Organometallic Chemistry 2021 Final Exam: June 24, 2021 at 8:00 AM PST

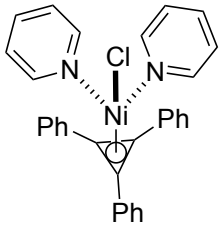
Directions: Please provide all answers, legibly, directly on this document and/or with appended pages as appropriate. Label all pages with your name in the top right corner and submit them as a single PDF in portrait orientation by emailing as an attachment to the instructor and TA's (each answer must be clearly paired with the respective problem by labeling and sequential organization). Do not put multiple conflicting answers for the same question, points will be taken off. The periodic table is attached on the last page.

_____ /31 Bonus + _____/140

_____%

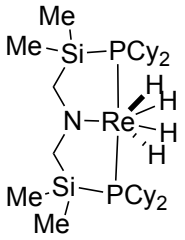
1. Provide the electron counting for the following structure. (4 points, 2 points each)

(a)



oxidation state	
d electron count	
electron count	
Coordination number	

(b)



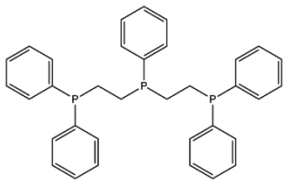
oxidation state	
d electron count	
electron count	
Coordination number	

2. Draw the most accurate structure from the formula. (8 points, 2 points each)

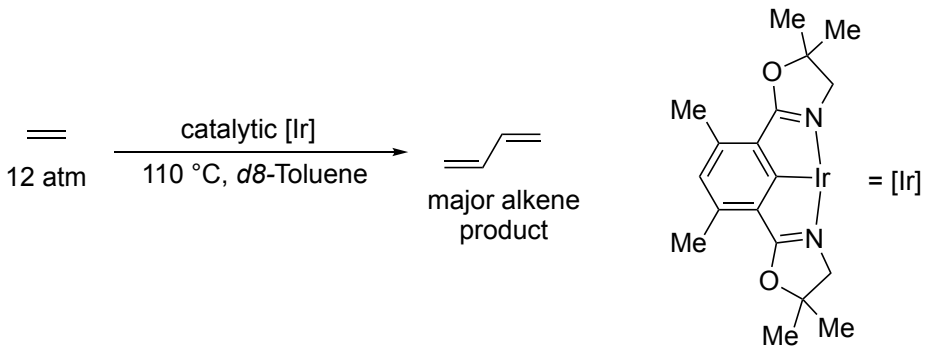
(c) $Co_2(CO)_8$

(d) $Mn_2(CO)_{10}$

(e) $Cp_2W(CO)_2$

(f) $[Pd(triphos)_2]^{+2}$ triphos = 

3. Consider the reaction of ethylene to form butadiene. (11 points)



(a) Draw a detailed catalytic cycle for the formation of butadiene and specify the byproduct of this reaction. (8 points)

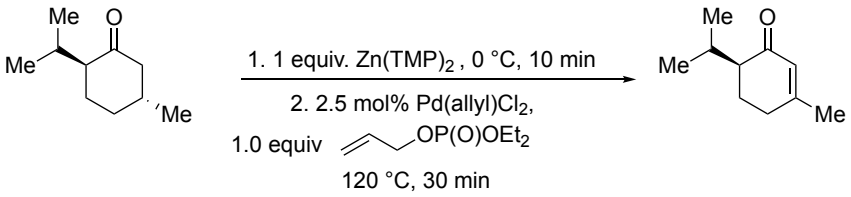
(b) Based on your mechanism, draw multiple potential byproducts. (3 points)

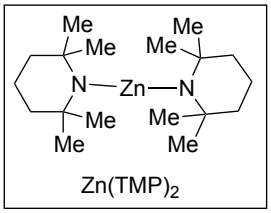
4. The Wacker Process is a widely used homogeneous catalyzed reaction in industry. (15 points)

(a) Provide the reactants and catalysts used for this industrial process and draw a detailed mechanism. (10 points)

(b) Using deuterium labeled reactants, (any D/H-permutation is available), propose a set of experiments that would help elucidate both nucleometallation and β-H elimination steps of the mechanism. (5 points)

