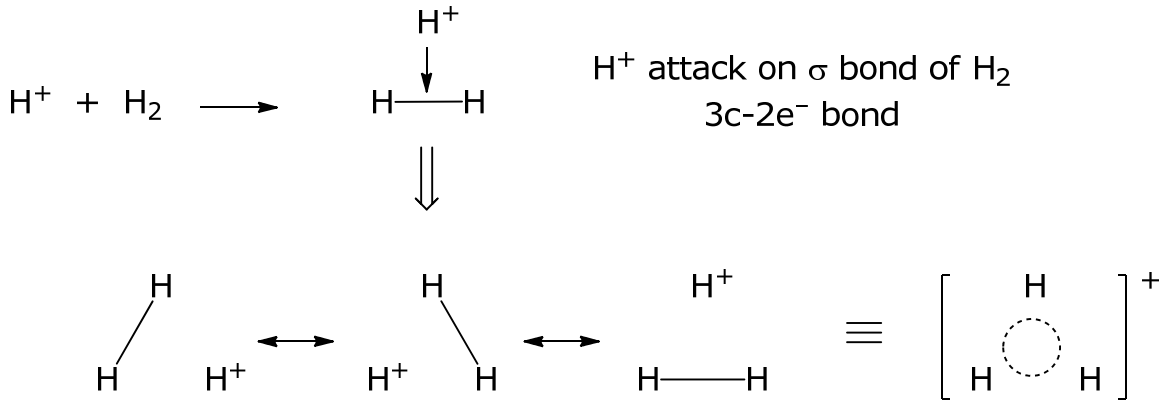
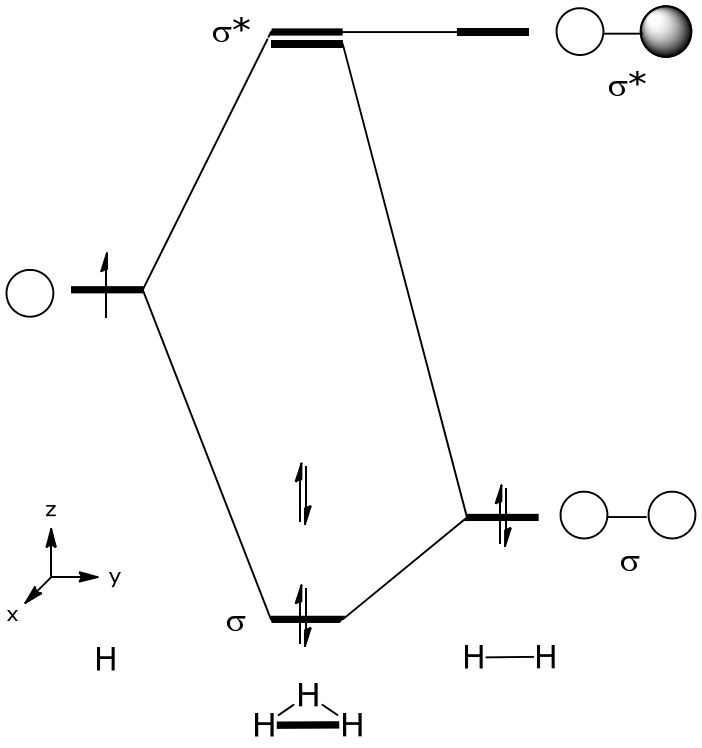
5.03, Inorganic Chemistry
Prof. Daniel G. Nocera
Lecture 6 Apr 11: Acid-Base Chemistry

Gas-Phase Acid-Base Reactions

The most straightforward acid-base reaction occurs by attack of H^+ on an atom or molecule (B) in the gas phase. Consider the attack of H^+ on H_2 to produce the simplest polyatomic molecule, H_3^+ (which has been detected by mass spectrometry in electrical discharges of H_2 gas).



H^+ attacks the HOMO of the base B for any protonation in the gas phase. For the example above, the bonding situation is described as follows:



The difference in the bond dissociation energies of H_2 and H_3^+ gives the energy for H^+ association to H_2,

$$H_3^+ \rightarrow 2H + H^+ \qquad \Delta H_1 = BDE(H_3^+) = 203 \text{ kcal mol}^{-1}$$

$$H_2 \rightarrow 2H \qquad \Delta H_2 = BDE(H_2) = 103 \text{ kcal mol}^{-1}$$

Thus the energy for protonation is

$$2H + H^+ \rightarrow H_3^+$$

$$H_2 \rightarrow 2H$$

$$H_2 + H^+ \rightarrow H_3^+ \qquad \Delta H_{assoc} = \Delta H_2 - \Delta H_1 = -100 \text{ kcal mol}^{-1}$$

and therefore the protonation of H_2 is comparable to its bond strength.

