SAND2016-0833PE

RE-cycle Efforts for Nationally Critical Elements: Fundamental Coordination Chemistry of Scandium

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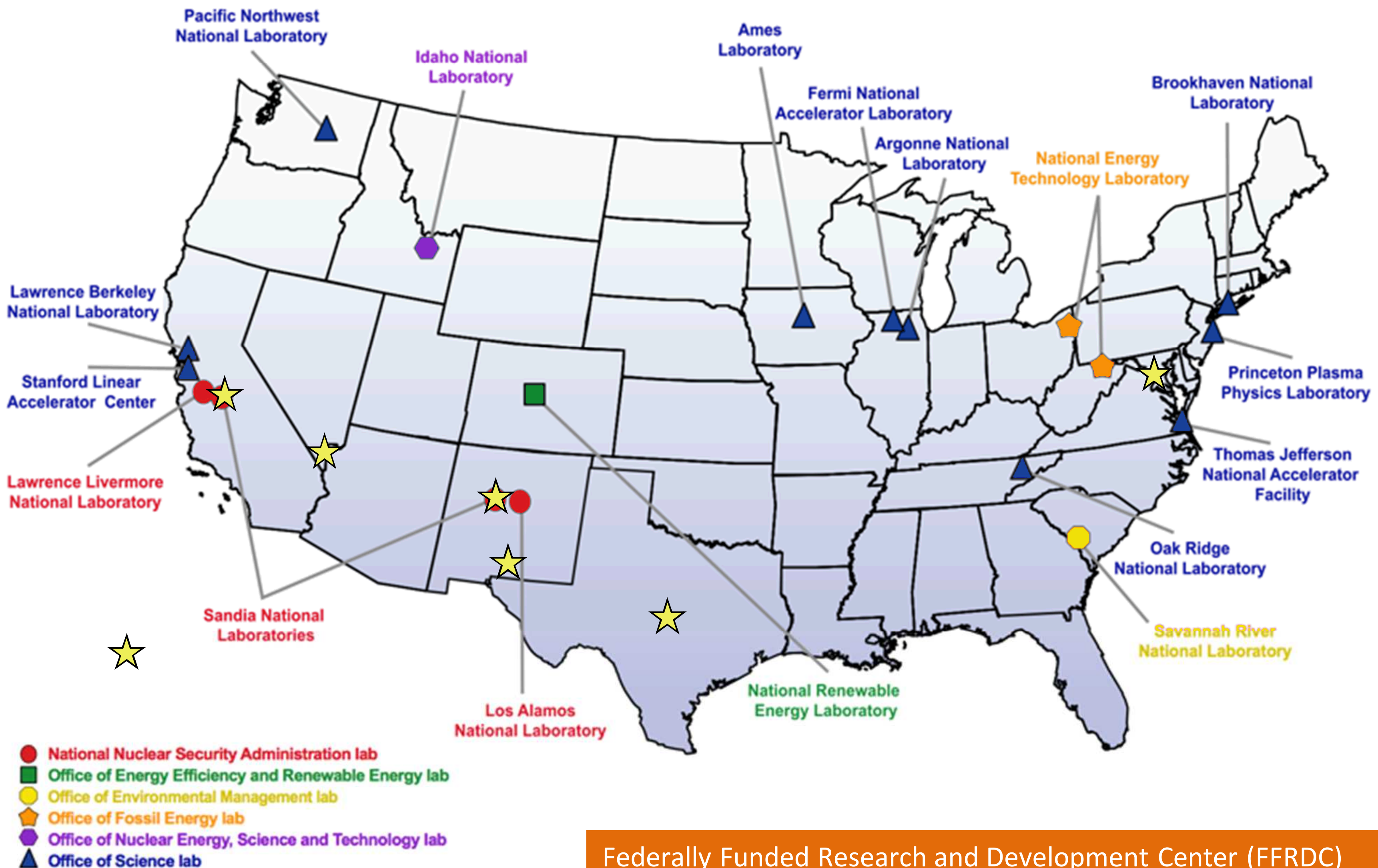
This work was supported by the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories and gratefully acknowledge the use of the Bruker X-ray diffractometer purchased via the National Science Foundation CRIF:MU at the University of New Mexico (CHE04-43580). Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

DEPARTMENT OF ENERGY NATIONAL LABORATORIES



Federally Funded Research and Development Center (FFRDC)
Government Owned/Contractor Operated (GO/CO)

Sandia National Laboratory sites are located across the nation

Albuquerque, New Mexico

Livermore, California

SNL's major facilities are located at Albuquerque, New Mexico; Livermore, California; and at a test range near Tonopah, Nevada.

Kauai, Hawaii

Waste Isolation Pilot Plant, Carlsbad, New Mexico

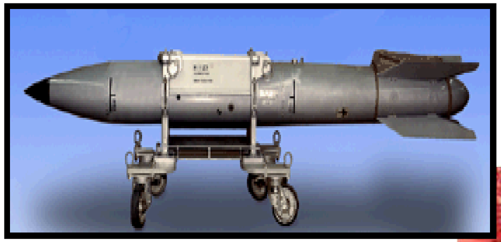
Pantex, Texas

188,300 acres.

Tonopah, Nevada

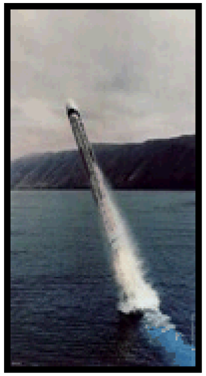
Sandia is a National Security Laboratory

Nuclear Weapons

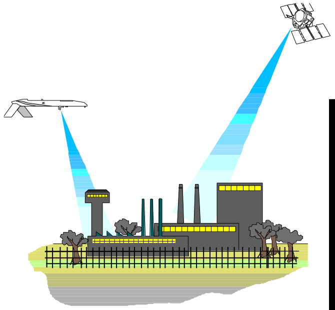


Safe, Secure,
Reliable Weapons

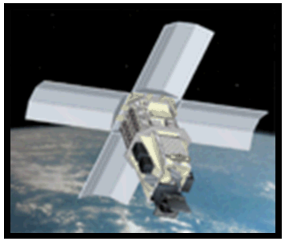
Defense Systems & Assessments



Defense

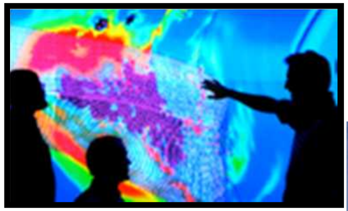


Detection

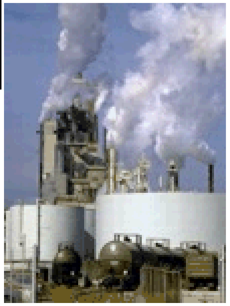


Surveillance

Energy, Climate, & Infrastructure Security



Modeling
& Analysis



Energy

Transportation

International, Homeland, & Nuclear Security

Incident response

Biological risk
management

Anti-crime and anti-
Terrorism technology

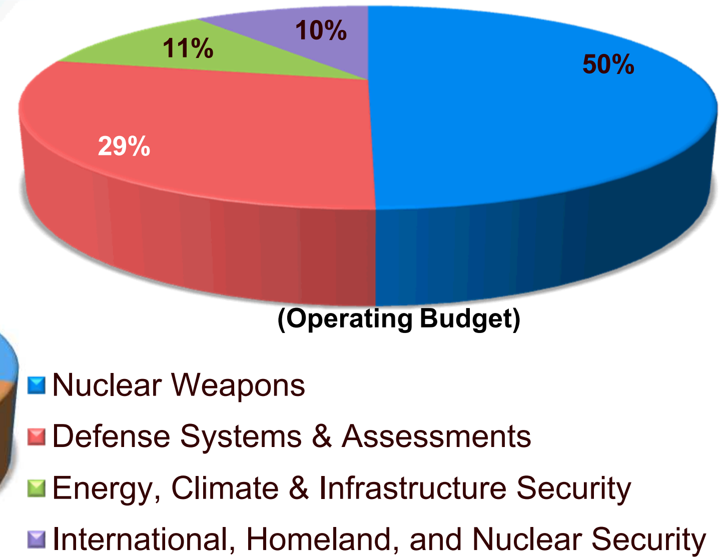
Science, Technology, & Engineering

People and Budget

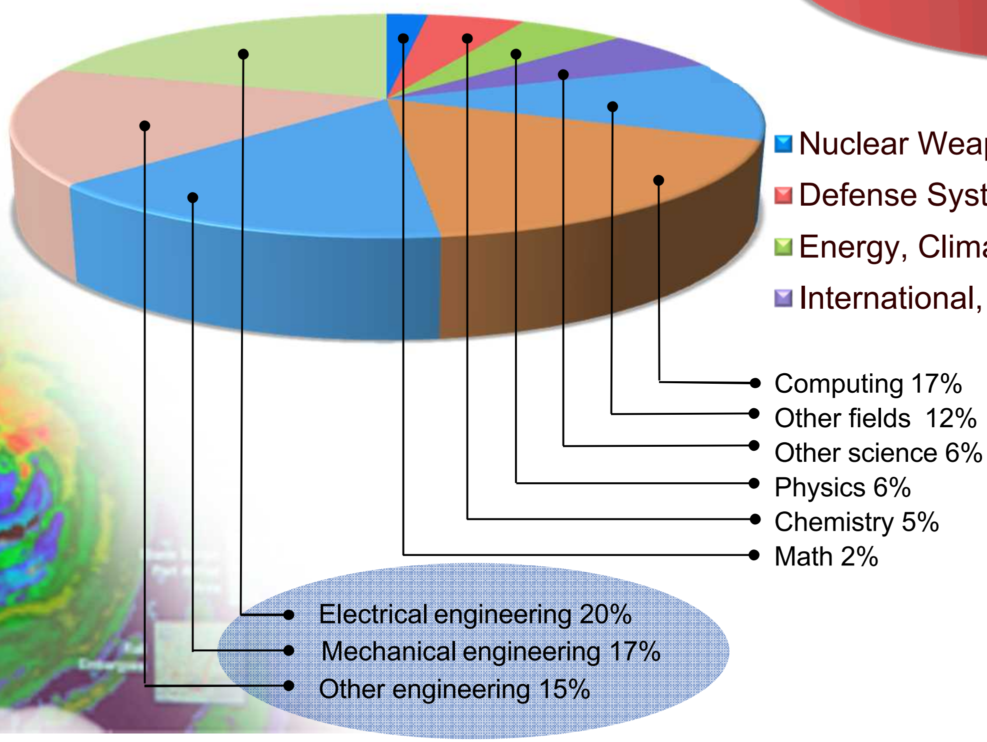
(As of October 11, 2011)

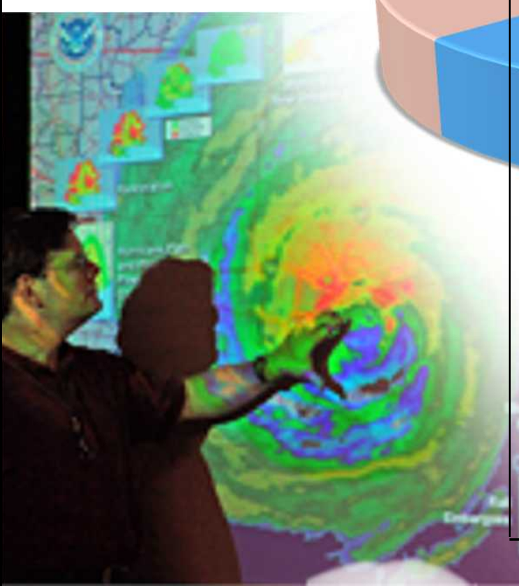
- On-site workforce: 11,876
- Regular employees: 9,122
- Gross payroll: ~$943 million

FY11 Operating Revenue $2.4 billion



Technical staff (4,557) by discipline





Cross-cutting, inter-discipline studies at AML/SNL requires integrated approach to research.

30 Sandia employees

+ technical staff,

+ technologists,

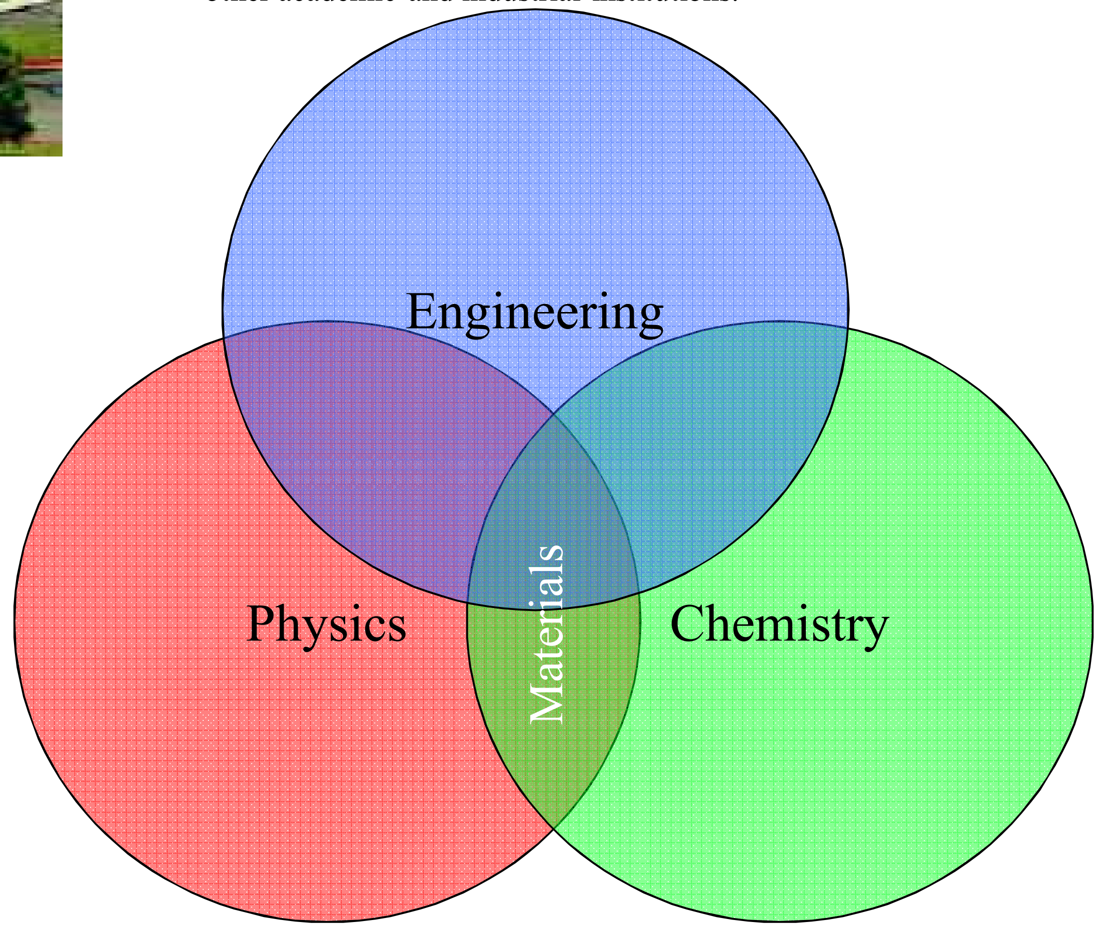
+ post docs, and

+ student interns

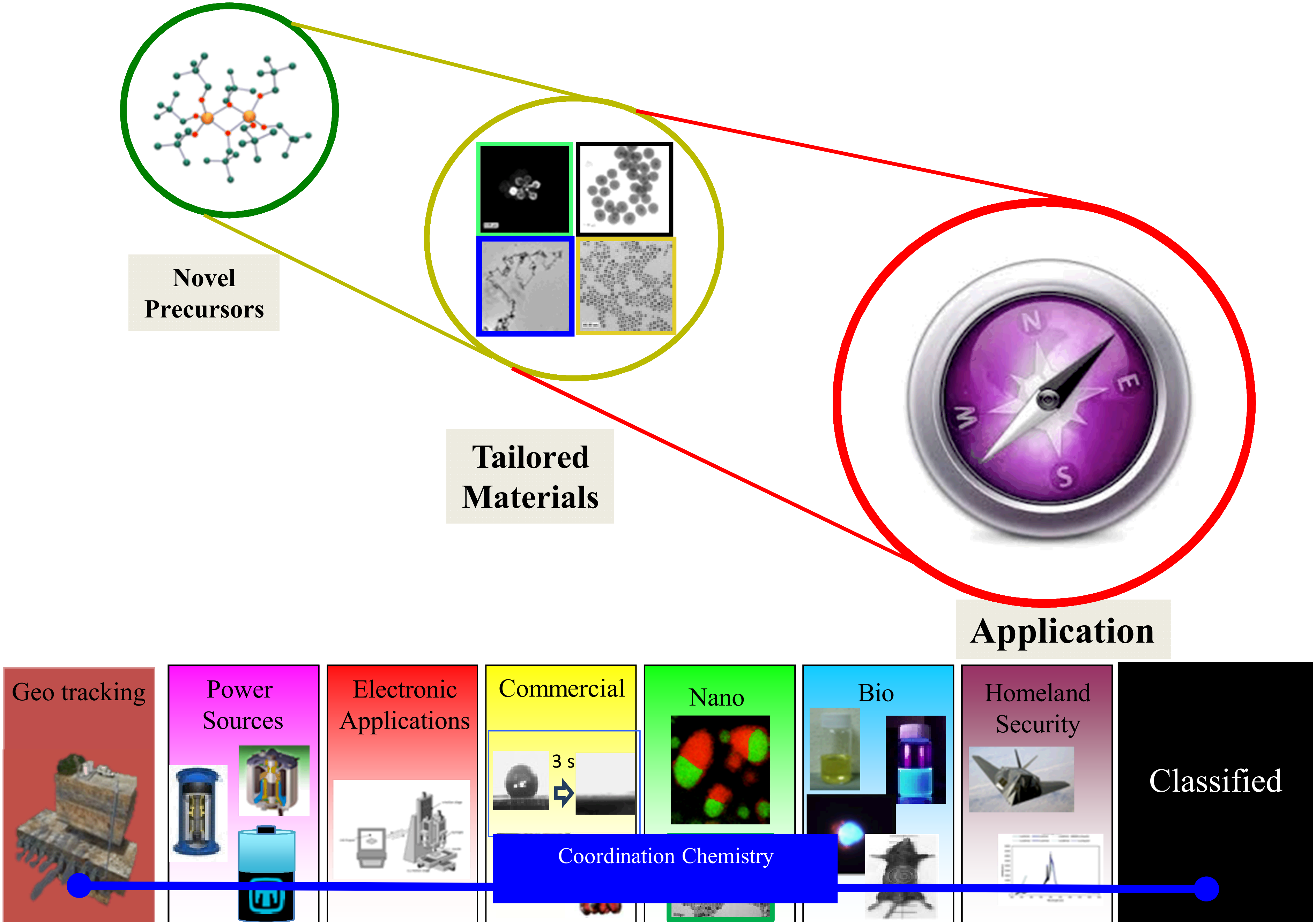
- hosts >30 students, faculty and researchers from UNM, and other academic and industrial institutions.

Work at the AML is focused on materials and process research in the areas of:

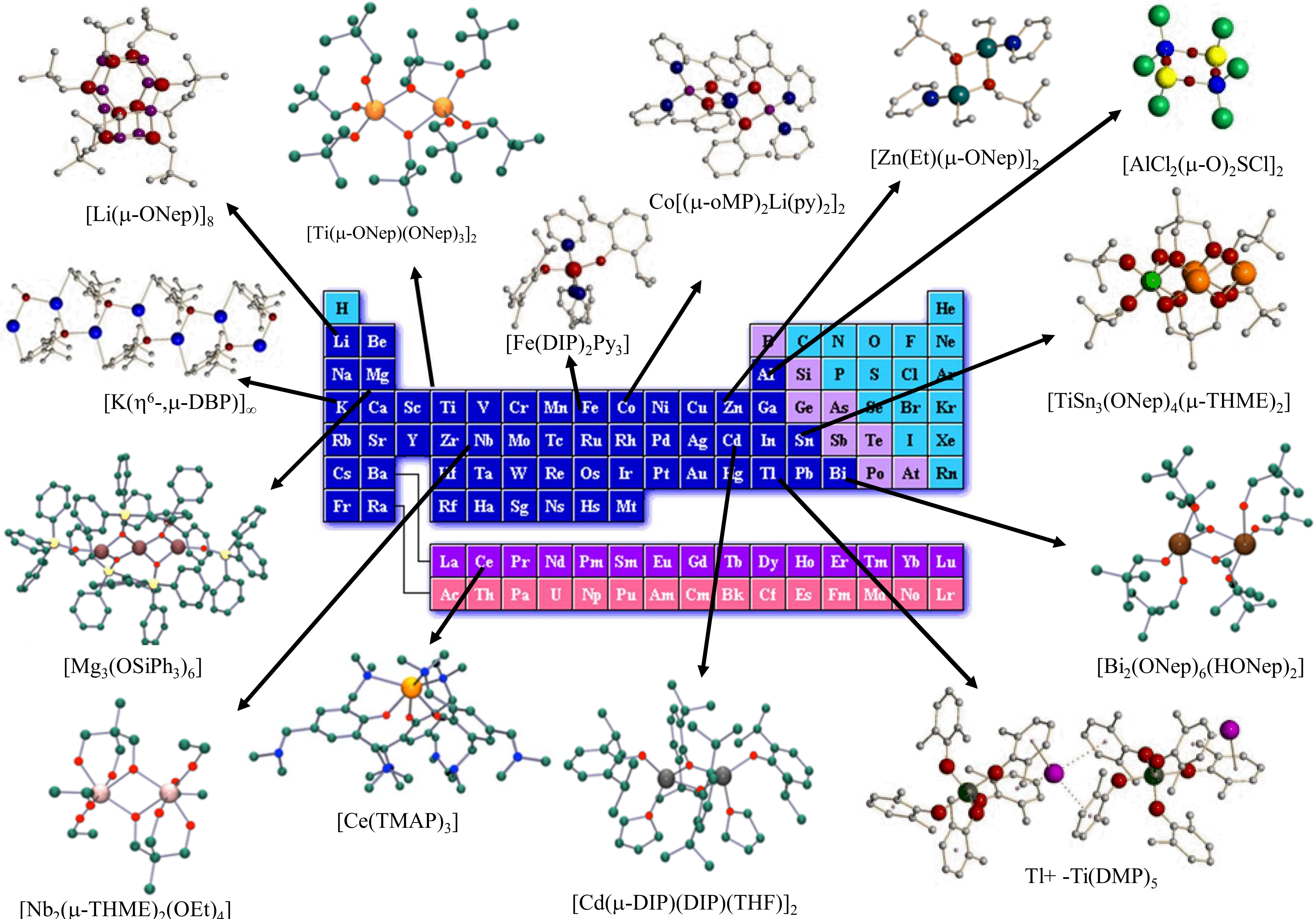
- **ceramics**,
- porous materials,
- catalysts,
- electronic materials,
- materials modeling,
- biomaterials,
- **synthesis.**



Approach and Projects of Boyle Research Group at Sandia

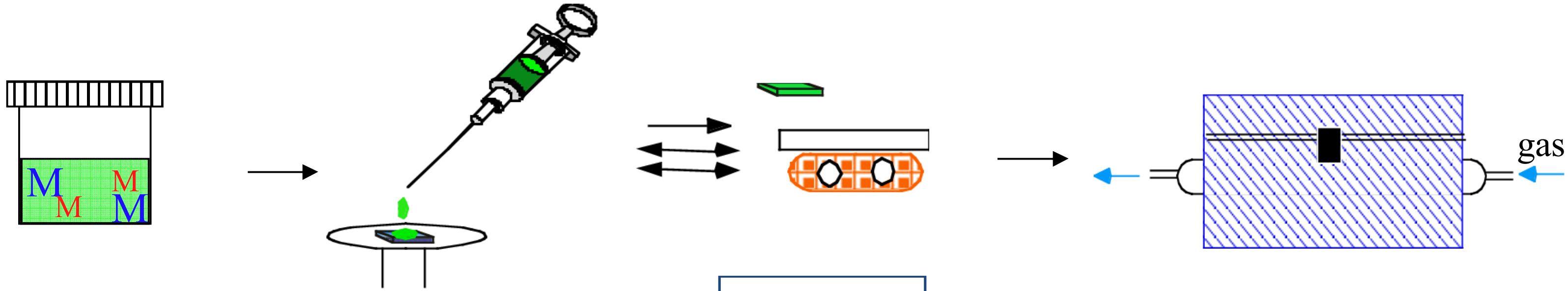


Precursors limited to the Periodic Table of Elements



Synthetic techniques for production of ceramic materials

Goal: Develop tailor-made precursors to generate optimized materials.

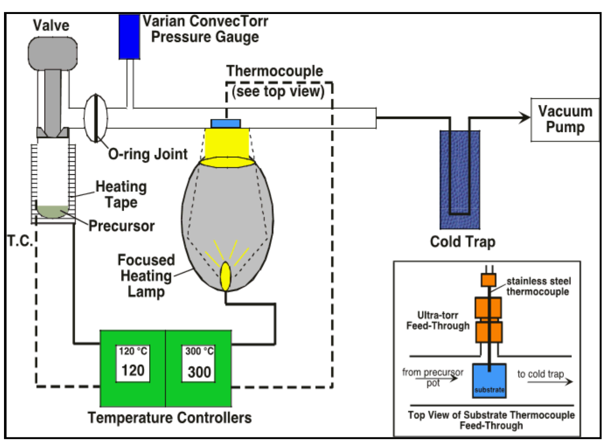


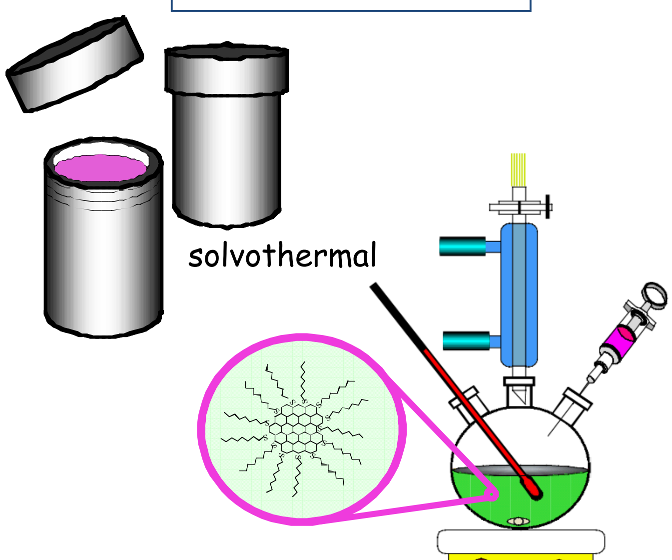
Sol-Gel

Spinning

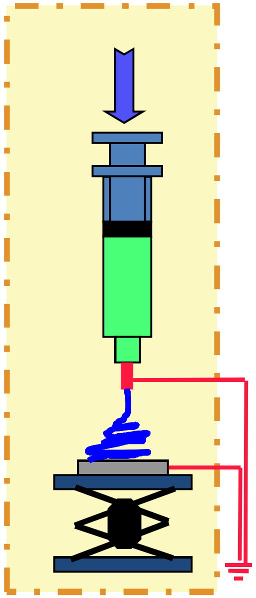
Nanoparticles

MOCVD

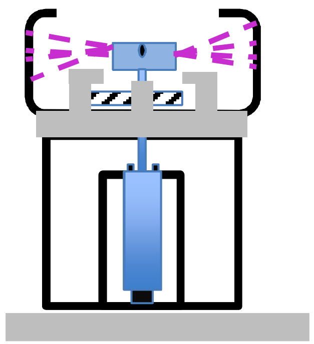




Solution precipitation

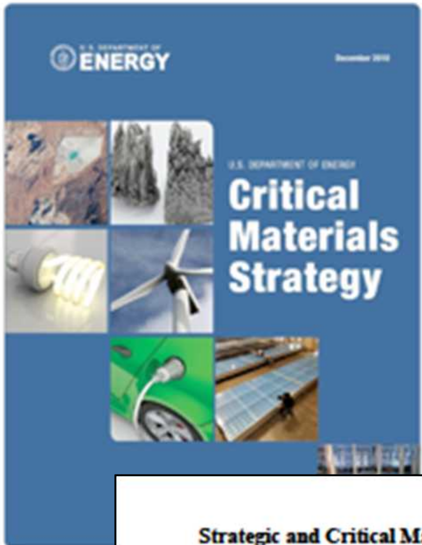


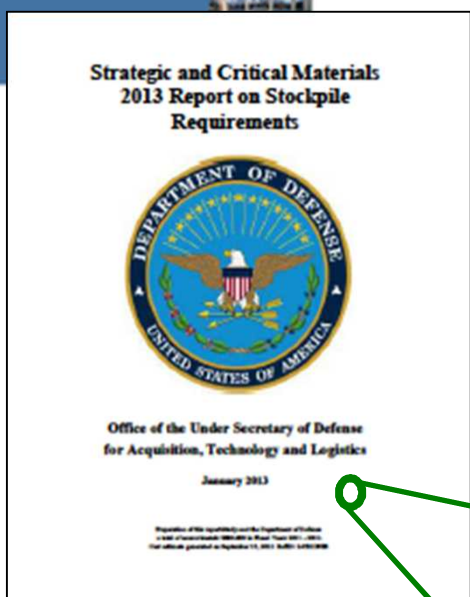
Electrospinning



Forcespinning

‘Nationally Critical Materials’ are necessary to maintain the nation’s economy.