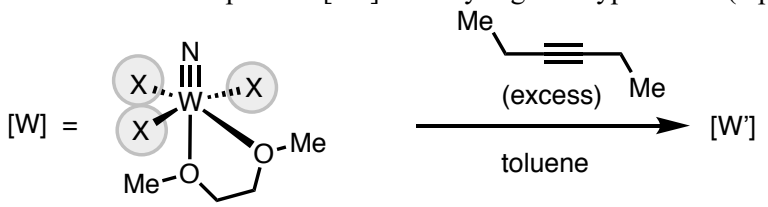
5. Consider the desaturation of this cyclic ketone. (8 points)
(a) Propose a catalytic cycle for the following transformation . (6 points)





(b) Based on the reagents in the reactions, predict a potential side product. (2 points)

6. In a stoichiometric experiment, treatment of [W] with excess 3-hexyne leads to formation of a new tungsten species [W'] as the major product. (15 points)
(a)Draw the structure of this new product [W'] and any organic byproducts. (4 points)



(b) Provide the electron counting for [W] and [W'] where X is a generic X-type ligand. (2 points)

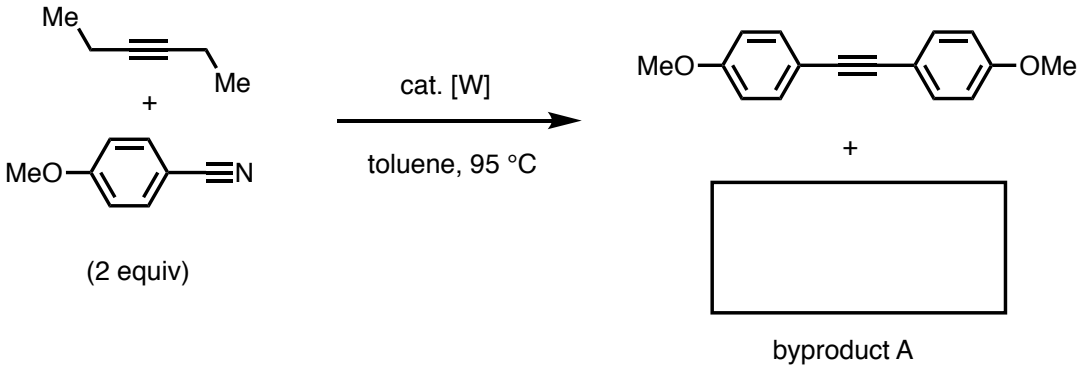
[W]

oxidation state	
d electron count	
electron count	
Coordination number	

[W']