The **proton affinity (PA)** is the energy released upon attack of H^+ on a species B in the gas phase,

$$B + H^+ \rightarrow BH^+ \qquad PA = -\Delta H_{assoc}$$

by convention, a positive value is exothermic

Can divide the protonation reaction in to two hypothetical reactions

$$B + H^+ \rightarrow B^+ + H \qquad \Delta H_1 = IE(B) - IE(H)$$

$$B^+ + H \rightarrow BH^+ \qquad \Delta H_2 = -BDE(BH^+)$$

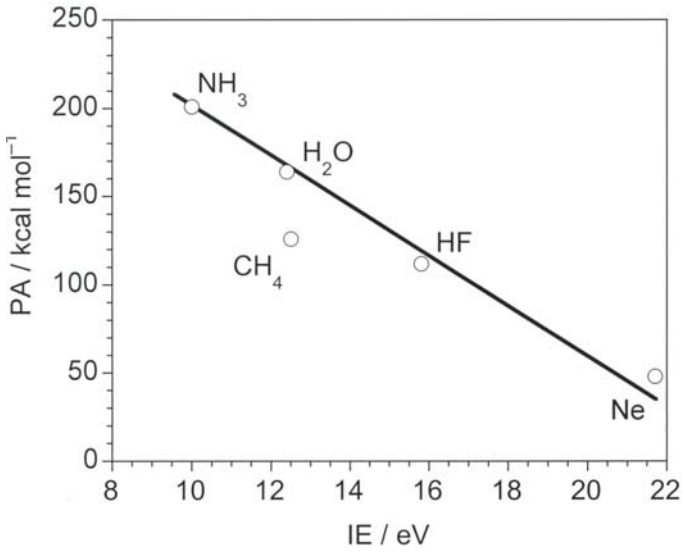
$$B + H^+ \rightarrow BH^+ \qquad \Delta H_{assoc} = IE(B) - IE(H) - BDE(BH^+)$$

$$PA = IE(H) - IE(B) + BDE(BH^+)$$

$$PA = 13.598 \text{ eV} - IE(B) + BDE(BH^+)$$

Protonation of B is therefore favored for small IE(B) … i.e., for small ionization energies of electrons in HOMO (or in other terms, electrons in higher energy HOMO are more easily attacked by the proton) and large bond dissociation energies.

Since changes in the bond ionization energies are generally much greater across a period than changes in BDEs, PA typically tracks IE(B). This is shown below for the simple B compounds below:



Note, even though CH_4 has no lone pair for attack by H^+, its PA is greater than that of F^-.

The PA increases with the activity of water:

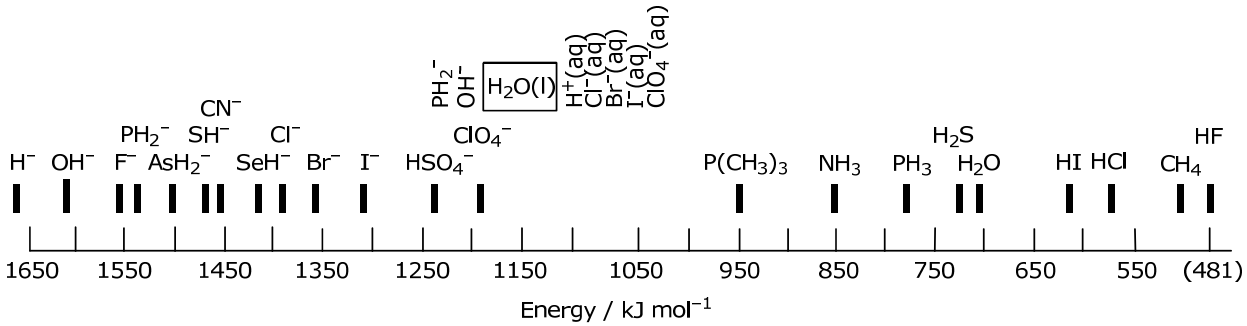
$H^+(g) + H_2O(g) \rightarrow H_3O^+(g)$	PA = 170 kcal mol^{-1}	Energy release from protonation increases with the formation of hydrogen bonds
$H^+(g) + 2H_2O(g) \rightarrow H_5O_2^+(g)$	PA = 218 kcal mol^{-1}	
$H^+(g) + 3H_2O(g) \rightarrow H_7O_3^+(g)$	PA = 272 kcal mol^{-1}	
$H^+(g) + 4H_2O(g) \rightarrow H_9O_4^+(g)$	PA = 328 kcal mol^{-1}	
$H^+(g) + H_2O(\ell) \rightarrow H^+(\ell)$	PA = 270 kcal mol^{-1}	

