SILATROPIC MIGRATION IN (1-TRIMETHYLSILYLINDENYL) (INDENYL) DIMETHYLSILANE, BIS(1-TRIMETHYL-SILYLINDENYL) DIMETHYLSILANE AND RELATED COMPOUNDS

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The relative silatropic migration ability of $SiMe_3$ and $IndSiMe_2$ in (1-trimethylsilylindenyl) (indenyl)dimethylsilane and bis(1-trimethyl-silylindenyl)dimethylsilane was estimated by molecular orbital calculations. Data show similar barriers (25-26 kcal/mol) for the [1,5] sigmatropic shifts for these groups. The molecular structure of bis(inden-1-yl)dimethylsilane determined by X-ray diffraction and by B3LYP/6-31G(d) molecular orbital calculations show an almost orthogonal arrangement of the two indenyl groups.

INTRODUCTION

Organometallic derivatives of Group 14 elements of the type $R_2ER'_2$ (E = Si(IV), Ge(IV), Sn(IV), and R' = bulky organic group with special electronic properties, like the 9-fluorenyl or 1-indenyl groups) have been intensively investigated for their catalytic properties. Significant industrial applications are foreseen for some of their metal complexes, for example as precursors to metallocenium catalysts for olefin polymerization [a review and some recent papers are cited in lit. 1-14]. These systems have also interesting structural peculiarities as shown in references 15-25.

Our interest in the synthesis and structure of bis(9-fluorenyl)derivatives with general formula $Me_2E(CR'R_2)(CR''R_2)$ where E = Si(IV), Ge(IV), Sn(IV) and CR_2 = fluorenyl[15-17] has been extended to mixed (9-fluorenyl)(1-indenyl) and to bis(1-indenyl) analogues. As in the case of bis(9-fluorenyl) derivatives we were interested in the reactivity of the mono- and dilithiated bis(inden-1-yl)dialkyl systems as intermediates to four membered rings

able to lead to mixed carbon/silicon materials and potential precursors in the synthesis of *ansa*-metallocenes with catalytic properties for the polymerization of olefines. This experiment is challenging due not only to the complexity brought in by the presence of the two chiral carbon atoms (giving the enantiomers **1** (**1S,1'S** and **1R,1'R**) and the meso isomer **1-meso** (**1S,1'R**)) but also due to the interesting dynamics brought in by the interconversion of the racemic and meso isomers observed by the aid of the ^{1}H-NMR spectra.[8,19,24,25] This interchange is monitored by the change in the ratio of the singlet due to the enantiotopic methyl groups in the *rac* mixture and the two signals for the diastereotopic methyls for the **1**-*meso* form.

The sigmatropic shift of an organometallic moiety, well known in the cyclopentadienyl derivatives[26] was observed even for monosubstituted indene like trimethylsilylindene, the consequence being the inversion of the absolute configuration of C1.[24] Molecular dynamic studies on bis(inden-1-yl)dimethylsilane based on various NMR techniques have been reported [18,19,24,25] and a mechanism implying symmetry-allowed suprafacial

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[1,5] sigmatropic shifts [19,24,25] rather than [1,3]-allylic shift[18] was suggested for the interconversion of **1-S** and **1-R** via **1-iso**. The [1,5] sigmatropic mechanism is supported by Diels-Alder trapping of the transient isoindene with reactive dienophiles such as tetracyanoethylene. [19,24,25] The isomer expected from [1,5] sigmatropic hydrogen shift, bis(inden-3-yl)dimethylsilane, **1c**, (nonchiral) was not observed in the NMR spectra yet reported.

