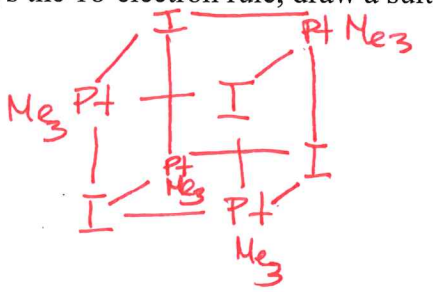
Chemistry 4000/5000
Midterm Examination #3 (December 8, 2021)

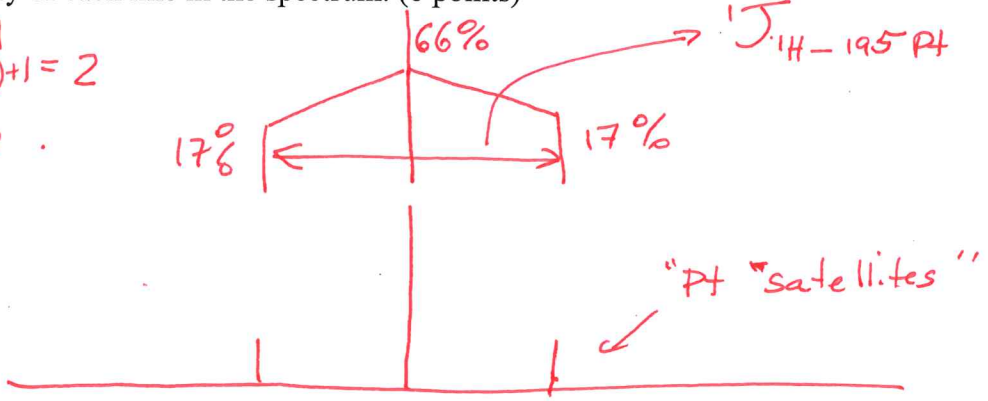
1. a) Given that $[Me_3Pt(\mu_3\text{-}I)]_4$ is highly symmetrical (only 1 resonance in the ^1H NMR spectrum) and obeys the 18-electron rule, draw a suitable structure. (4 points)



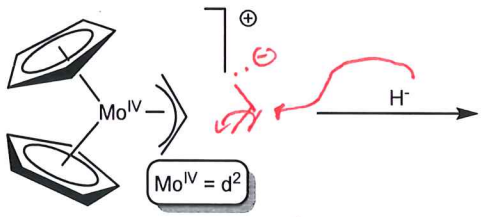
Pt (IV) d6 → 6e⁻
3 Me → 3x2e⁻ = 6e⁻
3 Ib → 3x2e⁻ = 6e⁻
18e⁻

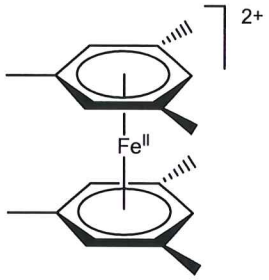
b) Assuming no coupling is observed between nuclei that are more than 3 bonds away from one another, predict the ^1H NMR spectrum of the compound you drew in part (a) using a tree diagram (^{195}Pt natural abundance = 33.8%, I = ½). Be sure to indicate the relative intensity of each line in the spectrum. (6 points)

$^1J_{^1H-^{195}Pt}$ $2nI+1$ $2(1)(\frac{1}{2})+1 = 2$
34 % of time.

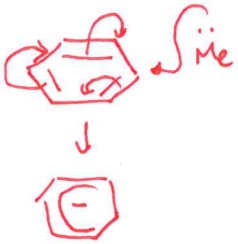


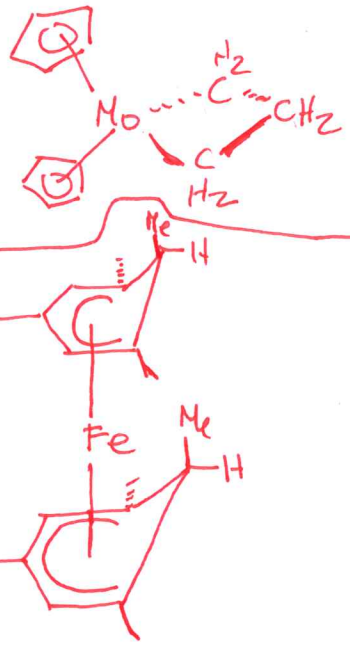
2. Use DGM rules to predict the products of the following reactions. *Very briefly* explain your reasoning. (8 points)





