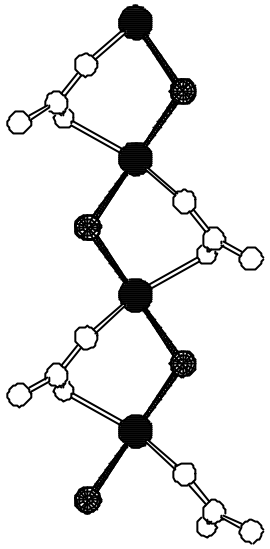
1D chain compound, with collinear Pd atoms

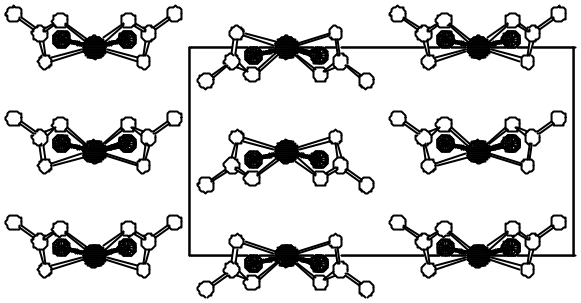


Relevant bond distances and angles: Pd···Pd 3.85(1) Å, Pd···Pd···Pd 180°; Pd-Cl 2.36(3) and 2.39(3) Å; Pd-Cl-Pd 108.9°; Pd-O 2.40(5), Pd-C2 2.16(6) Å; *trans*-Cl-Pd-Cl 161.4(4)°, *trans*-O-Pd-C2 161(2)°.

