One Step Synthesis of a Perchlorinated Cyclohexasilane from Trichlorosilane: A Route to New Materials for Flexible Electronics

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Background

β-Hydrosilylation of Acrylonitrile and Acrylates

$CH_2=CH\text{-}X + HSiCl_3 \rightarrow Cl_3Si\text{-}CH_2CH_2\text{-}X$

X = CN, COOR

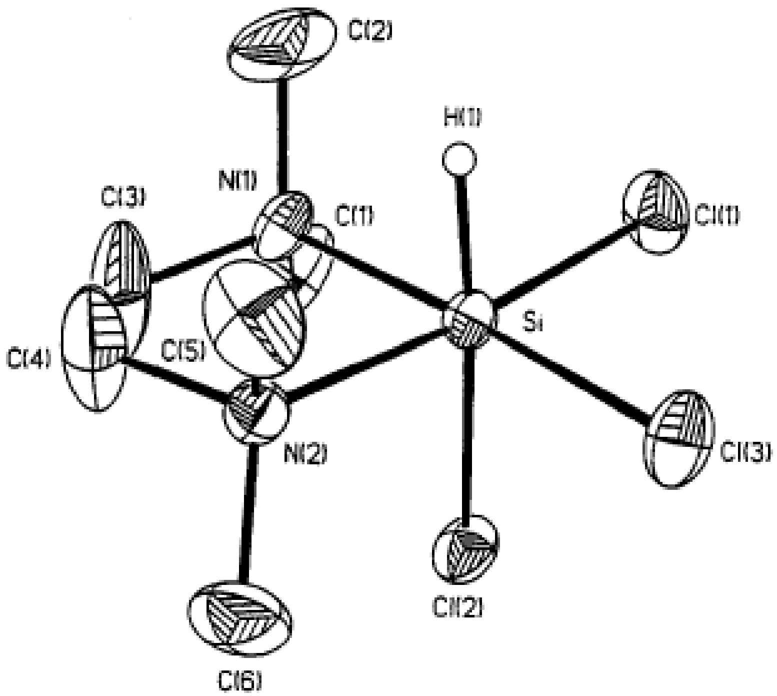
Catalyzed by Cu, Co halides or oxides with diamines

High yields, regiospecific

Looking for Intermediates in the Catalysis Reaction

Abundant literature on monoamine adducts of silanes,
very little on diamine and triamine adducts

(tmeda)$SiHCl_3$



Structural features

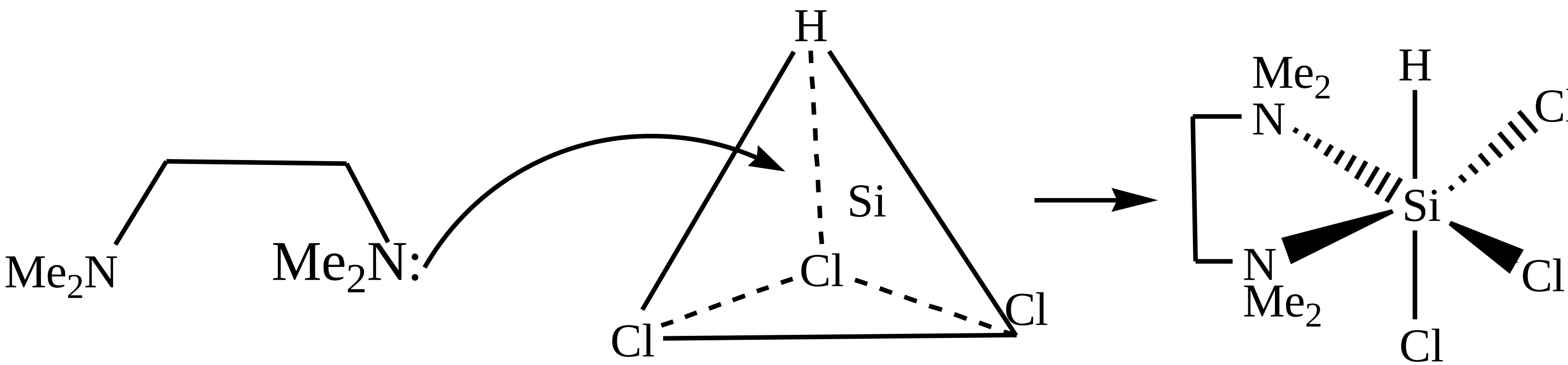
H-Si-Cl $_{(1,3)}$ ∠ 90.2^0; 92.9^0
H-Si-Cl$_{(2)}$ ∠ 175.5^0
N-Si-N ∠ 85.0^0

d(Si-H) = 1.363Å [Cl_3Si-H 1.454 calcd]
d(Si-Cl$_{(1,2,3)}$) = 2.205; 2.152; 2.202
d (Si-N$_{(1,2)}$) = 2.075; 2.087

Less stable isomer by ~16 kj/mol is formed

(using enSiH_2Cl_2 as model in MP2, MP4 calcns)

Dominant trend in 5 & 6 coordinate silanes is for more electronegative atoms to be *trans*



(tmeda)$SiCl_3H$

Attack at least hindered face produces final stereochemistry

Improve solubility with teeda? Yes, but with REDISTRIBUTION!

$$+ \ 2HSiCl_3 \longrightarrow (teeda)SiH_2Cl_2 \ + \ SiCl_4$$

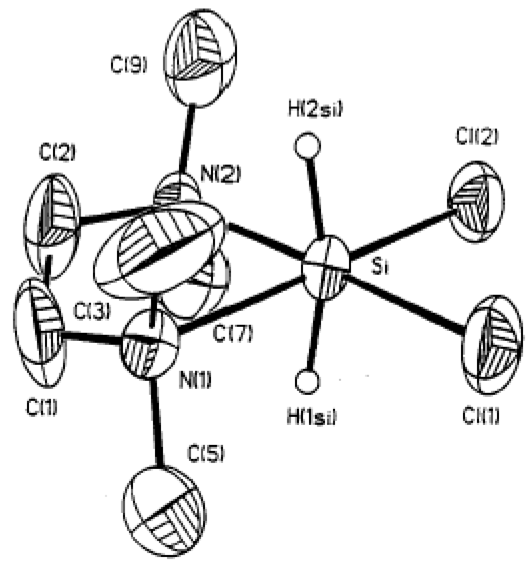
$(teeda)SiH_2Cl_2$ is nonflammable. Deliquesces in air

A very useful synthetic equivalent to H_2SiCl_2:

$$(teeda)SiH_2Cl_2 \ + \ 2\ RMgX \rightarrow R_2SiH_2 \quad >90\%$$

$$(teeda)SiH_2Cl_2 \ + \ 2\ RO^+ M^- \rightarrow (RO)_2SiH_2 \quad >80\%$$

Structural Features of (teeda)SiH_2Cl_2



d(Si-H) = 1.266 Å; 1.314   *d* (Si-N) = 2.134; 2.126   *d* (Si-Cl) = 2.223; 2.233

H_1-Si-H_2 ∠ 163.4^0 H_1-Si-Cl_2 ∠ 94.9^0 N_1-Si-N_2 ∠ 84.8^0

[$SiCl_2H_2$ calcd 1.469]   [$SiCl_2H_2$ e.d. 2.02]

Kinetic product is favored

Si 29 NMR data

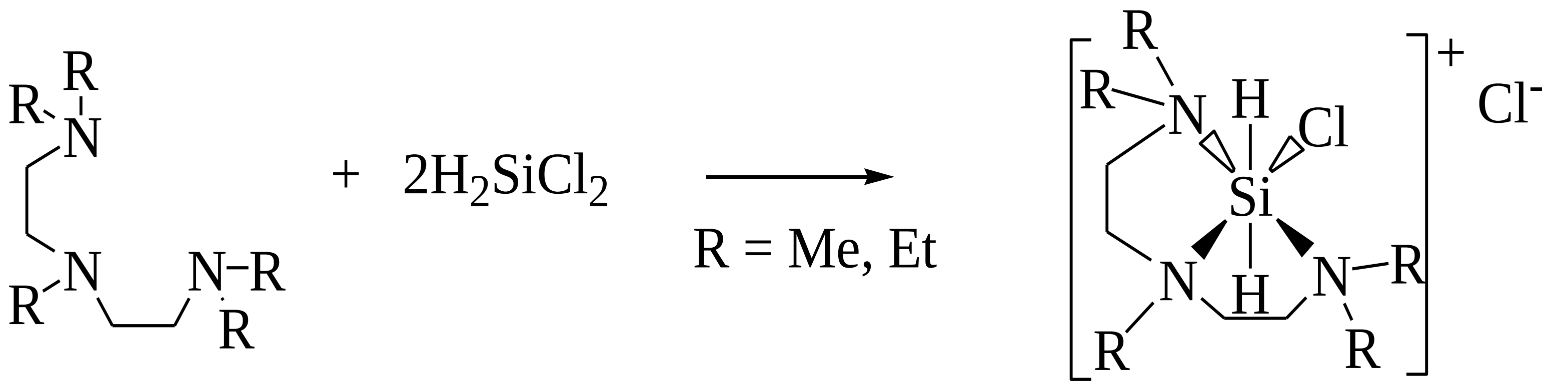
Complexing of simple chlorosilanes with diamines leads to very large Si-H coupling constants (Hz)

