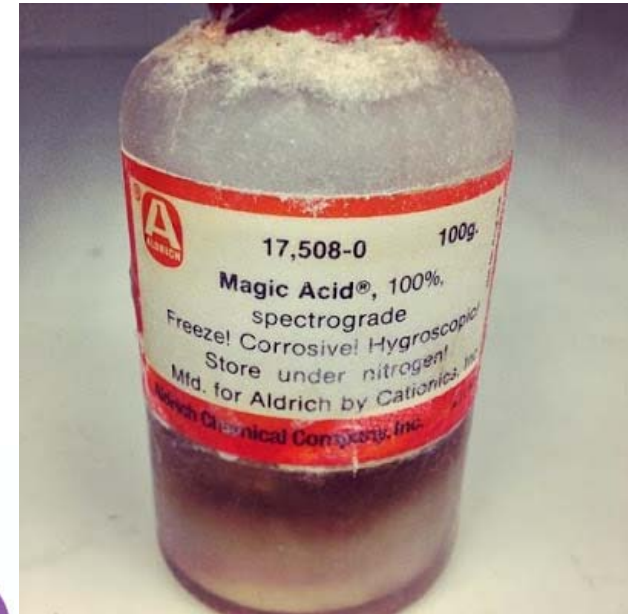
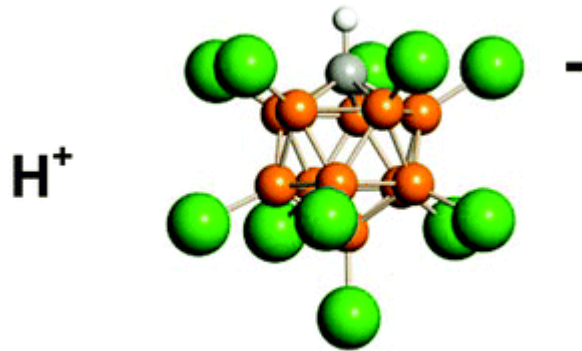
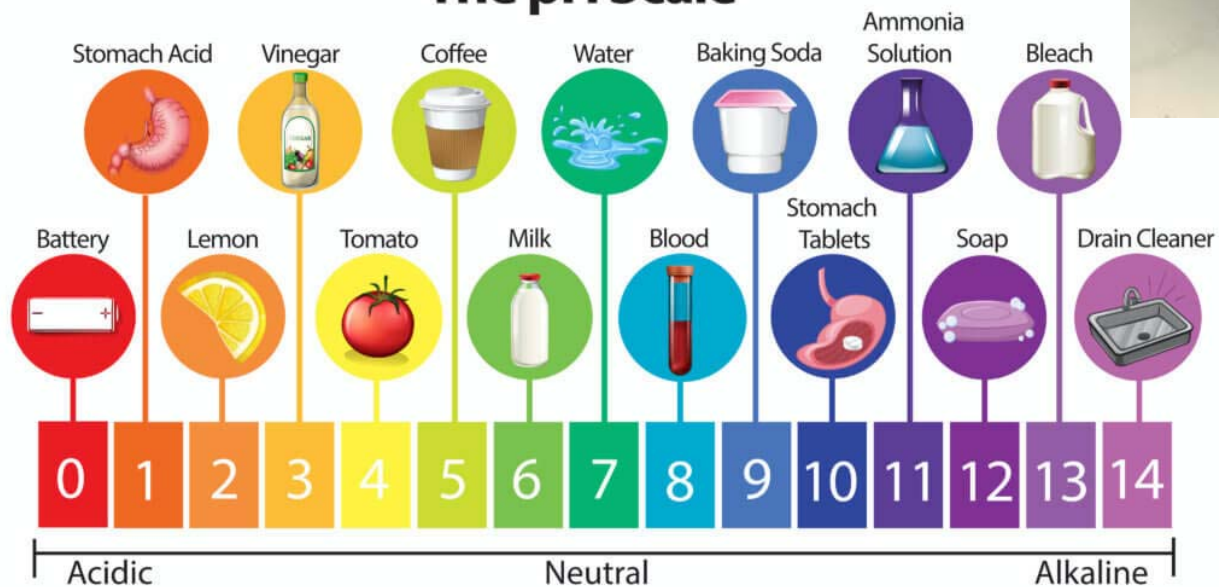


Acid-Base Chemistry



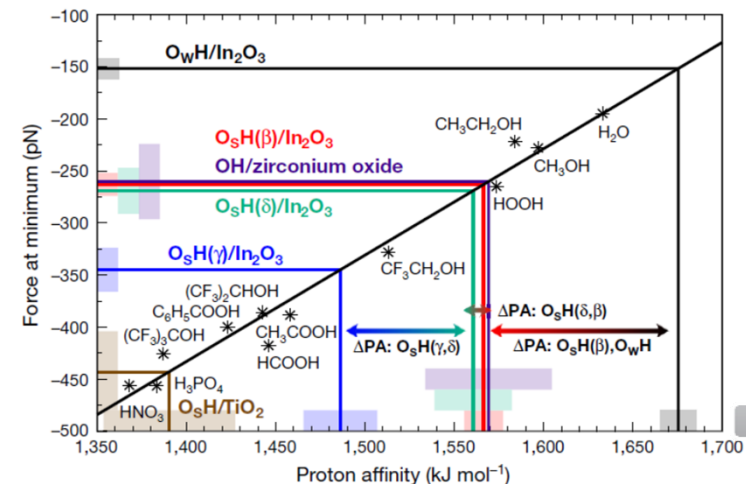
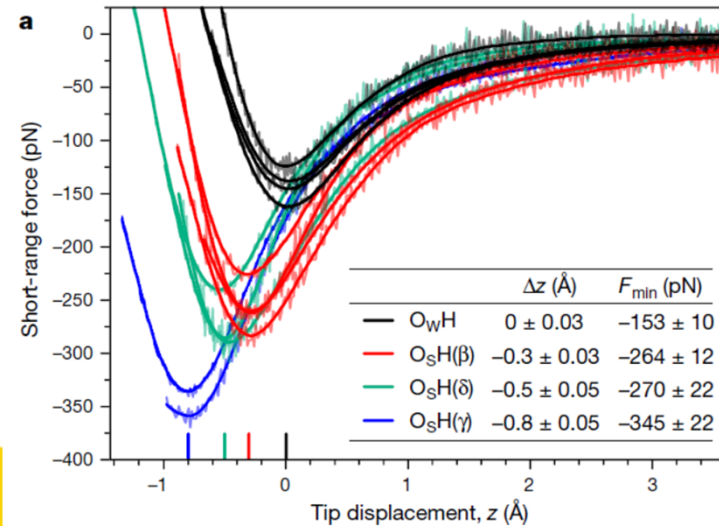
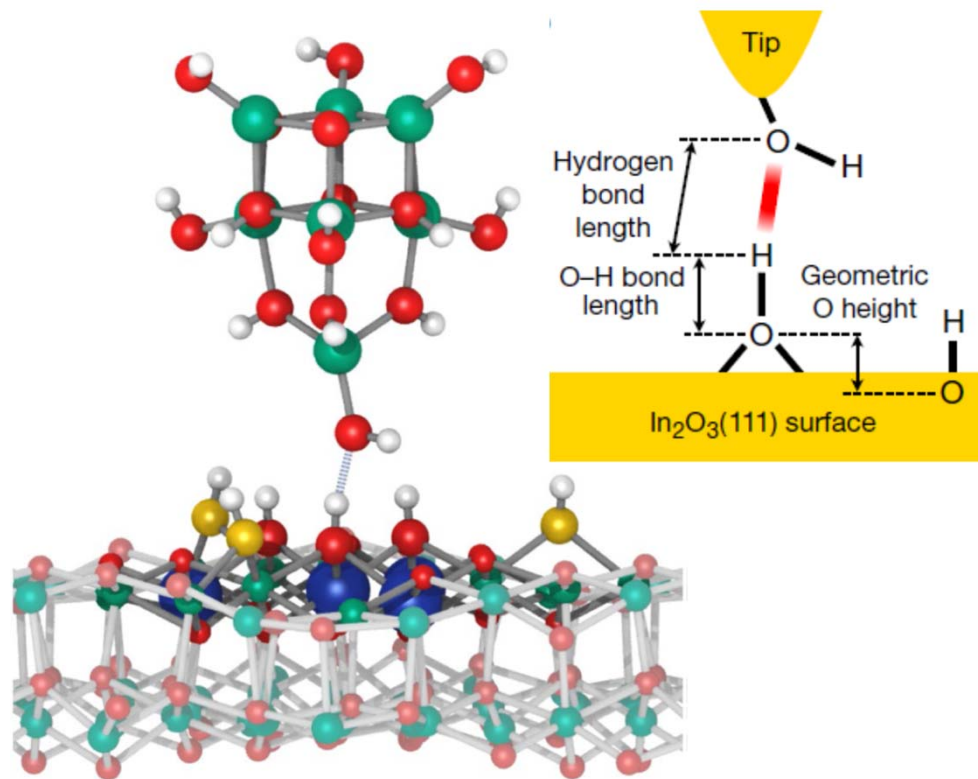
The pH Scale



Acidity of Surface OH by AFM

High-resolution non-contact atomic force microscopy (nc-AFM)

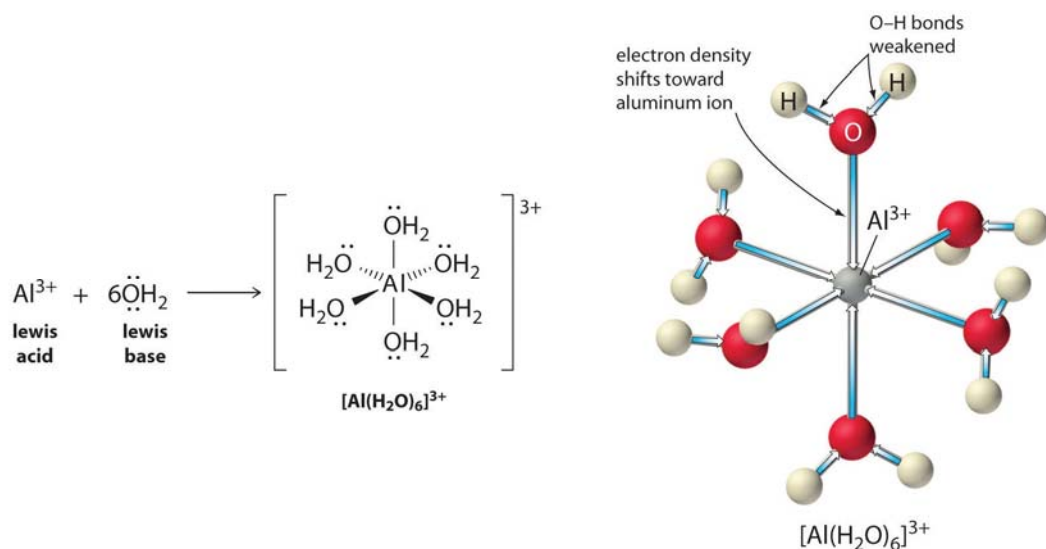
Hydroxyl (OH)-functionalized AFM tip



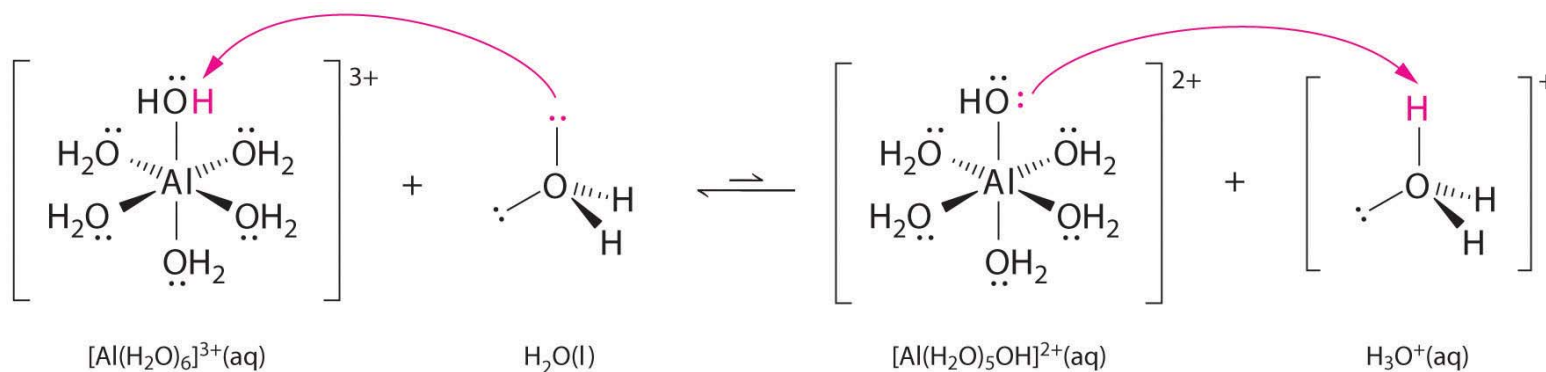
Nature 2021, 592, 722, /10.1038/s41586-021-03432-3