oxidation state	
d electron count	
electron count	
Coordination number	

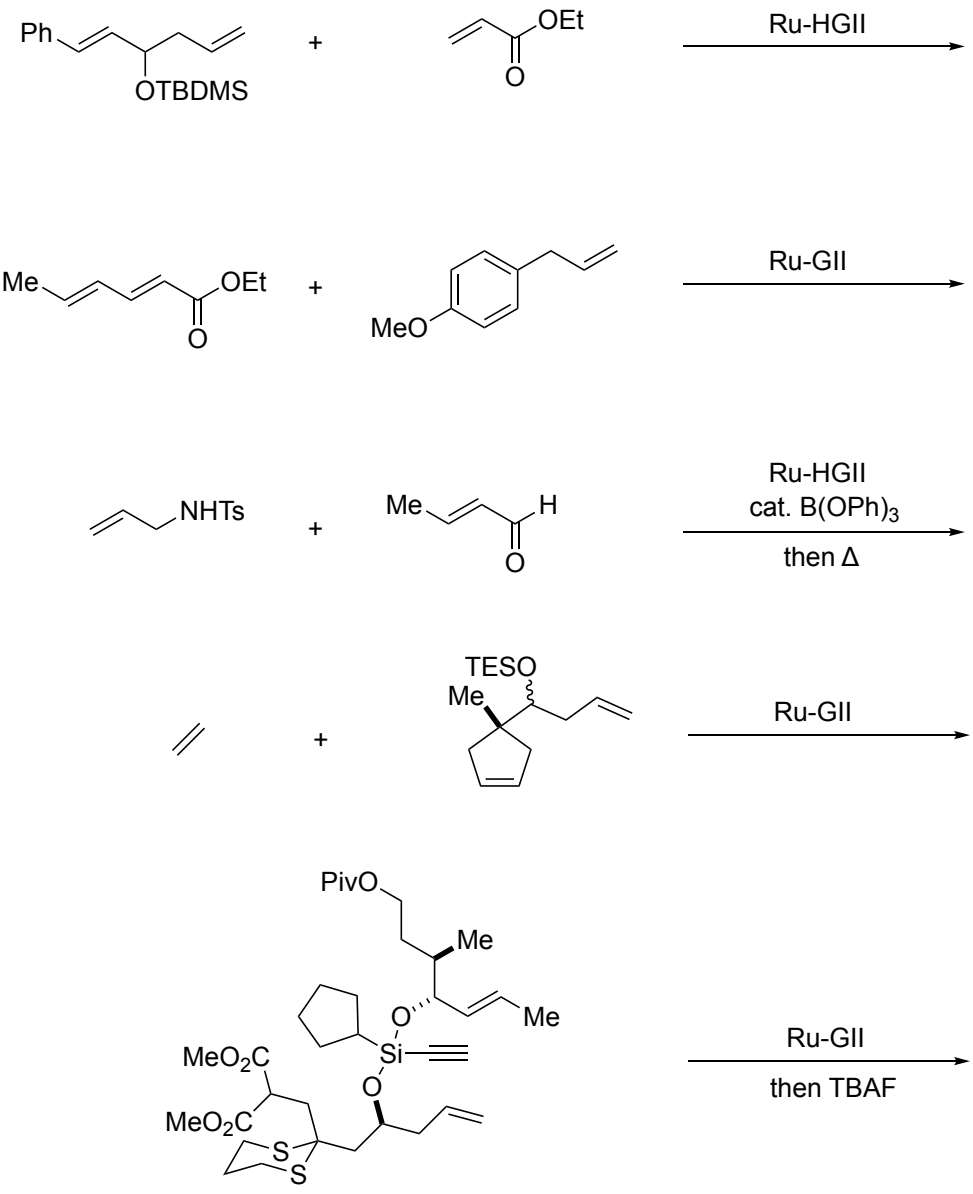
(c) Now consider the following catalytic reaction. Draw the structure of byproduct A that balances the above equation. (3 points)



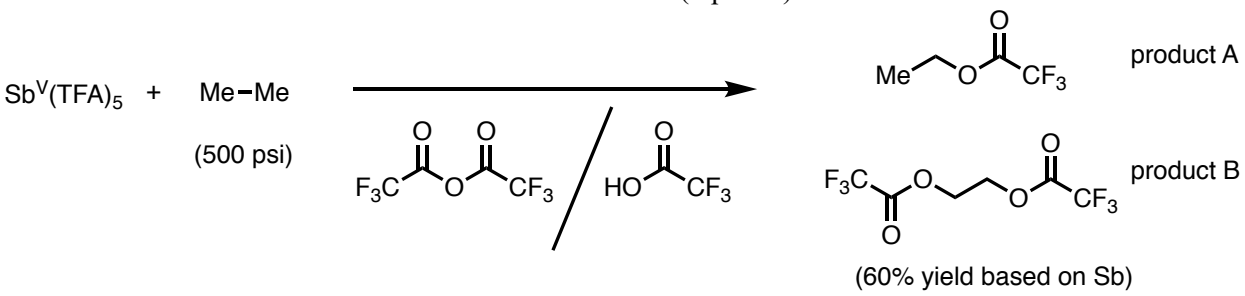
(d) Draw a catalytic cycle for this transformation. (6 points)

(e) (Bonus: +3 points) Based on your knowledge of catalysts used for related processes covered in class, propose specific ligands for X.

