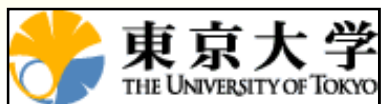


Organometallic Chemistry and Homogeneous Catalysis

Dr. Alexey Zazybin

Lecture N3

Kashiwa Campus, October 23, 2009



Properties

I. Nature of M

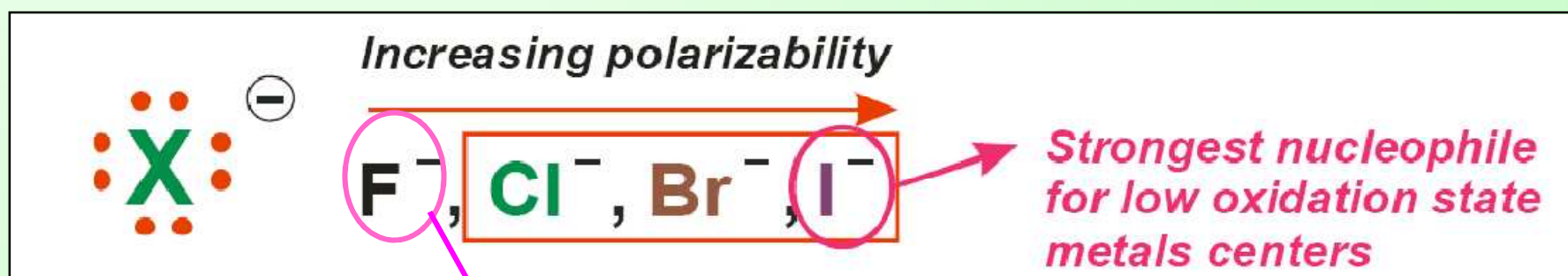
II. Nature of L

II.a. Ligands with C-atom attached to M

II.b. Ligands with other atoms attached to metal

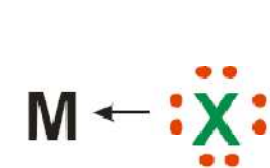
Halogen ligands (halide donors)

The halides are anionic donors that generally only donate $2e^-$ to a metal center. Due to their relatively high electronegativity they are not especially good σ -donor ligands. Although they can theoretically act as π -donor ligands, once again, the higher electronegativity limits them to simple $2e^-$ donor ligands.

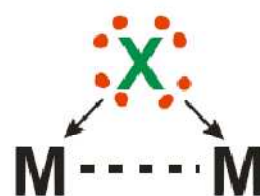


Fluoride is generally NOT a good ligand except for very high oxidation state metal centers. It is too electronegative to donate much of its electron density.

Bonding modes:



2e- terminal

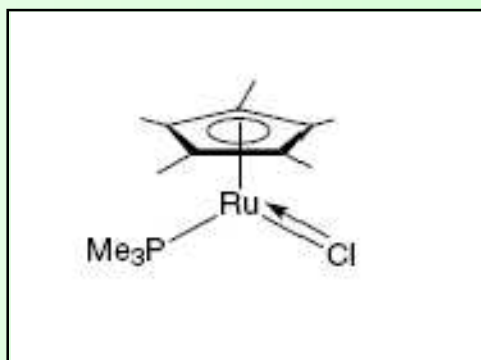


4e- μ -bridging

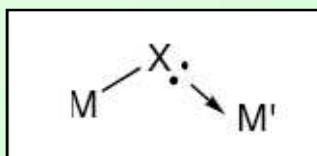


6e- μ_3 -bridging

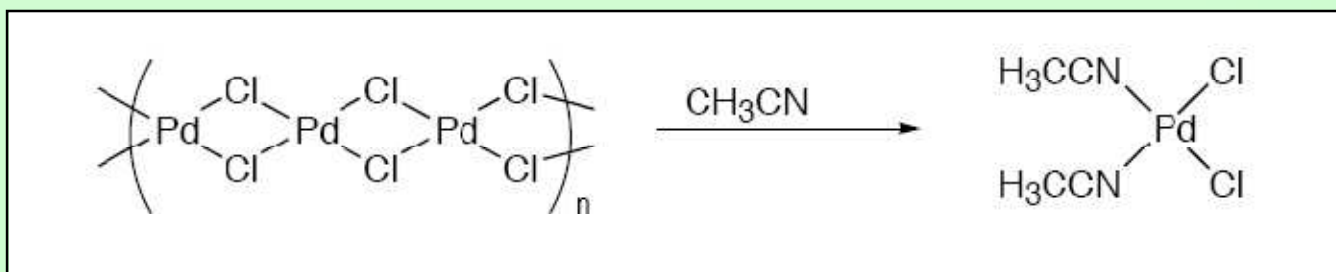
When coordinating to a single metal center usually we regard halides as $2e^-$ donors. $4e^-$ can be more easily donated by I than by any other halide, even so exceptions are possible:



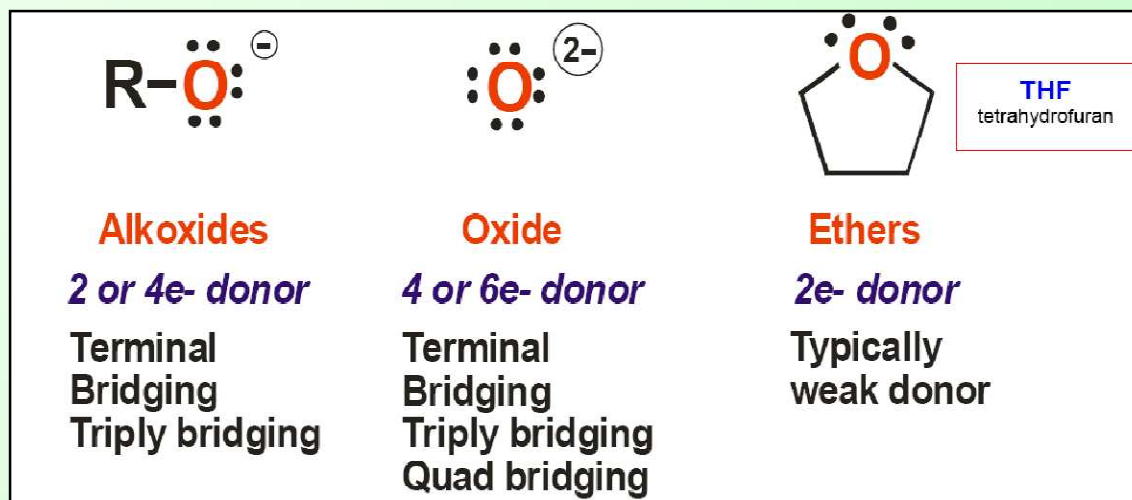
Bridging:



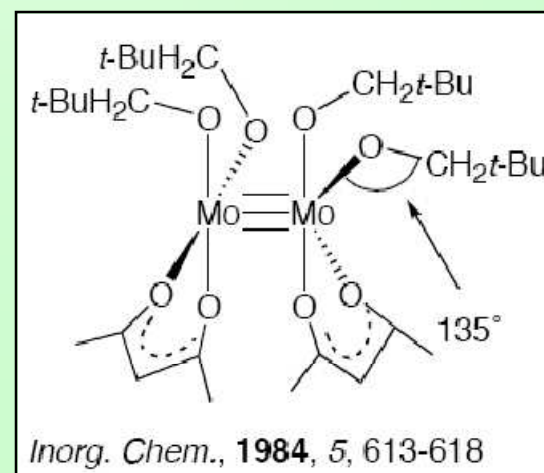
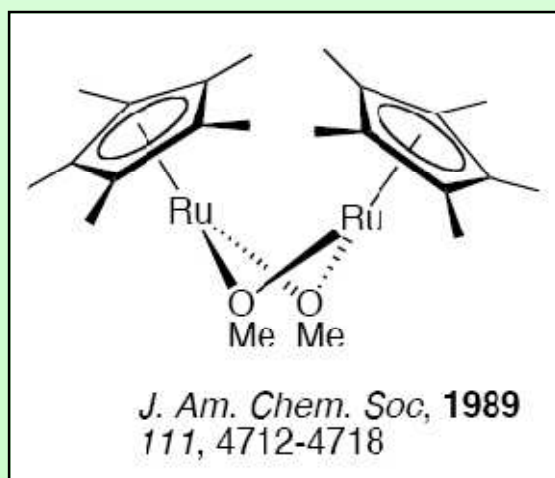
Coordinationally unsaturated metal halides often exist as insoluble polymers connected by bridging halides. PdCl_2 is a classic example. Ligands such as CH_3CN can displace the bridging halide to give the soluble square planar complex $(\text{CH}_3\text{CN})_2\text{PdCl}_2$.



Oxygen donors:



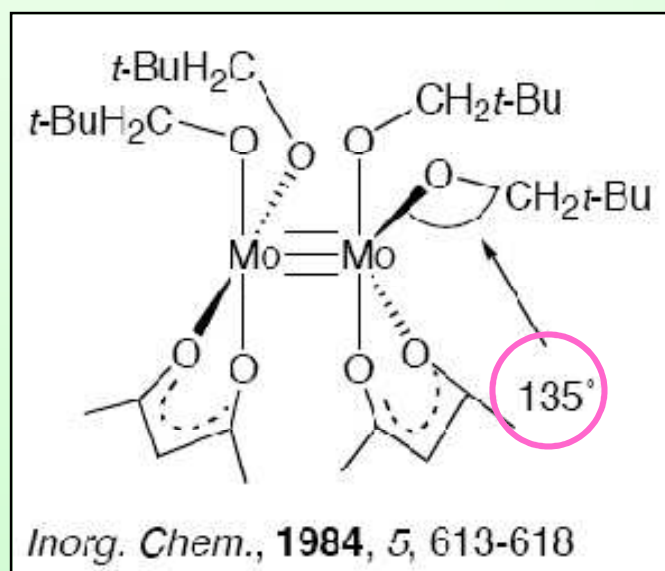
Alkoxides commonly act as bridging ligands for electropositive metals. To avoid formation of bridges, bulky alkoxides must be used. With high valent transition metals, π -donation becomes important.



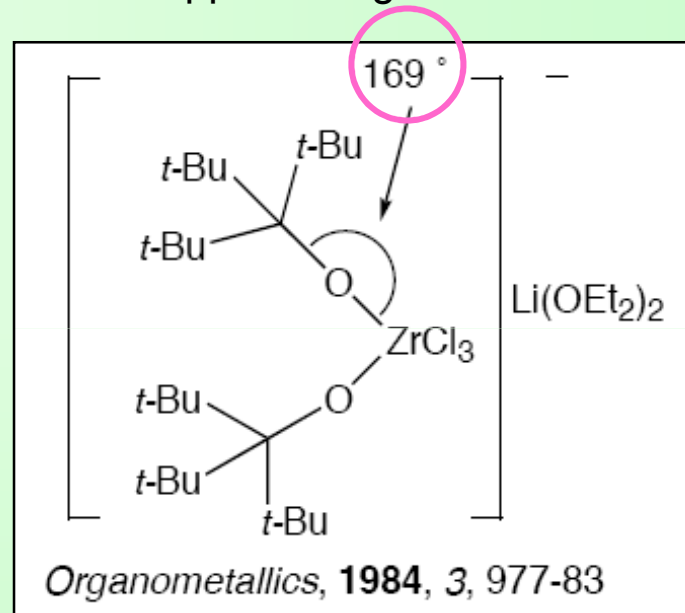
Important information about bonding type gives **M-O-C** angle:

Usually in ethers (like Et₂O) the C-O-C angle is about 110°

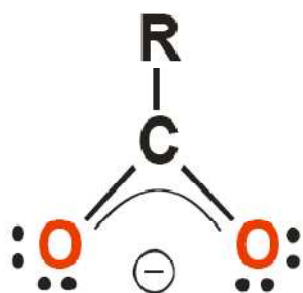
But in the metal-alkoxyde systems M-O-C angle is often approaching 120° or even 180°



An angle near 120° suggests that the O is sp² hybridized and acting as a 4 electron donor.



An angle near 180° suggests that the O is sp hybridized and acting as a 6 electron donor. In this case the alkoxide can be considered to be isoelectronic with the Cp ligand.



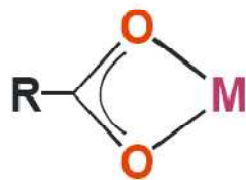
Carboxylates

2 or 4e- donor

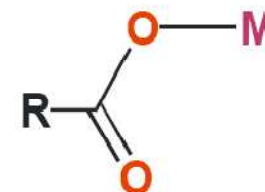
η^1 -terminal

η^2 -terminal

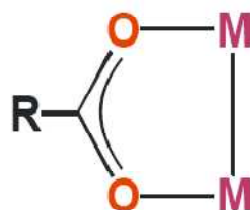
Bridging



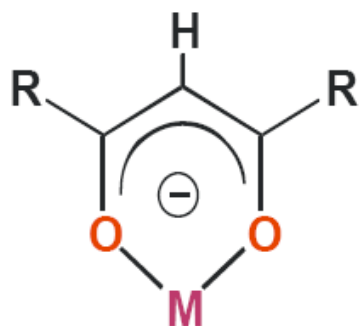
η^2 -chelating 4e-



η^1 2e- mode



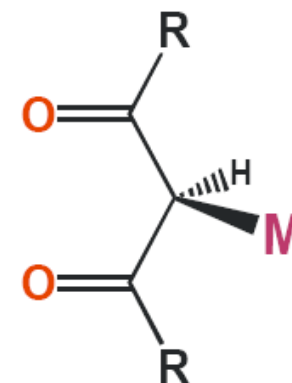
μ -bridging



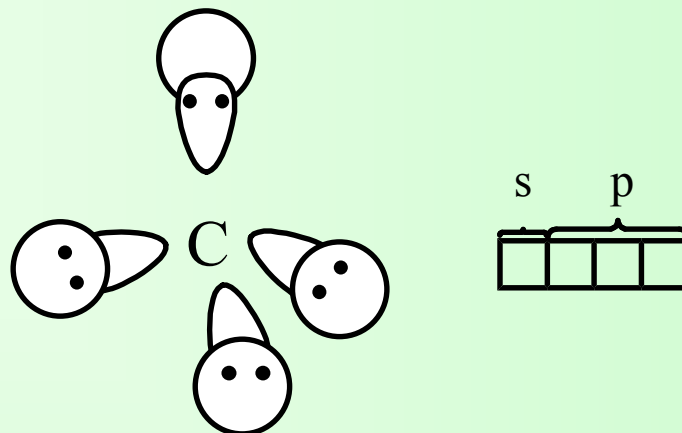
Acetoacetonates (acac)