For protonation of OH^-:

$H^+(g) + OH^-(g) \rightarrow H_2O(g)$	PA = 390 kcal mol^{-1}	PA decreases because must break hydrogen bonds
$H^+(g) + H_3O_2^-(g) \rightarrow 2H_2O(g)$	PA = 366 kcal mol^{-1}	
$H^+(g) + OH^-(\ell) \rightarrow H_2O(\ell)$	PA = 284 kcal mol^{-1}	

There is a *solvent leveling effect* on the PAs. In H_2O, the effective PA range is between 270-284 kcal mol^{-1}. Thus acids with PAs greater than 270 kcal mol^{-1} will not transfer H^+. The corollary is that no acid stronger than H_3O^+ can exist in solution since the PAs are such that H^+ transfer to H_2O is exothermic). Similarly no base stronger than OH^- can exist in solution since the PAs are such that the removal of a H^+ from water is exothermic. Thus there is a solvent leveling effect on

the PAs. The summary below shows the acid-base ranges in the gas phase and water.



Note that in gas phase, Cl^- has a higher PA than H_2O, so

$$HCl(g) + H_2O(g) \rightarrow NR$$

But in solution, Cl^- ion is stabilized by solvation and the PA of the ion is reduced considerably, so much so that the proton transfer becomes favorable,

$$HCl(aq) + H_2O(aq) \rightarrow Cl^-(aq) + H_3O^+(aq)$$

Acid Base Classifications

Common classifications of acids and bases are:

Arrhenius acids and bases. Acid produces hydronium ion, H_3O^+ and a base produces hydroxide ion, OH^- upon dissolution in H_2O. Arrhenius acids and bases are formed from a combination reaction of oxides and water. Metal oxides combine with water to produce bases,

$$\text{e.g., } MgO + H_2O \rightarrow Mg(OH)_2$$

Non-metal oxides react with water to form acids,

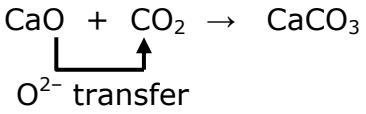
$$\text{e.g., } P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

Semiconducting metal (metalloid) oxides are amphoteric, i.e., depending on reaction conditions, oxides are acidic or basic,

$$Al_2O_3 + 6H_3O^+ \rightarrow 2Al^{3+} + 9H_2O$$

$$Al_2O_3 + 3H_2O + 2NaOH \rightarrow 2Na[Al(OH)_4]$$

Acids and bases react with each other to form salts; this is also true for the combination reaction of acidic and basic oxides,



Lux-Flood definition of acids and bases, base is O^{2-} donor, acid is O^{2-} acceptor

Brønsted-Lowry acids and bases. An acid loses H^+, a base gains H^+.

$$HA + B^- \leftrightarrows A^- + HB$$

$$K = \frac{[A^-]\,[HB]}{[HA]\,[B^-]}$$

⇩ defines a competition for H^+ between A^- and B^-

$$HA + H_2O \leftrightarrows A^- + H_3O^+ \qquad K = \frac{[A^-]\,[H_3O^+]}{[HA]}$$

$$HA + H_2O \leftrightarrows A^- + H_3O^+ \qquad K = \frac{[B^-]\,[H_3O^+]}{[HB]}$$

This definition of acids and bases can be extended by setting up a reference scaling to something other than water. For instance, the following equilibrium may be defined,

$$BH^+ + CH_3Hg^+ \leftrightarrows CH_3HgB^+ + H^+$$

(HA) $BH^+ \leftrightarrows B + H^+$ (HB) $CH_3HgB^+ \leftrightarrows CH_3Hg^+ + B$

pK Scale Referenced to CH_3HgB			
B	**pK(BH^+)**	**pK(CH_3HgB)**	**ΔpK**
F^-	2.8	1.50	1.35
Cl^-	−7.0	5.25	−12.3
Br^-	−9.0	6.62	−15.6
I^-	−9.5	8.60	−18.1
OH^-	15.7	9.37	6.3
S^{2-}	14.2	21.2	−7.0
NH_3	9.42	7.60	1.82
CN^-	9.14	14.1	−5.0

A relative scaling for the interaction of various bases B with H^+ vs CH_3Hg^+ (i.e., competition between CH_3Hg^+ and H^+ for B). Ordering for increasing strength of interaction with CH_3Hg^+:

$$OH^- < NH_3 < F^- < CN^- < S^{2-} < Cl^- < Br^- < I^-$$

"hard acid" nonpolarizable — "soft acid" polarizable

Hard-Soft Acid Base (HSAB) rule: hard acids prefer to bind to hard bases and soft acids prefer to bind soft bases. By studying various equilibria reactions, qualitative classification of hard and soft acid/bases may be established. This classification is shown in the tables below for ligands and metal ions.