2 Me$^-$

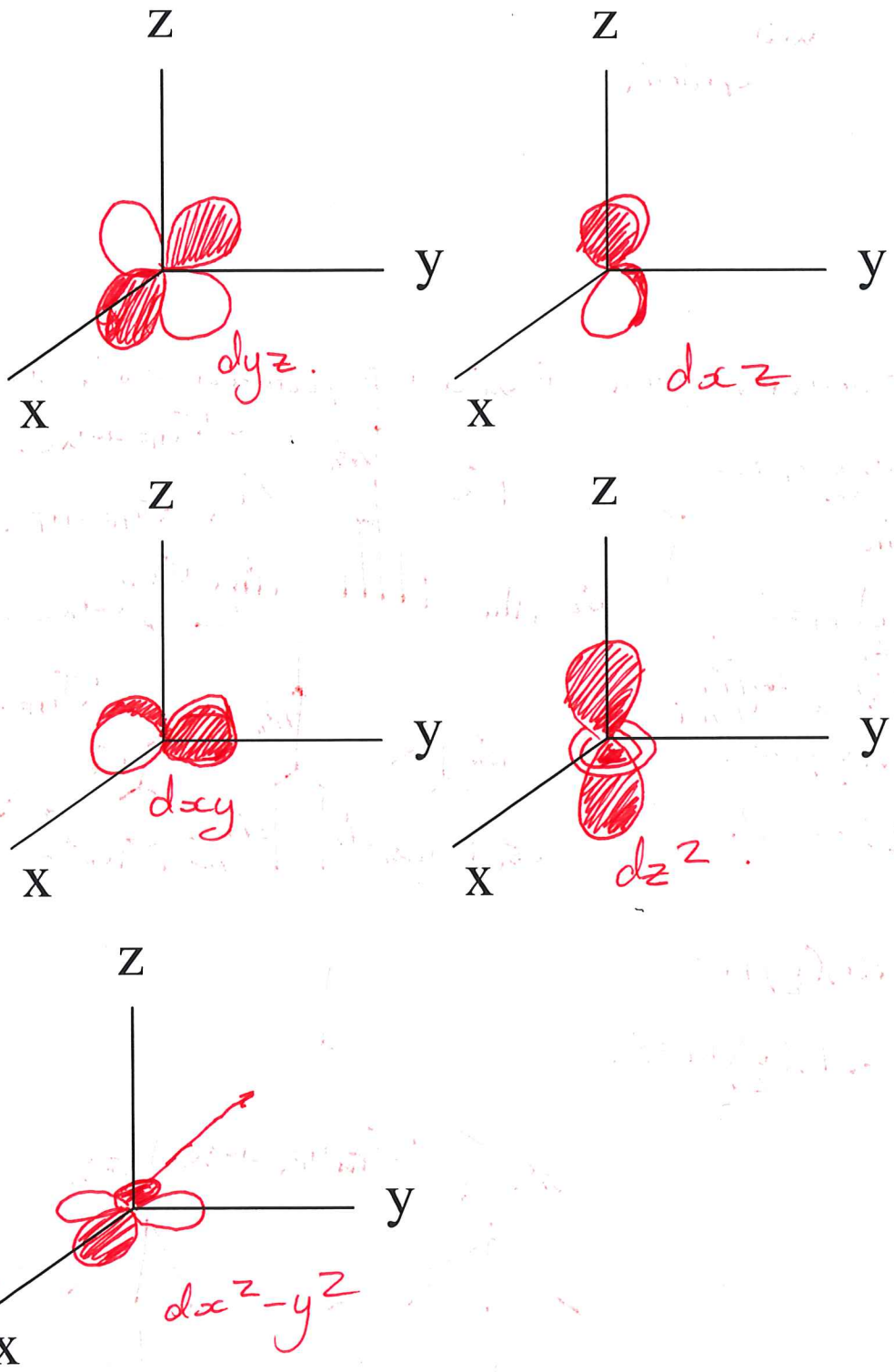




2) open > closed
3) for odd polyenes internal attack for metals that are not highly e⁻ withdrawing
↳ e.g. d² ω NO good π acceptor ligands
→ Dications usually react twice with nucleophiles
1) even > odd

3. **UNDERGRADUATE STUDENTS ONLY**

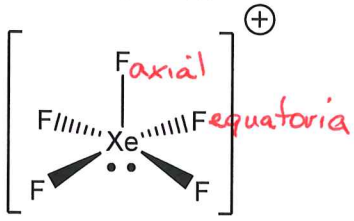
a) Draw and label the d-orbitals on the provided axes. (10 points)



4. Grubbs' catalyst is best known for what type of reactions? (6 points)

olefin metathesis

5. The XeF_5^+ cation formed from the reaction between XeF_6 and a strong Lewis acid exhibits a static square pyramidal structure:



^{19}F natural abundance = 100%, $I = ½$
^{129}Xe natural abundance = 26.44%, $I = ½$
^{131}Xe natural abundance = 21.18%, $I = 3/2$

(ASSUME THERE IS NO COUPLING TO ^{131}Xe)

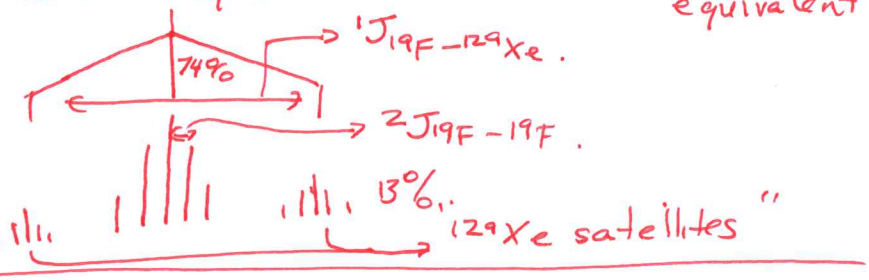
a) What would you predict the ^{19}F NMR spectrum of XeF_5^+ to look like? (How many signals and what multiplicity would those signals have?) Explain in words what you expect to see and simulate the spectrum using a tree diagram. Be sure to indicate the relative intensity of each line in the spectrum. (8 points)

* → two ^{19}F resonances from Faxial + Fequatorial which are not chemically equivalent.

