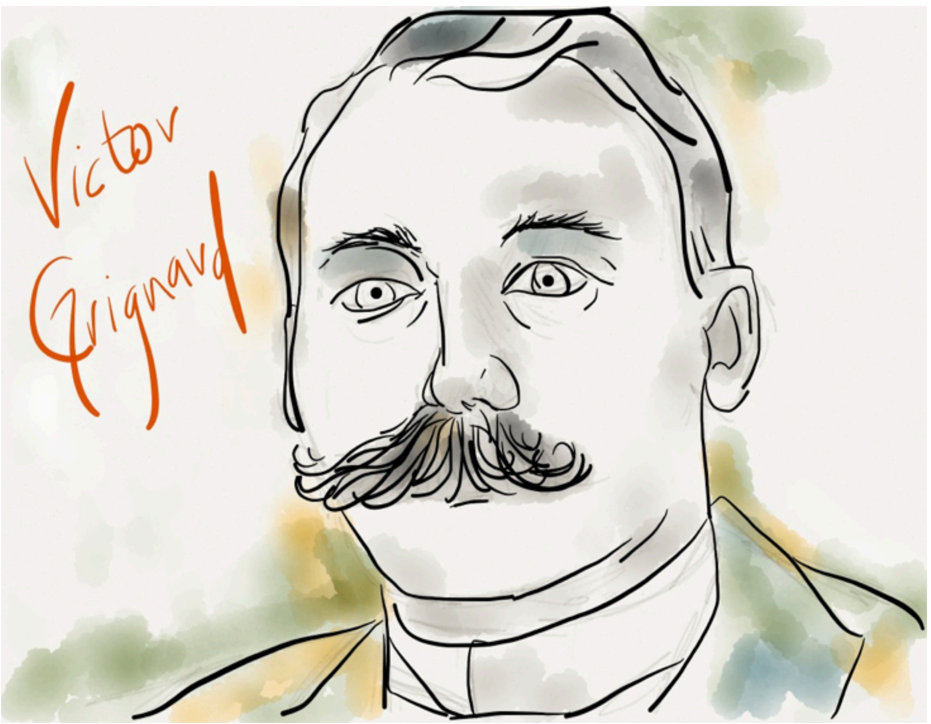
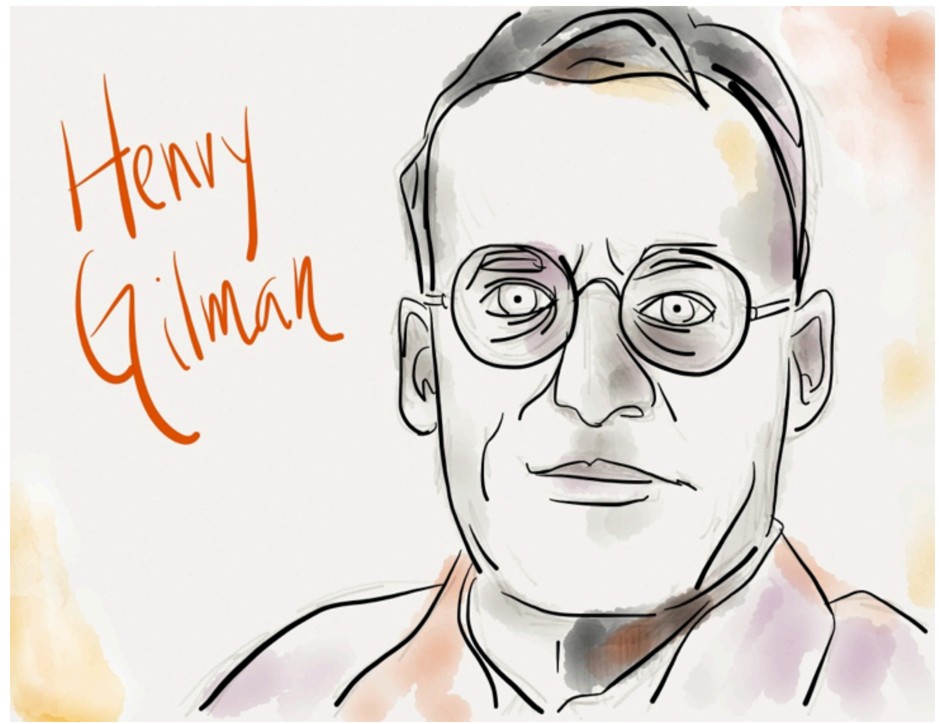
344 | Organic Chemistry Laboratory
Summer 2013





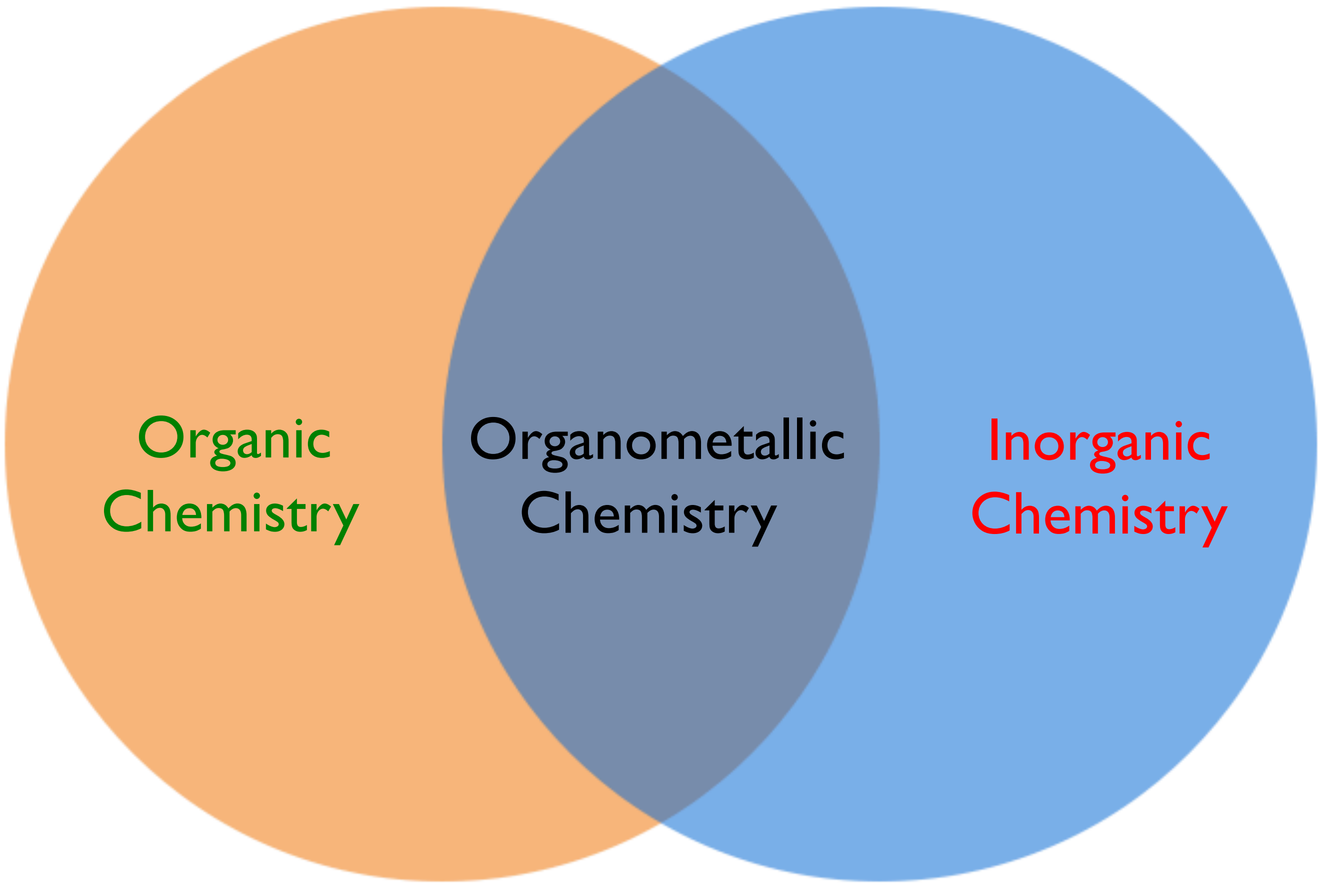
Lecture 5 Introduction to organometallic chemistry
July 29 2013

Portraits: http://scientistic.tumblr.com

What is organometallic chemistry?