1S,1'S   **1R,1'R**   **1-meso**   **1-iso**   **1c**
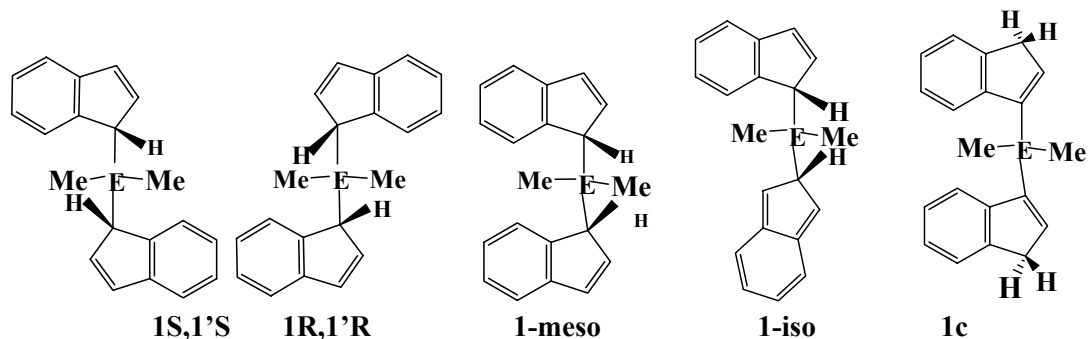
We report here the results obtained on the evaluation of the relative migration ability of SiMe$_3$, Me$_2$SiCl, Me, H and Me$_2$SiInd using AM1 semiempirical calculations in the reaction products of bis(inden-1-yl)dimethylsilane with n-butyllithium (1:1 and 1:2 molar ratio) followed by treatment of the lithiated product with trimethylsilylchloride or methyliodide (1:1 and 1:2 molar ratio).

The molecular structure of bis(inden-1-yl)dimethylsilane (**1**) in the gas-phase was obtained by B3LYP/6-31G(d) DFT calculation. A rough crystal structure of (R,R/S,S)-racemic bis(inden-1-yl)dimethylsilane, Me$_2$Si(Ind-H)$_2$ (**1**) is also reported.

RESULTS AND DISCUSSION

The reaction of bis(inden-1-yl)dimethylsilane (**1**) with n-butyllithium (1:1 and 1:2 ratio) followed by treatment of the lithiated products with methyliodide or trimethylsilylchloride was carried out at low temperature, in ethylic ether to get the 1-monosubstituted compounds **2a** and **2b** (**Scheme 1**) and 1,1'-disubstituted compounds **7a** and **7b** (**Scheme 4**), as for bis(9-difluorenyl)dimethylsilane.[15,32] The mass spectra of the oils obtained following the usual procedure of purification contain the molecular peaks of the expected products. Changes in the ^{1}H-NMR spectra recorded at various steps during the workup of the reaction mixtures were noticed suggesting the formation of new compounds in the process. Attempts to separate and to purify the products by usual chromatographic techniques were unsuccessful.

Another approach (described previously for preparing the substituted bis(9-difluorenyl) dimethylsilanes, -germanes, and stannanes[17]), was the lithiation of the substituted indenes (methylindene, **3a,** and trimethylsilylindene, **3b**) followed by reaction in 1:1 molar ratio with dichlorodimethylsilane to obtain (chloro)(dimethyl)(1-methylindenyl)silane (**4a**) and (chloro) (dimethyl)(1-trimethylsilylindenyl)silane (**4b**) (**Scheme 1**). Eventually, the reaction of **4a** or **4b** with indenyllithium was supposed to lead to (1-methylindenyl)(1-indenyl)dimethylsilane (**2a**) and (1-trimethylsilylindenyl)(1-indenyl)dimethylsilane (**2b**).

Silatropic migration was considered as the source of the mixture of compounds identified from the NMR spectra. Migration barriers of the substituents were calculated using semiempirical methods (AM1) for the starting materials (**1, 3a, 3b**), intermediates (**4a, 4b**) and reaction products (**2a, 2b**).

Based on the behaviour of 1-trimethysilylindene and bis(1,1-trimethylsilyl)indene described in the literature[24, 34-36] and also our experimental data, the equilibria described in **Scheme 2** were considered.