Strategic and Critical Materials
2013 Report on Stockpile
Requirements

Office of the Under Secretary of Defense
for Acquisition, Technology and Logistics

January 2013

- **no U.S. Government-wide definition exists** - broadly, if a vital sector of the economy requires a mineral in order to function, that mineral would likely be deemed “critical.”

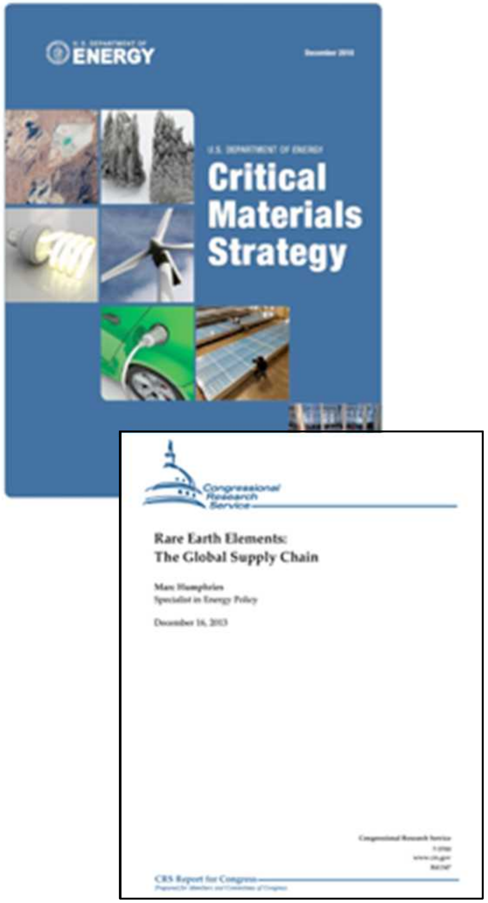
- from a national perspective, a strategic mineral may be defined as one that is important to the Nation’s economy, particularly for defense issues; doesn’t have many replacements; primarily foreign sourced.

- a nation’s ***perception of vulnerability to supply disruptions***, and of a need to safeguard its industries from repercussions of a loss of supplies.

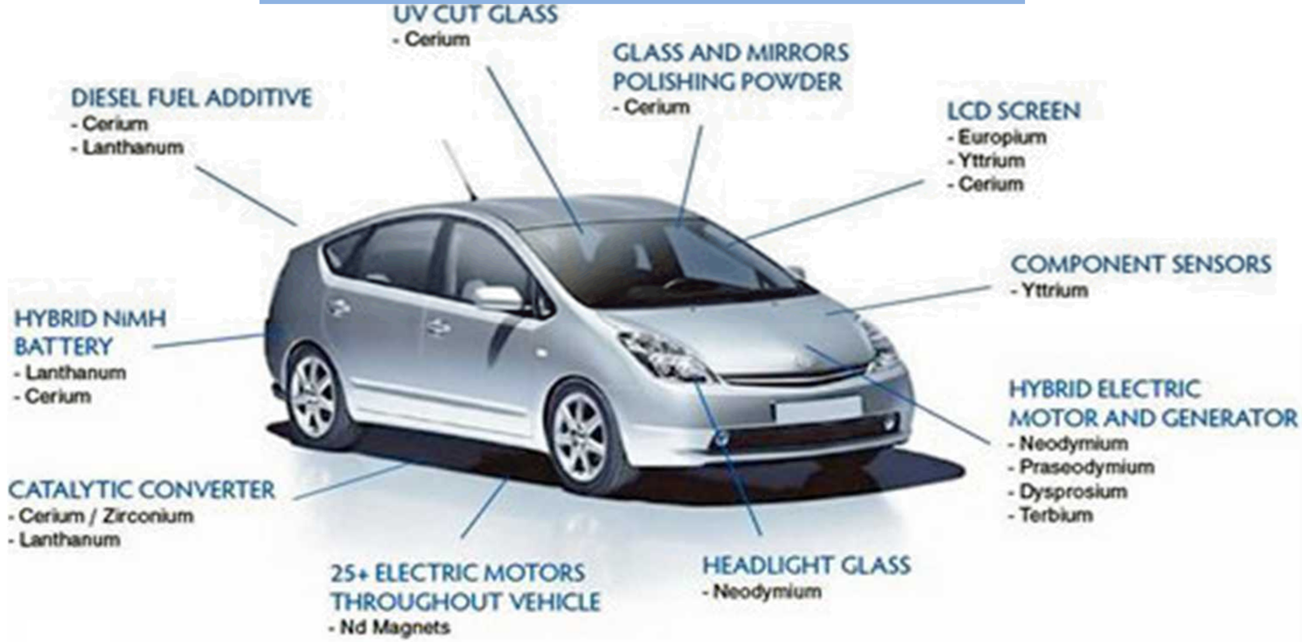
- Criticality to some extent is determined by the industrial and commercial uses of the raw materials.

> The concentration of production of rare earth elements (REEs) outside the United States raises the important issue of supply vulnerability. REEs are used for new energy technologies and national security applications. Two key questions of interest to Congress are: (1) Is the United States vulnerable to supply disruptions of REEs? (2) Are these elements essential to U.S. national security and economic well-being?

Surprisingly (!?) a number of these are the lanthanides (and Group 3 elements).



Toyota Prius and the lanthanides



* Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

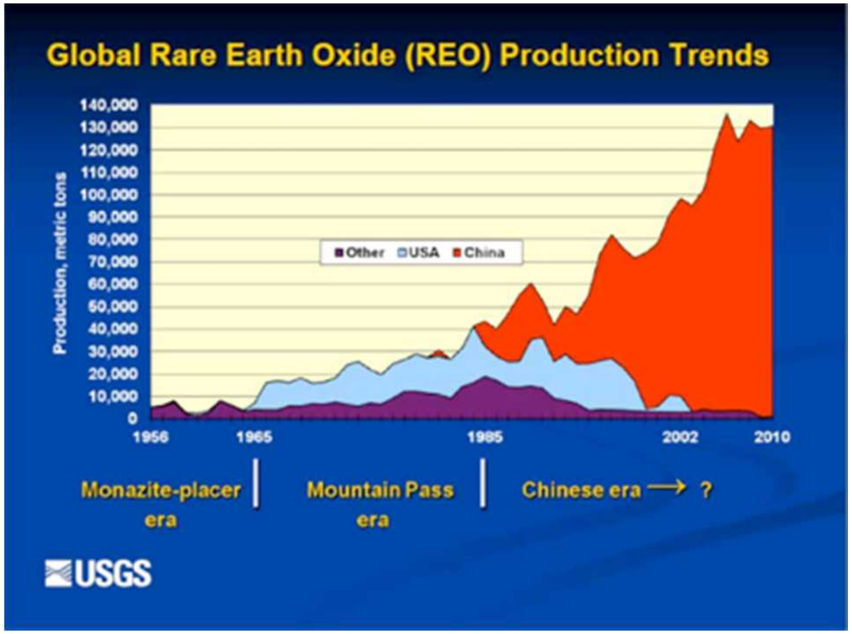
RE elements have found widespread utility:

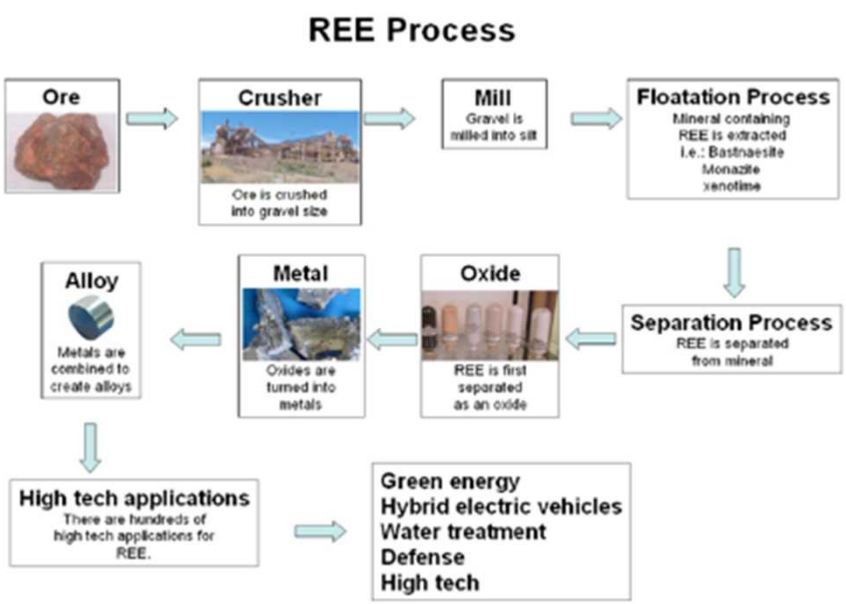
- *energy technology*
- *transportation*
- *electronic displays*
- *guidance systems*
- *national security*
- *lasers*
- *radar*
- *sonar systems*

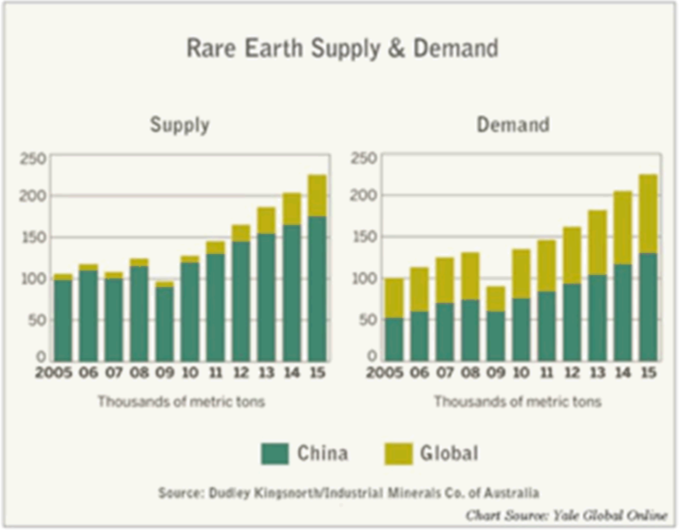
In the past few decades China has taken over the production of Ln_2O_3 materials.

<u>Ln Historically Abundant</u>

- 1950s: South Africa (monazite)
- 1960-1980: Mountain Pass (CA)
- 2010: Inner Mongolia, China
- 2011: MolyCorp resurrects Mountain Pass (CA) mine produces <95% Ln: only 37% world reserves, (2012 = 23 %)
- States Geological Survey (USGS) reveals US had 13 m metric tons Ln elements.







While RE are available in the US, the PUREX process to extract/isolate the elements limits utility.

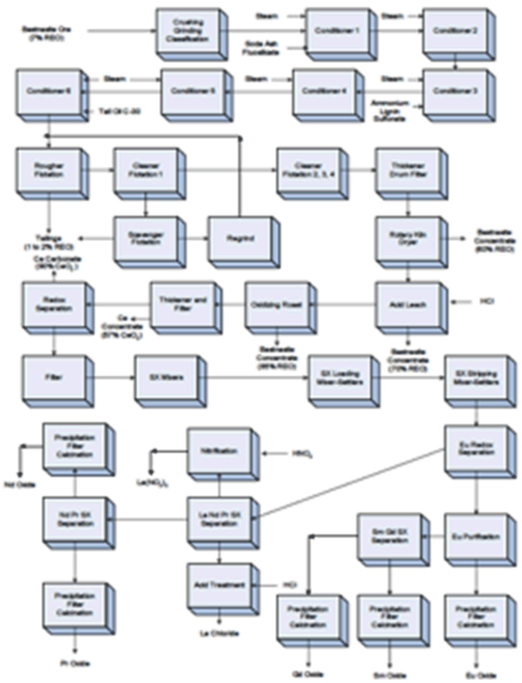


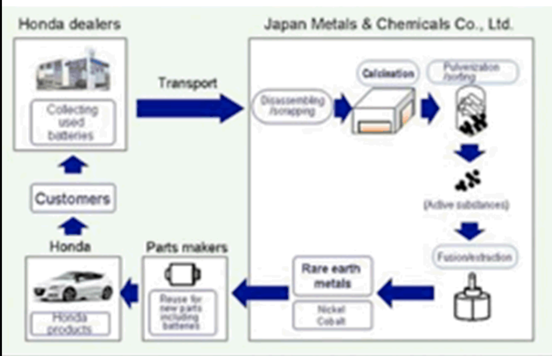
Figure 2. Rare earth elements mineral-processing flow sheet for the Mountain Pass mine, California, about 1995. From one type of ore, no less than 12 rare earth elements products were obtained. REO, rare earth oxides; Ce, cerium; Eu, europium; Gd, gadolinium; La, lanthanum; Nd, neodymium; Pr, praseodymium; Sm, samarium; HCl, hydrochloric acid. (Gupta and Krishnamurthy (2005), Castor and Hedrick (2006)).

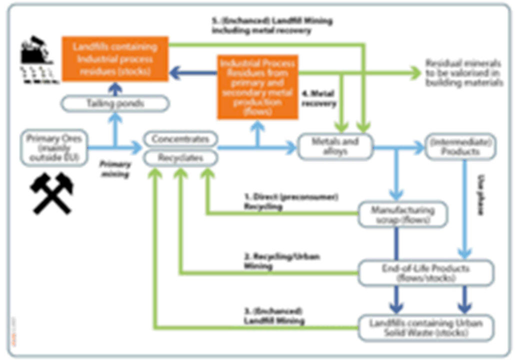
- **1949** - discovered by a uranium prospector who noticed the anomalously high radioactivity.
- **1952** - The Molybdenum Corporation of America bought the mining claims, and small-scale production began in 1952.
- **1960** - Production expanded greatly to supply demand for europium used in color television screens.
- **1965 – 1995** - larger scale; supplied most of the worldwide Re^{o}.
- **2002** - mine closed in response to environmental restrictions and lower prices for REEs.
- **2008** - Molycorp Minerals LLC revives the Mountain Pass mine
- **July 29, 2010**, Molycorp, Inc. became a publicly traded firm

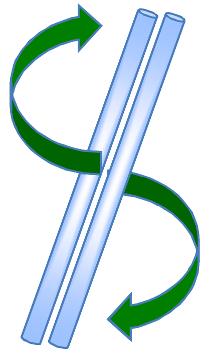
Molycorp filed for bankruptcy in June 2015.
In August 2015, it was reported that the mines was to be shutdown.

RE-cycle a possible route to reduced dependency.

Currently, only 1% of the RE-containing consumables are recycled.







- Honda (Japan) recently announced that key materials for their hybrid automobiles (which include RE oxides) will be recycled.

- Rhodia (France) has begun to reactivate its production plant to recover Tb and other RE elements from magnets, windmill components, electric vehicles and hard disks.

- Hitachi, Ltd. announced plans for recycling RE-magnets from hard disk drive motors, air conditioners, and other compressors. Developed machinery to separate and collect RE using an experimental dry process.

- Sandia 8700 kg of fluorescent waste, a loss $900,000 in RE material (per 2 yrs).

New extraction methods are necessary to aid in the RE-utilization of other ‘waste’ RE-materials (i.e., fluorescent bulbs and magnets).

Companies trying to take advantage of this need.

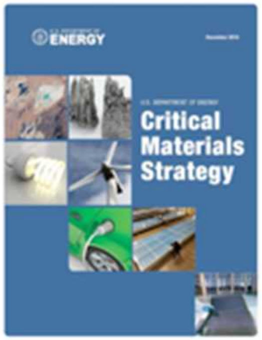
- REEcycle (U. Houston) has a patented method to extract Dy/Nd from neo-magnets.

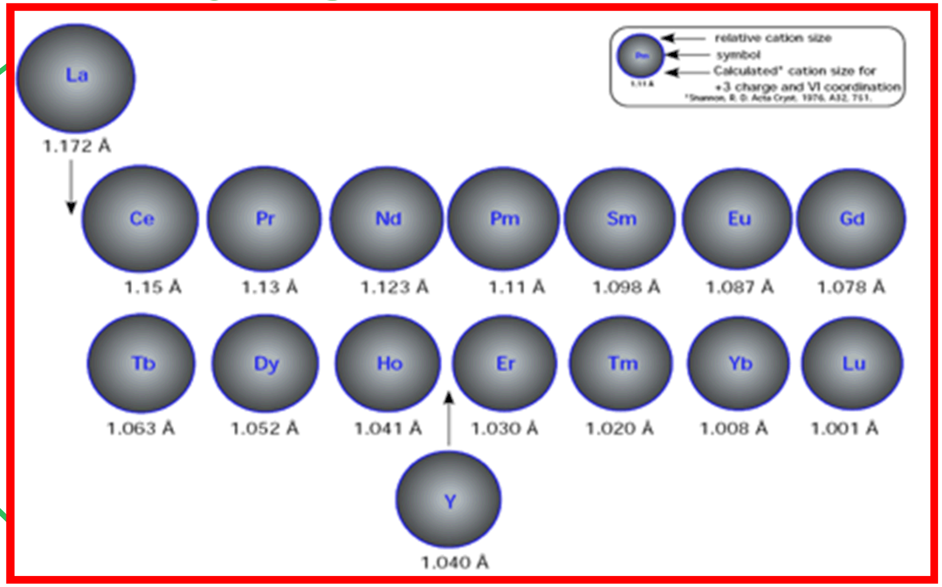
- Ames Laboratory and Critical Materials Institute has an imidazole borate ionic liquid to dissolve lanthanide oxides.

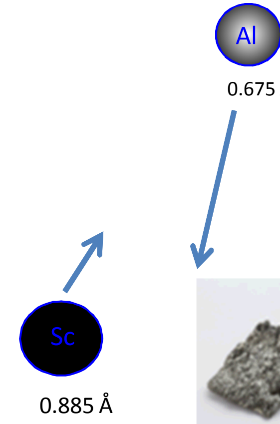
REEcycle

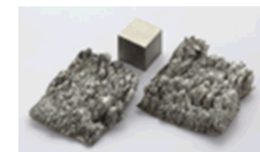
THE Ames Laboratory
Creating Materials & Energy Solutions
U.S. DEPARTMENT OF ENERGY

Everyone is studying Ln's. What happened to Sc?









Scandium:

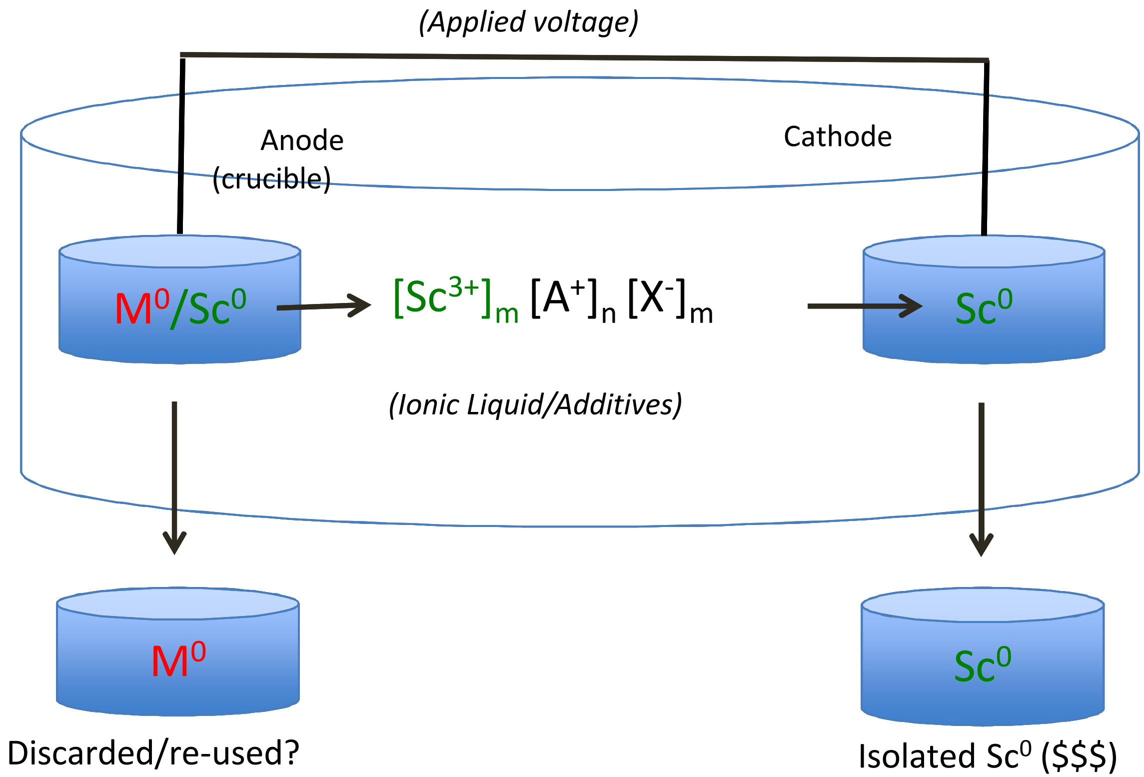
- discovered by Lars Fredrik Nilson, a Swedish chemist, in 1879
- Sc° was first produced in 1937 and the first pound (0.45 kilograms) produced in 1960.
- 18 to 25 ppm comparable to the abundance of Co (20–30 ppm).
- 50th most common element on Earth; 35th most abundant in the crust.
- trace amounts in many minerals: thortveitite, euxenite, and gadolinite.
- less than 22 pounds of Sc° is produced annually
- $75 – 270+ per gram.

Thortveitite
$(Sc,Y)_2Si_2O_7$ 24 % Sc

Sc has widespread utility –

- *20 kg (as Sc_2O_3) are used annually in the US for high intensity lights*
- *alloys – reduces crystallite precipitation; strenthens • Fuel cells •germination of seeds*
- *aerospace industry components • Hg vapor lights (sunlight) • tracing agents in oils*
- *sports equipment (bats, bicycles, lacrosse sticks, • firearms • dentists (Er,Cr:YSGG) lasers*

Primary Question:
How is elemental Sc^0 recovered with high purity?

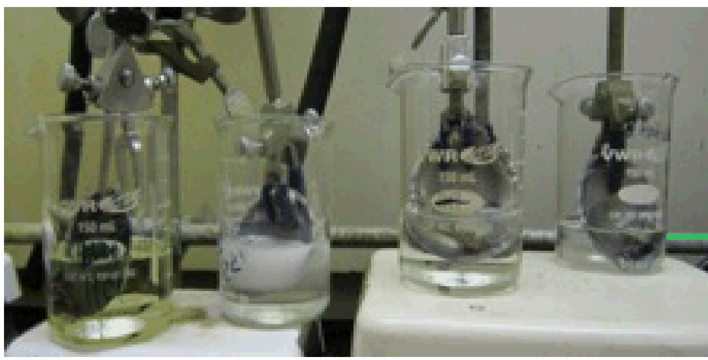


- Standard reduction potentials indicates selective oxidation is thermodynamically possible

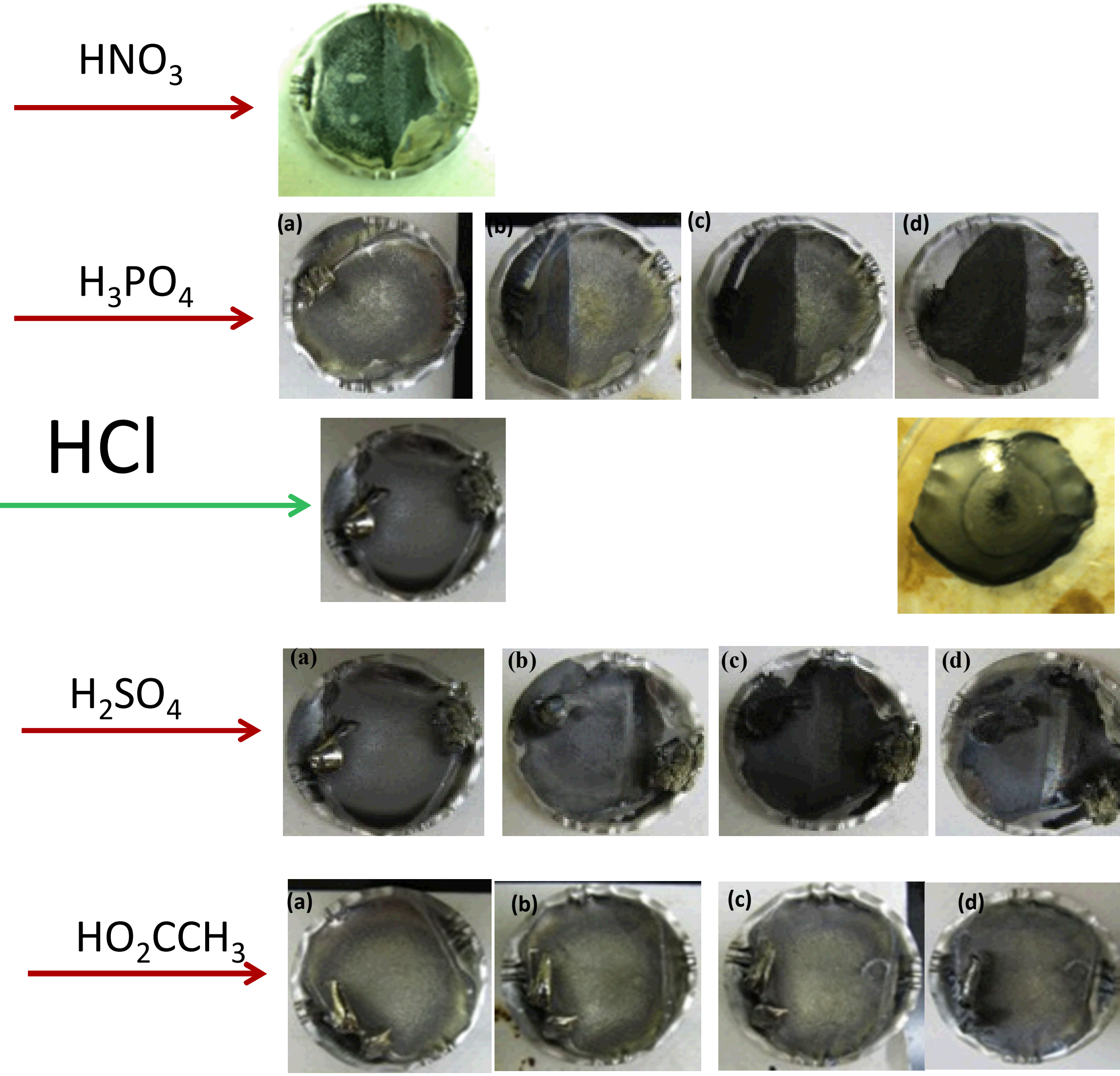
$Sc^{3+} + 3e^- = Sc^0 \; E^o = -2.03$ V

- Ionic Liquids$[A^+][X^-]$:
  - *electro-chemical window > 4-5 V*
  - *negligible vapor pressure*
  - *low viscosity*
  - *no H_2 generation*
  - *IP opportunities*

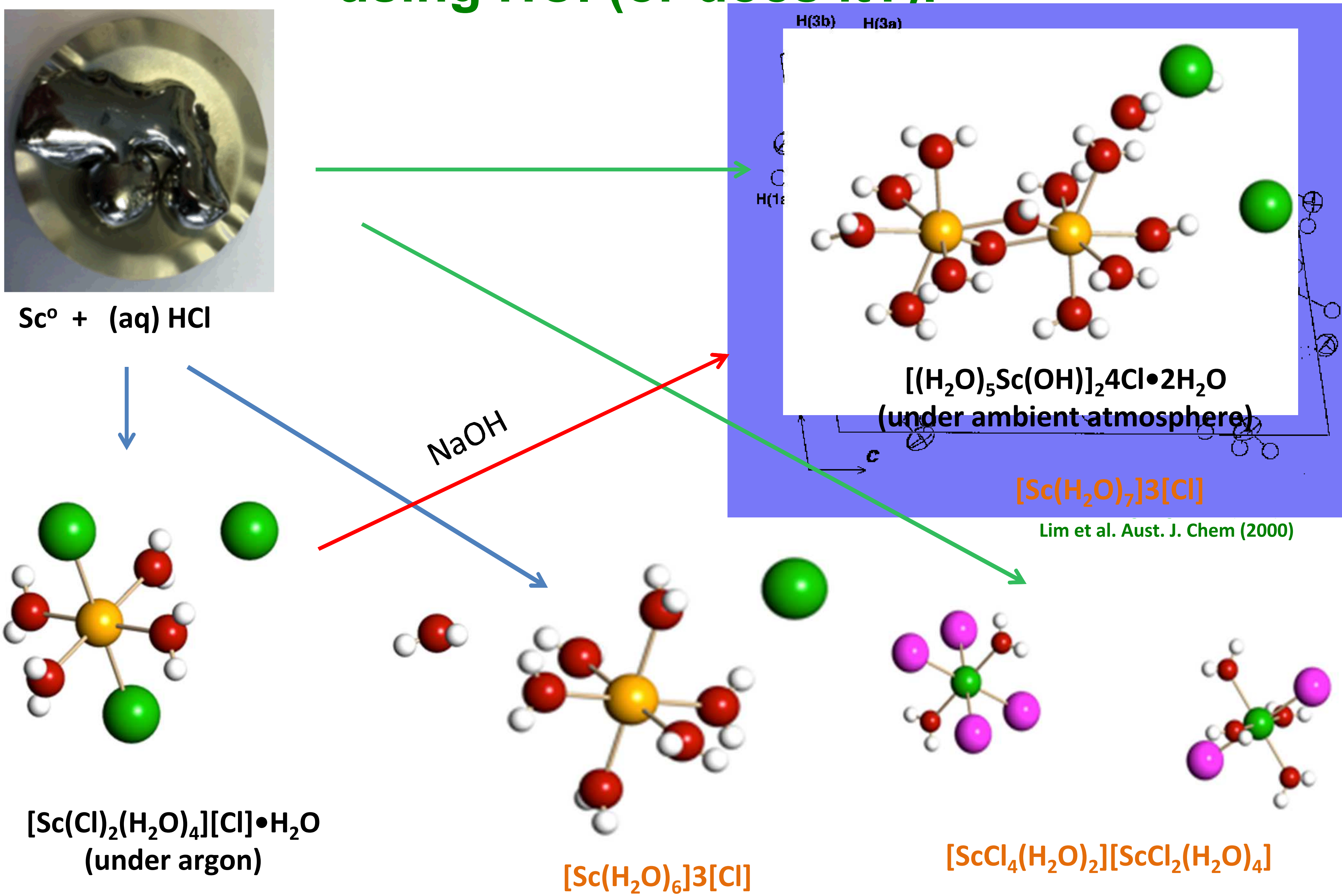
Dissolution of Sc° found to readily dissolve in (aq) HCl without disrupting the crucible (too much).