Axial

$^1J_{^{19}F-^{129}Xe}$ $2(1)(\frac{1}{2})+1=2$ ↑ 26.44% of time

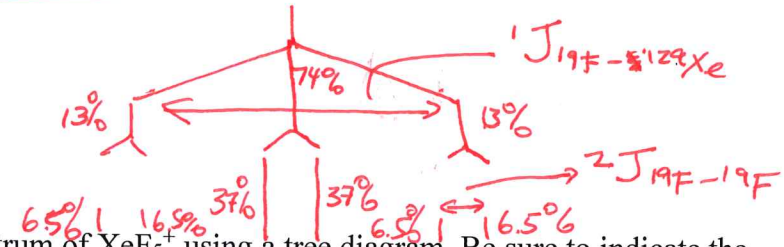
$^2J_{^{19}F-^{19}F}$ $2(4)(\frac{1}{2})+1=5$



Equatorial ↙ 26.44% of time

$^1J_{^{19}F-^{129}Xe}$ $2(1)(\frac{1}{2})+1=2$

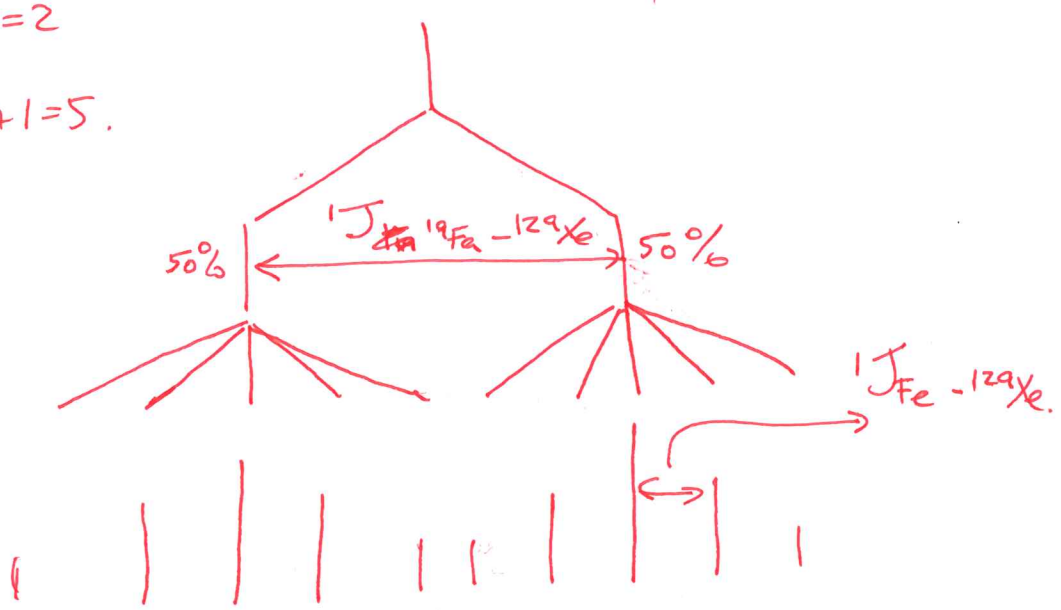
$^2J_{^{19}F-^{19}F}$ $2(1)(\frac{1}{2})+1=2$



b) Predict the ^{129}Xe NMR spectrum of XeF_5^+ using a tree diagram. Be sure to indicate the relative intensity of each line in the spectrum. (8 points)

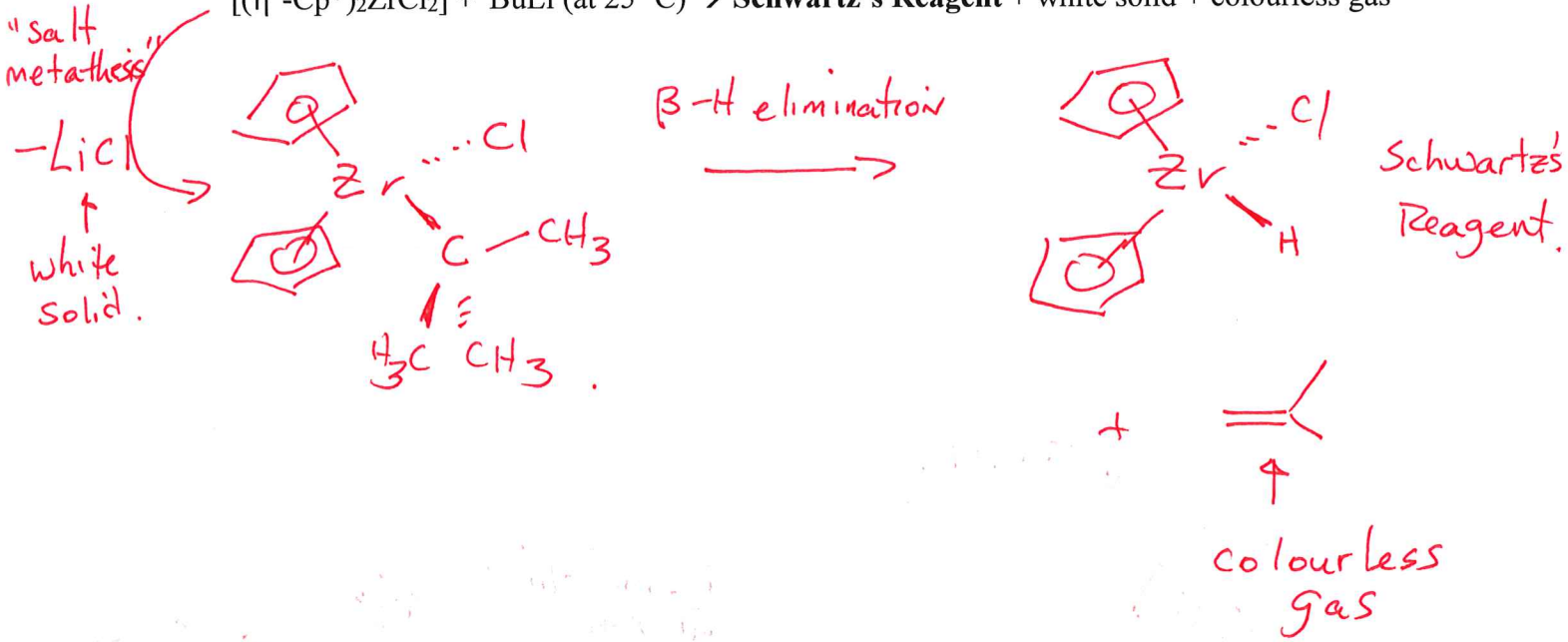
$^1J_{^{19}F_a-^{129}Xe}$ $2(1)(\frac{1}{2})+1=2$

$^1J_{^{19}F_e-^{129}Xe}$ $2(4)(\frac{1}{2})+1=5$.