392 (tmeda)$SiHCl_3$ 368 $SiHCl_3$

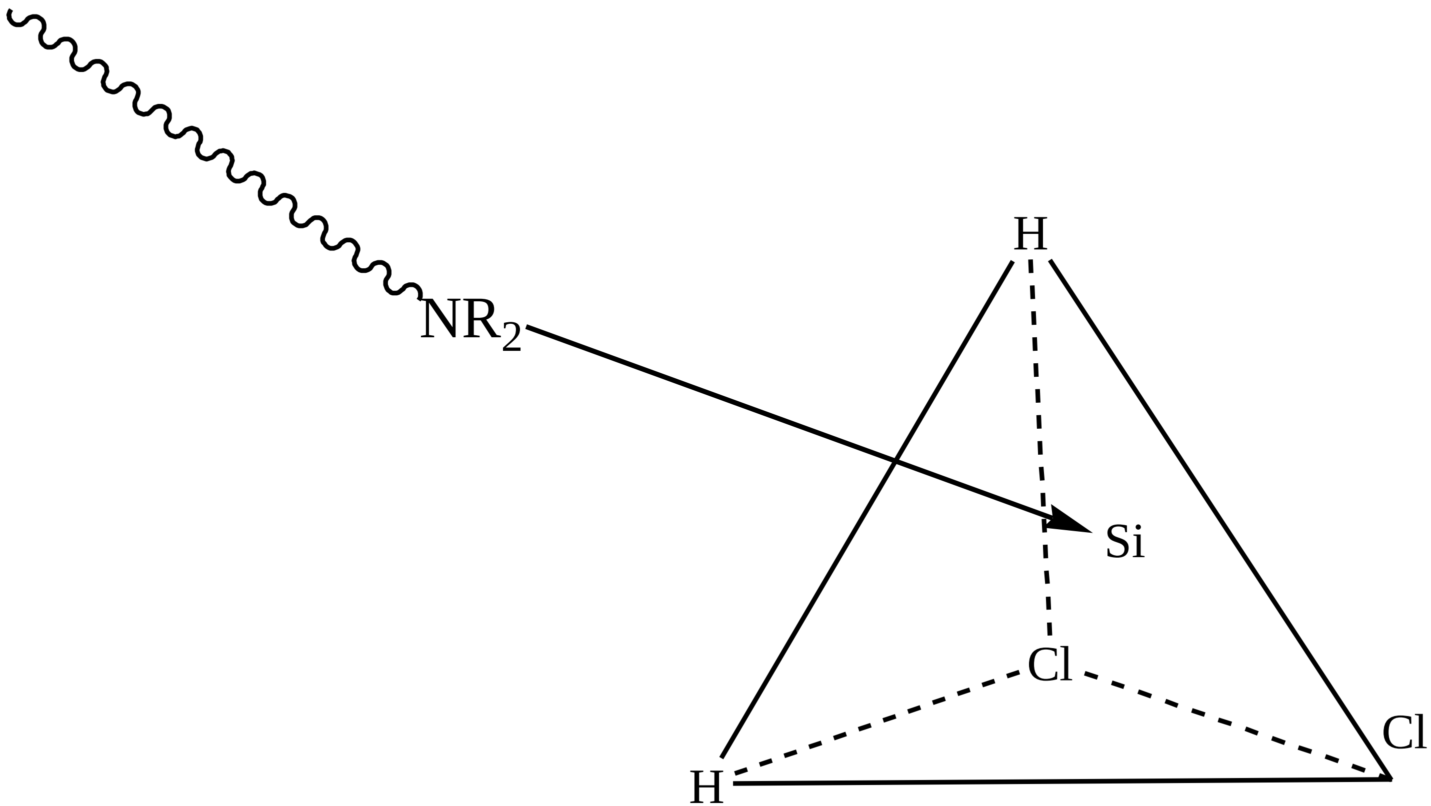
404 (teeda)SiH_2Cl_2 288 SiH_2Cl_2

Moving on to triamines

H_2SiCl_2 : Complexation + displacement with N-methyl and N-ethyl groups



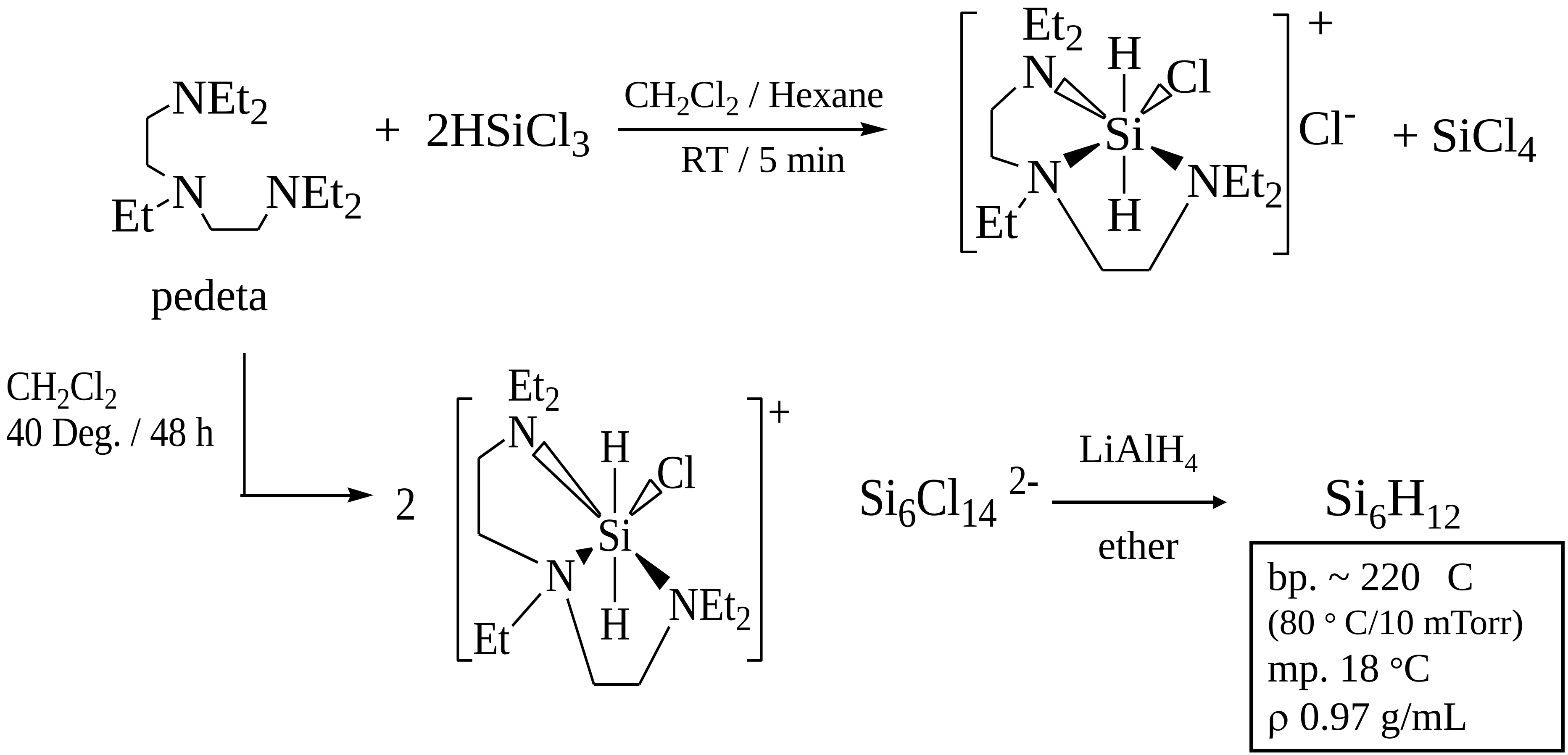
Attack on least hindered face (or edge) could explain stereochemistry



Reactions with tetraamines led to the complexation of only 3 of the 4 amines, no evidence of tetradentates

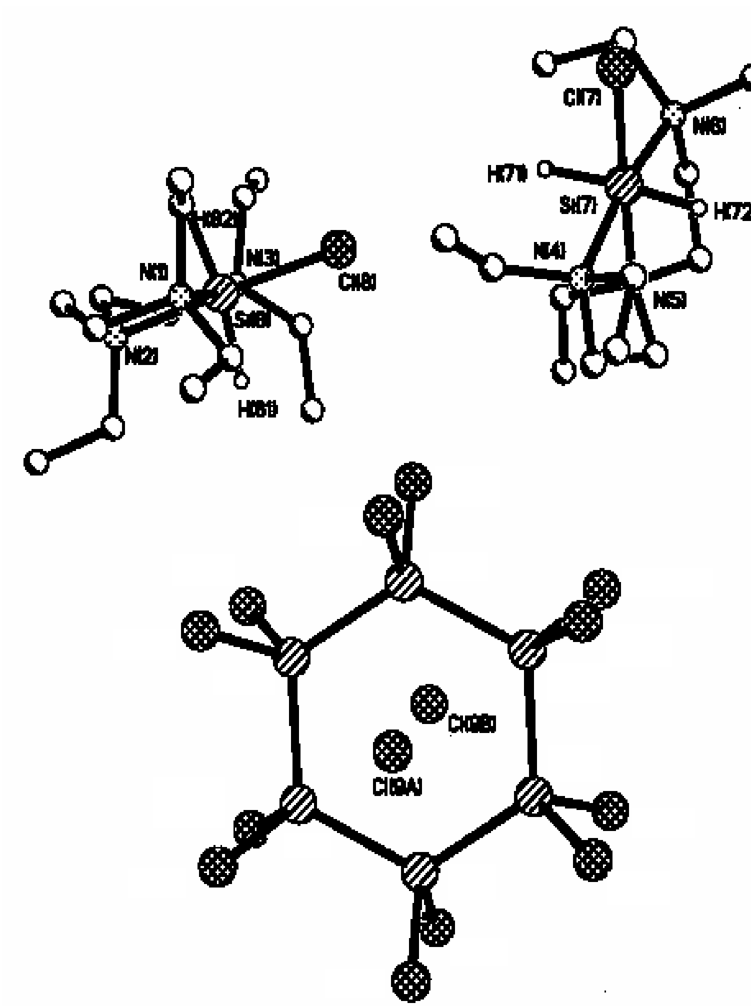
Cyclohexasilane Si_6H_{12} Chemistry

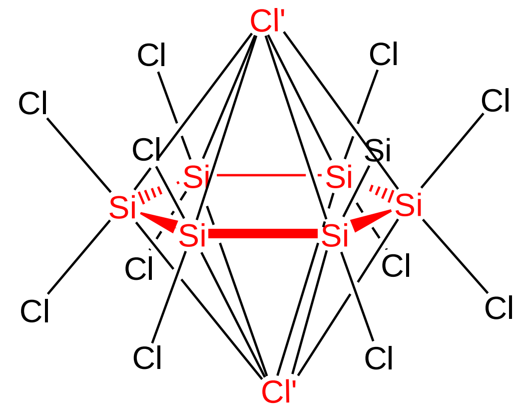
Amine-promoted displacement and redistribution: Si-Si bond formation



S.-B. Choi, B.-K. Kim, P. Boudjouk, D.G. Grier, *J. Am. Chem. Soc.* **2001,** *123*, 8117.

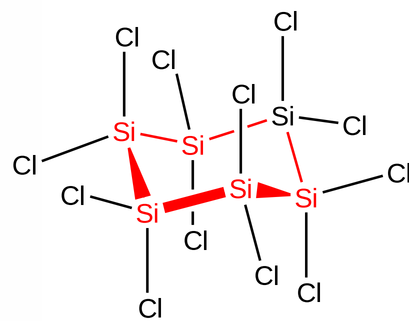
2[pedeta•H_2SiCl]$^+$ [Si_6Cl_{14}]$^=$



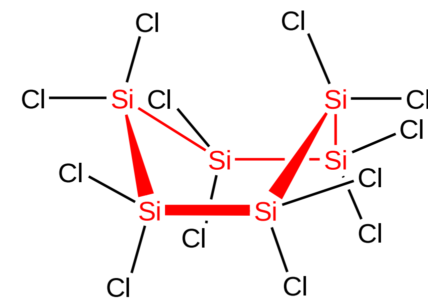


D6h

$\Sigma\angle Si_6ring$ = 719.5 (obs.)
720.0 (cal.)



D3d

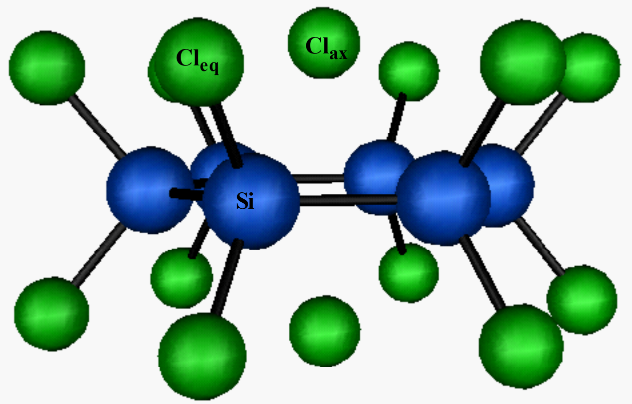


C2v

The PM3 calculated structure of Si_6Cl_{12} has D3d symmetry with Si -Si bond lengths of 2.463 Å, and Si-Cl bond lengths of 2.059 Å.

[i] Stuger, H.; Janoschek, R. *Phophorus, Sulfur, and Silicon*, **1992**, *68*, 129.