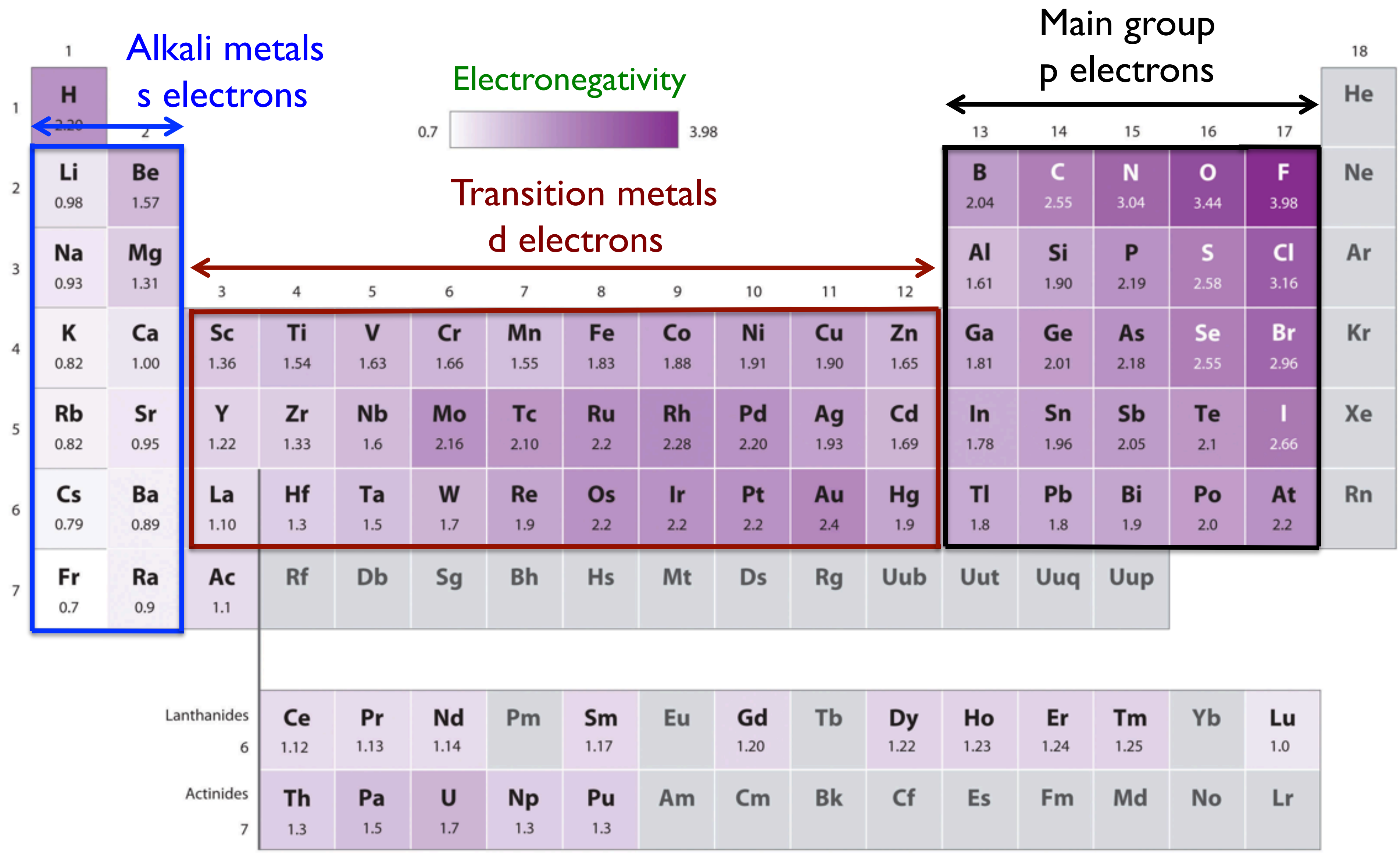
The chemistry of compounds containing a Carbon-Metal bond

Intersection of organic and inorganic chemistry



Organometallic chemistry = organic synthesis enabled by metals

Periodic Table



Periodic Table – typical organic compounds

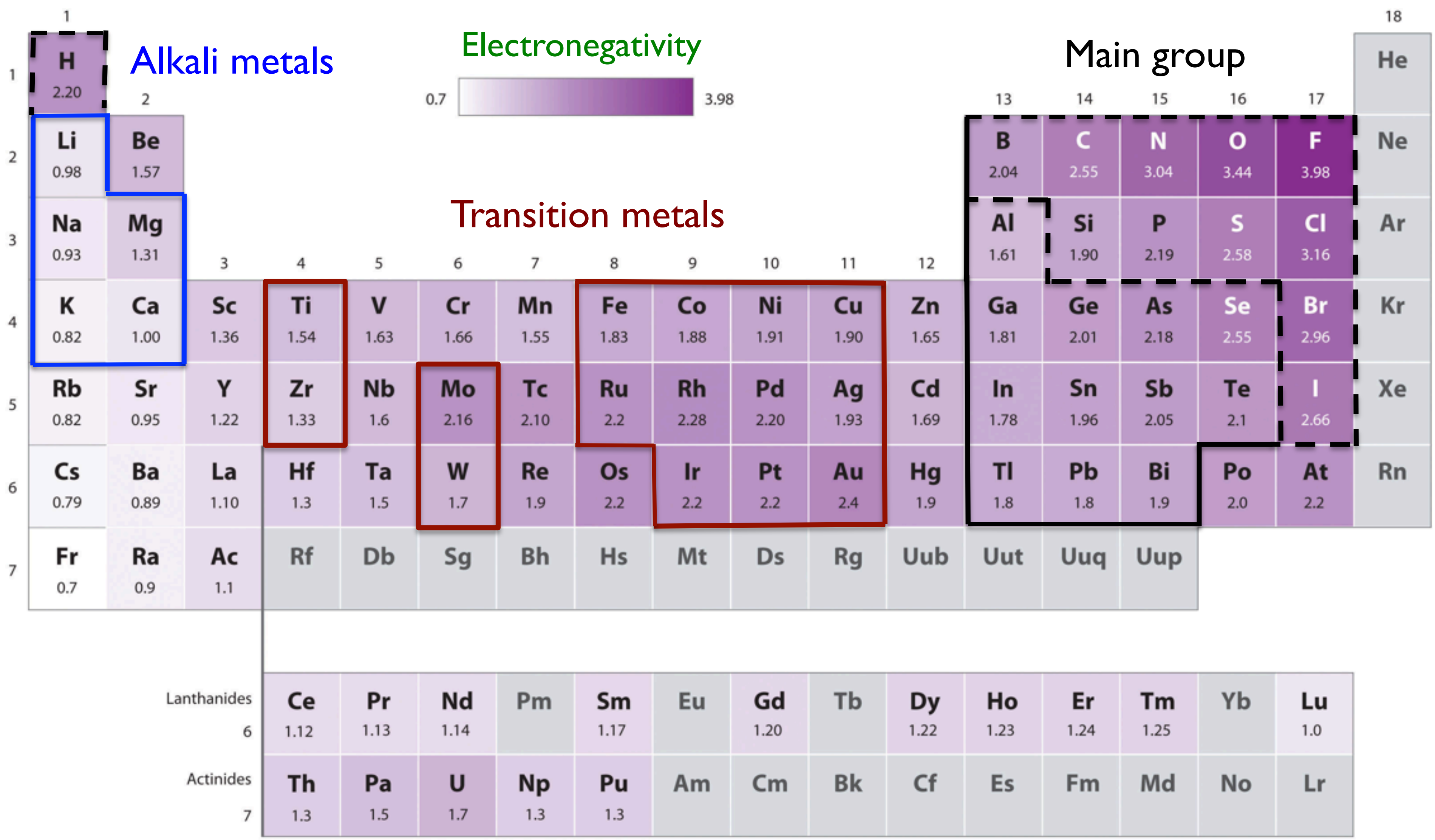
Electronegativity 0.7 — 3.98

Organic

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
6	Cs 0.79	Ba 0.89	La 1.10	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			

Lanthanides 6	Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb	Lu 1.0
Actinides 7	Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Periodic Table – common organometallics

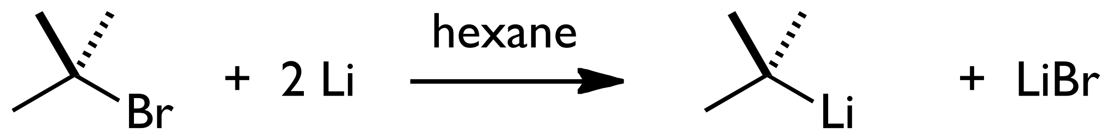


Much more to play with!!