Acidity of Metal Ions in Water



$$pK_a = -\log \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$



Acidity of Metal Ions in Water

The **smaller** the metal ion, the **more acidic** it is:

$$pK_a = -\log \frac{[H_3O^+][A^-]}{[HA]}$$

Metal ion	Ionic radius (Å)	pK _a
Be ²⁺	0.27	5.6
Mg ²⁺	0.74	11.4
Ca ²⁺	1.00	12.7
Sr ²⁺	1.18	13.2
Ba ²⁺	1.36	13.4

The **higher the charge** on metal ions of about the same size, the **more acidic** will the metal ion be:

Metal ion:	Ionic radius (Å)	pK _a
Na ⁺	1.02	14.1
Ca ²⁺	1.00	12.7
La ³⁺	1.03	8.5
Th ⁴⁺	0.94	3.2



Acidity of Metal Ions in Water

Electronegativity

The closer a metal is to **Au** in the periodic table, the higher its electronegativity

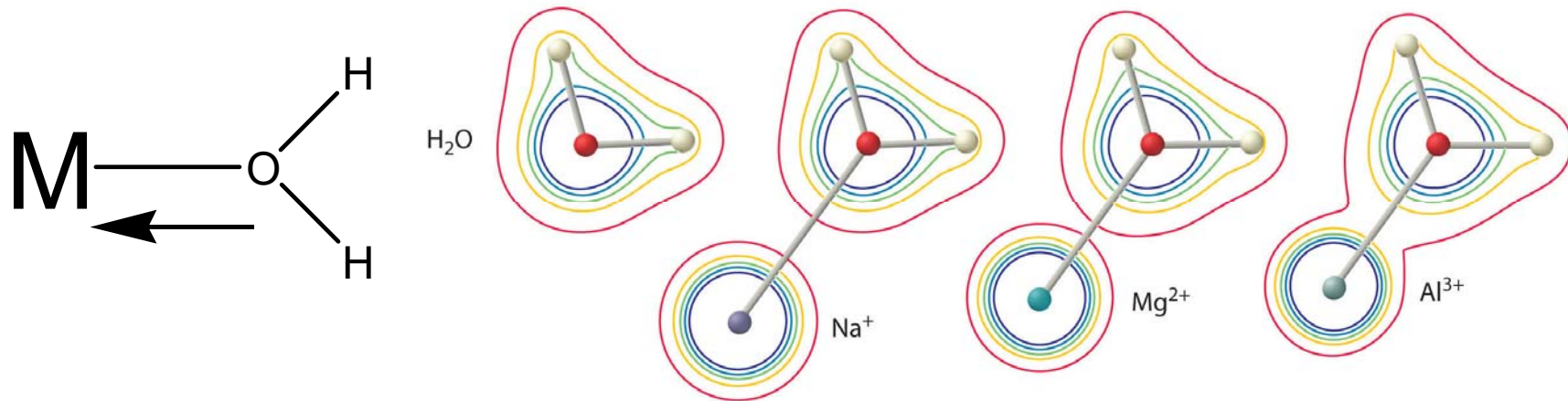
Electronegativity tends to override the charge/size factors in controlling the acidity of metal aqua ions, and metal ions **of higher electronegativity** will be much **more acidic** than metal ions of similar size and charge of low electronegativity:

Metal ion	Ionic radius (Å)	pK _a
Na ⁺	1.02	14.1
Ag ⁺	1.15	12.0
Sr ²⁺	1.19	13.2
Pb ²⁺	1.18	8.0
Ca ²⁺	1.00	12.7
Hg ²⁺	1.02	3.4
Y ³⁺	0.90	7.7
Tl ³⁺	0.89	0.6

$$pK_a = -\log \frac{[H_3O^+][A^-]}{[HA]}$$



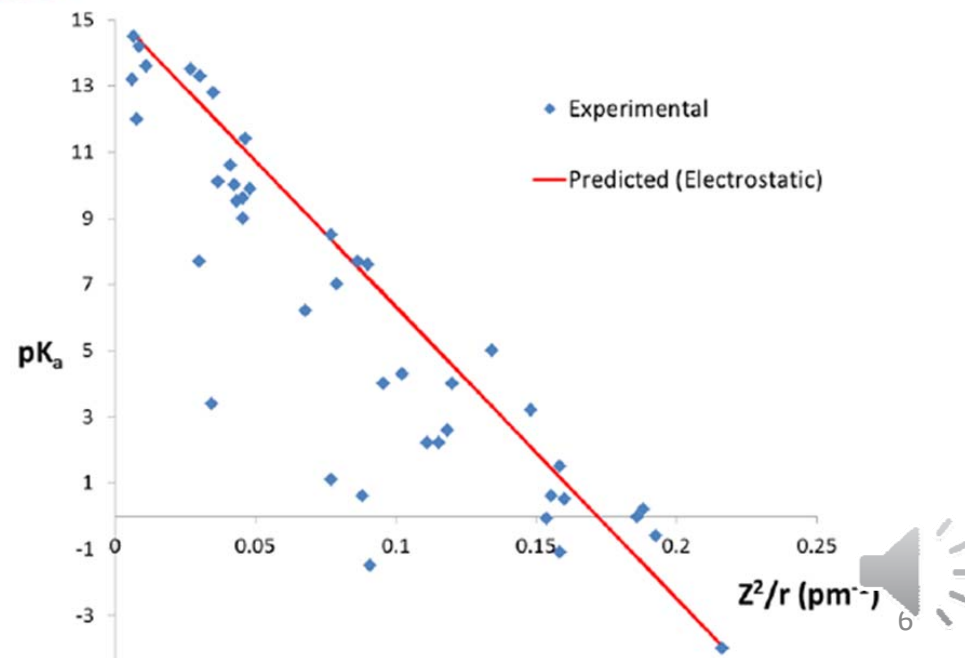
Acidity of Metal Ions in Water



Wulfsberg – an empirical equation for predicting the pK_a of metal ions in water based on **ion size and charge**:

$$pK_a = 15.14 - 88.16 \frac{Z^2}{r}$$

Z - the charge on the metal ion
r - ionic radius in pm



Acidity of Metal Ions in Water

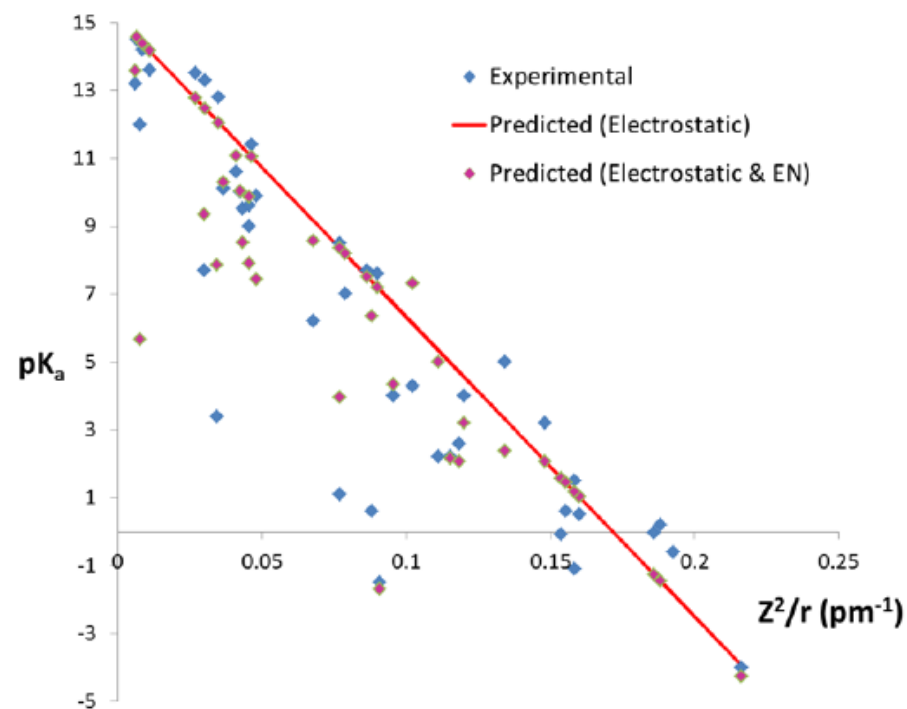
Improved empirical relationship that has been proposed to account for the effect of **electronegativity**:

$$pK_a = 15.14 - 88.16 \left(\frac{Z^2}{r} + 0.096(\chi - 1.50) \right)$$

r - ionic radius in pm

χ - Pauling electronegativity

Metal ion	pKa
Be ²⁺	5.6
Cu ²⁺	7.5
Fe ²⁺	9.5
Zn ²⁺	9.6
Mg ²⁺	11.4
Ca ²⁺	12.7
Sr ²⁺	13.2
Ba ²⁺	13.4
Al ³⁺	5



Acidity of Metal Ions in Water

Cation **hardness or softness** according to Pearson's Hard-Soft Acid Base Principle (HSAB)

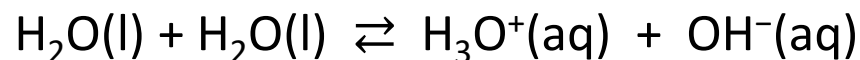
Soft cations are **more acidic** than hard cations of the same charge and radius

Cation	Classification	Radius (pm)	pK _{a1}
K ⁺	hard	1.33	14
Ag ⁺	soft	1.26	10
Mg ²⁺	hard	0.65	12.2
Cu ²⁺	soft	0.69	7.3
Ca ²⁺	hard	0.99	12.6
Cd ²⁺	soft	0.97	9.0
Sr ²⁺	hard	1.13	13.1
Hg ²⁺	soft	1.10	3.6



Solvent Theory of Acids and Bases

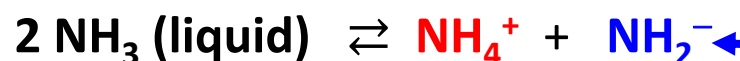
Autoionisation



$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1 \cdot 10^{-14} \text{ (at } 25 \text{ }^\circ\text{C)}$$

Lyonium ion
Solvent cation

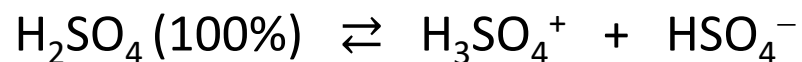
1905
Franklin



Lyate ion
Solvent anion

Autoionisation constant (as K_w in water)

$$K = [\text{NH}_4^+] [\text{NH}_2^-] = 2 \cdot 10^{-33} \text{ (at } -50 \text{ }^\circ\text{C)}$$



