

## **Catalyst design for synthesis, Midterm Exam**

**November 8, 2023**

**Name (First name, Last name):**

**Student ID number:**

PCs must not be used. No material other than the exam paper is permitted.

**Overall 32 points.**

You can also write the answer on the back of the exam paper if you run out of space; if you choose to do so, make a clear indication in the exam paper.

You have a maximum of **90 minutes** to finish the exam.

# THE PERIODIC TABLE

|                                            |                                       |                                        |                                            |                                                  |                                         |                                         |                                        |                                         |                                          |                                          |                                      |                                       |                                       |                                       |                                        |                                      |                                       |             |  |                 |  |             |  |
|--------------------------------------------|---------------------------------------|----------------------------------------|--------------------------------------------|--------------------------------------------------|-----------------------------------------|-----------------------------------------|----------------------------------------|-----------------------------------------|------------------------------------------|------------------------------------------|--------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|----------------------------------------|--------------------------------------|---------------------------------------|-------------|--|-----------------|--|-------------|--|
| THE PERIODIC TABLE                         |                                       |                                        |                                            |                                                  |                                         |                                         |                                        |                                         |                                          |                                          |                                      |                                       |                                       |                                       |                                        |                                      |                                       | 18<br>VIIIA |  |                 |  |             |  |
| 1<br>IA                                    |                                       |                                        |                                            |                                                  |                                         |                                         |                                        |                                         |                                          |                                          |                                      |                                       |                                       |                                       |                                        |                                      |                                       |             |  |                 |  |             |  |
| 1<br><b>H</b><br>1<br>1.008<br>Hydrogen    |                                       |                                        |                                            |                                                  |                                         |                                         |                                        |                                         |                                          |                                          |                                      |                                       |                                       |                                       |                                        |                                      | 2<br><b>He</b><br>2<br>4.00<br>Helium |             |  |                 |  |             |  |
| 2<br>IIA                                   |                                       |                                        |                                            |                                                  |                                         |                                         |                                        |                                         |                                          |                                          |                                      |                                       |                                       |                                       |                                        |                                      |                                       |             |  |                 |  |             |  |
| 2<br><b>Li</b><br>3<br>6.94<br>Lithium     | <b>Be</b><br>4<br>9.01<br>Beryllium   |                                        |                                            |                                                  |                                         |                                         |                                        |                                         |                                          |                                          |                                      |                                       |                                       |                                       |                                        |                                      |                                       |             |  |                 |  |             |  |