Experimental setup for Sc°/crucible



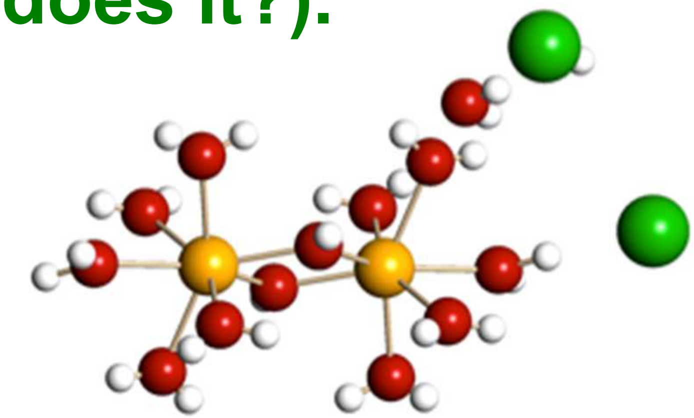
Dissolution of Sc° follows established chemistry using HCl (or does it?).



Dehydration of $ScCl_3$•$6H_2O$ follows established chemistry using HCl (or does it?).

Sc^o + (aq) HCl

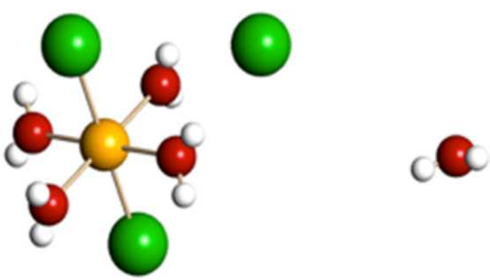
(aq) HCl →



$[(H_2O)_5Sc(OH)]_2 4Cl$•$2H_2O$
(at high temperature)

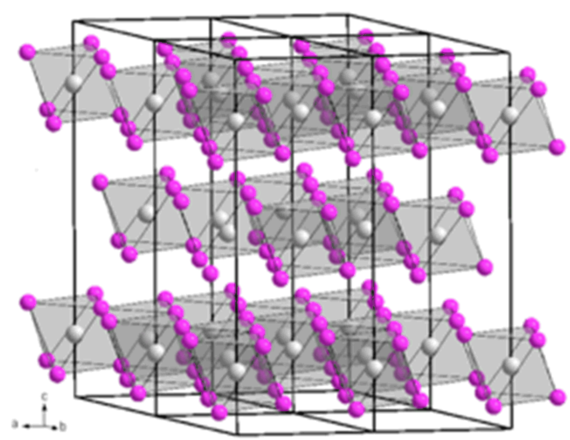
↓ SO_2Cl_2, THF

(aq) HCl ↓



$[Sc(Cl)_2(H_2O)_4]Cl$•H_2O
(at low temperature)

NH_4Cl or SO_2Cl_2 →

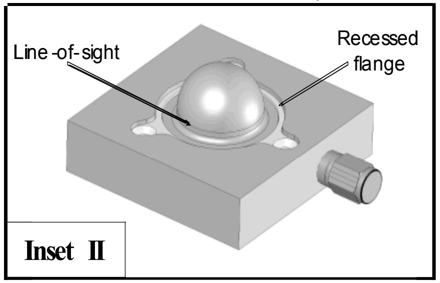


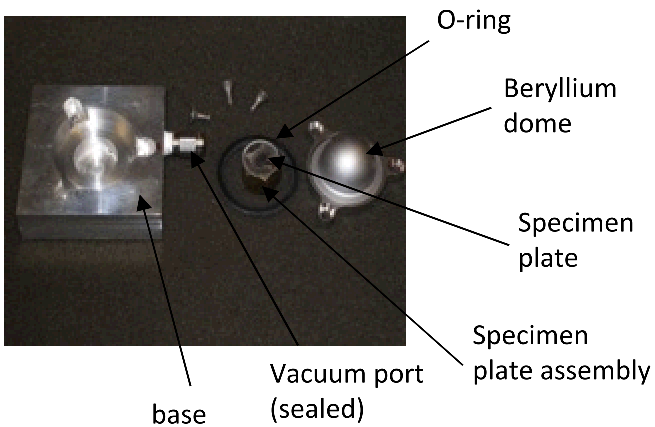
$ScCl_3$

https://de.wikipedia.org/wiki/Scandiumchlorid

‘Dry’ $ScCl_3$ verified(?) using. . .

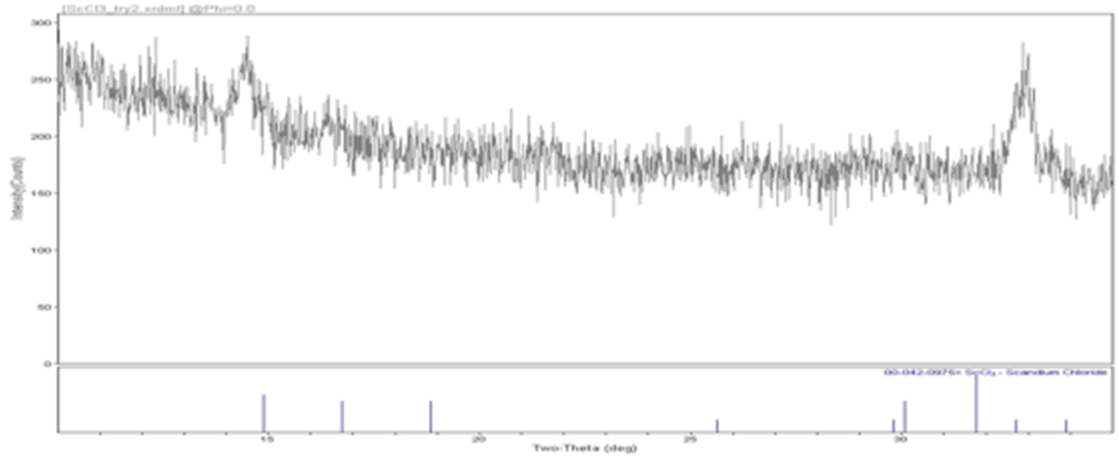
BeD-XRD



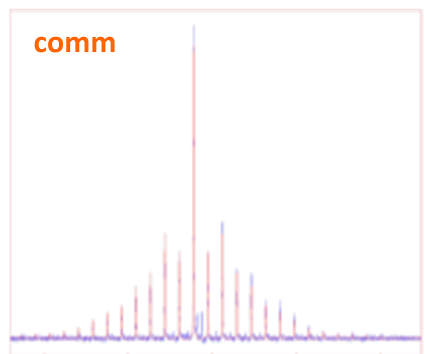


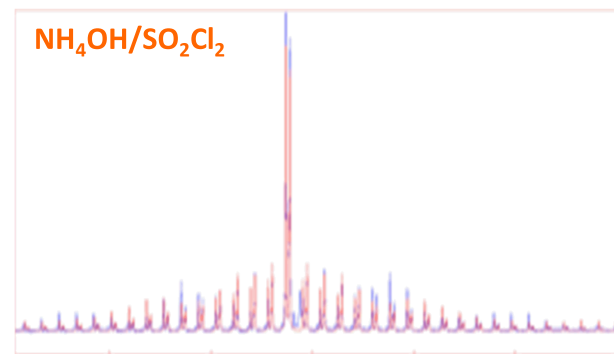
Complexometric titration:
$ScCl_3$ (29.7, %Sc):
comm. (29.7),
dried (19.6)

PXRD

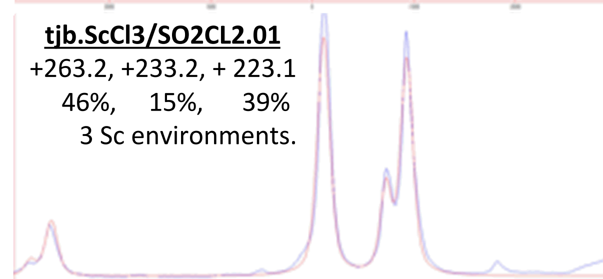


^{45}Sc NMR





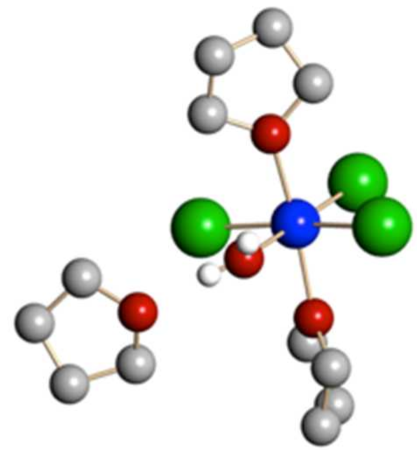
tjb.ScCl3.comm.01
+221.5 (100 %)



tjb.ScCl3/SO2CL2.01
+263.2, +233.2, + 223.1
46%, 15%, 39%
3 Sc environments.

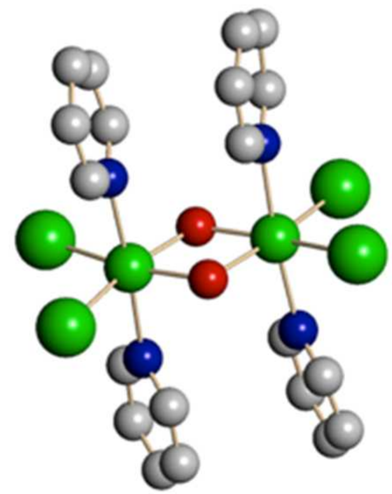
… (un)verified using single crystal X-ray diffraction

$ScCl_3 \cdot nH_2O$ —(NH$_4$OH dried)→ / —(SO$_2$Cl$_2$ dried)→ $ScCl_3$ —(THF)→



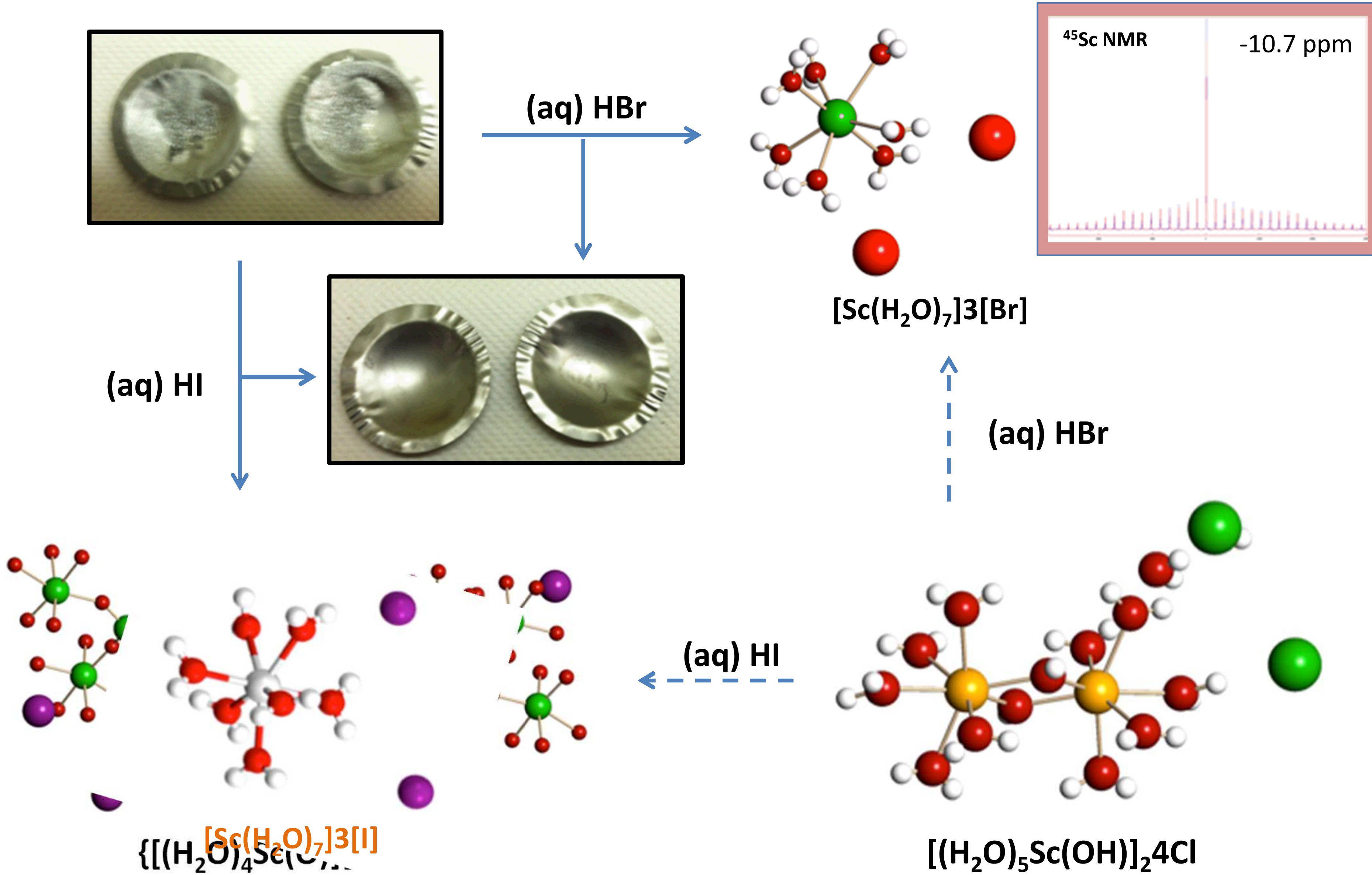
$[(H_2O)Sc(THF)_2] \bullet THF$

$[(H_2O)_5Sc(\mu\text{-}OH)]_2 4Cl \cdot 2H_2O$ —(NH$_4$OH dried)→ $ScCl_3$ —(py)→

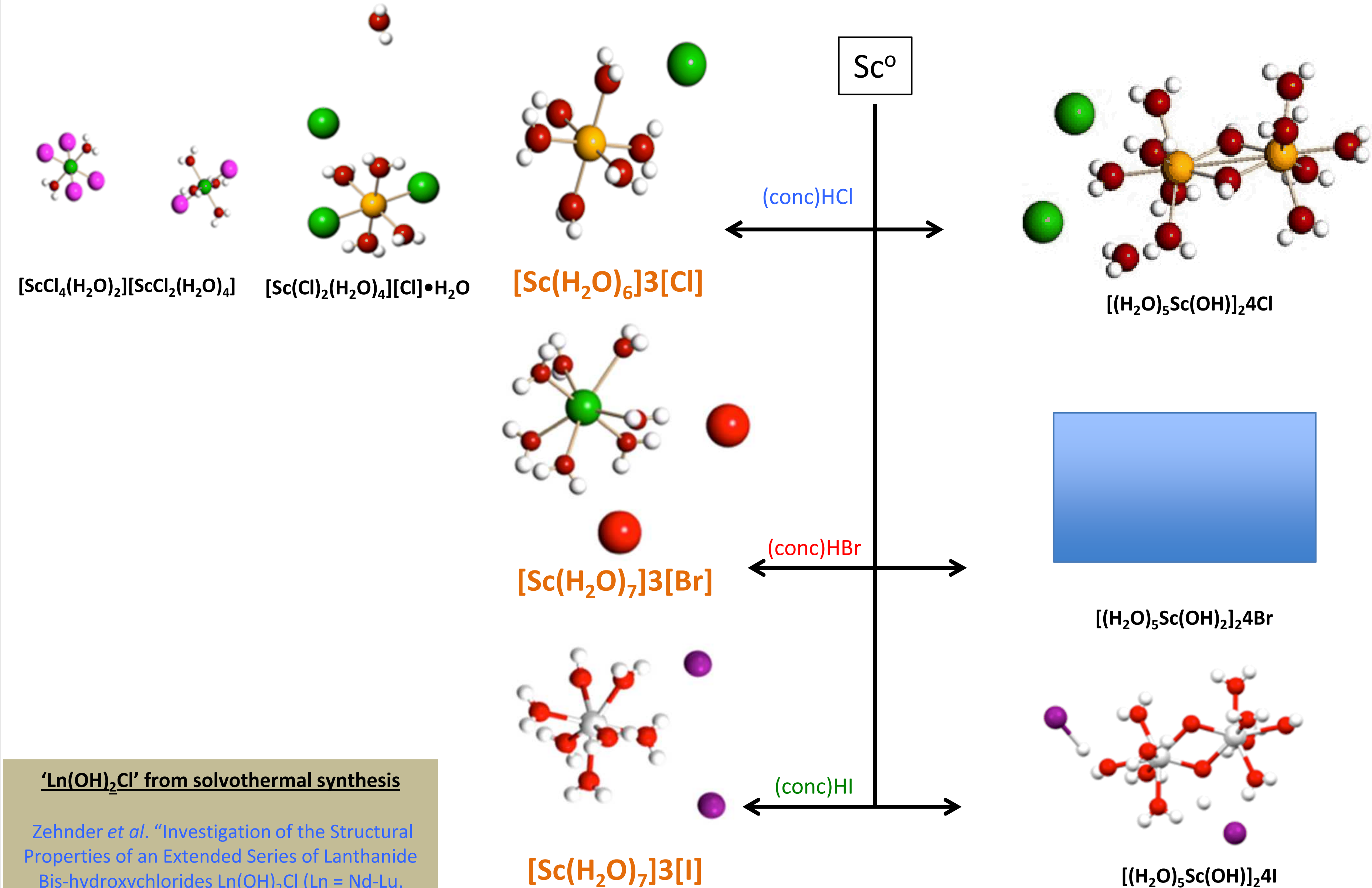


$[(py)_2Cl_2Sc(\mu\text{-}OH)]_2$

Other acids form hydrates as well from metal; from ‘$ScCl(OH)_2$’?



Halogenation of Sc is more complex than expected.



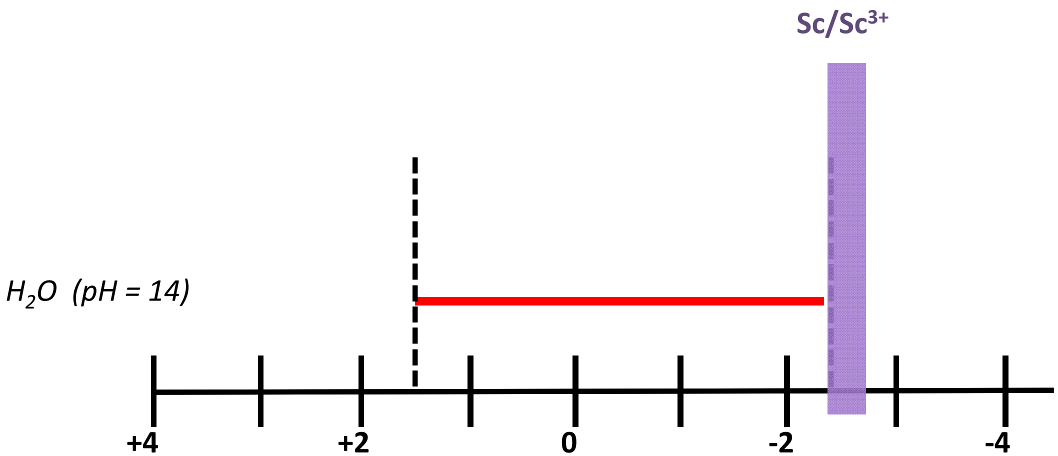
<u>'Ln(OH)$_2$Cl' from solvothermal synthesis</u>

Zehnder *et al.* "Investigation of the Structural Properties of an Extended Series of Lanthanide Bis-hydroxychlorides Ln(OH)$_2$Cl (Ln = Nd-Lu, except Pm and Sm)" *Inorg. Chem.* (**2010**) 4781.

Possible to reduce the Cl/H_2O species?

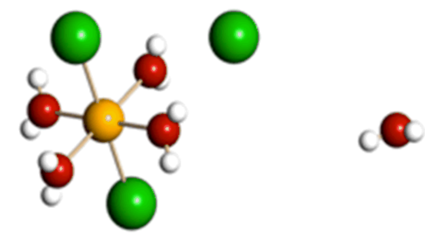
Sc^o ⇄ $ScCl_3 \bullet nH_2O$ *and/or* $[Sc(OH)(H_2O)_5]_2 4[Cl]$

(e^- reduction, dashed arrow to the left; **HCl**, arrow to the right)

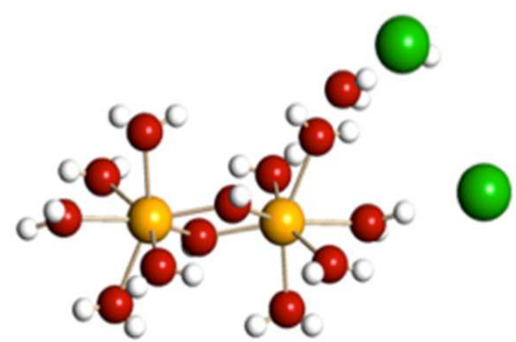


Potential (V vs Fc/Fc⁺)
vs ferrocene
(voltage limit set a 1 mA/cm²)

(Fc/F⁺) is 0.4 vs NHE)



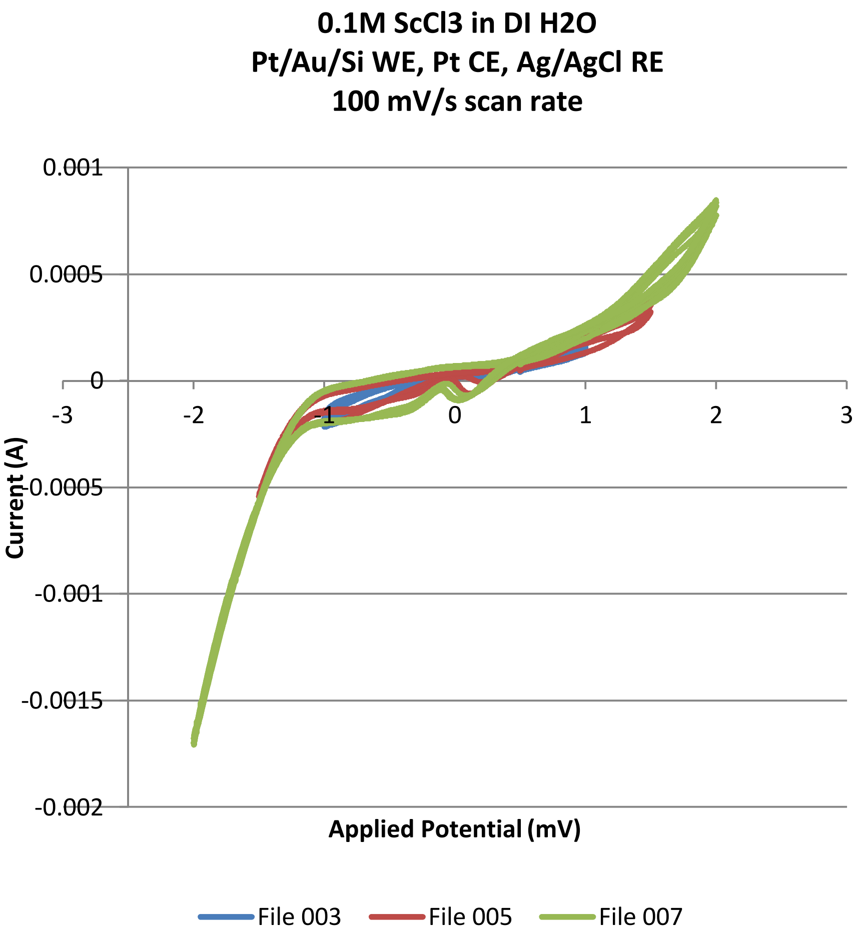
$[Sc(Cl)_2(H_2O)_4]Cl \bullet H_2O$



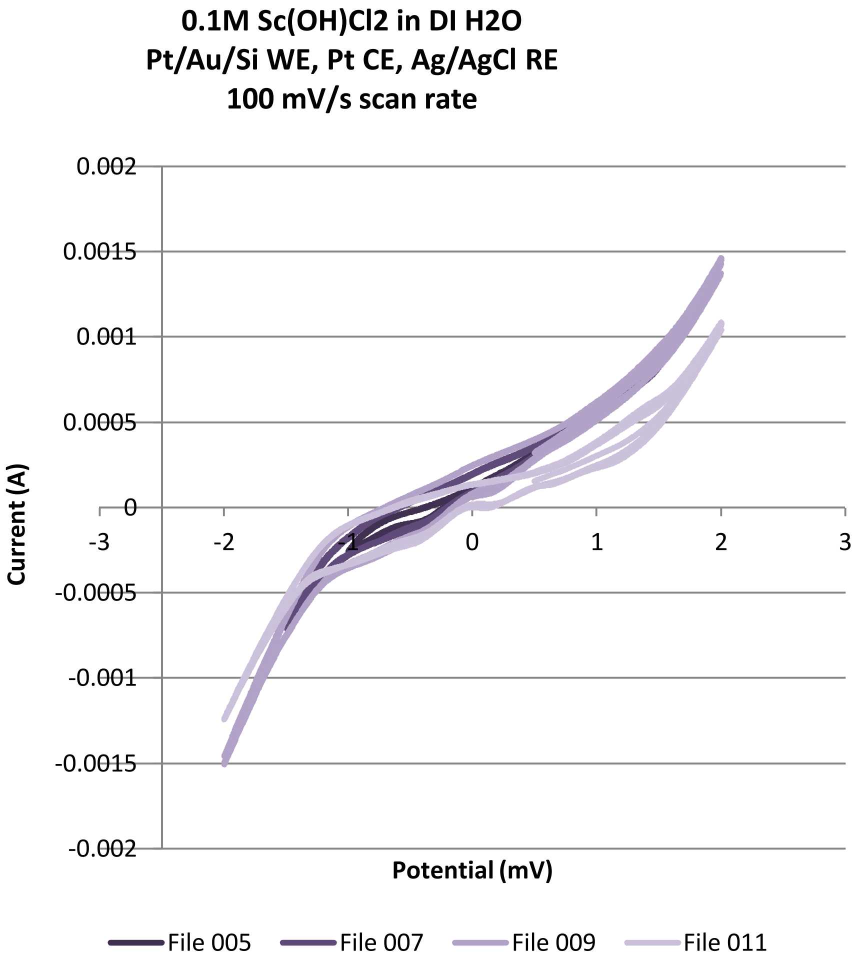
$[(H_2O)_5Sc(OH)]_2Cl_4$

Izutsu et al. "Electrochemistry in Nonaqueous Solutions"

Electrochemical reduction, in water, of $[ScCl_2(H_2O)_6]Cl \cdot H_2O$ and $[(H_2O)_5Sc(OH)]_2 4Cl$



