Main group organometallics - Homework solutions

Q Ex 1,6,7,10,16,17 and Prob. 1,4,6,7

1) Organometallic compounds must contain a carbon-“metal” bond
   a) BMe₃ - not strictly an organometallic as boron is a nonmetal but...
   b) B(OMe)₃ - not organometallic
   c) (NaMe)₄ - organometallic
   d) SiCl₃Me - not strictly an organometallic as Si is a nonmetal but...
   e) NMe₃ - not organometallic as nitrogen is a nonmetal
   f) sodium acetate - not an organometallic
   g) Na[BPh₄] - not strictly an organometallic anion as boron is a nonmetal but.....

6) Aluminum is the only member of the group that readily forms bridged species with methyl in the bridge. Boron is so small that forming bridges with anything larger than hydrogen causes steric problems. Aluminum is sufficiently large that bridges with methyl can be formed without steric difficulties and it is sufficiently small that orbital overlap in the bridge is OK. For indium and gallium bridging methyl is not commonly found as poor orbital overlap would lead to weak bonding.

7) 
   a) (MeLi)₄ - good carbanion nucleophile and strong reducing agent
   b) ZnMe₂ - reasonable carbanion nucleophile, mild Lewis acid, reducing agent
   c) MeMgBr - good carbanion nucleophile
   d) BMe₃ - mild Lewis acid
   e) Al₂Me₆ - good carbanion nucleophile, strong reducing agent
   f) SiMe₄ - mild Lewis acid
   g) AsMe₃ - mild Lewis base

10) 
   a) Na[C₁₀H₈] as the extra electron is not as well delocalized
   b) Na₂[C₁₀H₈] as the their is more negative charge on the anion and hence more electron-electron repulsion.
16)  
a) PbMe$_4$ is less thermally stable than SiMe$_4$ as a consequence of the lower metal carbon bond strength in the lead compound (poor orbital overlap).

b) BMe$_3$ > SiMeCl$_3$ > SiMe$_4$ > Li$_4$Me$_4$
Boron has a vacant valence orbital unlike all the other compounds. LiMe is going to be basic rather than acidic there is no obvious acidic center.
Silicon can become hypervalent so there is a possibility for Lewis acid behavior. The chlorinated silane is likely to be more acidic due to the electron withdrawing nature of the chloride.

c) SiMe$_4$ will not act as a Lewis base it has no appropriate electron pair. AsMe$_3$ will be the better Lewis base as it has a lone pair.

d) LiMe will more readily displace halide from GeCl$_4$ than HgMe$_2$ as LiMe is more nucleophilic and the formation of LiCl provides a strong thermodynamic driving force for the reaction.

17)  
a) LiMe, Schlenk / inert atmosphere techniques  
b) BMe$_3$, Vacuum line as it is volatile  
c) Al$_2$iBu$_6$, possibly vacuum line depends on volatility or schlenk ware if volatility is low.  
d) AsPh$_3$, should be OK in air  
e) Me$_3$SiOSiMe$_3$ can handle in air.

Prob 1)  
Triethylaluminum can be made in bulk by direct reaction of aluminum hydrogen and ethene. This is a cheap process. Trimethyaluminum has to be made via a more expensive route such as MeCl and aluminum to form Al$_2$Me$_4$Cl$_2$ followed by treatment with sodium metal. The sodium metal and MeCl are not cheap when compared to ethene.

Prob 4
The $\pi - \pi^*$ separation in the germanium compounds will be even less than that found for the disilenes due to worse orbital overlap in the germanium compounds. This difference will be reflected in, i) an increased susceptibility to attack by nucleophiles and electrophiles, ii) easy isomerization and, iii) increased tendency to be nonplanar.

Prob 6)

Germaethene synthesis [J. Am. Chem. Soc. 109, 4411 (1987)]

$\text{Mes}_2\text{GeF}_2 + \text{R}_2\text{CHLi} \rightarrow -50^\circ \text{C ether} \rightarrow \text{Mes}_2\text{GeF} - \text{CHR}_2 + \text{LiF}$

$R -$ is a very bulky ligand

Reaction presumably driven by the very low solubility and high stability of LiF.

$\text{Mes}_2\text{GeF} - \text{CHR}_2 + \text{tBuLi} \rightarrow \text{Mes}_2\text{Ge}==\text{CR}_2 + \text{LiF} + \text{tBuH}$

Deprotonation driven by very powerful sterically hindered base. Substitution of F by tBu does not take place due to steric hinderance. Loss of LiF is driven by low solubility and high stability of LiF.

A Lewis base will attack the $\pi^*$ orbital of the product to form an adduct. The $\pi^*$ orbital is low lying in this molecule compared to that in an alkene. This is because of the poor p orbital overlap and weak bonding in the germanium compound.

Prob 7)

$\text{GeMe}_3\text{Cl} + \text{LiH} \rightarrow \text{GeMe}_3\text{H} + \text{LiCl}$

or $\text{GeMe}_3\text{Cl} + \text{LiAlH}_4 \rightarrow \text{GeMe}_3\text{H} + ....$

By analogy with hydrosilation,

$\text{GeMe}_3\text{H} + \text{CH}_2\text{CPh}_2 \rightarrow (\text{H}_2\text{PtCl}_6) \rightarrow \text{Me}_3\text{GeCH}_2\text{CHPh}_2$