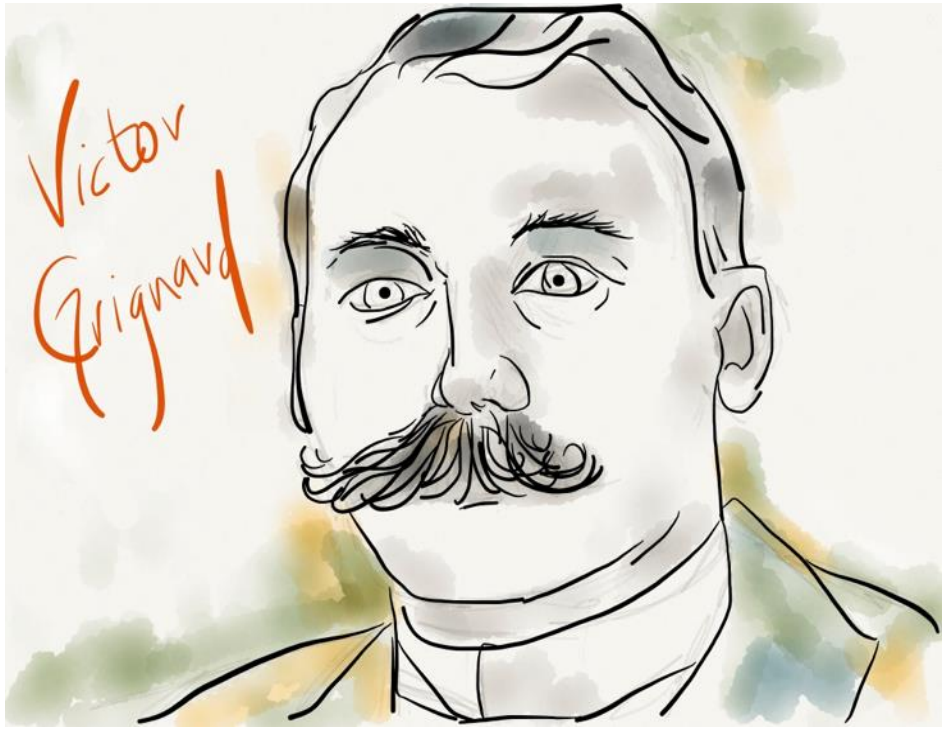
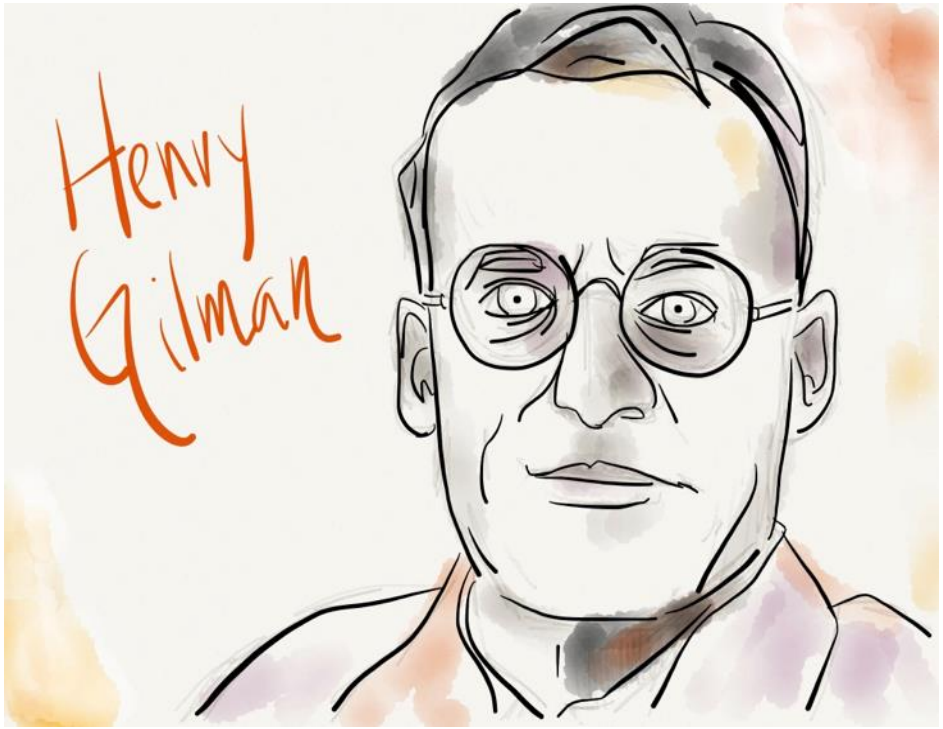
344 | Organic Chemistry Laboratory
Spring 2014