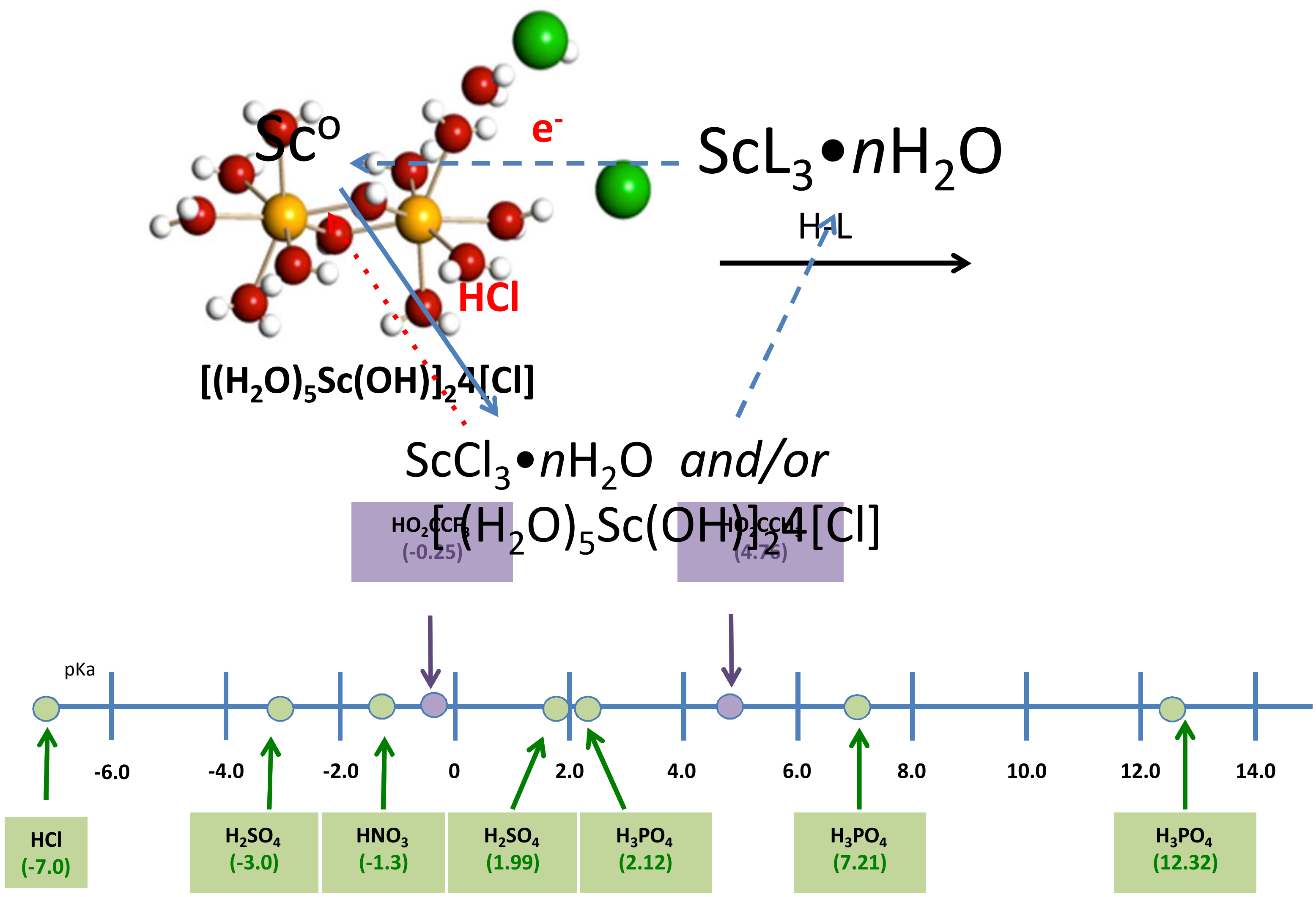
$[Sc(Cl)_2(H_2O)_6]Cl \cdot H_2O$



$[(H_2O)_5Sc(OH)]_2 4[Cl]$

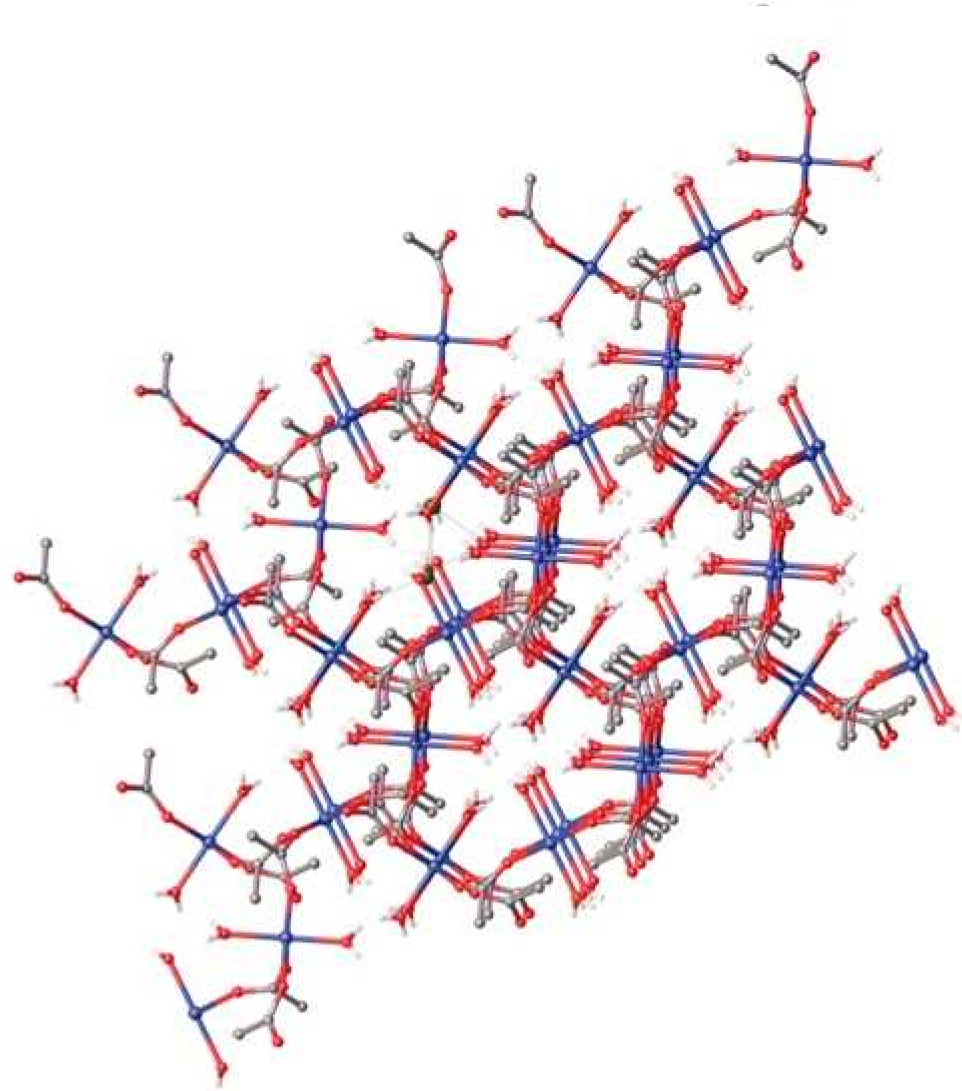
Chloride's not going to work for the reduction of Sc^{3+}.

Alternative approach, generate alternative ligand set with less complicated product set.



pKa of Inorganic and oxo-acids (http://evans.harvard.edu/pdf/evans_pka_table.pdf)

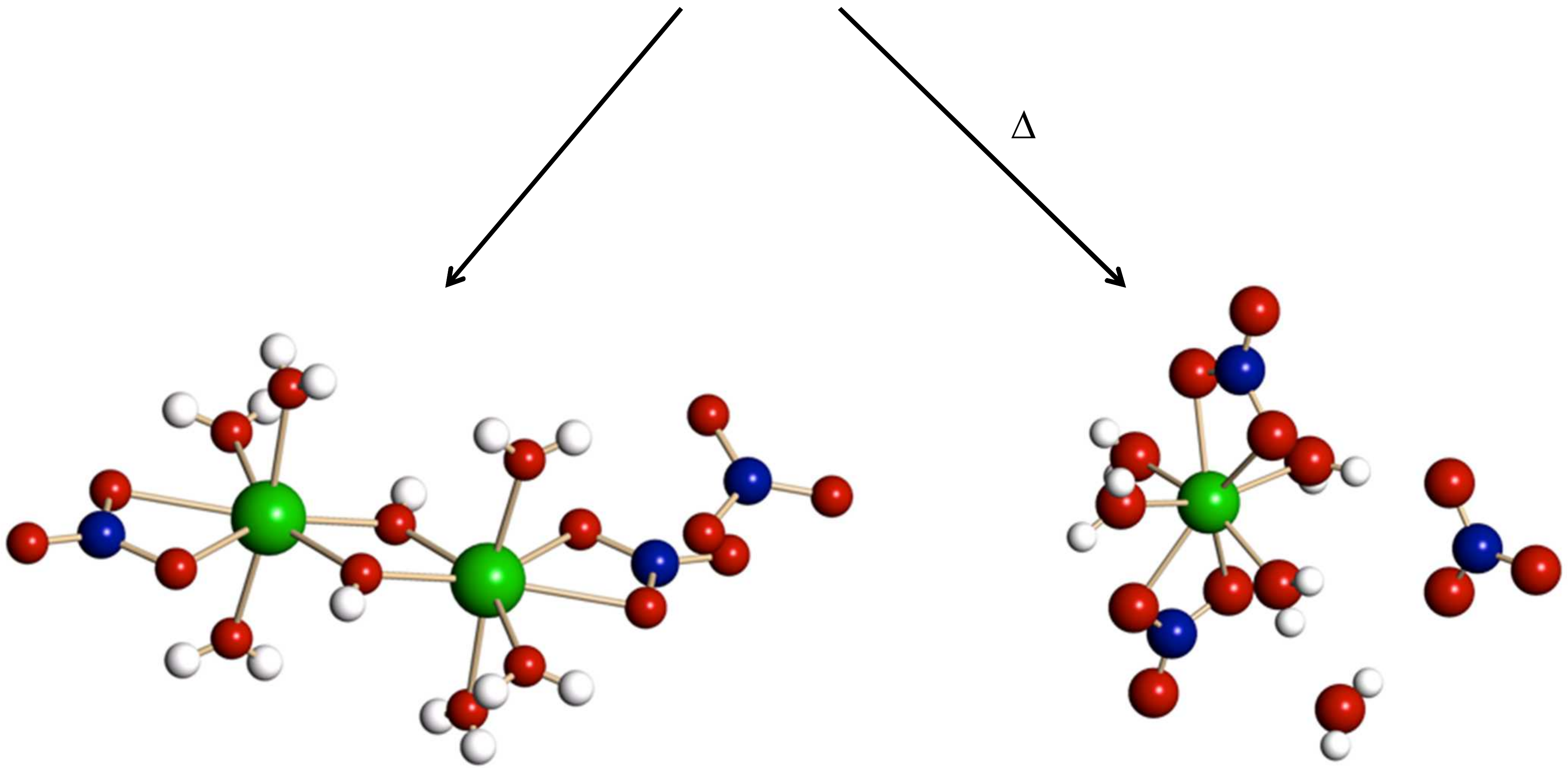
$[(H_2O)_5Sc(\mu\text{-}OH)]_2 4Cl \cdot 2H_2O + (xs)\ HO_2CCH_3 \longrightarrow$



$[Sc_6(\mu\text{-}OAc)_{12}(H_2O)_{12}]6[Cl]$

Fuchs, R.; Strahle, J., *Z. Naturforsh., B: Chem. Sci.* **1984,** *39*, 1662.

$[Sc(\mu\text{-}OH)(H_2O)_5]_2 4[Cl]\bullet H_2O$ + (xs) HNO_3



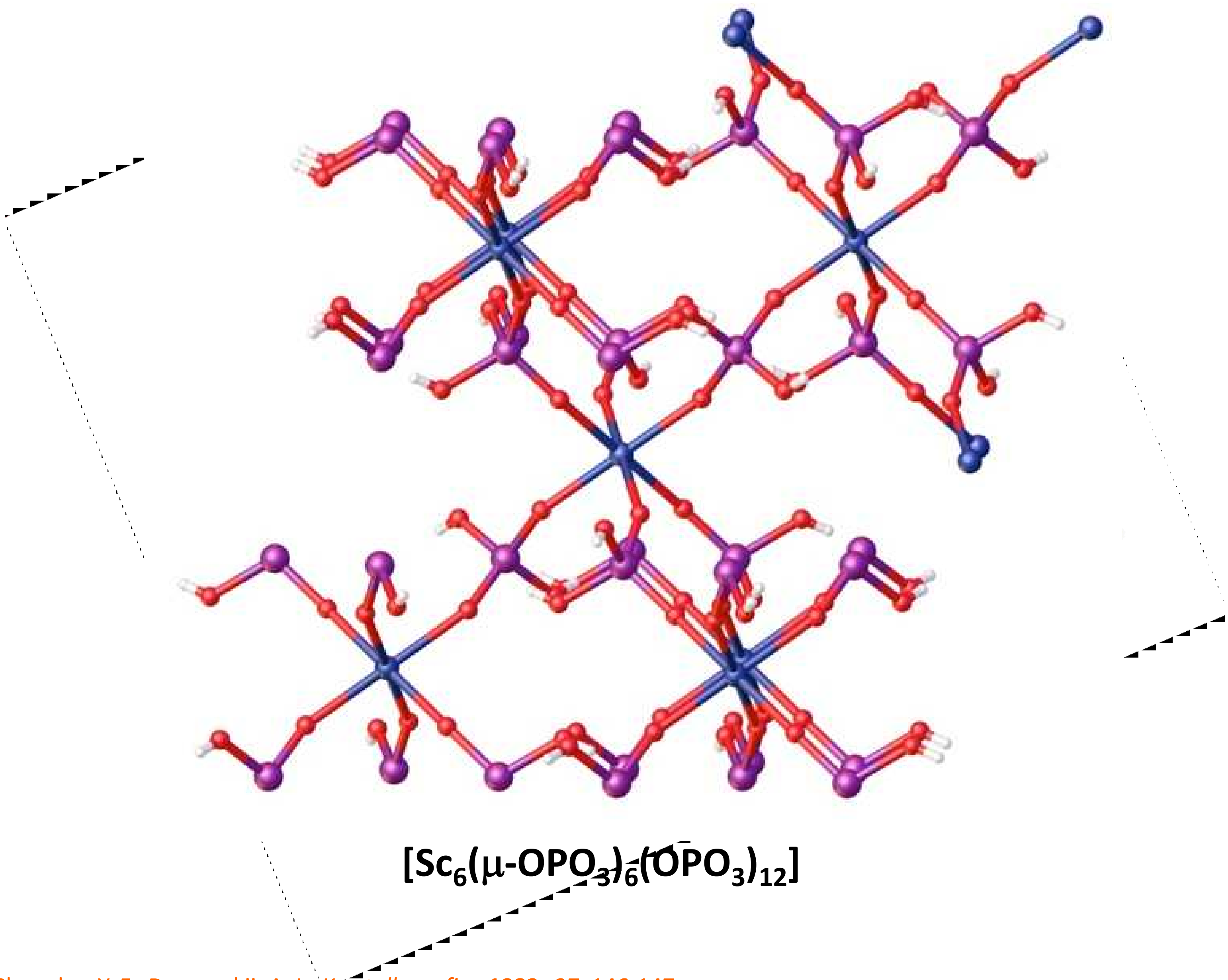
$[Sc(\mu\text{-}OH)(NO_3)^c(H_2O)_3][NO_3]$

$[Sc(O_2NO)^c{}_2(H_2O)_4][NO_3]\bullet H_2O$

Arif, A. M.; Hart, F. A.; Hursthouse, M. B.; Thornton-Pett, M.; Zhu, W., *J. Chem. Soc., Dalton Trans.* **1984**, 2449-2454.

Brown, M. D.; Levason, W.; Murray, D. C.; Popham, M. C.; Reid, G.; Webster, M., *J. Chem. Soc., Dalton Trans.* **2003**, 857-865.

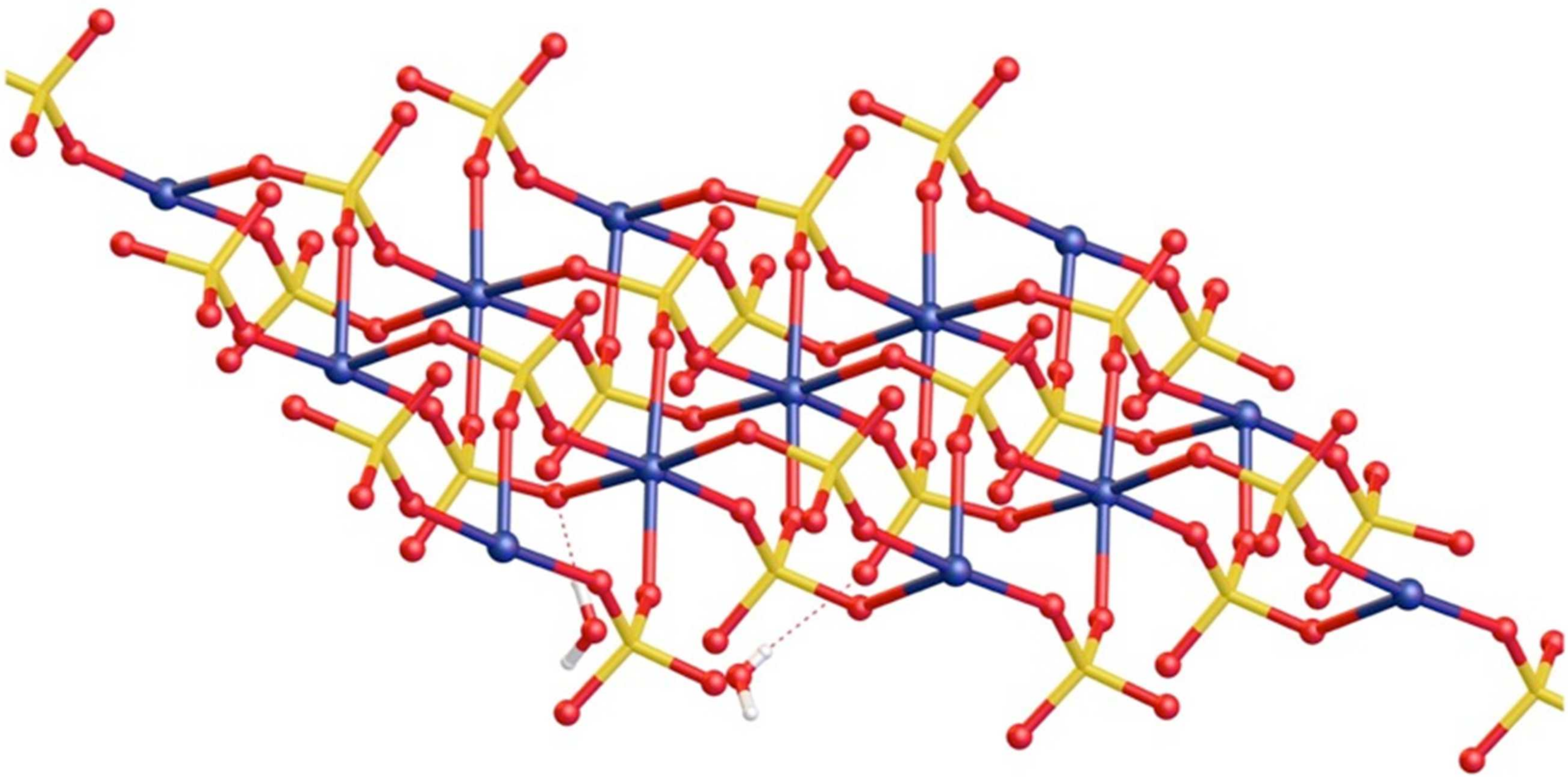
$Sc(\mu\text{-}OH)(H_2O)_5]_2 4[Cl] \cdot H_2O + (xs)\ H_3PO_4 \longrightarrow$



$[Sc_6(\mu\text{-}OPO_3)_6(OPO_3)_{12}]$

Sholin, Y. I.; Shepelev, Y. F.; Domanskii, A. I., *Krystallografiya* **1982,** *27*, 146-147;

$[Sc(\mu\text{-}OH)(H_2O)_5]_2 4[Cl] \bullet H_2O + (xs)\ H_2SO_4 \longrightarrow$



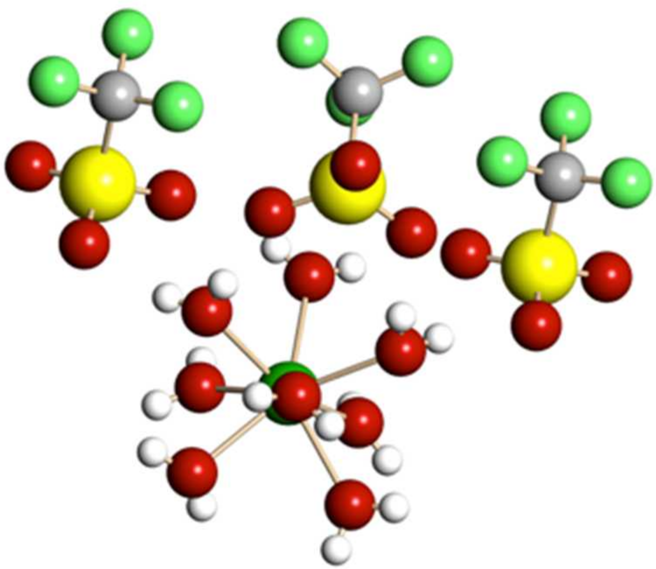
$[Sc_2(\mu\text{-}OSO_4)_3(H_2O)_2]_n$

Wickleder, M. S., *Z. Anorg. Allg. Chem.* **2000,** *626*, 1468-1472.

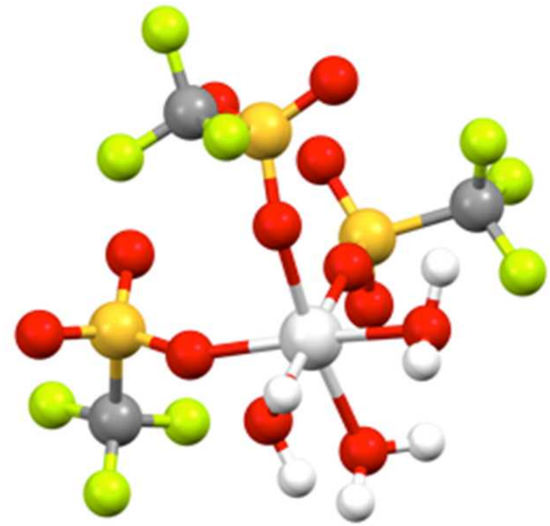
$Sc(\mu\text{-}OH)(H_2O)_5]_2 4[Cl]\cdot H_2O$ + (xs) $H_x\text{-}SO_n\text{-}R$

H-OTf →

F_3CSO_3H →



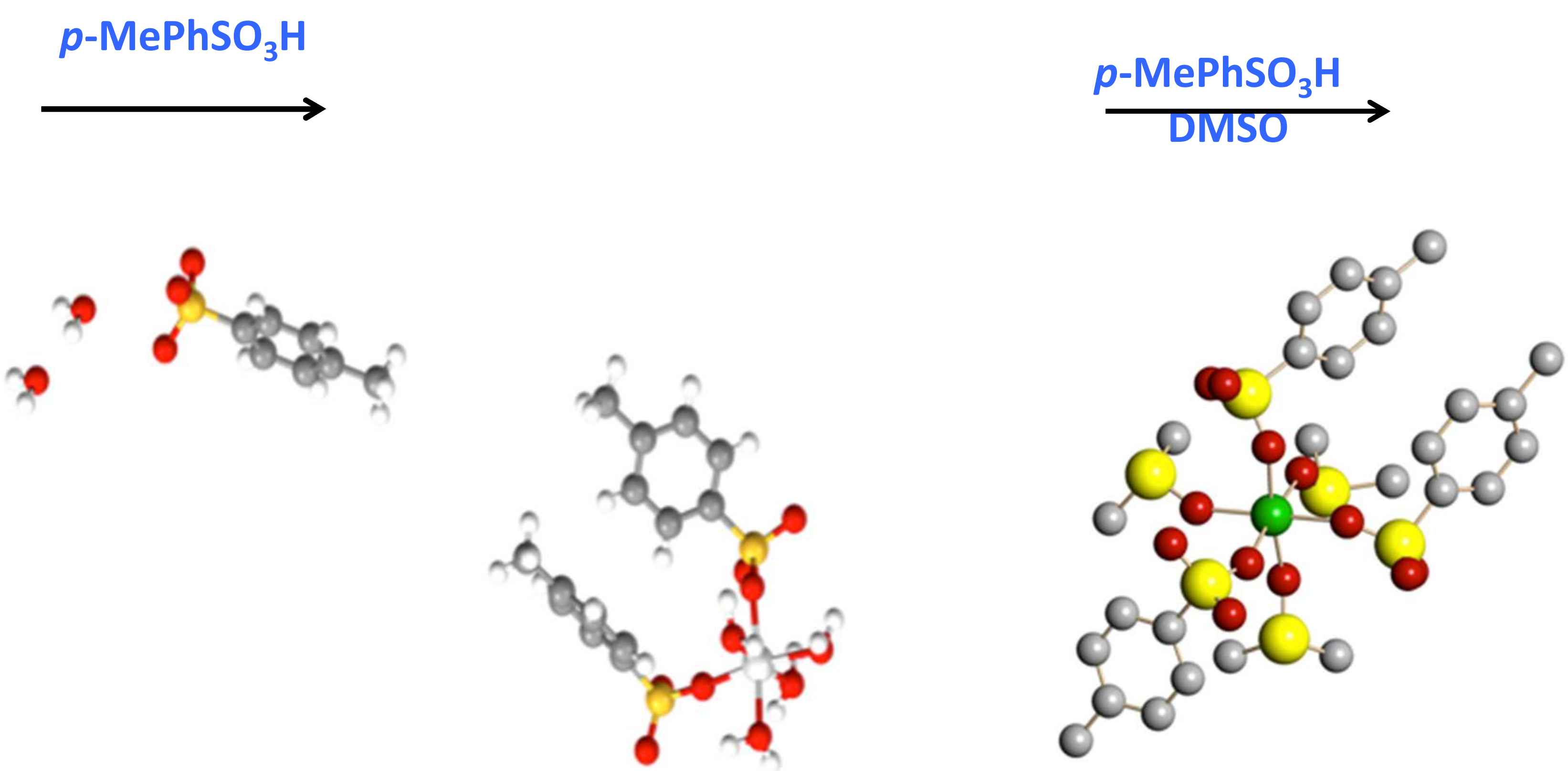
$[Sc(H_2O)_8]OTf_3$



$[Sc(O_3SCF_3)_3(H_2O)_3]$

Abbasi, A.; Lindqvist-Reis, R.; Eriksson, L.; Sandstrom, D.; Lidin, S.; Persson, I.; Sandstrom, M., *Chem-Eur. J.* **2005,** *11*, 4065-4077.

$Sc(\mu\text{-}OH)(H_2O)_5]_2 4[Cl] \cdot H_2O$ + (xs) $H_x\text{-}SO_n\text{-}R$



$[Sc(O_3SPhMe)_2(H_2O)_4][HSO_3PhCH_2(H_2O)_2]$

$(DMSO)_4Sc(Otf)_3$

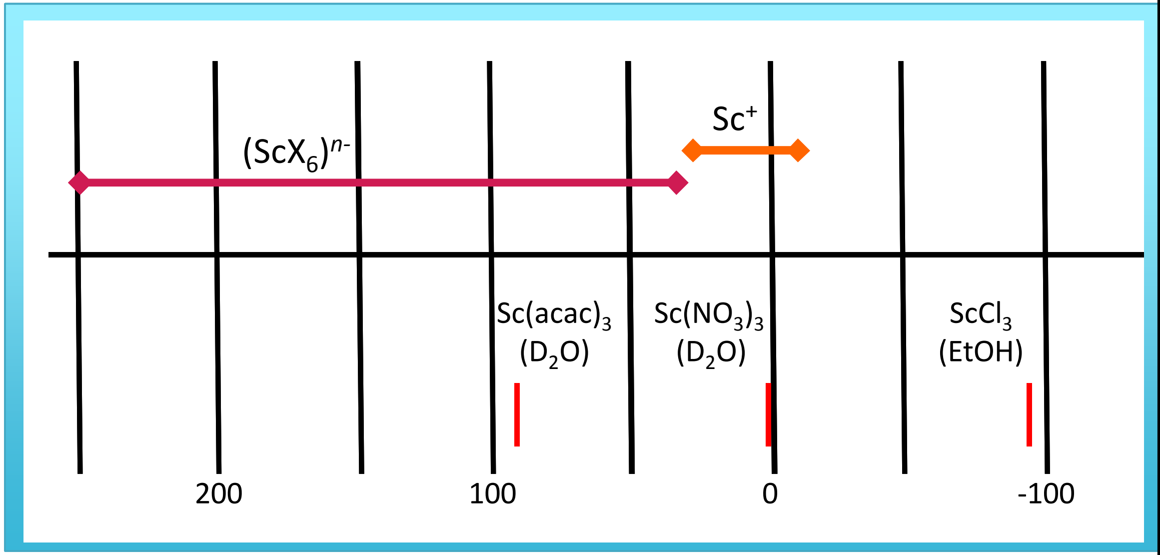
Ohki, Y.; et al *Bull Chem Soc Jpn.* 1988.

^{45}Sc NMR is surprisingly simple to obtain.

^{45}Scandium NMR

^{45}Scandium (45Sc) is a high sensitivity nucleus but with a 100% natural abundance that yields broad lines even in symmetric environments over a wide chemical shift range. 45Sc is a spin 7/2 nucleus and is therefore quadrupolar. As a result, the signal width increases with asymmetry of the environment.

