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Main Group Chemistry: From Counterintuitive Bonding to Energy Applications

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11 - 21 - 13

Part 1: Fundamental Bonding in Heavier Group 14 (Si-Pb) Carbene Analogues: Sub 90° Interligand Angles

- Synthesis and characterization**
- Bonding trends: new and unusual**

Part 2: Materials Development for Energy Applications

- Hydrogen storage: ionic liquids and ammonia-borane**
- Ion Gels: flexible, solid state electrolytes**
- Chemical modification of graphene oxide for ORR catalysis**

Part 1: Fundamental Bonding in Heavier Group 14 (Si-Pb)

Carbene Analogues: Sub 90° Interligand Angles

- Dichalcogenolates of heavier group 14 elements
 - Very bulky ligands produce acute Ch-E-Ch bond angles
- Metallylene (divalent, group 14 element) → Carbene analogues
 - Acyclic, two-coordinate monomers
 - R_2Si = Silylene
 - R_2Ge = Germylene
 - R_2Sn = Stannylene
 - R_2Pb = Plumbylene

E = Si, Ge, Sn, Pb

Ch = O, **[S]** Se

Introduction

- Tetravalent group 14 chemistry: decades of research
- Divalent chemistry comparatively young
 - Renaissance ~20 years
- Catalysis
 - Carbene-transition metal complexes demonstrate robust chemistry
 - Heavier analogues (Si, Ge, Sn, Pb) being explored
- Synthetic precursors
 - CVD
 - Nanowires
- Novel bonding and reactivity
 - Main group elements can behave like TM

[Alkene hydrosilylation catalyst]

[Germanium oxide nanowires]

Power, P. P. *Nature*, **2010**, 463, 171

Fasulo, M. E.; Lipke, M. C.; Tilley, T. D. *Chem. Sci.* **2013**, 4, 3882

Gerung, H.; Boyle, T. J.; Tribby, L. J.; Bunge, S. D.; Brinker, C. J.; Han, S. M. *J. Am. Chem. Soc.* **2006**, 128, 5244

Interligand Angles in Heavier Metallylenes

- Acyclic examples are known for Ge, Sn, Pb
 - No stable Si derivative
- Most interligand bond angles range from 95 - 115°
 - General exceptions
 - Very large substituents widen bond angle
 - Strongly electronegative substituents narrow angle
- Narrow to acute angles common for E(ChR)₂
- 23 species of Ge and Sn with -O-E-O- moiety
 - Most 90 ± 5°
 - No Pb examples
- S-E-S: Only Sn(SMes*)₂²

O-Sn-O = 88.8°

S-Sn-S = 85.4°

Ligands

Synthesis of Germylene, Stannylene and Plumbylene Dichalcogenolates

E = Ge, Sn, Pb

Ch = O, S, Se

Ar = Ar^{Me6}, Ar^{iPr4}, Ar^{iPr6}, Ar^{iPr8},

Cetinkaya, B.; Gümrükcü, I.; Lappert, M. F. *J. Am. Chem. Soc.*, **1980**, 102, 2088

Stanciu, C.; Richards, A. F.; Stender, M.; Olmstead, M. M.; Power, P. P. *Polyhedron*, **2006**, 25, 477

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Ge, Sn, Pb Dithiolates

S-Sn-S angle decreases with larger ligands

- Same trend present in Ge
- Pb shows little effect

^{119}Sn NMR: $\delta = 764$

S-Sn-S = 86.4°

C-C-S-Sn = 39.3°

^{119}Sn NMR: $\delta = 827$

S-Sn-S = 78.3°

C-C-S-Sn = 28.0°

^{119}Sn NMR: $\delta = 919$

S-Sn-S = 73.2°

C-C-S-Sn = 3.6°

What about Silicon?

- All previously reported stable, two-coordinate silylenes are cyclic
- Transient acyclic species
 - Oligomerize
 - Undergo C-C, C-H bond activation

^{29}Si NMR: $\delta = -577$

^{29}Si NMR: $\delta = 78.3$

^{29}Si NMR: $\delta = 567$

Silylene Synthesis

$\text{Br}_2\text{Si}(\text{SAr}^{\text{Me}_6})_2$

$[\text{IMes}(\text{Mg})]_2$

Si-S:	2.158(3) Å	Si-S WBI = 0.97
S-C:	1.791(2) Å	Dec = 146° C
S-Si-S:	90.52(2)°	
Si-S-C:	102.93(6)°

R_2Si or R_2SiH_2 ?