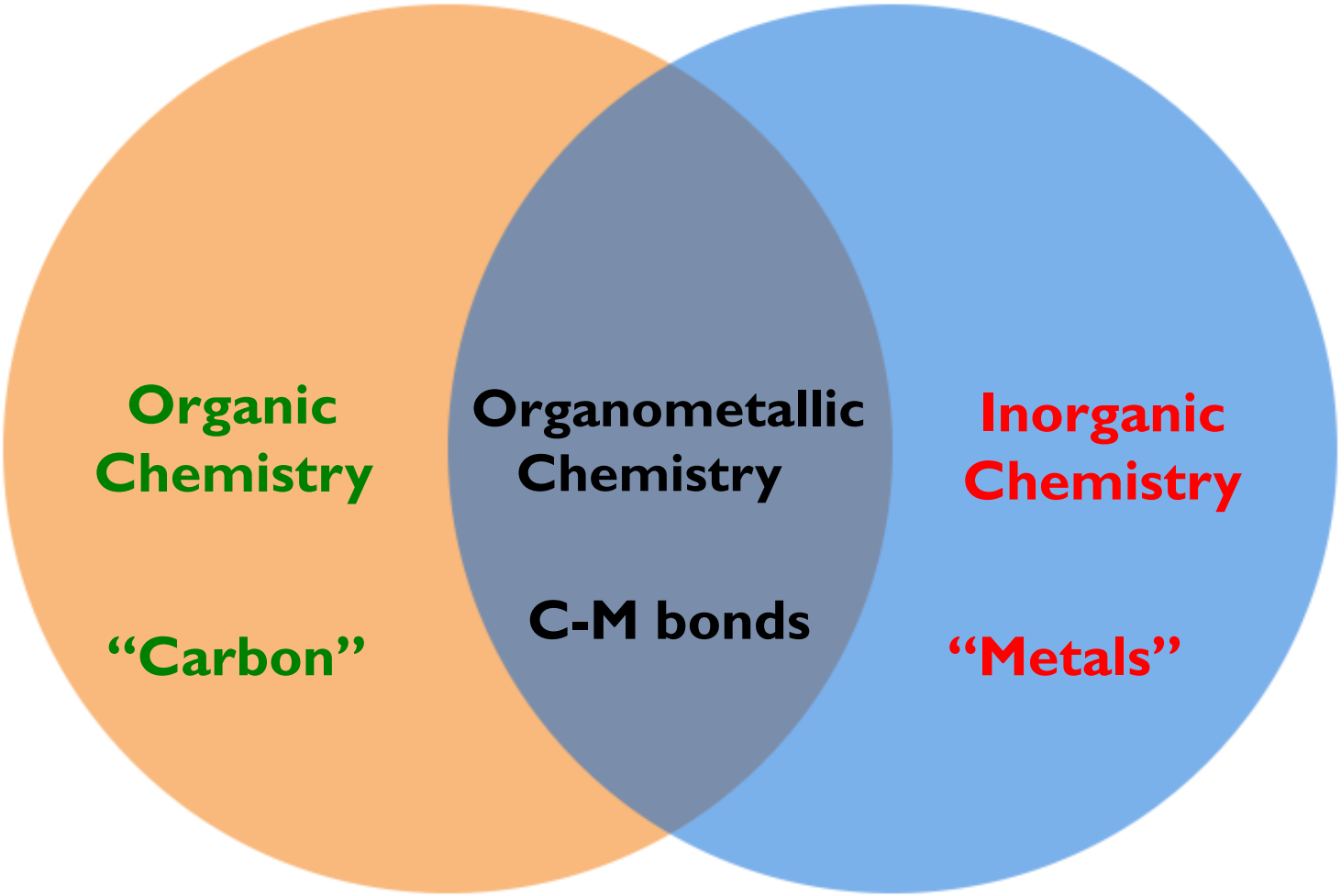




Introduction to organometallic chemistry

Portraits: http://scientistic.tumblr.com

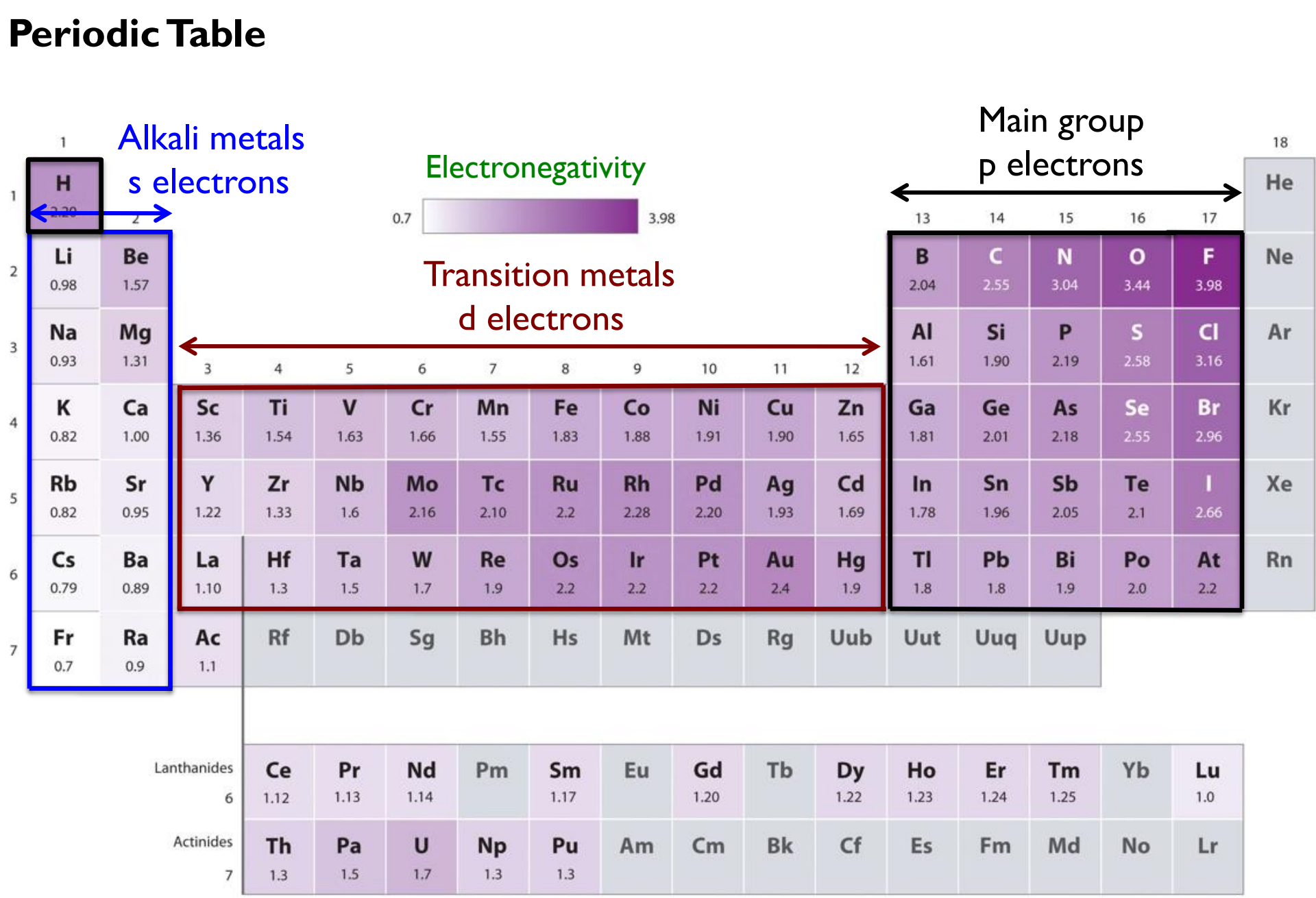
What is organometallic chemistry?



Organometallic chemistry = Study of compounds containing a Carbon-Metal bond

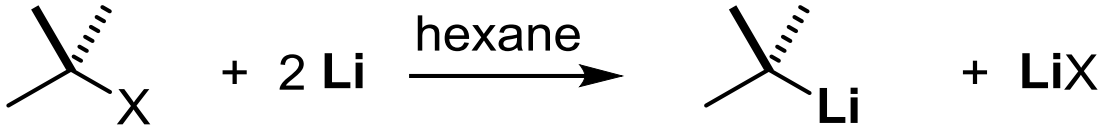
Organometallic chemistry = Organic synthesis using metals

Periodic Table



Organometallics – s-block metals

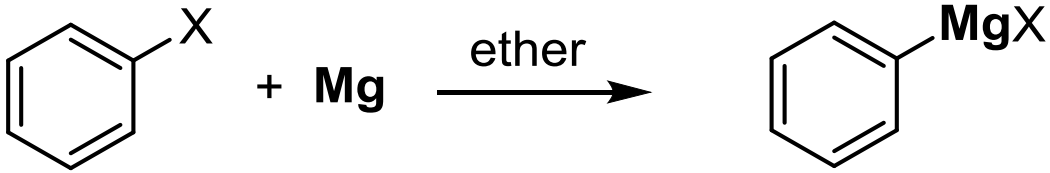
Organolithiums