|                                            |                                       | <b>H</b><br>1<br>1.008<br>Hydrogen     |                                            | SYMBOL<br>ATOMIC NUMBER<br>ATOMIC WEIGHT<br>NAME |                                         |                                         |                                        |                                         |                                          |                                          |                                      |                                       |                                       |                                       |                                        |                                      |                                       |             |  | ( ) = ESTIMATES |  |             |  |
| 3<br>IIIB                                  | 4<br>IVB                              | 5<br>VB                                | 6<br>VIB                                   | 7<br>VIIB                                        | 8<br>9<br>10<br>VIII                    |                                         |                                        | 11<br>IB                                | 12<br>IIB                                | 13<br>IIIA                               | 14<br>IVA                            | 15<br>VA                              | 16<br>VIA                             | 17<br>VIIA                            |                                        |                                      |                                       |             |  |                 |  |             |  |
| 3<br><b>Na</b><br>11<br>22.99<br>Sodium    | <b>Mg</b><br>12<br>24.31<br>Magnesium |                                        |                                            |                                                  |                                         |                                         |                                        |                                         |                                          |                                          |                                      |                                       |                                       |                                       |                                        |                                      |                                       |             |  |                 |  |             |  |
| 4<br><b>K</b><br>19<br>39.10<br>Potassium  | <b>Ca</b><br>20<br>40.08<br>Calcium   | <b>Sc</b><br>21<br>44.96<br>Scandium   | <b>Ti</b><br>22<br>47.88<br>Titanium       | <b>V</b><br>23<br>50.94<br>Vanadium              | <b>Cr</b><br>24<br>52.00<br>Chromium    | <b>Mn</b><br>25<br>54.94<br>Manganese   | <b>Fe</b><br>26<br>55.85<br>Iron       | <b>Co</b><br>27<br>58.93<br>Cobalt      | <b>Ni</b><br>28<br>58.69<br>Nickel       | <b>Cu</b><br>29<br>63.55<br>Copper       | <b>Zn</b><br>30<br>65.39<br>Zinc     | <b>Ga</b><br>31<br>69.72<br>Gallium   | <b>Ge</b><br>32<br>72.61<br>Germanium | <b>As</b><br>33<br>74.92<br>Arsenic   | <b>Se</b><br>34<br>78.96<br>Selenium   | <b>Br</b><br>35<br>79.90<br>Bromine  | <b>Kr</b><br>36<br>83.80<br>Krypton   |             |  |                 |  |             |  |
| 5<br><b>Rb</b><br>37<br>85.47<br>Rubidium  | <b>Sr</b><br>38<br>87.62<br>Strontium | <b>Y</b><br>39<br>88.91<br>Yttrium     | <b>Zr</b><br>40<br>91.22<br>Zirconium      | <b>Nb</b><br>41<br>92.91<br>Niobium              | <b>Mo</b><br>42<br>95.94<br>Molybdenum  | <b>Tc</b><br>43<br>(97.9)<br>Technetium | <b>Ru</b><br>44<br>101.07<br>Ruthenium | <b>Rh</b><br>45<br>102.91<br>Rhodium    | <b>Pd</b><br>46<br>106.42<br>Palladium   | <b>Ag</b><br>47<br>107.87<br>Silver      | <b>Cd</b><br>48<br>112.41<br>Cadmium | <b>In</b><br>49<br>114.82<br>Indium   | <b>Sn</b><br>50<br>118.71<br>Tin      | <b>Sb</b><br>51<br>121.76<br>Antimony | <b>Te</b><br>52<br>127.60<br>Tellurium | <b>I</b><br>53<br>126.90<br>Iodine   | <b>Xe</b><br>54<br>131.29<br>Xenon    |             |  |                 |  |             |  |
| 6<br><b>Cs</b><br>55<br>132.91<br>Cesium   | <b>Ba</b><br>56<br>137.33<br>Barium   | <b>La</b><br>57<br>138.91<br>Lanthanum | <b>Hf</b><br>72<br>178.49<br>Hafnium       | <b>Ta</b><br>73<br>180.95<br>Tantalum            | <b>W</b><br>74<br>183.85<br>Tungsten    | <b>Re</b><br>75<br>186.21<br>Rhenium    | <b>Os</b><br>76<br>190.2<br>Osmium     | <b>Ir</b><br>77<br>192.22<br>Iridium    | <b>Pt</b><br>78<br>195.08<br>Platinum    | <b>Au</b><br>79<br>196.97<br>Gold        | <b>Hg</b><br>80<br>200.59<br>Mercury | <b>Tl</b><br>81<br>204.38<br>Thallium | <b>Pb</b><br>82<br>207.2<br>Lead      | <b>Bi</b><br>83<br>208.98<br>Bismuth  | <b>Po</b><br>84<br>(209)<br>Polonium   | <b>At</b><br>85<br>(210)<br>Astatine | <b>Rn</b><br>86<br>(222)<br>Radon     |             |  |                 |  |             |  |
| 7<br><b>Fr</b><br>87<br>223.02<br>Francium | <b>Ra</b><br>88<br>226.03<br>Radium   | <b>Ac</b><br>89<br>227.03<br>Actinium  | <b>Rf</b><br>104<br>(261)<br>Rutherfordium | <b>Db</b><br>105<br>(262)<br>Dubnium             | <b>Sg</b><br>106<br>(263)<br>Seaborgium | <b>Bh</b><br>107<br>(262)<br>Bohrium    | <b>Hs</b><br>108<br>(265)<br>Hassium   | <b>Mt</b><br>109<br>(266)<br>Meitnerium | Unnamed<br>Discovery<br>110<br>Nov. 1994 | Unnamed<br>Discovery<br>111<br>Nov. 1994 | Unnamed<br>Discovery<br>112<br>1996  |                                       | Unnamed<br>Discovery<br>114<br>1999   |                                       | Unnamed<br>Discovery<br>116<br>1999    |                                      | Unnamed<br>Discovery<br>118<br>1999   |             |  |                 |  |             |  |
| ALKALI METALS                              |                                       | ALKALI EARTH METALS                    |                                            |                                                  |                                         |                                         |                                        |                                         |                                          |                                          |                                      |                                       |                                       |                                       |                                        |                                      |                                       |             |  | HALOGENS        |  | NOBLE GASES |  |

ALKALI  
METALS

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EARTH  
METALS

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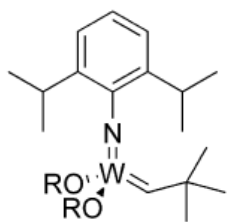
LANTHANIDES

