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Regio- and stereo-selectivity in the silylation of 2,6-diethyl-3,4,7,8-tetramethyl-1,5-dihydro-s-indacene

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Disilylation of 2,6-diethyl-3,4,7,8-tetramethyl-1,5-dihydro-s-indacene is regioselective and stereoselective. The stereoselectivity was modified by changing the experimental conditions, allowing an understanding of the reaction mechanism. The structure of the 'meso' diastereoisomer was established by X-ray diffraction. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: hexaalkyl-1,5-dihydro-s-indacenyl dianion; regioselective and stereo selective silylation

INTRODUCTION

Derivatives of s-indacene are of great interest in various areas of chemistry[1–4] and biochemistry.[5,6] In this paper we present a general and selective route to tetra- and hexaalkylsubstituted-1,5-dihydro-s-indacenes[1] in order to prepare new metallocene complexes[3] and organometallic polymers. One of the best routes to these compounds is to use the corresponding lithium derivatives. In our previous work,[1] the mono and dilithium derivatives were characterized *in situ* by silylation, which was found to be very selective. In the present work we investigate the dimetallation (Li, Si) of 2,6-diethyl-3,4,7,8-tetramethyl-1,5-dihydro-s-indacene and the stereoselectivity of the reactions depending on experimental conditions.

RESULTS AND DISCUSSION

Lithium derivatives of cyclopentadienyl or polynuclear aromatic compounds are usually considered as ion pairs with a delocalized anion and solvated lithium cation or as complexes in which lithium is π coordinated to the delocalized anion[7,8] and solvated by a nucleophilic solvent (THF, TMDA, DME, etc.).[7,9–11] Since it was observed[1] that lithiated polyalkyl-s-indacenes are highly stabilized in THF, the most credible structure for the monolithiated compound appears to be the $\eta 3$ coordinated lithium–THF complex.

The monosilylation of 3,4,7,8-tetramethyl-2,6-diethyl-1,5-dihydro-s-indacene $\mathbf{P_0}$ was achieved by reacting the monolithiated compound **X** with trimethylchlorosilane. The reaction is regioselective, leading only to the 1-trimethylsilylderivative $\mathbf{P_1}$ (Scheme 1).[1]

Hyperchem (AM1) calculations showed that the difference in the relative stabilities of the two possible isomeric forms $\mathbf{P_1}$ and $\mathbf{P_2}$ (Scheme 2) cannot explain the observed selectivity. Using Hyperchem (AM1) calculations, the different possible routes of the chemical reaction were examined in the hope of finding the most probable one. All possible transition states or, within the precision of this type of semi-empirical calculation, the reaction states **T** near the real transition state having a dynamic leading to the final known silylated product were considered (Scheme 3).

The **T** states resulting from a *cis*/Li or a *trans*/Li approach of the organochlorosilane to the two limiting zwitterionic forms **A** and **B** of the monolithiated compound **X** were compared (Scheme 3).

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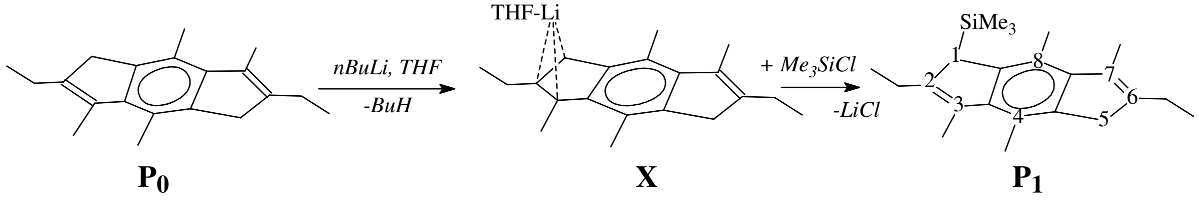
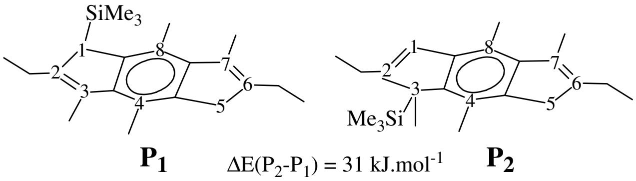


Scheme 1.