alkyl halide
(X = halide)

tert-butyl lithium

Organomagnesium halides
(Grignard reagents)



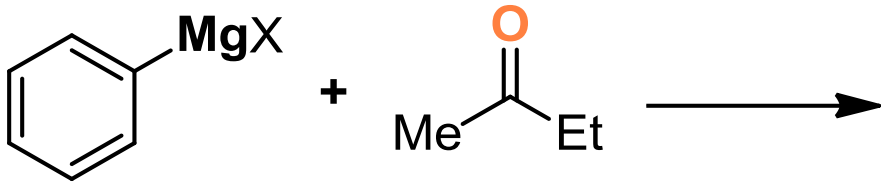
aryl halide

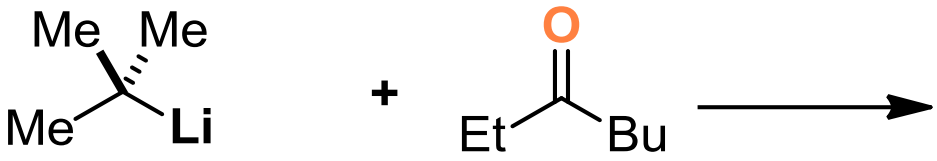
phenylmagnesium halide

Lithium diorganocuprates
(Gilman reagents)

lithium diethylcuprate

Organometallics – s-block compounds



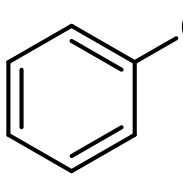


organolithium reagent

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

Why do Grignards and organolithiums react as carbon nucleophiles?