STRUCTURE

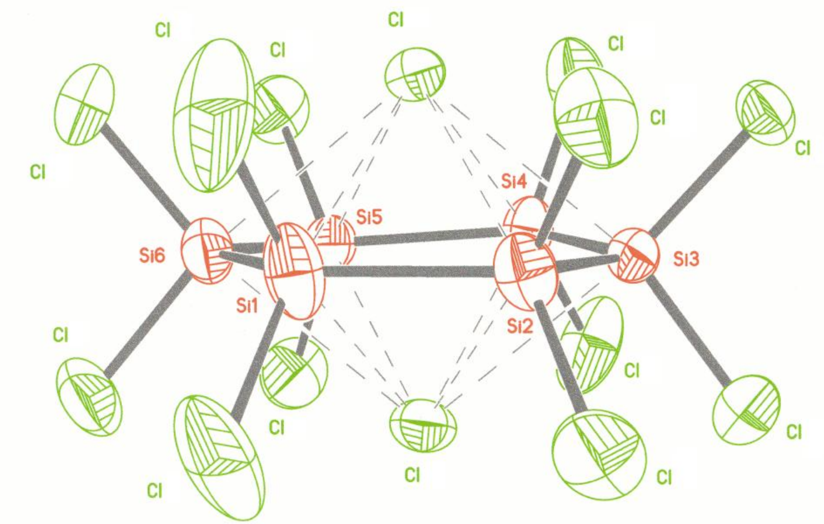


R (Si-Si) = 2.34Å (calc), ~2.32Å (expt)

R ($Si-Cl_{eq}$) = 2.10Å (calc), ~2.08Å (expt)

R ($Si-Cl_{ax}$) = 3.06Å (calc), 3.00Å (expt)

Crystal structures



$[pedeta•H_2SiCl]^+_2\ [Si_6Cl_{14}]^=$

$[pedeta•H_2SiBr]^+_2\ [Si_6Br_{14}]^=$

Selected Bond Lengths of $[Si_6X_{14}]^{2-}$

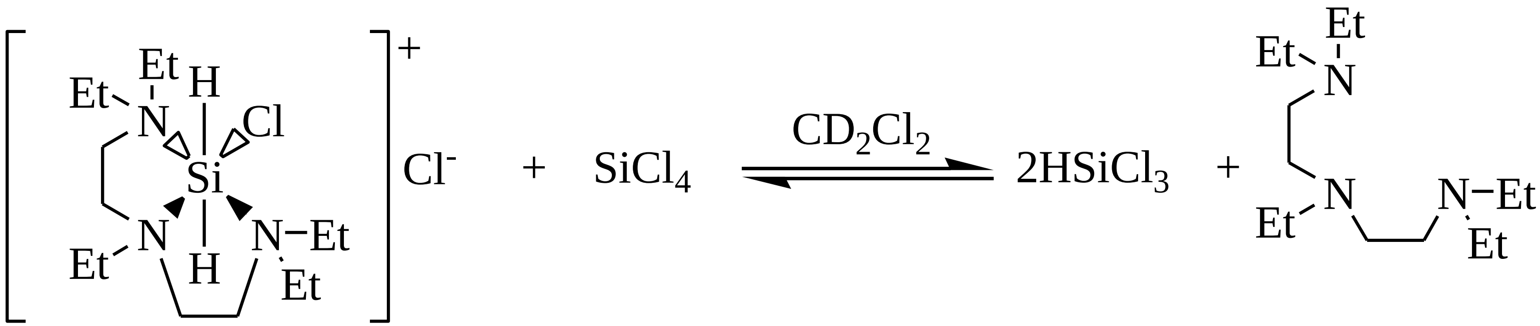
	X = Cl, X' = Cl	X = Br, X' = Br
Si - X	2.078	2.237
Si - X'	3.000	3.114
Si - Si	2. 319	2.345
X - plane of Si6 ring	1.60	1.73
X' - plane of Si6 ring	1.91	2.05
X' - X'	3.81	4.100

r_{cov} (Si) = 1.17 Å, r_{vdw}(Si) = 2.10 Å

r_{cov} (Cl) = 0.99 Å, r_{vdw}(Cl) = 1.80 Å; r_{cov} (Si-Cl) = 2.16 Å; r_{vdw}(Si-Cl) = 3.90 Å)

r_{cov} (Br) = 1.14 Å; r_{vdw}(Br) = 1.90 Å; r_{cov} (Si-Br) = 2.31 Å; r_{vdw}(Si-Cl) = 4.00 Å)

^{1}H & ^{29}Si NMR study in CD_2Cl_2



$SiCl_4$, $HSiCl_3$ and $Cl_3Si{:}^-$ observed by ^{29}Si nmr

Complexed, protonated, and free amines observed by ^{1}H nmr

Alternate Routes to $Si_6X_{14}{}^{2-}$

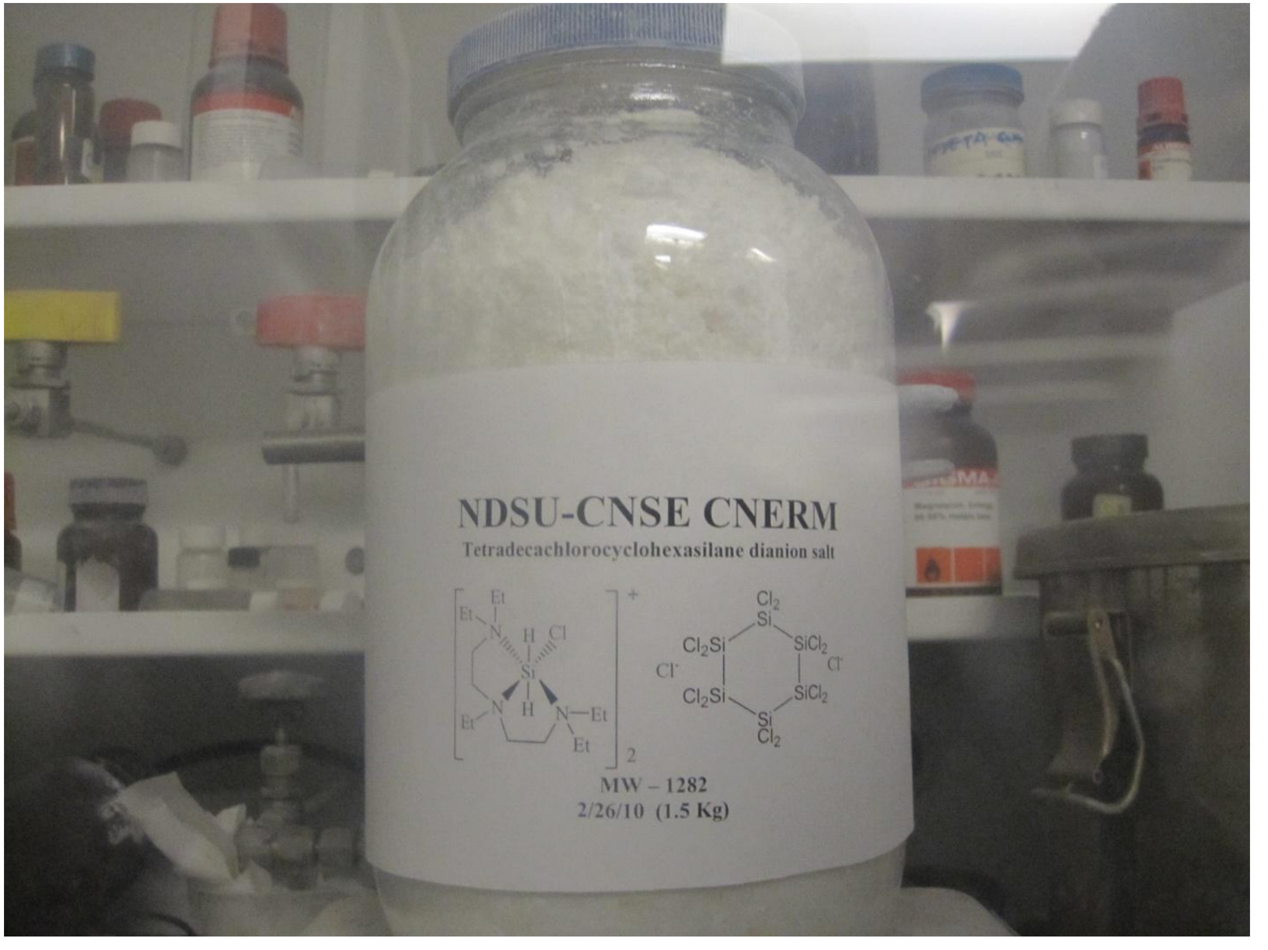
$[\text{pedeta}\bullet H_2SiCl]^+ Cl^- + SiCl_4 \rightarrow 2[\text{pedeta}\bullet H_2SiCl]^+ [Si_6Cl_{14}]^{2-}$

$[\text{pedeta}\bullet H_2SiCl]^+ Cl^- + SiBr_4 \rightarrow 2[\text{pedeta}\bullet H_2SiBr]^+ [Si_6Br_{14}]^{2-}$

$\text{pedeta} + Cl_3SiH + Ph_4PCl \rightarrow 2[Ph_4P]^+ [Si_6Cl_{14}]^{2-}$

(good quality crystals)

1.5 Kg of $[Si_6Cl_{14}^{=}]\ 2[NR_4^{+}]$



$Si_6Cl_{14}^{2-}$ Useful Precursor to Si_6H_{12} and Si_6X_{12}

$$\mathrm{Ph_2SiCl_2} \xrightarrow{\mathrm{Li}} \underset{1.8\%}{\mathrm{Ph_{12}Si_6}} \xrightarrow[\mathrm{AlCl_3}]{\mathrm{HX,\ RX}} \underset{60\%}{\mathrm{Si_6X_{12}}} \xrightarrow{\mathrm{LAH}} \underset{>90\%}{\mathrm{Si_6H_{12}}}$$

$$\mathrm{Cl_3SiH} \xrightarrow{\mathrm{pedeta}} \underbrace{\underset{80\%}{\mathrm{Si_6Cl_{14}^{2-}}} \xrightarrow{\mathrm{LAH}} \underset{>90\%}{\mathrm{Si_6H_{12}}} \xrightarrow{\mathrm{X_2}} \underset{>90\%}{\mathrm{Si_6X_{12}}}}_{65\%}$$

Approximately 72% yield of Si_6H_{12} from Cl_3SiH

Basic Reactions of $Si_6Cl_{14}^{2-}$

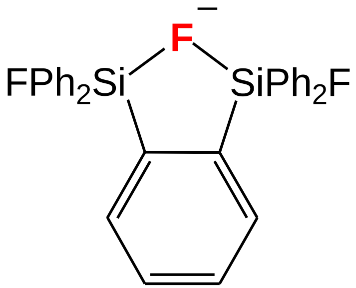
$$2R^+ \; Si_6Cl_{14}^{2-} \quad + \quad xs\ MeMgBr \quad \rightarrow \quad Si_6Me_{12}$$

$$2R^+ \; Si_6Cl_{14}^{2-} \quad + \quad xs\ PhMgBr \quad \rightarrow \quad Si_6Ph_{12}$$

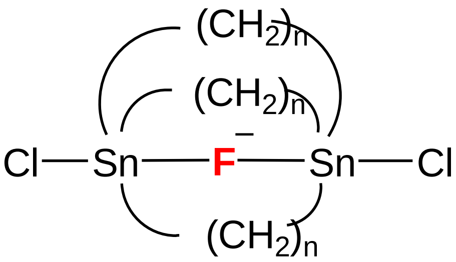
$$2R^+ \; Si_6Cl_{14}^{2-} \quad + \quad xs\ LiAlH_4 \quad \rightarrow \quad Si_6H_{12}$$

Yields $> 90\%$

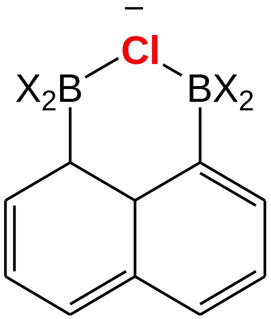
Intermolecular Complexation of Multidentate Lewis Acid hosts and Lewis Base Guests



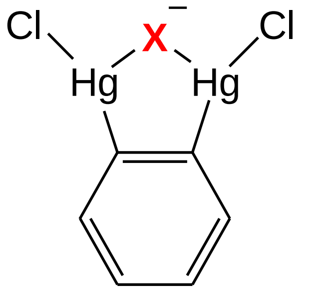
1990, Tamao & Ito
^{13}C, ^{19}F, ^{29}Si NMR, X-ray