From these four theoretical cases, only the one corresponding to a *cis*/Li approach on **A** led to only one dynamic transition state $\mathbf{T_1}$ (Scheme 4), which has a pentacoordinated silicon, a well-known intermediate.[12]

In $\mathbf{T_1}$ (hyperchem representation with the protons localized) there is the formation of a silicon carbon bond (1.90 Å) and a lengthening of the Si–Cl bond (Scheme 4). The chlorine migrates into the coordination sphere of the lithium, which at the same time expels THF. We also verified that the difference in the relative stabilities of the cationic intermediates **C** and **D**, which would arise from release of the anion chlorine preceding the formation of LiCl, although not significant, would be favorable to the formation of the 1-sililated isomer $\mathbf{P_1}$ (Scheme 5).

Thus, the high regioselectivity of the monosilylation reaction would come from the formation of the only possible transition state **T1** resulting from a *cis*/Li approach of the trimethylchlorosilane to the monolithiated indacene and its selective attachment in position 1.

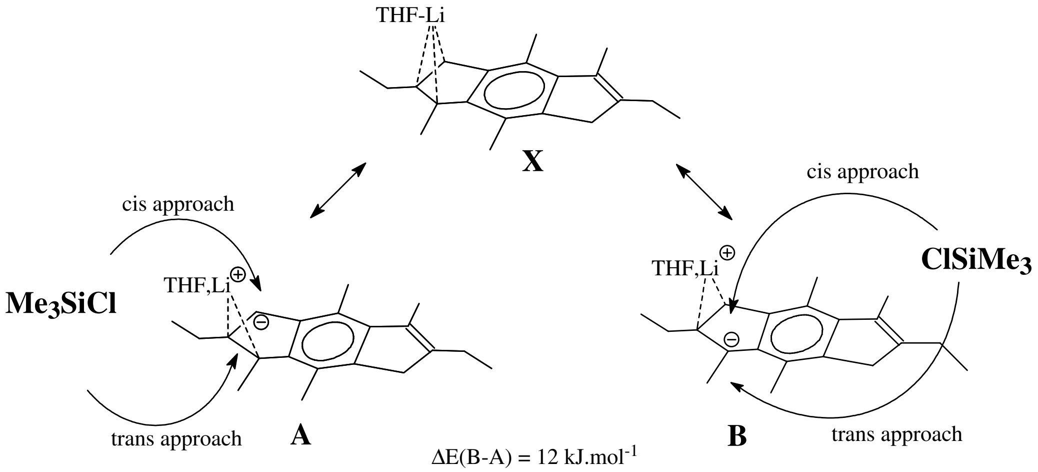


Scheme 2.

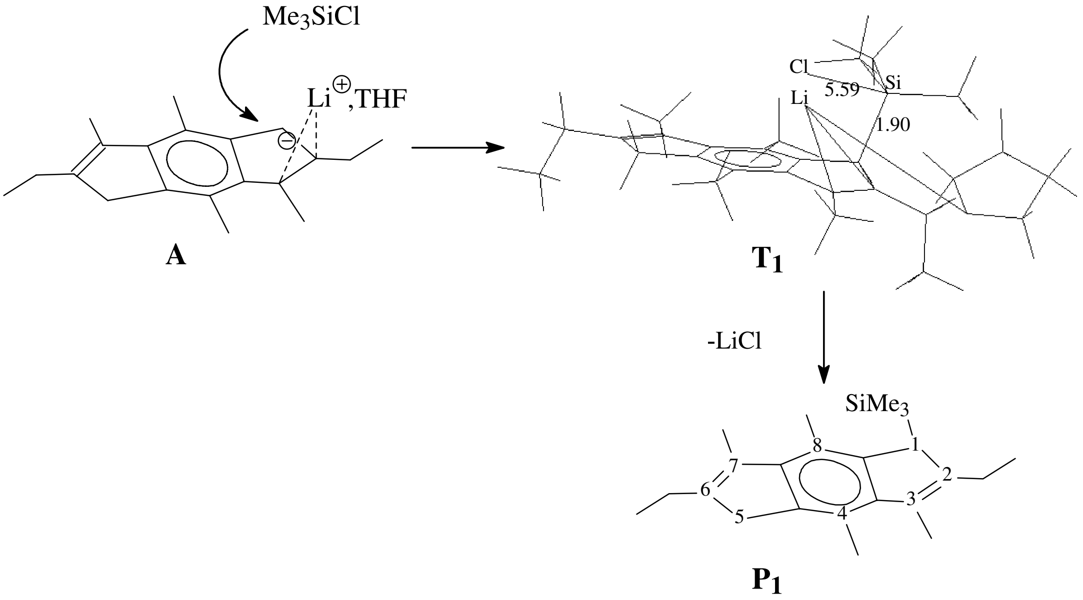
In the case of disilylation of the 3,4,7,8-tetramethyl-2,6-diethyl-1,5-dihydro-s-indacene $\mathbf{P_0}$, a complete regioselectivity in 1 and 5 positions was observed, as evident by the absence of any ethylenic proton in its ^{1}H NMR spectra. However, because of the two asymmetric carbons (1, 5), two diastereoisomers $\mathbf{P_3}$ (*cis*) and $\mathbf{P_4}$ (*trans*) (Scheme 6) were detected by GC/MS and ^{1}H NMR, but were not identified.[1] One is a solid, $\mathbf{P_4}$, and the other, $\mathbf{P_3}$, a liquid. The *trans* derivative, $\mathbf{P_4}$ (a meso isomer), was identified by X-ray diffraction analysis (Fig. 1). $\mathbf{P_4}$ is always the major compound formed in the reaction regardless of the experimental conditions.