ACTINIDES

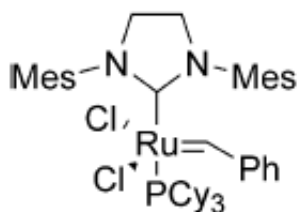
|                                      |                                           |                                        |                                        |                                       |                                        |                                         |                                       |                                         |                                          |                                       |                                          |                                        |                                          |
|--------------------------------------|-------------------------------------------|----------------------------------------|----------------------------------------|---------------------------------------|----------------------------------------|-----------------------------------------|---------------------------------------|-----------------------------------------|------------------------------------------|---------------------------------------|------------------------------------------|----------------------------------------|------------------------------------------|
| <b>Ce</b><br>58<br>140.12<br>Cerium  | <b>Pr</b><br>59<br>140.91<br>Praseodymium | <b>Nd</b><br>60<br>144.24<br>Neodymium | <b>Pm</b><br>61<br>(145)<br>Promethium | <b>Sm</b><br>62<br>150.36<br>Samarium | <b>Eu</b><br>63<br>152.97<br>Europium  | <b>Gd</b><br>64<br>157.25<br>Gadolinium | <b>Tb</b><br>65<br>158.93<br>Terbium  | <b>Dy</b><br>66<br>162.50<br>Dysprosium | <b>Ho</b><br>67<br>164.93<br>Holmium     | <b>Er</b><br>68<br>167.26<br>Erbium   | <b>Tm</b><br>69<br>168.93<br>Thulium     | <b>Yb</b><br>70<br>173.04<br>Ytterbium | <b>Lu</b><br>71<br>174.97<br>Lutetium    |
| <b>Th</b><br>90<br>232.04<br>Thorium | <b>Pa</b><br>91<br>231.04<br>Protactinium | <b>U</b><br>92<br>238.03<br>Uranium    | <b>Np</b><br>93<br>237.05<br>Neptunium | <b>Pu</b><br>94<br>(240)<br>Plutonium | <b>Am</b><br>95<br>243.06<br>Americium | <b>Cm</b><br>96<br>(247)<br>Curium      | <b>Bk</b><br>97<br>(248)<br>Berkelium | <b>Cf</b><br>98<br>(251)<br>Californium | <b>Es</b><br>99<br>252.08<br>Einsteinium | <b>Fm</b><br>100<br>257.10<br>Fermium | <b>Md</b><br>101<br>(257)<br>Mendelevium | <b>No</b><br>102<br>259.10<br>Nobelium | <b>Lr</b><br>103<br>262.11<br>Lawrencium |

1. (8 points)

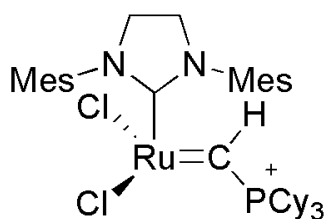
Describe the oxidation state and the number of electrons at the metal for the following complexes.



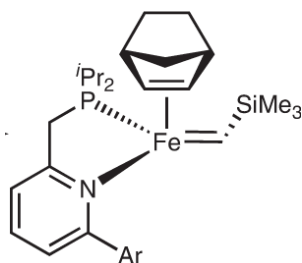
W (VI) or (+6); 0 electron at metal. (1 point each answer)



Ru(IV) or (4+); 4 electrons at metal (1 point each answer)

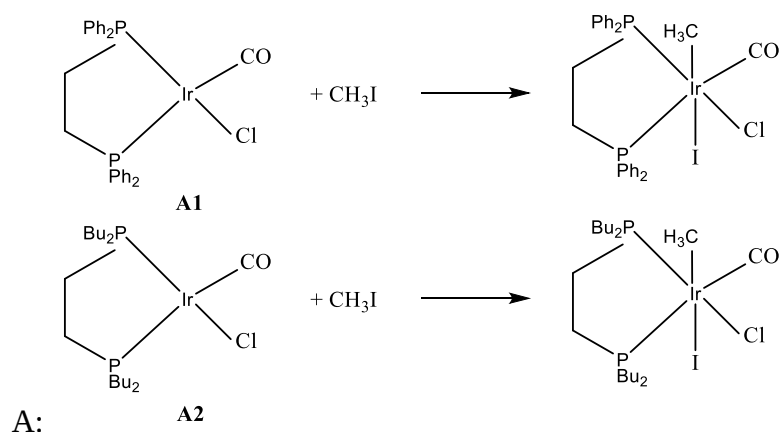


$[\text{B}(\text{C}_6\text{F}_5)_4]^-$  Ru(IV) or (4+); 4 electrons at metal (1 point each answer)