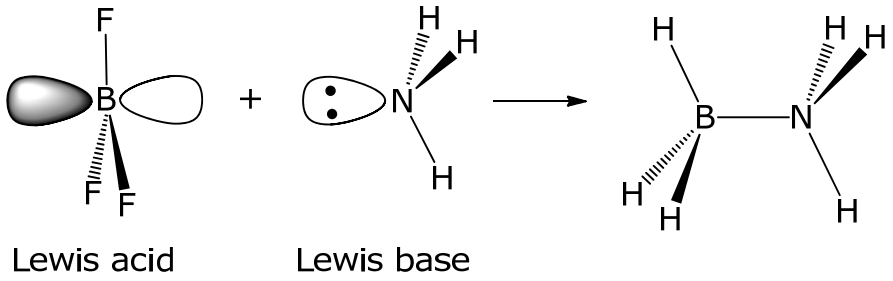
Hard bases	*Borderline bases*	*Soft bases*
		H^-
F^-, Cl^-	Br^-	I^-
H_2O, OH^-, O^{2-}		H_2S, HS^-, S^{2-}
ROH, RO^-, R_2O, CH_3COO^-		RSH, RS^-, R_2S
NO_3^-, ClO_4^-	NO_2^-, N_3^-	SCN^-, CN^-, RNC, CO
CO_3^{2-}, SO_4^{2-}, PO_4^{3-}	SO_3^{2-}	$S_2O_3^{2-}$
NH_3, RNH_2, N_2H_4	$C_6H_5NH_2$, C_5H_5N, N_2	R_3P, $(RO)_3P$, R_3As
		C_2H_4, C_6H_6

SOURCE: Adapted from R. G. Pearson, *J. Chem. Educ.*, **1968**, *45*, 581.

Hard acids	*Borderline acids*	*Soft acids*
H^+, Li^+, Na^+, K^+		
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^2		
BF_3, BCl_3, $B(OR)_3$	$B(CH_3)_3$	BH_3, Tl^+, $Tl(CH_3)_3$
Al^{3+}, $Al(CH_3)_3$, $AlCl_3$, AlH_3		
Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{3+}	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} Rh^{3+}, Ir^{3+}, Ru^{3+}, Os^{2+}	Cu^+, Ag^+, Au^+, Cd^{2+}, Hg_2^{2+}, Hg^{2+}, CH_3Hg^+, $[Co(CN)_5^{3-}]$, Pd^{2+}, Pt^{2+}, Pt^{4+}
Ions with oxidation states of 4 or higher		Br_2, I_2 Metals with zero oxidation state
HX (hydrogen-bonding molecules)		π acceptors: trinitrobenzene, quinones, tetracyanoethylene, etc.

SOURCE: Adapted from R. G. Pearson, *J. Chem. Educ.*, **1968**, *45*, 581.

Lewis acids and bases. A Lewis base is an electron pair donor; a Lewis acid is an electron pair acceptor. In a Lewis acid-base reaction, the HOMO of the base interacts with the LUMO of the acid to form a bond,



Lewis acid Lewis base

In the above reaction, the N lone pair of NH_3 (the HOMO of NH_3) attacks the empty p_z orbital of B (the LUMO of BF_3).

Superacids

Concepts of H^+ concentration and pH are most meaningful only for dilute aqueous solutions of acids. At high concentration of acid or in other media, **Hammett acidity** function, $\mathbf{H_0}$, is a useful concept.