Table 1 shows that a change in the experimental conditions leads to a change in the ratio $\mathbf{P_3}$:$\mathbf{P_4}$. When trimethylchlorosilane is added to the dilithium compound of $\mathbf{P_0}$, the reaction occurs with a low concentration of Me_3SiCl and leads to the lowest yield of $\mathbf{P_4}$, while an inverse addition leads to the highest yield of $\mathbf{P_4}$.

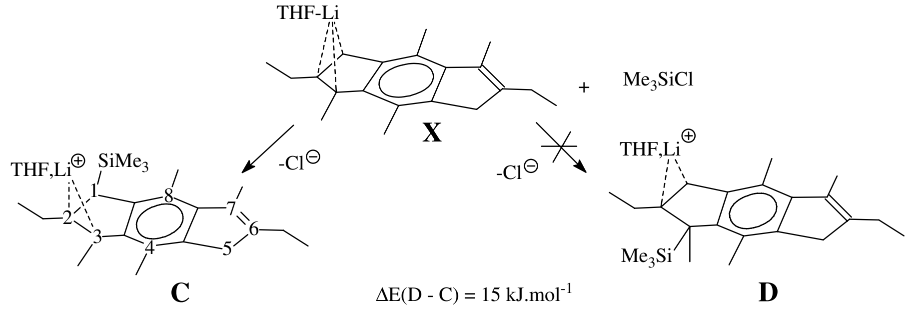
The stereo selectivity cannot be a consequence of the relative stability of **E** and **F** [$\Delta E(F - E) = 10\ \mathrm{kJ\ mol^{-1}}$, Scheme 6], but appears experimentally dependant on the trimethylchlorosilane concentration. Therefore, we thought that competition between a concerted disilylation and a disilylation in two steps would be possible.



Scheme 3.



Scheme 4.



Scheme 5.

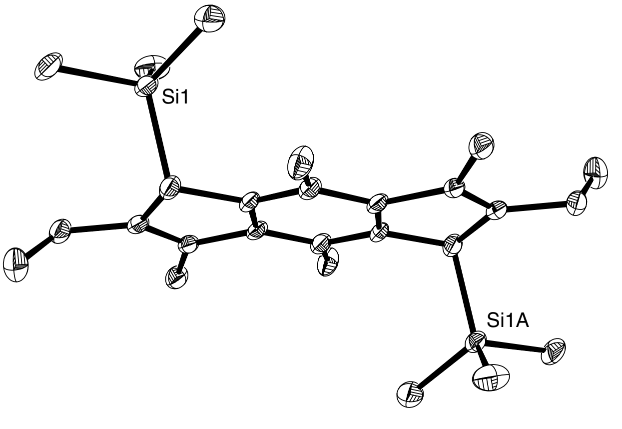


Figure 1. Solid state molecular structure of meso isomer $\mathbf{P_4}$.