^{45}Sc NMR is rarely used because scandium is rare and has a limited chemistry and when it is used it is to study the chemical environment of the scandium. Each type of Scandium compound has its characteristic chemical shift (fig. 2).



http://chem.ch.huji.ac.il/nmr/techniques/1d/row4/sc.html

^{45}Sc-NMR Properties

natural abundance = 100 %

spin (I) = 7/2;

Solution chemical shift range 350 ppm (-100 to 250 ppm)

Reference compound 0.06 M $Sc(NO_3)_3$ in D_2O

gyromagnetic ratio = 6.50880 x 10^7 rad/Ts (similar to ^{13}C)

magnetic moment (m) = 5.3933489 m_N

quadrapole moment (Q) = 0.22 x10^{-28} m^2 or -0.22 barn

$\nu_o(^{45}Sc)$ = 97.4 MHz (9.4 T) and 112.0 MHz (11.75 T)

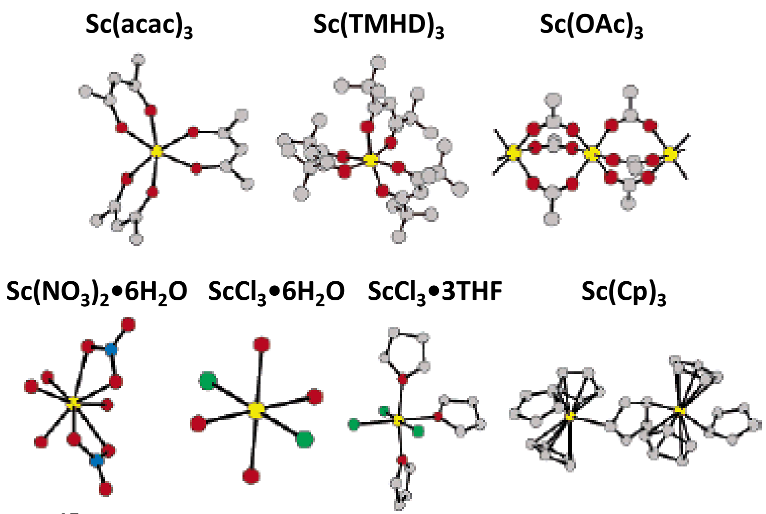
$T_1 = 5 \times 10^{-3}$ s

Frequency to ^{1}H (100 MHz) = 24.291747%

Relative receptivity to ^{13}C = 1730 (0.302 to ^{1}H)

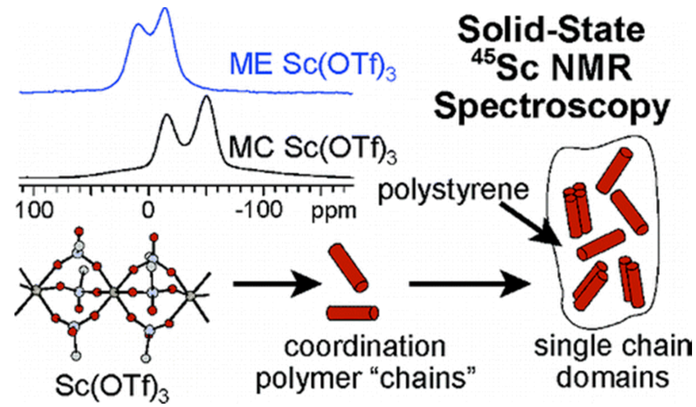
Linewidth parameter 66 fm^4

^{45}Sc NMR supposed to show coordination environment.



"^{45}Sc NMR signals are affected by both the symmetry of the coordination environment and nature of the bonding."

Rossini and Schurko *J. Am. Chem. Soc.* (**2006**).



"^{45}Sc quadrupolar coupling constants (C_Q) range from 3.9 to 13.1 MHz and correlate directly with the symmetry of the scandium coordination environment."

"^{45}Sc NMR isotropic chemical shifts and quadrupole coupling constants of several Sc-containing solid oxides prove to be sensitive to local structure. In these materials the ^{45}Sc isotropic chemical shift appears to be dominated by the coordination number."

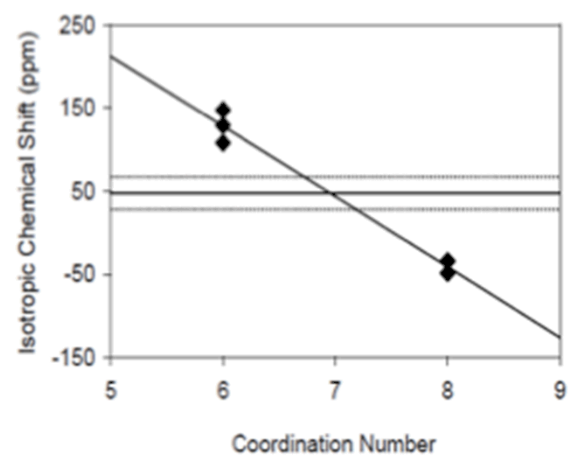
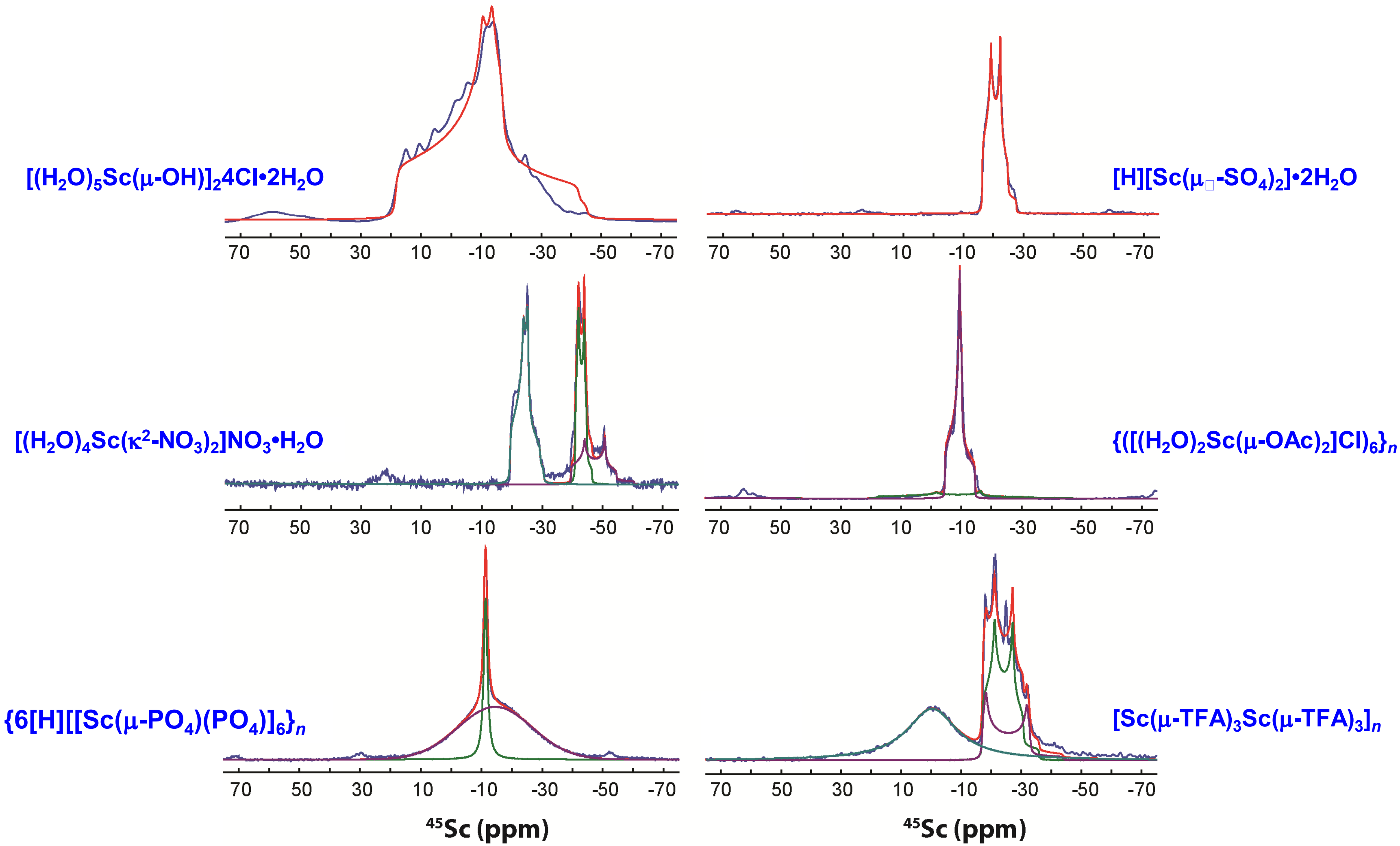


Figure 3. Isotropic chemical shifts for ^{45}Sc in model compounds (diamonds), vs. observed values for Sc-doped zirconia (horizontal lines).

Stebbins *Chem. Mater.* (**2006**).

^{45}Sc NMR solid state used to characterize the various $ScL_3(H_2O)_n$ compounds.

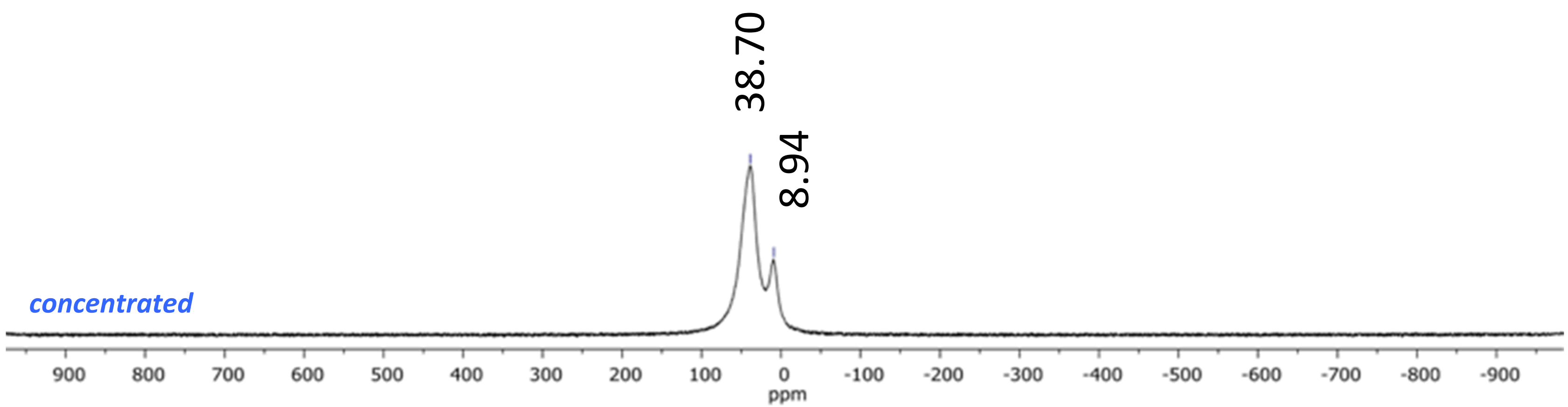


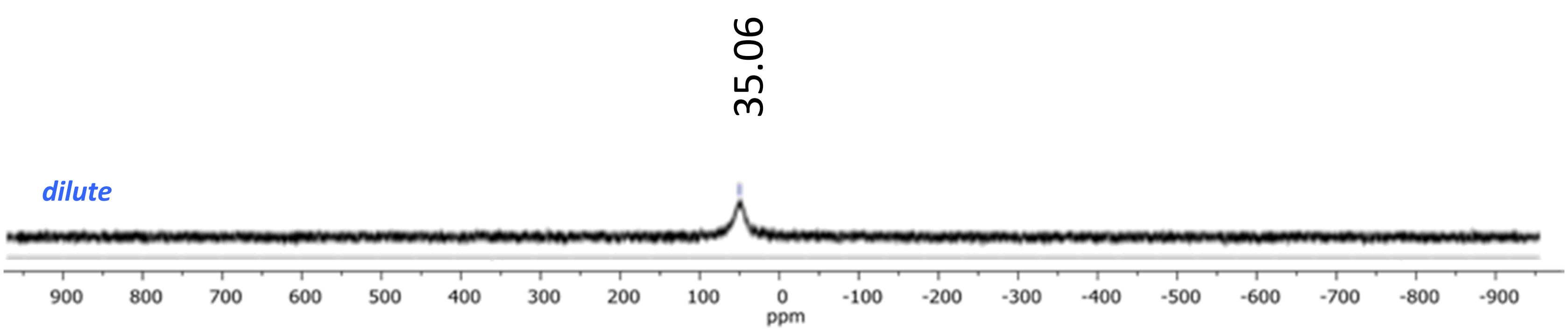
Solution state ^{45}Sc NMR of $[Sc(OH)Cl_2(H_2O)_4]_2$ compounds indicates equilibrium.

$[(H_2O)_5Sc(OH)]_2 4Cl$

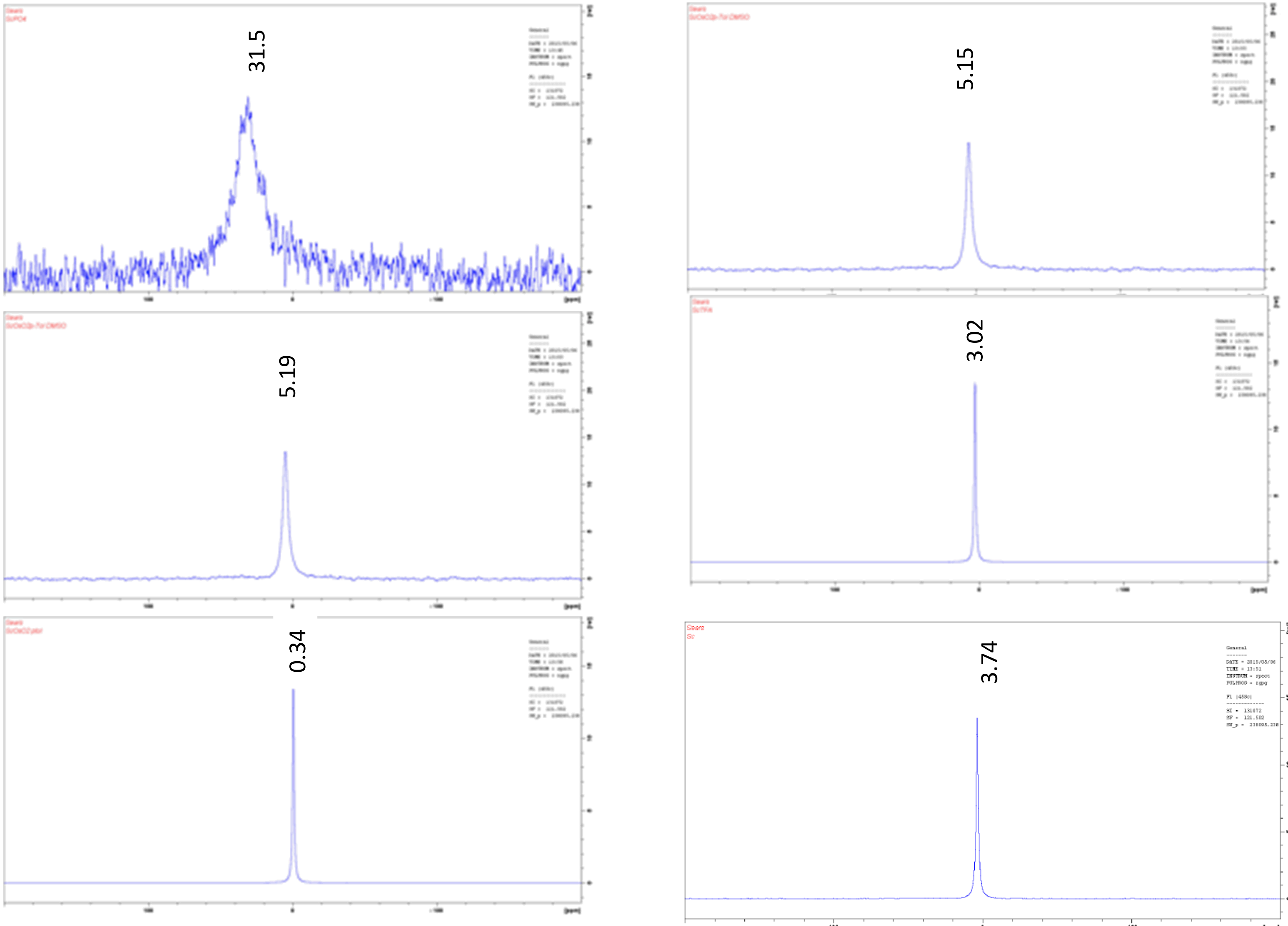
$[(H_2O)_5Sc(\mu\text{-}OH)]_2Cl_4 \xrightarrow[-\,H_2O]{+\,H_2O}$ "$[Sc(OH)Cl(H_2O)_5]Cl$" $\underset{-\,H_2O}{\overset{+\,H_2O}{\rightleftarrows}}$ "$[Sc(OH)(H_2O)_6]Cl_2$"

innersphere Cl — *outersphere Cl*





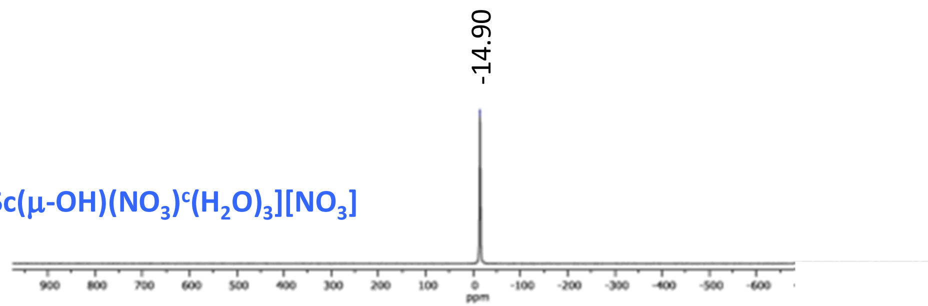
^{45}Sc NMR solution state of $ScL_3(H_2O)_n$ in H_2O all have resonance around 0.0 ppm



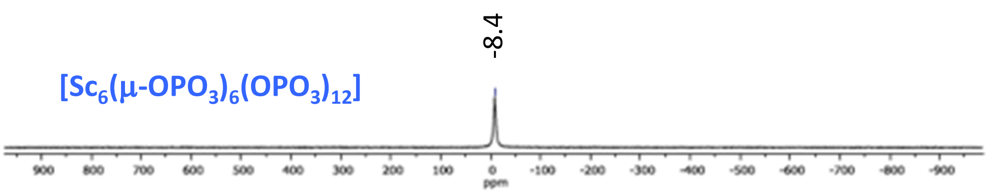
The fact that all the Sc-L species formed the $[Sc(H_2O)_6]^{3+}$ species means WATER is not a good choice of solvent for e-chem Sc^o RE-cycle.

^{45}Sc NMR solution state of $ScL_3(H_2O)_n$ in H-L all have different resonances.

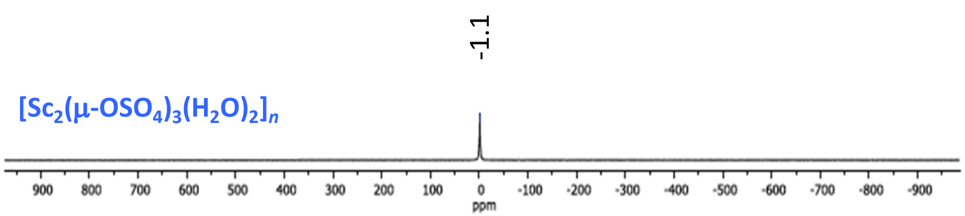
[Sc(μ-OH)$(NO_3)^c(H_2O)_3$][NO_3]



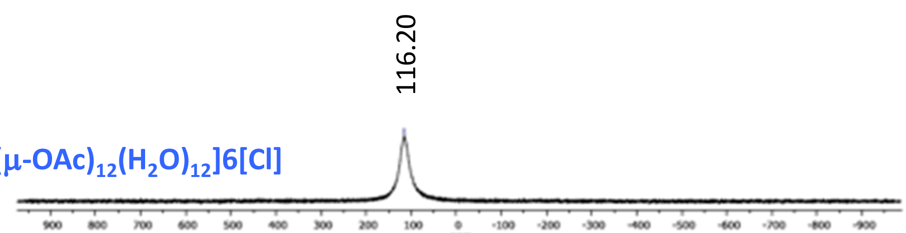
[Sc_6(μ-$OPO_3)_6(OPO_3)_{12}$]



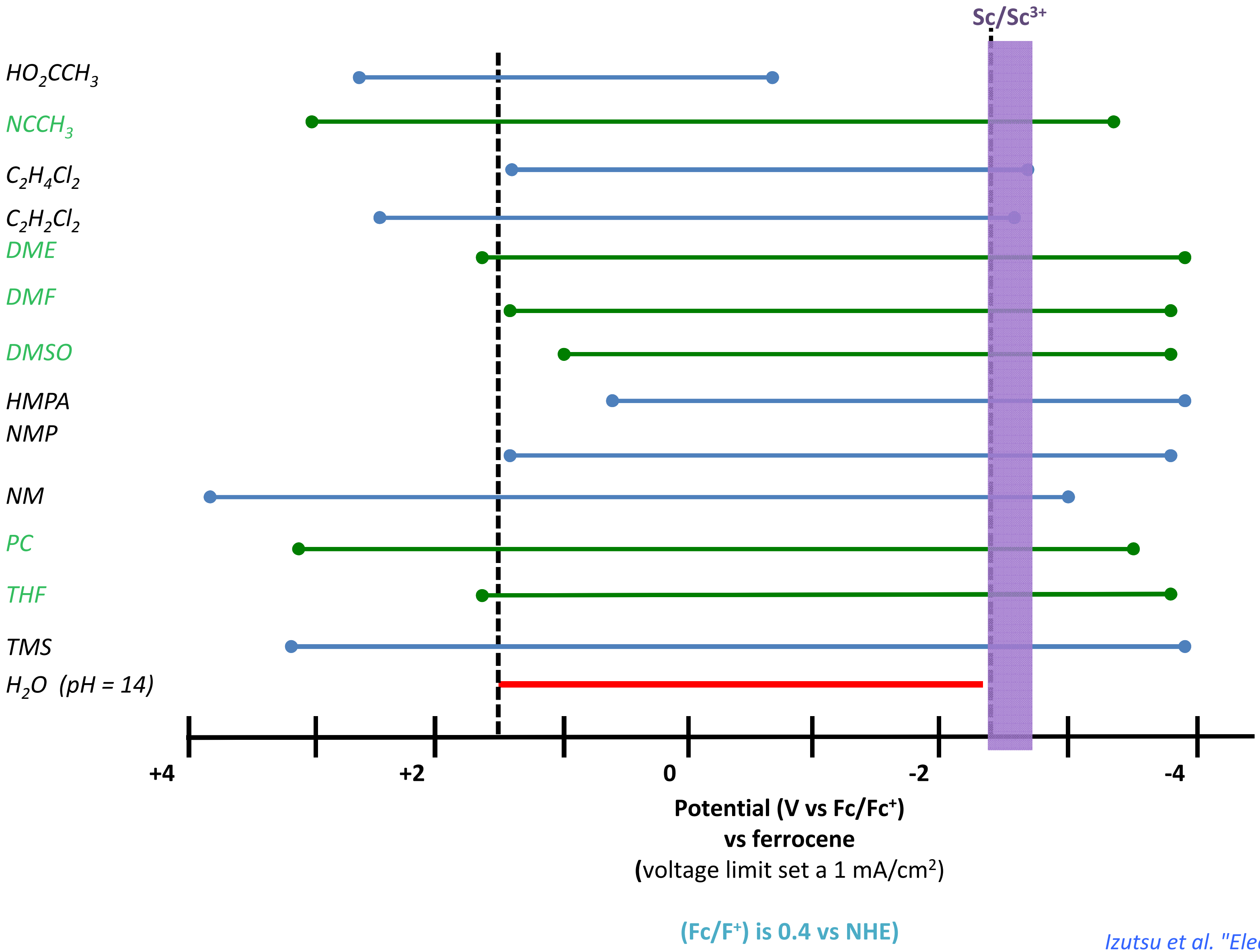
[Sc_2(μ-$OSO_4)_3(H_2O)_2]_n$



[Sc_6(μ-OAc)$_{12}(H_2O)_{12}$]6[Cl]



Select solvents with large enough window to reduce Sc^{3+}; determine solution structure.

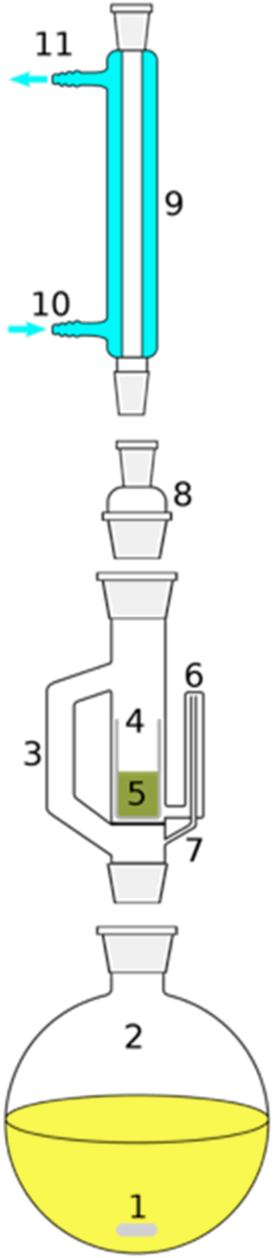


Izutsu et al. "Electrochemistry in Nonaqueous Solutions"

How to dry $ScCl_3(H_2O)_n$?

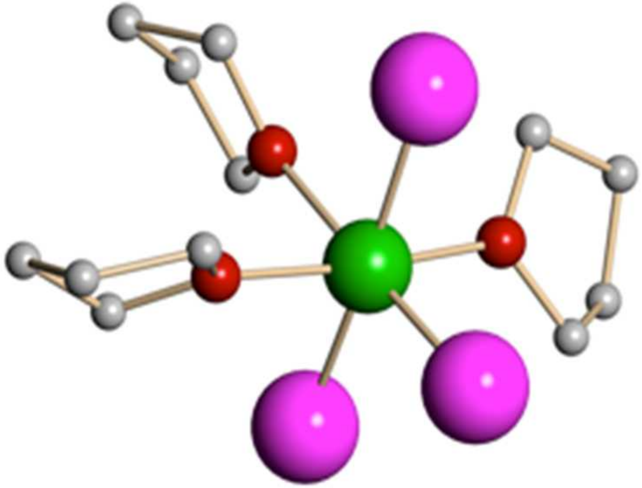
- DME/SO_2Cl_2
- Soxhlet Extraction in THF

Amico et al. "Improved preparation of anhydrous LNCl3 under mild conditions" Inorg. Chim. Acta (1995) 1 – 3.



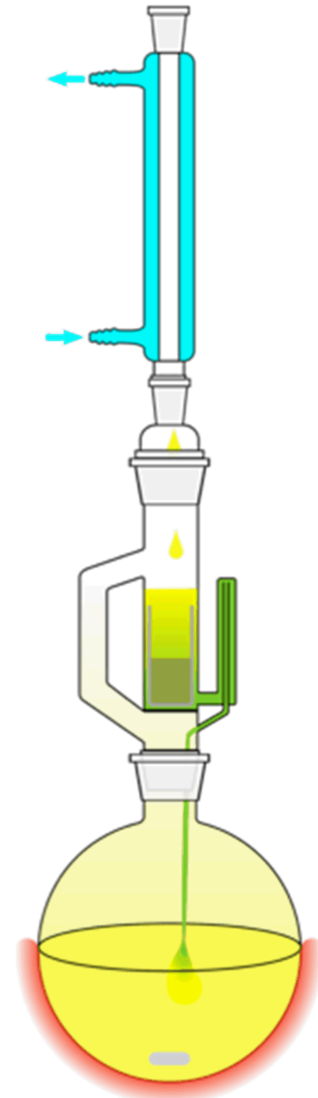
NMR ScCl3(THF)3

PXRD ScCl3(THF)3



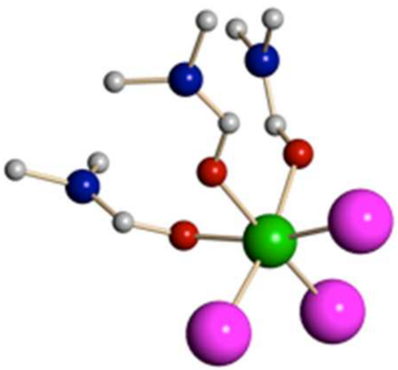
$[ScCl_3(THF)_3]$

Atwood & Smith Dalton Trans (1974)



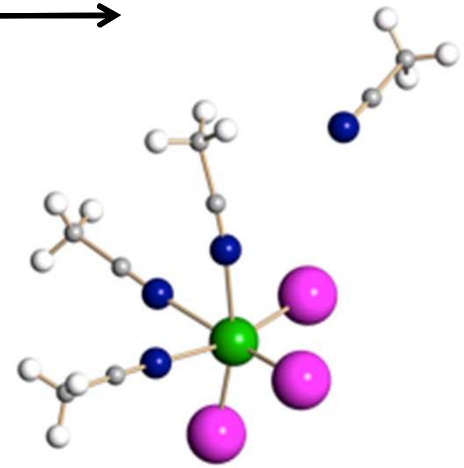
Solvates of $[ScCl_3(THF)_3]$ are structurally diverse.