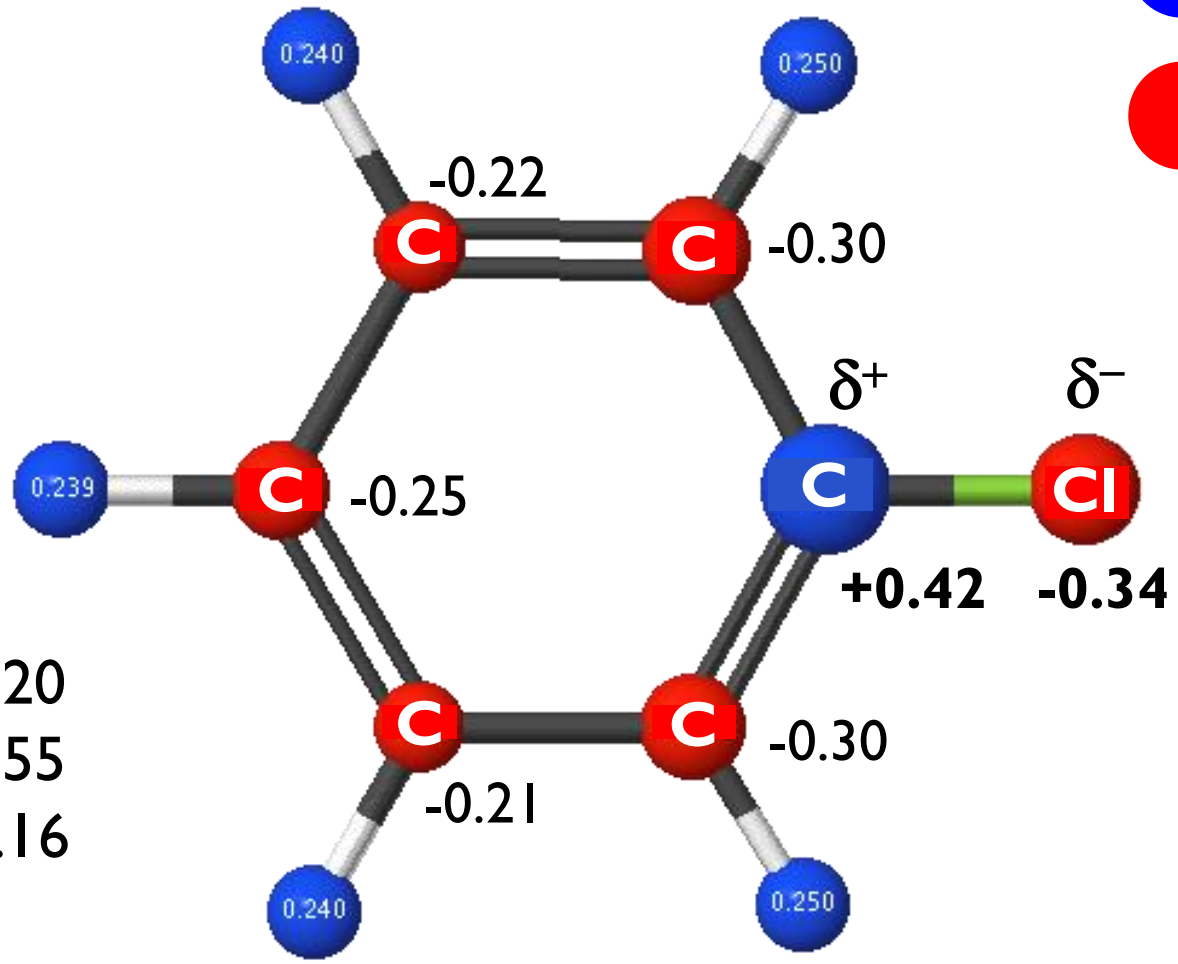
Charge distribution – Chlorobenzene



A typical organic compound

= positively charged

= negatively charged

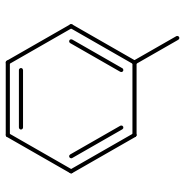


$X_H = 2.20$
$X_C = 2.55$
$X_{Cl} = 3.16$

X = Pauling electronegativity

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

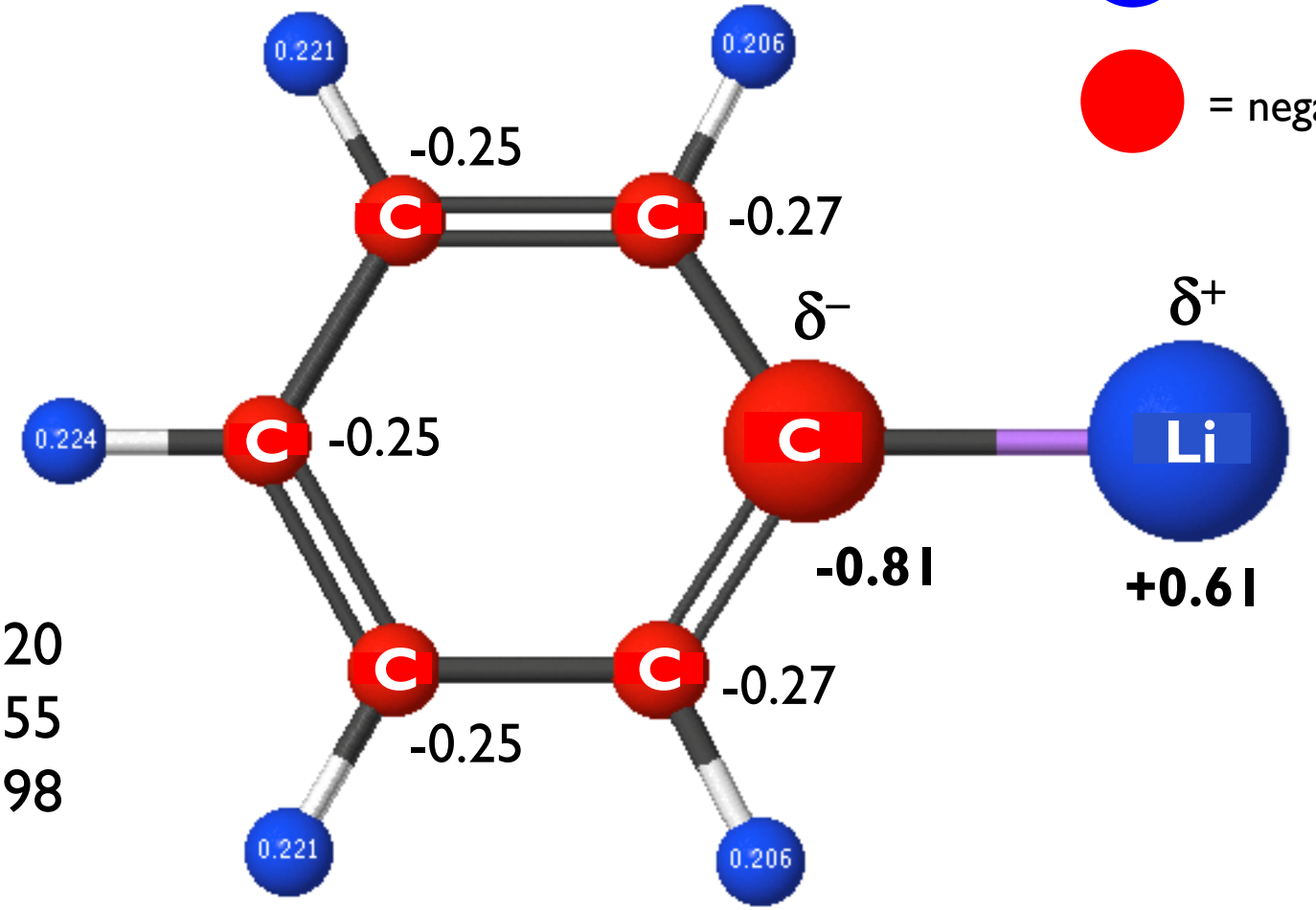