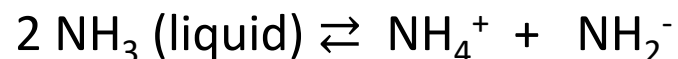
$$K = [\text{H}_3\text{SO}_4^+] [\text{HSO}_4^-] = 1 \cdot 10^{-5} \text{ (at } 25 \text{ }^\circ\text{C)}$$



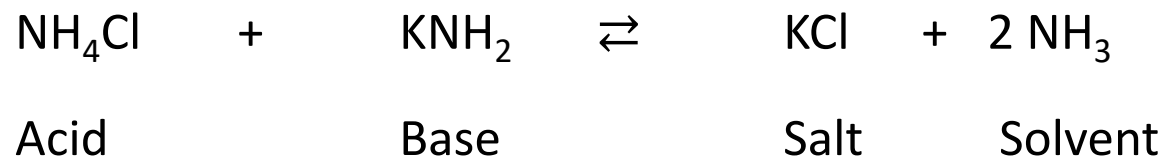
Solvent Theory of Acids and Bases

Acids are compounds that increase the concentration of the **lyonium** - solvent cation

Bases are compounds that increase the concentration of the **lyate** solvent anion



Neutralization titration in liquid NH_3



In liquid NH_3 (liquid), HAc is a stronger acid than in water
In H_2SO_4 (100%), HAc is a weaker acid than in water

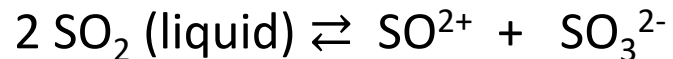


Solvent Theory of Acids and Bases

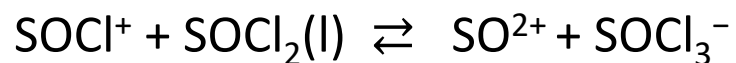
Aprotic solvent acids and bases

Exchange of solvent fragments

Autoionisation - Exchange of O²⁻



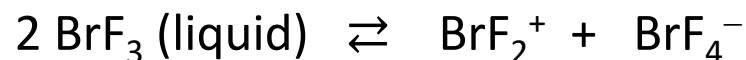
Acid = SOCl₂ Base = MgSO₃



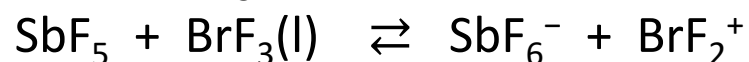
Solvent Theory of Acids and Bases

Aprotic solvent acids and bases

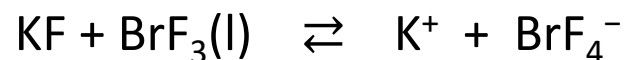
Autoionisation - Exchange of F⁻



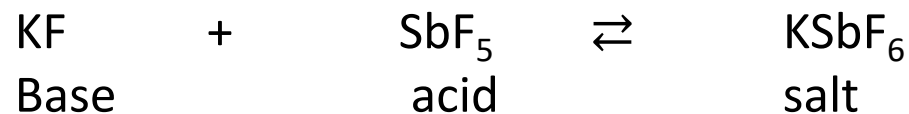
Acid = SbF₅



Base = KF



Acid-base neutralisation reaction



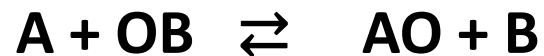
Lux-Flood Acid-Base Theory

Geochemistry and electro/chemistry of molten salts

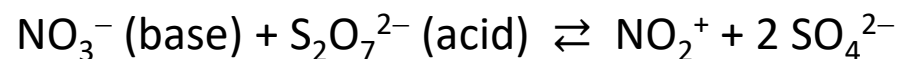
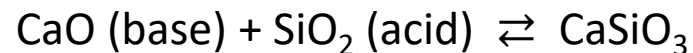
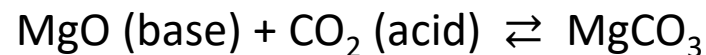
Definition

An acid = an **oxide** ion (O^{2-}) **acceptor**

A base = an **oxide** ion **donor**



For example:



Usanovich Acid-Base Theory

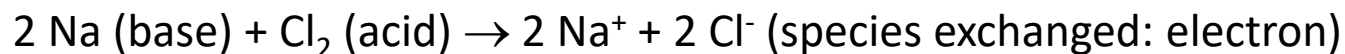
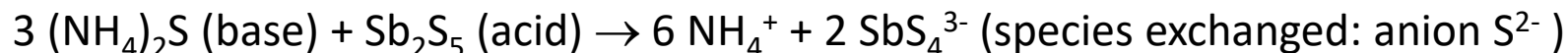
1938 - a general theory that does not restrict acidity to hydrogen-containing compounds, more general than the Lewis theory

An acid = anything that *accepts negative species, anions or electrons or donates positive ones, cations*

A base = the reverse - *accepts cations, furnishes anions or electrons*

Could be applied to the concept of redox reactions (oxidation-reduction) as a special case of acid-base reactions

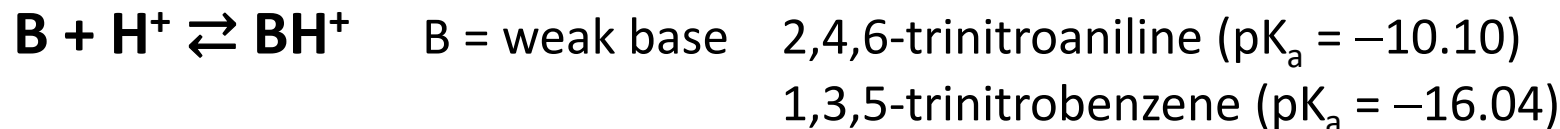
Examples of Usanovich acid-base reactions :



The Usanovich concept encompasses all of the others - it is too general to be useful.



Hammet Function



UV/VIS spectrophotometric or NMR measurements

Acidity constant of BH^+

$$K_{BH} = \frac{[B][H^+]}{[BH^+]}$$



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

$H_0 = \text{pH}$ but not concentration of H^+

e.g., HSO_3F - the reactivity (protonating power) of the solvated hydrogen ions is 10^{15} times greater than the reactivity of the hydrated hydrogen ions in an aqueous solution of $\text{pH} = 0$

Acid	H_0	
HF	-11	
H_2SO_4 (100%)	-12.1	
$\text{CF}_3\text{SO}_3\text{H}$	-14.1	
Oleum	-15	
HSO_3F	-15.1	
$\text{H}(\text{CHB}_{11}\text{F}_{11})$	-18	
$\text{HSO}_3\text{F} + \text{SbF}_5$	-21	Mixed Brønsted + Lewis acids
$2 \text{ HF} + \text{SbF}_5$	-31	



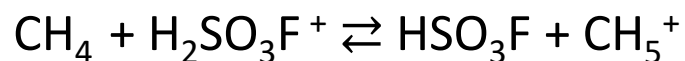
Superacids

Superacid = an acid with an acidity stronger than H_2SO_4 (100%)
Extremely poor proton acceptor

Magic acid



Protonation of methane



Stable carbocations, NMR study, refining oil and gas, catalysis



George A. Olah
(1927 – 2017)

Nobel Prize in Chemistry 1994

Carborane Superacids

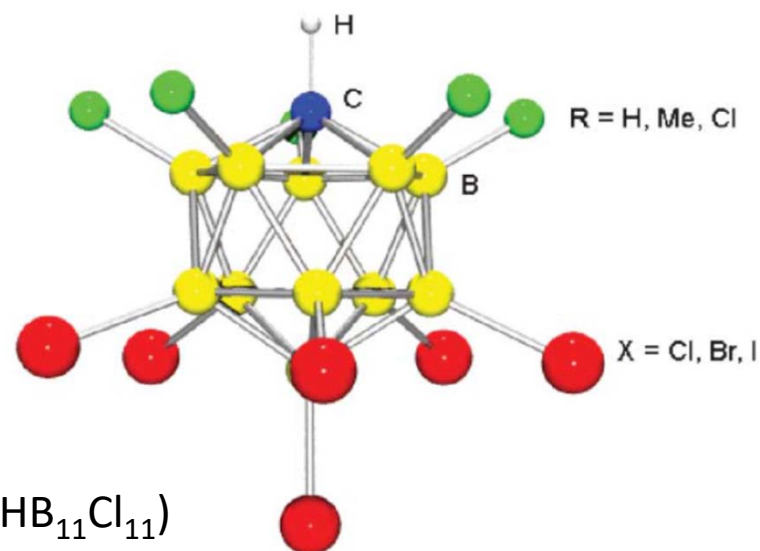
The **carborane** superacids $\text{H}(\text{CHB}_{11}\text{X}_{11})$ - high acidity, icosahedral anion

The acid anion is very stable and substituted with electronegative substituents
Separate protic acidity from anion nucleophilicity and oxidative capacity

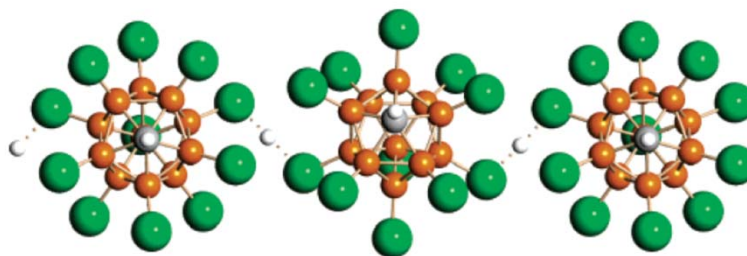


Christopher A. Reed
Angew. Chem. Int Ed, **2004**,
43, 5352 and **2014**, 53, 1131

Can be stored in a bottle
Fluoroantimonic acid is
corrosive to glass



Solid state structure of $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$
Intermolecular Cl–H–Cl bridges

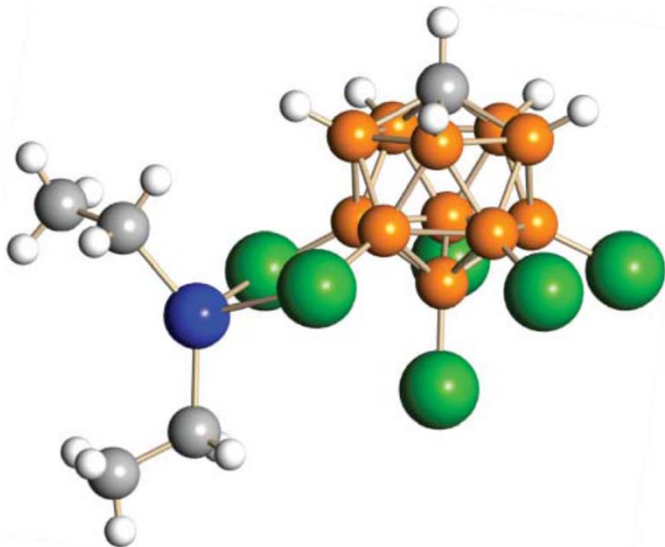


Carborane Superacids

The carborane superacid $\text{H}(\text{CHB}_{11}\text{X}_{11})$

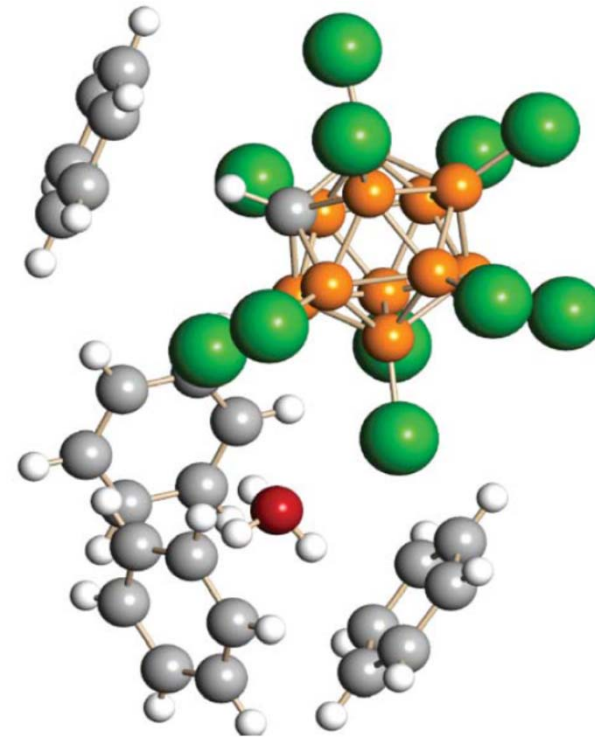
- **High acidity ($\text{H}_0 \sim -18$)**
- **High anion stability**
- **Low nucleophilicity**
- **Non-oxidative**
- **Good crystallization properties**