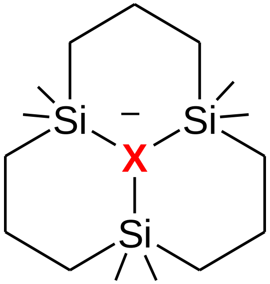
1987, 1989, Newcomb
^{119}Sn NMR, X-ray



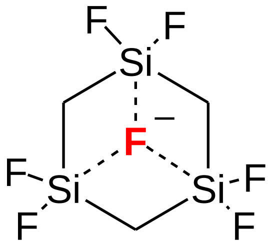
1987, Katz
X-ray



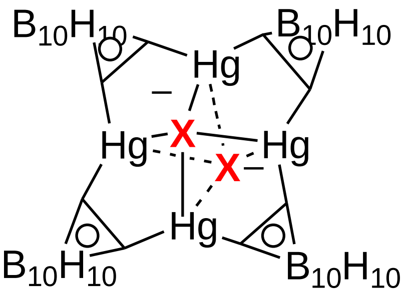
1985, Wuest
X-ray



1988, Jung
Transport studies



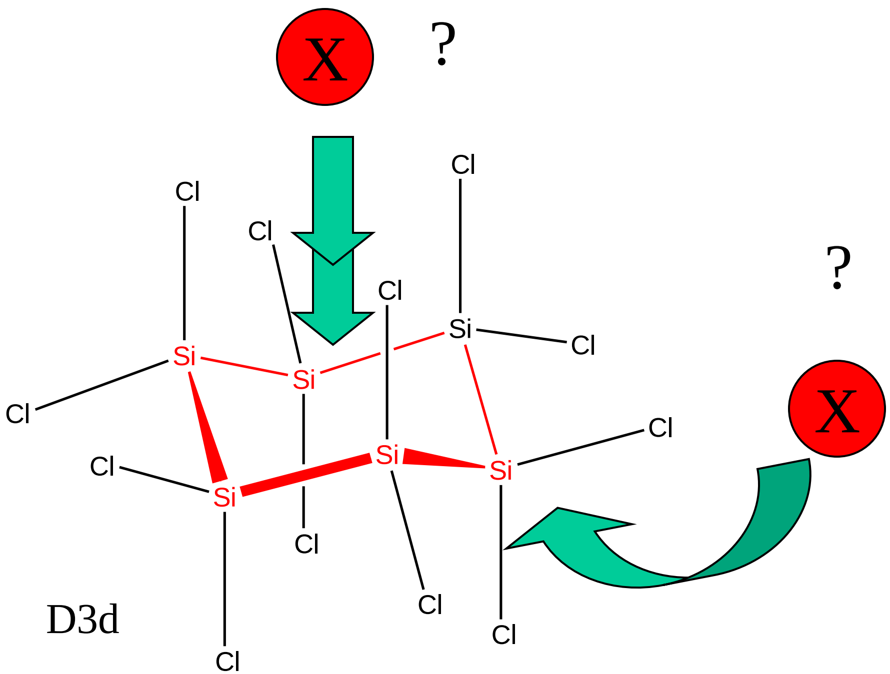
1996, Corriu, X-ray
^{19}F, ^{29}Si NMR (-25.56, s)



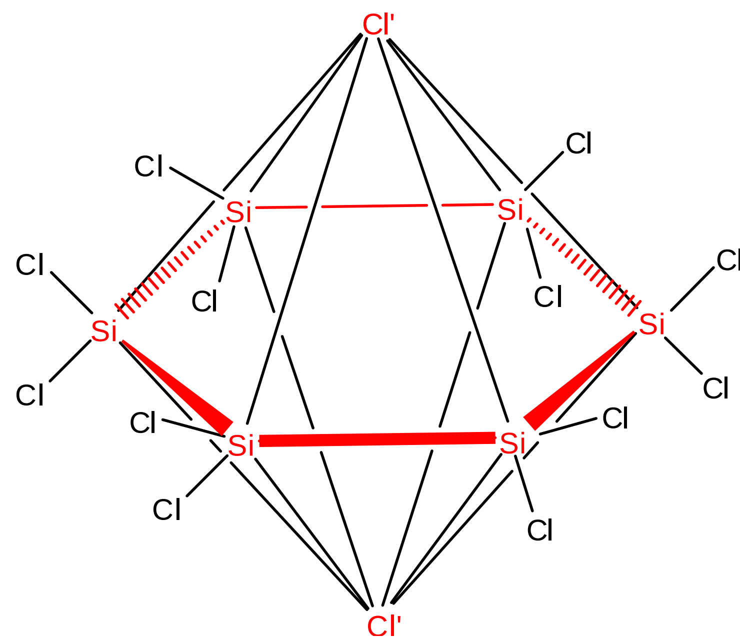
1992, Hawthorne,
X-ray

Dodecachlorocyclohexasilane as a Multidentate Lewis Acid Host

$$Si_6Cl_{12} \quad + \quad 2RX \longrightarrow R_2[Si_6Cl_{12}X_2]$$



D3d



Synthesis of $R_2\,[Si_6Cl_{12}X_2]$ from Si_6Cl_{12}

$$Si_6Cl_{12} \quad + \quad 2R^+\,X^- \;\rightarrow\; 2\,R^+\,[Si_6Cl_{12}X_2]$$

X = Cl, Br, I R = [Pedeta•H_2SiCl], $BnEt_3N$ and Ph_4P

White crystals, yield: 75 - 95%

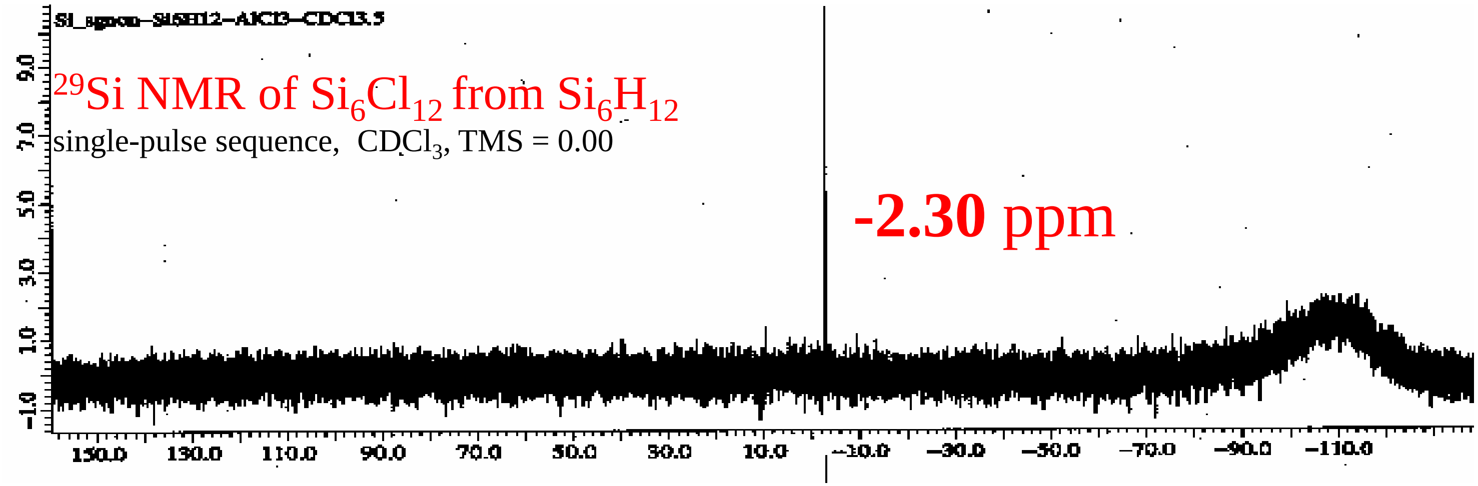
	Compound	C/H(/N) (Cal)	C/H(/N) (Found)
1	X = Cl, R = H_2SiCl•pedeta	26.22/5.50/ 6.55	26.25/5.42/6.45
2	X = Br, R = $BnEt_3N$	27.43/3.90/2.46	27.22/3.75/2.39
3	X = Br, R = Ph_4P	40.24/2.81	39.32/2.81
4	X = I, R = Ph_4P	37.77/2.64	36.44/2.54

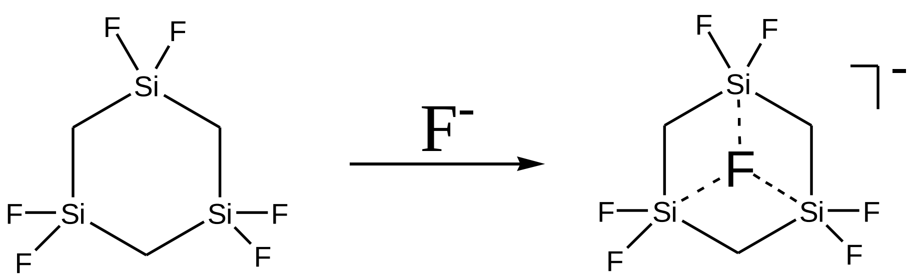
^{29}Si NMR Data

$$^{29}\text{Si (ppm)} = -22.05 \ ([\text{pedeta}\bullet\text{H}_2\text{SiCl}]^+_2\ [\text{Si}_6\text{Cl}_{14}]^= \text{ in } \text{CD}_3\text{CN})$$

$$= -22.71 \ ([\text{n-Bu}_4\text{N}]^+_2\ [\text{Si}_6\text{Cl}_{12}\text{Br}_2]^= \text{ in } \text{CD}_2\text{Cl}_2)$$

downfield from that of dodecachlorocyclohexasilane (-2.5 ppm).[i] Hengge, E. *Monatsh. Chem.* **1979**, *110*, 1295.