Space Group Pbca

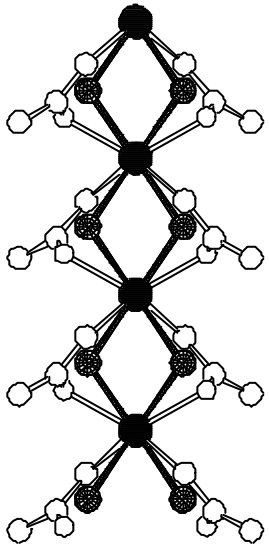
Ordered Chains

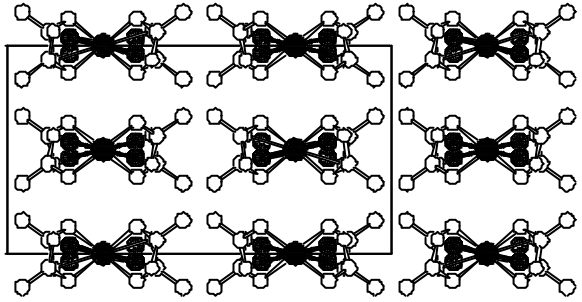




Space Group Ibca

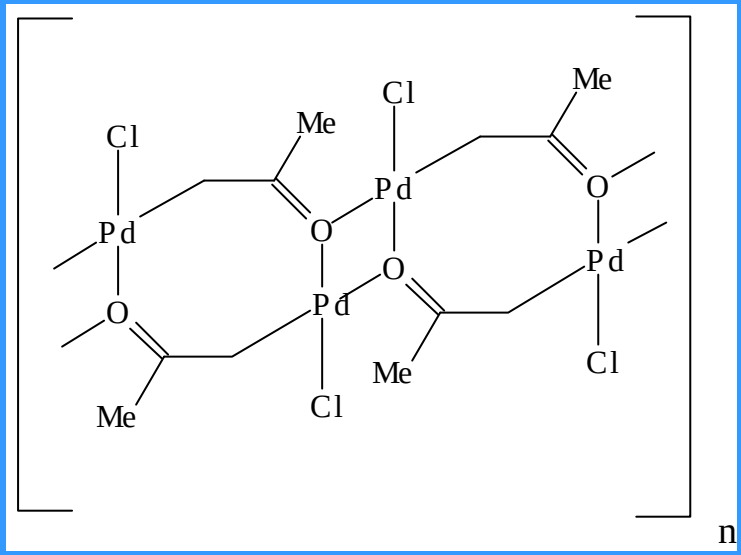
Disordered Chains





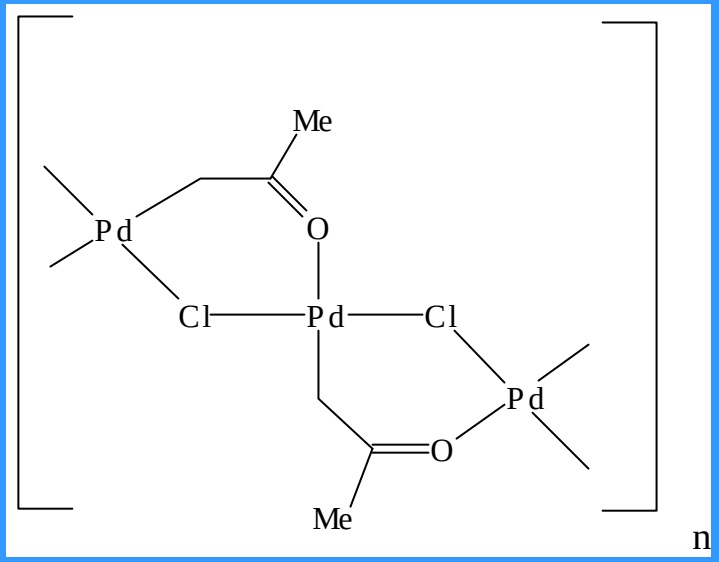
Proposed Connectivity

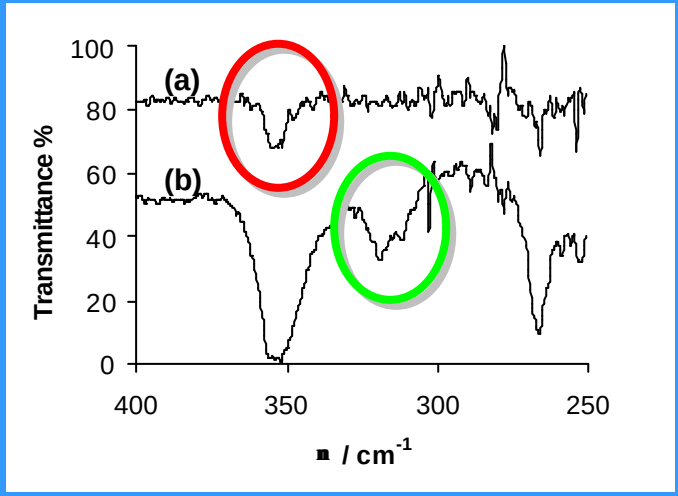
μ_3,η^1,η^2-acetonyl, Terminal Cl^-



True Connectivity

μ_2,η^1,η^1-acetonyl, Bridging Cl^-





IR spectra (nujol mull) in the 400-250 cm^{-1} region a) Diluted and b) Concentrated

Peaks at 268 and 354 cm^{-1}

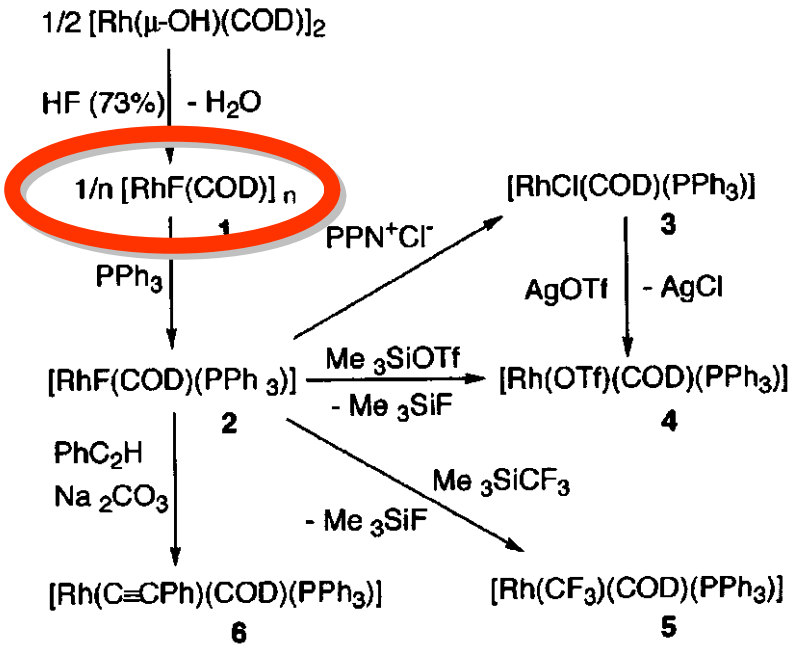
Polymeric $[Rh(COD)F]_n$

"Synthesis and Reactivity of Fluoro Complexes"

J.Vicente, et al.