The ^{1}H- and ^{13}C-NMR spectra of the product separated from reaction **ii**, R = SiMe$_3$, (**Scheme 1**) are consistent with the presence of a unique, pure compound with the structure **4b'**. The attack of the base directly in the position 3 might be also considered. In order to check the preference of such reagents for one of the 1-3 positions of the indenyl ring, semiempirical (AM1) and B3LYP/6-31G(d) geometry optimizations on **3b** and its deprotonated forms have been carried out. The total energies and the electrostatic charges on **C1-C3** are given in Table 1.
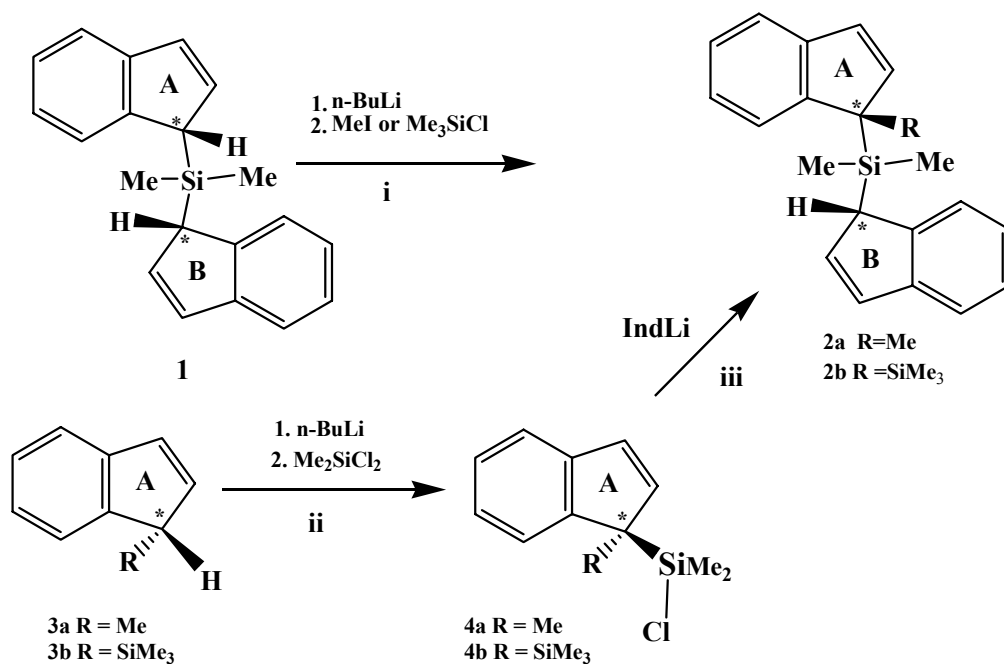
Scheme 1
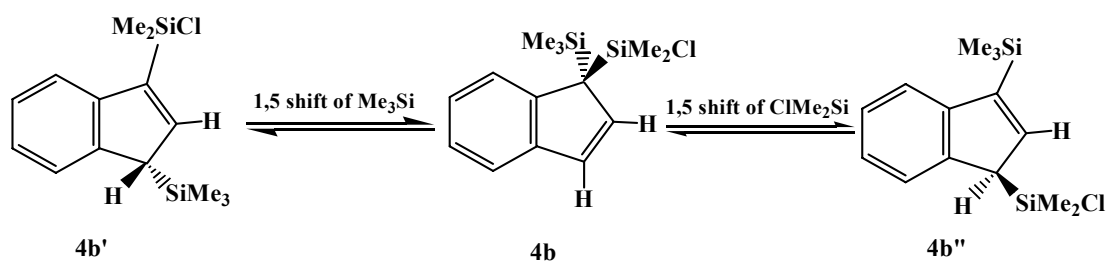
Scheme 2

Table 1

Total (relative) energies and electrostatic charges of **3b** and its deprotonated forms

	AM1 enthalpy of formation (kcal/mol)	Total energy B3LYP/6-31G(d) (a.u.)	AM1/B3LYP calculated charges		
			C1	C2	C3
3b		-756.439982	-0.476/-0.377	-0.050/-0.125	-0.283/-0.374
3b -H(C1)	-20.06 (0.0)	-755.863207 (0.0)	-0.732/-0.730	0.002/-0.017	-0.505/-0.534
3b -H(C2)	30.69 (+50.75)	-755.785723 (+48.62)	0.117/0.371	-0.867/-0.920	-0.046/0.087
3b -H(C3)	39.81 (+59.87)	-755.775894 (+54.79)	-0.632/-0.600	0.349/0.357	-1.222/-1.142

Both levels of calculations give similar trends in the energies and charges on the considered atoms. Thus, in **3b** C1 has the highest negative charge and this way favors the attack of BuLi at this site. The lowest energy anion is formed when the proton of C1 is abstracted, and the other anions (**3b -H(C2)** and **3b -H(C3))** are over 50 kcal/mol higher. Thus, **3b -H(C1)** seems to be the favored deprotonated form and an electrophile ($^+$SiMe$_2$Cl)

might attack rather at **C1** (q=-0.732 e) than at C3 (q=-0.505). So, the lithiation of **3b** followed by addition of Me$_2$SiCl$_2$ should lead to **4b**.