Organometallics – s-block compounds

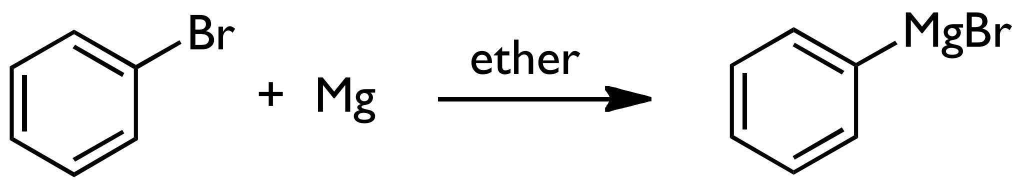
You are already familiar with some simple organometallic compounds from CHEM 343/345

Organolithiums



tert-butyl lithium

Organomagnesium halides
(Grignard reagents)



phenylmagnesium bromide

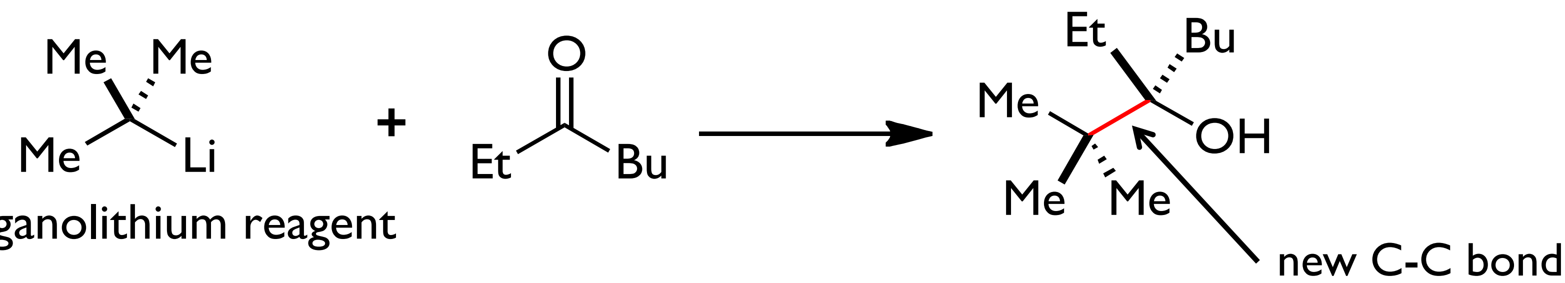
Lithium diorganocuprates
(Gilman reagents)

$$2\,EtLi + CuI \xrightarrow{\text{ether}} Et_2CuLi + LiI$$

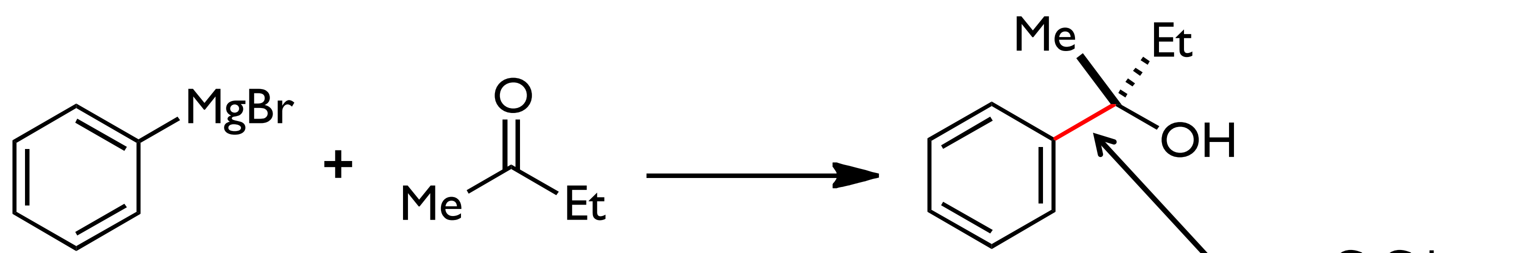
lithium diethylcuprate

Organometallics – s-block compounds

You are already familiar with some simple organometallic compounds from CHEM 343/345



organolithium reagent



Grignard reagent

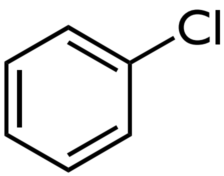
Organic fragment of reacting as a **nucleophile**, has carbanion character

Reactivity of C-atom in a typical organic compound is as an electrophile

Carbon nucleophile + carbon electrophile = new C-C bond

Why do Grignards and organolithiums react as carbon nucleophiles?