2 or 4e- donor

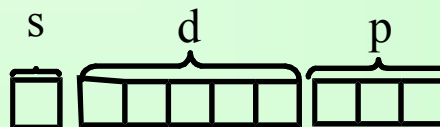
**Unusual C-bonded
acac**



For organic compounds: maximum 8 electrons on C:



For metal complexes: maximum 18 electrons on M:



Complexes with 18 e⁻ counts are referred to as saturated, because there are no empty low-lying orbitals to which another incoming ligand can coordinate.

Complexes with less than 18e⁻ are called unsaturated and can electronically bind additional ligands



Cationic 2e⁻ donor: NO⁺ (nitrosyl)

Neutral 2e⁻ donors: PR₃ (phosphines), CO (carbonyl), R₂C=CR₂ (alkenes), RC≡CR (alkynes, can also donate 4 e⁻), N≡CR (nitriles)

Anionic 2e⁻ donors: Cl⁻ (chloride), Br⁻ (bromide), I⁻ (iodide), CH₃⁻ (methyl), CR₃ (alkyl), Ph⁻ (phenyl), H⁻ (hydride)

The following can also donate 4 e⁻ if needed, but initially count them as 2e⁻ donors (unless they are acting as bridging ligands):

OR⁻ (alkoxide), SR⁻ (thiolate), NR₂⁻ (amide), PR₂⁻ (phosphide)

Anionic 4e⁻ donors: C₃H₅⁻ (allyl), O²⁻ (oxide), S₂⁻ (sulfide), NR₂⁻ (imide), CR₂⁻ (alkylidene)

and from the previous list: OR⁻ (alkoxide), SR⁻ (thiolate), NR₂⁻ (amide), PR₂⁻

Anionic 6e⁻ donors: Cp⁻ (cyclopentadienyl), O₂⁻ (oxide)



Electron Count Oxidation State Coordination Number

- Basic tools for understanding structure and reactivity.
- Doing them should be “automatic”.
- Not always unambiguous \Rightarrow don't just *follow* the rules, *understand* them!

The basis of counting electrons

- Every element has a certain number of valence orbitals:

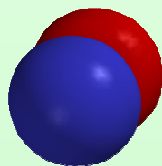
1 (1s) for H

4 (ns , $3 \times np$) for main group elements

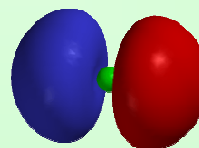
9 (ns , $3 \times np$, $5 \times (n-1)d$) for transition metals



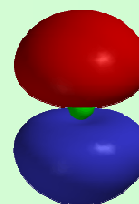
s



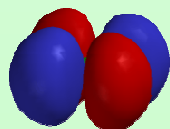
px



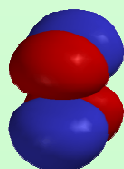
py



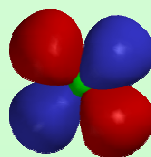
pz



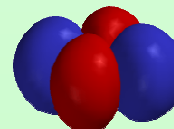
dxy



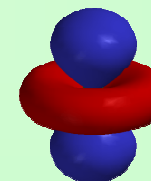
dxz



dyz



dx^2-y^2

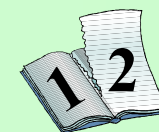


dz^2



The basis of counting electrons

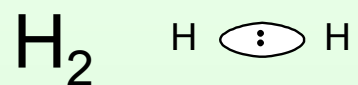
- Every orbital wants to be “used”, i.e. contribute to binding an electron pair.
- Therefore, every element wants to be surrounded by 2/8/18 electrons.
- The strength of the preference for *electron-precise* structures depends on the position of the element in the periodic table.



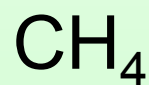
The basis of counting electrons

- **Too few electrons:**
An empty orbital makes the compound very electrophilic, i.e. susceptible to attack by nucleophiles.
- **Too many electrons:**
There are fewer covalent bonds than one would think (not enough orbitals available). An ionic model is required to explain part of the bonding. The "extra" bonds are relatively weak.
- **Metal-centered (unshared) electron pairs:**
Metal orbitals are fairly high in energy. A metal atom with a lone pair is a strong σ -donor (nucleophile) and susceptible to electrophilic attack.

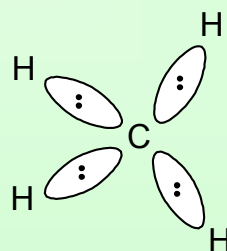
Use a localized (valence-bond) model
to count electrons



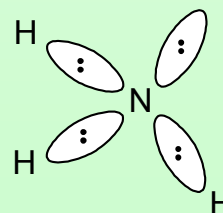
Every H has 2 e. *OK*

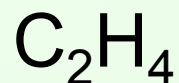


H has 2 e, C 8. *OK*

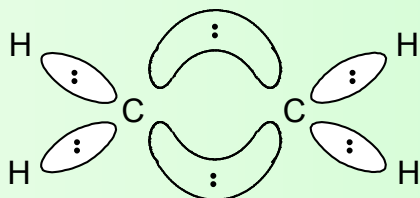


N has 8 e. Nucleophile! *OK*

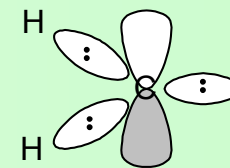




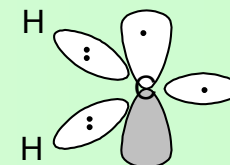
C has 8 e. *OK*

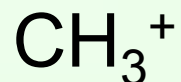


C has only 6 e, and an empty p_z orbital:
extremely reactive ("singlet carbene").
Unstable. Sensitive to nucleophiles and
electrophiles.

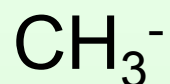
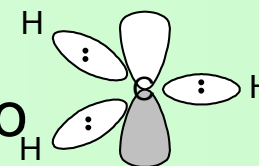


C has only 6 e, is a "biradical" and
extremely reactive ("triplet carbene"), but
not especially for nucleophiles or
electrophiles.

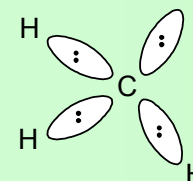




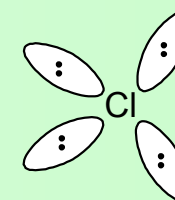
C has only 6 e, and an empty p_z orbital:
extremely reactive. Unstable. Sensitive to
nucleophiles.