DMF →



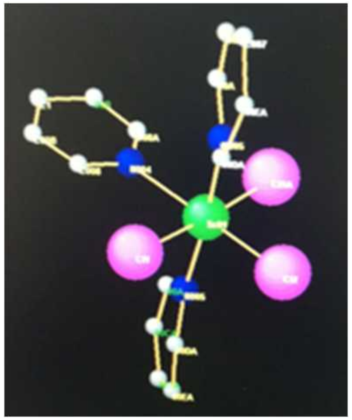
$[ScCl_3(DMF)_3]$

MeCN →



$[ScCl_3(MeCN)_3]$

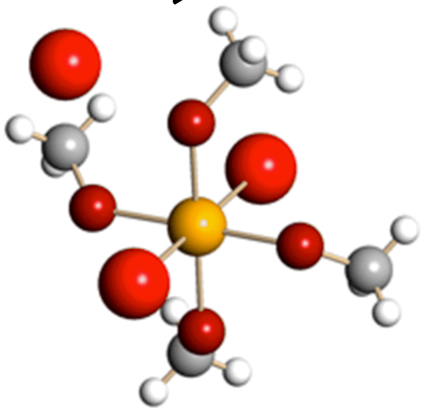
py →



$[ScCl_3(py)_3]$

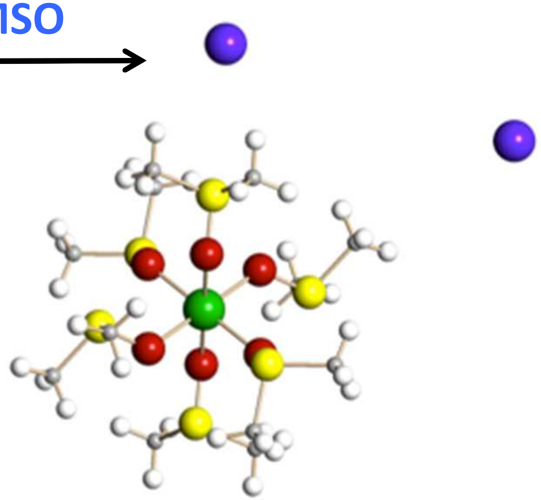
Hubert-Pfalzgraf et al Polyhedron (1999): DME/MeCN & diglyme

MeOH →



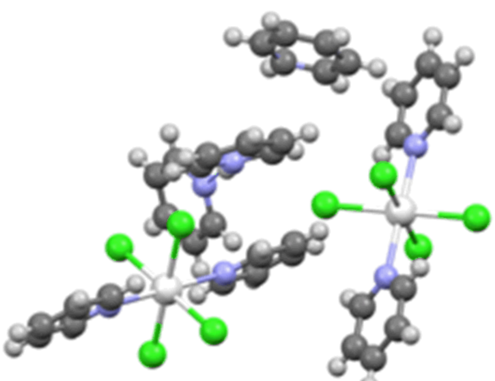
$[ScBr_2(MeOH)_4][Br]$

DMSO →



$[Sc(DMSO)_6]3[Cl]$

py →

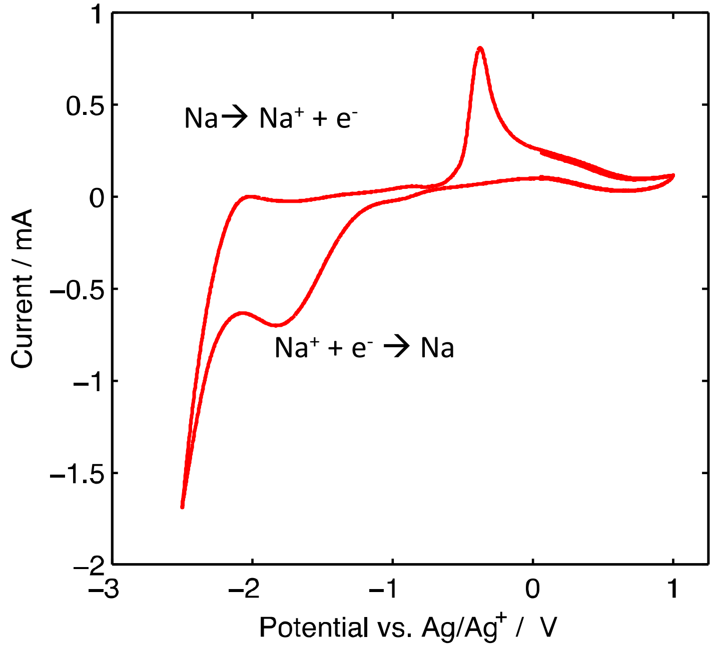


$\{[ScCl_4(py)][py\text{-}H\text{-}py]\}_2$

Selected voltammagrams of commercially available samples investigated show no reduction for Sc^{+3}.

Pt in 0.1 M $Sc(NTf_2)_3$ in DMF 100 mV/s

bis(trifluoromethylsulfonyl)imide (NTf_2)



- Na (identified by EDS)
- impurities electroplated

Pt in 0.1 M $Sc(OTf)_3$ in DMF 100 mV/s

trifluoromethanesulfonate (OTf)

Potential vs. Ag/Ag$^+$ / V

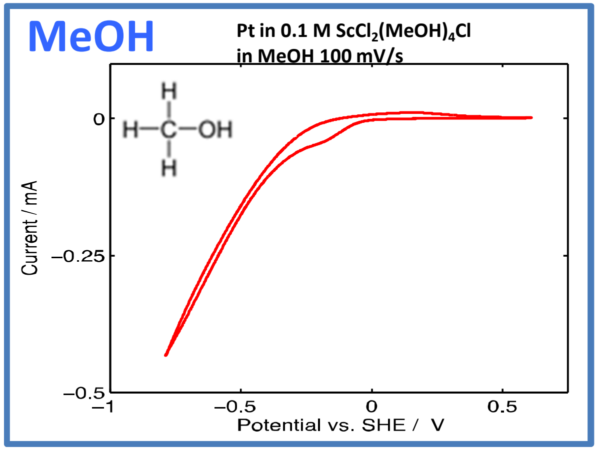
- Redox peaks w/0 film deposition
- unclear as to what the redox active species is

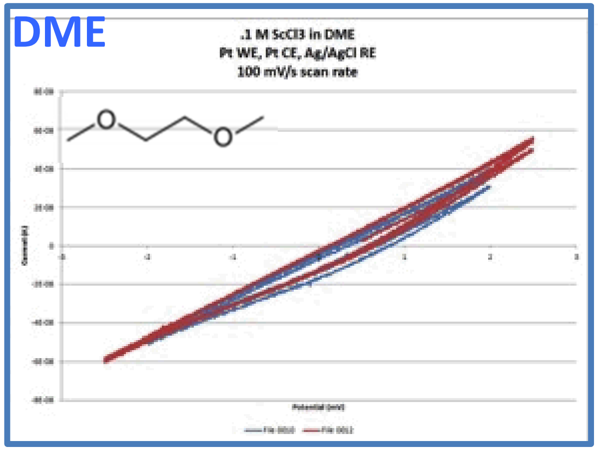
Deposit onto 100 nm Pt/40 nm Ti/SiO_2/Si (100) for 2 hours at constant potential.

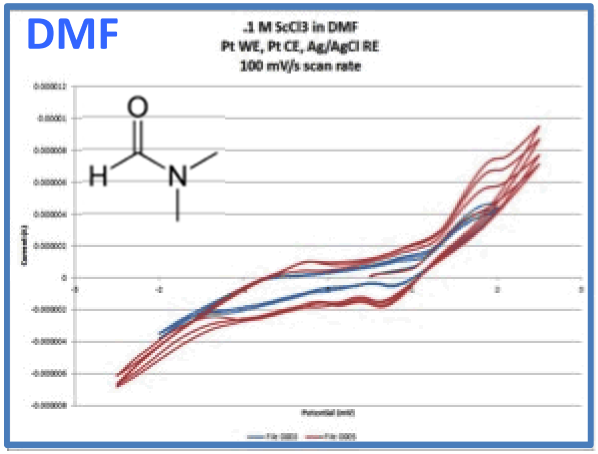
[1]Anhydrous DMF kept with 3Å sieves.
[2]All ILs and Sc salts dried at 100 °C, <0.5 mTorr for 72 hrs

Thermodynamic vs. Kinetic

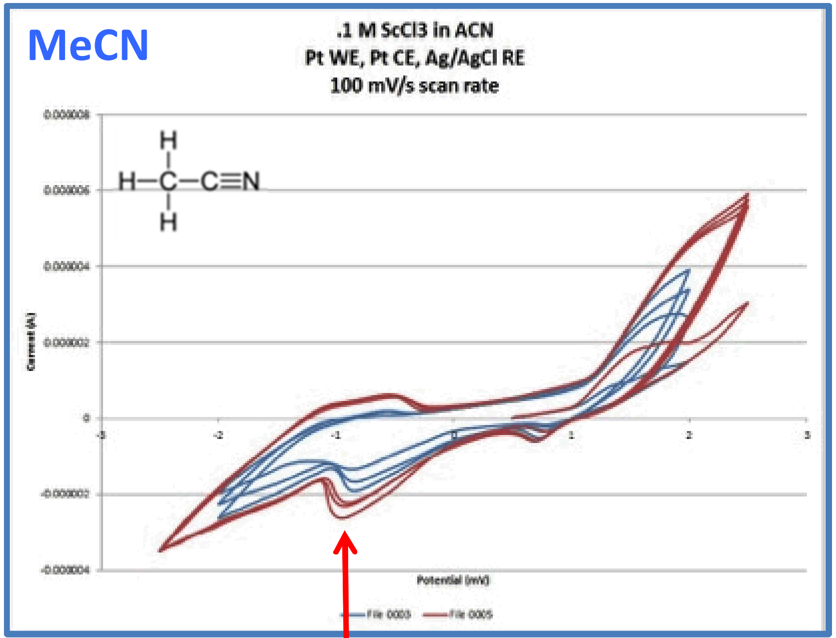
E-chem results of [$ScCl_3(solv)_x$] species reveal:

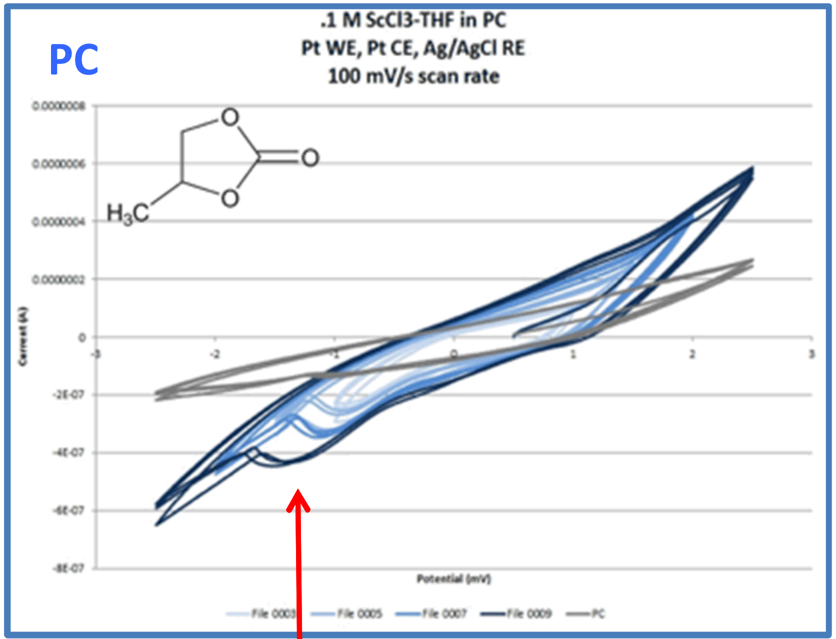






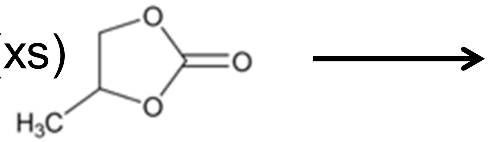
- poor solvent choice (MeOH red)
- No re-dox observed
- unusual re-dox, small



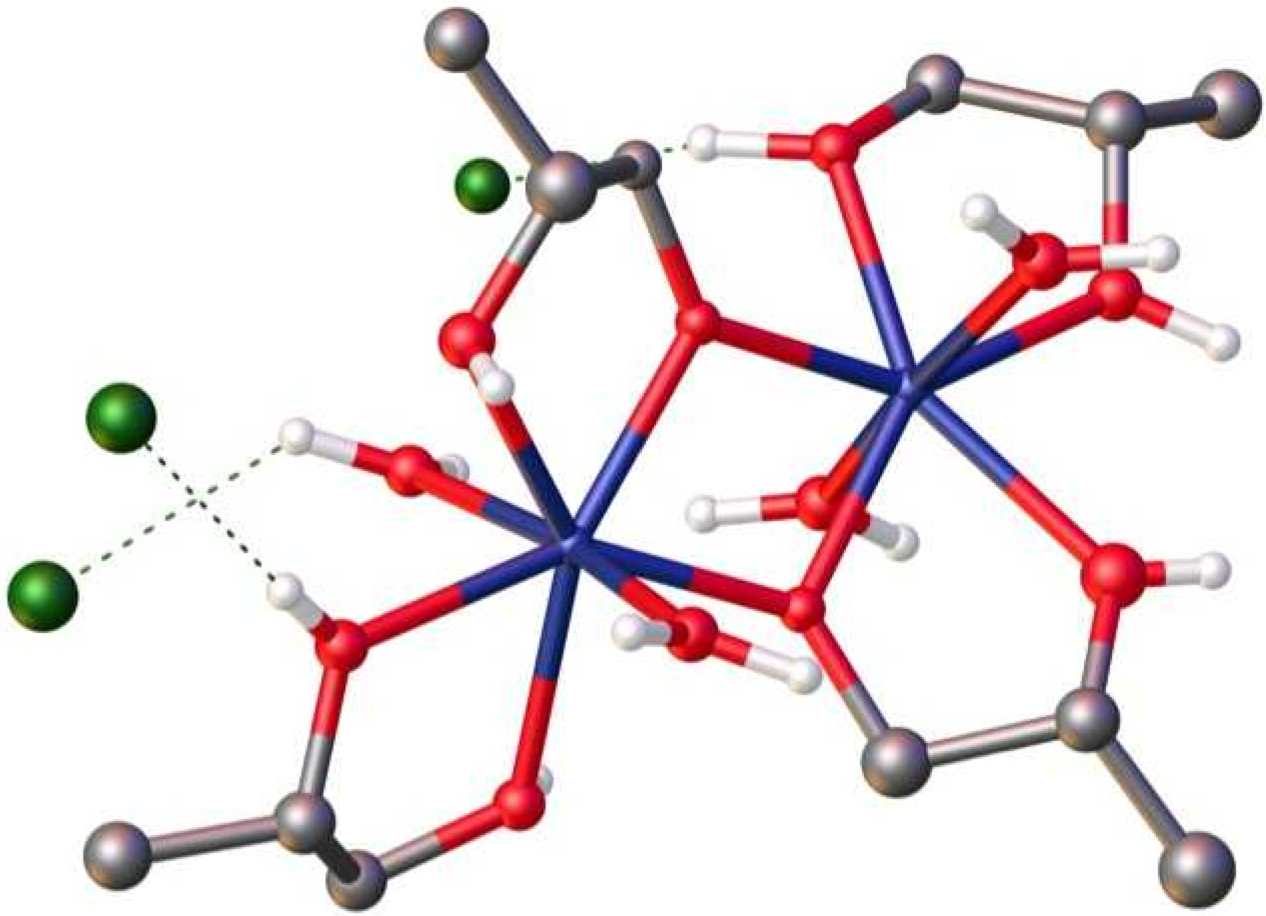


- redox observed
- reduction observed

PC solvate of $[(H_2O)_5Sc(OH)]_2 4Cl$ is Odd and not a solvate!

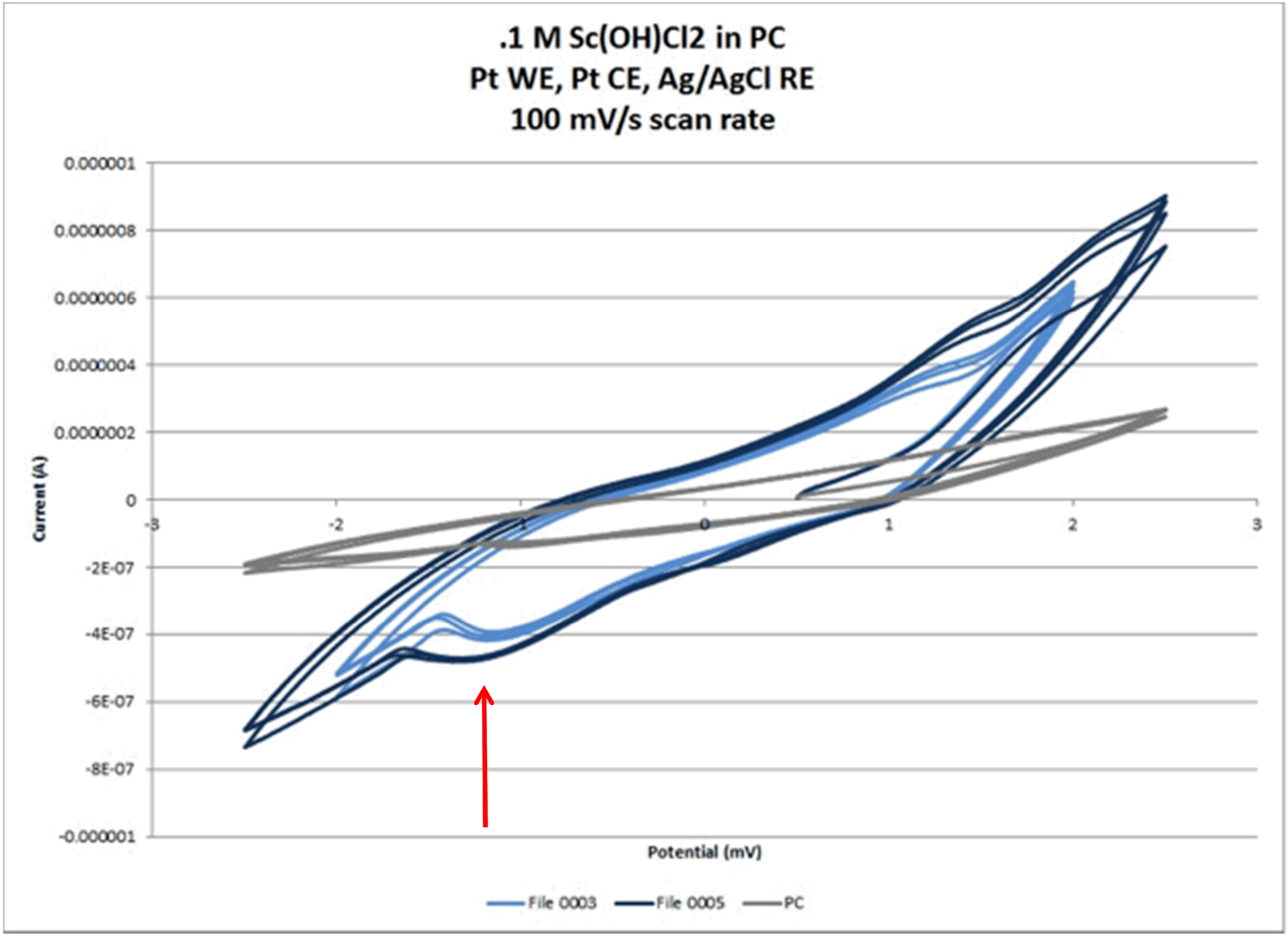
$[(H_2O)_5Sc(OH)]_2 4Cl$ + (xs) 

Propylene carbonate

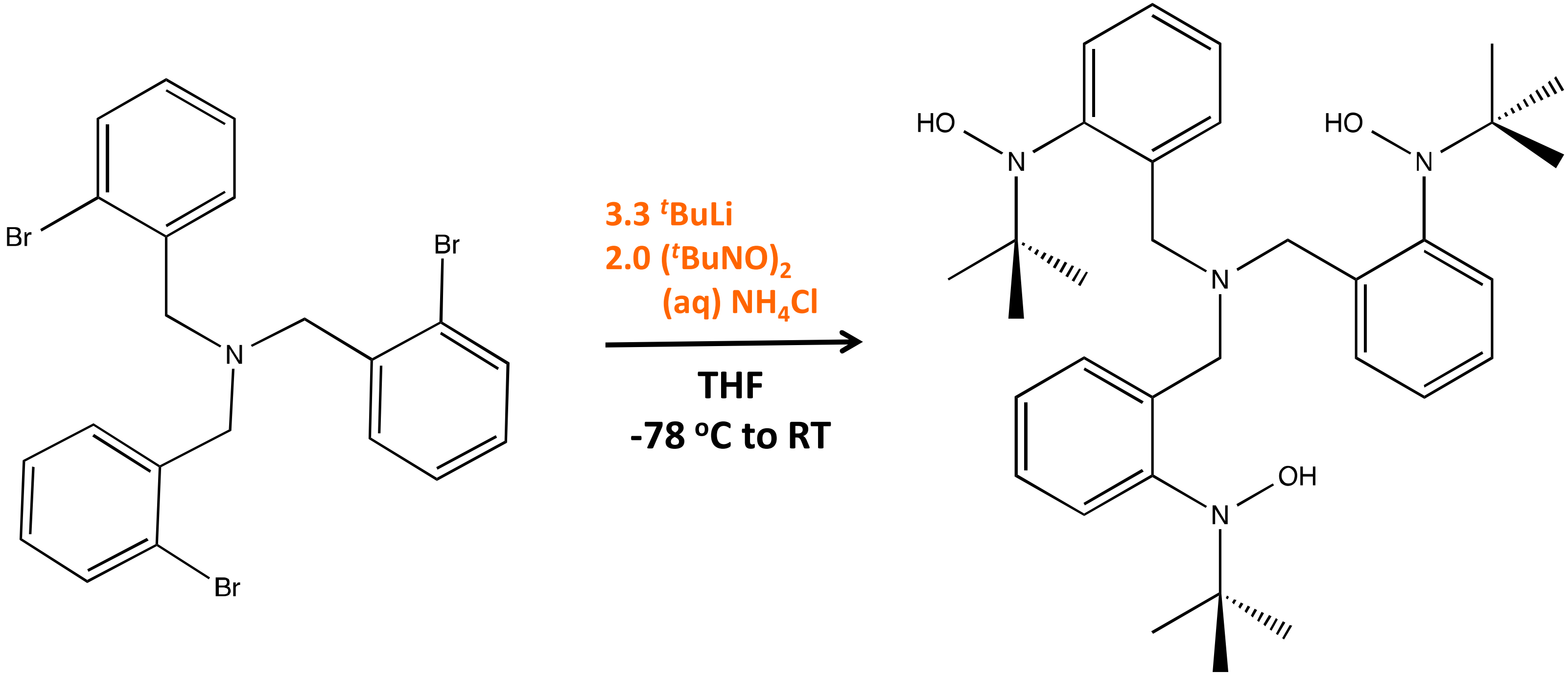


$[(\kappa^2(O,O')\text{-}(OPr^i(OH)_2)Sc(\kappa^2(O,O')\mu(O)\text{-}OPr^i(OH))(H_2O)_2]_2 4Cl$

E-chem results of PC-Sc(OH)Cl2 shows odd RED peak



Tripodal nitroxide ligand used to extract Nd and Dy



[{2-^{t}BuNOH)$C_6H_4CH_2$}$_3$N]

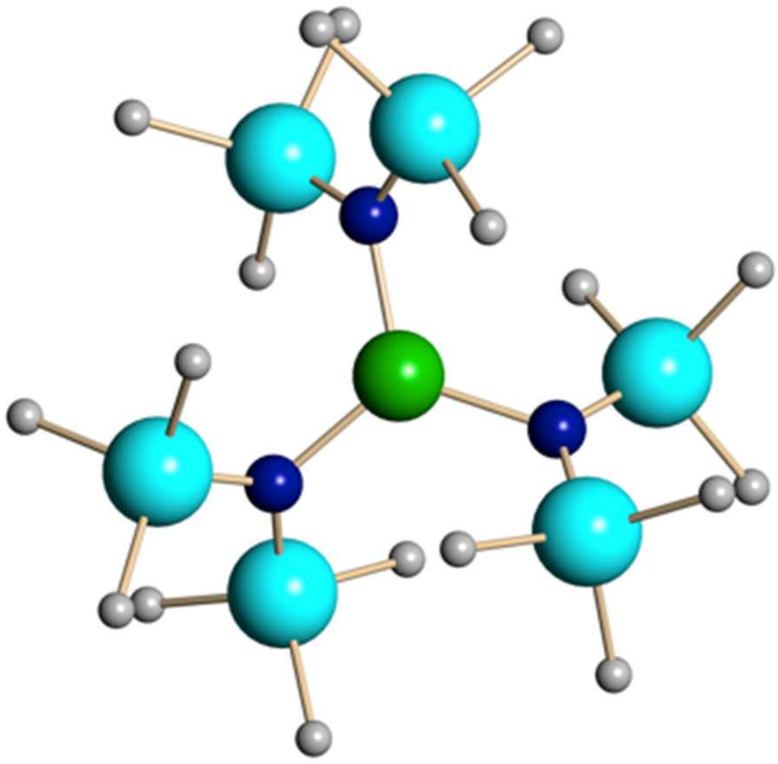
H_3-TriNox

Exposure of the metal cations in the aperture induces a self-associative equilibrium comprising [M(TriNOx)thf]/$[M(TriNox)]_2$ . . . Nd/Dy separations through leaching with a separation ratio of $S_{Nd/Dy}$ = 359.

Bogart et al. "An operationally simple method for separating the Rare-Earth elements Nedodymium and Dysprosium" *Angewandte Commun.* (**2015**) 8222.

Switch to different ligated precursors (Sc-X to Sc-N).

$$ScCl_3(THF)_3 + 3\ KNR_2 \xrightarrow{THF} Sc(NR_2)_3 + 3\ KCl$$



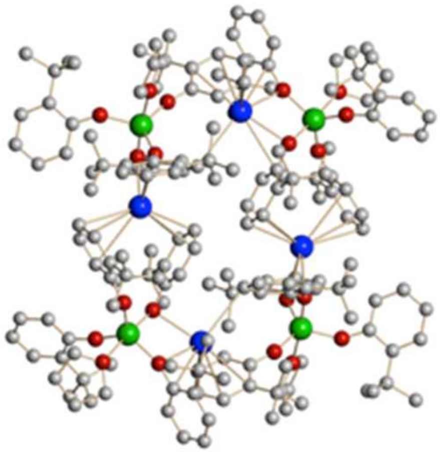
tris(bis(trimethylsilyl)amino)scandium
Chemical Formula: $C_{18}H_{54}N_3ScSi_6$
Molecular Weight: 526.12

Single crystal[1]
a: 16.160 *b:* 16.160 *c:* 8.530
α: 90 β: 90 γ: 120 V = 1929.124
a: 16.05 *b:* 16.01 *c:* 8.32
α: 89.91 β: 89.91 γ: 60.11 V = 1854

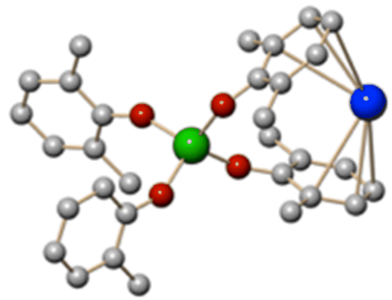
1: Ghotra, Hursthouse, Welch *Chem. Commun.* **1973**, 669.

Alkali metal derivatives observed. . .oops! . . .being explored for scintillator applications.

