SUBSTITUENT EFFECTS ON THE FLUXIONAL REARRANGEMENTS AND
ISOMERIZATION OF INDENYL SILANES AND STANNANES

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Recent studies have shown that the *monohapto* indenyl compounds (I) of a number of main

group and transition series metals exhibit dynamic intramolecular (fluxional) rearrangements.[1]

In the case of the indenylsilanes (Ia) a kinetically slower hydrogen migration occurs, giving

rise to non-fluxional positional isomers.[2] From the relatively low activation energies for the

migrations and the demonstrated intramolecularity of the reactions, it has been proposed that

the rearrangements proceed through transition states and/or intermediates which involve little

if any charge separation during the migration process.[3] The transition state for rearrange-

ment can be pictured as consisting of an indenyl radical and a radical formed from the migrating

group M. Examination of the normalized π-electron populations for the indenyl radical (ob-

tained from Hückel MO - calculations) reveals that the smallest π-electron density occurs at

C(4) and C(7), while the largest π-electron density occurs at C(2). Thus, substitution of

electron donating groups at C(4) and C(7) might be expected to stablize the transition state

or intermediate for rearrangement, whereas substitution at C(2) would be expected to destabi-

lize the transition state or intermediate relative to the unsubstituted compounds.

Accordingly, we have synthesized the 2-methyl- (II) and 4,7-dimethyl-indenyl (III) deriva-

tives of trimethylsilane and -stannane, and we report here the activation parameters for the

metallotropic shift and in the case of the silanes the prototropic isomerization.

Ia M=SiMe$_3$
b M=SnMe$_3$

IIa M=Si(CH$_3$)$_3$
b M=Sn(CH$_3$)$_3$

IIIa M=Si(CH$_3$)$_3$
b M=Sn(CH$_3$)$_3$
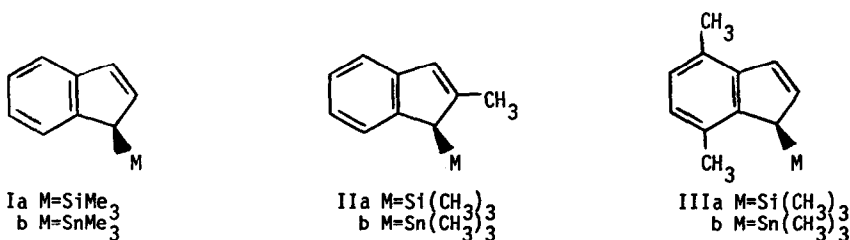
At room temperature, compounds IIa and IIb exhibit NMR spectra characteristic of the slow-exchange, limiting spectrum. Heating IIa to 185° results in coalescence of the multiplet assigned to $CH_3(2)$ and changes in the H(1) and H(3) resonances characteristic of the onset of fluxional behavior. Compound IIb exhibits coalescence of the H(1) and H(3) signals at 110°. By contrast for compound IIIa the coalescence of the $CH_3(4)$ and $CH_3(7)$ signals occurs at 125° while for IIIb the corresponding methyl resonances coalesce at -15° and the coalescence of H(1) and H(3) occurs at 27°. The activation parameters for these rearrangements are given in Table I. It is noteworthy that variation of the position of the methyl substituent(s) alters the $\Delta G^{\ddagger}$ for both Si and Sn migration by ~20 kJ mol^{-1} (~4.5 kcal mol^{-1}) in a manner parallel to that predicted from consideration of the π-electron densities in the indenyl moiety.

Ring substitution in the case of the silanes profoundly affects both the rate of isomerization (via hydrogen migration) and the product distribution at thermal equilibrium. Compound IIa is converted upon themolysis at 200° for 24 hrs to a mixture of 91% IIa and 9% 3-isomer while compound IIIa isomerizes in 35 min at 182° to 15% IIIa and 85% 2-isomer with no evidence for the formation of the 3-(trimethylsilyl)isomer. The equilibrium distributions of positional isomers are given in Table II. The free energies of activation for the reversible isomerization of IIIa to the 2-trimethylsilyl isomer are 146 kJ mol^{-1} (34.8 kcal mol^{-1}) and 139 kJ mol^{-1} (33.2 kcal mol^{-1}) respectively.

It should be noted that steric factors may be at least in part responsible for the effects observed in these compounds, although these alone seem insufficient to account for the observed results.[4]

Table I

Activation Parameters for the Fluxional Rearrangements of Substituted Indenyl Silanes and Stannanes ($\Delta G^{\ddagger}$ in kJ mol^{-1})[a].

Compound	Ia	Ib	IIa	IIb	IIIa	IIIb
$\Delta G^{\ddagger}$	100[b]	63	111	78	91	59
	(23.8)[c]	(15.0)	(26.5)	(18.6)	(21.8)	(14.0)

a) Evaluated at the coalescence temperature from the equation

$$k = (kT/h)\ exp(-\Delta G^{\ddagger}/RT)\ \text{where}\ k = (\pi/\sqrt{2})(\Delta\gamma)\ \text{at coalescence.}$$

b) Data from reference 1a.

c) Parenthetical values in kcal mol^{-1}.

Table II

Isomer Distribution[a] at Thermal Equilibrium.

1-isomer   2-isomer   3-isomer

R(2)	R(3)	R(4)	R(7)	1-isomer	2-isomer	3-isomer
H	H	H	H	54	31	15
Me	H	H	H	91	b	9
H	Me	H	H	84	16	b
H	H	Me	Me	15	85	b

a) mole percent

b) not observed (<2%)

References

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2. P. E. Rakita and G. A. Taylor, Inorg. Chem., 1972, 11, 2136.

3. J. Dalton and C. A. McAuliffe, J. Organometal. Chem., 1972, 39, 251.

4. Thermolysis of diphenylmethylsilylindene gives at equilibrium 34% 1-isomer, 38% 2-
    isomer, and 28% 3-isomer compared with 54%, 31%, and 15% respectively for trimethyl-
    silylindene. Unfavorable steric interaction between the bulkier diphenylmethylsilyl
    group in the 3-position and the 4-hydrogen would be expected to reduce the amount of
    the 3-isomer relative to the trimethylsilyl analog. G. A. Taylor and P. E. Rakita,
    to be published.