Since the calculated barrier of migration of SiClMe$_2$ is higher than that of SiMe$_3$ (28.41 kcal/mol versus 24 kcal/mol), **4b'** should be the favoured migration product. These data are in excellent agreement with the experimental NMR data which yielded an activation energy barrier of

24 kcal/mol[33-36] and with the AMPAC/MOPAC UHF results reported by Rigby *et al.*[33] Extending the calculations on other halosilyl groups we found that the migration barrier increases with the number of chlorine atoms on the halosilyl group (29.97 kcal/mol for $SiCl_2Me$ and 31.17 kcal/mol for $SiCl_3$).

Literature data report that these barriers might be reduced by modifying the arene part of the indene. Thus, methyl groups in 4,7[37,38] or incorporation of one fused benzo ring[33,39] lower the barrier of the migration of $SiMe_3$ to ca. 22 kcal/mol.

Incorporation of two fused benzo rings is even more in favor of migration (a barrier of 18 kcal/mol).[33,39] We should mention that the [1,5] shift of the hydrogen atom is ruled out because the corresponding barriers are much higher (43 kcal/mol).[33]

The 1-monosubstituted indenylsilanes **2** can be transformed via the [1,5] silatropic shifts into their isomers **5** (shift of the R substituents on the A ring) and **6** (shift of $IndSiMe_2$ on the A ring) **(Scheme 3)**.

6a R = Me
6b R = SiMe₃   2a R=Me
                             2b R =SiMe₃   5a R = Me
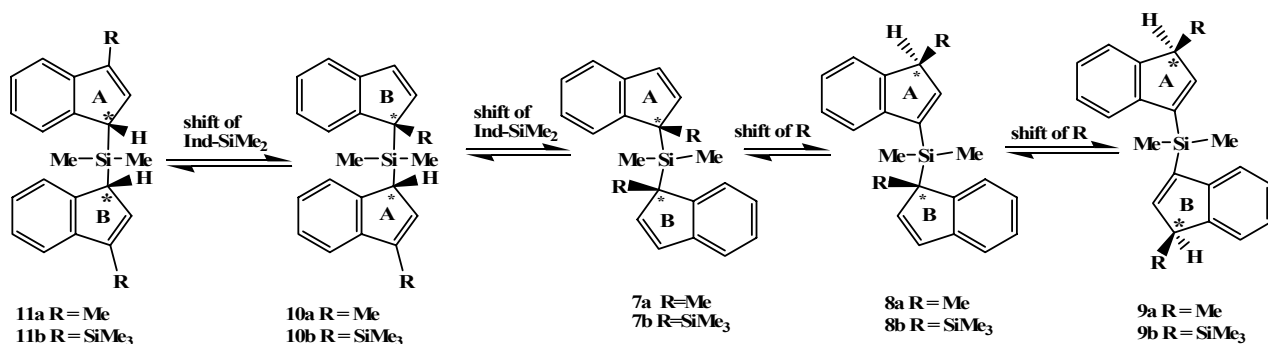   5b R = SiMe₃
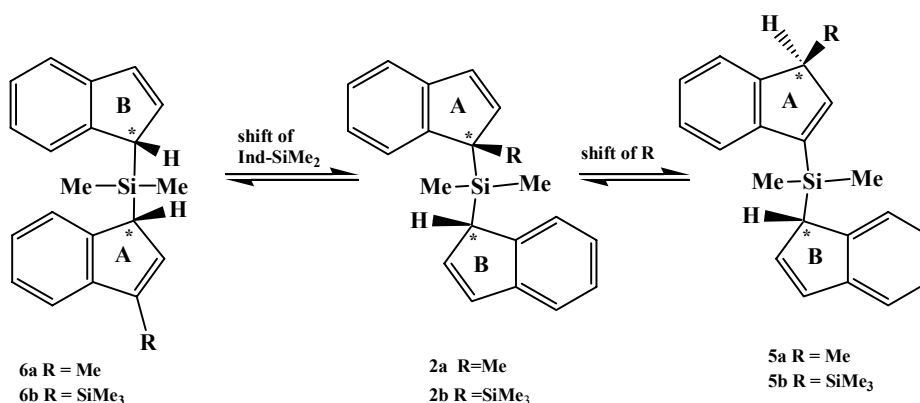
Scheme 3

The identification of the reaction products was facilitated by the fact that the reaction of **4b'** with indenyllithium led mainly to **5b**. A ratio of **2b** to **5b** of 8:1 based on $SiMe_3$ signals could be roughly estimated from the ^{1}H-NMR spectra recorded on a fresh solution obtained through path **i** in **Scheme 1.** This ratio was changed during the separation procedures and moreover, the final mixture contains **6b** together with isomers **2b** and **5b**. However, the system is rather complicated and it was not possible to establish a relation between the composition of the reaction mixture and the solvent or the temperature (up to 80°C).