Charge distribution – Phenyl lithium



An organometallic compound

= positively charged

= negatively charged

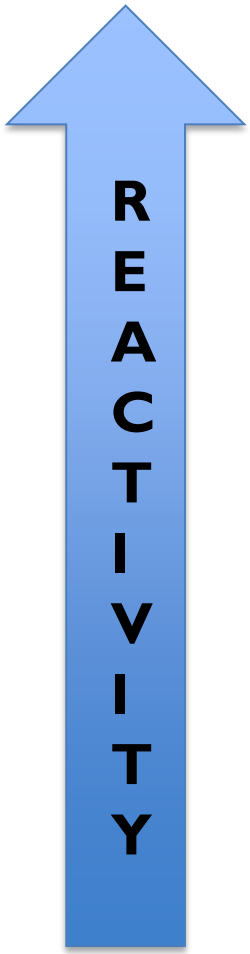


X_H = 2.20
X_C = 2.55
X_{Li} = 0.98

X = Pauling electronegativity

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

Carbon-Metal bond polarity drives reactivity

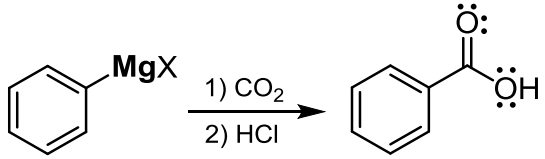


