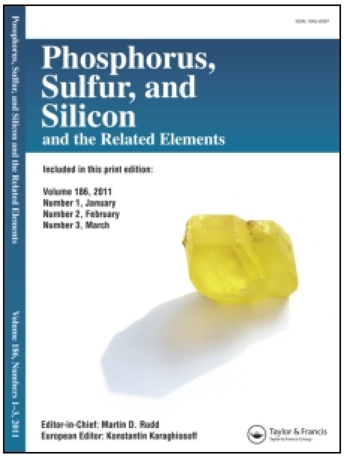


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Group VI Heteroatomcyclopolysilanes Syntheses and NMR Properties

H. Stüger[a]; M. Eibl[a]; I. Kovacs[b]
[a] Institut für Anorganische Chemie Technische Univ., Graz, Austria [b] Institute of Inorganic Chemistry Techn. Univ., Budapest, Hungary

To cite this Article Stüger, H. , Eibl, M. and Kovacs, I.(1992) 'Group VI Heteroatomcyclopolysilanes Syntheses and NMR Properties', Phosphorus, Sulfur, and Silicon and the Related Elements, 65: 1, 29 — 32
To link to this Article: DOI: 10.1080/10426509208055311
URL: http://dx.doi.org/10.1080/10426509208055311

Phosphorus, Sulfur, and Silicon, 1992, Vol. 65, pp. 29–32
Reprints available directly from the publisher
Photocopying permitted by license only

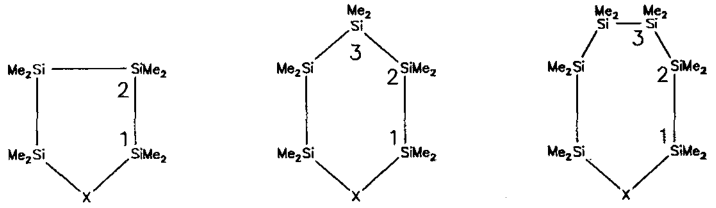
GROUP VI HETEROATOMCYCLOPOLYSILANES SYNTHESES AND NMR PROPERTIES

H. STÜGER, M. EIBL
Institut für Anorganische Chemie Technische Univ. Graz Austria
I. KOVACS
Institute of Inorganic Chemistry Techn. Univ. of Budapest Hungary

Abstract Group VI heterocyclopolysilanes have been synthesized from α,ω-dichloropolysilanes and Li_2S/Li_2Se or by simple hydrolysis. Si-Si NMR coupling constants correlate satisfactorily with electronegativities of the heteroelements indicating dominant Fermi contact contributions.

INTRODUCTION

Just one systematic study dealing with permethylheterocyclopolysilanes has been published so far by West and coworkers[1]. Because we are generally interested in Si-Si bond/substituent interactions, we decided to attempt the selective synthesis of group VI heterocyclopolysilanes exhibiting structural formulae as depicted below and to investigate their spectral properties.



X = O, S, Se

SYNTHESES

The oxygen containing heterocycles are readily formed after careful hydrolysis of the corresponding α,ω-dichlorooligosilanes followed by condensation of the α,ω-diol intermediates:

$$Cl-(SiMe_2)_n-Cl \xrightarrow[-2HCl]{2H_2O} HO-(SiMe_2)_n-OH \xrightarrow{-H_2O} cyclo\text{-}(SiMe_2)_nO \qquad (1)$$

The sulfur and selenium derivatives are easily obtained, when the α,ω-dichloroprecursors are reacted with Li_2S or Li_2Se prepared in situ from S or Se and $Li[(BEt_3)H]$ in THF[2]:

$$Li_2X\cdot BEt_3 + Cl(SiMe_2)_nCl \xrightarrow{-2LiCl} cyclo\text{-}(SiMe_2)_nX + BEt_3 \qquad (2)$$

$$(X = S, Se)$$

TABLE 1 Si-Si coupling constants in [Hz] obtained by the INEPT-INADEQUATE technique and ^{29}Si chemical shifts in [ppm] relative to TMS of permethylheterocyclooligosilanes

	$^1J_{Si1Si2}$	$^1J_{Si2Si3}$	$^2J_{Si1Si3}$	δ Si1	δ Si2	δ Si3
Si_4Me_8O	81.27	-	10.6	14.84	-	-50.4
$Si_5Me_{10}O$	83.96	58.29	7.2	9.74	-49.6	-45.8
$Si_6Me_{12}O$	88.07	60.58	7.4	8.32	-47.1	-42.4
Si_4Me_8S	75.85	-	13.0	9.24	-	-44.2
$Si_5Me_{10}S$	76.06	61.74	8.17	1.99	-44.9	-43.8
$Si_6Me_{12}S$	77.19	63.76	8.50	2.65	-42.4	-40.8
Si_4Me_8Se	73.82	-	13.1	5.28	-	-41.4
$Si_5Me_{10}Se$	74.06	62.63	8.6	-2.90	-44.1	-43.3
$Si_6Me_{12}Se$	74.84	64.47	8.7	-2.18	-42.1	-40.1
Si_4Me_8NMe	82.56	-	9.71	1.82	-	-53,2
$Si_5Me_{10}NMe$	81.50	60.28	7.63	0.21	-48.4	-47.4
$Si_6Me_{12}NMe$	82.90	60.06	8.07	1.56	-44.9	-42.2
$Si_4Me_8PMe^a$	67.00	-	14.75	-8.27	-	-41.8
$Si_5Me_{10}PMe^a$	67.60	58.7	9.1	-16.8	-43.5	-43.0
$Si_6Me_{12}PMe^a$	69.27	-	8.85	-16.1	-42.9	-42.4