The systems become even more complex with one substituent on each indenyl ring of **1**. The independent [1,5] sigmatropic shifts of the **R** and of the **Ind(R)-SiMe₂** groups is shown in **Scheme 4**. The combined **R-** shift on one indenyl and **Ind(R)-SiMe₂** shift on the other indenyl fragment is not included in the scheme but should not be ruled out.

11a R = Me   10a R = Me   7a R=Me   8a R = Me   9a R = Me
11b R = SiMe₃   10b R = SiMe₃   7b R=SiMe₃   8b R = SiMe₃   9b R = SiMe₃

Scheme 4

The migration barriers of R = $SiMe_3$ groups in the systems shown in **Scheme 4** are presented in **Figure 1**.
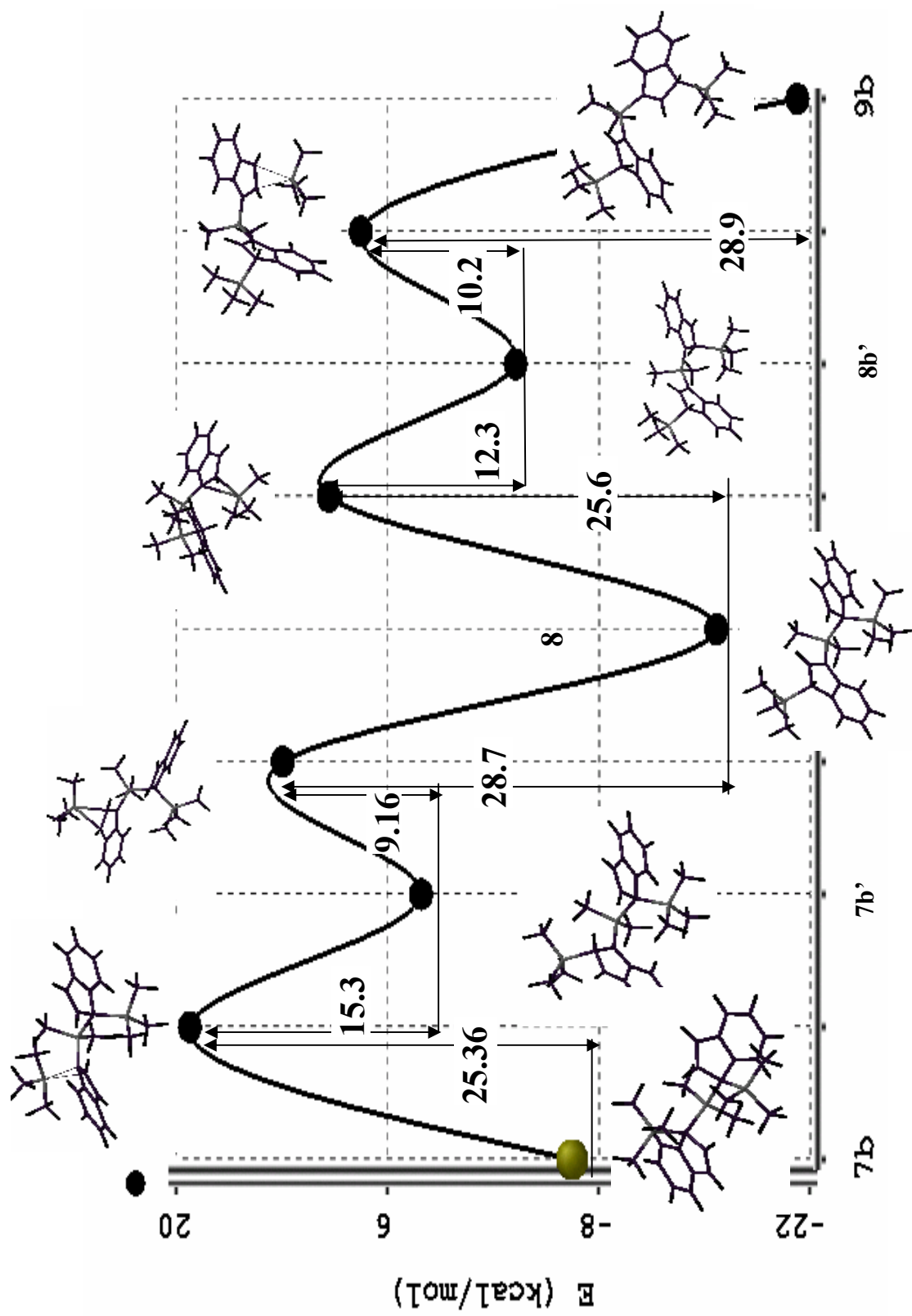
Fig. 1 – Potential energy profile for the [1,5]shift of the two SiMe$_3$ groups in **7b**.