7. Draw the expected cross-metathesis products with relative stereochemistry. (2 points, 4 points for last q, 12 points) Bonus: draw the full catalyst structure for HGII and GII +2 each



8. In 2019, it was reported that the *p*-block compound $Sb(TFA)_5$ (TFA = trifluoroacetate) is able to mediate functionalization of methane and ethane. (8 points)

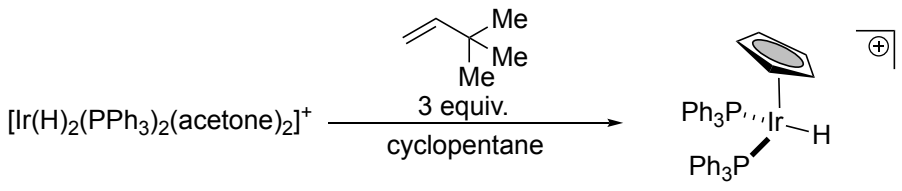


(a) One of the TFA ligands is κ^2. Based on this information draw the structure and name the geometry. (2 points)

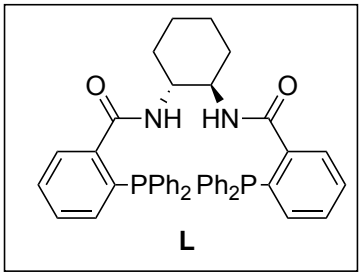
(b) Propose a mechanism for formation of product A. (6 points)

(c) (Bonus: +6 points) Control experiments revealed that product B is formed from product A. Draw two or more mechanisms by which this could take place and design one or more experiments to distinguish between them.

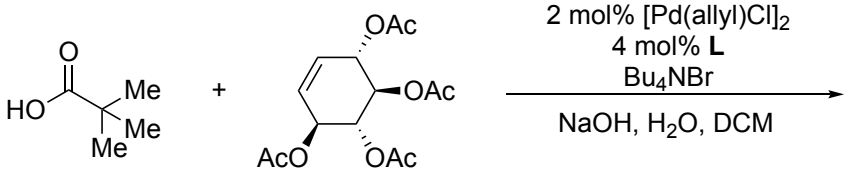
9. Draw the mechanism for the formation of the iridium complex below. (8 points)

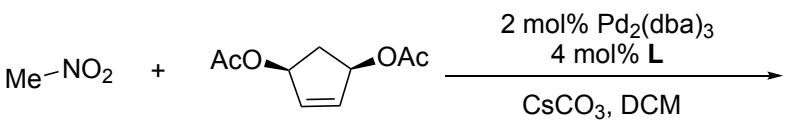


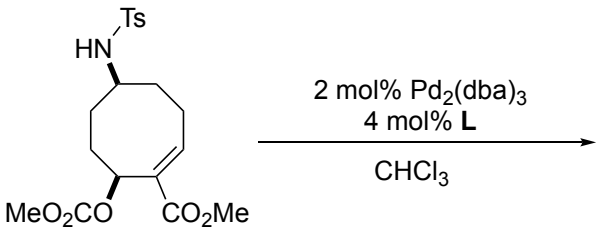
10. Draw the products with relative stereochemistry. (10 points, 2 points each)

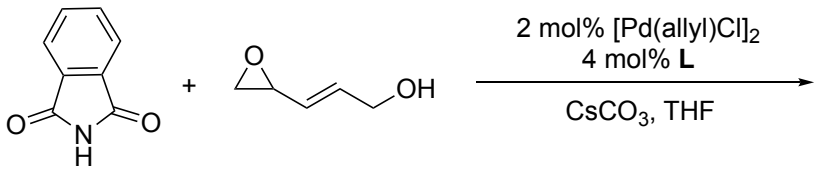


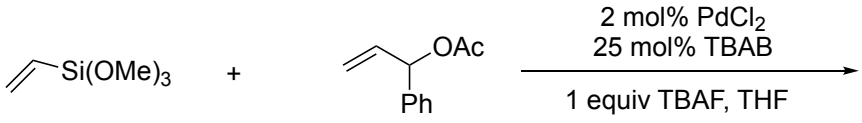
L









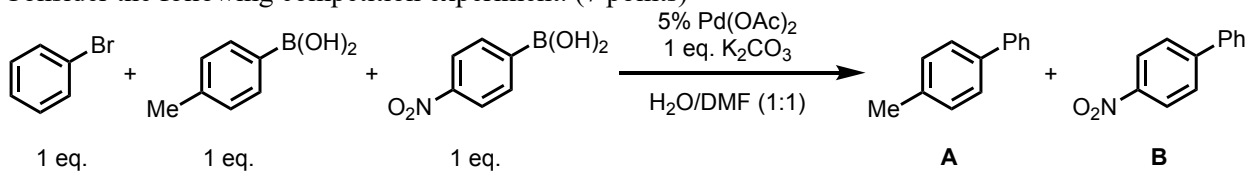


11. Palladium catalyzed reactions that go through Mizoroki-Heck type insertions can give a variety of products based on the conditions. (24 points)