Aluminium $\text{Et}_2\text{Al}(\text{CHB}_{11}\text{H}_5\text{Cl}_6)$

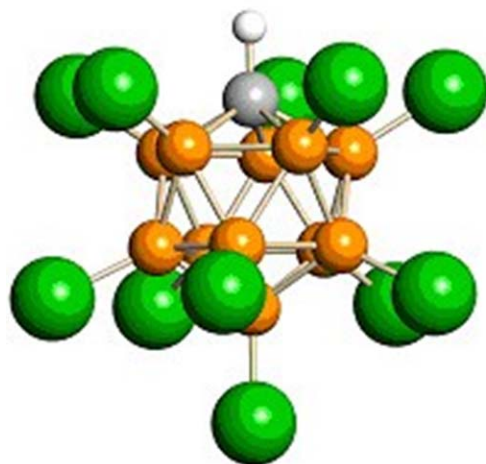
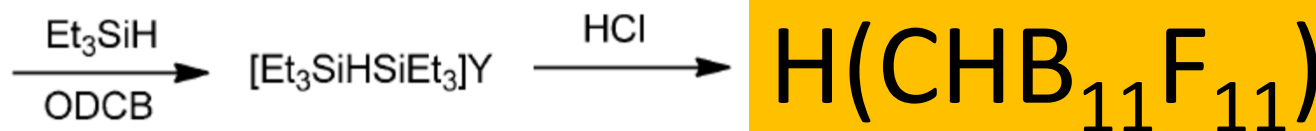
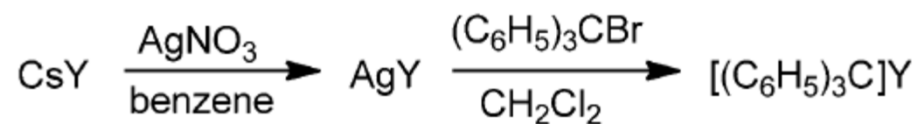
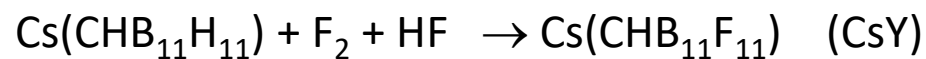


Oxonium

$[\text{H}_3\text{O}^+\cdot 3\text{benzene}][\text{CHB}_{11}\text{Cl}_{11}]\cdot \text{benzene}$



Carborane Superacid $\text{H}(\text{CHB}_{11}\text{F}_{11})$

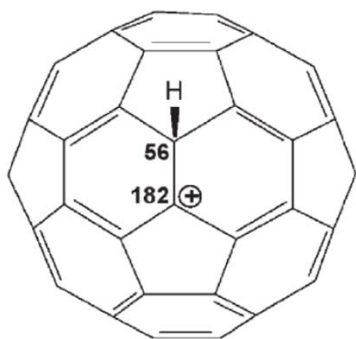
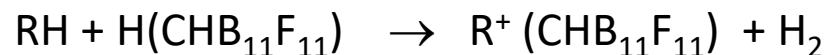


Angew. Chem. Int Ed, 2014, 53, 1131



Carborane Superacid $\text{H}(\text{CHB}_{11}\text{F}_{11})$

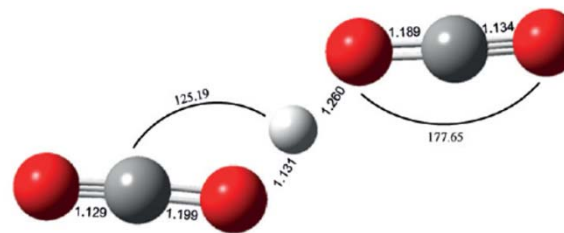
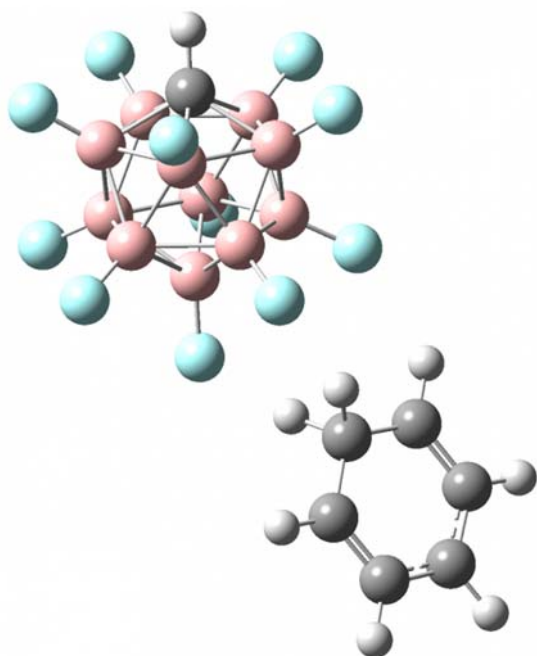
The strongest known acid



The only acid capable of protonating C₆₀ without side reactions
Solid state ¹³C CPMAS NMR - 1,2-carbocation static structure
Solution ¹³C NMR - a single sharp resonance - the proton in the HC₆₀⁺ cation is a globetrotter

The only acid capable of protonating CO₂ to produce [H(CO₂)₂]⁺

Protonates benzene to yield C₆H₇⁺ salt
A sigma complex, stable to 150 °C

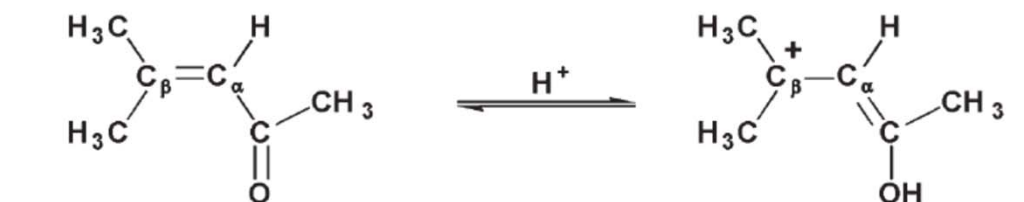


$\Delta\delta$ Mesityl Oxide Scale

The **acidities** of carborane acids cannot be measured in the conventional manner of an H_0 Hammett acidity function because carborane acids are solids not liquids

The $\Delta\delta$ mesityl oxide scale

Liquid SO_2 , the ^{13}C NMR chemical shift difference ($\Delta\delta$) between the C_α and C_β carbon atoms of mesityl oxide which increases with increasing protonation as the reaction equilibrium is shifted to the right hand side



Acid	^{13}C $\Delta\delta$ (ppm)	H_0
H(CHB ₁₁ Cl ₁₁)	84.0 \pm 0.1	<i>a</i>
H(CHB ₁₁ H ₅ Cl ₆)	83.8 \pm 0.1	<i>a</i>
H(CHB ₁₁ H ₅ Br ₆)	83.8 \pm 0.1	<i>a</i>
H(CHB ₁₁ H ₅ I ₆)	83.3 \pm 0.1	<i>a</i>
FSO ₃ H	73.8 \pm 0.5	-15.1
CF ₃ SO ₃ H	72.9 \pm 0.4	-14.1
HN(SO ₂ CF ₃) ₂	72.0 \pm 0.4	<i>a</i>
H ₂ SO ₄	64.3 \pm 3.1 ^b	-12.1
Mesityl oxide (unprotonated)	32.4 \pm 0.1	

Leveling effect

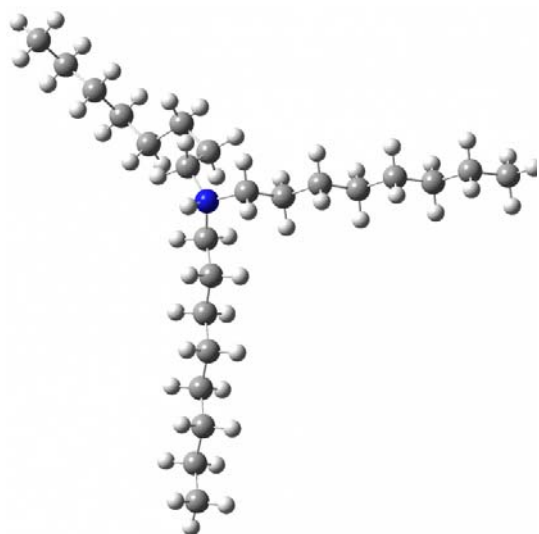
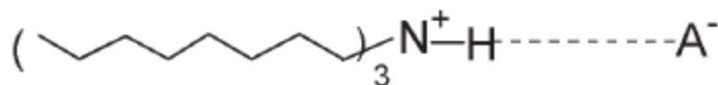


ν NH Basicity Scale

Ranks the hydrogen bond acceptor ability of A^- anions in complexes with the **trioctylammonium ion** in CCl_4 , contact ion pairs

The stronger the basicity of A^- anion, the weaker is the corresponding HA acid and the lower is the N–H stretching frequency

IR ν N–H frequencies will decrease with increasing A^- basicity, correlating with HA acidity



Conjugate base	ν N–H/ $\pm 1 \text{ cm}^{-1}$	$\Delta\nu/\text{cm}^{-1}$
${}^a\text{CHB}_{11}\text{Cl}_{11}^-$	3163	0
$\text{CHB}_{11}(\text{CH}_3)_{11}^-$	3156	7
${}^a\text{CHB}_{11}\text{H}_5\text{Cl}_6^-$	3148	15
$\text{Co}^{\text{III}}(\text{C}_2\text{B}_9\text{H}_8\text{Cl}_3)_2^-$	3145	18
$\text{CHB}_{11}(\text{CH}_3)_5\text{Cl}_6^-$	3143	20
$\text{CHB}_{11}\text{H}_{11}^-$	3129	34
${}^a\text{CHB}_{11}\text{H}_5\text{Br}_6^-$	3125	38
$\text{CHB}_{11}(\text{CH}_3)_5\text{Br}_6^-$	3120	43
${}^a\text{CHB}_{11}\text{H}_5\text{I}_6^-$	3097	6
$\text{CHB}_{11}(\text{CH}_3)_5\text{I}_6^-$	3091	72



Tris(pentafluorophenyl)borane $B(C_6F_5)_3$

$B(C_6F_5)_3$ – an “ideal Lewis acid”

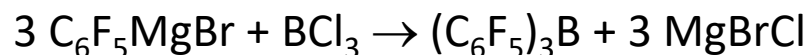
- strong Lewis acidity between BF_3 and BCl_3
- inertness of the B-C bonds, hydrolytically more stable than BF_3 , related fluoro-substituted boron compounds, such as $B-CF_3$, decompose with formation of B-F bonds
- steric bulkiness - the hydride and alkyl group abstraction, a catalyst activator in Zeigler Natta and metallocene based olefin polymerization reactions



- preparing frustrated Lewis acid-base pairs for activation of H_2 , alkynes, CO_2 , etc.
- preparing Xe-C bonded compounds

Prepared from a Grignard reagent derived from bromopentafluorobenzene

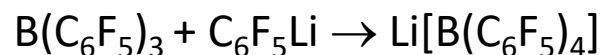
Original synthesis employed C_6F_5Li , but this reagent can detonate, elimination of LiF