The barrier of migration of one SiMe$_3$ group of **7b** with the formation of isoindene **7b'** (25.4 kcal/mol) is similar with the barrier of migration of the second SiMe$_3$ group on the other ring **8b** to **8b'** (25.7 kcal/mol). According to these calculations, bis(1-trimethylsilylindenyl-3)dimethylsilane **9b** was found to be the lowest energy isomer. On the other hand, the migration of (Me$_3$Si)IndSiMe$_2$ group in **7b** implies a barrier of 26.04 kcal/mol which is comparable with the above value of 25.4 kcal/mol and with the experimental value of 24.2 kcal/mol reported for **1**.[19]

Crystal and Molecular structure of Me$_2$Si(Ind)$_2$

Crystal and molecular structure of bis(inden-1-yl)dimethylsilane (**1**) has been determined by X-ray diffraction (data have been deposited with the Cambridge Crystallographic Data Centre: CCDC 617386). In spite of the poor diffraction quality of the crystals the main aim of the work getting the geometric configuration of the molecule in the solid state and the intermolecular interactions was attained. The geometrical parameters of the system (Table 2, Figure 2) do not differ from those found in other indenyl derivatives of Group 14. Thus, the Si-C1(indenyl) distances are in the same range as in tris(inden-1-yl)silane (1.889(4)–1.911(4))[16] or [*rac*-{1-AlMe$_2$(1,4-dioxane)$_{0.5}$-2-Me-1-indenyl}$_2$SiMe$_2$]$_n$ (1.880(3) - 1.929(3) Å)[5] and the Si-Me distances are similar to those from reference Moreover, B3LYP/6-31G(d) geometry optimization of the (R,R) stereoisomer (selected as the lowest energy conformer of C2 symmetry) also points to the parameters found in the solid state (Table 2).

A notable feature of (**1**) is the fact that the two indenyl groups are almost orthogonal, the dihedral angle being 84.68°.
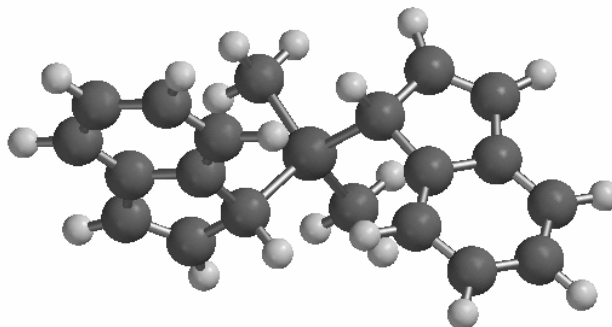

Fig. 2 – The calculated minimum energy molecular structure of (R,R)-Me$_2$Si(Ind)$_2$.

Table 2

Main molecular parameters for the Me$_2$Si(Ind)$_2$ (DFT calculated values are given in parentheses)

Bond lengths (Å)		Bond angles (°)	
Si-C(Me)	1.853(7) (1.889)	C(Me)-Si-C(Me)	112.5(4) (110.91)
Si-C(Me')	1.868(7) (1.889)	C(Ind)-Si-C(Ind')	109.1(3) (109.98)
Si-C(Ind)	1.896(7) (1.934)	C(Ind)-Si-C(Me)	109.1(4) (109.22)
Si-C(Ind')	1.919(7) (1.934)	C(Ind)-Si-C(Me')	107.1(4) (108.75)
		C(Ind')-Si-C(Me)	109.7(3)(108.75)
		C(Ind')-Si-C(Me')	109.2(3)(109.22)

The crystals of **1** are built of pairs of (R,R) and (S,S) enantiomers disposed along the b axis (Figure 3). The two isomers forming a pair are held together mostly through weak C-H···π interactions as suggested by the (Indenyl)H···C(Indenyl) distances (3.005Å) calculated by optimizing the geometry of the dimer by using the same DFT procedure. The interaction energy thus calculated (as the difference between the energy of the dimer and that of two isolated molecules of **1**) is 1.78 kcal/mol which is in the range of CH···π interactions.[40] Alternatively, this interaction might be characterized by the H…Centroid of the opposite ring distance which is 3.30 Å in the crystal (Figure 3).