- Prepared $H_2Si(SAr^{Me_6})_2$
- NMR: $^1J_{Si,H} = 256 \text{ Hz}$
- IR: Si-H stretching vibrations
 $\nu = 2182(s), 2168(s) \text{ cm}^{-1}$
- Hybrid PBE1PBE exchange-correlation functional
 - def2-TZVP basis set

	$Si(SAr^{Me_6})_2$		$H_2Si(SAr^{Me_6})_2$	
	Exp.	Calc.	Exp.	Calc.
Si-S (Å)	2.158(3)*	2.153	2.139(1)*	2.143
S-C (Å)	1.791(2)*	1.775	1.787(3)*	1.778
Si-Cent. (Å)	3.431*	3.606	3.546*	3.649
S-Si-S (°)	90.52(2)	90.04	93.5(2)*	95.74
C-S-Si (°)	102.93(6)*	104.36	107.8(1)*	107.05

* = Average

Electronic Spectrum

Experimental Energy [nm ($M^{-1}cm^{-1}$)]	Calculated Energy [nm]	Oscillator strength	Dominant contributions		
382 (8300)	386	0.047	97a	→ 96b	(97 %)
318 (23,000)	318	0.120	96a	→ 96b	(89 %)
	296	0.079	97a	→ 97b	(90 %)
291 (20,000)	291	0.107	94a	→ 96b	(59 %)
			95a	→ 96b	(23 %)
			93a	→ 96b	(13 %)
269 (25,000)	265	0.053	96a	→ 97b	(47 %)
			97a	→ 98b	(36 %)

Reactivity

No Reaction

No Reaction

Bulkier Silylenes

- $\text{Br}_2\text{Si}(\text{SAr}^{\text{iPr}_n})_2$ $n = 4, 6$
- $[\text{IMes}(\text{Mg})]_2$
 - Too bulky

Reduction - Magnesium

- Rieke's Mg + 5 % anthracene

- Acute S-Si-S angle

- Thermally very stable

- $(\text{Br})_2\text{Si}(\text{SAr}^{\text{Me}_6})_2 + \text{Mg}^\circ$
 $\neq \text{Si}(\text{SAr}^{\text{Me}_6})_2$

– ^{29}Si NMR : $\delta = 50.5$

– Likely a silylenoid intermediate

S-Si-S = $84.97(5)^\circ$

m.p. = 203°C

^{29}Si NMR: $\delta = 271.3$

S-Si-S = $85.78(12)^\circ$

m.p. = 254°C

^{29}Si NMR: $\delta = 270.9$

Bonding Trends

6 C	7 N	8 O
14 Si	15 P	16 S
32 Ge	33 As	34 Se
50 Sn	51 Sb	52 Te
82 Pb	83 Bi	84 Po

Bond Angle vs Ligand Bulk

- Si, Ge, Sn- Increase in ligand bulk: Decrease in S-E-S angle
- Pb- Increase in ligand bulk: Little change in S-E-S angle
- Si - Pb: Increase in ligand bulk: increase in C-S-M angle

S-E-S Angle vs. Ligand Bulk

C-S-E Angle vs. Ligand Bulk

S-E-S Angle vs $n \rightarrow p$ Transition Energy

- $n \rightarrow p$ transition = HOMO-LUMO
- Si, Ge, Sn- Decrease in S-M-S angle: Decrease in $n \rightarrow p$ transition energy
 - Pb: Increase in S-Pb-S angle: Decrease in $n \rightarrow p$ transition energy
- Si-Pb: Increase of C-S-E angle: Decrease in $n \rightarrow p$ transition energy

S-E-S Angle vs. HOMO-LUMO

C-S-E Angle vs. HOMO-LUMO

Selenolato Derivatives

- $\text{Ge}(\text{SeAr}^{\text{iPr}_4})_2$ and $\text{Sn}(\text{SeAr}^{\text{iPr}_4})_2$
 - 1st structurally characterized examples of Ge(II) and Sn(II) selenolates
 - M-Se distance 0.11 and 0.12 Å longer than E-S
 - $\Delta r_{\text{S,Se}} = 0.13 \text{ Å}$