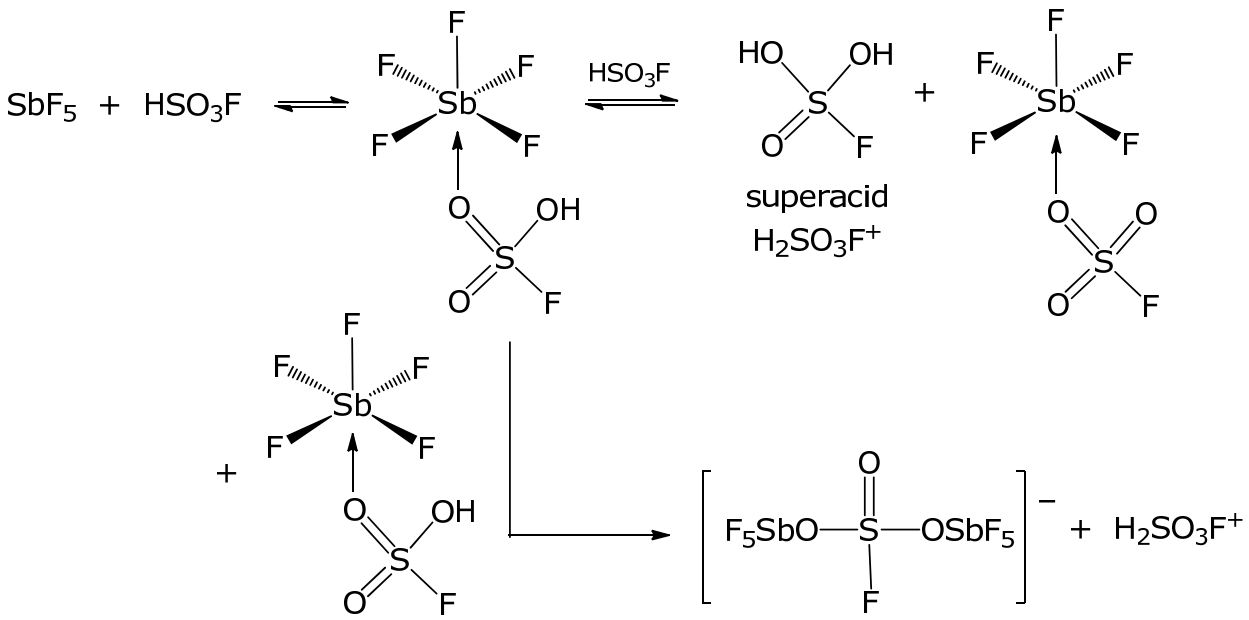
$$B + H^+ \leftrightarrows BH^+$$

$$H_0 = pK_{BH^+} = -\log \frac{[BH^+]}{[B]}$$

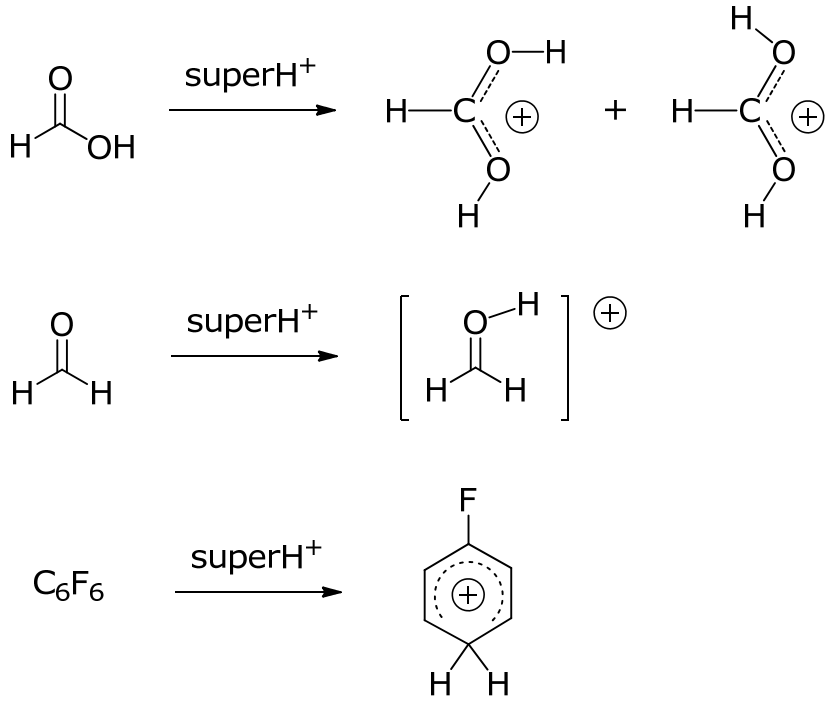
In dilute solutions, H_0 is synonymous with pH. For a number of acids in aqueous solution up to concentrations of 8 M, H_0 is similar, suggesting acidity to be independent of anion.