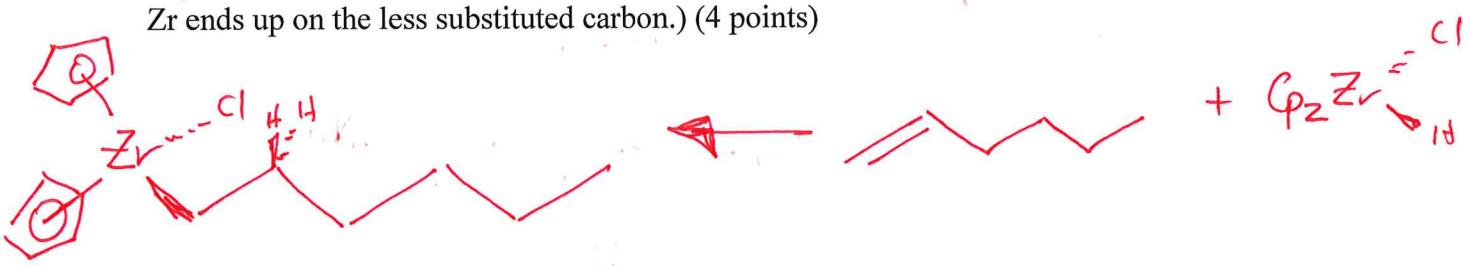


6. a) Schwartz's Reagent is prepared by the reaction of zirconocene dichloride and one equivalent of ^{t}BuLi, as outlined below. Identify the three products of this reaction and *briefly* explain how they form. (8 points)

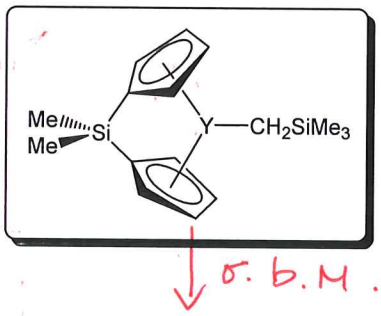
$[(\eta^5\text{-Cp}^*)_2ZrCl_2]$ + ^{t}BuLi (at 25 °C) → **Schwartz's Reagent** + white solid + colourless gas

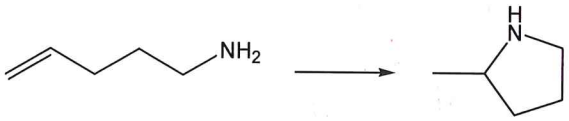


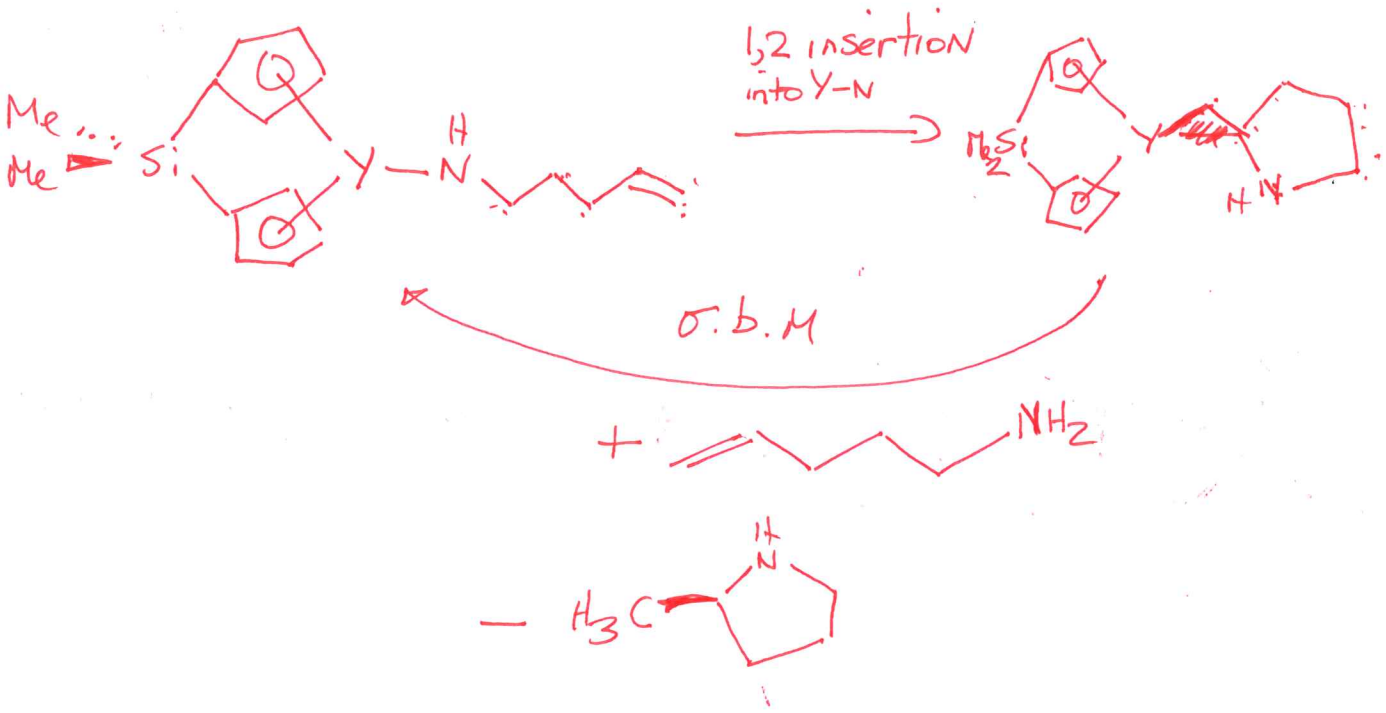
b) Schwartz's Reagent is valuable for participating in hydrozirconation reactions. Draw the product of a reaction between Schwartz's Reagent and 1-hexene. No explanation is required. (Hint: Hydrozirconation reactions proceed in a regiospecific fashion wherein the Zr ends up on the less substituted carbon.) (4 points)



