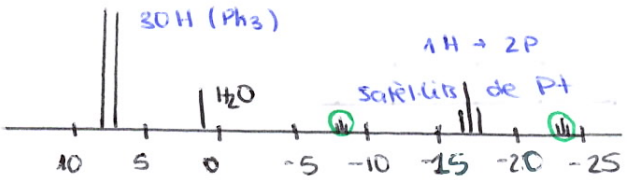
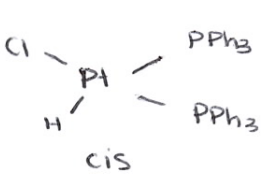
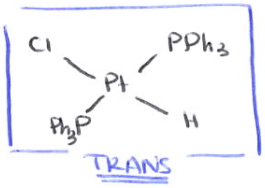
- PROBLEMES T4: RMN -

21/01/19

4.1 $[PtHCl(PPh_3)_2]$ RMN - ^1H







$^{195}Pt^{(*)}$ → $I = 1/2$ (Ab. 33,8 %)
Pt inactiu $I = 0$ (Ab. 66,2 %)

^{31}P → $I = 1/2$

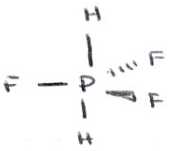
$P-Ph_3$ → $5 \times 3 = 15\,H \times 2 = 30\,H$

30 H → Singlet: químicament equivalents (pla)
↳ S'acobla a 1P / 3Ph $I = 1/2$
$2 N_p I_p + 1 = 2 \cdot 1 \cdot 1/2 + 1 =$ Doblet

H → Singlet → S'acobla a 2P en cis $2 \cdot 2 \cdot 1/2 + 1 = 3$ TRIPLET
↳ S'acobla al Pt^*?
Pt inactiu ($I = 0$) (66,2 %)
Pt^* $2 \cdot 1 \cdot 1/2 + 1 = 2$ (33,8 %)

Satèl·lits de Pt^*

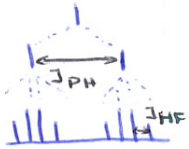
4.2. RMN ^1H, ^{19}F, ^{31}P $J_{PF} > J_{PH} > J_{HF}$ $I_H = 1/2$ $I_F = 1/2$ $I_{31P} = 1/2$



• RMN - ^1H 2H axials → químicament equivalents → Singlet ∫2.

→ 1 enllaç 1P → $2 \cdot 1 \cdot 1/2 + 1 =$ Doblet

→ 2 enllaços 3F → $2 \cdot 3 \cdot 1/2 + 1 =$ Quadruplet

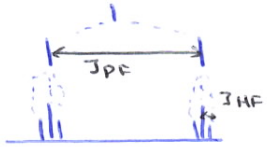


Doblet de quadruplets

• RMN - ^{19}F: 3 ^{19}F equatorials → químicament equivalents. Singlet ∫3.

→ 1 enllaç 1P → Doblet

→ 2 enllaços 2H → $2 \cdot 2 \cdot 1/2 + 1 =$ Triplet



Doblet de triplets

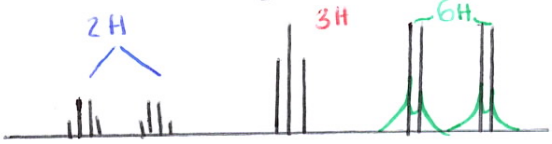
RMN - ^{31}P: ^{31}P → Singlet ∫1.

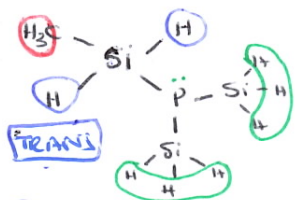
→ 1 enllaç 3F → Quadruplet

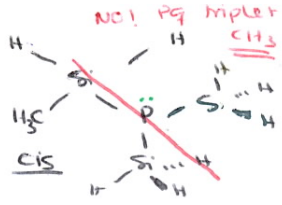
→ 1 enllaç 2H → Triplet

Quadruplet de triplets

4.3 RMN - ^1H $(SiH_3)_2PSiH_2CH_3$







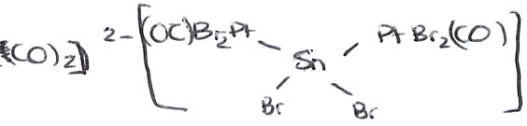
3 H químicament equivalents singlet → Triplet? 2 H químicament equivalents !) $2 \cdot 2 \cdot 1/2 + 1 = 3$

6H químicament equivalents 1P a 1 enllaç → Doblet

Ha i Hb ≠ 1 P a 2 enllaços → Doblet + 3 enllaços 3 H → Quadruplet

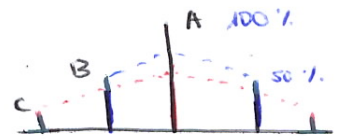
OK.