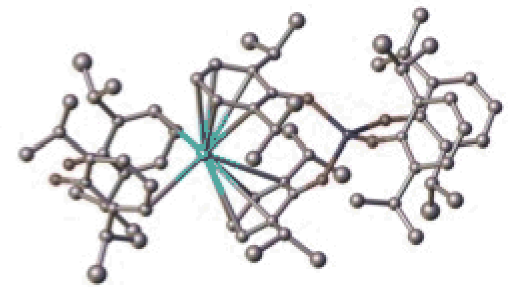
$$[Sc(NR_2)_3] + 3\,HOR \xrightarrow{tol} [Sc(OR)_3] + 3\,HNR_2 + \ldots$$



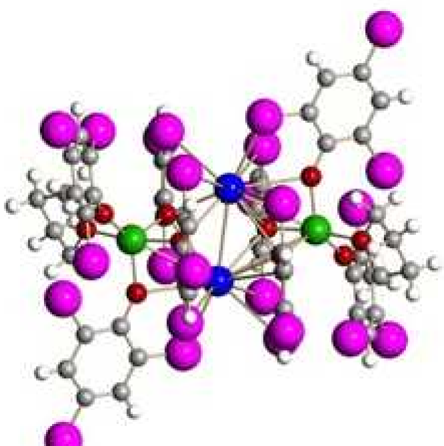
$[(\eta 6\text{-}K)(\mu\text{-}oBP)_2Sc(oBP)_2]_4$



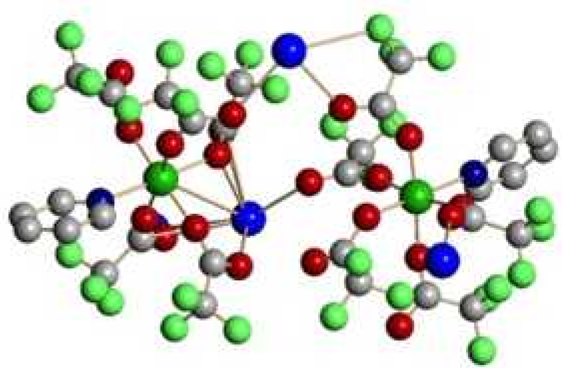
$[(\eta 6\text{-}K)(\mu\text{-}DMP)_2Sc(\mu\text{-}DMP)_2]_n$



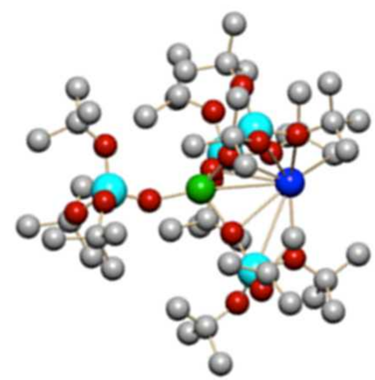
$[(\eta 6\text{-}K)(\mu\text{-}DIP)_2Sc(\mu\text{-}DIP)_2]_n$



$[KSc(TCP)_4]_2$



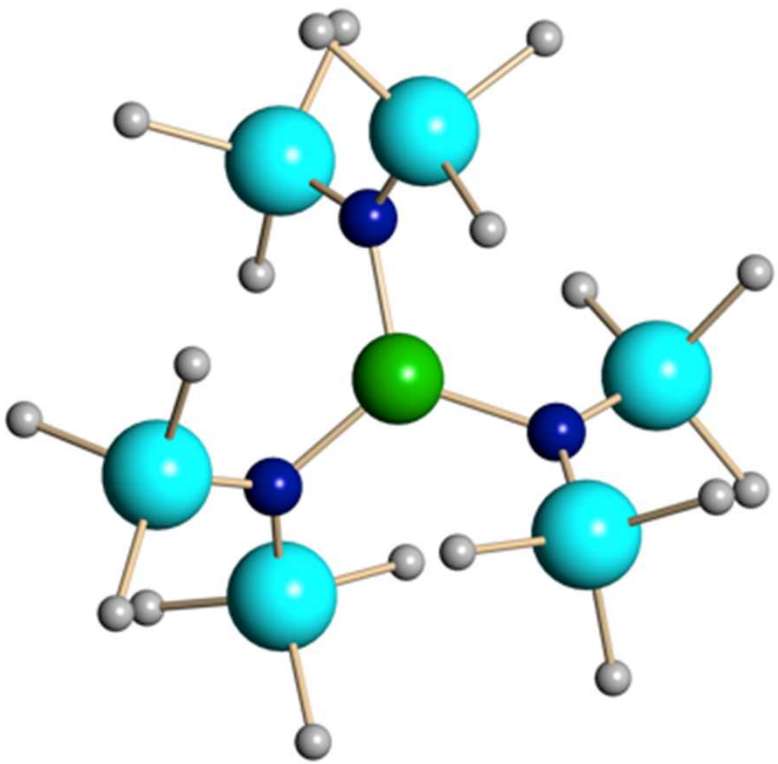
$[NaSc(TFA)_4(py)]_n$



$[K(\mu\text{-}TOBS)_2Sc(\mu\text{-}TOBS)]_n$

Switch to different ligated precursors (Sc-X to Sc-N).

$$ScCl_3(THF)_3 + 3\ KNR_2 \xrightarrow{THF} [Sc(NR_2)_3] + 3KCl$$



<u>tris(bis(trimethylsilyl)amino)scandium</u>

FTIR

Chemical Formula: $C_{18}H_{54}N_3ScSi_6$

Molecular Weight: 526.12

Elemental Analysis:

calcd: C, 41.09; H, 10.35; N, 7.99; Sc, 8.54; Si, 32.03

Found: 41.57%C, 10.07% H,, 6.83%N

Single crystal[1]

a: 16.160 *b:* 16.160 *c:* 8.530

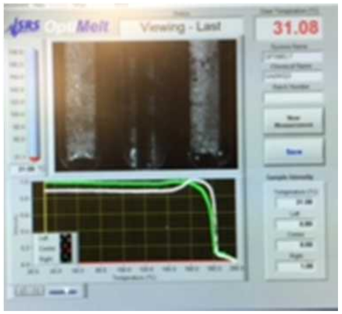
α: 90 β: 90 γ: 120 V = 1929.124

a: 16.05 *b:* 16.01 *c:* 8.32

α: 89.91 β: 89.91 γ: 60.11 V = 1854

Melt Temp: 169-174 °C[2]

172 °C



NMR* ^{1}H δ 0.93 ppm

^{13}C δ xxx ppm;

^{45}Sc δ xxx ppm

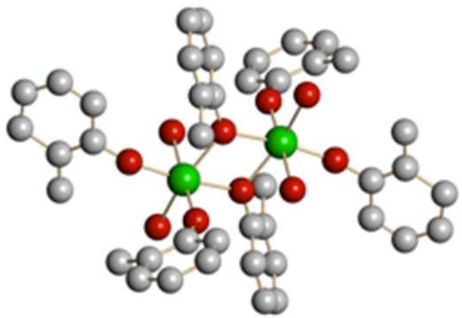
* 18 mg/0.2 mL $CDCl_3$

1: Ghotra, Hursthouse, Welch *Chem. Commun.* **1973**, 669.

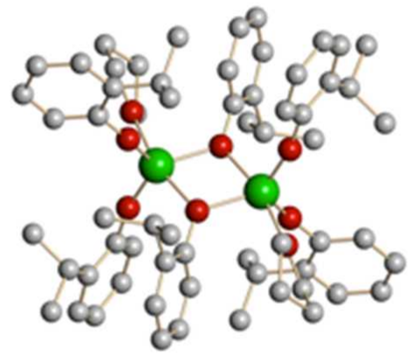
2: https://www.americanelements.com/tris-n-n-bis-trimethylsilyl-amide-scandium-iii-37512-28-0

New family of Sc-Alkoxides being developed

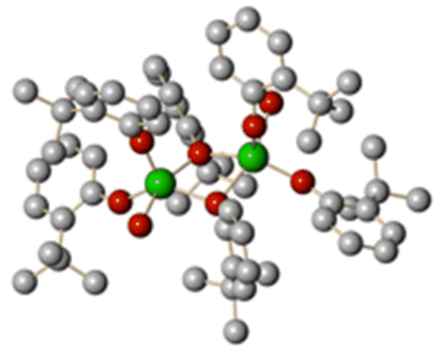
$$[Sc(NR_2)_3] + 3\ HOR \xrightarrow{tol} [Sc(OR_2)_3] + 3\ HNR_2$$



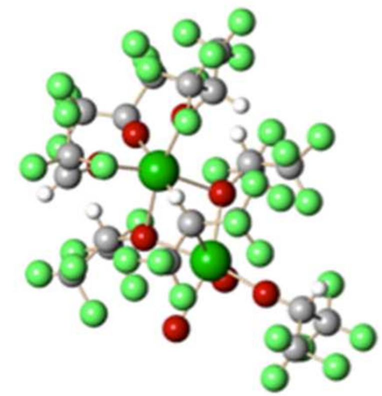
$[Sc(oMP)_3]_2$



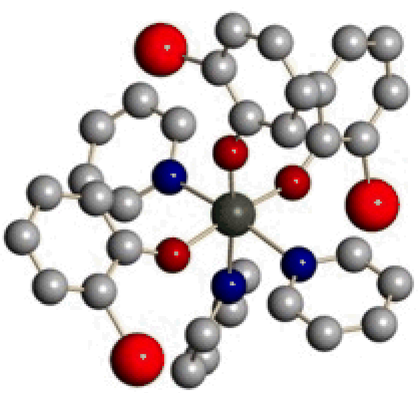
$[Sc(oPP)_3]_2$



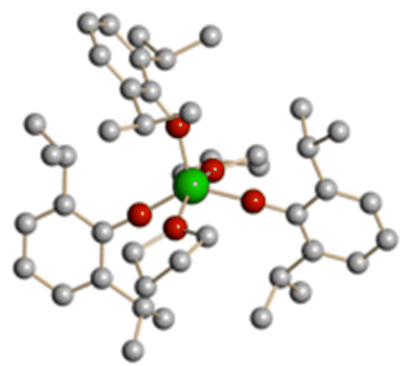
$[Sc(oBP)_3]_2$



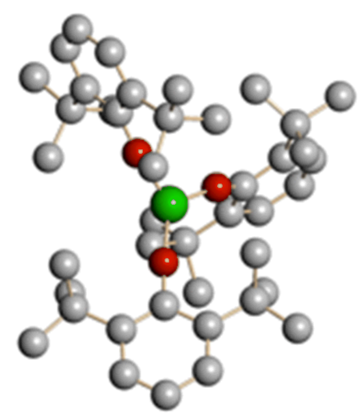
$[(OPr^{i}\text{-}F)_6Sc_2(H_2O)_2]$



$[Sc(BP)_3(py)_3]$



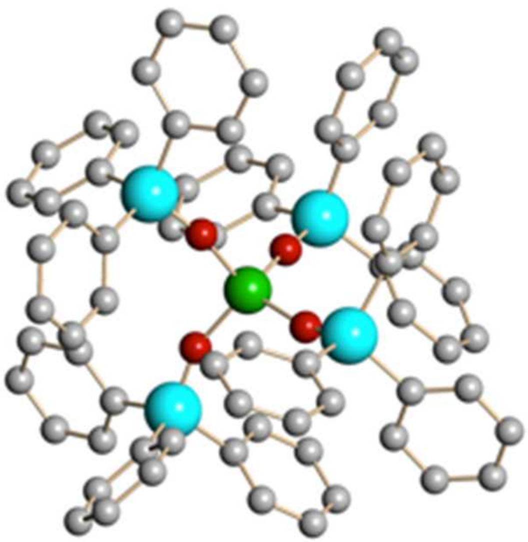
$[Sc(DIP)_3(THF)_2]$



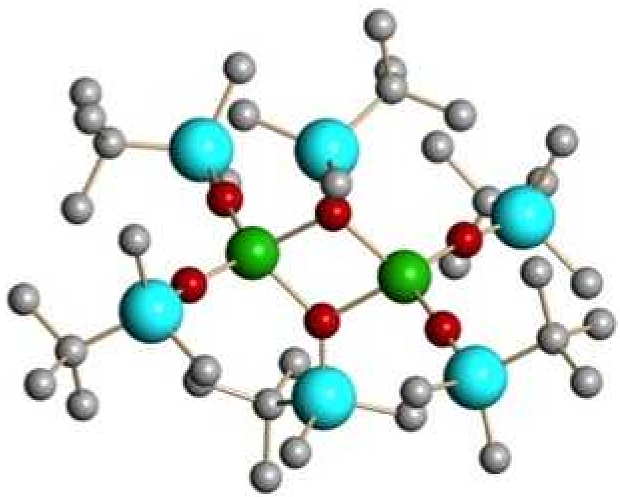
$[Sc(DBP)_3]$

Sc-siloxides of interest for e-chem studies and alternative materials applications.

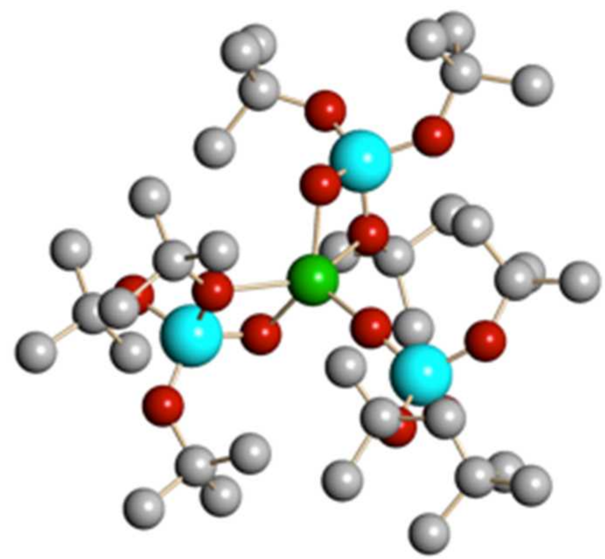
$$[Sc(NR_2)_3] + 3\ HOSiR_3 \longrightarrow [Sc(OSiR_3)_3] + 3\ HNR_2$$



[Sc(TPS)$_3$(H-TPS)]

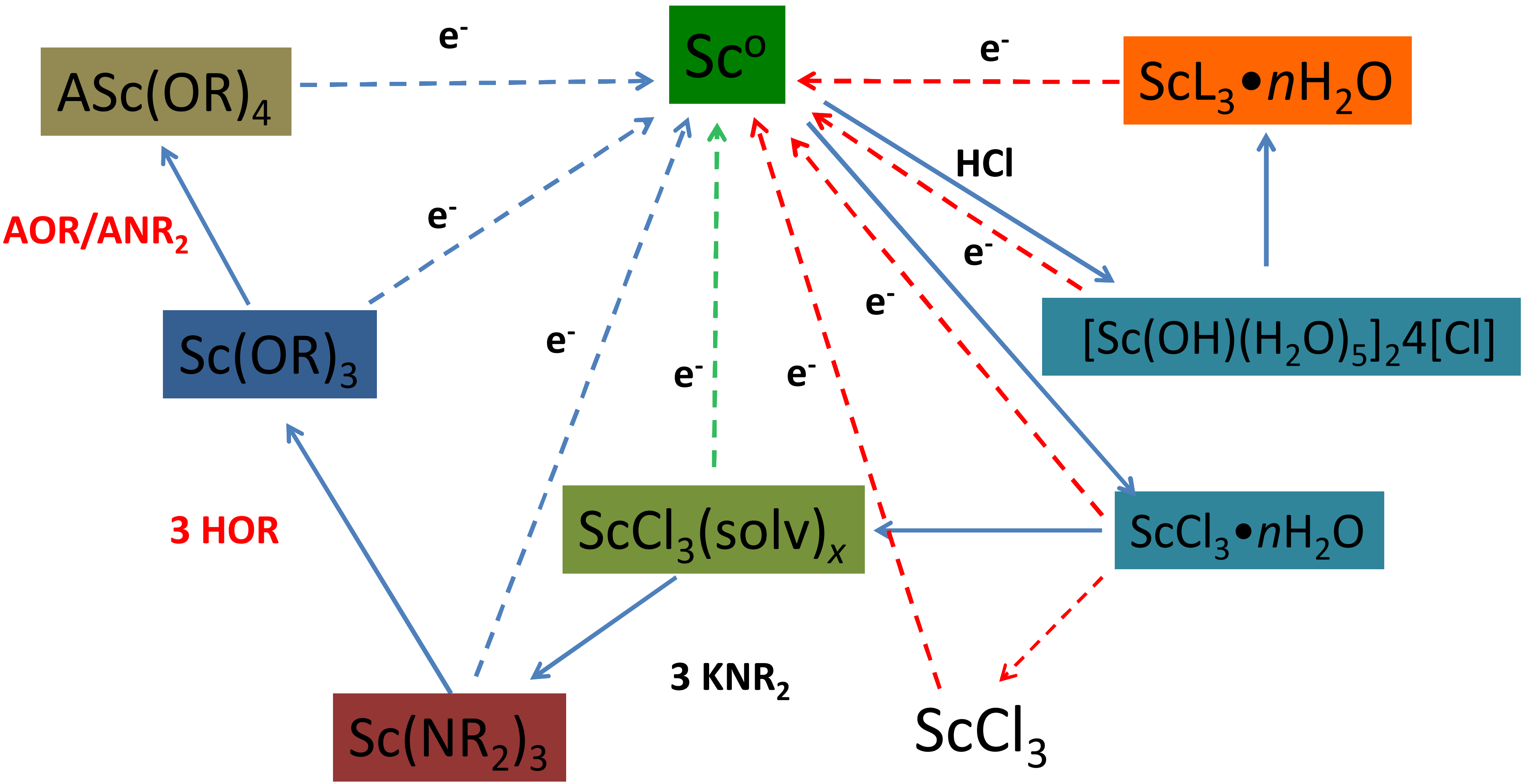


[Sc(μ-DMBS)(DMBS)$_2$]



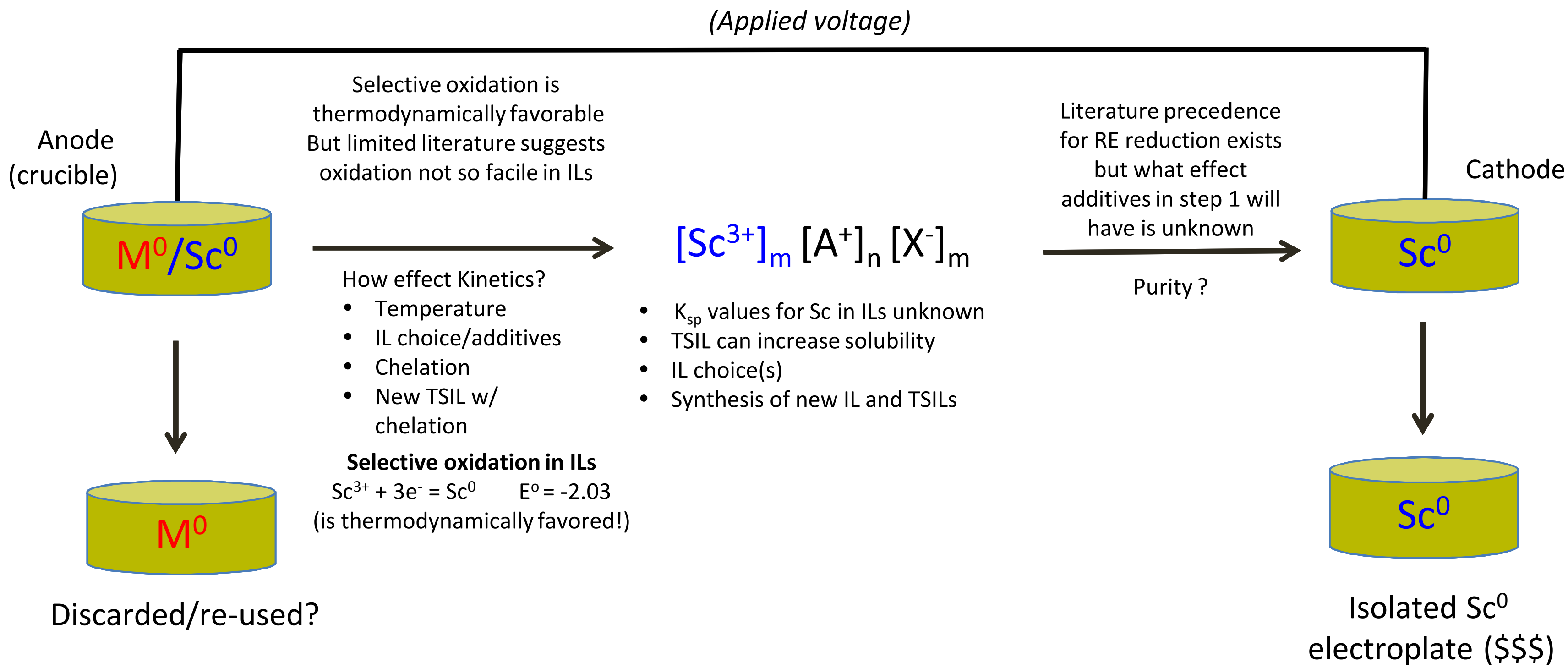
[Sc(TOBS)$^c{}_2$(TOBS)]

Alternative approach, generate amides or alkoxides

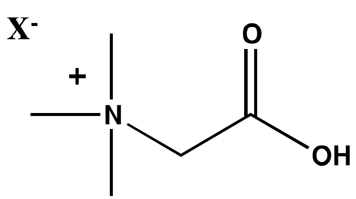


Potential RE-cycle

S&T questions in developing a Sc° recovery technology



TSIL = Task specific Ionic Liquids
e.g. Chelating IL from commodity chemical betaine

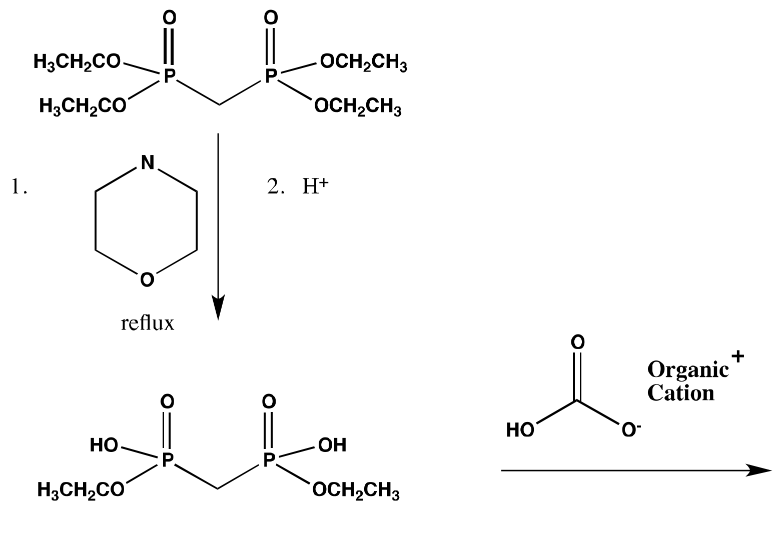


Ionic Liquids$[A^+][X^-]$:
- electro-chemical window > 4-5 V
- negligible vapor pressure
- low viscosity
- no H_2 generation
- IP opportunities

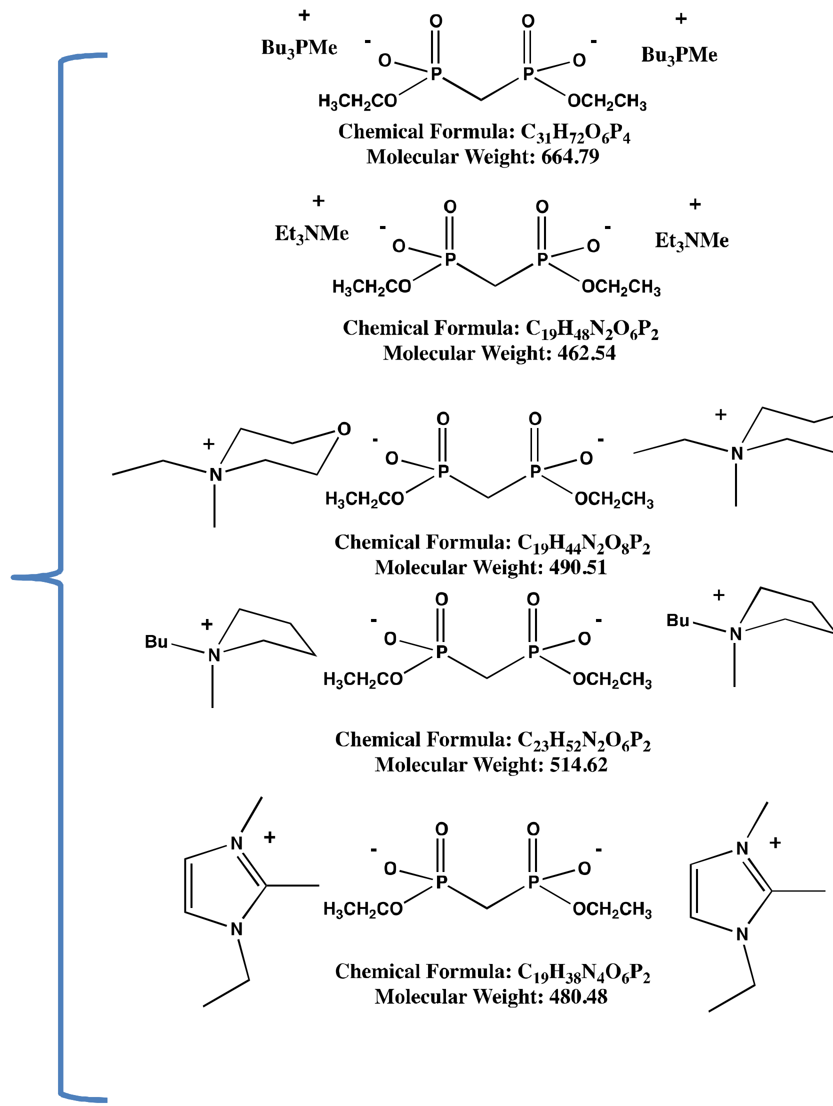
- Precedence for reduction for Rare Earths
- Oxidation has not been demonstrated but high temperature oxidation in ILs of inert metals has – even Pt has been reported!

Tailored made ILs based on methylene bisphosphonates and $Sc(NR_2)_3$ not altered upon crystallization.

Synthesized in two steps in high yield



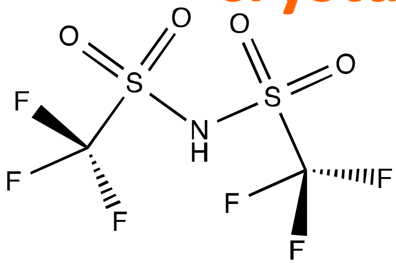
Ionic Liquids (IL)



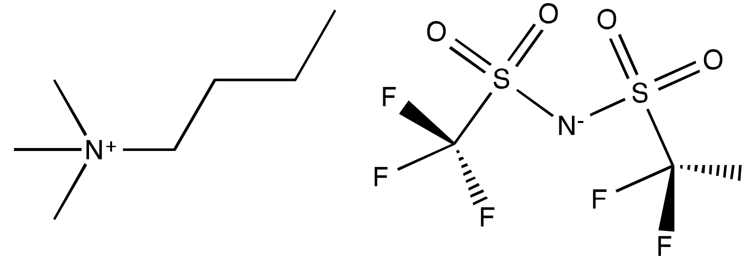
Characterization ongoing

Most thick oils at room temperature

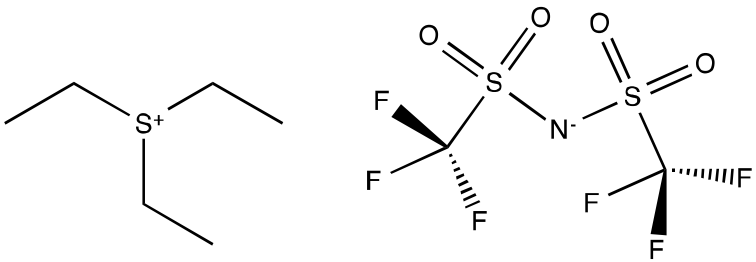
Structural properties of and $Sc(NR_2)_3$ not altered upon crystallization from sulfonyl-imide IL.