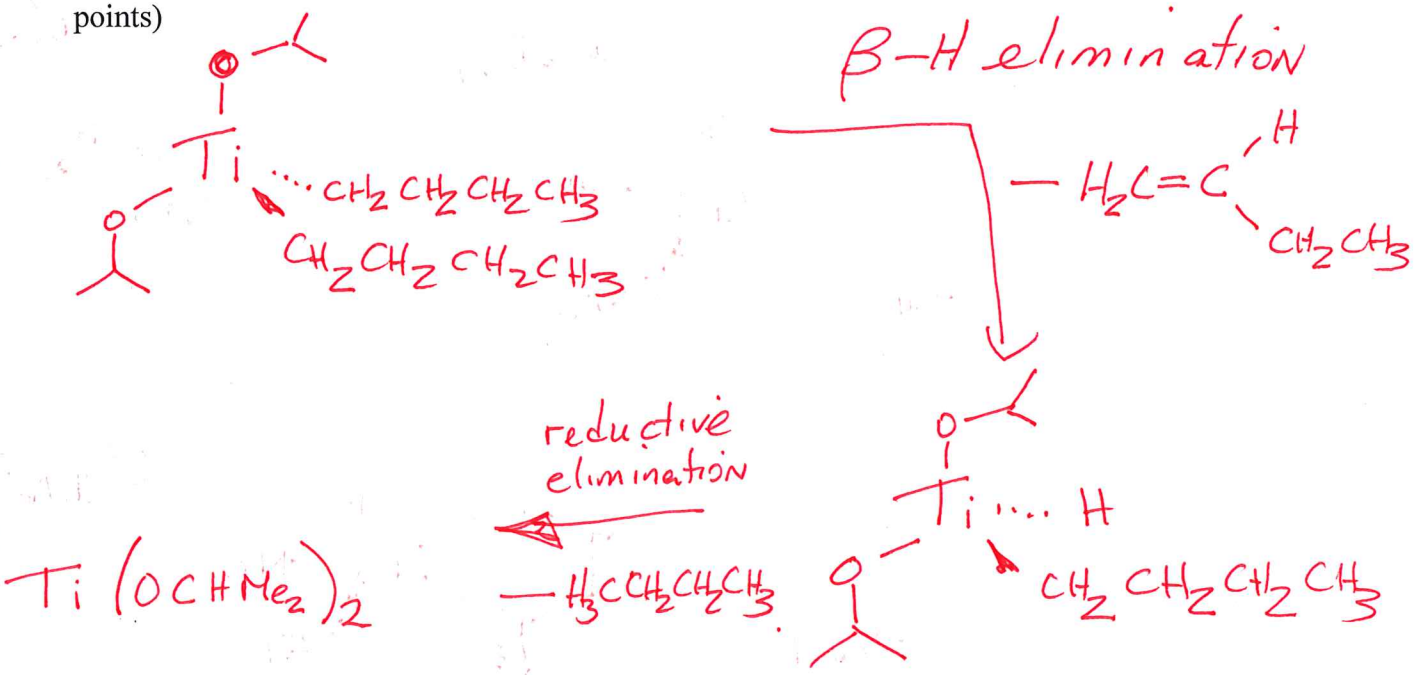
7. **Graduate Students Only (Undergraduate students may attempt for bonus marks).**
The following transformation is catalyzed by the yttrium (III) d^0 complex shown below. Note that the active catalyst is generated in one step from this complex during which one equivalent of $SiMe_4$ is released. Propose a catalytic cycle based on the fundamental reaction types you have learned. Note that it is not necessary to indicate electron movement, but the structure of every intermediate is required. Indicate in words (5 or less/reaction) what kind of fundamental organometallic reaction(s) are taking place in each step of the catalytic cycle. (10 points)