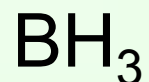


C has 8 e, but a lone pair. Sensitive to
electrophiles.

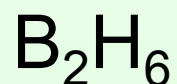
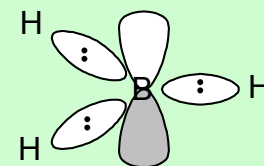


Cl has 8 e, 4 lone pairs. **OK** Somewhat
sensitive to electrophiles.

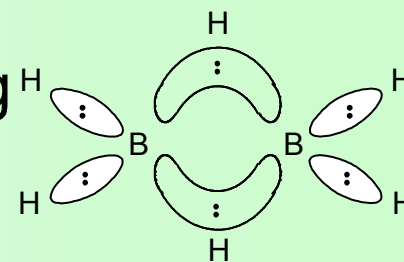




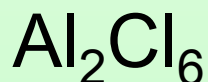
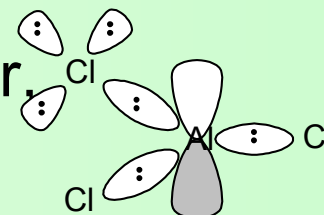
B has only 6 e, not stable as monomer,
forms B_2H_6 :



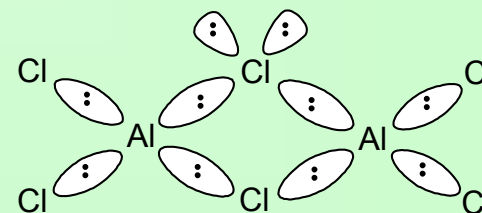
B has 8 e, all H's 2 (including the bridging H!). 2-electron-3-center bonds! *OK*

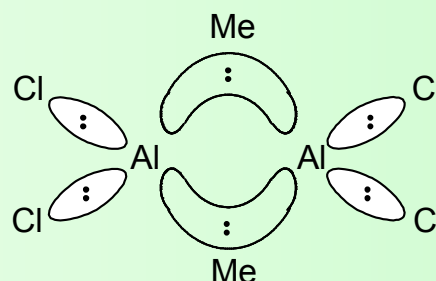
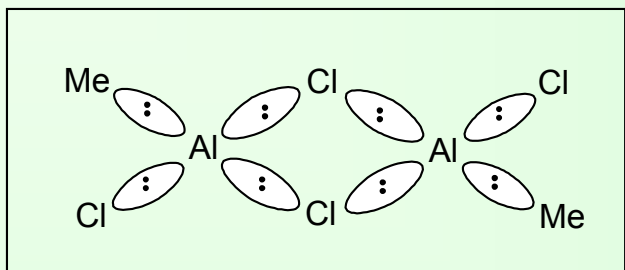
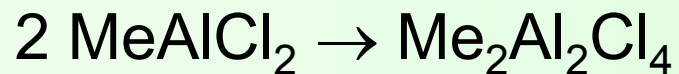


Al has only 6 e, not stable as monomer,
forms Al_2Cl_6 :

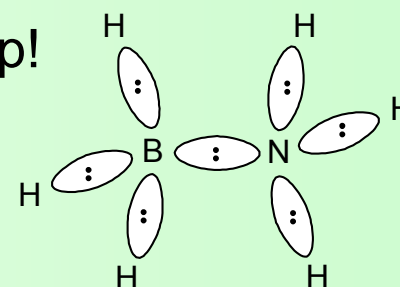
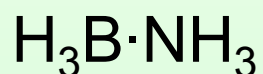


Al has 8 e, all Cl's too (including the bridging Cl!). Regular
2-electron-2-center bonds! *OK*



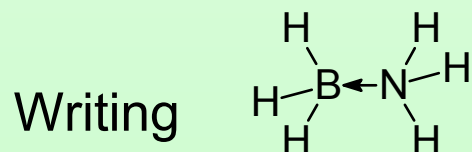
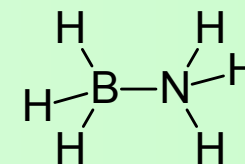


2-electron-3-center bonds are a stopgap!

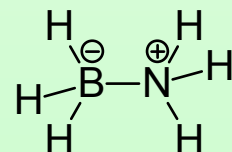


N-B: donor-acceptor bond (nucleophile NH_3 has attacked electrophile BH_3).

Organometallic chemists are "sloppy" and write:



or



would be more

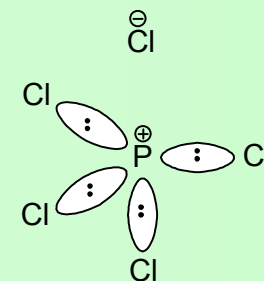
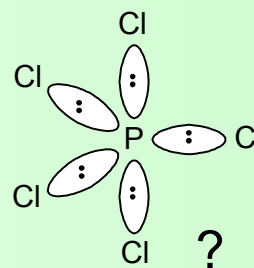
correct (although the latter does not reflect the "real" charge distribution).

PCl₅

P would have 10 e, but only has 4 valence orbitals, so it cannot form more than 4 "net" P-Cl bonds.

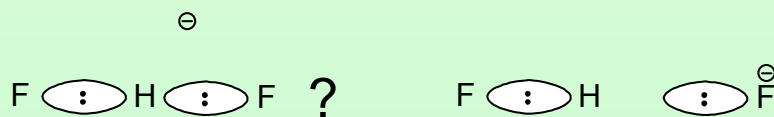
You can describe the bonding using ionic structures (hyperconjugation).

Easy dissociation in PCl₃ + Cl₂.



HF₂⁻

Write as FH·F⁻, mainly ion-dipole interaction.



Examples of electron counting:



1. Nature of central atom (oxidation state, number of electrons)

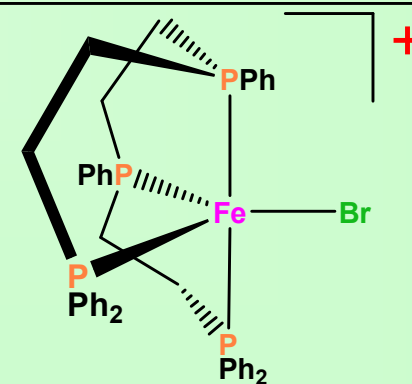
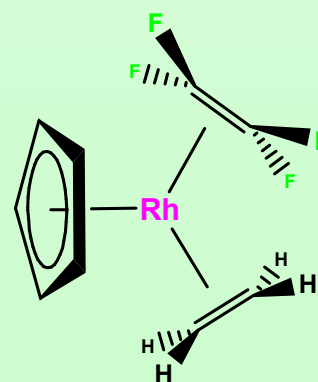
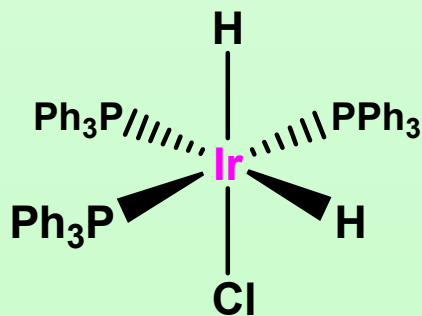
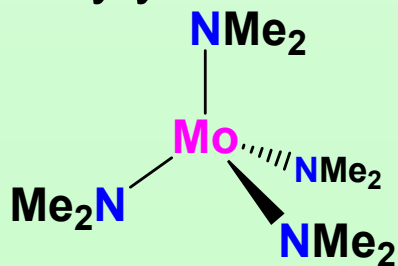
Charge of the complex: **0** Charge of the non-neutral ligands: $2 * (-1) = -2$ Metal oxidation state: **+2**