(a) For the following scheme below give general reaction conditions, specify what X could be, and draw the product for the neutral Heck, cationic Heck, reductive Heck, oxidative Heck, and carbonylative Heck. (4 points each)

(b) Reactions using C(sp^3)-halides for the Heck reaction are exceptionally challenging and rare in the literature. Give 1 potential deleterious pathway that would prevent such a reaction from happening selectively. (4 points)

12. Consider the following competition experiment. (7 points)



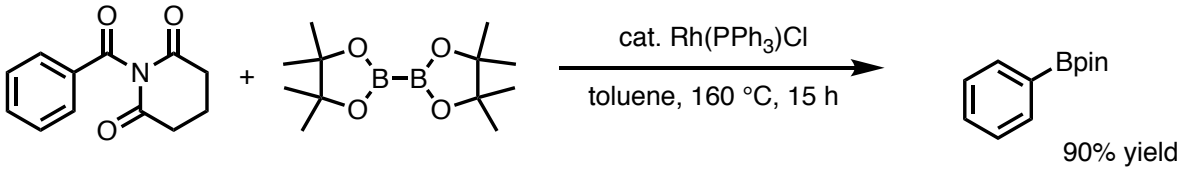
(a) Draw the active transmetalating species that leads to formation of product **A**. (3 points)

(b) With 1 eq. of K_2CO_3, **B** is the predominant product. With 2.6 eq. of K_2CO_3, **A** is the predominant product. Explain why this is the case. (4 points)

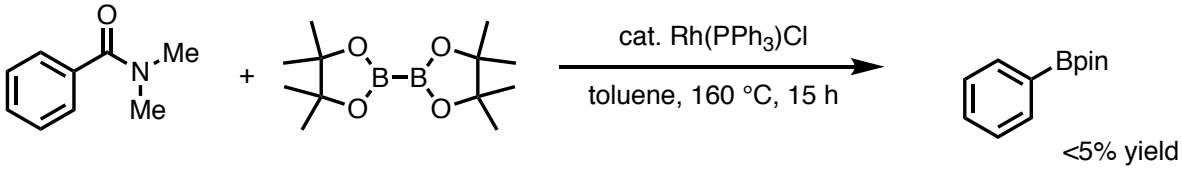
(c) (Bonus: +3 points) It is necessary to use more than 2 eq. of K_2CO_3 to see the maximum ratio of **A** to **B**. Why is this the case?

13. 10 Points

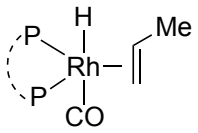
(a) Propose a catalytic cycle for the following reaction. (6 points)



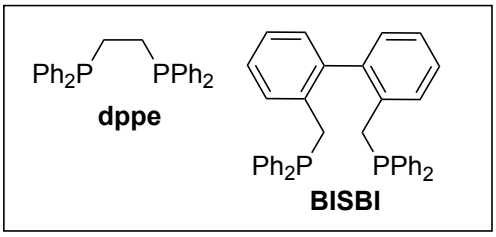
(b) When the amide from part (a) is replaced with the substrate below, the reaction does not take place. Explain this result. (4 points)



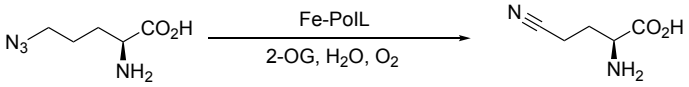
14. (Bonus: +10 points) Explain the effects of Berry pseudo rotation on the following 3 rhodium species, and the effects on selectivity in hydroformylation.