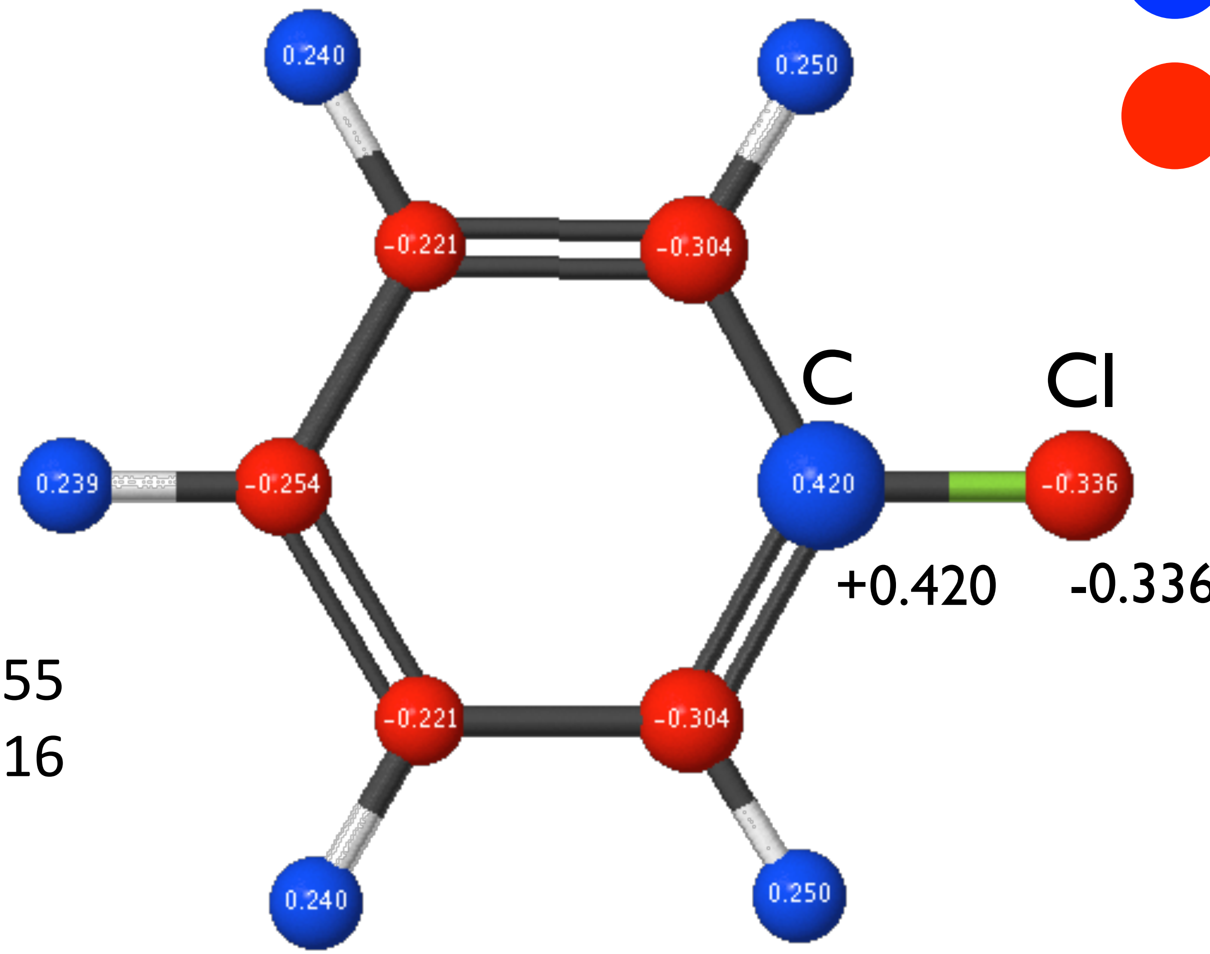
Charge distribution – Chlorobenzene



A typical organic compound

= positively charged

= negatively charged



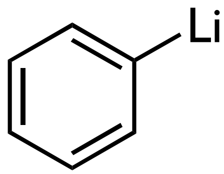
X_C = 2.55
X_{Cl} = 3.16

C-atom in C-Cl bond is positively charged

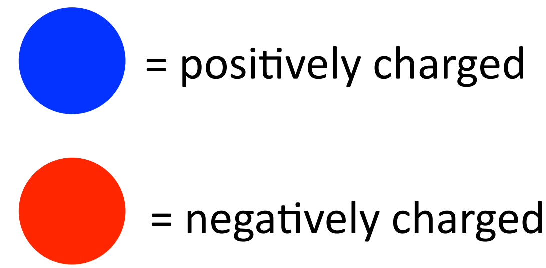
X = Pauling electronegativity

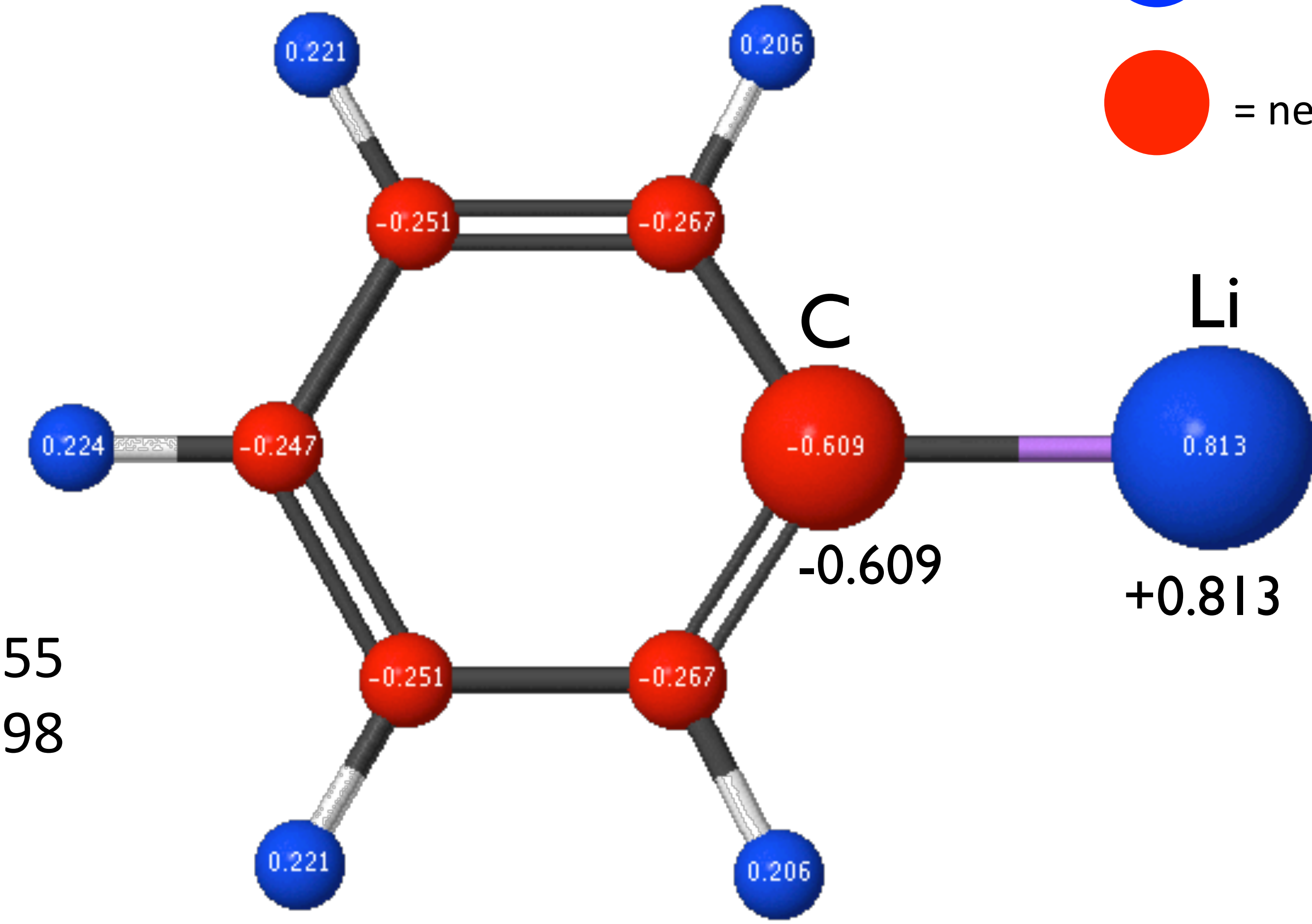
NPA charges, B3LYP/6-31G(d)

Charge distribution – Phenyl lithium



An organometallic compound





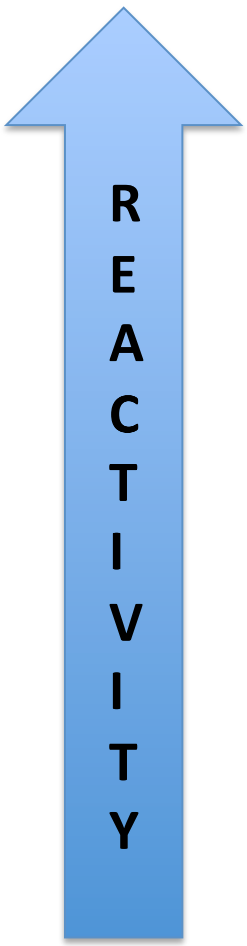
X_C = 2.55
X_{Li} = 0.98

Reversal of bond polarity…C-atom of C-Li bond is negatively charged

X = Pauling electronegativity

NPA charges, B3LYP/6-31G(d)

Carbon-Metal bond polarity



C-M bond	Δ Electronegativity#	% ionic character*
C-K	2.55 – 0.82 = 1.73	68
C-Na	2.55 – 0.93 = 1.62	63
C-Li	2.55 – 0.98 = 1.57	61
C-Mg	2.55 – 1.31 = 1.24	48
C-Ti	2.55 – 1.54 = 1.01	40
C-Al	2.55 – 1.61 = 0.94	37
C-Cu	2.55 – 1.90 = 0.65	25
C-B	2.55 – 2.04 = 0.51	20
C-Cl	2.55 – 3.16 = - 0.61	24
C-Br	2.55 – 2.96 = - 0.41	16
C-H	2.55 – 2.20 = 0.35	14

Ionic

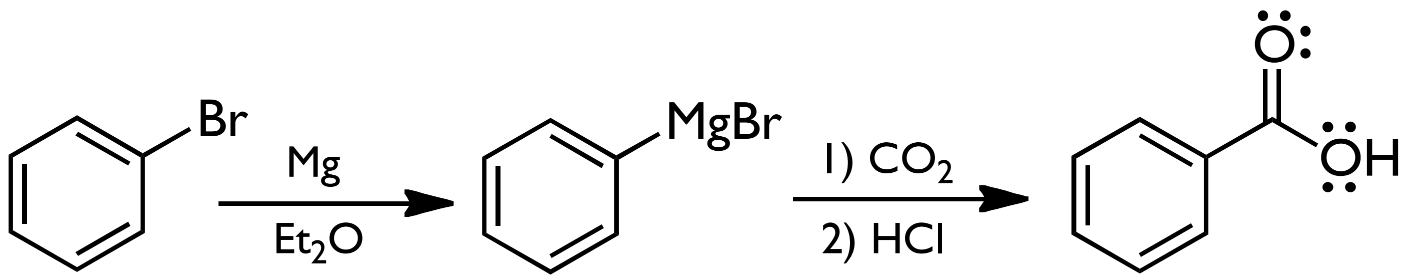
Polar covalent

Covalent

Pauling electronegativity, X

* % ionic character = [(X_C – X_M) ÷ X_C]

Grignard lab – Synthesis of benzoic acid



What you need

Dry + clean glassware

Drierite column

Anhydrous Et_2O

Dry ice

Bromobenzene

Mg bits

Small chip of iodine

Drierite column

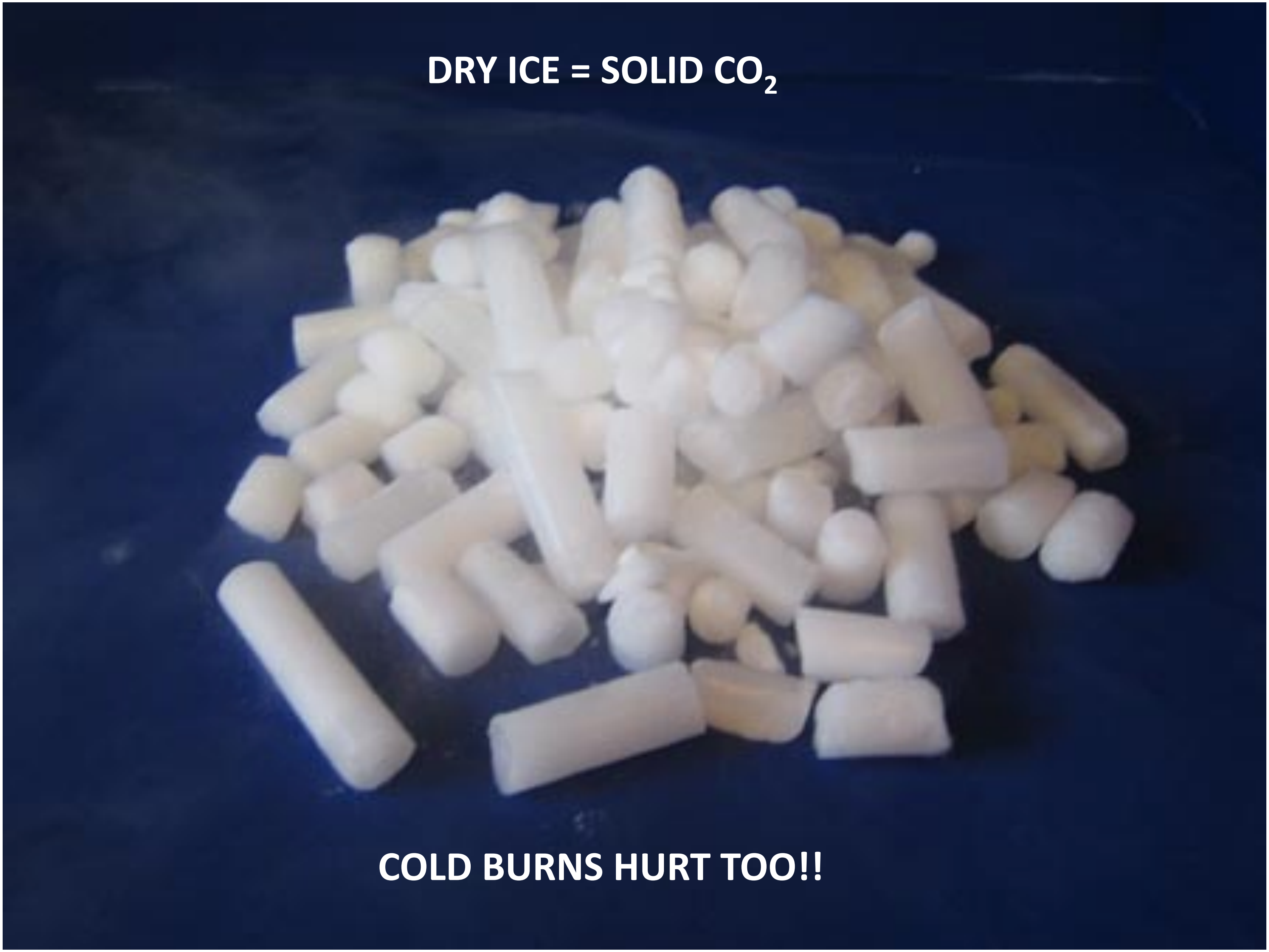
A column of drierite sits atop the condenser