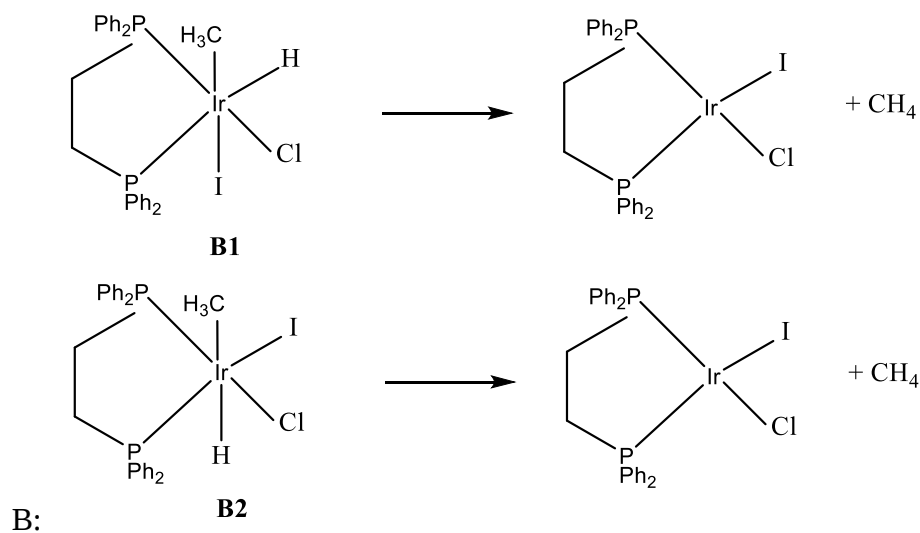


Fe(II) or (2+); 6 electrons at metal. (1 point each answer)

2. For the following reactions, choose the complex that has the higher reaction rate, and explain why. (4 points)

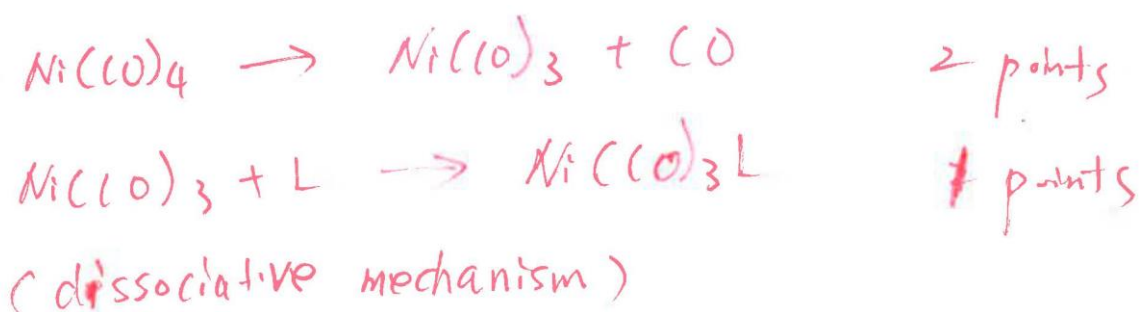


The reaction of A2 is faster, (1 point) because Bu group is more electron donating than Ph group, which is better for oxidative addition. (1 point)



The reaction of B1 is faster, (1 point) because the CH<sub>3</sub> group and H group are cis to one another, which is for reductive elimination than in B2, where the two groups are trans. (1 point)

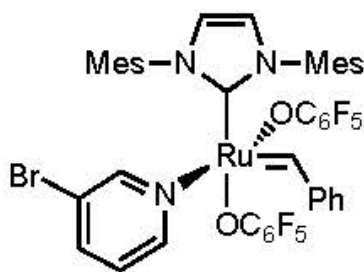
3.  $\text{Ni}(\text{CO})_4$  can undergo substitution reaction with an incoming neutral ligand L to give  $\text{Ni}(\text{CO})_3\text{L}$ . Kinetic studies show that the rate is first order in Ni and zero order in L. Draw a mechanism of the ligand substitution reaction. Explain the observed kinetics using this mechanism. (5 points)



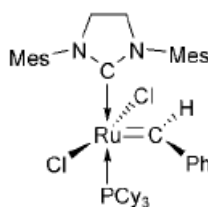
For kinetics, first dissociative step is rate limiting,  
 so first order in Ni, and zero order in L.