Number of electrons for Pt^{2+} : for Pt^0 according to the periodic table 10,
For Pt^{2+} : $8e^-$

2. Nature of ligands (number of electrons donating to the metal)

$4 * (2e^- \text{ - ligands}) = 8e^-$ Final result: $8 + 8 = 16 e^-$

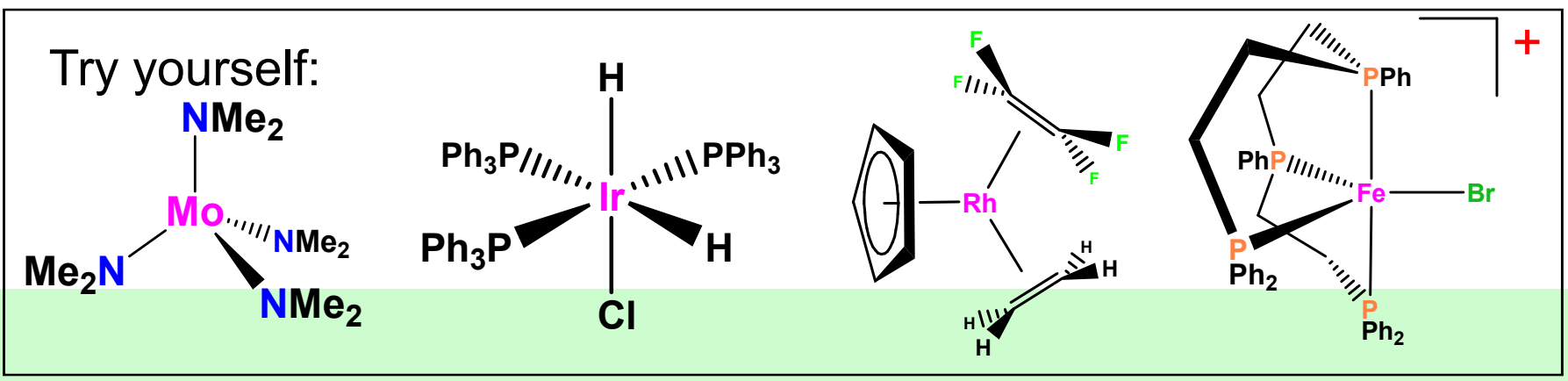
Try yourself:



Periodic Table of the Elements

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								

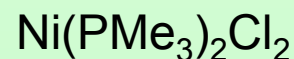
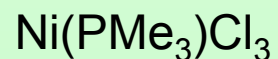
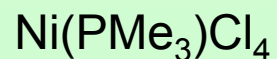
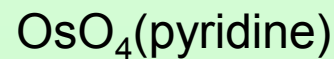
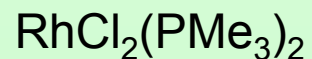
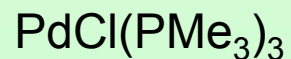
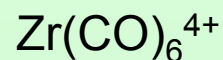
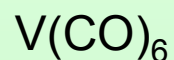
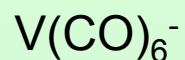
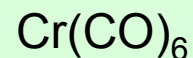
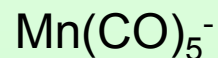
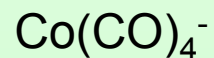
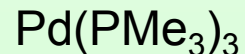
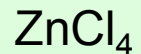
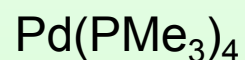
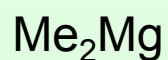
- hydrogen
- alkali metals
- alkali earth metals
- transition metals
- poor metals
- nonmetals
- noble gases
- rare earth metals

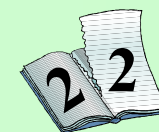




Exercises

Give electron count and oxidation state for the following compounds.
Draw conclusions about their (in)stability.





Main group organometallic chemistry

Compound	Category	Bonding	Structure
KMe	ionic	ionic	$K^+ CH_3^-$ ionic lattice
CsMe	ionic	ionic	$Cs^+ CH_3^-$ ionic lattice
$[Be(CH_3)_2]_x$	polymeric	(3c,2e)	doubly-bridged polymeric chain
$[Mg(CH_3)_2]_x$	polymeric	(3c,2e)	doubly-bridged polymeric chain
Li_4Me_4	electron poor	(4c,2e)	(tetrahedron structure)
$Zn(CH_3)_3$	electron poor	(2c,2e)	linear
$HgMe_2$	electron precise	2c,2e normal bond	linear
$Al_2(CH_3)_2$	electron poor	(3c,2e and 2c,2e)	

Often: ionic bonding, di-, tetra-, polymeric structure

Group I: Li, Na, K, Rb, Cs



Organolithium Compounds

- Ionic character
- Electron-deficient

- Strongly basic
- Strongly nucleophilic

- Reducing
- Oligomeric or polymeric structures
- Applications in organic synthesis

Organo Na, K, ... compounds

- "Purely" ionic

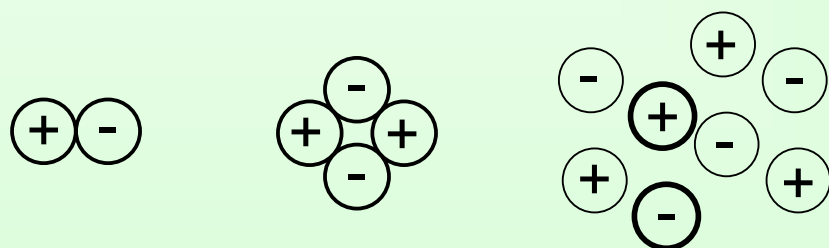
- Very strong bases

- Polymeric structures, mostly insoluble

- Few applications

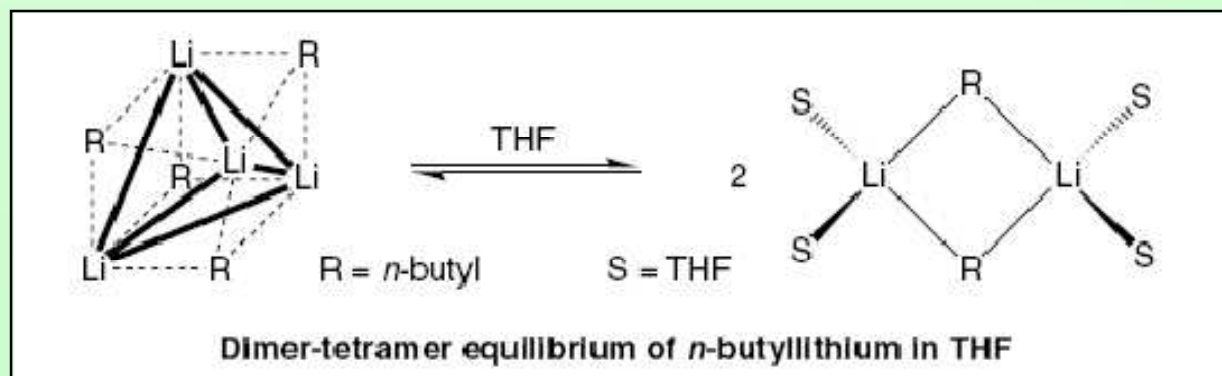
Oligomeric Li compounds: ionic interpretation

The polarity of the metal-carbon bond increases upon going down in the periodic table: the lithium alkyls have some covalent character and form tetrameric clusters, whereas cesium alkyls are purely ionic.