- $\text{Ge}(\text{ChAr}^{\text{iPr}_4})_2$; Ch = S, Se
 - Se-Ge-Se: 3.5° wider
 - Ge-Se-C: 5° narrower

- $\text{Sn}(\text{ChAr}^{\text{iPr}_4})_2$; Ch = S, Se
 - Very similar angles
 - ^{119}Sn NMR
 - Ch = S; $\delta = 814.8$
 - Ch = Se; $\delta = 1148$

$\text{Ge}(\text{SeAr}^{\text{iPr}_4})_2$

Se-Ge-Se: $84.71(1)^\circ$

Ge-Se-C: $108.78(5)^\circ$

$\lambda_{\text{n} \rightarrow \text{p}}$: 435 nm

^{77}Se NMR: $\delta = 657.5$

$\text{Sn}(\text{SeAr}^{\text{iPr}_4})_2$

S-Sn-S: $78.71(2)^\circ$

Sn-S-C: $112.35(4)^\circ$

$\lambda_{\text{n} \rightarrow \text{p}}$: 434 nm

^{77}Se NMR: $\delta = 526.9$

Alkoxo Derivatives

- O-E-O wider than S-E-S / Se-E-Se
 - Ge: *ca.* 11.3°
 - Sn: *ca.* 13.5°
 - Pb: *ca.* 22.0°
- 1st structurally characterized 2-coordinate Ch-Pb-Ch species

O-M-O: 99.3(6)°

Pb-O-C: 126.7(2)°

$\lambda_{\text{n} \rightarrow \text{p}}$: 370 nm

^{207}Pb NMR: $\delta = 1070$

S-M-S: 77.21(4)°

Pb-S-C: 113.42(11)°

$\lambda_{\text{n} \rightarrow \text{p}}$: 422 nm

^{207}Pb NMR: $\delta = 4303$

Ch-M-Ch Angle vs. Chalcogen

- Thiolates produce narrowest Ch-M-Ch angle
- Phenoxides produce widest C-Ch-M angle
- Contradict Bent's Rule
 - Ligands: More EN $\rightarrow$ narrower angles

Stanciu, C.; Richards, A. F.; Stender, M.; Olmstead, M. M.; Power, P. P. *Polyhedron*, **2006**, 25, 477

Dickie, D. A.; MacIntosh, I. S.; Ino, D. D.; He, Q.; Labeodan, O. A.; Jennings, M. C.; Schatte, G.; Walsby, C. J.; Clyburne, J. A. C. *Can. J. Chem.* **2008**, 86, 20

Calculations for Smaller Chalcogenolates

Small Aryls: $\text{Ch-E-Ch} \geq 90^\circ$

E	O	S	Se
C	104°	114°	115°
Ge	92°	94°	95°
Sn	90°	93°	94°

E = Si, Ge, Sn, Pb

- Replacing Ph with *m*-terphenyl has small effect

E	O	S	Se
Ge	90°	92°	93°

- Bigger substituents: $\theta \leq 90^\circ$

Going *Big*

- Larger ligands cause greater distortion

- Interligand repulsion

- Narrowest angle: Ch = Sulfur

- (-OAr) greater local sterics
 - bond pair – bond pair repulsion
 - Se: Less strain → less distortion

- Packing effects ignored

E = Si, Ge, Sn, Pb

- Results are improved with Dispersion correction correction (Grime's DFT-D3)

	<u>Si</u>			<u>Ge</u>			<u>Sn</u>			<u>Pb</u>		
Angles (θ)	Exp.	Calc.	Disp. Corr.	Exp.	Calc.	Disp. Corr.	Exp.	Calc.	Disp. Corr.	Exp.	Calc.	Disp. Corr.
SES	N/A	84.4	82.2	77.01(2)	82.2	77.8	73.09(2)	78.3	74.1	80.07(2)	79.0	73.6
CSE	N/A	117.2	116.4	119.42(6)	117.6	117.6	119.15(8)	117.9	119.0	117.4(9)	118.1	119.8

Deformation

Valence Kohn-Sham MOs of H-S-Ge-S-H and their energies (eV)