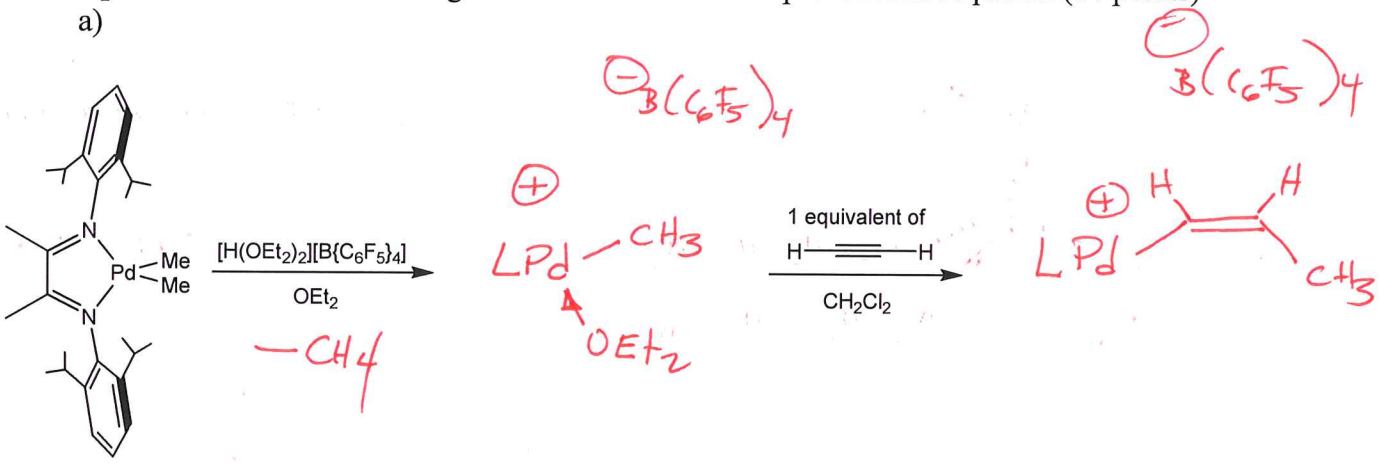
8. At room temperature, the $[Ti(nBu)_2(OCHMe_2)_2]$ decomposes to the unusual **Ti(II) species** $[Ti(OCHMe_2)_2]$, releasing 1-butene, followed by *n*-butane. Provide a mechanism for this reaction. Note that it is not necessary to indicate electron movement, but the structure of every intermediate is required. Indicate in words (5 or less/reaction) what kind of fundamental organometallic reaction(s) are taking place in each step of the mechanism. (12 points)



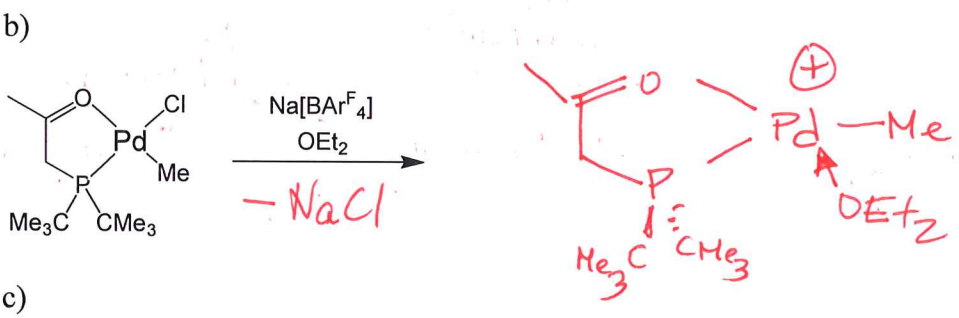
9. **Answer part a and any two of b-e.**

For the reactions below, provide the correct products (both inorganic and organic). **None of the reactants or starting materials are present in excess of the amount shown in the equations.** No additional reagents can be added. No explanation is required. (14 points)

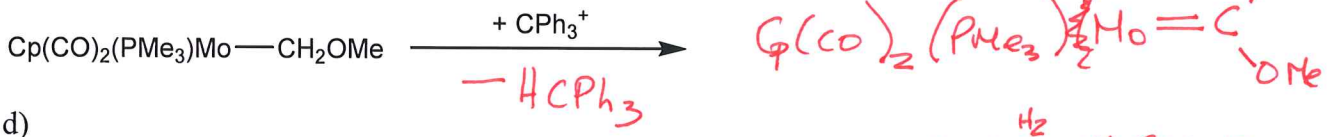
a)



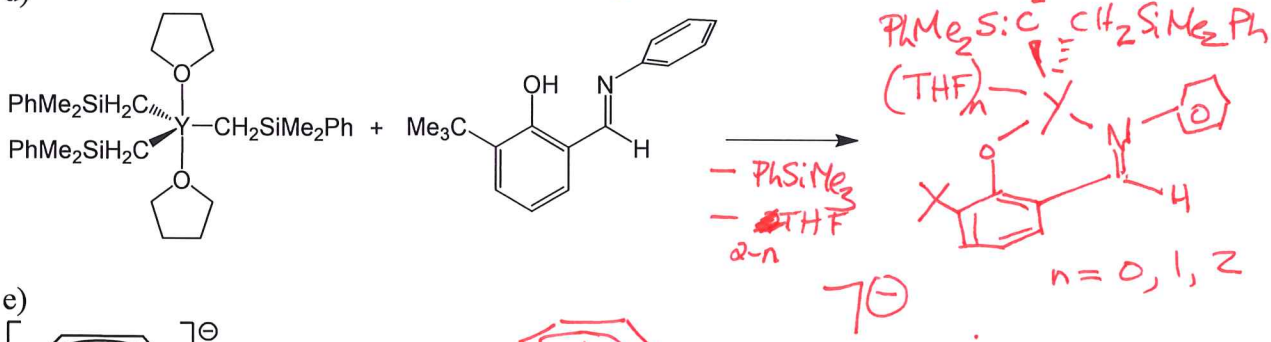
b)



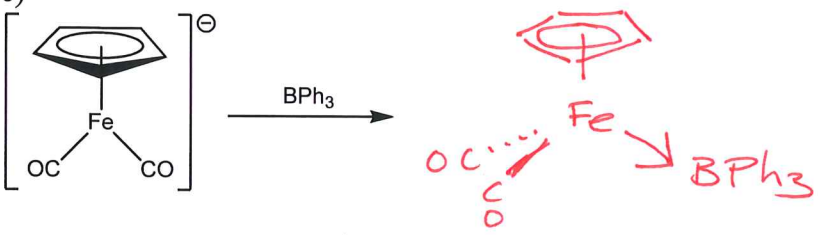
c)