	H_0	
HSO_3F + SbF_5 (14.1 mol %)	26.5	
HF + SbF_5 (0.6 mol%)	21.1	← Acidity of HF increases substantially with the addition of Lewis acids
HSO_3F	15	
$H_2S_2O_7$	15	
CF_3SO_3H	14.1	
H_2SO_4	12.1	
HF	11	← Acidity decreases with addition of F^- ($HF + F^- \leftrightarrows HF_2^-$)
HF + NaF (1 M)	8.4	←
H_3PO_4	5.0	
H_2SO_4	4.9	
HCO_2H	2.2	

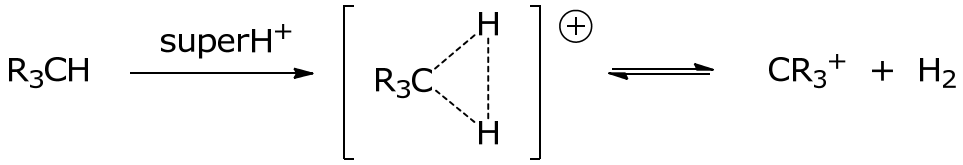
Acid media with $-H_0$ values >6 are often referred to **superacids**. One of the more acidic solutions, SbF_5—FSO_3H is very complicated,



Virtually all organic compounds react with superacids,



George Olah received the NP for his studies of the carbonium ion, produced by hydride abstraction with superH$^+$,



Metal carbonyls react with superH$^+$,

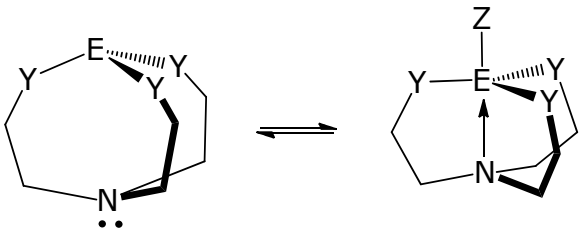
$Fe(CO)_5$ + superH$^+$ ⇆ $[HFe(CO)_5]^+$

Cp_2Fe + superH$^+$ ⇆ $[CpFe_5H]^+$

$C_8H_8(CO)_3$ + superH$^+$ ⇆ $[C_8H_9Fe(CO)_3]^+$

Superbases

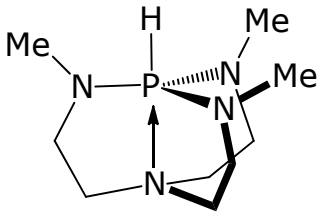
Will focus on atranes,



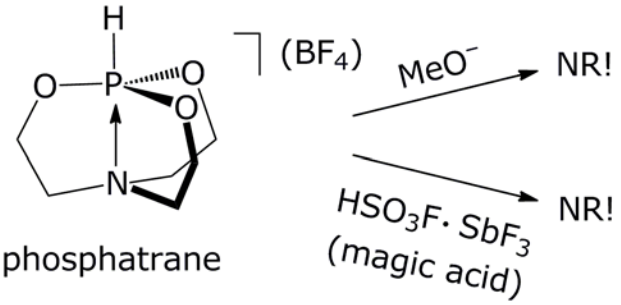
pro-atrane atrane

for Y = O, NR
- Z = O, NR; E = group 5 or 15
- Z = R, SR, NR, OR; E = group 4 or 14
- Z = N, group 16
- Z = nothing, E group 13
- Z = lone pair, group 15