- Ch-E-Ch and CSE angle can both greatly impact orbital energy
 - Change order
 - $^{119}\text{Mössbauer}$ spectra of Sn derivatives supports calculations
- $n \rightarrow p$ transition can result from either $E_n \rightarrow E_p$ or $\text{Ch}_n \rightarrow E_p$

Conclusions from Part 1

- First Examples
 - Stable acyclic silylenes
 - First complete series of acyclic, heavier metallylenes (Si-Pb)
- The principal forces leading to the sub-90° bond angles are:
 - Intramolecular steric repulsion
 - Attractive dispersion forces between the bulky substituents
- The P.E.S. of the Ch-E-Ch is shallow (1-2 kJ mol⁻¹ per 5°)
- The size of the chalcogen has a large effect on the geometry of the metallylenes
 - Electronegativity play a minor role
- The HOMO can change depending on the interligand angle
- Exceptions to Bent's Rule can occur under strained condition

Part II: Materials Development for Energy Applications

Hydrogen Storage

Ion Gel Electrolytes

ORR Catalysts

Declining Petroleum Quality: A Prelude to Developing New Energy Storage Media

DOE: H₂ is part of the future

2005 initiative established 3 Centers of Excellence to address the long term issue

- Adsorbents
- Metal Hydrides
- Chemical Hydrides

All Major Auto Companies Believe Fuel Cells Are Central to the Industry's Future

Materials investigated in search of the “Fuel of the Future”

Ammonia-borane

Remaining Issues

Product PB (polyborazylene) is solid!

Volatile Impurities

Goal: Develop AB/IL mixtures that have sufficient:

H₂ capacity (8.7% as of May 2013)

Release kinetics

Stability

Little or no impurities

Transferability-Material is a fluid after H₂ release

The Solution is Keeping the Product in Solution

The Solution is Keeping the Product in Solution

Initial studies using mixtures of N-substituted amineboranes and AB produce a liquid product

Picture @ Room Temperature

20 wt. %AB in hexylAB (6.0 wt. % H_2) transforms from a slurry to liquid upon dehydrogenation

Solution: Develop substituted amineboranes that are also ionic liquids

B. D. Rekken, B. L. Davis, 2013, Patent Application: S-129386

B. L. Davis, A. Carré-Burritt, B. D. Rekken, H. Kalviri, N. Mack, R. T. Baker, T. Semelsberger. *Submitted*

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Ammonia-borane Substituted Ionic Liquids

Cations and anions investigated

Work has focused on the N-substituted AB-ILs (N-ABILs)

Cations

Imidazolium

Pyrrolidinium

Pyrazolium

$n = 2, 3$

$n' = 1, 2$

Anions

Halide

Triflate

Bistriflimide

N-Substituted Amine-Borane Ionic Liquids (N-ABILs)

Alternative cations can be prepared by the same method

N-substituted Amine-Borane Ionic Liquids

	Material	Initial State (20 °C)	Wt % H ₂
N-ABIL 1	Solid	2.46
N-ABIL 2	Solid	1.50
N-ABIL 3	Solid	2.28
N-ABIL 4	Oily Wax	1.43
N-ABIL 5	Solid	2.12
N-ABIL 6	Liquid	1.36
N-ABIL 7	Liquid	0.96
N-ABIL 8	Solid	2.09
N-ABIL 9	Liquid	1.32
N-ABIL 10	Solid	2.13

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N-ABIL 7

Liquid in the **Charged** State

Liquid in the **Spent** State

Viscosity (cP)
650 (33 °C)

Melting Point (°C)
< -20

Anion Greatly Impacts Dehydrogenation Temperature

Additives likely to co-oligomerize if dehydrogenation coincides with AB dehydrogenation

Structure of N-ABILs: Charged and Spent State

X-Ray Crystal Structure of N-ABIL 2

B-N Distance: (1.604(2) Å)

Anion-Cation Distances:

OTf-imidazolium ring (3.200(2) Å)

OTf-ammonium moiety (2.248(4) Å)

Charged

Size-Exclusion Chromatography

Anion Effects

- Chlorides = trimer
- Bistriflimides = Dimer
- AB Blends break-up IL only oligomers

Chloride

Bistriflimide

Bistriflimide/AB Blend

Spent

N-ABIL 7 with Ammonia-Borane (AB)

Material	Eq. AB	Initial/Final State	Wt. % H ₂
N-ABIL 7	0.5	Fluid/Viscous Liquid	1.4
N-ABIL 7	1	Fluid/Viscous Liquid	1.9
N-ABIL 7	2	Fluid/Viscous Liquid	2.8
N-ABIL 7	3	Slurry/Taffy	3.5
N-ABIL 7	5	Slurry/Solid	4.9
70% N-ABIL 7 30% MBPyrro NTf ₂	5	Slurry/Solid	4.7

Spent N-ABIL 7/AB Liquid

Ion Gels: Flexible electrolytes and supercapacitors

One of the major drawbacks of DSSC is the electrolyte stability over a period of time

Liquid electrolyte (rt.)