Metal can = anhydrous

Wash bottle = “Wet”

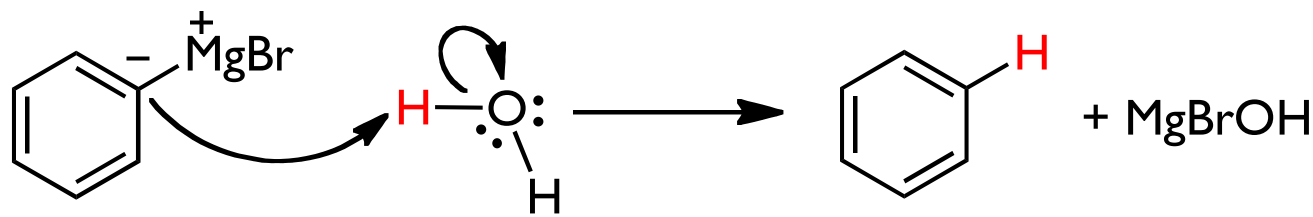
USE ANHYDROUS ETHER
FOR GRIGNARD REACTION

DO NOT USE “WET” ETHER
FOR GRIGNARD REACTION


DRY ICE = SOLID CO_2
COLD BURNS HURT TOO!!

Grignard lab – Synthesis of benzoic acid

Why do we need anhydrous solvent and a drying column?



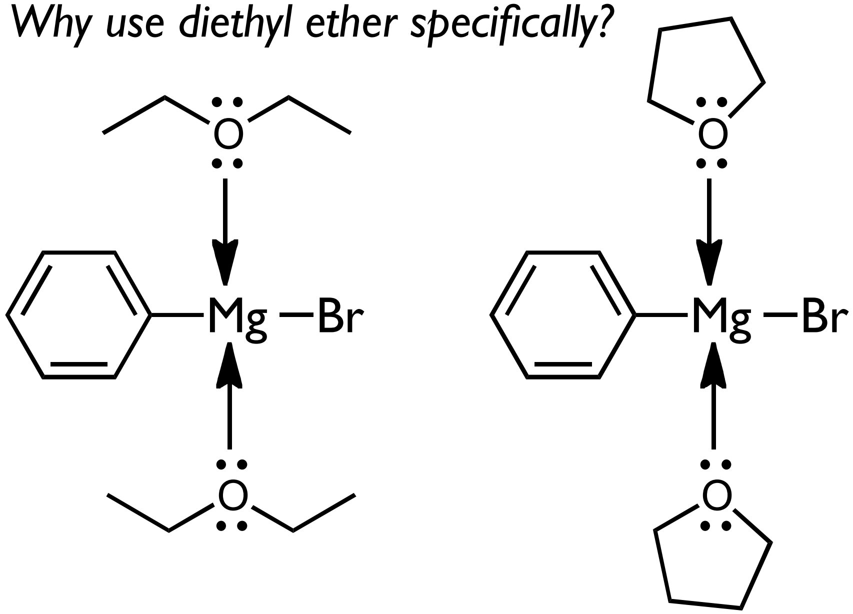
PhMgBr   water

pKa ~43   pKa 15.7

The nucleophilic C-atom of the Grignard reagent is strongly basic

Water quenches the Grignard reagent as it is formed.

Why use diethyl ether specifically?

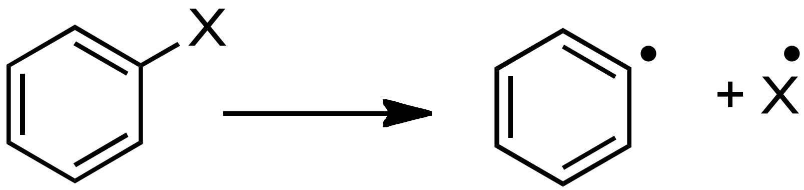


Et_2O and THF are able to coordinate to Mg

Stabilizes compound and enhances solubility

Grignard lab – Synthesis of benzoic acid

Why use bromobenzene specifically?



X = F, Cl, Br

BDE = ($E_{Ph\ radical}$ + $E_{X\ radical}$) - E_{PhX}

C-X bond	Calculated BDE (kcal/mol)	C-X bond distance (Å)
C-F	122	1.36
C-Cl	90	1.75
C-Br	78	1.92

Why not use aryl iodides?

More expensive, less "green", side-product issues

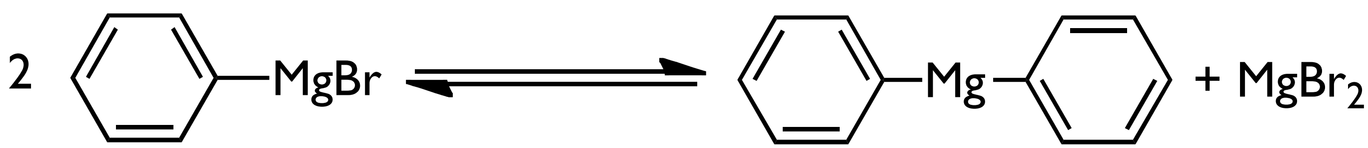
Structure of Grignard reagents

Typically show a Grignard in the form RMgX on paper

…..but in solution its much more complicated

Schlenk equilibrium

$$2\,RMgX \rightleftharpoons R_2Mg + MgX_2$$

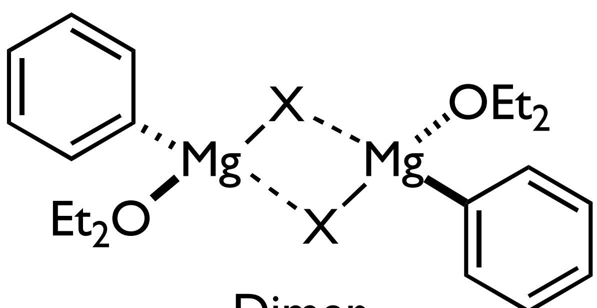


A B

A and **B** cannot be distinguished by reaction product (i.e. their reactivity is exactly the same)