Table 1. Dependency of the ratio $\mathbf{P_4:P_3}$ on experimental conditions

Condition of addition	Percentage $\mathbf{P_4}$	Percentage $\mathbf{P_3}$
$2Me_3SiCl$ on $\mathbf{P_0}Li_2$	60	40
$\mathbf{P_0}Li_2$ on 2 Me_3SiCl	73	27

Regarding disilylation in two steps, we calculated by AM1 calculations the first interactions, *cis*/Li and *trans*/Li, of trimethylchlorosilane with the **E** and **F** isomeric forms of the dilithium derivative of $\mathbf{P_0}$ (Schemes 7–9). In the case of **E**, the *cis*/Li and *trans*/Li approach of trimethylchlorosilane (Scheme 7) do not lead to any transition state.

On the contrary, the *cis* or *trans* approach of Me_3SiCl to **F** led to two possible transition states, $\mathbf{T_2}$ (Hyperchem representation with the protons localized, Scheme 8) and $\mathbf{T_3}$ (Scheme 9).

In the case of $\mathbf{T_3}$, the *trans*/Li approach is favored by a possible suprafacial lithium chlorine interaction and a simultaneous migration of Li^+ towards the negative center on the other side. A comparison between the relative stabilities

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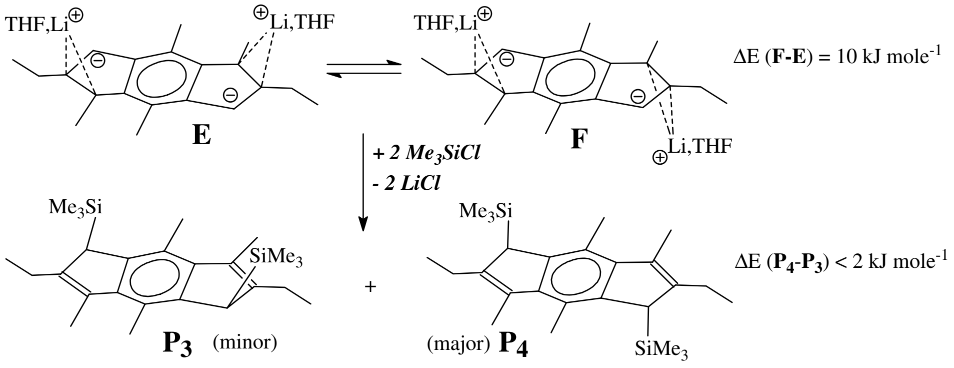
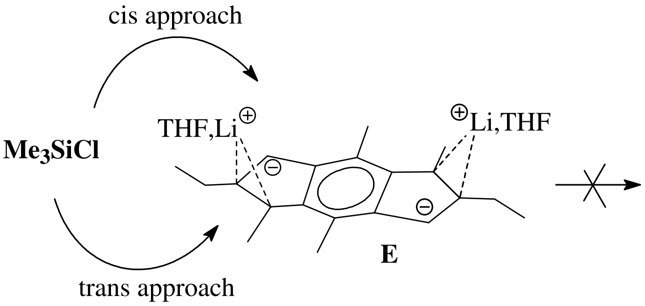


Scheme 6.



Scheme 7.

of T_2 and T_3 shows that, in this particular case, the *trans*/Li approach is unusually favored by 68 kJ mol^{-1}, a consequence of the possible suprafacial Li–Cl interaction (Scheme 10).

Thus, the two transition states T_2 and T_3 give rise to two possible stereo isomeric silylated lithium derivatives of P_0: **G** and **H** (Scheme 11).