Very strong bases,

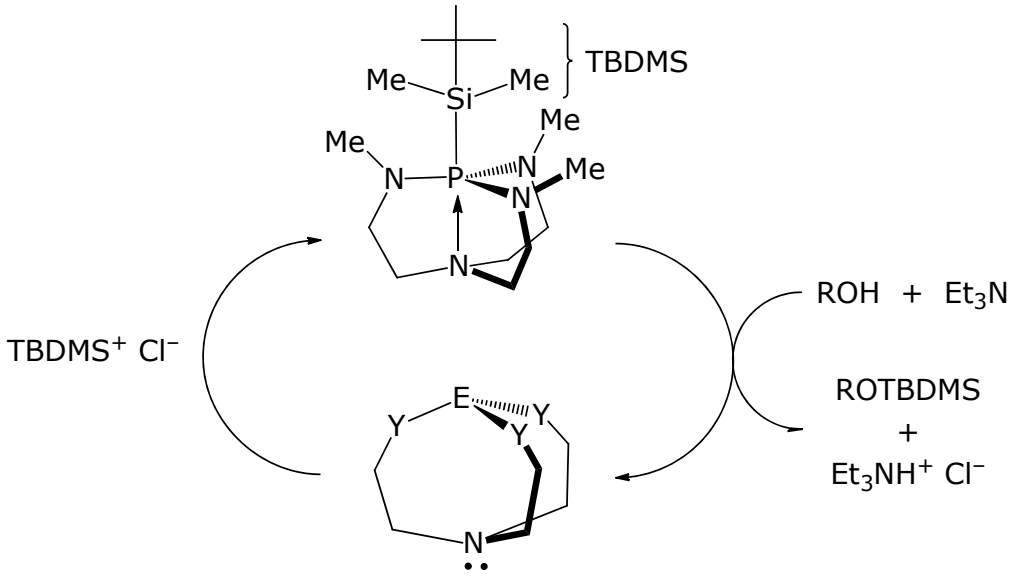


pK_a = 26.8



phosphatrane

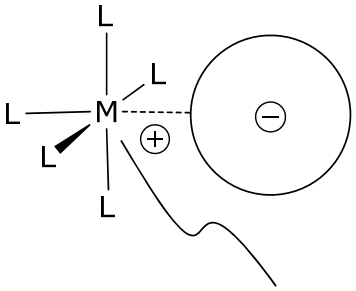
Superbases can catalyze unusual transformations. Here is one that provides a convenient way to protect alcohols,



Weakly Coordinating Anions

Coordination chemists can enhance reactivity (see Ziegler Natta polymerization module) using large and weakly coordinating anions.

Classical noncoordinating anions are ClO_4^-, $SO_3CF_3^-$, SO_3F^-, BF_4^-, PF_6^-, AsF_6^-, SbF_6^-. By making the anion bulkier, even more weakly coordinating anions may be realized,



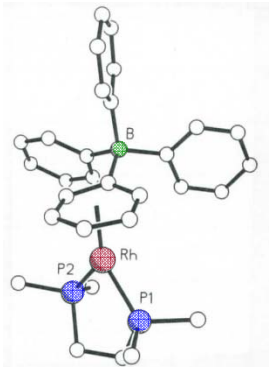
to minimize interaction between cation and anion, decrease Coulomb potential by:

1) large bulky anion
2) low charge (usually −1)
3) delocalize charge over entire anion
4) place atoms with high EN at the periphery

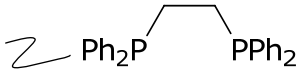
"vacant" coordination site usually coordinated by solvent; when donor number of solvent decreases sufficiently, anion will occupy coordination site

Some examples of weakly coordinating anions follow.

Tetraarylborates



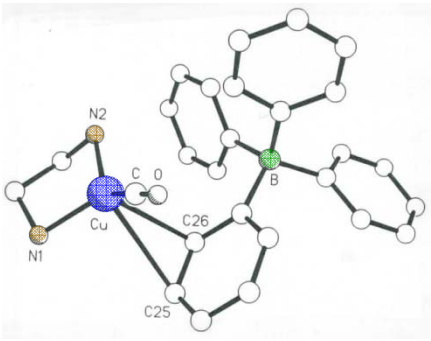
Rh(BPh$_4$)(diphos)



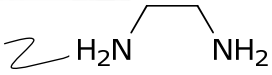
the η^6 coordination of BPh_4^-, allows the EAN of 18 to be satisfied

phenyl groups omitted from structure for clarity, only ipso carbon shown

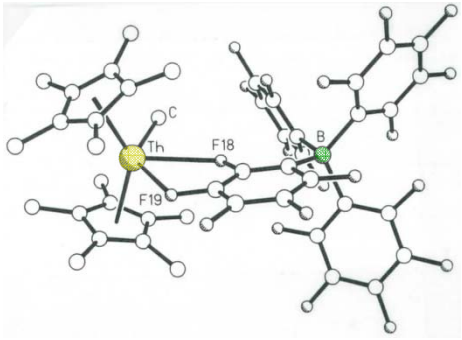
Coordination of BPh_4^- is often dictated by the electron count. Here BPh_4^- assumes an η^2 coordination to satisfy 18 EAN



Cu(BPh$_4$)(CO)(en)



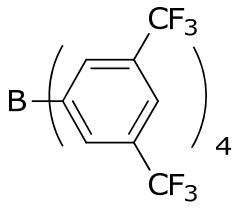
Can reduce coordinating ability of anion further by attenuating the ligating ability of the phenyl rings. One strategy is to make them poorer donors, by fluorination of the phenyl rings. For $B(C_6F_5)^-$, η^2 coordination is unusual.