Ionic interactions are "soft" but not weak!

The degree of clusterification of lithium alkyls varies with the nature of the solvent between dimer (LiCH₃: TMEDA) and hexamer (Li-*n*-C₄H₉: cyclohexane)

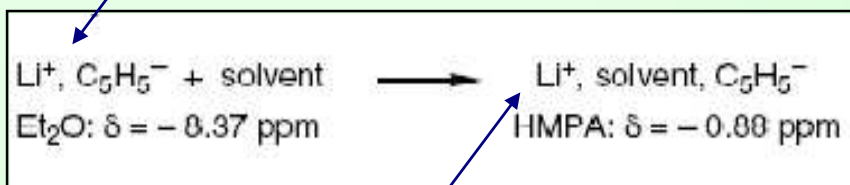




NMR of Li-organic compounds:

^7Li NMR:

With LiC_5H_5 , the chemical shifts in ^7Li NMR for the Li^+ cation in the contact ion pair



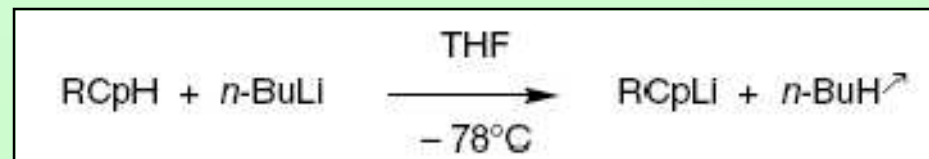
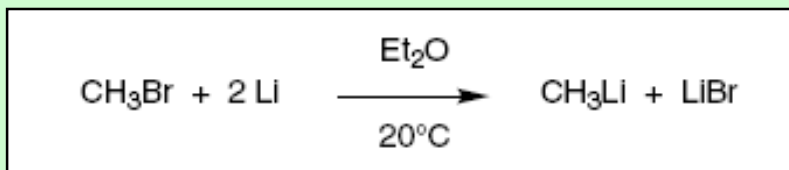
and the solvent-separated ion pair are very different

^1H NMR:

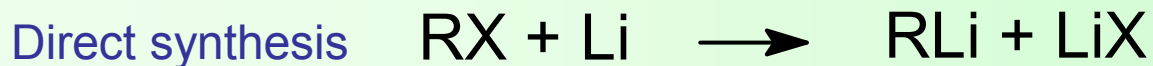
The concentrations of ^1H lithium-alkyls can be easily followed by ^1H NMR using the signal of the protons α to Li whose values are found near -1 ppm.

Synthesis of Organolithium Compounds

Lithium metal and *n*-butyllithium in hexane solution being commercial, the two following methods of syntheses of lithium-alkyl complexes are currently used:



Synthesis of Organolithium Compounds



- Reactivity:
alkyl > aryl,
Cl < Br < I,
Li < Na etc
- Side reaction: Wurtz coupling, especially for X = I (Better to use RCl)
- In apolar or weakly polar solvents (any active H atoms "kill" organolithium compounds)
- Radical mechanism



- Faster for more basic R'^-
- Faster in polar and/or coordinating solvents
- Works well if product capable of intramolecular coordination



Reactivity of Organolithium Compounds

General Li-R bond is polar covalent rather than ionic. Polarity is due to small size of lithium metal cation. Li^+ acts like a hard acid polarising the e^- cloud of e.g. CH_3^- . Due to its polar/covalent character LiR are less reactive than NaR and in many ways more useful, selective.

1. Deprotonation-metallation (basic nature)

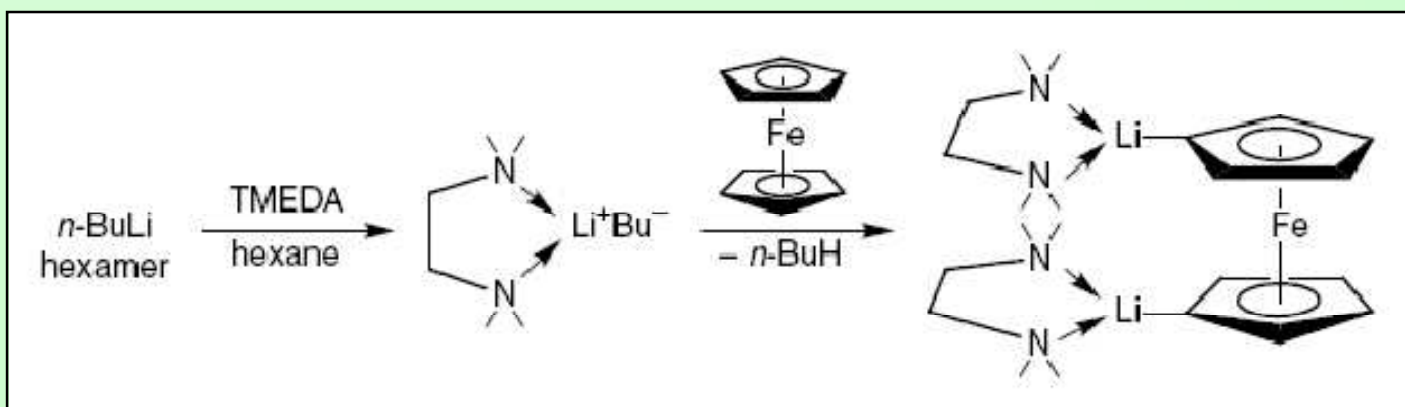
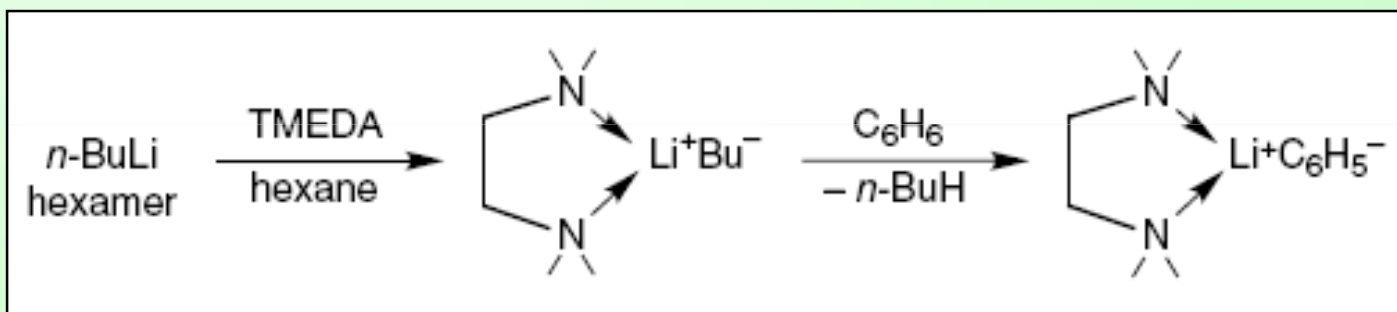
n-Butyllithium is one of the most currently used bases in organic synthesis. The hydrocarbon's C-H bonds are considered as acidic. And *n*-butyllithium as the base corresponding to butane ($pK_a = 44$). The deprotonation of the following hydrocarbons by *n*-butyllithium is thus thermodynamically favorable:

Hydrocarbon	cyclopentadiene	fluorene	acetylene	toluene	benzene
pK_a	15	21	24	35	37

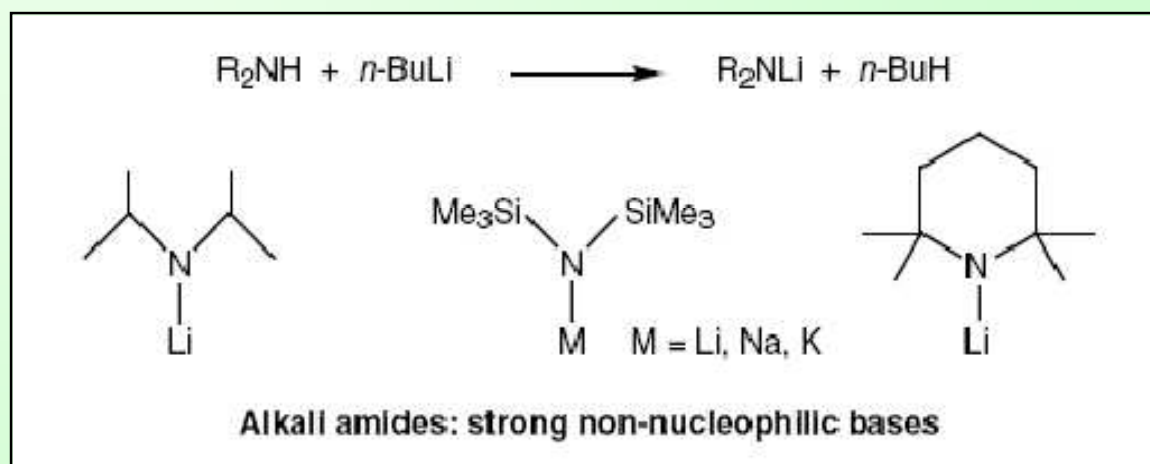
In the case of benzene, the large kinetic barrier does not allow the reaction to proceed.

However benzene deprotonation is possible in the presence of TMEDA.

The role of this chelate⁺ ligand is first to break the hexameric cluster in hexane by complexation of the Li⁺ cation, which strongly polarizes the Li-C bond. The addition of benzene or ferrocene then rapidly leads to deprotonation-metallation of the aromatic derivative, because the *n*-C₄H₉⁻ anion is rendered more basic once it is disengaged from the covalent bond with Li.



The only restriction of using BuLi is that it can sometimes act not only as a base but also as a nucleophile. In these cases, it is necessary to prepare a bulky base by reaction of *n*-butyllithium with a bulky amine such as diisopropylamine, bis(trimethylsilyl)amine or tetramethylpiperidine.

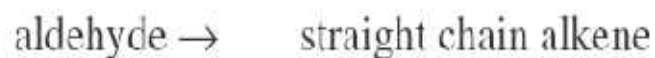
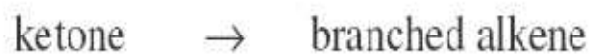
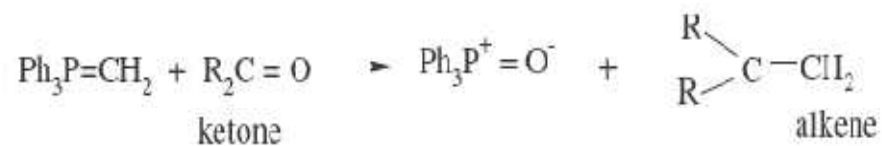
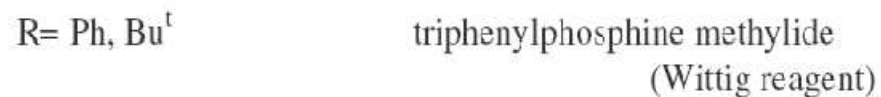
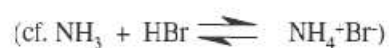