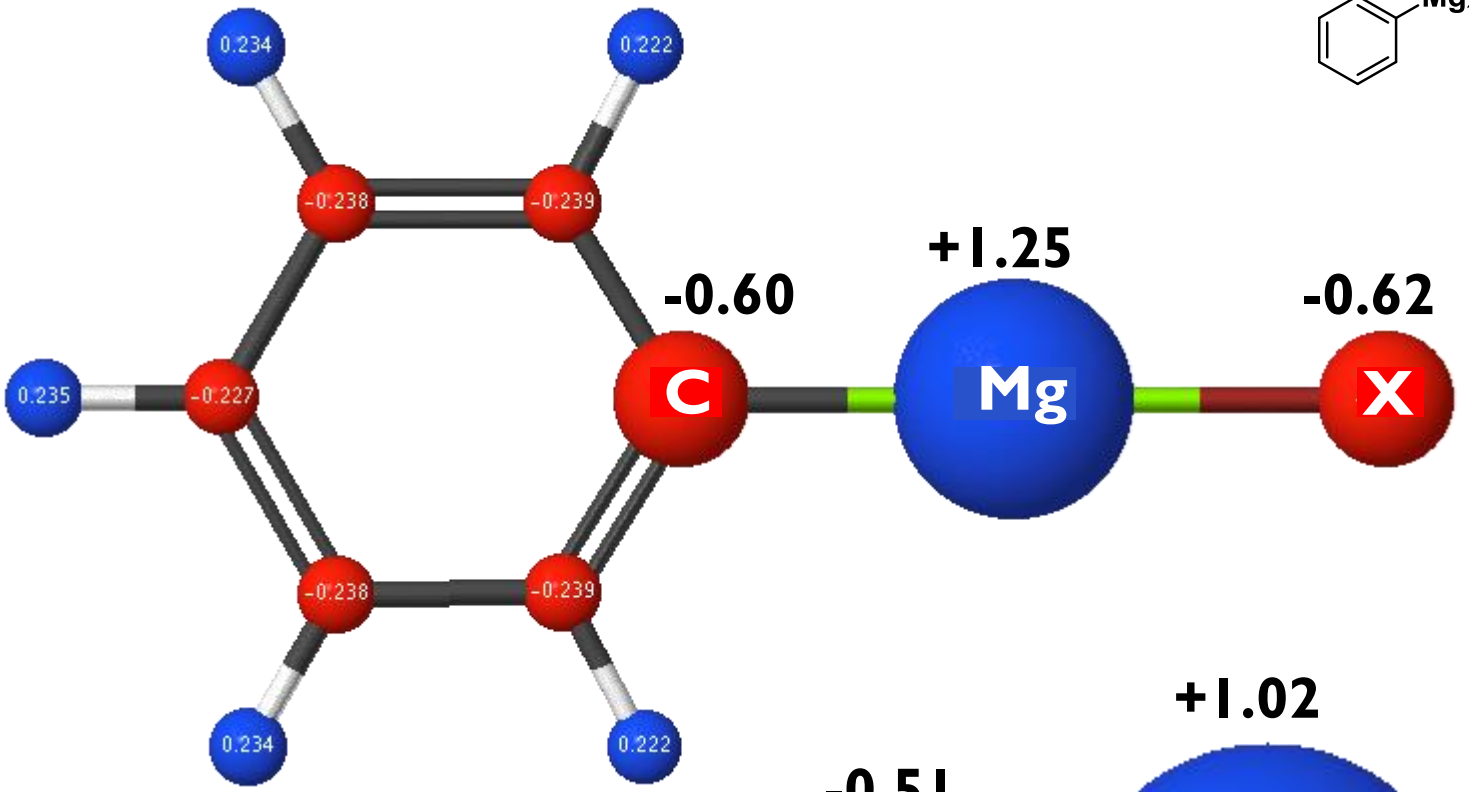
C-M bond	Δ Electronegativity#	% ionic character*
C-K	2.55 – 0.82 = 1.73	68
C-Na	2.55 – 0.93 = 1.62	63
C-Li	2.55 – 0.98 = 1.57	61
C-Mg	2.55 – 1.31 = 1.24	48
C-Ti	2.55 – 1.54 = 1.01	40
C-Al	2.55 – 1.61 = 0.94	37
C-Cu	2.55 – 1.90 = 0.65	25
C-O	2.55 – 3.44 = -0.89	35
C-Cl	2.55 – 3.16 = -0.61	24
C-Br	2.55 – 2.96 = -0.41	16
C-H	2.55 – 2.20 = 0.35	14