4.4 RMN-^{119}Sn $[Sn\,Br_2(PtBr_2(CO)_2)_2]^{2-}$



^{119}Sn $I = 1/2$

^{195}Pt $I = 1/2$



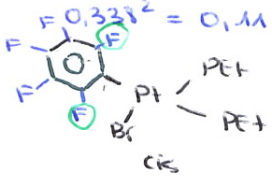
Quintuplet (= I)

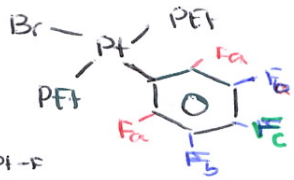
A: 1 Sn singlet 1 $\frac{662 \cdot 66,2}{10000} = 0,44 \rightarrow 100\,\%$

B: (1) 1 Pt* $2 \cdot 1 \cdot 1/2 + 1 = 2$ Doblet $\frac{66,2 \cdot 33,8}{1000} = 0,22 \rightarrow 50\,\%$

C: 2 P* Triplet $F\ 0,33^2 = 0,11 \rightarrow 25\,\%$

4.5. $^{195}P\{^1H\}$ PQ





$2F_b$ → triplet

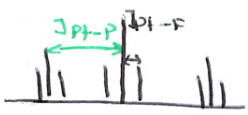
$1F_c$ → doblet

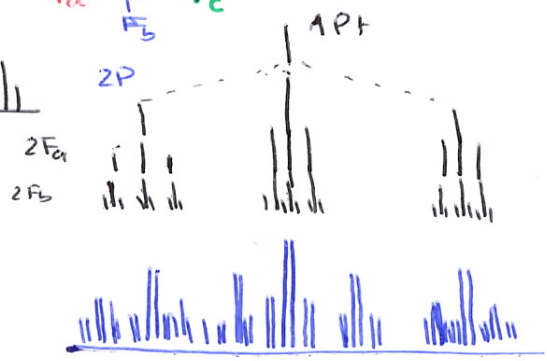
TRANS

A: 1 Pt singlet

2 P q. eq. → Triplet

$2F_a$ q. eq → Triplet





CIS

1 Pt singlet

$1P_{trans}$ → doblet

$1P_{cis}$ → doblet

2 F q. eq. → triplet

NO!

Triplet de triplets de triplets de doblets !

4.6. S

RMN-F

RMN-^{31}P

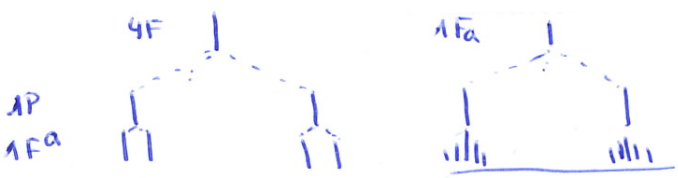
1 P Singlet

$1F_a$ JP-Faxial (1)

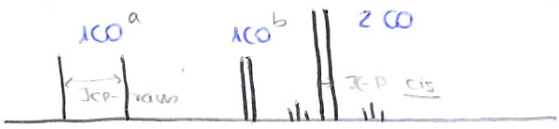
4 Fb

Quintuplet

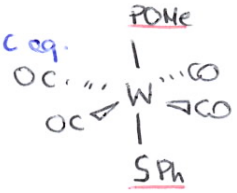
Oh



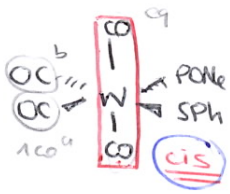
4.7. RMN - $^{13}C\{^1H\}$ CO

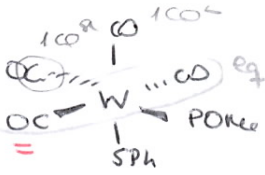


2/4C eq.



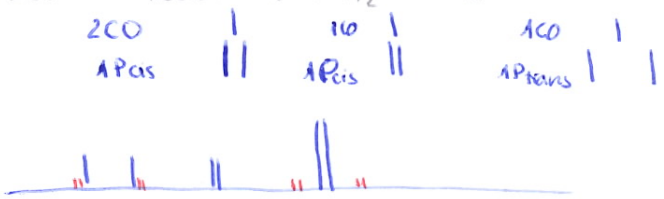
TRANS



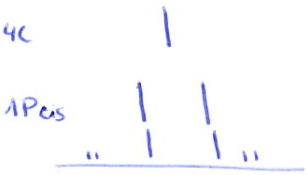


^{183}W ($I = 1/2$)
14, 28 %.
Wreactiu = 85, 72 %.