Position of equilibrium depends on solvent, temperature, concentration, R-group

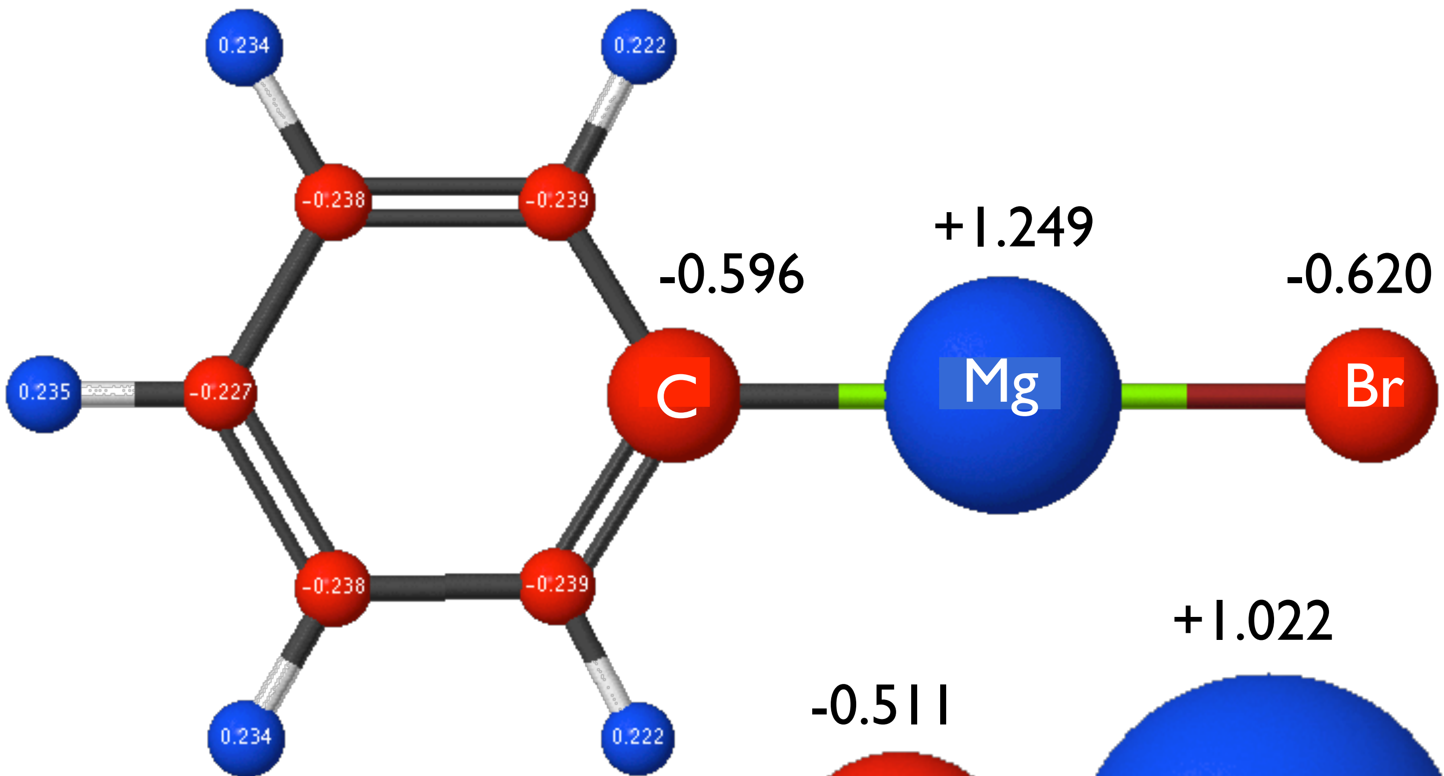
Grignard reagents are not monomeric across all concentrations

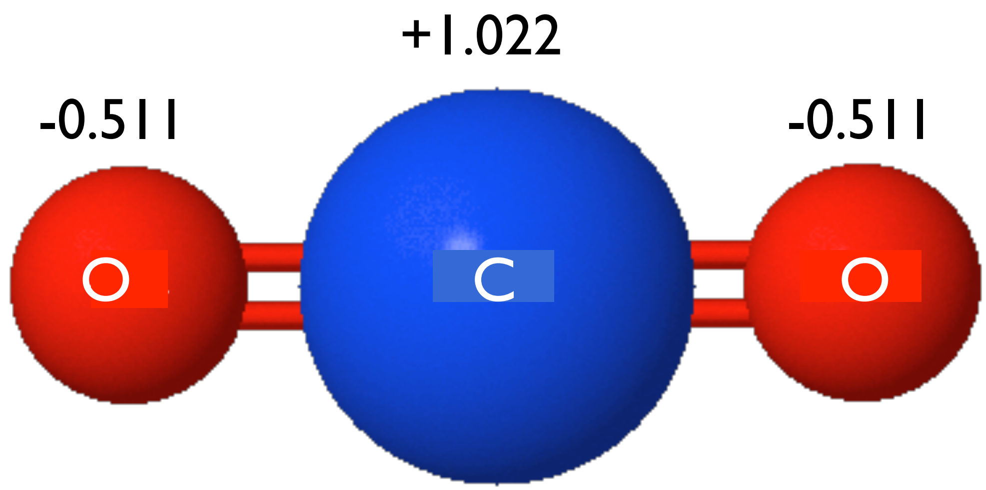


Dimer

- Solution behavior of Grignard reagents is highly complex
- Many reactive species in solution
- RMgX works just fine to explain our chemistry