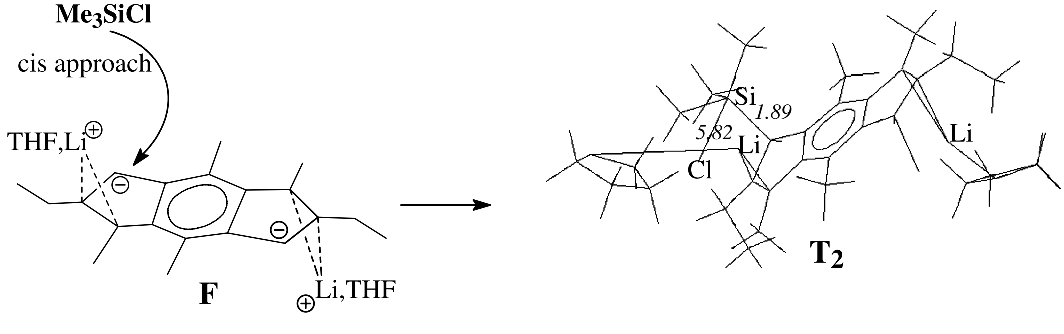
We continued with Hyperchem (AM1) calculations of the four possibilities: *cis*/Li and *trans*/Li approach of the second trimethylchlorosilane on **G** and **H** (Scheme 12).

It appears that only a *cis*/Li approach of trimethylchlorosilane to **G** and **H** can lead to transition states, respectively, T_4 and T_5 (of almost the same stability, Scheme 12), yielding the disilylated stereo isomers P_3 and P_4 (also having the same stability, Scheme 12). Therefore, the two step process of disilylation of P_0 should give two diastereoisomers, P_3 and P_4, in equivalent amounts, which was not the experimental result.

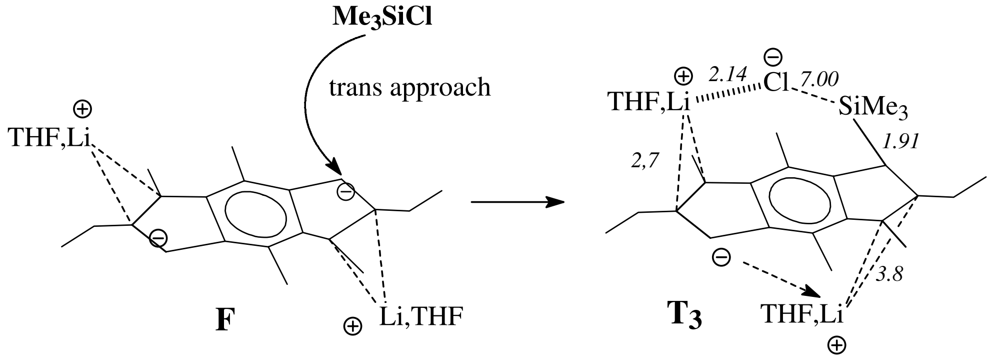
An investigation of the simultaneous disilylation of P_0 using the same Hyperchem (AM1) calculation shows that the simultaneous *cis*/Li or *trans*/Li approach of trimethylchlorosilane on **F** (the dilithiated derivative of P_0) both produce a possible intermediate state, respectively T_6 and T_7, T_7 being thermodynamically the most stable for the suprafacial interaction Li–Cl (Scheme 13). In any case, this two transition states T_6 and T_7, through LiCl elimination, form only the *trans* stereoisomer P_4 (Scheme 13).

At this point, a competition between this two disilylation processes appears the most credible hypothesis to explain the observed major formation of P_4. To verify this hypothesis experimentally, we studied the silylation of the monosilylated compound P_1 on which no simultaneous process could occur. The lithiated derivatives **G** and **H** were prepared from P_1 using *n*-butyllithium (Scheme 14) and then combined with an excess of trimethylchlorosilane, leading to the expected same amount of stereo isomers P_3 and P_4.

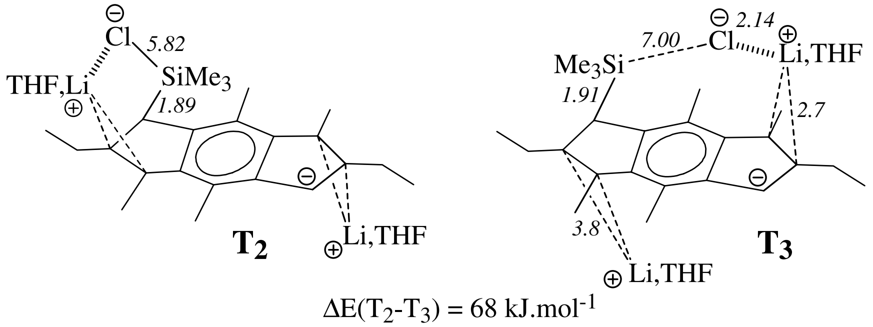
In conclusion, the major formation of the *trans* diastereosisomer P_4 in the disilylation of 3,4,7,8-tetramethyl-2,6-diethyl-1,5-dihydro-s-indacene formed by reacting its