2 points

4. The following Ru catalyst (Ru-a) was found to be more active than the Grubbs II catalyst in ring-closing metathesis. Explain why (2 points)



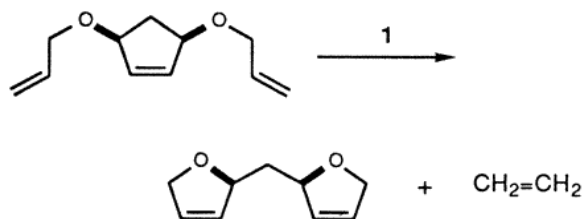
(Ru-a)



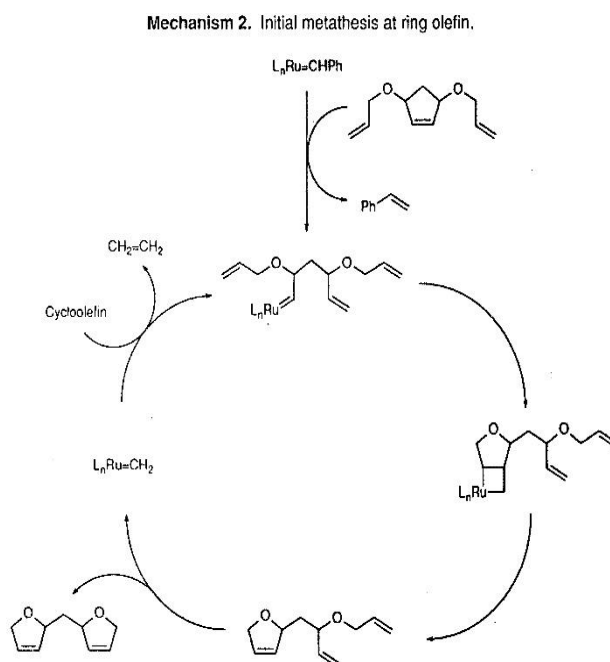
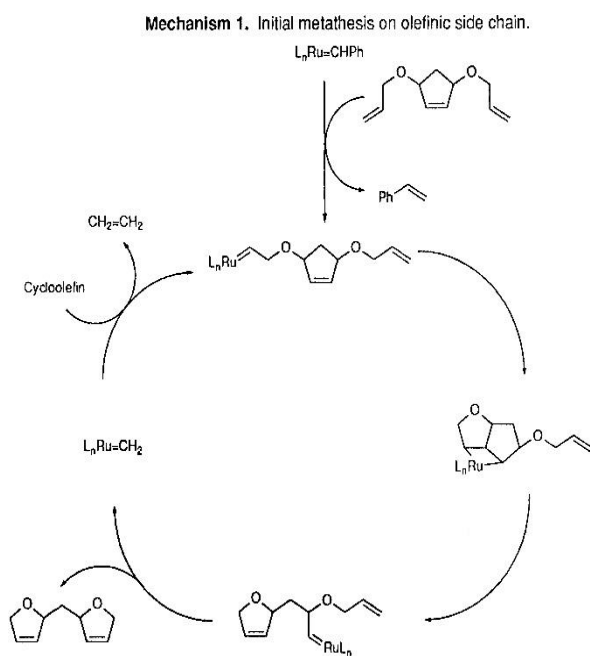
(Grubbs-II)

Ru-a has a pyridine ligand, which is more labile than PCy<sub>3</sub> ligand. Thus, Ru-a can be more quickly activated, leading to a more active catalyst. (2 points; along this idea)

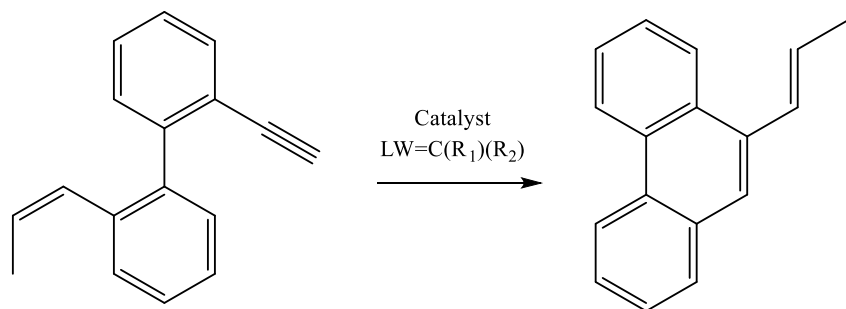
5. The following reaction was catalyzed by Grubbs-I catalysts ( $L_nRu=CHPh$ ). Please propose a mechanism for this reaction. (5 points)



Either one of the two possibilities below, or a reasonable variation of it. Each step 1 point.



6. Enyne metathesis is a metathesis reaction between an alkene and an alkyne. Mechanistically it is similar to alkene metathesis. Please draw the mechanism of the following enyne metathesis. (8 points)



Something like this: each major step 2 points (reasonable variations ok)