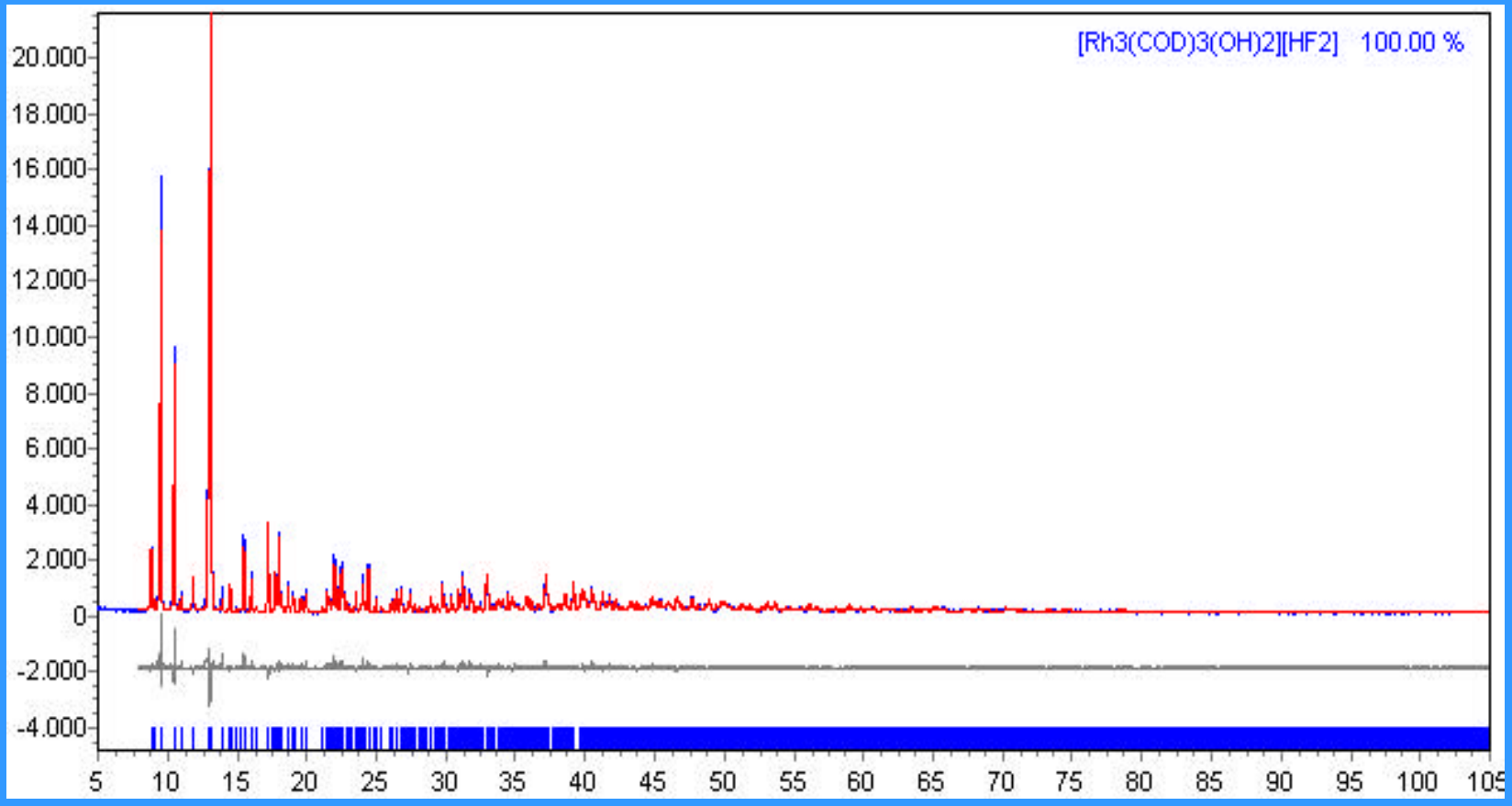
***Inorg.Chem.* 2001, *40*, 2636**

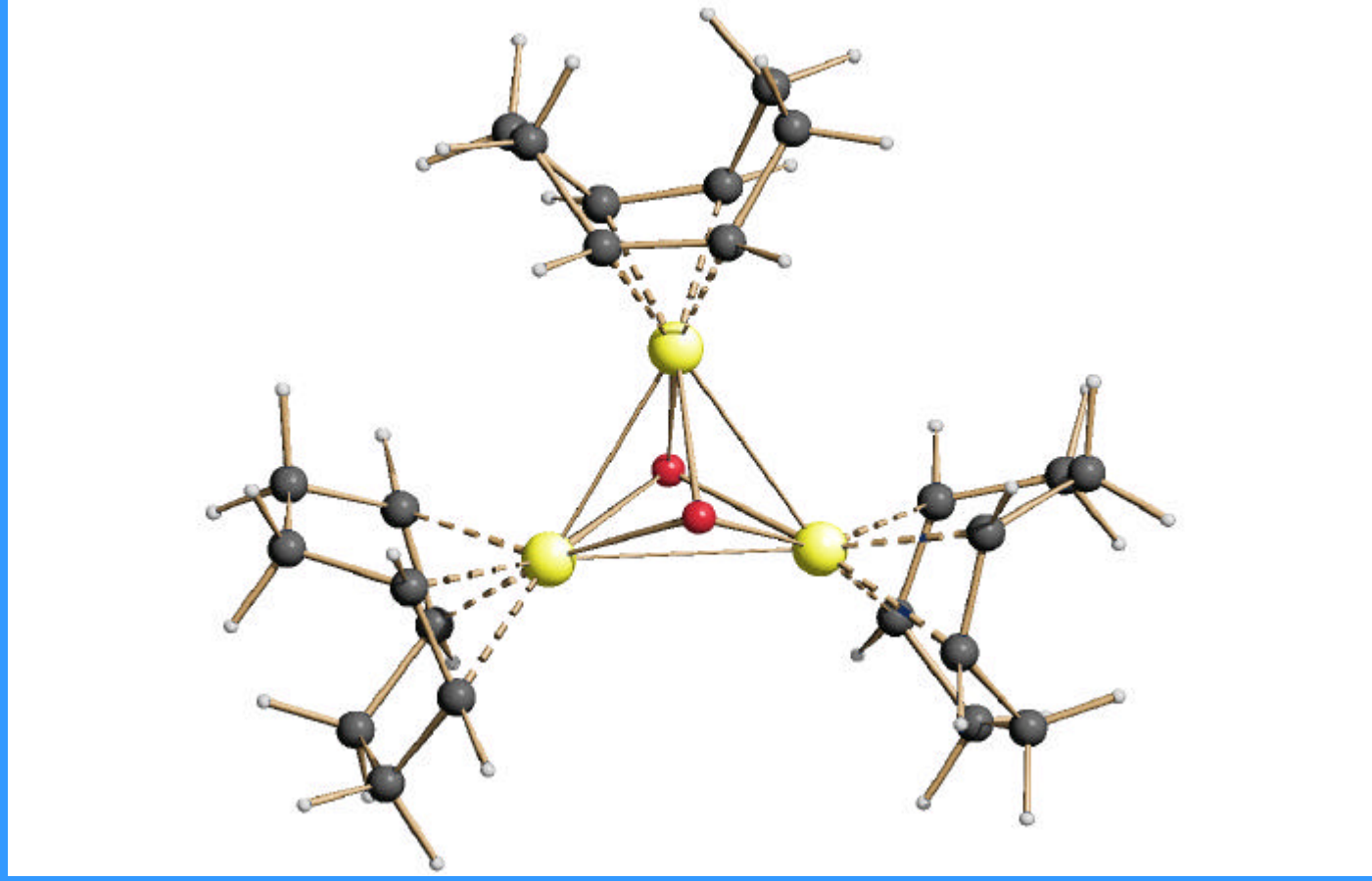
Scheme 1

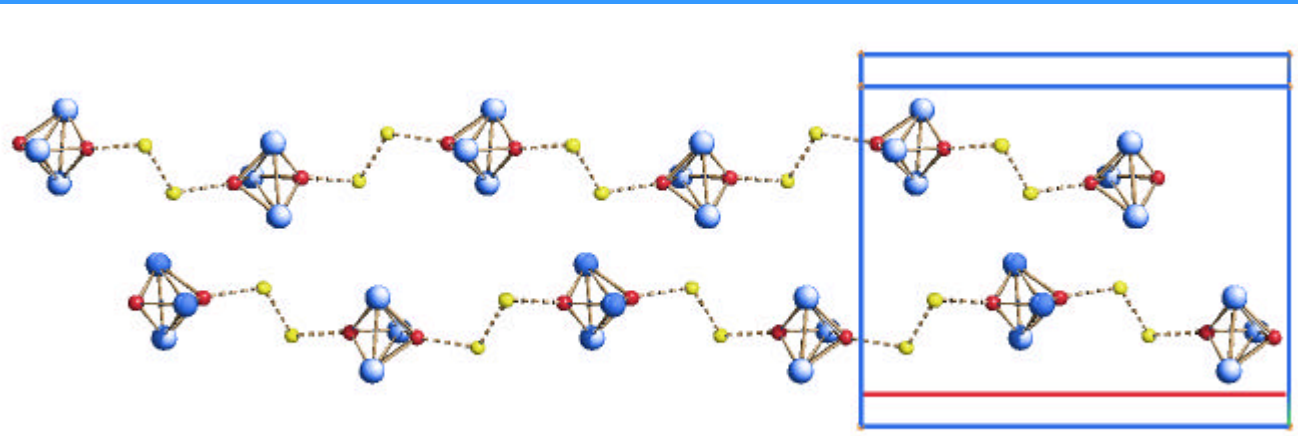


Solution by Patterson, Simulated Annealing (TOPAS-R) and Difference Fourier Methods (WINGX); Refinement by TOPAS-R.

Rp 0.079; Rwp 0.103; R(Bragg) 0.051; $10 < 2\theta < 105°$







Formula	Experimental	$[Rh(COD)F]_n$	$[Rh_3(COD)_3(OH)_2][HF_2]$
Analysis, %	C 41.76, H 5.53	C 41.42, H 5.66	C 40.81, H 5.58
^{1}H, ^{13}C NMR (RT)	COD only	COD only	COD + deshielded H's