Preparation of Ion Gels: An Evolution

Hydrolysis and Condensation of Silica Precursor

Gelation Time
1-2 Days

TMOS

CVD Reactor

Gelation Time
2 Hours

Microwave Process

Gelation Time
5 Minutes

Ion Gel Impedance Characterization

High Energy Density Graphene Oxide Micro-Supercapacitors

- High energy density

$$E = \frac{1}{2} CV^2 / m$$

- Mechanical strength and flexibility

- High resolution laser patterning to increase surface area

- Chemical modification of GO to increase ionic conductivity

Non-Precious Metal Heterogeneous ORR Catalysis

- Fuel cells use catalysts to rapidly reduce O_2
- Pt and other precious metals are standard
 - Grid-scale prohibitive: cost, scarcity
- Catalysts using non-precious metals or metal-free are being explored
- N, Fe-doped graphitic species have demonstrated activity close to that seen for Pt

Amination of “holy” graphene oxide

Metal Starting
Materials

Rekken, B. D.; Martinez, U.; Purdy, G.; Mack, N.; Gupta, G.; Dattelbaum, A. *Unpublished Results*
C. Su et. al. *Nature. Comm.* **2012**, 3, DOI: 10.1038/ncomms2315

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Low-temperature synthesis of NGO from GO

Part II conclusions

- **Several new classes of ionic liquids have been synthesized, isolated and characterized**
- **New anhydrous method for anion-exchange in ILs**
- **N-ABILs were demonstrated to be a liquid before and after dehydrogenation**
- **Mixed N-ABIL/AB blends were shown to co-oligomerize to give a liquid product**
- **Ion gels were prepared that display very low impedance for a solid-state electrolyte**
 - Ionic liquid used in synthesis can have a large impact on the properties
- **Low-temperature, chemical pathways to NGO were prepared**
 - Materials display ORR catalytic activity

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Thank You

Extra Slides

Synthesis of Terphenyl Chalcogenols

Ar^{Me_6} : R = 2,4,6-Me₃, R' = H Ch = O, S, Se

Ar^{iPr_4} : R = 2,6-iPr₂, R' = H

Ar^{iPr_6} : R = 2,4,6-iPr₃, R' = H

Ar^{iPr_8} : R = 2,4,6-iPr₃, R' = 3,5-iPr₂

Stanciu, C.; Richards, A. F.; Stender, M.; Olmstead, M. M.; Power, P. P. *Polyhedron*, **2006**, 25, 477-483

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Substituent Effects on the NMR Shift

^{119}Sn NMR

$\text{Sn}(\text{SAr}^{\text{Me}_6})_2$: $\delta = 764$

$\text{Sn}(\text{SAr}^{\text{iPr}_4})_2$: $\delta = 815$

$\text{Sn}(\text{SAr}^{\text{iPr}_6})_2$: $\delta = 827$

$\text{Sn}(\text{SAr}^{\text{iPr}_8})_2$: $\delta = 919$

$\text{Sn}(\text{SeAr}^{\text{iPr}_4})_2$: $\delta = 1148$

- Paramagnetic contribution to NMR shift strongly affected by chalcogen
 - Electronegative = Upfield
 - Electropositive = Downfield
- Moderate steric effect
 - Narrower S-M-S angle = Downfield

$\text{Sn}(\text{OAr}^{\text{iPr}_4})_2$: $\delta = -290$

Effect of Acute Interligand Angles on Torsion Angles

- C-C-S-E torsion angles decrease with narrowing S-M-S moiety, bulkier ligands
 - Si, Ge, Sn

$\theta = 39.5^\circ$

$\theta = 3.3^\circ$

Extra Slide 1: Table of distances and angles

Table 1. Selected distances (Å) and angles (°), for M(SAr)₂ (M = Si, Ge, Sn, Pb) compounds.