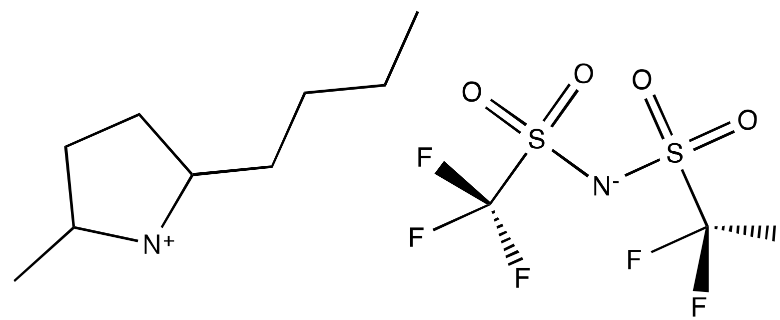
Bis(trifluoromethanesulfonyl)imide



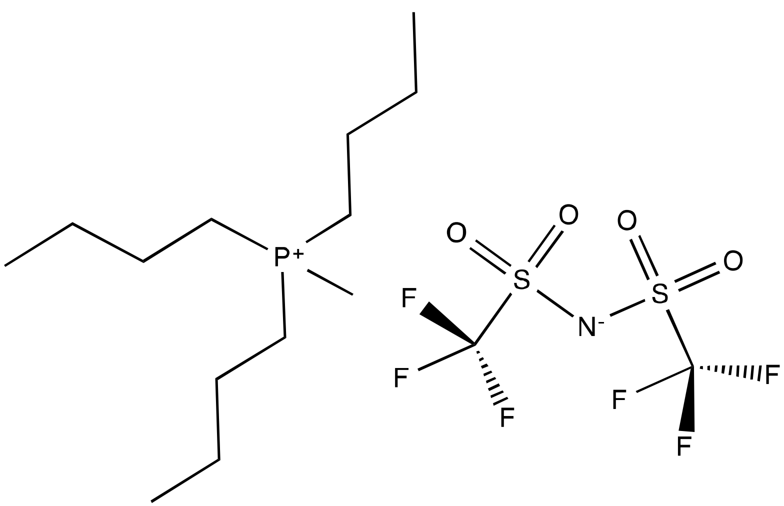
Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide



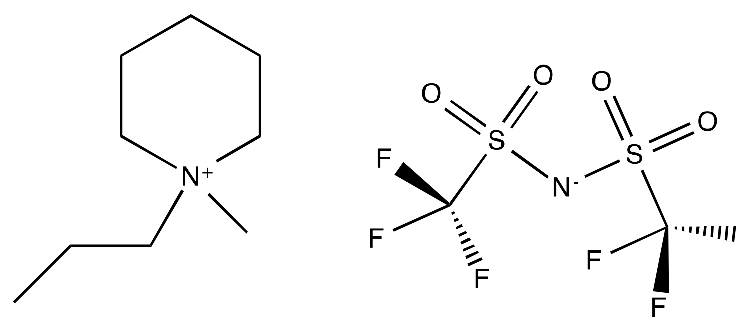
triethylsulfonium bis(triflurometh ylsulfonyl)imide



1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide

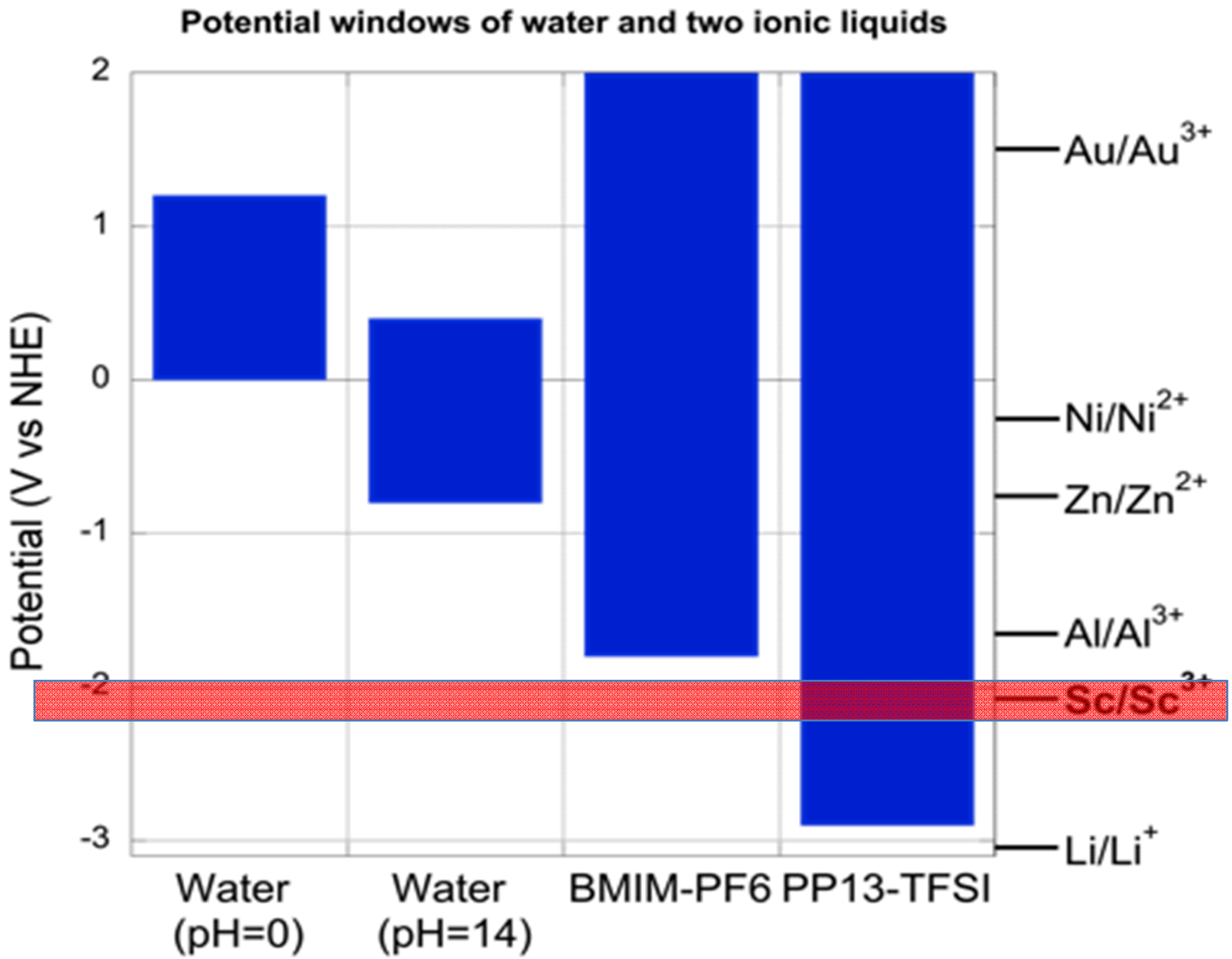


Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide



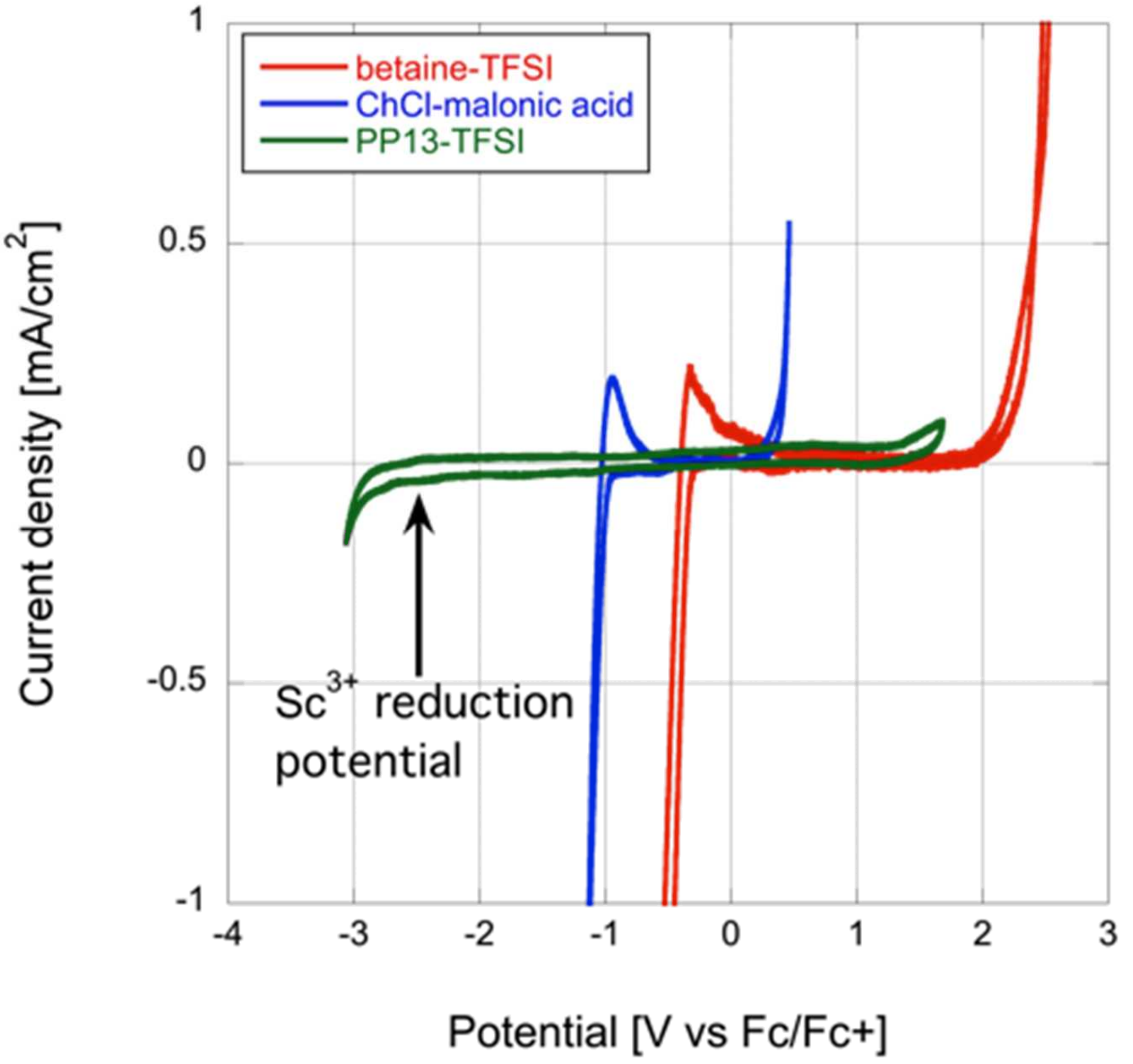
1-Methyl-1-propylpiperidinium bis[(trifluoromethyl)sulfonyl]azanide

Solution reduction of Sc^{3+} may be possible using Ionic Liquids (IL).

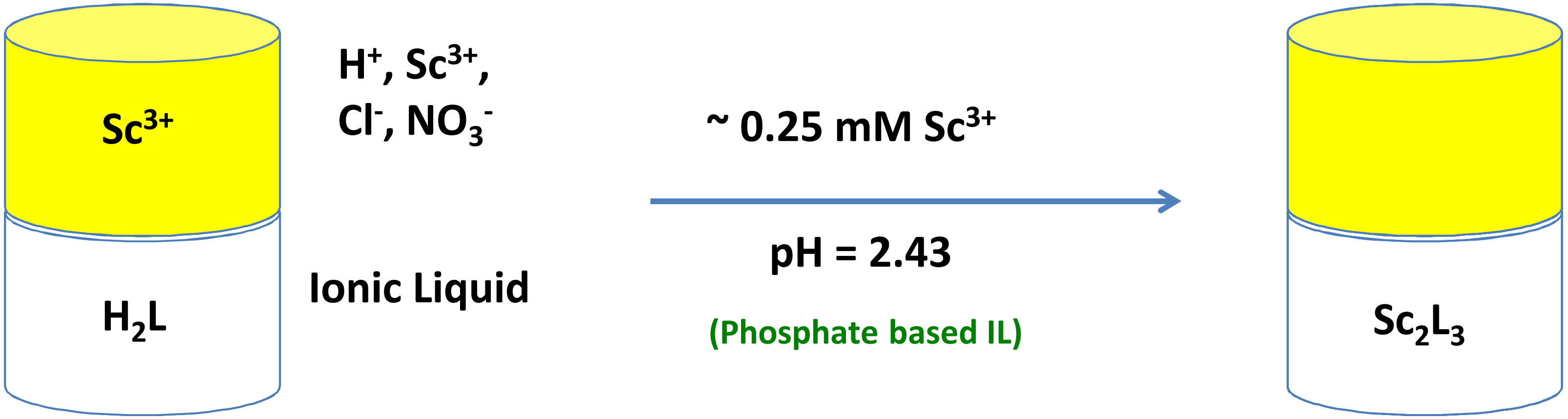


- Need to determine if ionic liquids of interest are compatible with Sc electrodeposition
- No standard reference electrode for all ionic liquids
  - Use ferrocene as an internal standard
- Sc deposition estimated below -2.5 V vs. Fc/Fc

E-Chem analysis of the Sc precursors indicate that solution reduction of Sc^{3+} may be possible.



Sc^{3+} was successfully extracted from HCl solutions with high efficiency.



Ligand Concentration	$-PO_2-OH$ Concentration	$Sc^{3+}_{(aq)}$ before Extraction	$Sc^{3+}_{(aq)}$ after Extraction	% Extracted
0.125 mM	0.250 mM	0.293 mM	0.270 mM	8.2
0.250 mM	0.500 mM	0.293 mM	0.103 mM	65
0.375 mM**	0.750 mM	0.293 mM	0.048 mM	84

**Conditions were 17.2 % excess Sc^{3+} - high extraction!

Sc^{3+} electro-reduction reduction not observed, yet!!

	Solvent	Salts supplied by T. Boyle	CVs suggest dep?	Deposition Potential	Film contents via EDS
6	[1-butyl-3-methylimidazolium Cl]$_3$Sc(OTf)$_3$[2]	(25 mol% Sc(OTf)$_3$)	N/A	N/A	IL decomposed into wax. Catalyzed by Sc(OTf)$_3$?
7	[1-butyl-3-methylimidazolium Cl]$_3$ScCl$_3$	(25 mol% ScCl$_3$)	N/A	N/A	IL phase separated or decomposed.
8	NH_3	(Sc metal)	*In progress*		

Deposit onto 100 nm Pt/40 nm Ti/SiO_2/Si (100) for 2 hours at constant potential.

[1]Anhydrous DMF kept with 3Å sieves.
[2]All ILs and Sc salts dried at 100 °C, <0.5 mTorr for 72 hrs

Chemical Reduction of Sc° derivatives explored as an alterative approach to e-chem studies.

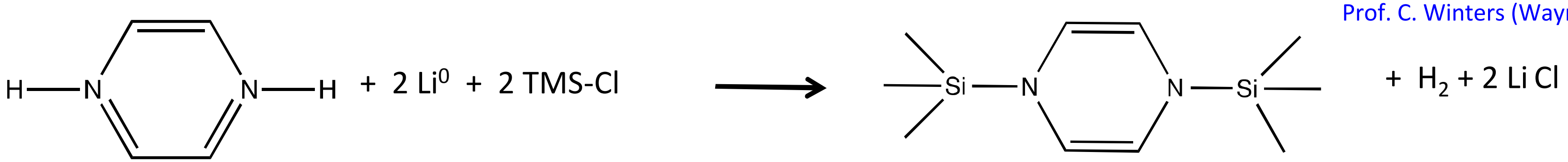
• larger scale, more rapid routes possible • less setup necessary • simple routes that can be ‘farmed-out’

Na/K or Na/Hg or $LiAlH_4$ or $NaBH_4$

$ScCl_3$ + 3/2 TMS_2-Pyrazine → Sc° + TMS-Cl + H_2-pyrazine

• demonstrated for Al and Ti
• nanoparticles produced
• simple setup – heated toluene

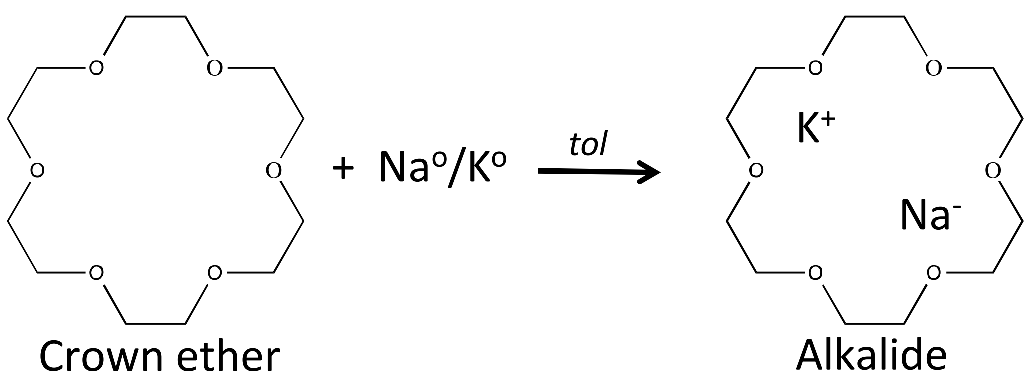
Private communication
Prof. C. Winters (Wayne State)



Iqbal et al. Angew. Chem. IEEE. (1971) **10** 127.

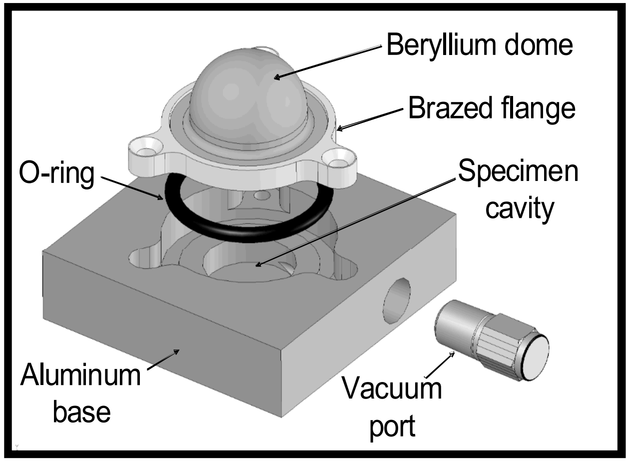
2 $ScCl_3$ + 3 K^+-(crown)-Na^- → 2 Sc° + K^+-(crown)-Cl^- + 3 NaCl

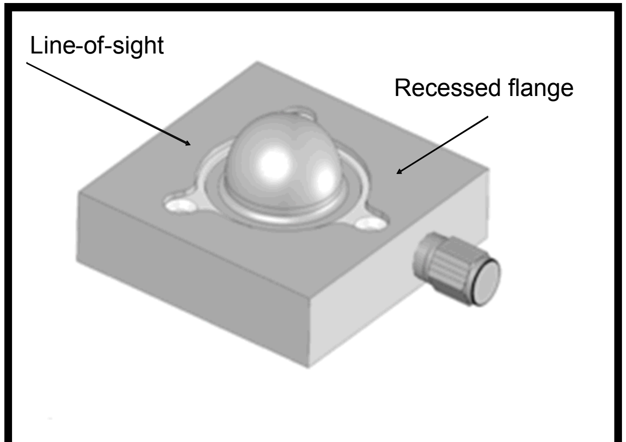
• complex setup
• nanoparticles produced
• proven for Dy and Gd
• suggest other Ln NP possible

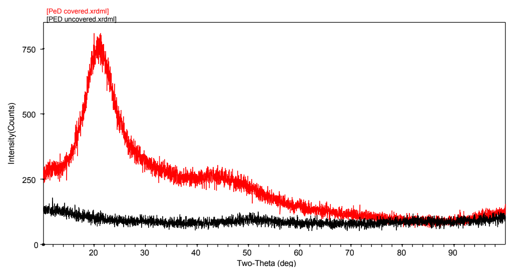


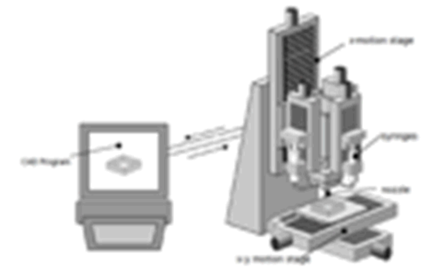
Wagner et al. J. Mater. Chem. (2003) **13** 857.

Chemical Reduction of Sc° derivatives explored as an alterative approach to e-chem studies.







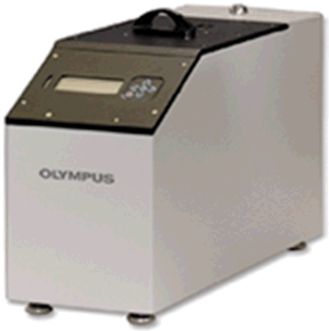


Beryllium Dome
(BeD)
$10 K

Plastic Dome
(PeD)
$500

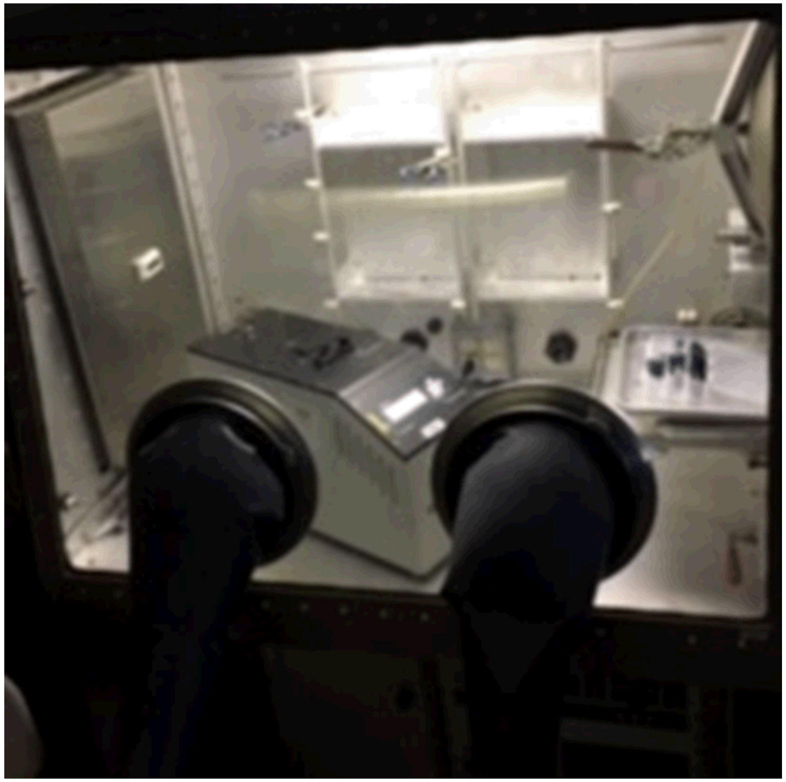
Direct Write PeD
(DW-PeD)
2 for $80

New PXRD is so small put in a glovebox and operates through BlueTooth.



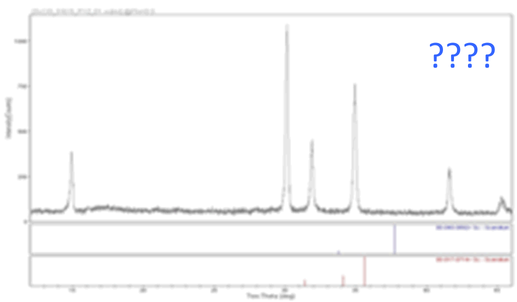
BTX II Compact Benchtop X-ray Diffraction System

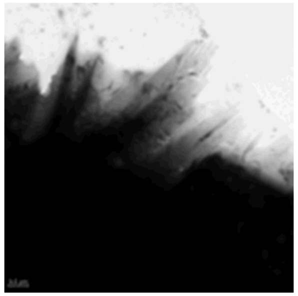
The BTX II Bench-top XRD System is a fast, low cost, small footprint, bench-top XRD for full phase ID of major, minor and trace components and quick XRF scan of elements Ca - U. Its unique, minimal sample prep technique and sample chamber allow for fast, bench-top analysis rivaling the performance of large costly lab units.

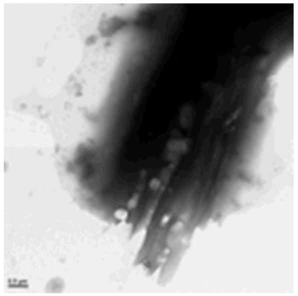


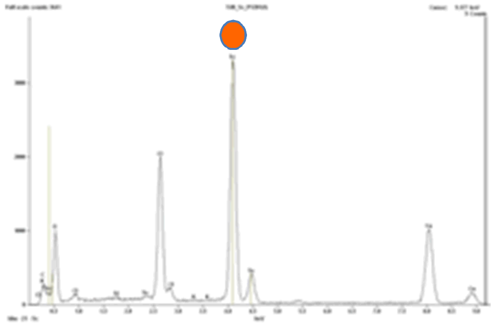
Chemical Reduction of Sc^{Cl}_3 derivatives found to generate:

$ScCl_3$ + 3/2 TMS_2-Pyrazine → Sc^o + TMS-Cl + H_2-pyrazine

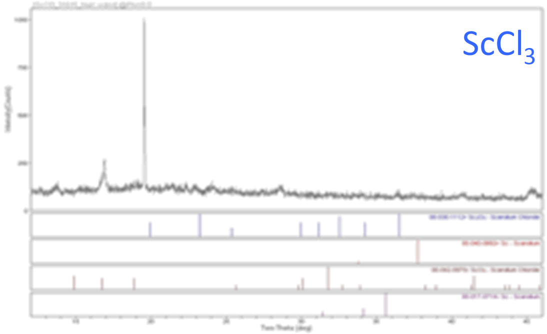


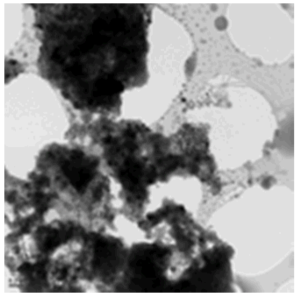


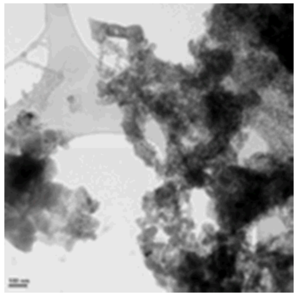


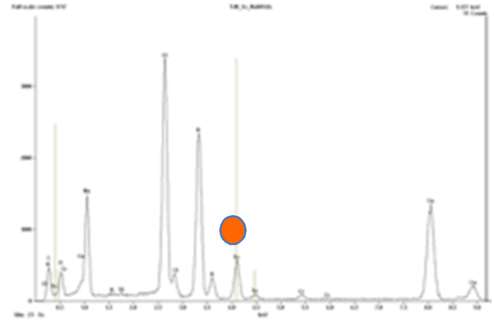


2 $ScCl_3$ + 6 K/Na → Sc^o + 3 KCl + 3 NaCl

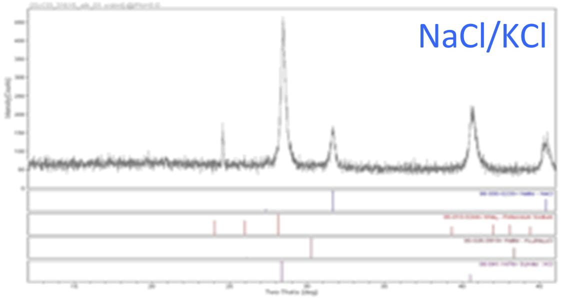


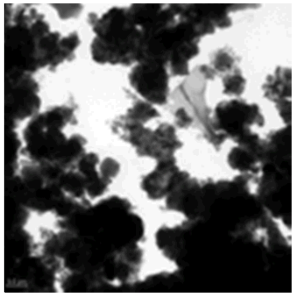


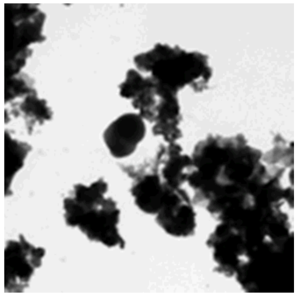


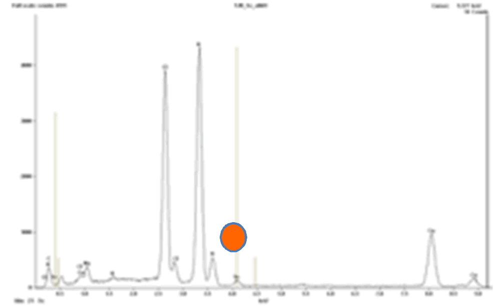


2 $ScCl_3$ + 3 K^+-(crown)-Na^- → 2 Sc^o + K^+-(crown)-Cl^- + 3 NaCl





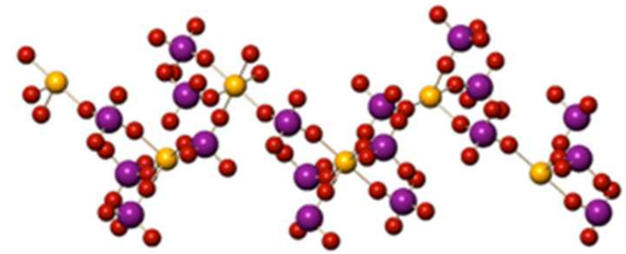




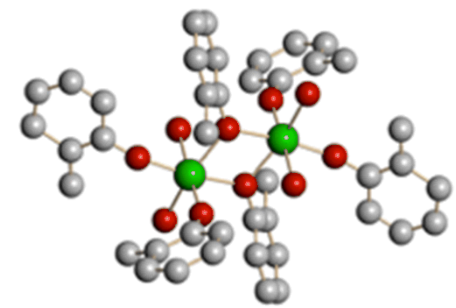
Summary and Conclusions

Coordination chemistry

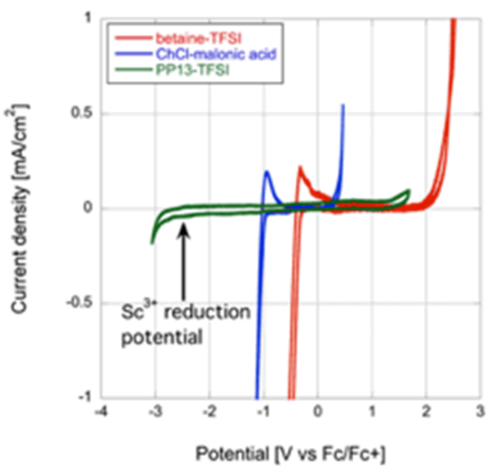
- Re-developing aqueous Sc^0 reactivity with hydrohalic acids
  - + Chlorides much more complicated than expected
  - + Bromide and Iodide being studied
  - + Sc-45 NMR valuable tool for characterization.
- Solvation of $ScCl_3$ reveals simple CN-6 solvation for some solvents but others lead to outersphere halides or salt formation
- Alkoxide ligated species appears to favor dinuclear structures
- Alternative siloxides and alkali alkoxide families being synthesize
- Sc chemistry *not* same as Ln nor Al.



$[Sc_6(\mu\text{-}OPO_3)_6(OPO_3)_{12}]$



$[Sc(oMP)_3]_2$



Ionic liquid

- New phosphate IL system developed
- amide stable in phosphate and sulfonyl imid systems
- large windows available.
- $Sc\text{-}NR_2$ stable in IL investigated

Electrochemical reduction

- PC reduction observed (?)
- thermodynamics vs kinetic? controlling reduction
- new precursors and solvent systems being investigated.

Chemical reduction

- ?????
- ?????
- ??????