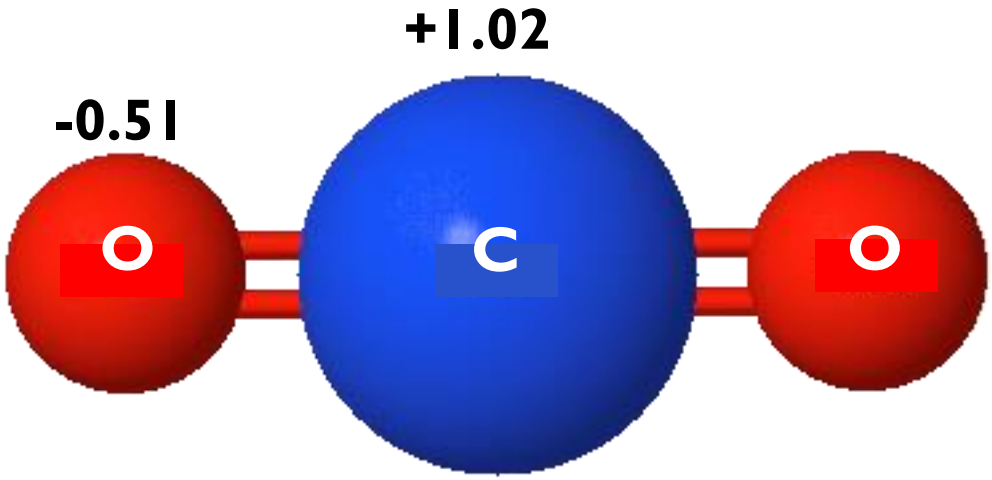
Pauling electronegativity, X

* % ionic character = $[(X_C - X_M) \div X_C]$

Reactivity of Grignard reagents



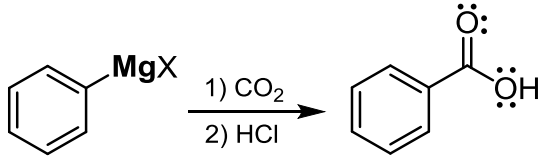


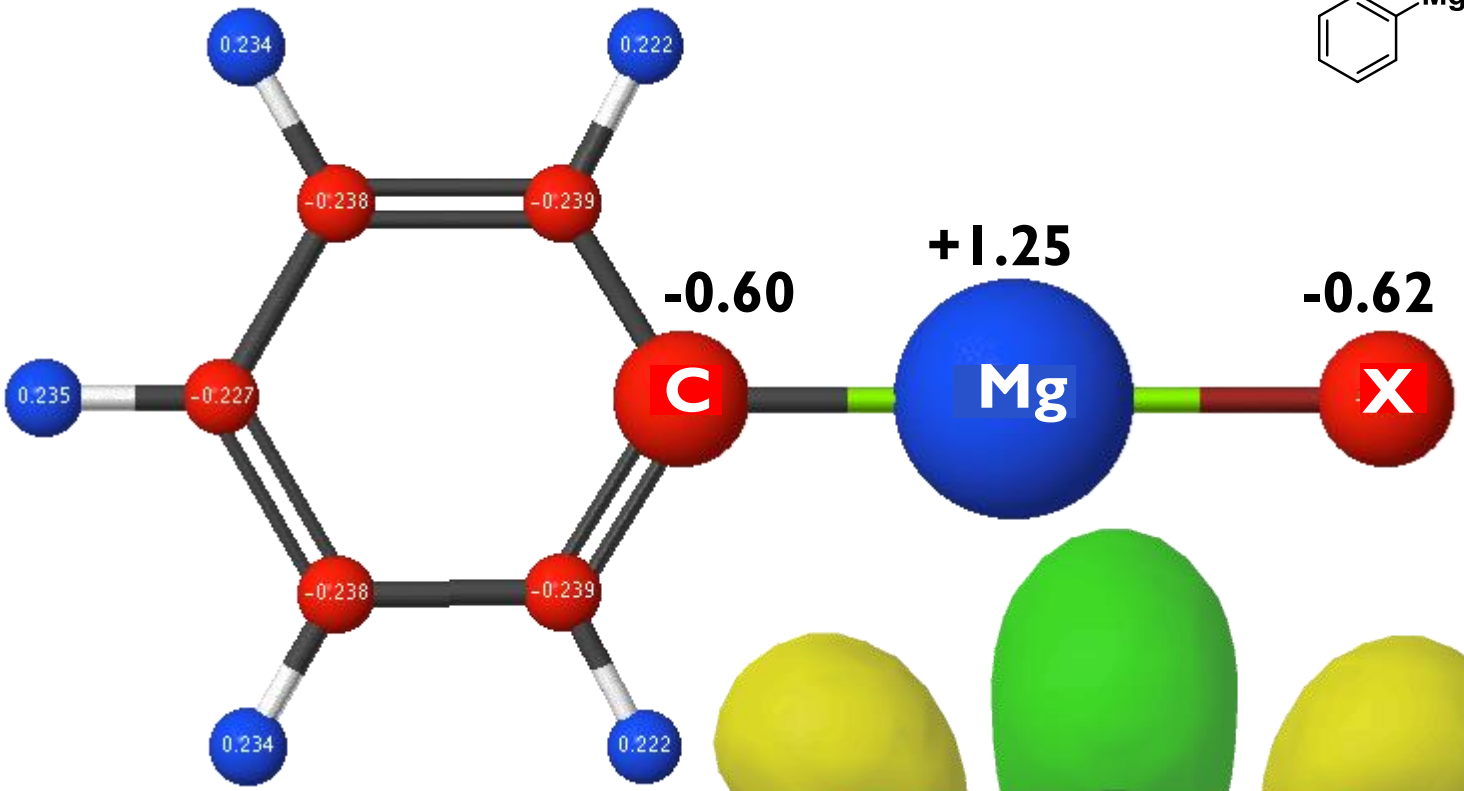


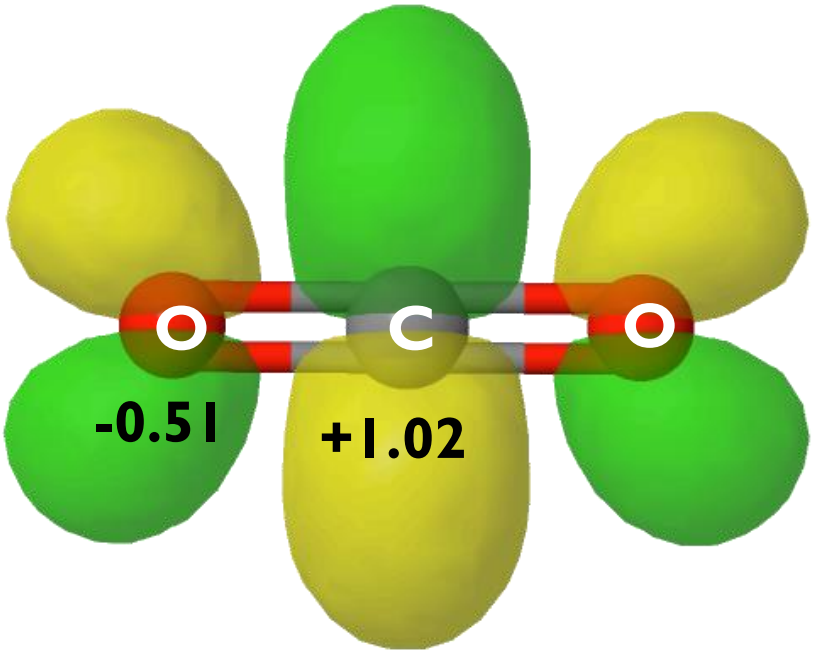
C-Mg bond % ionic character = 2.55 – 1.31 = **48%**

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

Reactivity of Grignard reagents



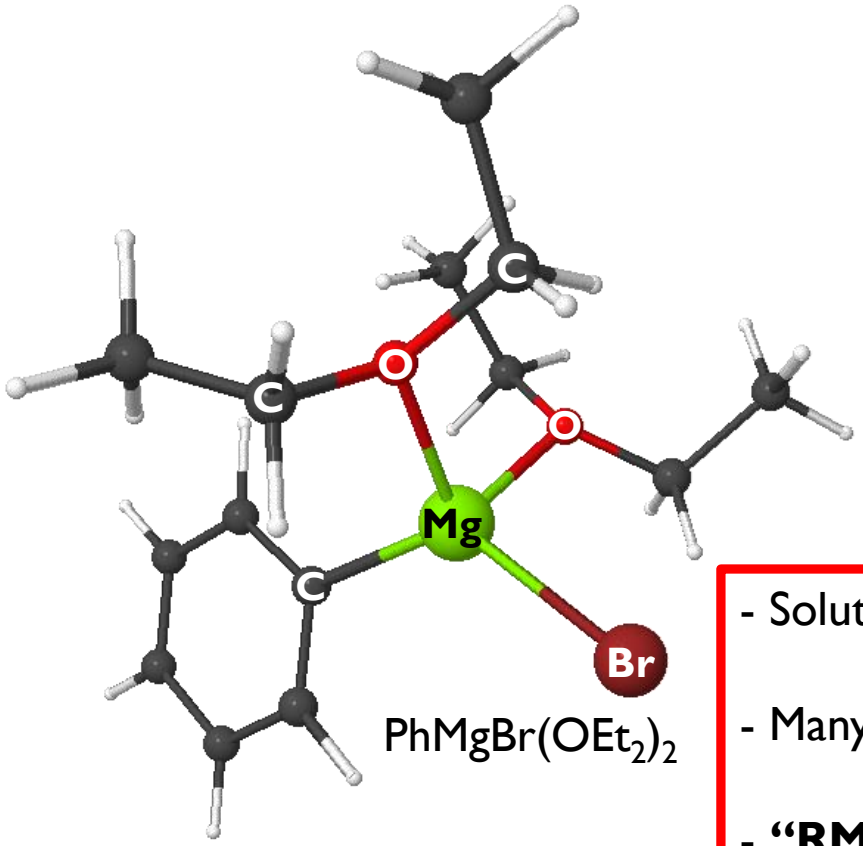




NBO calculation, B3LYP/6-31G(d)

Grignard lab – Synthesis of a benzoic acid

Why the need to use anhydrous solvent and a drying column?



$PhMgBr(OEt_2)_2$

B3LYP/6-31G(d)

Why use diethyl ether as the solvent?

- Solution behavior of Grignard reagents is highly complex

- Many reactive species in solution

- **"RMgX" works just fine to explain our chemistry**

Summary

Organometallic chemistry

- the chemistry of compounds containing a Carbon-Metal 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
- main reactivity is 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
- think about which C-X bond is more reactive to insertion of Mg