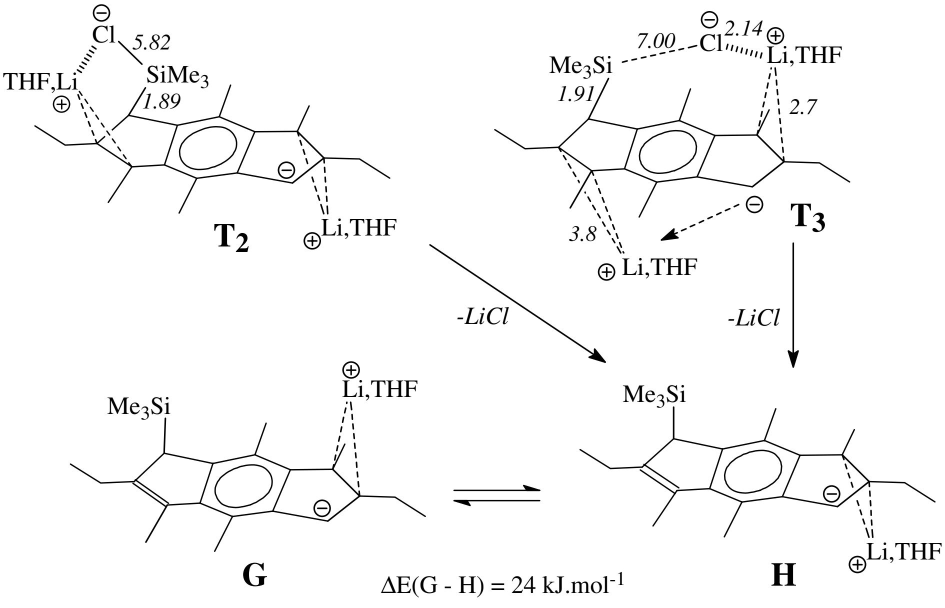
Scheme 8.



Scheme 9.



Scheme 10.



Scheme 11.

dilithium derivatives with trimethylchlorosilane can be explained by a competition of simultaneous disilylation processes, one concerted and the other occurring by two steps.

EXPERIMENTAL

All reactions were carried out under nitrogen or argon and in dry solvents using standard Schlenk techniques. NMR