Weakly Coordinating Anions

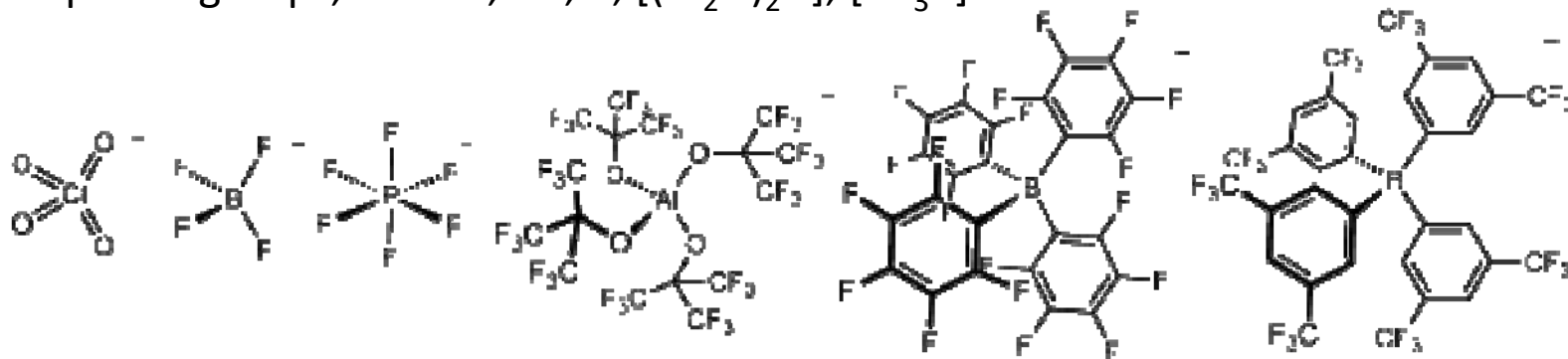
Weakly coordinating anions - unreactive nonbasic, nonnucleophilic counteranions, stabilisation of reactive low coordinate cationic metal and main-group complexes: AuXe_4^{2+} , Xe^{2+} , HC_{60}^+ , Mes_3Si^+ , $\text{Ag}(\text{CO})_2^+$, N_5^+

Tetrakis(pentafluorophenyl)borate – reaction of $\text{B}(\text{C}_6\text{F}_5)_3$ with pentafluorophenyllithium



$[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{Al}(\text{OR}^F)_4]^-$ (R^F = fluoroalkyl), $[\text{HCB}_{11}\text{X}_{11}]^-$ (X = halogen)

$[\text{BAR}^F_4]^-$ BARF (Ar^F = 3,5-(CF_3) $_2\text{C}_6\text{H}_3$), solubility and crystallinity, and simple NMR-reporter groups, M^+ = Li, Na, K, $[(\text{Et}_2\text{O})_2\text{H}]$, $[\text{Ph}_3\text{C}]$



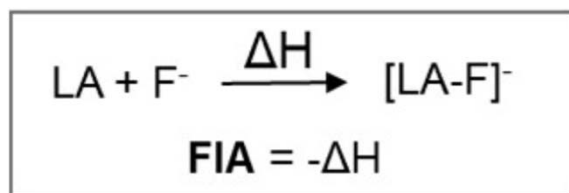
Fluoride Ion Affinity (FIA)

Lewis Superacids = molecular Lewis acids, which are stronger than monomeric SbF_5 in the gas phase

FIA = a quantitative measure for Lewis acidity

Lewis acids with a FIA higher than that of monomeric SbF_5 (489 kJ mol^{-1}) are **Lewis superacids**

FIA = the negative enthalpy of the gas phase reaction between a **fluoride** ion and a Lewis acid



F^- - small size and polarizability minimizes steric repulsion, charge transfer, π -backbonding, and dispersion forces

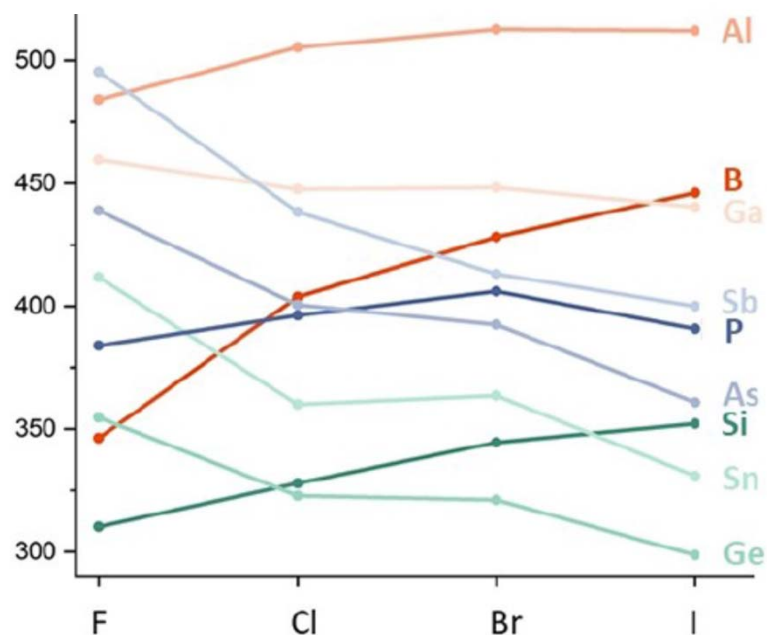
Anion	Symmetry	FIA [kJ mol ⁻¹]
BF_4^-	T_d	338
PF_6^-	D_{4h}	394
AsF_6^-	D_{4h}	426
SbF_6^-	D_{4h}	489
$\text{Sb}_2\text{F}_{11}^-$ vs Sb_2F_{10}	C_1	549
$\text{Sb}_3\text{F}_{16}^-$ vs Sb_3F_{15}	C_i	582
$\text{Sb}_4\text{F}_{21}^-$ vs Sb_4F_{20}	C_{2v}	584
$[\text{B}(\text{OTeF}_5)_4]^-$	C_1	550
$[\text{As}(\text{OTeF}_5)_6]^-$	C_3	593
$[\text{Sb}(\text{OTeF}_5)_6]^-$	C_3	633
$[\text{Al}(\text{OR})_4]^-$ (R = C(CF ₃) ₃)	S_4	537
$[(\text{RO})_3\text{AlFAl}(\text{OR})_3]^{-[\text{b,e}]}$	C_i	685 ^[b]
$[\text{B}(\text{C}_6\text{H}_5)_4]^-$	S_4	342
$[\text{B}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4]^-$	S_4	471
$[\text{B}(\text{C}_6\text{F}_5)_4]^-$	S_4	444
$[\text{B}(\text{CF}_3)_4]^-$	T	552



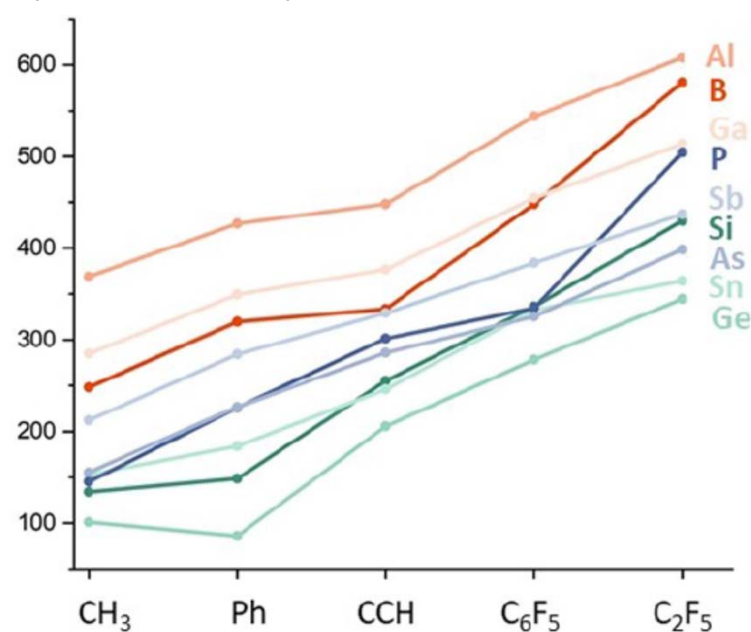
Fluoride Ion Affinity (FIA)

- Halides - In their highest oxidation states, maximum FIA are obtained for light element acceptors with heavy element substituents (e. g., BI_3) or heavy element acceptors with light element substituents (e. g., SbF_5)
- Nonfluorinated C-ligands - an increase in FIA for $\text{sp}^3 < \text{sp}^2 < \text{sp}$ hybridized C in line with their increasing group electronegativity
- C_6F_5 group is effective for FIA boosting, C_2F_5 substituent is the strongest

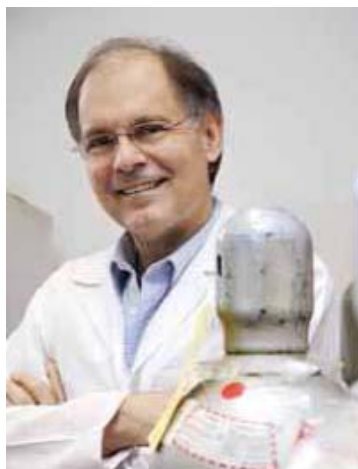
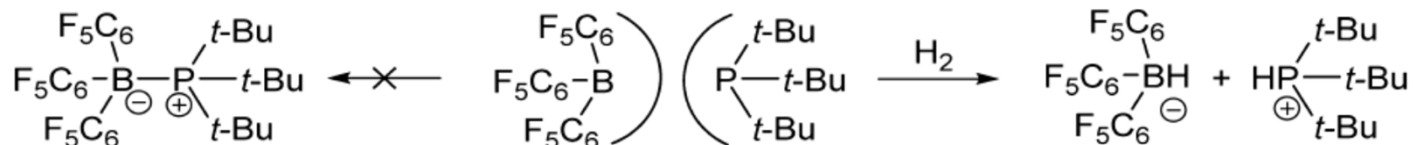
(FIA, kJ mol^{-1})



(FIA, kJ mol^{-1})



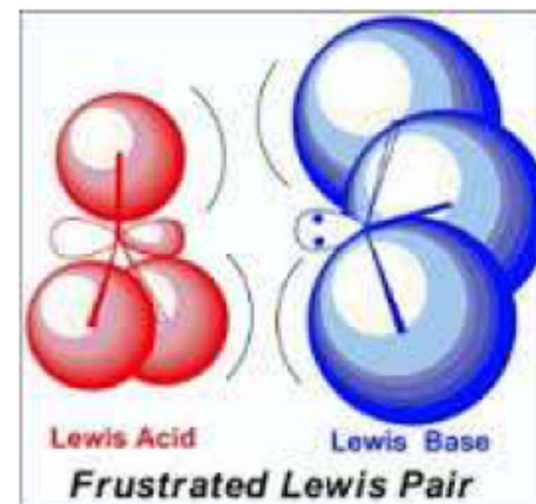
Frustrated Lewis Pair (FLP)



Douglas W. Stephan

Combinations of **Lewis acids and bases** which are **sterically** prevented from forming the classical Lewis acid-base adducts

Lewis acidity and basicity available for activation of a third molecule



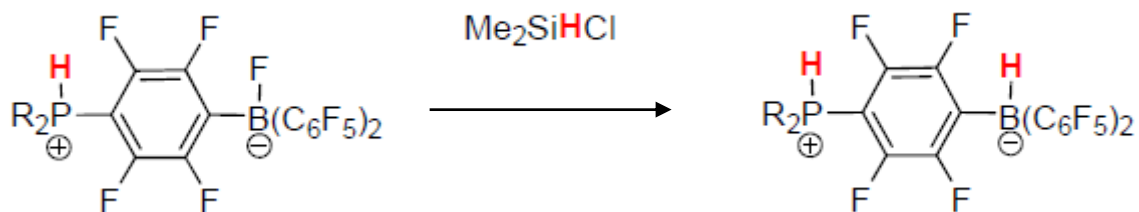
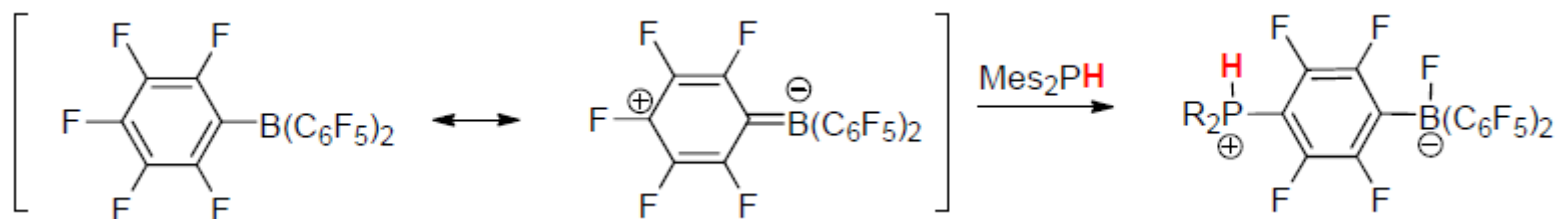
Boron – phosphorus, due to their unquenched reactivity, such molecules are able to heterolytically cleave dihydrogen molecule making them potential metal free hydrogenation catalysts



Frustrated Lewis Pair (FLP)

Frustrated Lewis pair is a compound or mixture containing a **Lewis acid** and a **Lewis base** that, due to **steric hindrance**, cannot combine to form an adduct. Due to their unquenched reactivity, such systems are **very reactive**.