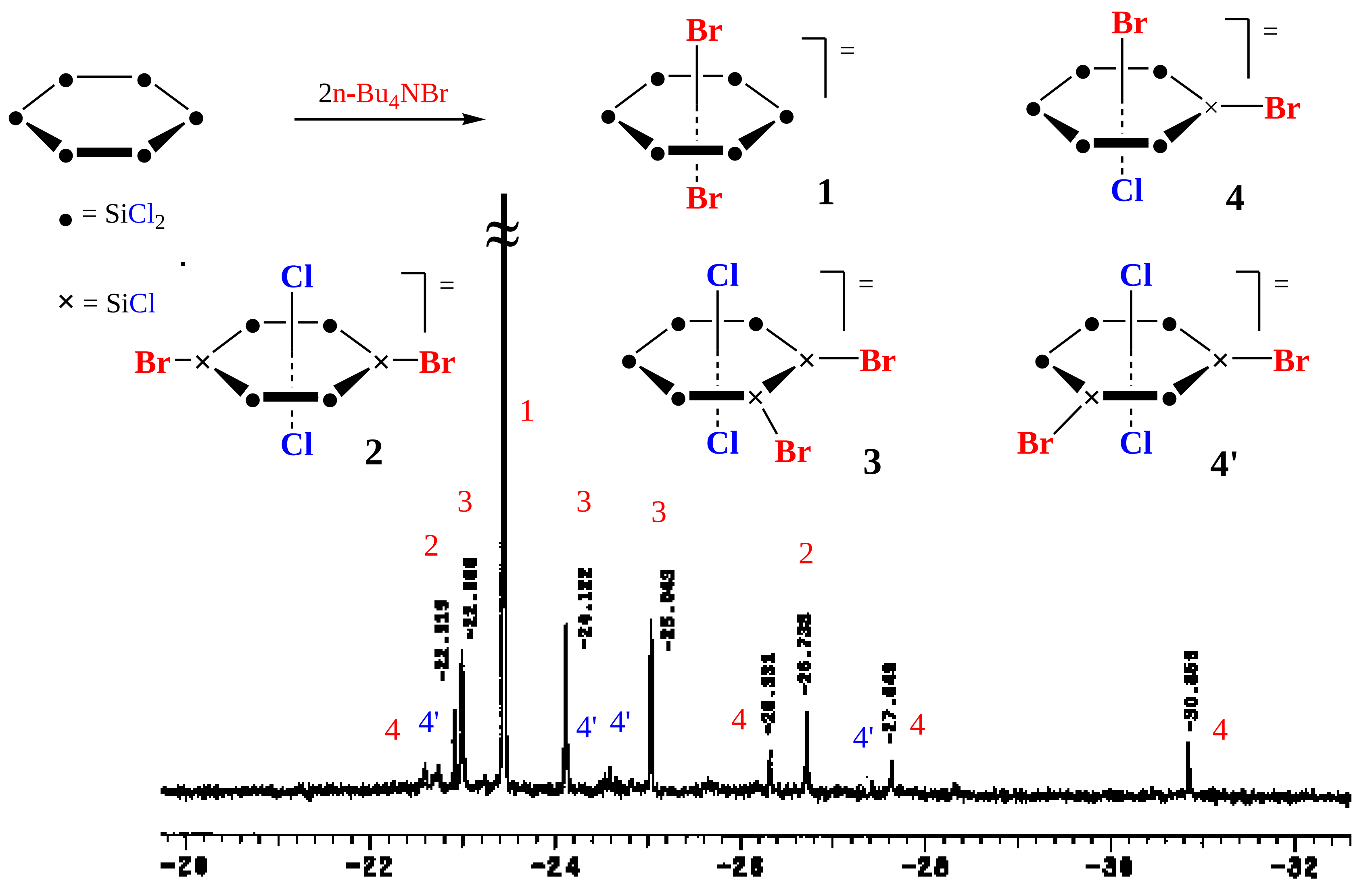
δ = -2.38 ppm

-25.56 ppm

Corriu, R. J. P. *ACIEE.* **1996**, *35*, 324.

^{29}Si-NMR Study of the reaction of Si_6Cl_{12} with n-Bu_4NBr

Si_6Cl_{12} + 2n-Bu_4NBr ⟶ (n-$Bu_4N)_2Si_6Cl_{12}Br_2$ White crystal, high yield



Possible Mechanism

$$SiCl_3H \quad + \quad teeda \quad \rightleftharpoons \quad teedaH^+ \quad + \quad Cl_3Si^-$$

$$Cl_3Si^- \quad + \quad SiCl_3H \quad \rightleftharpoons \quad Si_2Cl_5H \quad + \quad Cl^-$$

$$Cl_3Si^- \quad + \quad Si_2Cl_5H \quad \rightleftharpoons \quad Si_3C_7H \quad + \quad Cl^-$$

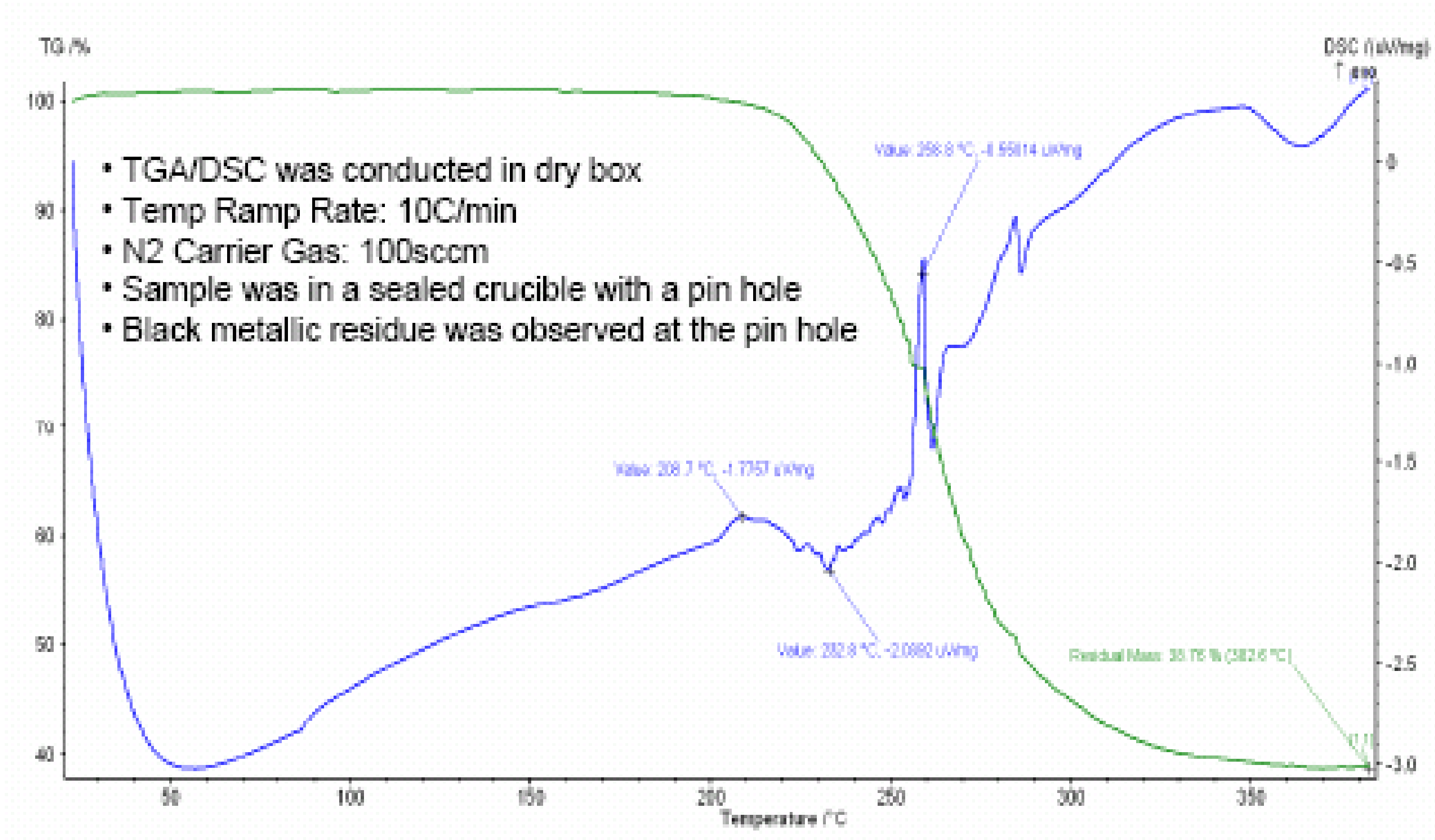
$$Si_3Cl_7H \quad + \quad teeda \quad \rightleftharpoons \quad Si_3Cl_7^- \quad + \quad teedaH^+$$

$$2Si_3Cl_7^- \longrightarrow Si_6Cl_{14}^{2-}$$

Some Properties of CHS

- Clear colorless liquid, bp 80^{o}/10-15 torr
- Flammable in air
- Stores indefinitely at $0^{o}C$ under nitrogen
- Amenable to Direct Write Applications
- Can be monochlorinated with $HgCl_2$ …
- Thermally stable at $100^{o}C$ for 12 hr
- Loses H rapidly above $220^{o}C$

TGA/DSC of Cyclohexasilane



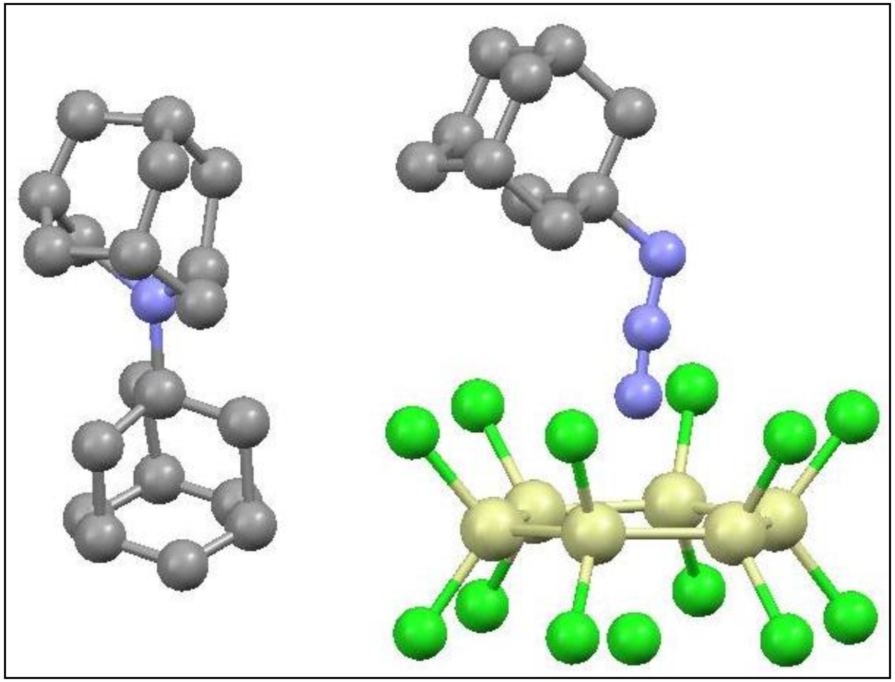
CHS is stable at 100 degC for at least 12 h

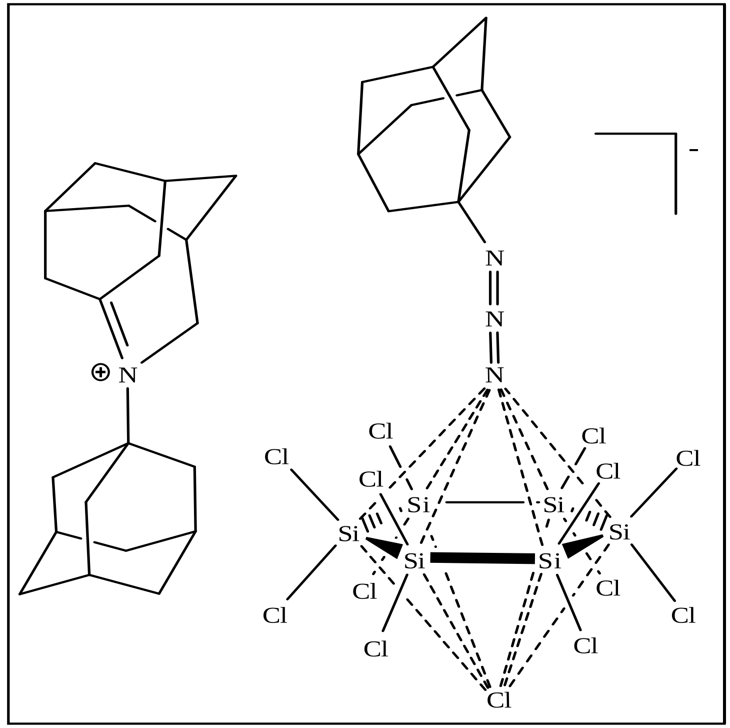
In Search of Neutral Adducts to the Si-6 Ring

Si_6Cl_{12} + 2 AdN_3 → white crystals

simple addition of one or two AdN_3?

Surprise!