2. Transmetalation (nucleophilic nature)

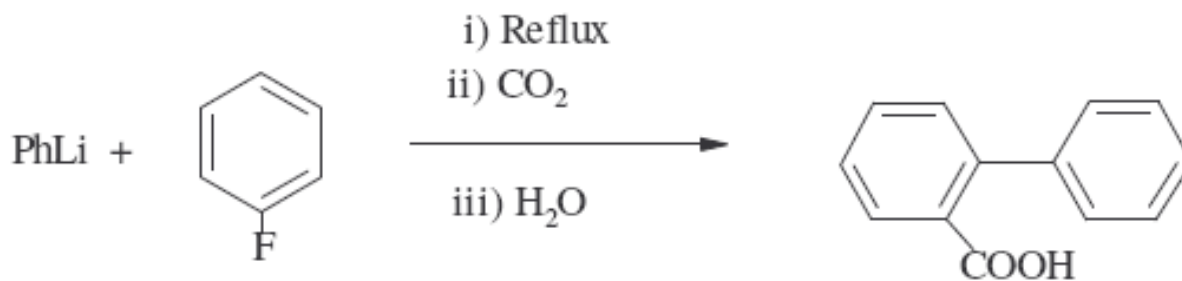




3. Synthesis of Wittig reagents

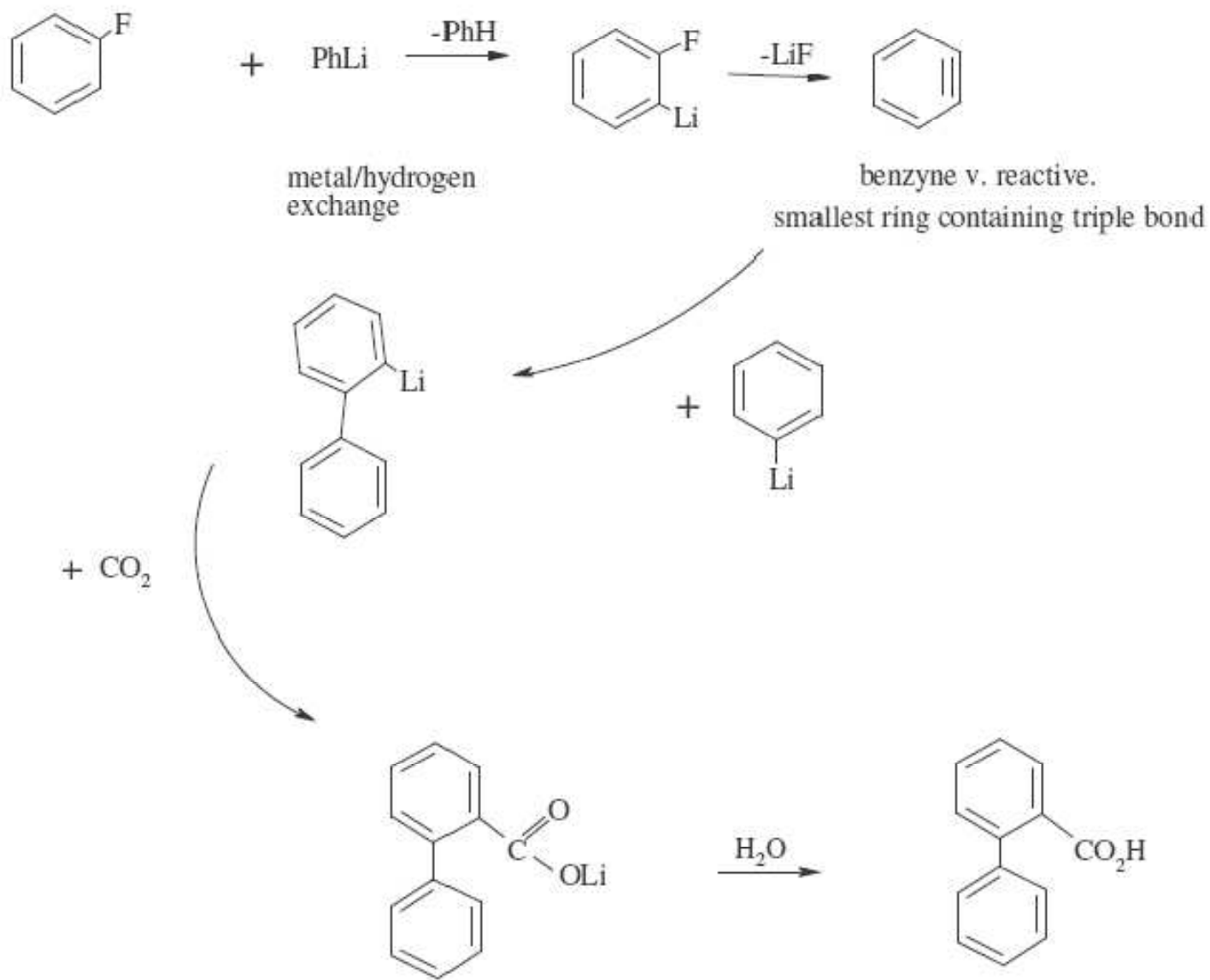


4. Reaction of LiR with Organofluorines



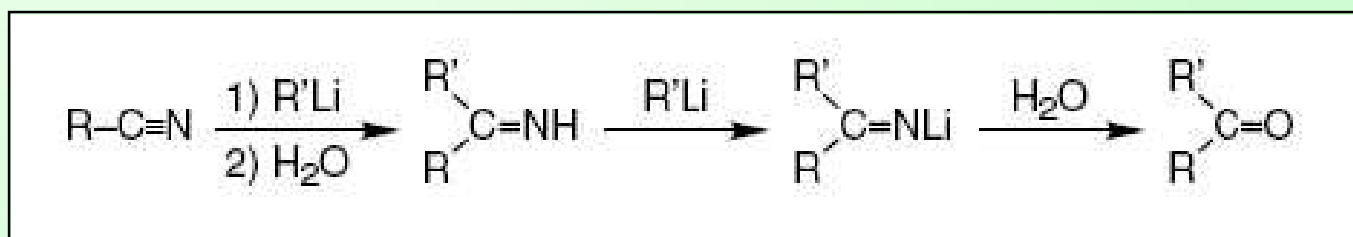
fluorobenzene, ortho H are a little acidic.

Mechanism:



5. Addition to the other multiple bonds

These additions are of synthetic interest. For instance, the addition of lithium compounds on nitriles is a synthetic route to ketones, whereas the addition of lithium compounds on *N,N*-dimethylformamide leads to aldehydes:



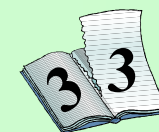
Special issues when working with organolithium species:

(I) work under inert atmosphere (N_2) Ar

Using N_2 in preparation of R-Li gives Li_3N (purple solution)

(II) dry, degassed solvents/reagents

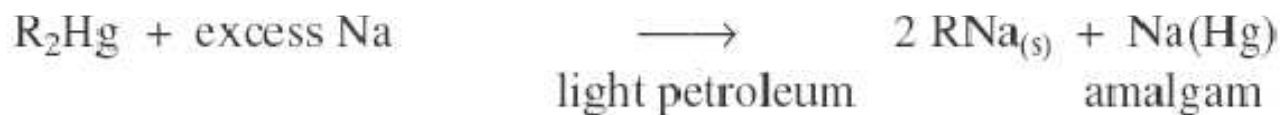
(III) dry apparatus



Heavier Group I Organometallics (Na, K...)

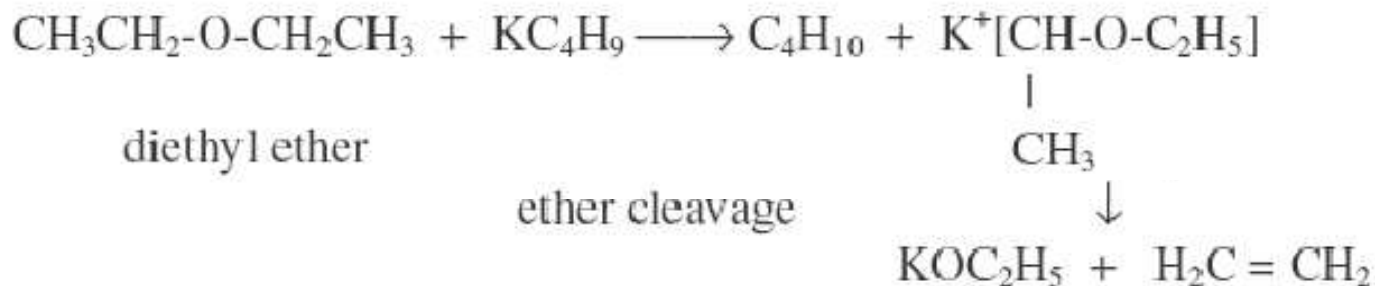
Limited use: ionic character of M-C increases down group. Generally very reactive even slowly metallate hydrocarbons (in which they are insoluble).

Synthesis:



Not prepared from organochlorides due to coupling (!)

Reactivity:



More strong bases (!)