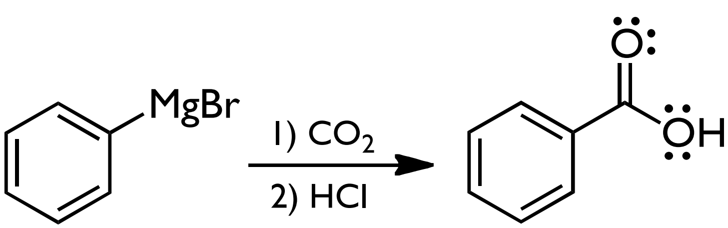
Reactivity of Grignard reagents





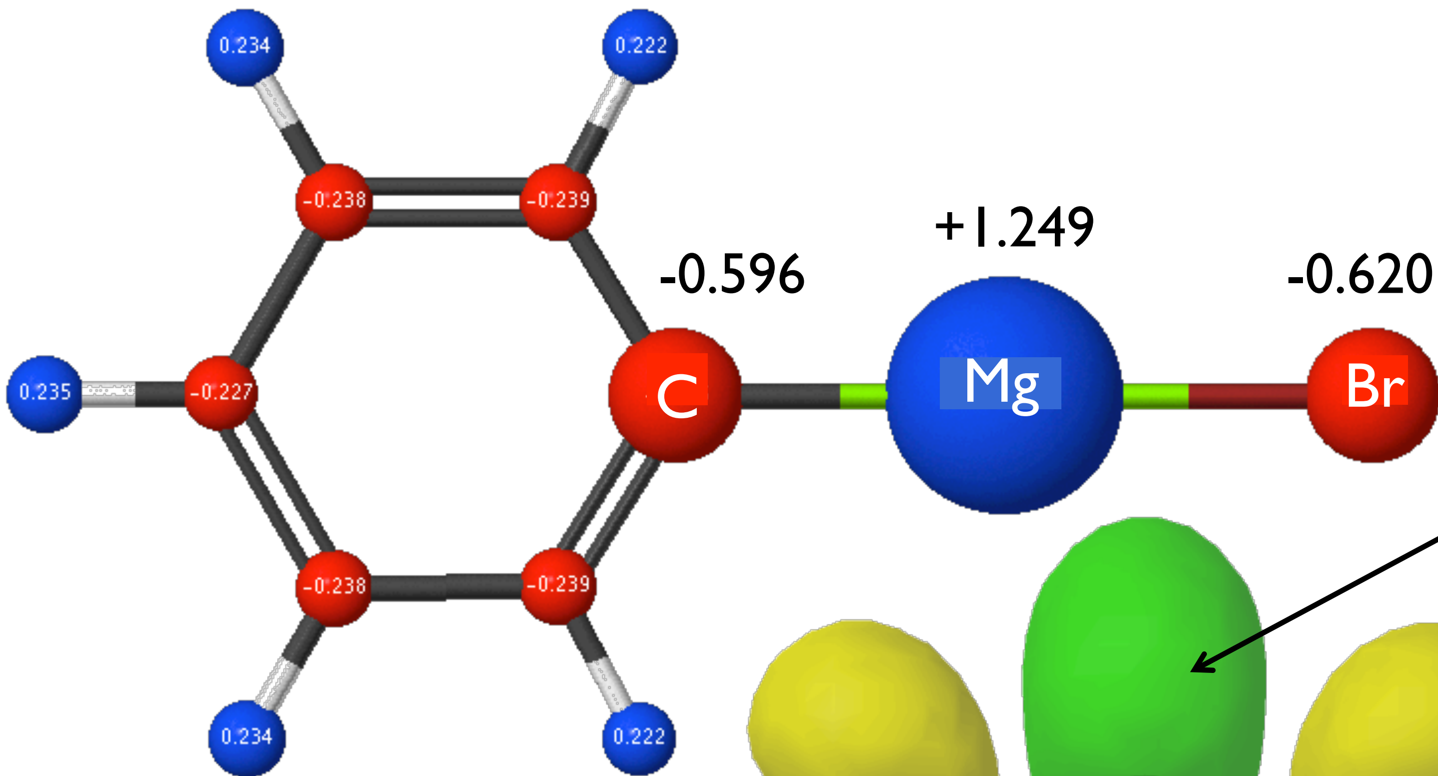
C-atom of Grignard is Nucleophilic

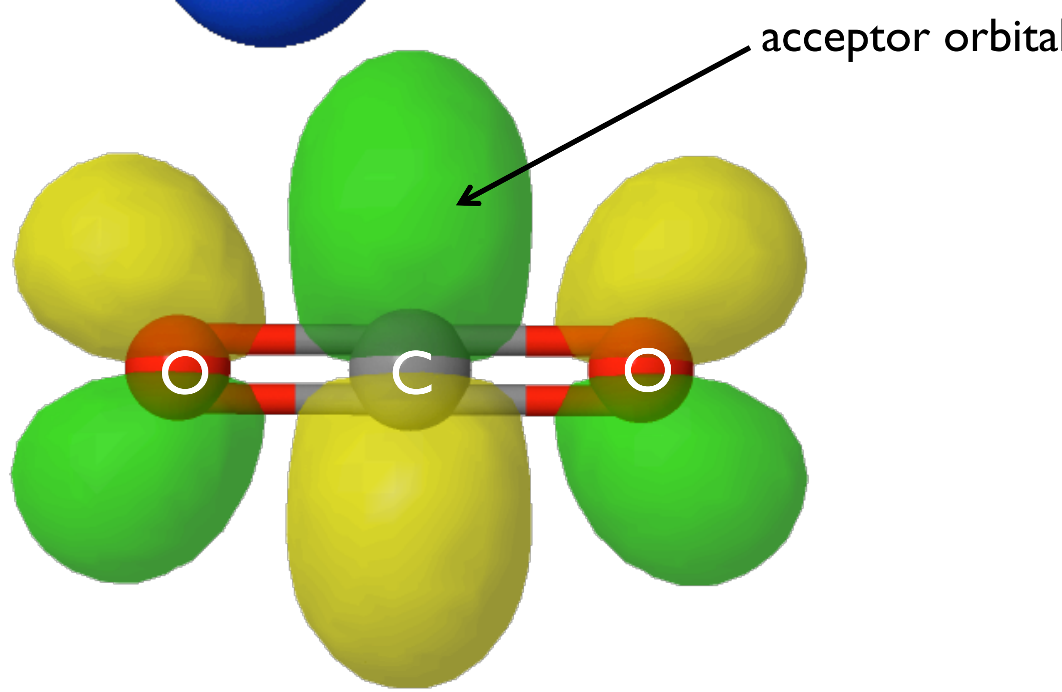
C-atom of CO_2 is Electrophilic



NPA charges, B3LYP/6-31G(d)

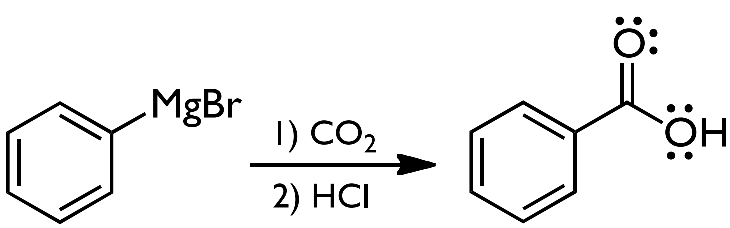
Reactivity of Grignard reagents





C-atom of Grignard is Nucleophilic

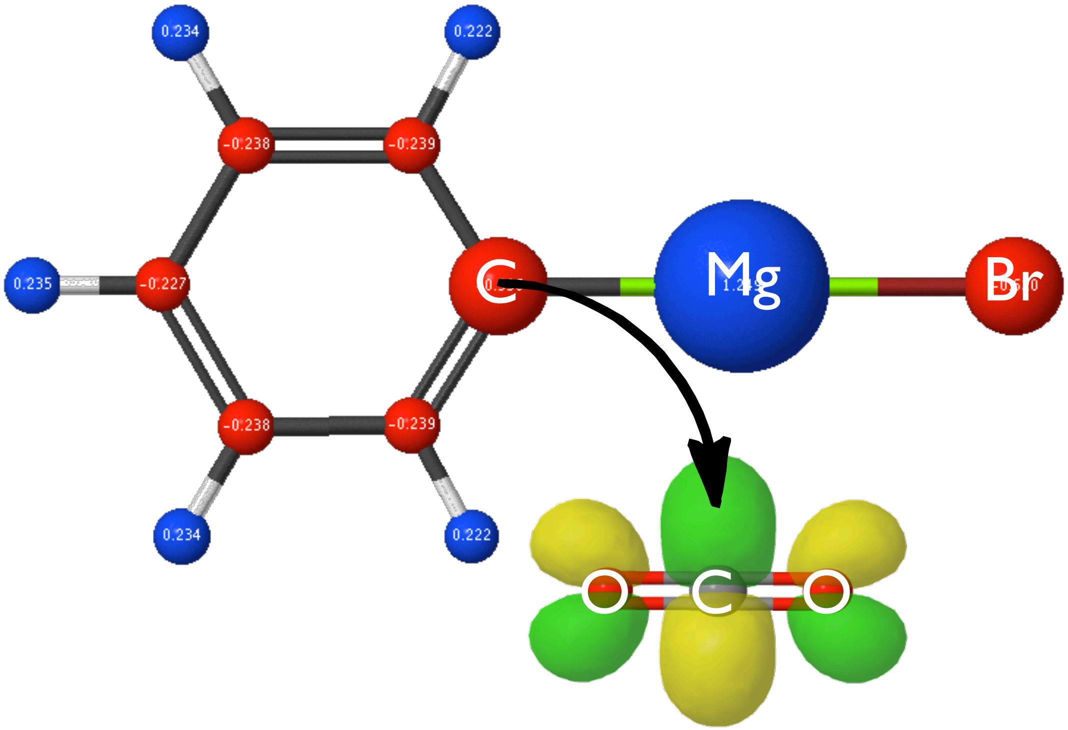
C-atom of CO_2 is Electrophilic

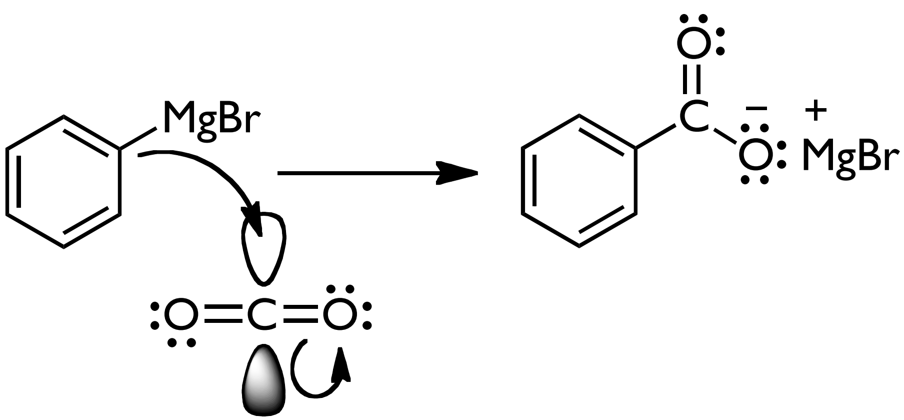


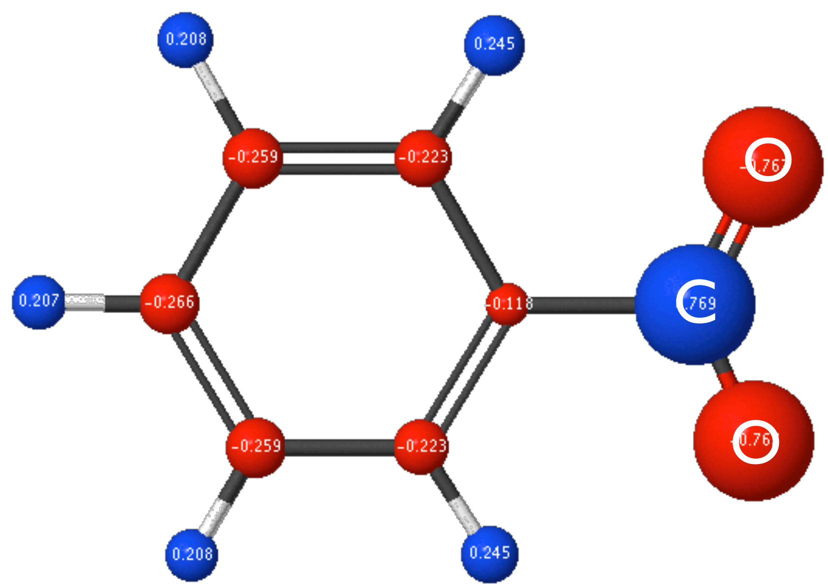
LUMO of CO_2

NBO calculation, B3LYP/6-31G(d)