Compound	S-M	S-M-S	C-S-M	M-S-C-C	C-S	M-Centroid	S---S	Reference
(1) Si(SAr ^{Me6}) ₂	2.158(3)*	90.52(2)	102.93(6)*	44.9(1)*	1.791(2)*	3.431*	3.0666(4)	25
(2) Si(SAr ^{Pri4}) ₂	2.137(1)	85.08(5)	113.80(9)	38.2(2)	1.775(2)	3.249	2.8903(9)	This Work
(3) Si(SAr ^{Pri6}) ₂ ^a	2.089(9)*	84.8(1)*	118.(1)*	29(7)*	1.77(1)	3.31(6)*	2.817(3)*	This Work
(4) Ge(SAr ^{Me6}) ₂	2.265(1)*	88.68(2)	103(3)*	40(6)*	1.785(1)*	3.28(5)*	3.1656(6)	This Work
(5) Ge(SAr ^{Pri4}) ₂	2.284(4)	81.26(2)	113.58(5)	32.3(1)	1.778(1)	3.094	2.9749(6)	This Work
(6) Ge(SAr ^{Pri6}) ₂ ^a	2.24(4)*	79.6(2)	114(1)*	27(7)*	1.79(3)*	3.3(1)*	2.867(7)	This Work
(7) Ge(SAr ^{Pri8}) ₂	2.2940(6)	77.01(2)	119.42(6)	3.6(2)	1.782(2)*	3.302	2.8566(6)	This Work
(24) Sn(SMes*) ₂	2.4356(3)	85.4(1)	101.64	86.34	1.8087(2)	4.383	3.3034(5)	23
(8) Sn(SAr ^{Me6}) ₂	2.479(5)*	85.555(3)	104(5)*	38(10)*	1.7815(9)*	3.22(9)	3.3677(4)	This Work
(9) Sn(SAr ^{Pri4}) ₂	2.470(1)	78.63(3)	113.8(1)*	31.2(3)*	1.778(4)*	3.082*	3.130(1)	This Work
(10) Sn(SAr ^{Pri6}) ₂	2.46(6)*	78.2(2)*	113(1)*	34(6)*	1.774(2)*	3.3(2)*	3.10(2)*	This Work
(11) Sn(SAr ^{Pri8}) ₂	2.5009(6)	73.09(2)	119.15(8)	3.8(2)	1.776(2)	3.220	2.9783(8)	This Work
(12) Pb(SAr ^{Pri4}) ₂	2.5656(9)	77.21(4)	113.42(11)	31.0(1)	1.771(3)	3.046	3.202(1)	26
(13) Pb(SAr ^{Pri6}) ₂	2.579(5)*	77.27(2)	114.9(7)*	28(8)*	1.772(2)*	3.12(5)*	3.2207(7)	This Work
(14) Pb(SAr ^{Pri8}) ₂	2.587(7)*	80.07(2)	117.4(9)*	29(4)*	1.782(1)*	3.08(2)*	3.3281(7)	This Work
* = Averaged Values								
a. Data for these two structures could not be refined to a low residual value.								

Table 2. Selected distances (Å) and angles (°) for compounds M(OAr)₂, M = Ge, Sn, Pb

Compound	O-M	O-M-O	C-O-M	M-O-C-C	C-O	M-Centroid	O---O	Reference
(17) Ge(OAr ^{Pri4}) ₂	1.8271(16) *	92.54(6)	128.03(13) *	36.9(4)*	1.378(3)*	3.377*	2.640(2)	40
(18) Sn(OAr ^{Me6}) ₂	2.041(3)*	87.32(11)	126.7(3)*	30.0*	1.343(6)*	2.961*	2.818(5)	31
(19) Sn(OAr ^{Pri4}) ₂	2.0472(17) *	92.18(6)	129.25(15) *	30.6*	1.360(3)*	3.163*	3.13	40
(20) Pb(OAr ^{Pri4}) ₂	2.216(8)*	99(1)*	127(2)*	26(5)	1.354(2)*	2.95(3)*	3.38(3)*	11
(21) Ge(OAr ^{*Me}) ₂	1.807(9)*	92.0(4)	124.7(7)*		1.44(2)*			8a
(22) Sn(OAr ^{*Me}) ₂	2.009(5)*	88.8(2)	125.2(5)*		1.371(7)*			8a
(23) Pb(OAr ^{*Me}) ₂	2.14(2)*	86.2(4)	124(2)*		1.36(1)*			8b
* = Average Value								
Ar*Me = C ₆ H ₂ Bu ^t ₂ -2,6-Me-4								