[a] chemical shift values are consistent with data reported in ref.[1]

NMR SPECTROSCOPY

^{29}Si-NMR data of group VI heterocyclopolysilanes are summarized in TABLE 1 together with data of the corresponding N and P containing compounds[3]. ^{29}Si chemical shift values of silicon atoms directly bonded to the heteroelements are shifted downfields with increasing electronegativity of the heteroatoms. Although there seems to be a general relationship between electronegativity and chemical shifts, the correlation is rather poor. The absolute magnitude of $^{1}J_{Si(1)Si(2)}$ in permethylheterocyclopolysilanes satisfactorily can be correlated with the electronegativity of the heteroatoms (FIGURE 1).

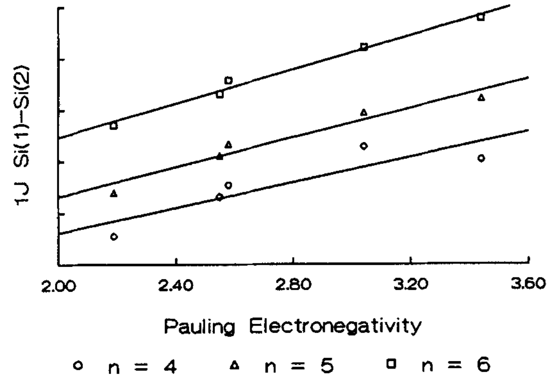


FIGURE 1 Dependence of $^{1}J_{Si(1)Si(2)}$ from heteroatom electronegativity for permethylheterocyclopolysilanes *cyclo*-$(SiMe_2)_nX$ (X = O, S, Se, NMe, PMe)

Similar correlations observed for $^{1}J_{(C-C)}$, $^{1}J_{(Si-C)}$ and $^{1}J_{(C-H)}$ in numerous systems[4,5,6] are usually taken to indicate the dominance of the Fermi contact contribution to spin-spin coupling. According to simple views of Fermi contact coupling the electronegative heteroatoms on Si(1) concentrate silicon s-character in hybrid orbitals directed toward Si(2) leading to higher values of $^{1}J_{Si(1)Si(2)}$. Only limited support to this crude model is given by preliminary results of semi-empirical PM3 calculations[7]. Linear correlations between

$^1J_{Si(1)Si(2)}$ and bond orders or silicon 3s orbital densities at Si(1) and Si(2), as suggested by equation (3), could not be obtained.

$$J_{SiSi} = \frac{16\beta^2\gamma_{Si}^2}{9\Delta E} . s_1(0)^2 s_2(0)^2 . P_{s1s2}^2 \qquad (3)$$

ΔE = mean electronic excitation energy

P_{s1s2} = Si(1)3s-Si(2)3s bond order

$s_1(0)$, $s_2(0)$ = silicon 3s orbital densities

CONCLUSIONS

Possible explanations for the inconsistence between theory and experiments are:

1. *Insufficient theory* The simple MO approach, for instance, relating bond orders to the magnitude of coupling constants by equation (3) might not be appropriate for the compounds investigated in this study.
2. *Molecular geometry* Fully optimized geometries have been used in the PM3 calculations. Virtually conformer mixtures exist giving rise to different average charge distributions and hybridizations.
3. *Coupling mechanism* The Fermi contact term does not alone determine the magnitude of coupling constants in heterocyclopolysilanes. Possibly there are also considerable contributions from the dipolar or/and spin-orbital terms.

REFERENCES

[1] T.H.Newman, R.West and R.T.Oakley, J.Organomet.Chem., 197, 159 (1980)

[2] M.R.Detty and M.D.Seidler, J.Org.Chem, 47, 1354 (1982)

[3] for the synthesis of aza- and phosphacyclopolysilanes compare Lit.1

[4] R.K.Harris and B.J.Kimber, J.Magn.Res., 17, 174 (1975)

[5] G.E.Maciel, J.W.McIver, N.S.Ostlund and J.A.Pople, J.Am.Chem.Soc., 92, 1 (1970)

[6] V.J.Bartuska and G.E.Maciel, J.Magn.Res., 5, 211 (1971)

[7] PM3 calculations have been performed by G.Czonka of the Techn.Univ.of Budapest. Detailed results will be published elsewhere.