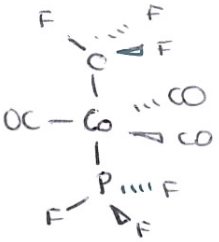
★ 2CO → Doblet $2 \cdot 1 \; 1/2 + 1 = 2$



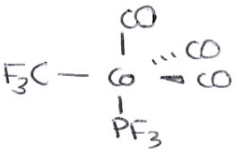
TRANS 4C



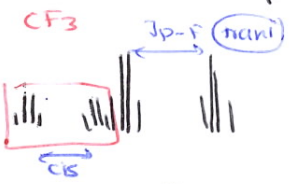
4.8. RMN - ^{19}F

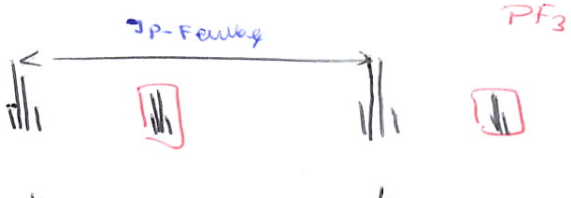


MER-

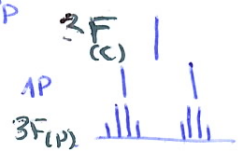


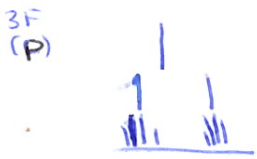
FAC-





MER ^{19}F ; ^{31}P

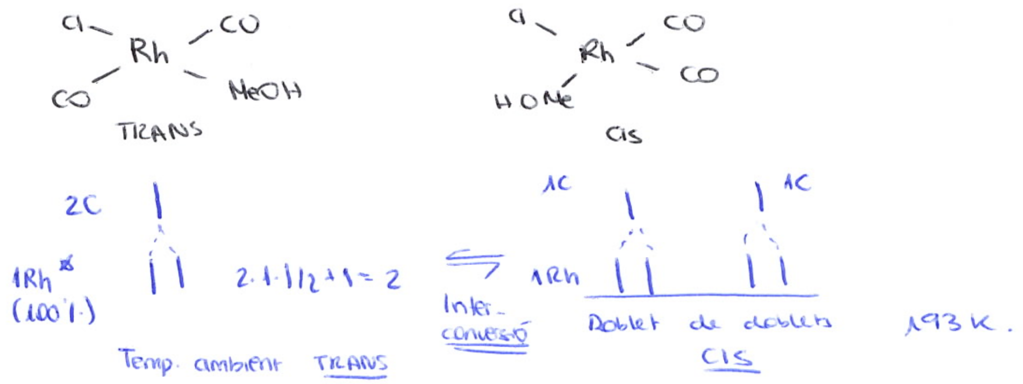




A T↓ interconversió mer - fac ? sí. cis ⟷ < ⟷ trans

A T↑ interconversió molt ràpida pont intermig Co He.

4.9.

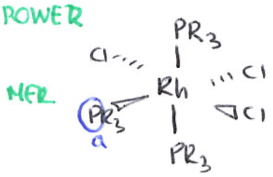


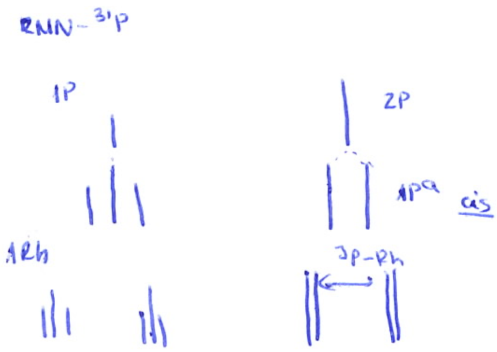
AP.1 POWER: sistemes dinàmics

Pt* no s'acobla.

A T falta 4P ⊖

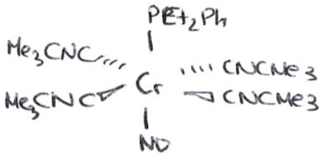
AP.2 POWER

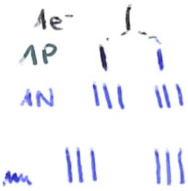




- PROBLEMES T5: RSE -

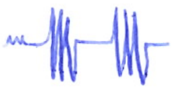
5.1. trans - $[Cr(NO)(PEt_2Ph)(CNCMe_3)_4]^{2+}$, $[Cr(NO)(dppe)_2F]$, $[Cr(NO)(CNCMe_3)_3\ dppe]^{2+}$



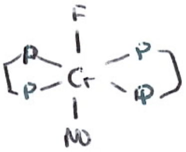


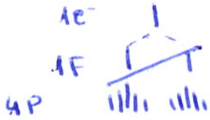
$2 \cdot 1 \cdot 1 + 1 = 3$

$2 \cdot 1 \cdot 3/2 + 1 = 4$

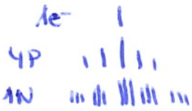


a)