The first example of such a system was prepared from $B(C_6F_5)_3$, most of the examples use $B(C_6F_5)_3$ as the Lewis acid or a compound having $B(C_6F_5)_2$ group.

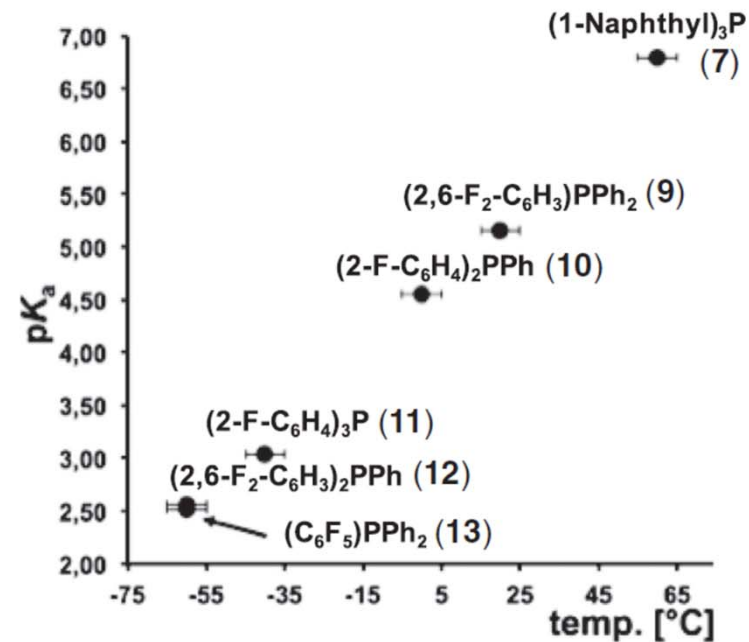
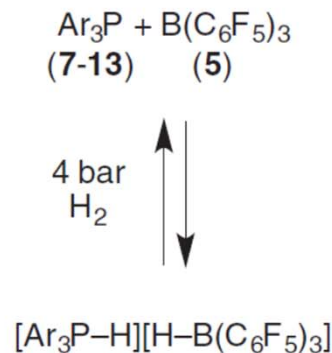
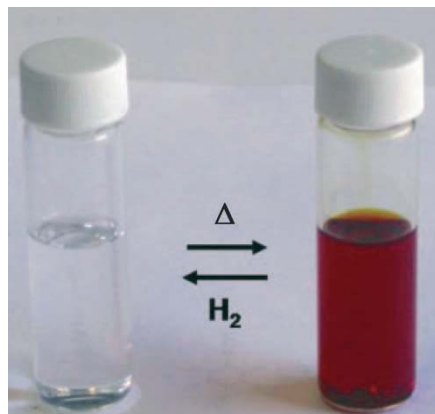
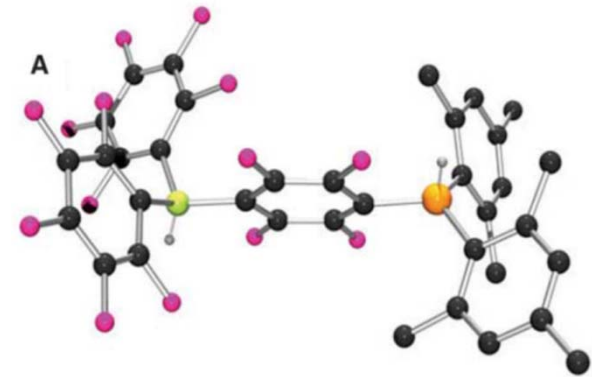
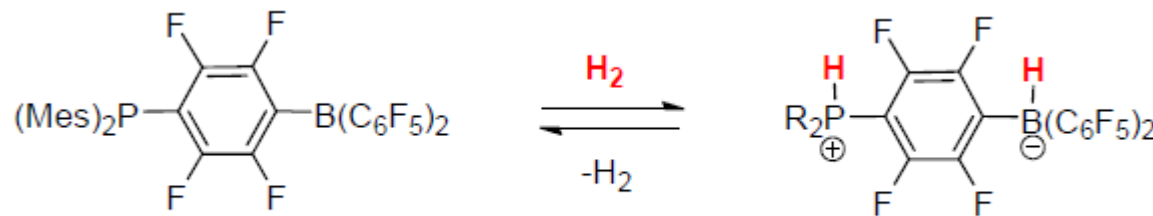


Stephan, D. *et al.*, *Science* **2006**, 314, 1124



Dihydrogen Activation

H–H bond of dihydrogen is the simplest covalent bond
Bond energy - the strongest homoatomic single bond

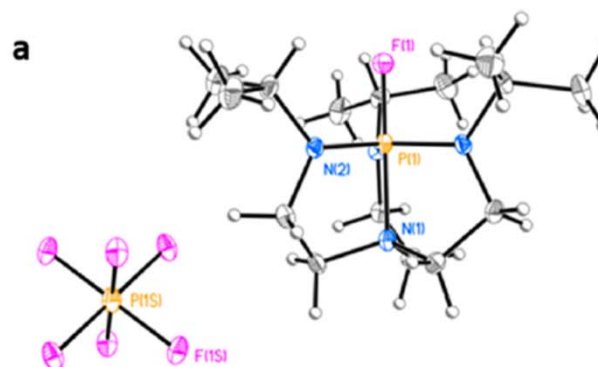
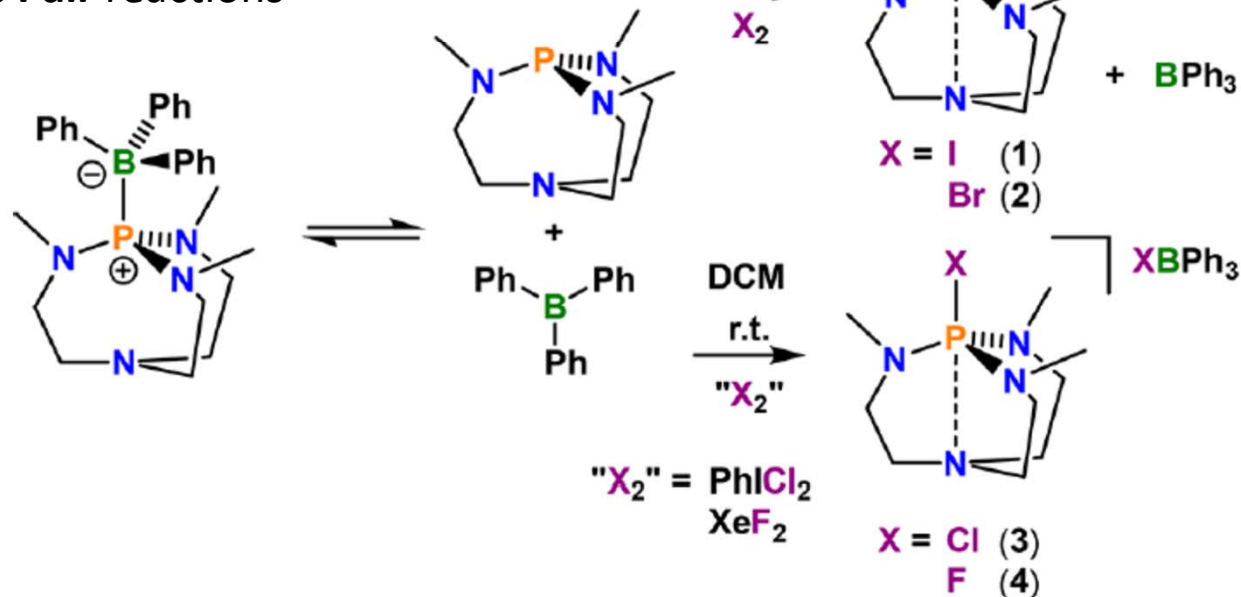


Synthesis of Haloazaphosphatranes

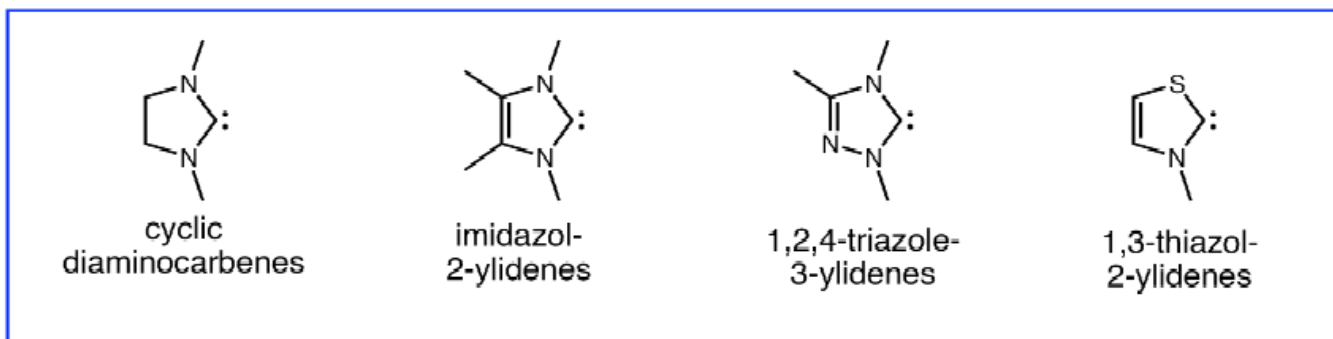
Direct fluorination of **Verkade's base** with XeF_2 leads to cage destruction and formation of PF_6^-



Frustrated Lewis Pair reactions



Carbene Bases

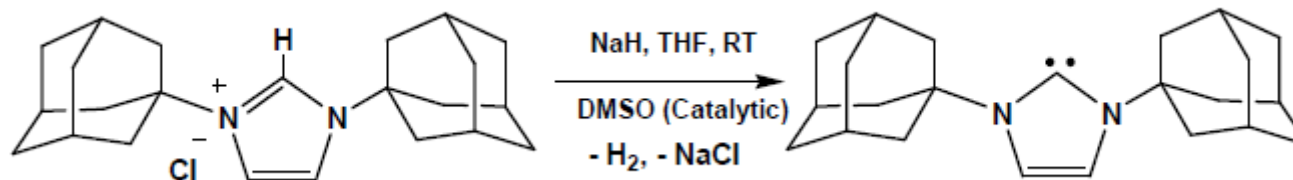


N-heterocyclic carbenes (NHCs)