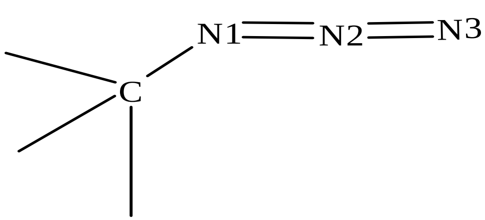
Si-Si: 2.33-2.35 (Å),
Si-Cl: 2.05-2.08 (Å)
Si-Cl': 3.07-3.15 (Å)
Si- N: 3.03 – 3.20 (Å)
Si-Si-Si: 119.15(8)-120.95(8)°

R (I>2σ(I)]: 0.0632
R (all data): 0.2279
N3-Si6(centroid): 2.043 (Å)
Cl-Si6(centroid): 1.897 (Å)

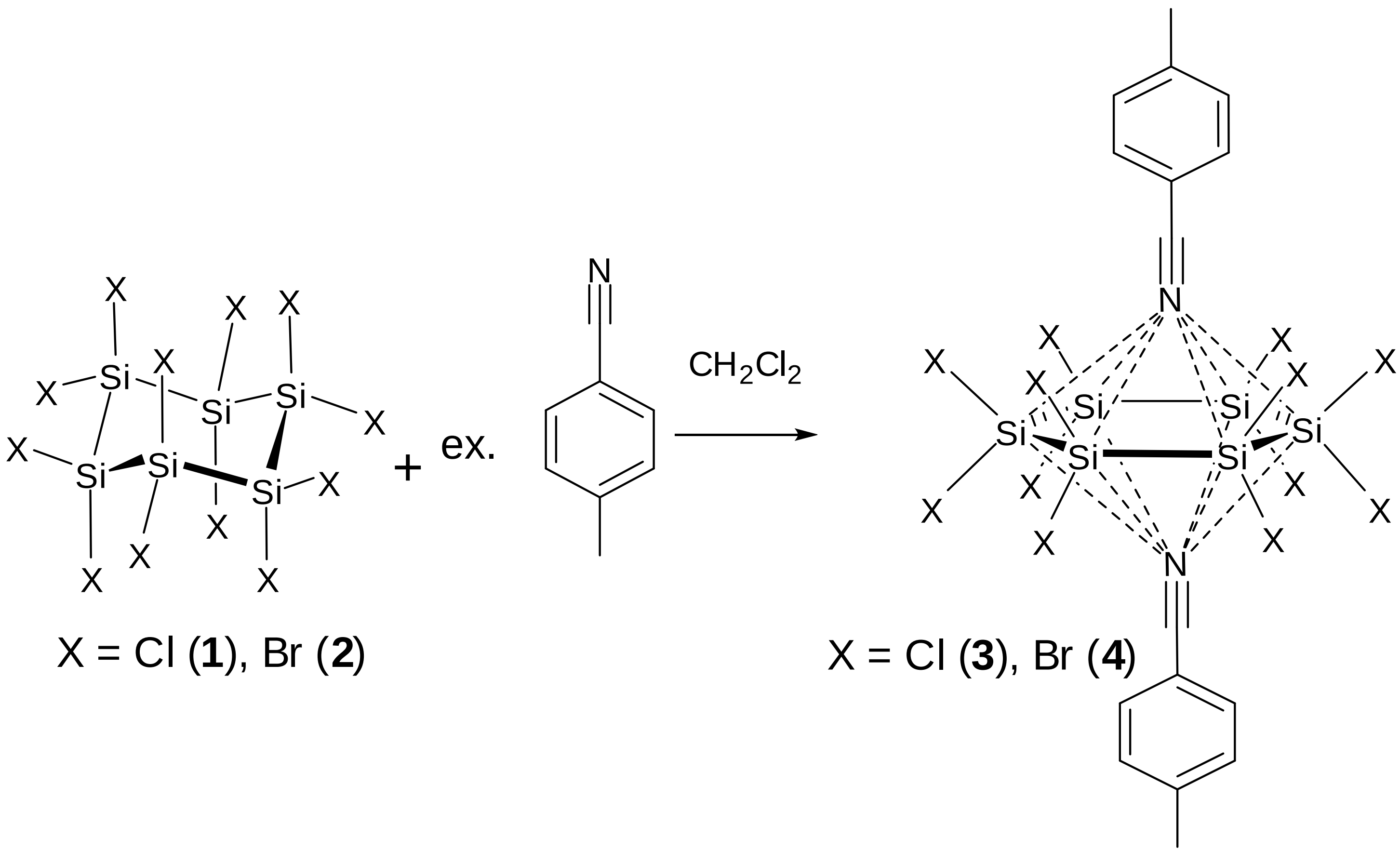
Comparison of Coordinated Azide and Free Organoazide

Compound	Bond Distance (Å)			Angles (deg.)	
	C-N1	N1-N2	N2-N3	C-N1-N2	N1-N2-N3
$[AdN_3\ Si_6Cl_{12}\ Cl]^-$	1.523(8)	1.21(1)	1.112(8)	116.7(7)	174.4(7)
$[HBPz^F{}_3]Cu\text{-}N_3Ad$ [a]	1.509(4)	1.219(4)	1.136(4)	116.1(3)	173.1(3)
MeN_3 [b]	1.472	1.244	1.162	115.2	172.5

a: Dias, H. V. R. *et al*, Inorg. Chem., **2000**, 39, 3894.
b: Nguyen, M. T., *et al*, J. Phys. Chem., **1996**, 100, 6499, the data are calculated results.

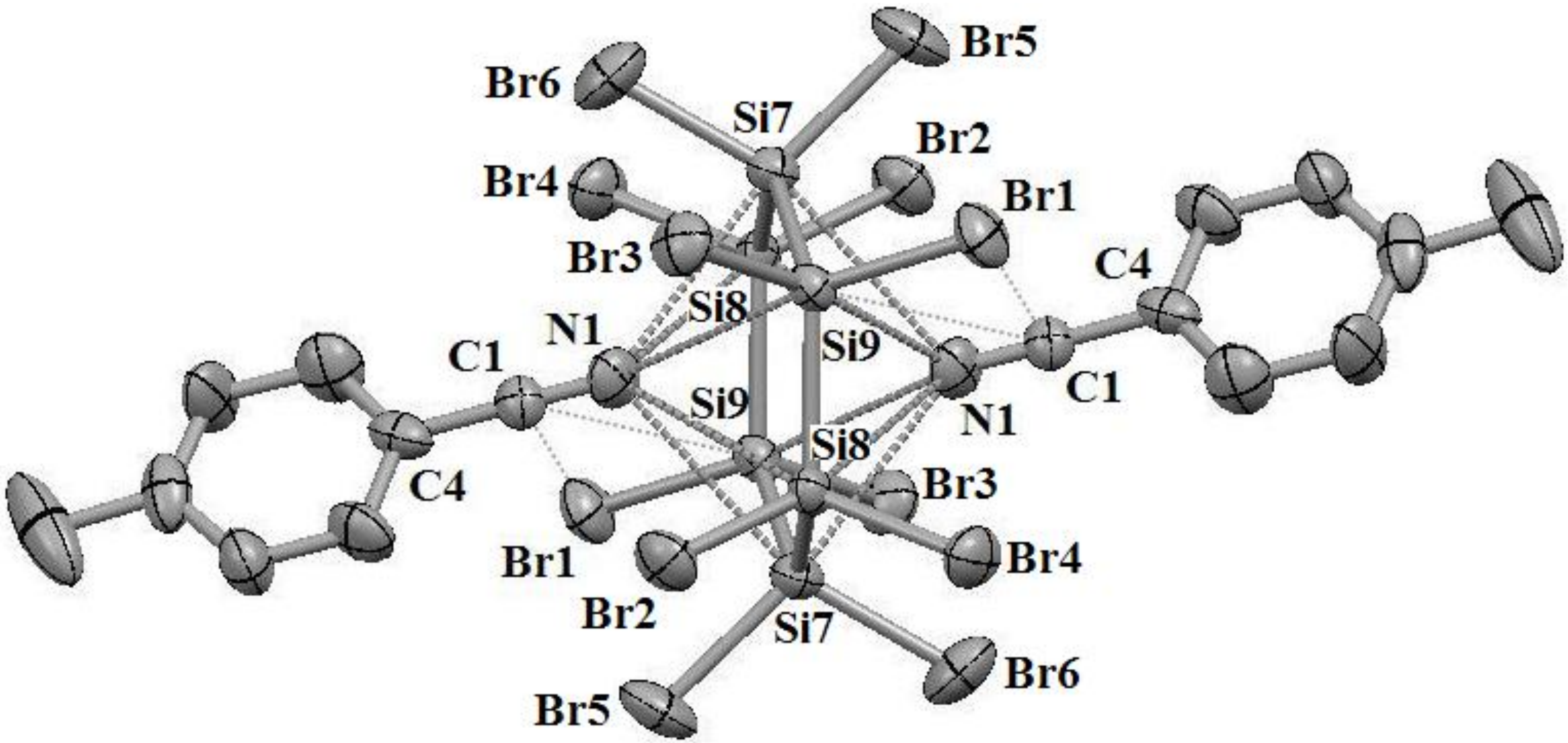


Inverse Sandwich Chemistry
Addition of Tolunitrile to Si_6Cl_{12}



X = Cl (**1**), Br (**2**)

X = Cl (**3**), Br (**4**)

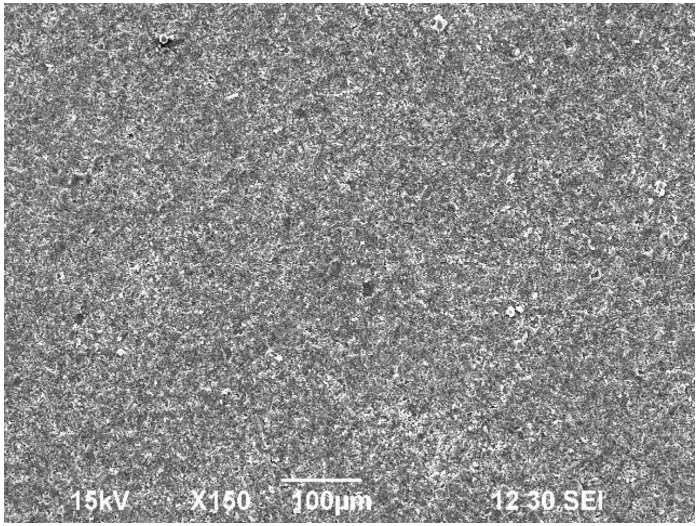

Br5
Br6
Si7
Br2
Br4
Br1
Br3
C4
Si8
N1
Si9
C1
C1
Si9
N1
Si8
C4
Br3
Br1
Br4
Br2
Si7
Br6
Br5