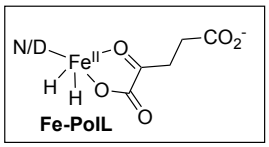


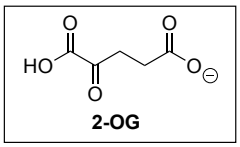
P = 2x PPh_3, dppe, BISBI

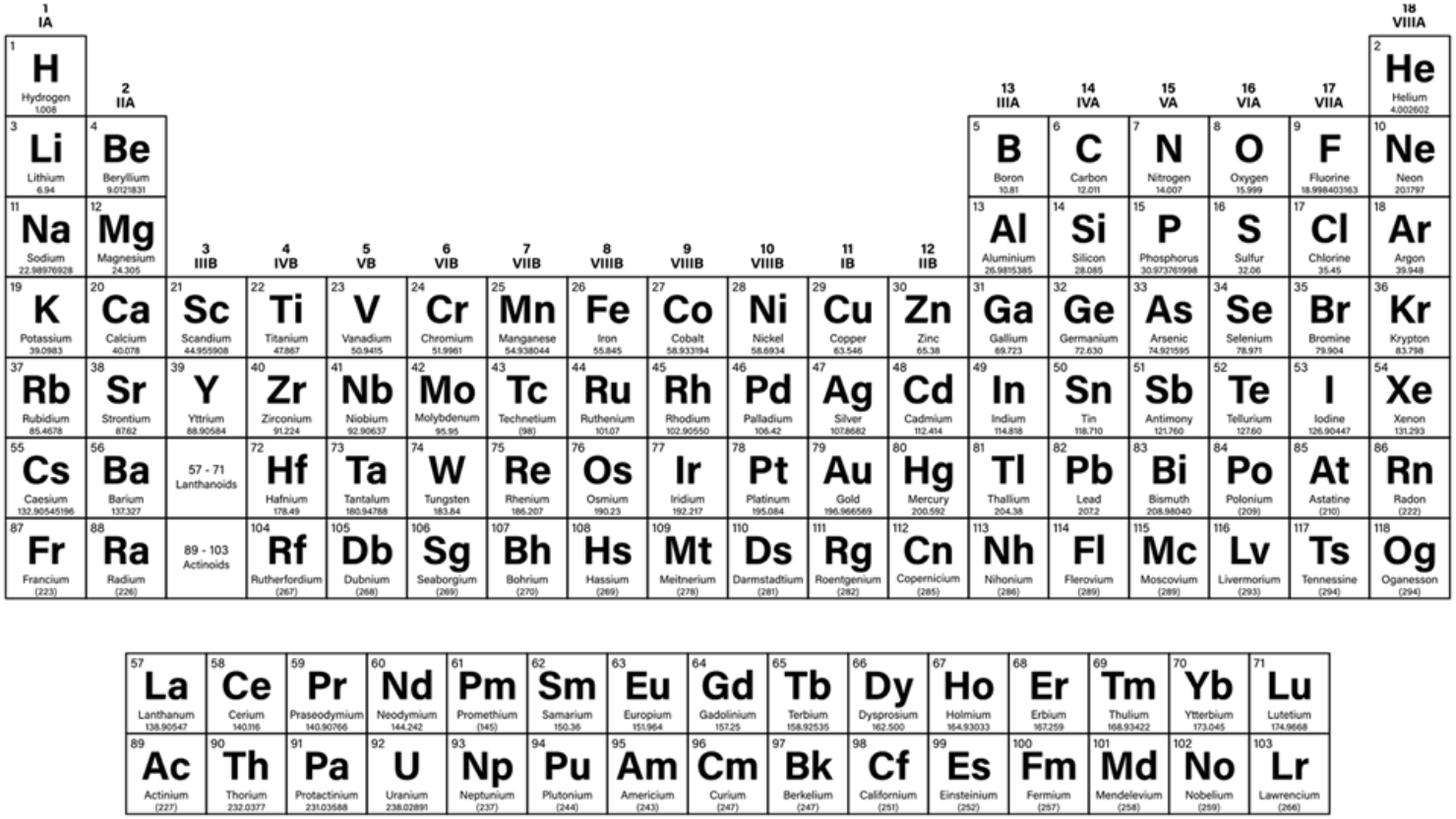


15. (Bonus +5) Draw a potential reaction pathway for the following reaction catalyzed by nonheme iron hydroxylase PoIL.