The dimers are in contact along the **a** axis through short (2.701 Å) C9….H11 distances while the columns of dimers such formed are held together through C13...H3 interactions (2.824 Å) along the **b** axis and give rise to a 2-D network.
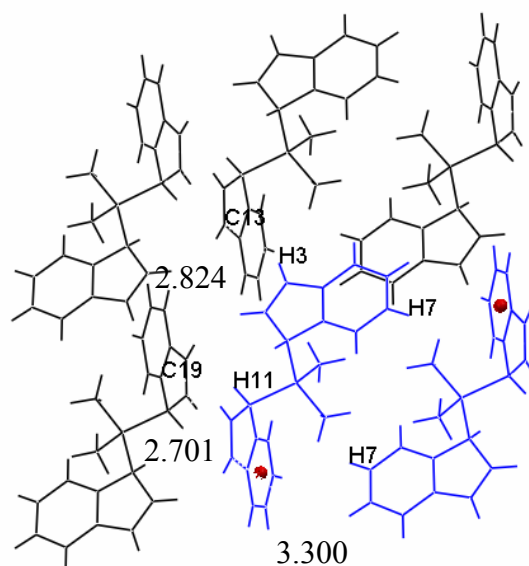
Fig. 3 – Packing of (R,R) and (S,S) pairs of **1** disposed along the **a** and **b** axis.

EXPERIMENTAL

Semiempirical AM1 geometry optimizations have been carried out for all the investigated systems, determining the minimum energies as well as the energy of the transition states for the sequences of the [1,5]sigmatropic shifts. All calculations have been performed using Spartan'04[27] suite of programs. In addition DFT B3LYP/6-31G(d) full geometry optimizations of the $Me_2Si(Ind)_2$ and their (R,S) dimers have been undertaken in order to evaluate the interaction energy.

$Me_2Si(Ind)_2$ obtained according to the literature[28-31] has been repeatedly recrystallized from dichloromethane. However, all attempts to grow single crystals led only to very thin needles, wherefrom eventually a sample has been chosen for X ray diffraction.

Synthesis

The monolithiated $Me_2Si(Ind)_2$ obtained from **1** in diethylether and n-BuLi 1.6 M in hexane at room temperature was cooled at –78°C and the stoichiometric amount of MeI or Me_3SiCl was added. The reaction mixture was stirred for several hours at room temperature. Lithium halides were filtered out and the solvents evaporated in vacuo and replaced by pentane.

Disubstituted derivatives were synthesized starting from the dilithiated **1** and two equivalents of the halides.

Chloro-(1-trimethylsilyl-inden-1-yl)-dimethylsilane, 4b'

One equivalent of Me_2SiCl_2 was added dropwise to a solution of 1-trimethylsilyl-indenyl lithium in Et_2O (prepared from 1-trimethylsilylindene and nBuLi at -78°). After 1 hour of stirring at room temperature LiCl was removed by filtration and the solvent evaporated in vacuo. The compound was obtained as a pure yellow oil (yield = 94 %).

^{1}H-NMR(ppm) (CDCl$_3$): 0.36 s, 0.49 s (C**H3**)$_2$Si, 0.62 s (C**H3**)$_3$Si, 4.06 d **H1**, 7.12 d **H2**, J$_{(H1H2)}$:1.8 Hz, 7.86 m (aromatic C**H**).

^{13}C-NMR(ppm) (CDCl$_3$): -0.11, 0.02 (C**H**$_3$)$_2$Si, 0.80 (C**H**$_3$)$_3$Si, 49.71 **C1**, 122.59, 123.68, 124.40, 125.94, **C4-7**, 143.09, 144.04, 144.72, 148.04 **C2, C3, C8 ,C9**.

Mz: 280 (FAB+)

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