Table 3. Selected distances (Å) and angles (°) for compounds M(SeAr)₂, M = Ge, Sn

Compound	Se-M	Se-M-Se	C-Se-M	M-Se-C-C	C-Se	M-Centroid	Se---Se	Reference
(15) Ge(SeAr ^{Pri4}) ₂	2.396(5)*	84.715(1))	108.8(5)*	36(1)*	1.939(4) *	3.17(3)*	3.2301(6))	This Work
(16) Sn(SeAr ^{Pri4}) ₂	2.594(3)*	78.60(3)	112.1(3)*	26(7)*	1.935(9) *	3.17(7)*	3.286(1)	This Work
* = Average Value								

Table 5. ^{29}Si , ^{77}Se , ^{119}Sn , and ^{207}Pb Heteronuclear NMR chemical shifts for tetrylene dichalcogenolates				
	δ : ^{29}Si	δ : ^{77}Se	δ : ^{119}Sn	δ : ^{207}Pb
(1) $\text{Si}(\text{SAr}^{\text{Me6}})_2$	285.5			
(2) $\text{Si}(\text{SAr}^{\text{Pri4}})_2$	270.4			
(3) $\text{Si}(\text{SAr}^{\text{Pri6}})_2$	270.9			
(8) $\text{Sn}(\text{SAr}^{\text{Me6}})_2$			763.8	
(9) $\text{Sn}(\text{SAr}^{\text{Pri4}})_2$			814.8	
(10) $\text{Sn}(\text{SAr}^{\text{Pri6}})_2$			827.4	
(11) $\text{Sn}(\text{SAr}^{\text{Pri8}})_2$			919.4	
(12) $\text{Pb}(\text{SAr}^{\text{Pri4}})_2$				4283
(13) $\text{Pb}(\text{SAr}^{\text{Pri6}})_2$				4299
(14) $\text{Pb}(\text{SAr}^{\text{Pri4}})_8$				4335
(15) $\text{Ge}(\text{SeAr}^{\text{Pri4}})_2$				
		657.5		
		526.9		
(16) $\text{Sn}(\text{SeAr}^{\text{Pri4}})_2$		*	1148	
(18) $\text{Sn}(\text{OAr}^{\text{Me6}})_2$			-344	
(19) $\text{Sn}(\text{OAr}^{\text{Pri4}})_2$			-289.7	
(20) $\text{Pb}(\text{OAr}^{\text{Pri4}})_2$				1070
* $^1J_{\text{SeSn}} = 516 \text{ Hz}$				

Co-Published with Our Results

Si-B: 2.066(1) Å
Si-N: 1.731(1) Å
B-Si-N: 109.7(1)°

^{29}Si NMR: $\delta = 439.7$

HOMO-LUMO: 2.04 eV

Published back-to-back with
 $\text{Si}(\text{SAr}^{\text{Me}_6})_2$

Metal-Free Anion Exchange

Traditional Methods

- Classic procedures use silver and lithium salt that can be difficult to purify or do not metathesize
- Produces a waste product
- Amine-boranes are intolerant with H₂O which is often used in the purification

New Method

Easy Purification: Co-product (TMSCl) is highly volatile, allowing for easy separation

Waste Reduction: TMSCl can be reused in the synthesis of the silylamine

AB Compatible: Anhydrous method does not react with amine-borane moiety

X = OTf, NTf₂,

Ionic Liquid Choice Matters!

Ionic Liquid 1

Ionic Liquid 2

Impedance Characterization

1. A serial resistance R_S , including the resistances of the electrolyte, the TCO glass, and cables.
2. The charge transfer resistance $2R_{CT}$ at both electrodes. Due to the symmetry of the cell both electrodes contribute to the charge transfer resistance and must be considered.
3. The double-layer capacitance CDL at both electrodes. Again, the double-layer capacitances at both electrodes are taken into account due to the symmetry of the cell.