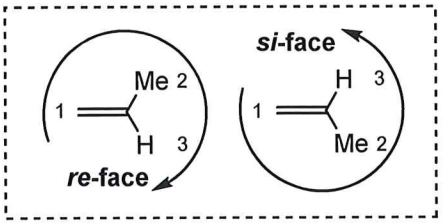
d)

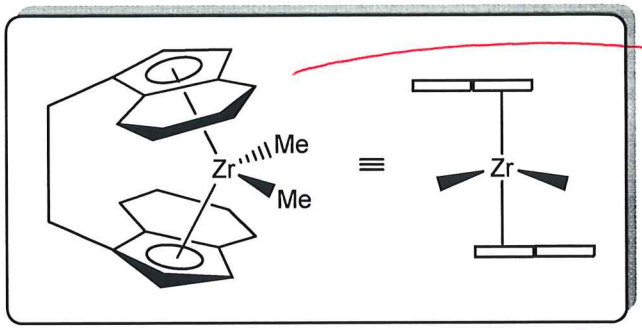


e)

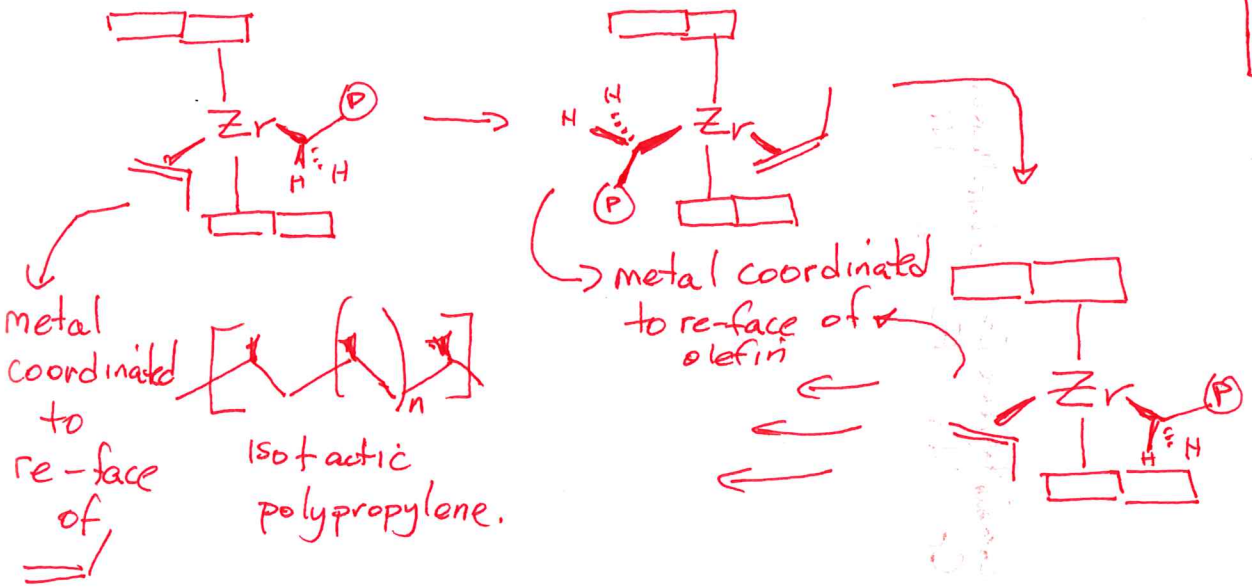


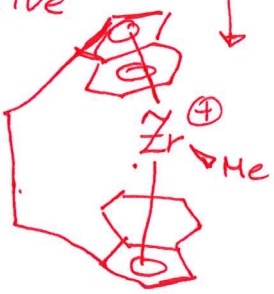
10. After activation with $[CPh_3]^+[B(C_6F_5)_4]^-$, would you expect the following complex to form atactic, isotactic, syndiotactic or hemiisotactic polypropylene? Draw a short sequence for this type of polypropylene, and explain how such a microstructure arises. (12 points)