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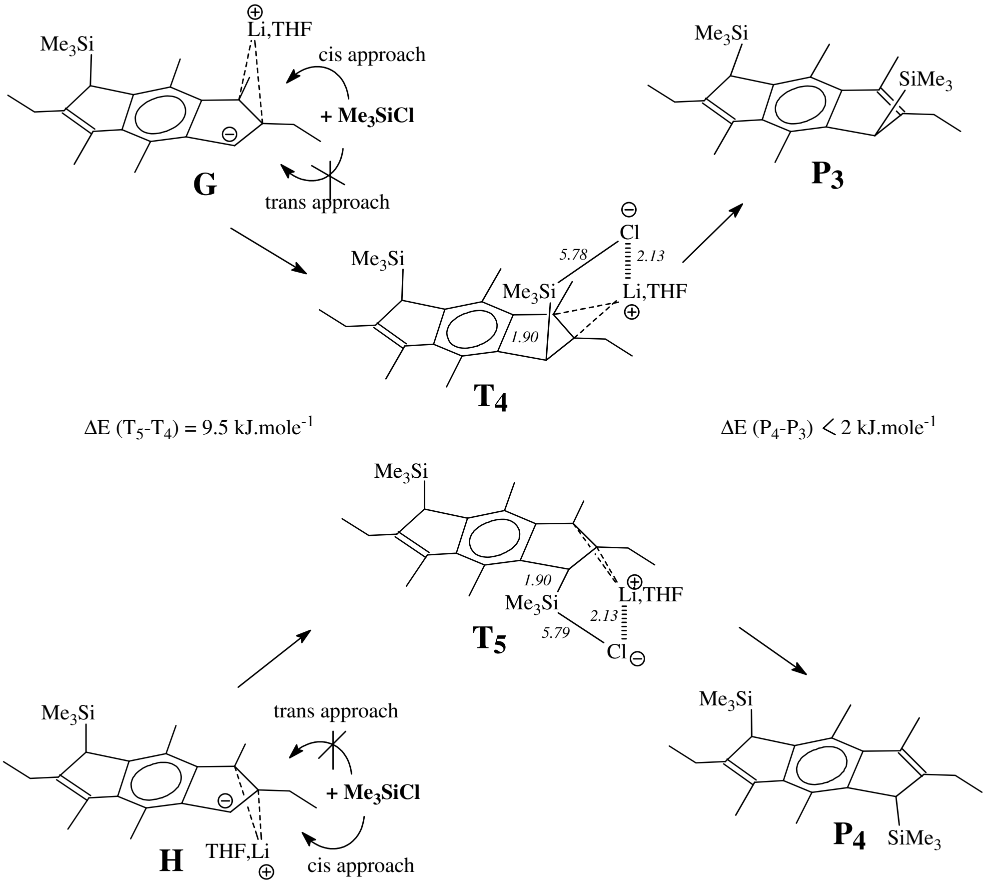
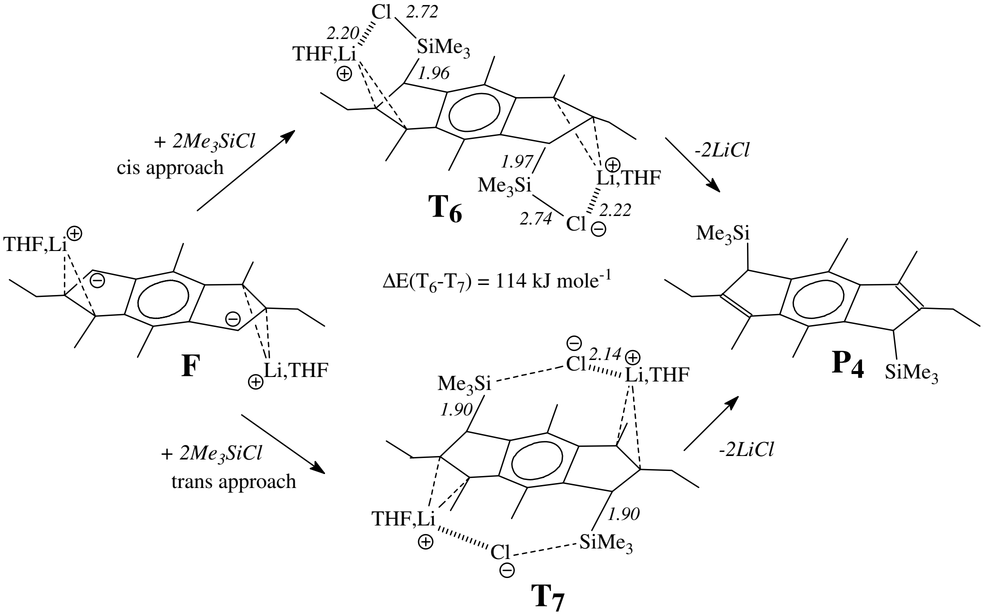
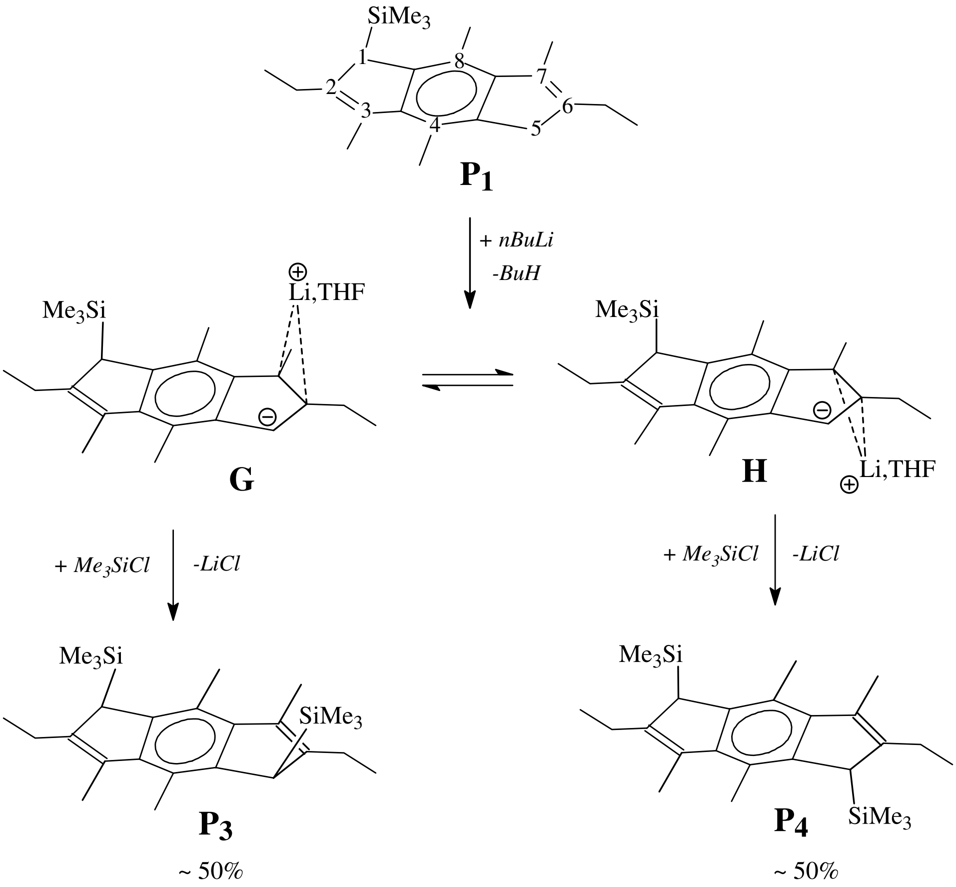