Cp_2*Th(Me)(B(C_6F_5)$_4$)

the anion interacts with anion through two of the peripheral fluorines

An even weaker coordinating anion is $BAr^F_4{}^-$,



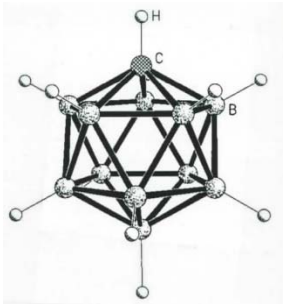
May assess coordination strength in many different ways. Mann showed that the following disproportionation reaction is promoted by X^-

$$2\ Rh_2(TM4)_4{}^{3+} + 2X^- \leftrightarrows Rh_2(TM4)_4{}^{2+} + Rh_2(TM4)_4X_2{}^{2+}$$

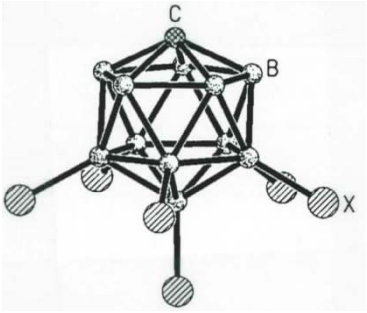
TM4 = 2,5-diisocyano-2,5-dimethylcyclohexane

X^-	$K_{disprop}$
Cl^-	$> 10^6$
$ClO_4{}^-$	18
$BF_4{}^-$	4
$PF_6{}^-$	0.09
$SbF_6{}^-$	0.008
$BArF_4{}^-$	$< 10^{-10}$

Carboranes

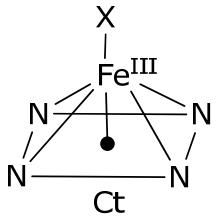


$CB_{12}H_{12}{}^-$



$CB_{11}H_6X_6{}^-$ (X = Cl, Br, I)

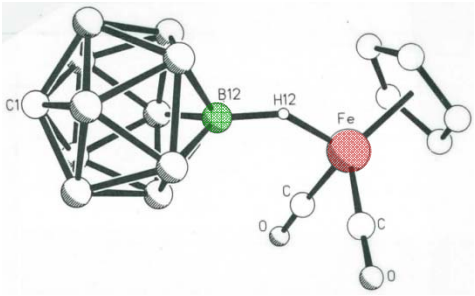
Consider the structural and spectroscopic properties of $[Fe^{III}TPP]^+$ (TPP = tetraphenylporphyrin)



Ct defines the center of the plane defined by the 4 nitrogen atoms of the porphyrin macrocycle

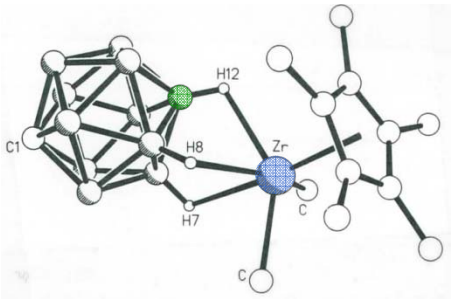
X^-	Fe—N / Å	Ct to N / Å	Fe to Ct /Å
Cl^-	2.049	2.013	0.38
ClO_4^-	2.001	1.981	0.30
SbF_6^-	1.978	1.974	0.15
$CB_{11}H_{12}^-$	1.961	1.955	0.10

All trends in above table point to a smaller metal ion radius as one moves down the table. Hence the carborane is the least interacting with the Fe^{III} center of the porphyrin.



$CpFe(CB_{11}H_{12})(CO)_2$

The B12-H12 bond is the most hydridic and it is the one that typically interacts with the metal (EAN = 18)



$Cp^*Zr(Me)_2$ $(CB_{11}H_{12})$

For metal cationic complexes with low electron counts (i.e., early TMs), hydride neighbors of B12-H12 also interact

EAN = 18 is satisfied with 3 Zr···H contacts ($6e^-$s to the count)

The coordinating ability of the carborane can be further hindered by replacing peripheral H^- with larger and more diffuse atoms (e.g., Br for H). Consider the following,

Y	ν_{CO} / cm^{-1}
I^-	2016
ClO_4^-	2049
$CB_{11}H_{12}^-$	2049
SbF_6^-	2050
$CB_9H_5Br_5^-$	2096
$CB_{11}Me_{12}^-$	2098
$CB_{11}H_6Br_6^-$	2108

for $[CpFe(CO)_2^+]Y^-$

The more positively charged the metal, the less π-backbonding and hence the higher the CO stretching frequency