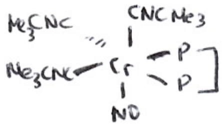




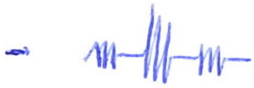
$I = 1/2$



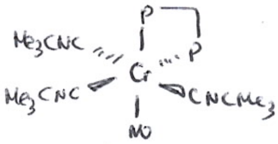
c)



FAC-



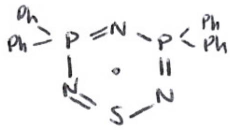
b)

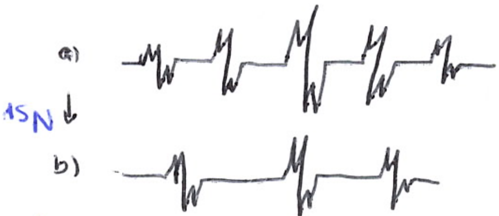


MER-

Els P en mer no són equivalents

5.2.





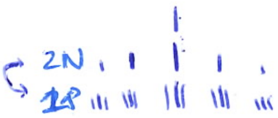
Quintuplet de ~~doblets~~ triplets

Triplet de ~~doblets~~ triplets

$^{31}P \rightarrow I = 1/2$

$^{14}N \rightarrow I = 1$

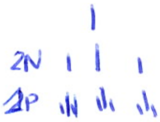
$^{15}N \rightarrow I = 1/2$



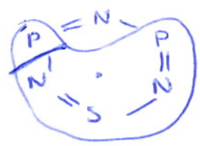
$2N \cdot 1 + 1 = 5 \rightarrow N_N = 2$

$2 \cdot 2 \cdot 1 + 1 = 5$

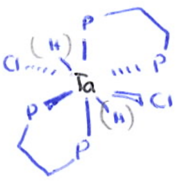
b) Triplet $^{15}I = 1/2 \rightarrow 2 \cdot 2 \cdot 1/2 + 1 = 3$



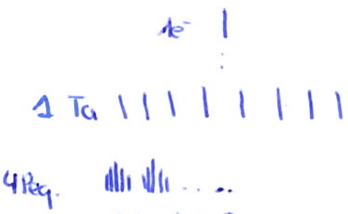
HOMO



5.3. H ↔ D no l'altera! No s'acobla a H Ta: $I = 7/2$ 100%.



TRANS



$2 \cdot 1 \cdot 7/2 + 1 = 8$

Octaplet ? de quintuplets.

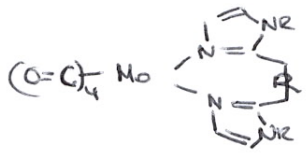
5.4. $[Co_3(CO)_9Se]$ Co: I = 7/2

$2 \cdot 3 \cdot 7/2 + 1 = 22$ senyals.

5.5. $[Mo(bmiq)(CO)_4]$ RSE

Oxidada $[Mo(bmiq)(CO)_4]^+$

Reduïda $[Mo(bmiq)(CO)_4]^-$



^{95}Mo ^{97}Mo | I = 7/2 | 15,8 % 9,6 %

(A) 1e⁻ |

OK

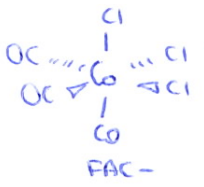
$2 \cdot 1 \cdot 5/2 + 1 = 6$ Només s'acaba a NO!

Satèl·lits de Mo.

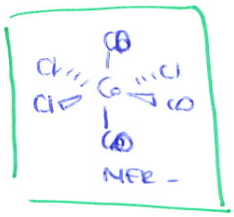
(B) 1e⁻ |

$2 \cdot 1 \cdot 1 + 1 = 3$ Només s'acaba a 1 N (AMINO)

5.6. $[NBu_4][Co(Cl)_3(CO)_3]$



FAC-



MER-

1e⁻ |

3C $2 \cdot 1/2 \cdot 3 + 1 = 4$

1Co $2 \cdot 1 \cdot 7/2 + 1 = 8$

MER-

1e⁻ |

(Co^8) $2 \cdot 1 \cdot 7/2 + 1 = 8$

$2\,^{13}C$ trans. $\rightarrow 2 \cdot 2 \cdot 1/2 + 1 = 3$

$1\,^{13}C \rightarrow 2 \cdot 1 \cdot 1/2 + 1 = 2$ Doblet

$2\,^{12}C$ 1e⁻ |

×8

$1\,^{13}C$ |

×8

(?) ✓ Triplet de doblet

5.7. $[VCl_4(PEt)_2]$ 1e⁻ |

2P

I (^{51}V) = 7/2

$2 \cdot 1 \cdot 7/2 + 1 = 8$