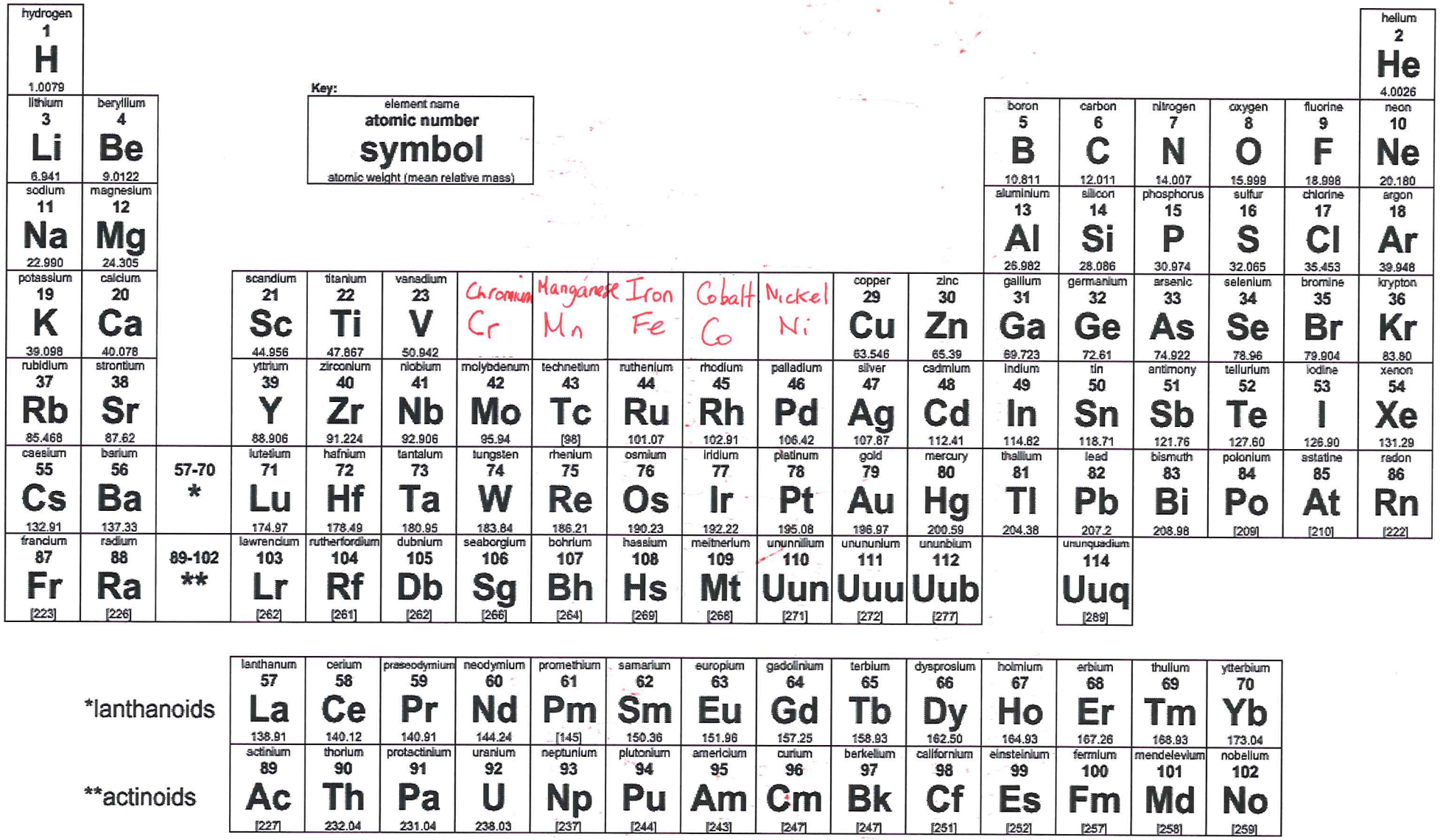
The catalyst will afford isotactic polypropylene as every insertion is selective (via coordination of the re-face of propylene).





BONUS:

The periodic table provided on the last page of this exam paper has 5 missing elements. Add in the symbol and name of the missing elements. (5 points)


Key:
element name
atomic number
symbol
atomic weight (mean relative mass)
hydrogen 1 H 1.0079
helium 2 He 4.0026
lithium 3 Li 6.941
beryllium 4 Be 9.0122
boron 5 B 10.811
carbon 6 C 12.011
nitrogen 7 N 14.007
oxygen 8 O 15.999
fluorine 9 F 18.998
neon 10 Ne 20.180
sodium 11 Na 22.990
magnesium 12 Mg 24.305
aluminium 13 Al 26.982
silicon 14 Si 28.086
phosphorus 15 P 30.974
sulfur 16 S 32.065
chlorine 17 Cl 35.453
argon 18 Ar 39.948
potassium 19 K 39.098
calcium 20 Ca 40.078
scandium 21 Sc 44.956
titanium 22 Ti 47.867
vanadium 23 V 50.942
Chromium Cr
Manganese Mn
Iron Fe
Cobalt Co
Nickel Ni
copper 29 Cu 63.546
zinc 30 Zn 65.39
gallium 31 Ga 69.723
germanium 32 Ge 72.61
arsenic 33 As 74.922
selenium 34 Se 78.96
bromine 35 Br 79.904
krypton 36 Kr 83.80
rubidium 37 Rb 85.468
strontium 38 Sr 87.62
yttrium 39 Y 88.906
zirconium 40 Zr 91.224
niobium 41 Nb 92.906
molybdenum 42 Mo 95.94
technetium 43 Tc [98]
ruthenium 44 Ru 101.07
rhodium 45 Rh 102.91
palladium 46 Pd 106.42
silver 47 Ag 107.87
cadmium 48 Cd 112.41
indium 49 In 114.82
tin 50 Sn 118.71
antimony 51 Sb 121.76
tellurium 52 Te 127.60
iodine 53 I 126.90
xenon 54 Xe 131.29
caesium 55 Cs 132.91
barium 56 Ba 137.33
57-70 *
lutetium 71 Lu 174.97
hafnium 72 Hf 178.49
tantalum 73 Ta 180.95
tungsten 74 W 183.84
rhenium 75 Re 186.21
osmium 76 Os 190.23
iridium 77 Ir 192.22
platinum 78 Pt 195.08
gold 79 Au 196.97
mercury 80 Hg 200.59
thallium 81 Tl 204.38
lead 82 Pb 207.2
bismuth 83 Bi 208.98
polonium 84 Po [209]
astatine 85 At [210]
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bohrium 107 Bh [264]
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unununium 111 Uuu [272]
ununbium 112 Uub [277]
ununquadium 114 Uuq [289]
*lanthanoids
lanthanum 57 La 138.91
cerium 58 Ce 140.12
praseodymium 59 Pr 140.91
neodymium 60 Nd 144.24
promethium 61 Pm [145]
samarium 62 Sm 150.36
europium 63 Eu 151.96
gadolinium 64 Gd 157.25
terbium 65 Tb 158.93
dysprosium 66 Dy 162.50
holmium 67 Ho 164.93
erbium 68 Er 167.26
thulium 69 Tm 168.93
ytterbium 70 Yb 173.04
**actinoids
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thorium 90 Th 232.04
protactinium 91 Pa 231.04
uranium 92 U 238.03
neptunium 93 Np [237]
plutonium 94 Pu [244]
americium 95 Am [243]
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berkelium 97 Bk [247]
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