^{19}F NMR	No Rh-F bond	Rh-F bond	No Rh-F bond
CP-MAS ^{19}F NMR	Single type of F	Single type of F	Single type of F
IR bands	1954 cm^{-1} (br)	?	F-H-F and O-H···F
ESI-MS (MeOH)	695 Da	?	$[Rh_3(COD)_3(OMe)_2]^+$
Synthesis	HF/H_2O + $[Rh(COD)OH]_2$	No OH groups	Presence of OH
Reactivity	With PPh_3	$RhF(COD)PPh_3$	$RhF(COD)PPh_3$ 59 %
Solubility in Organic Solvents	Very Poor	Polymer	Ionic Species

Summarizing:

Thanks to *ab-initio* studies on conventional XRPD data, a number of structural hypotheses based on chemical and spectroscopic evidence of various nature have been rejected, and new stoichiometries, connectivities and packing modes have been discovered.

But do not forget that:

An XRPD study is worthwhile only when suitable Single Crystals lack

Thank you all for your attention!

Acknowledgements

Prof. A.Sironi	Crystallography	Università di Milano
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Dr. S.Chardon	Electrochemistry	Université de Grenoble
Dr. S.Galli	Crystallography	Università dell'Insubria

* A number of undergraduate and graduate students

* $ MIUR, CNR, Chamber of Commerce of Como