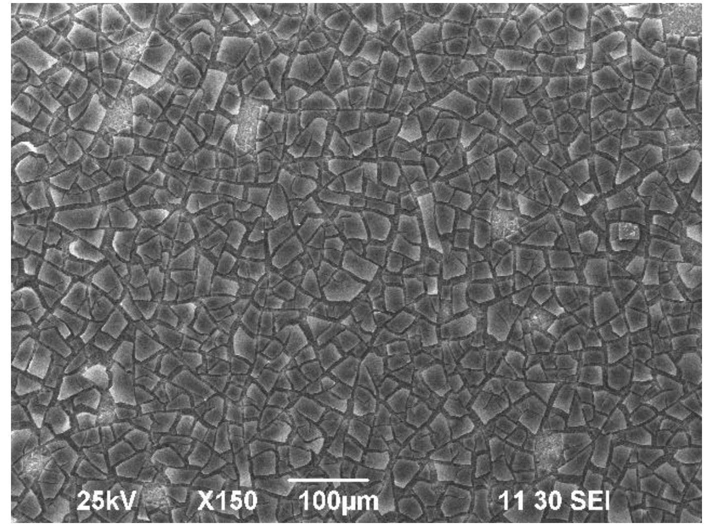
Printed Silicon – Thicker Films Crack

~1 µm

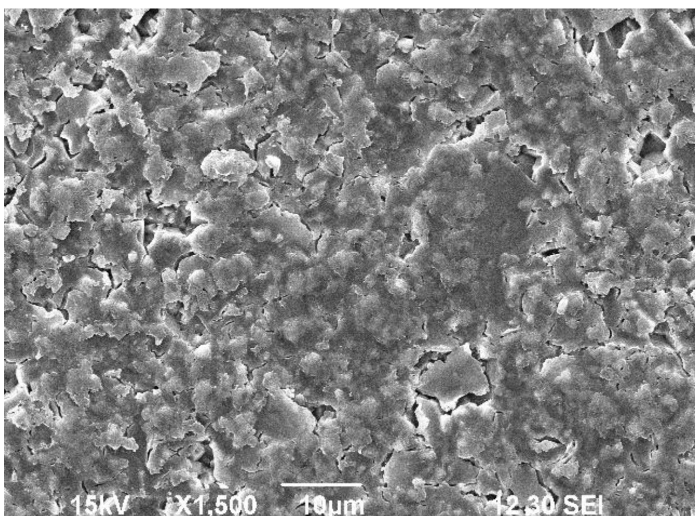
~3 µm

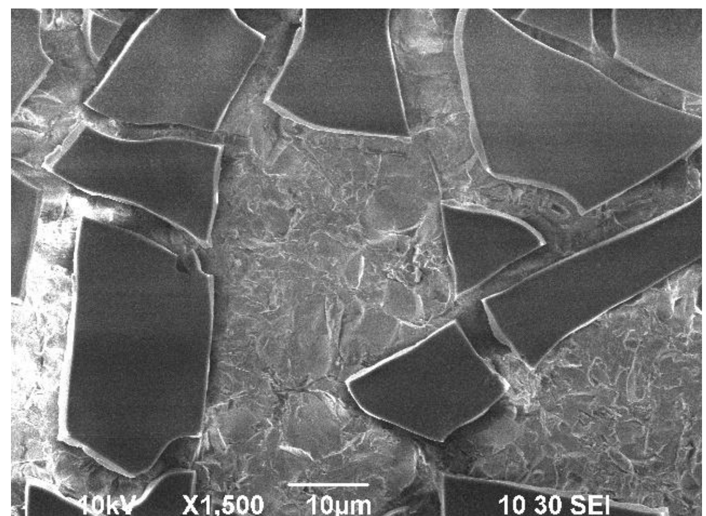
Low Magnification





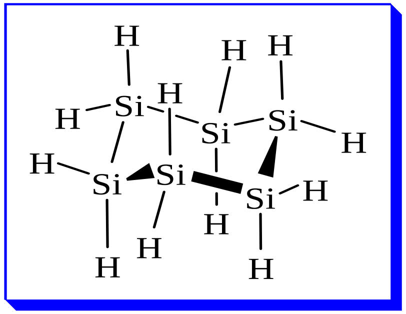
High Magnification

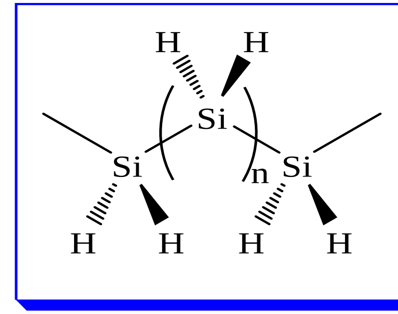




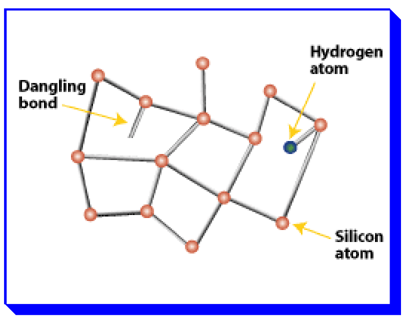
Si_6H_{12} readily transforms to a-Si:H and rc-Si

Cyclohexasilane $\xrightarrow{\text{Heat or UV irradiation}}$ **Polysilane**



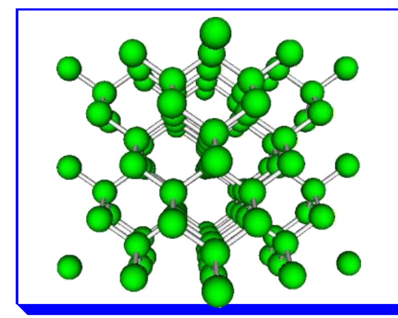


$\xrightarrow{\text{Heat}}$ **a-Si:H** $\xrightarrow{\text{Heat or laser}}$ **rc-Si**



amorphous silicon

a-Si:H and rc-Si used as photon absorber layers for solar cells and active layer in TFTs



recrystallized silicon

Cyclohexasilane-Enabled Printed Silicon

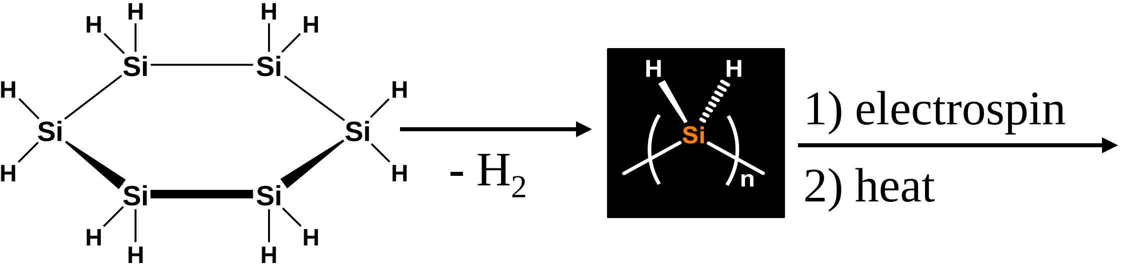
Si_6H_{12} (l) → printed circuits (5 um) via
Collimated Aerosol Beam-Direct Write Technology

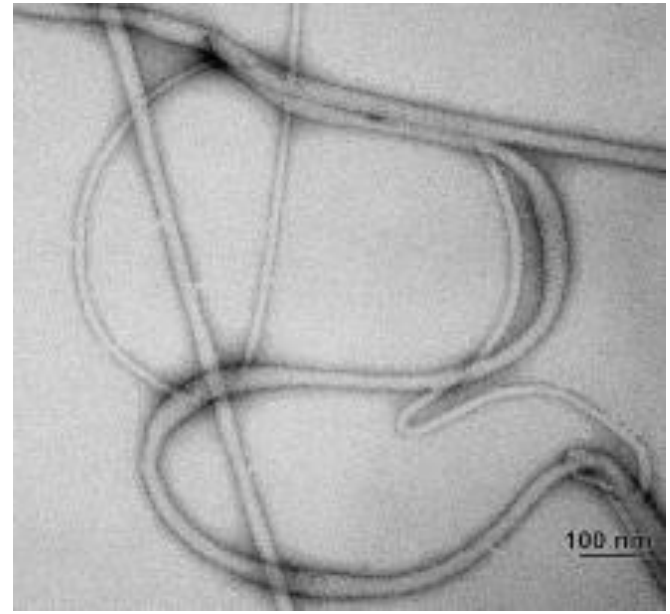
Potential Benefits in the Field of Printed Flexible Electronics

- Superior and proven electronic characteristics (vs. organic semiconductors)
- Improved shelf-life using "neat" ink (vs. doped Si-nanoparticle/ liquid silane)
- Lower temperature transformation to a-Si:H (plastic substrates)

•Other potential applications: solar cells, transistors

Electrospinning SiNWs from Si_6H_{12}-based Inks

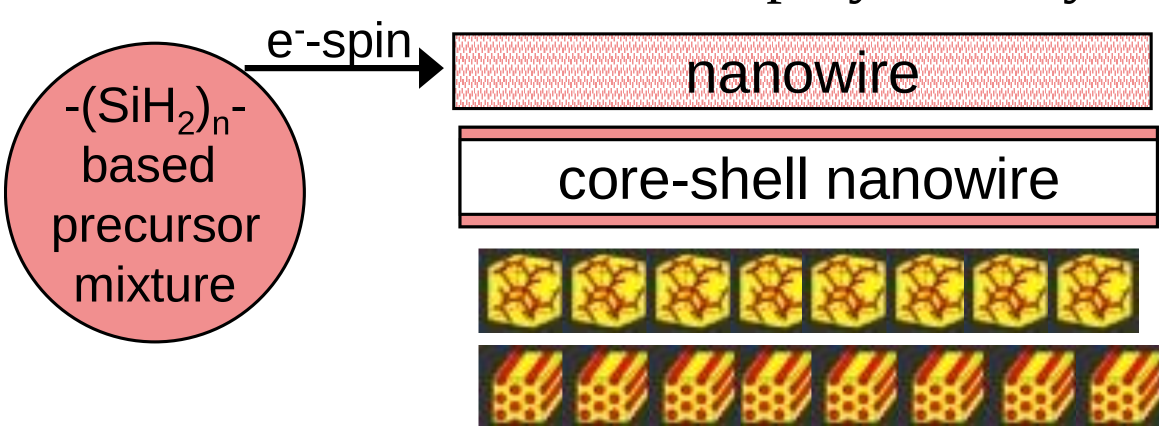




Si nanofibers as Li Ion Battery Anode

1) >10-fold increase in energy density compared to graphite
2) d<100 nm, amorphous structure
3) scalable process
4) low cycle loss

Potential for New Copolymer Physical Chemistry



statistical mixtures

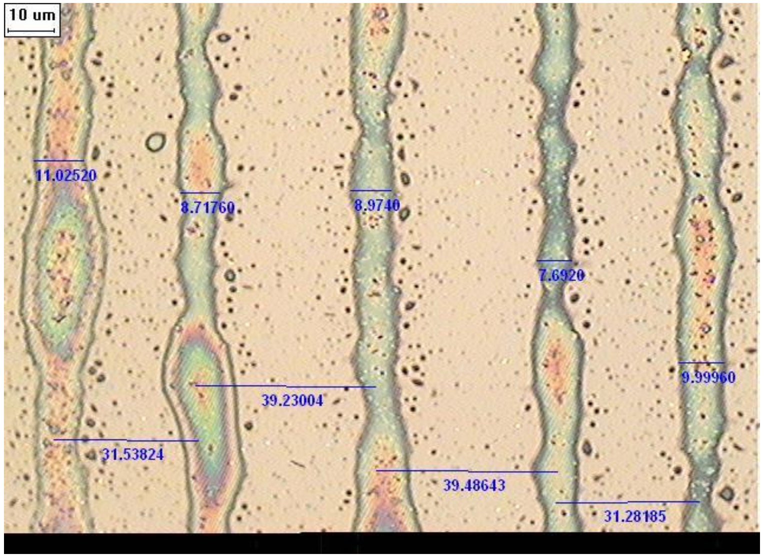
Co-polymers
surface energy,
phase miscibility

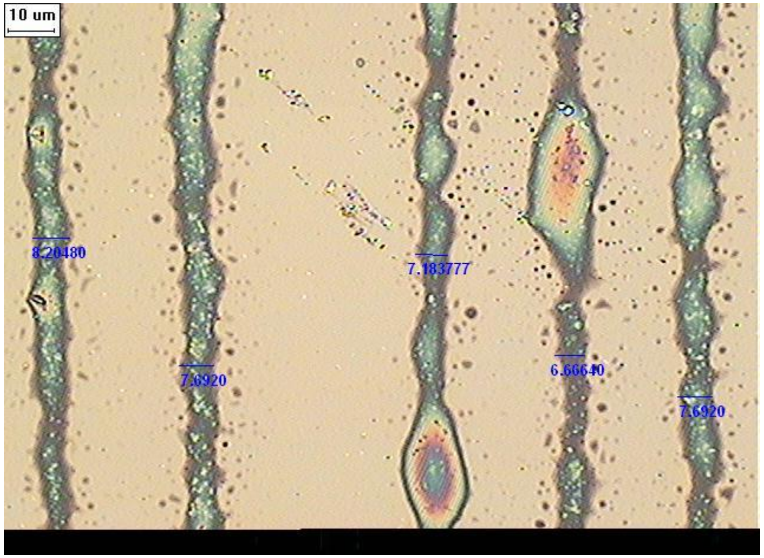
Having Si_6H_{12} Enables: Printing Silicon Lines