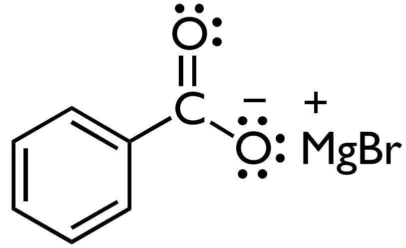
Reactivity of Grignard reagents



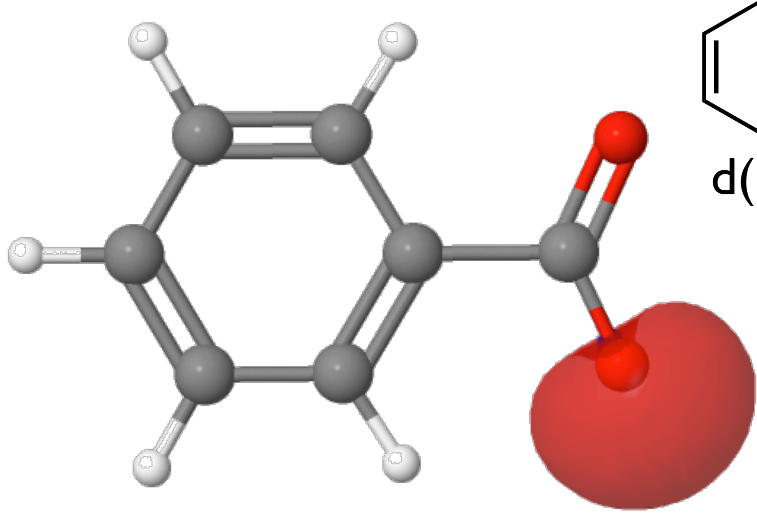




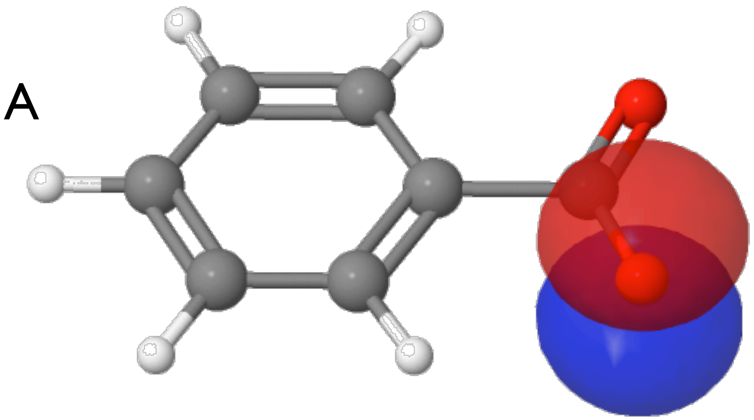
Nature of the carboxylate anion



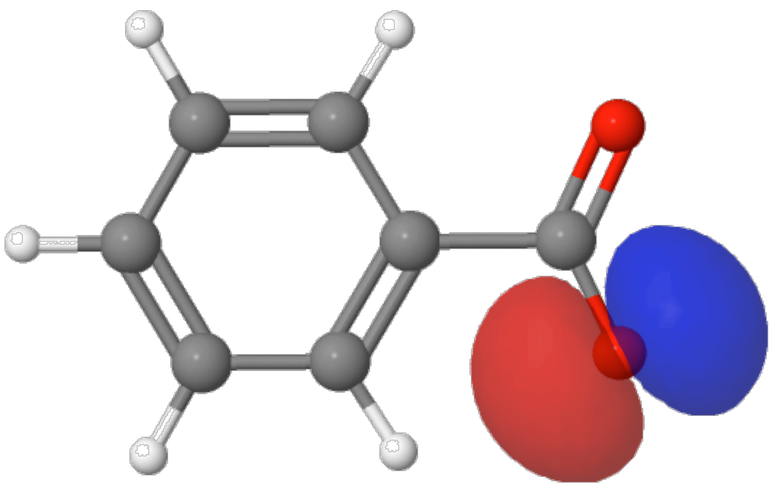
d(C-O) = 1.257 A



LP(1)O9 $sp^{0.65}$



LP(2)O9 s^0p^1



LP(3)O9 s^0p^1

Display Range 45 - 50 / 145

Orbital	Description	Occupancy	Energy
45	LP(1)O9 s(60.55%)p0.65(39.42%)d0.00(0.03%)	1.977180760	-0.456244162 Hartree
46	LP(2)O9 s(0.08%)p99.99(99.74%)d2.12(0.17%)	1.877813450	-0.014377923 Hartree
47	LP(3)O9 s(0.00%)p1.00(99.76%)d0.00(0.24%)	1.579947141	-0.007937662 Hartree
48	LP(1)O10 s(60.55%)p0.65(39.42%)d0.00(0.03%)	1.977180760	-0.456244162 Hartree
49	LP(2)O10 s(0.08%)p99.99(99.74%)d2.12(0.17%)	1.877813450	-0.014377923 Hartree
50	LP(3)O10 s(0.00%)p1.00(99.76%)d0.00(0.24%)	1.579947141	-0.007937662 Hartree

Summary

Organometallic chemistry

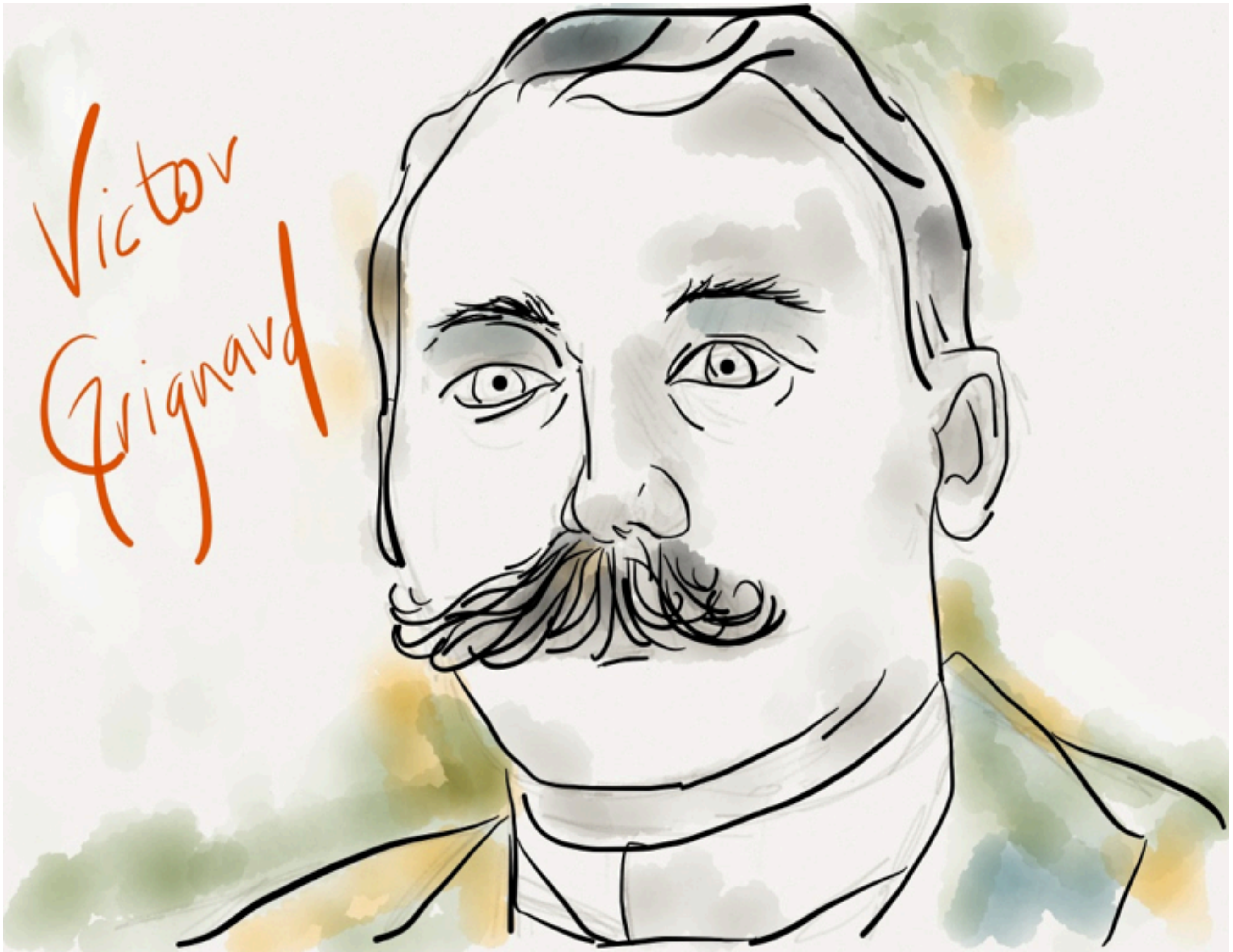
- the chemistry of compounds containing a C-M bond
- intersection of organic and inorganic chemistry
- allows "impossible" organic reactions to occur

Organolithium and Grignard reagents

- Polar C-M bonds = reactive toward water/oxygen
- nucleophilic carbon atom, carbanion character
- strongly basic
- reactive toward carbonyl groups
- used in stoichiometric amounts (i.e. 1:1 or greater)

Grignard lab

- use dry clean glassware
- use dry ether for reaction solvent, regular ether for everything else
- tiny chip of I_2 to assist with initiation of reaction
- dry ice burns ya!
- think about which layer contains crude benzoic acid
- think about purification steps



Portraits: http://scientistic.tumblr.com

YES!