- stronger σ -donors than the most electron rich phosphines
- less likely to dissociate from the metal during the reaction
- replaced phosphines in many organometallic and organic reactions
- useful spectator ligands, **tunable** electronically and sterically
- most frequently prepared via deprotonation of the corresponding azolium salts



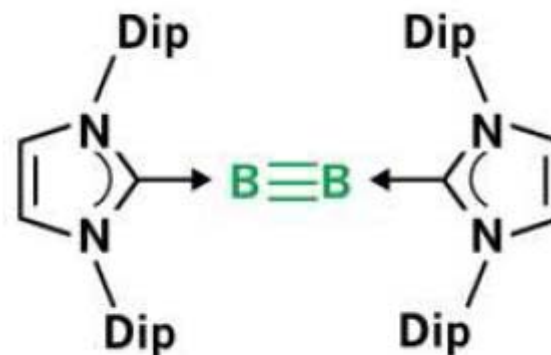
Anthony J Arduengo



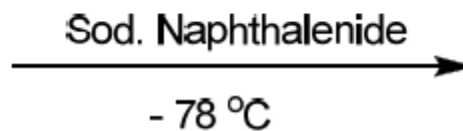
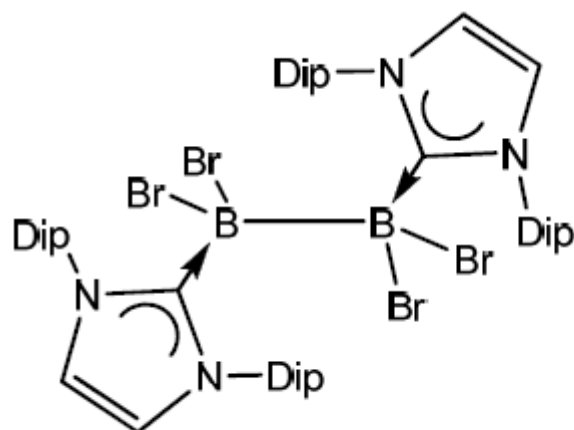
Carbene Bases



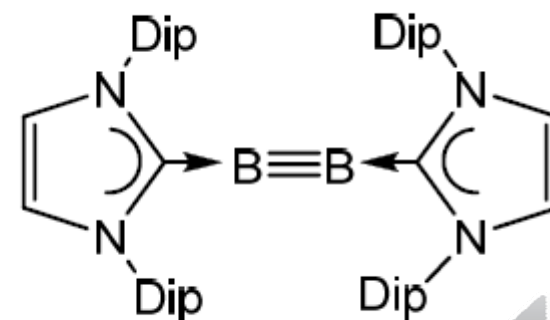
Holger Braunschweig



The first example of a stable **diboryne** having a $B\equiv B$ and stabilized by N-heterocyclic carbenes prepared in 2012



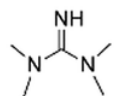
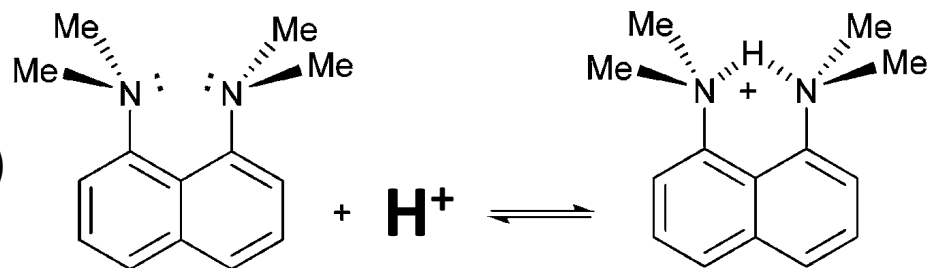
Dip = 2,6 diisopropylphenyl



Superbases

Proton Sponge

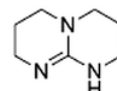
1,8-bis(dimethylamino)
naphthalene



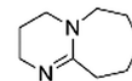
TMG ($pK_{BH^+}=23.3$)



Bispidine ($pK_{BH^+}=21.5$)

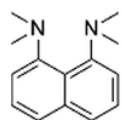


TBD ($pK_{BH^+}=26.0$)

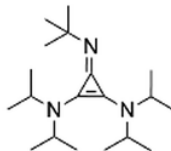


DBU ($pK_{BH^+}=24.3$)

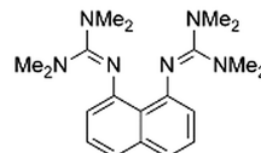
$$K_{BH} = \frac{[B][H^+]}{[BH^+]}$$



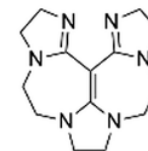
DMAN ($pK_{BH^+}=18.2$)



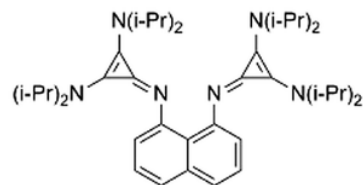
DAC ($pK_{BH^+}=26.9$)



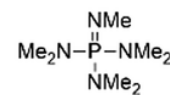
TMGN ($pK_{BH^+}=25.1$)



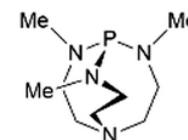
Vinamidine ($pK_{BH^+}=29.2$)



DACN ($pK_{BH^+}=27.0$ *)



P1 Base ($pK_{BH^+}=27.5$)



Verkade's Base ($pK_{BH^+}=32.8$)

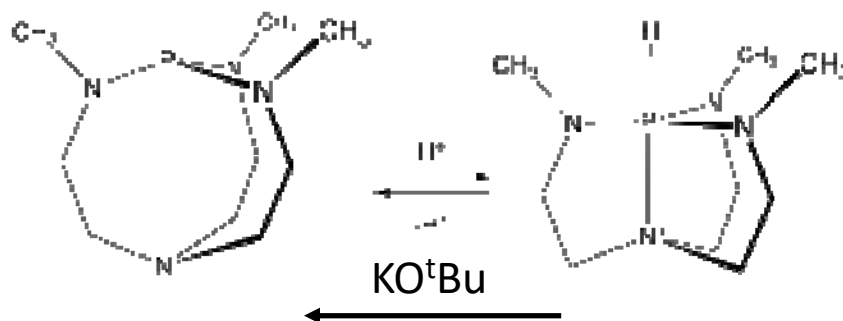
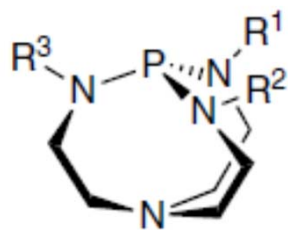


Superbases

Verkade's Bases - aminophosphine – proazaphosphatrane – strongly basic, only weakly nucleophilic - catalysts in a variety of organic reactions



John G. Verkade
1935 - 2016



Transannular P→N
bond stabilizes the
P–H bond

Gas phase
basicity (GB)

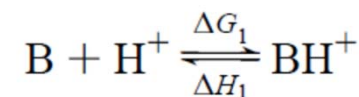
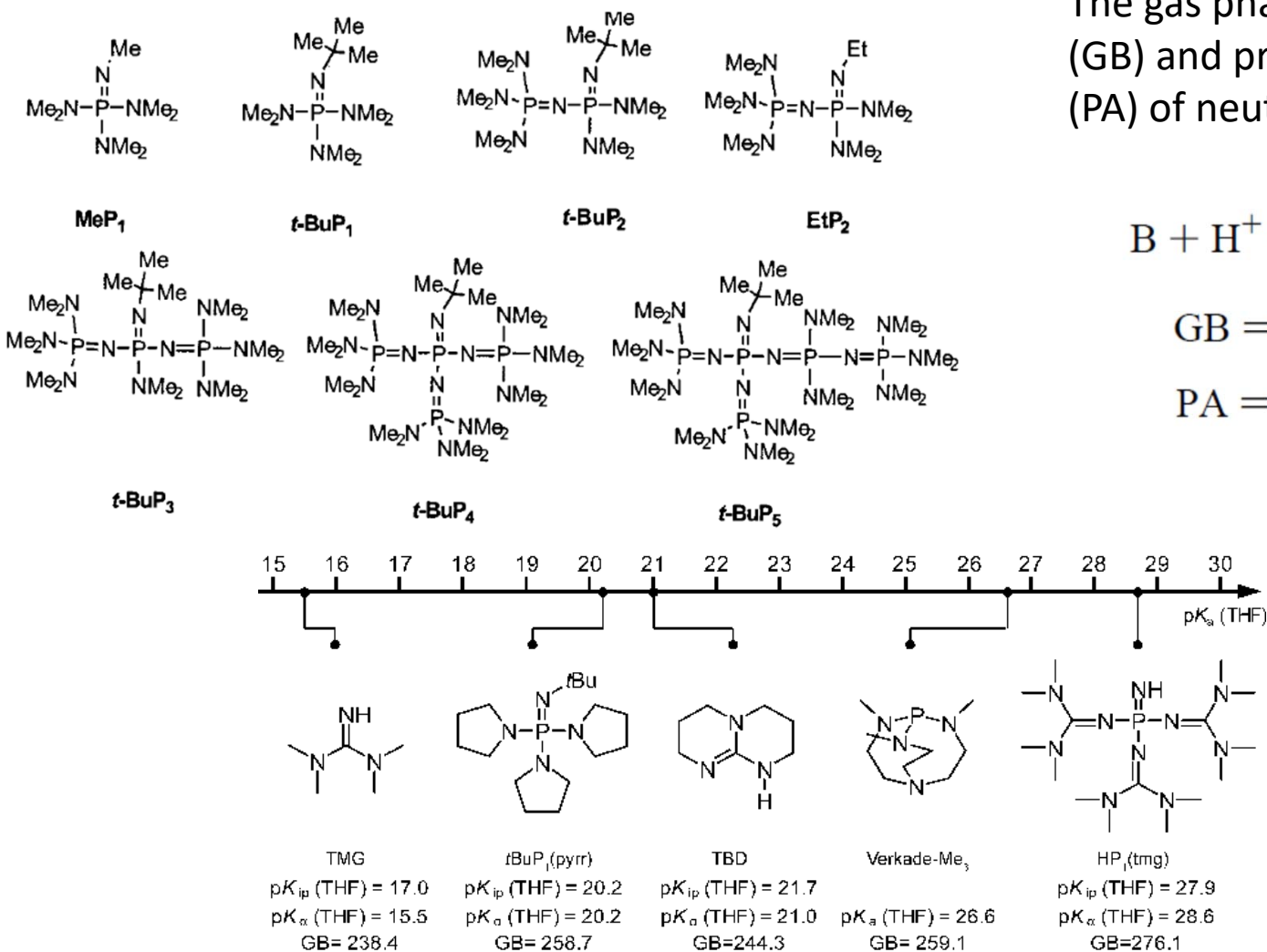
R ¹	R ²	R ³	pK _a (MeCN)	pK _a (DMSO)	pK _a (THF)	GB [85]
H	H	H		29.6		
<i>i</i> Pr	H	H	34.49			
<i>i</i> Pr	<i>i</i> Pr	<i>i</i> Pr	33.63			
<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu	33.53			260.8 (261.7)
Me	Me	Me	32.90; 32.82 (41.2)	26.8	26.6 [102]	259.1
Piv	Piv	Piv	32.84			
CH ₂ Ph	CH ₂ Ph	CH ₂ Ph		26.8		

Superbases

Phosphazene imines

Reinhard Schwesinger

The gas phase basicities (GB) and proton affinities (PA) of neutral bases (B)



$$GB = -\Delta G_1$$

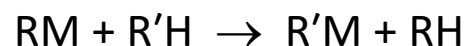
$$PA = -\Delta H_1$$



Superbases

Deprotonation of diverse weakly acidic organic and organometallic compounds, metalation replaces C–H with C–M, metal-hydrogen exchange