Optical Micrographs of Printed Silicon via CAB-DW

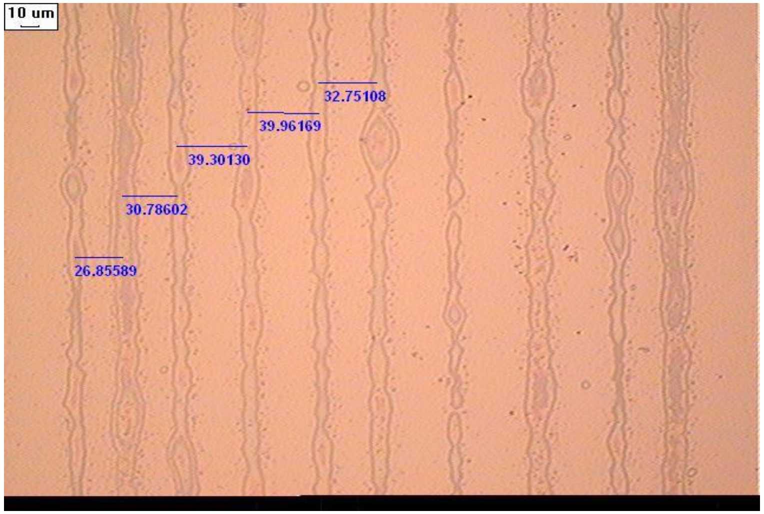
After UV | After UV + 350 °C

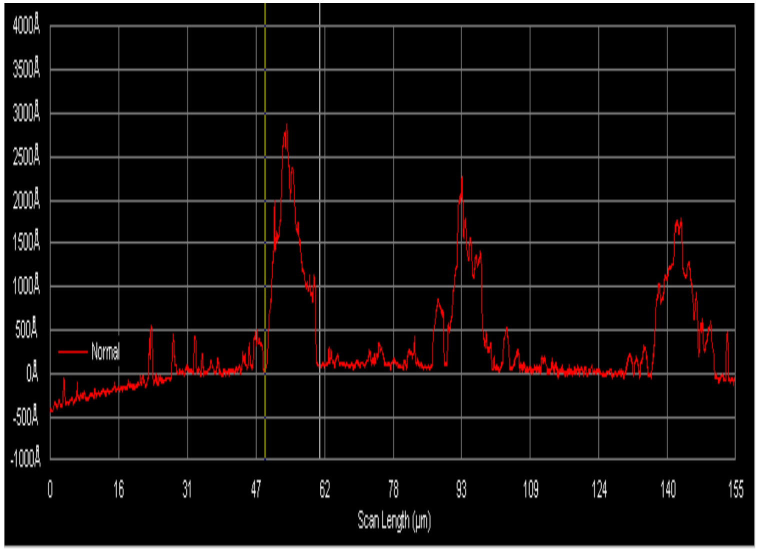
50 X mag



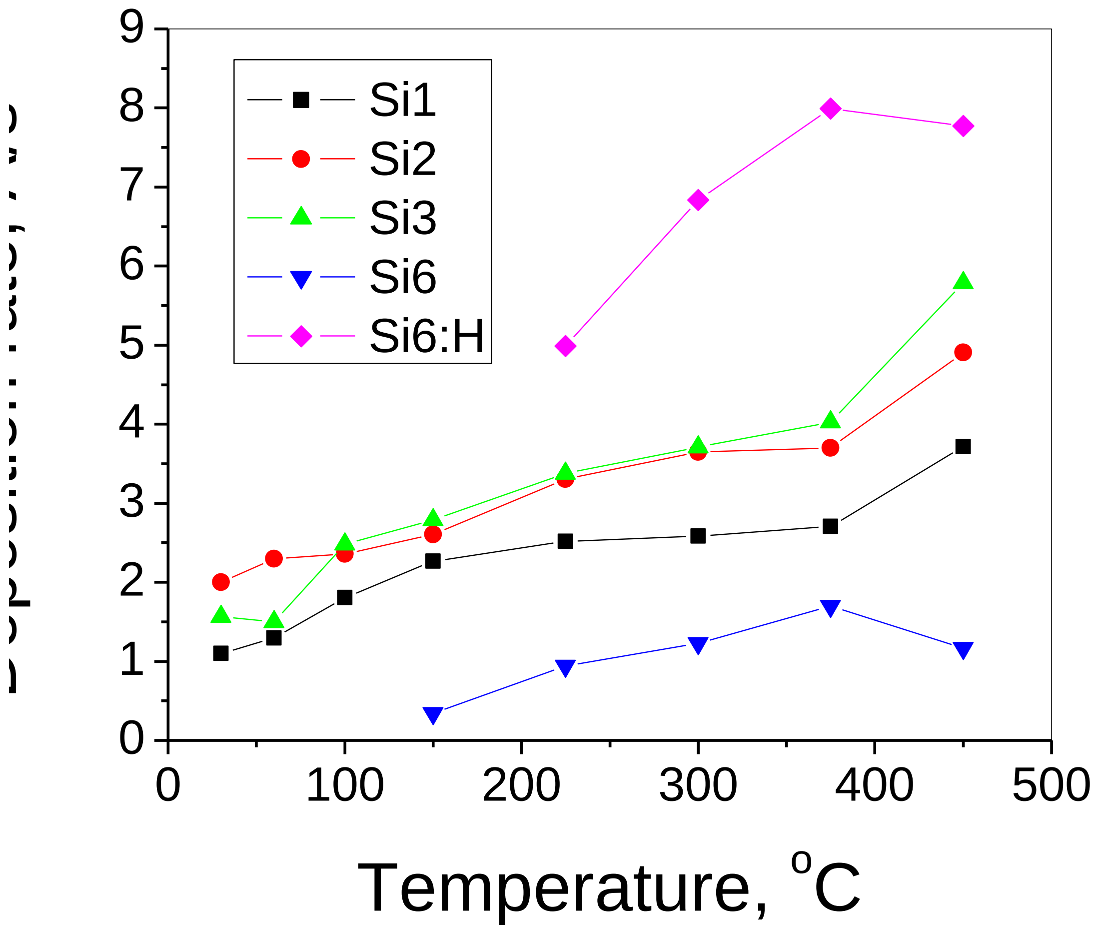


20 X mag





PECVD a-Si Deposition Rates

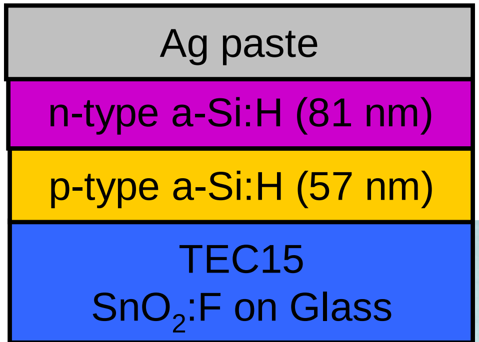


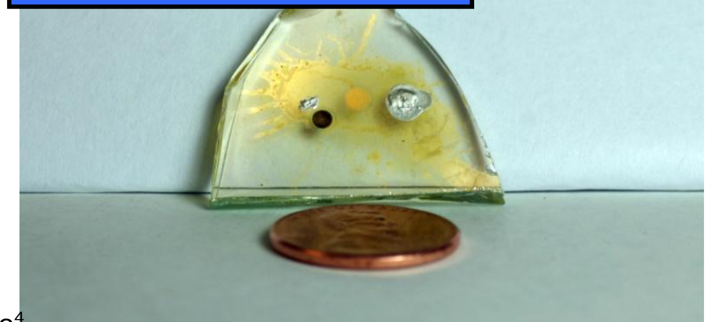
Si_6H_{12} with H_2 Dilution Is Superior

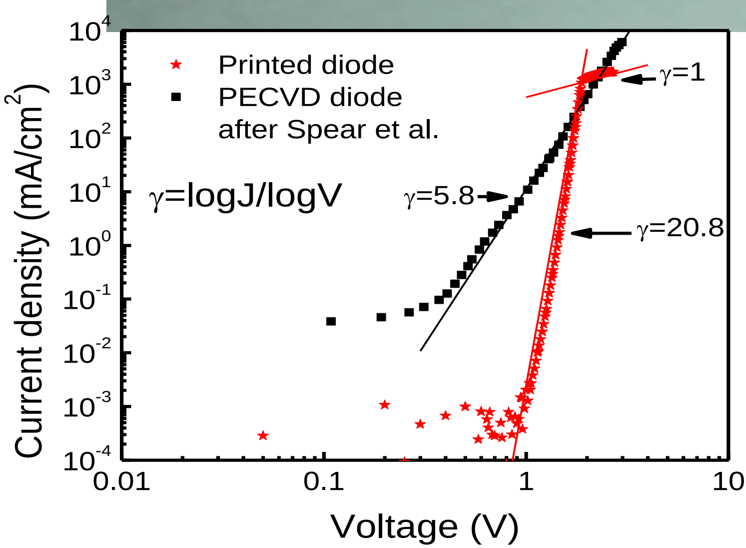
34th IEEE Photovoltaics Specialist Conference, pp. 1758-1760

Liquid Silane Precursors to Printed Silicon

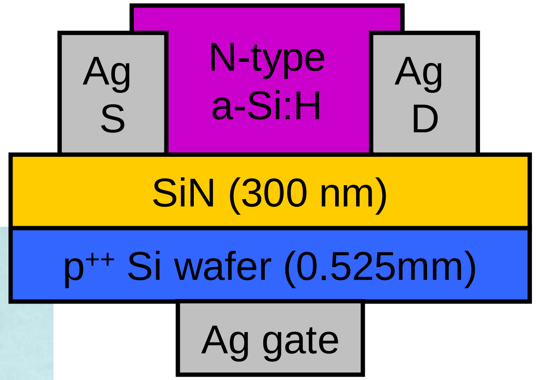
First Diode

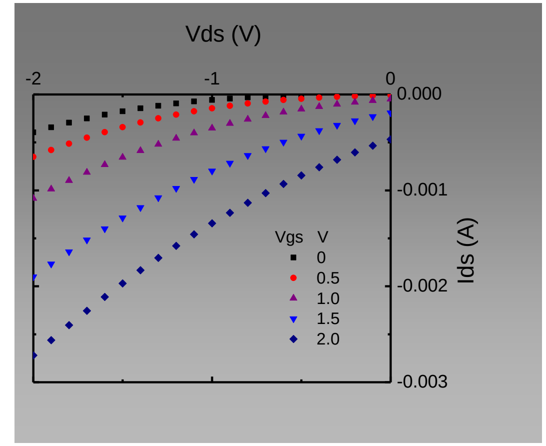


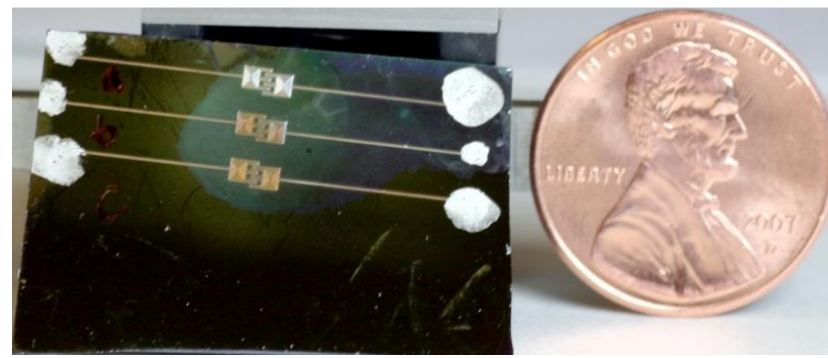




First Transistor







Film thicknesses < 200 nm

J. Non-Cryst. Solids, **2008**, *354*, 2623-2626

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