1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8 VIIIB
9 VIIIB
10 VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
1 H Hydrogen 1.008
2 He Helium 4.002602
3 Li Lithium 6.94
4 Be Beryllium 9.012183l
5 B Boron 10.81
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
9 F Fluorine 18.998403163
10 Ne Neon 20.1797
11 Na Sodium 22.98976928
12 Mg Magnesium 24.305
13 Al Aluminium 26.9815385
14 Si Silicon 28.085
15 P Phosphorus 30.973761998
16 S Sulfur 32.06
17 Cl Chlorine 35.45
18 Ar Argon 39.948
19 K Potassium 39.0983
20 Ca Calcium 40.078
21 Sc Scandium 44.955908
22 Ti Titanium 47.867
23 V Vanadium 50.9415
24 Cr Chromium 51.9961
25 Mn Manganese 54.938044
26 Fe Iron 55.845
27 Co Cobalt 58.933194
28 Ni Nickel 58.6934
29 Cu Copper 63.546
30 Zn Zinc 65.38
31 Ga Gallium 69.723
32 Ge Germanium 72.630
33 As Arsenic 74.921595
34 Se Selenium 78.971
35 Br Bromine 79.904
36 Kr Krypton 83.798
37 Rb Rubidium 85.4678
38 Sr Strontium 87.62
39 Y Yttrium 88.90584
40 Zr Zirconium 91.224
41 Nb Niobium 92.90637
42 Mo Molybdenum 95.95
43 Tc Technetium (98)
44 Ru Ruthenium 101.07
45 Rh Rhodium 102.90550
46 Pd Palladium 106.42
47 Ag Silver 107.8682
48 Cd Cadmium 112.414
49 In Indium 114.818
50 Sn Tin 118.710
51 Sb Antimony 121.760
52 Te Tellurium 127.60
53 I Iodine 126.90447
54 Xe Xenon 131.293
55 Cs Caesium 132.90545196
56 Ba Barium 137.327
57 - 71 Lanthanoids
72 Hf Hafnium 178.49
73 Ta Tantalum 180.94788
74 W Tungsten 183.84
75 Re Rhenium 186.207
76 Os Osmium 190.23
77 Ir Iridium 192.217
78 Pt Platinum 195.084
79 Au Gold 196.966569
80 Hg Mercury 200.592
81 Tl Thallium 204.38
82 Pb Lead 207.2
83 Bi Bismuth 208.98040
84 Po Polonium (209)
85 At Astatine (210)
86 Rn Radon (222)
87 Fr Francium (223)
88 Ra Radium (226)
89 - 103 Actinoids
104 Rf Rutherfordium (267)
105 Db Dubnium (268)
106 Sg Seaborgium (269)
107 Bh Bohrium (270)
108 Hs Hassium (269)
109 Mt Meitnerium (278)
110 Ds Darmstadtium (281)
111 Rg Roentgenium (282)
112 Cn Copernicium (285)
113 Nh Nihonium (286)
114 Fl Flerovium (289)
115 Mc Moscovium (289)
116 Lv Livermorium (293)
117 Ts Tennessine (294)
118 Og Oganesson (294)
57 La Lanthanum 138.90547
58 Ce Cerium 140.116
59 Pr Praseodymium 140.90766
60 Nd Neodymium 144.242
61 Pm Promethium (145)
62 Sm Samarium 150.36
63 Eu Europium 151.964
64 Gd Gadolinium 157.25
65 Tb Terbium 158.92535
66 Dy Dysprosium 162.500
67 Ho Holmium 164.93033
68 Er Erbium 167.259
69 Tm Thulium 168.93422
70 Yb Ytterbium 173.045
71 Lu Lutetium 174.9668
89 Ac Actinium (227)
90 Th Thorium 232.0377
91 Pa Protactinium 231.03588
92 U Uranium 238.02891
93 Np Neptunium (237)
94 Pu Plutonium (244)
95 Am Americium (243)
96 Cm Curium (247)
97 Bk Berkelium (247)
98 Cf Californium (251)
99 Es Einsteinium (252)
100 Fm Fermium (257)
101 Md Mendelevium (258)
102 No Nobelium (259)
103 Lr Lawrencium (266)