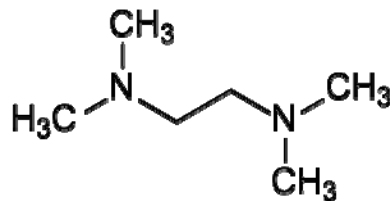
The Schorigin reaction



Butyllithium reagents: n-butyl-, sec-butyl-, and tert-butyllithium - not sufficiently basic to deprotonate extremely weakly acidic compounds such as benzene and ethylene

Basicity enhanced by using

- donor solvents, such as diethyl ether and THF
- a chelating tertiary diamine such as N,N,N',N'-tetramethylethylenediamine (TMEDA)



Superbases

1946 Avery A. Morton at MIT

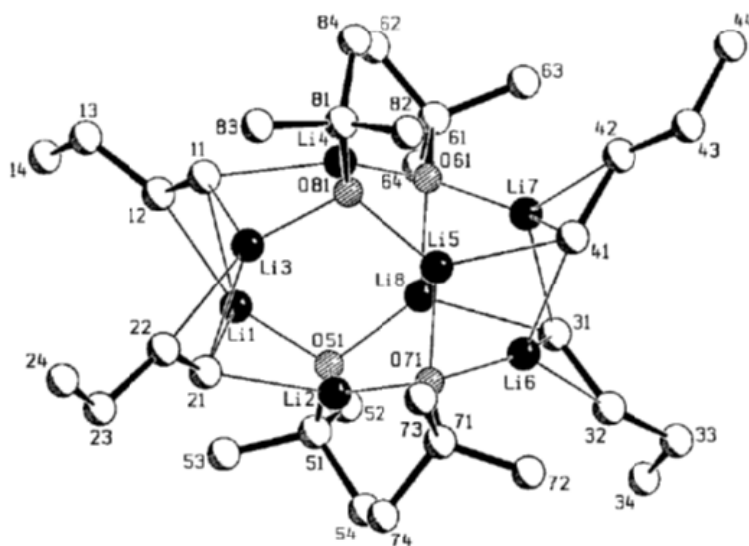
n-amylsodium + *i*PrONa - metalate ethylene directly to give vinylsodium

The “alkoxide effect” - never cited by the later workers

1964 Rediscovered by 3 groups (US, DE, CZ)

L. Lochmann at the Inst. of Macromolecular Science

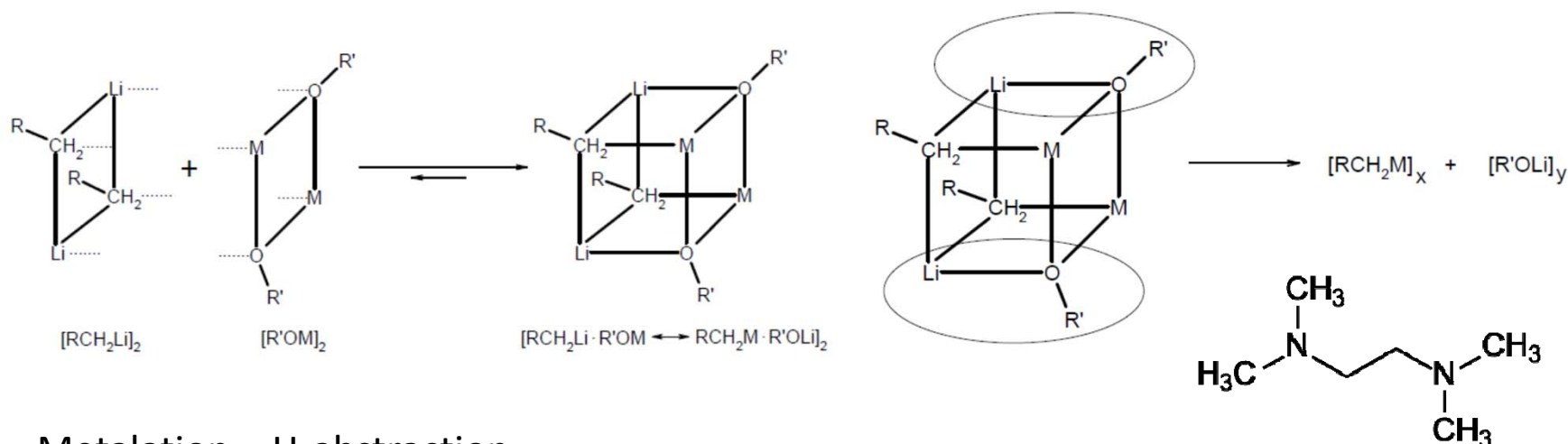
n-butyl-, *sec*-butyl-, and *tert*-butyllithium, were “activated” by the addition of a potassium or sodium alkoxide



Superbases

$n\text{-C}_4\text{H}_9\text{Li} \cdot \text{tert-C}_4\text{H}_9\text{OK}$ - LICKOR - Lochmann-Schlosser base - a very reactive metalation agent

Metal-metal exchange reaction – driven by HSAB (Hard and Soft Acids and Bases)



Metalation = H-abstraction

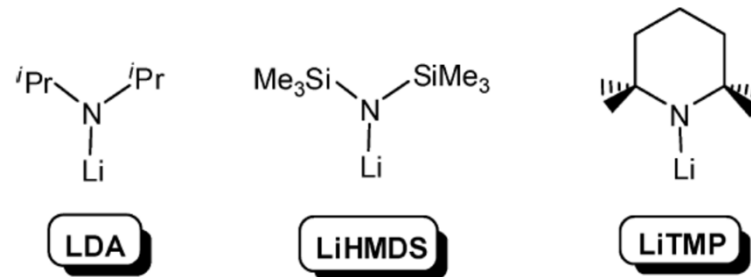


Anionic polymerization of dienes, styrene-butadiene copolymers, methyl methacrylate, ethylene oxide



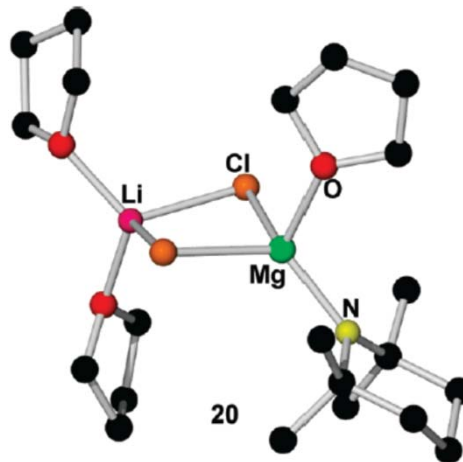
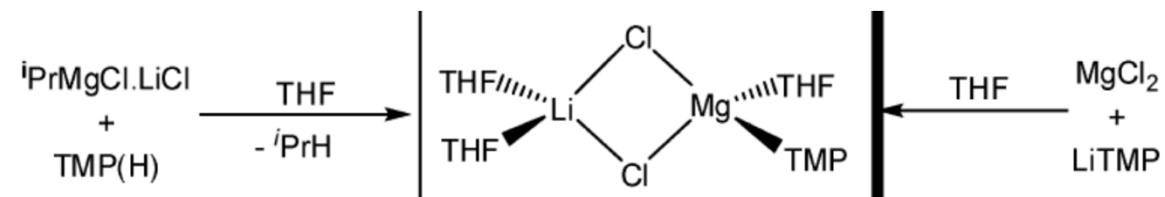
Superbases

Alkali metal amides



TMP = 2,2,6,6-tetramethylpiperidine

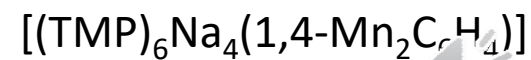
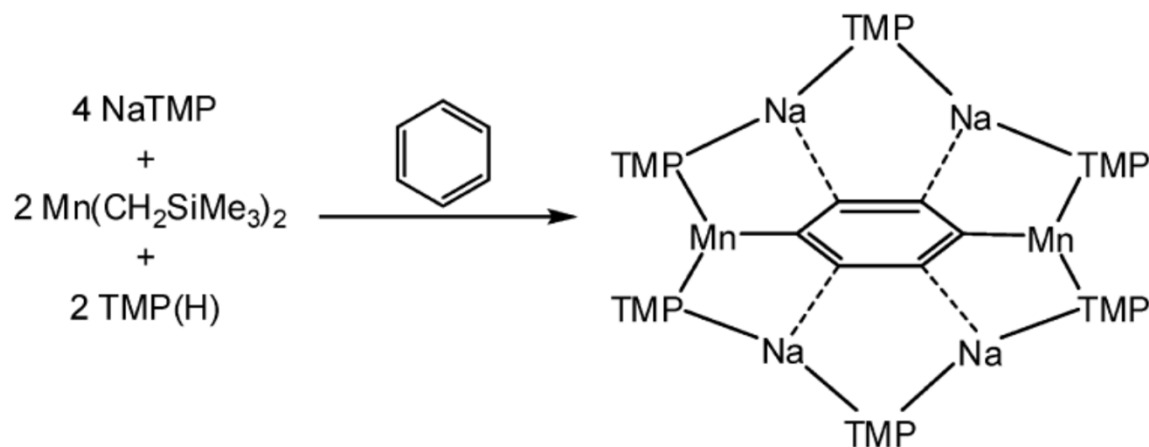
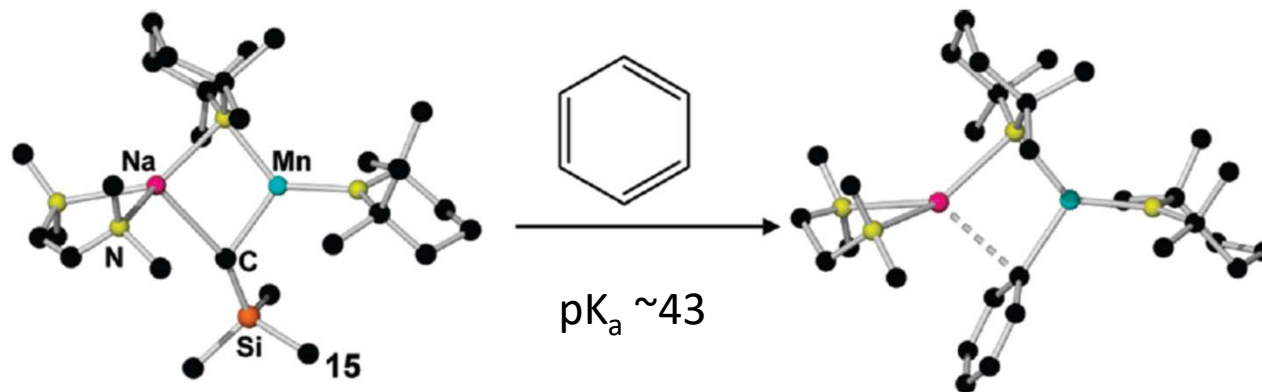
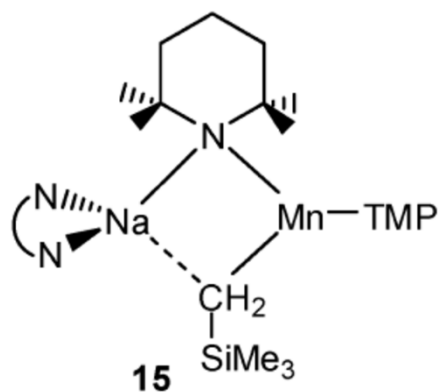
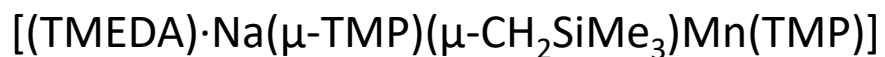
Knochel - Turbo-Grignard reagent





Robert E. Mulvey

Superbases



Dictionary of Used Terms

AFM atomic force microscopy = rastrovací sondová mikroskopie