Scheme 12.



Scheme 13.



Scheme 14.

spectra were recorded on a Bruker AC80 (80.13 MHz) and ARX 400 (400.13 MHz) (^{1}H), AC200 (50.32 MHz) and an ARX 400 (100.62 MHz) (^{13}C), (δ ppm/TMS) instruments; IR spectra on a Perkin Elmer 1600FT IR spectrometer; and mass spectra on an HP5989 instrument in the electron impact (EI) mode (70 eV). Elemental analyses were performed by the 'Service Central de Microanalyse' of 'Ecole Nationale Supérieure de Chimie de Toulouse'. For crystallized compounds, melting points were measured on a Leitz microscope. Molecular calculations were performed with Hyperchem program at the AM1 level.

Disilylation of 2,6-diethyl-3,4,7,8-tetramethyl-1,5-dihydro-s-indacene

First experimental conditions: adding Me$_3$SiCl to the dilithium derivative of 2,6-diethyl-3,4,7,8-tetramethyl-1,5-dihydro-s-indacene

Following a previously published procedure,[1] *n*BuLi (1.6 M in hexane, 1.88 ml, 3.1 mmol) was added to 2,6-diethyl-3,4,7,8-tetramethyl-1,5-dihydro-s-indacene **P$_0$** (0.37 g, 1.39 mmol, freshly purified by sublimation) in 6 ml THF, at −60 °C. The mixture was warmed to 0 °C and Me$_3$SiCl (0.52 ml, 4.1 mmol) was added drop wise with stirring. After 2 h at room temperature and 1 h of reflux, THF was evaporated under vacuum and replaced by 15 ml pentane to eliminate LiCl by filtration through celite. Evaporation of pentane in vacuum yielded a light yellow sticky residue, identified as a mixture of two diastereoisomers by GC and GC/mass analyses (EI) ($M^{+\bullet} = 410$); 0.54 g, yield 95%. The first product detected (60%, $M^{+\bullet} = 410$) was identified as the meso disilylated isomer **P$_4$** by comparison with the isolated crystals whose structure was established by X-ray diffraction (see hereafter), the second one (40%) being the threo isomer **P$_3$** ($M^{+\bullet} = 410$).

Second experimental conditions: adding Me$_3$SiCl to the dilithium derivative of 2,6-diethyl-3,4,7,8-tetramethyl-1,5-dihydro-s-indacene

The dilithium derivative of 2,6-diethyl-3,4,7,8-tetramethyl-1,5-dihydro-s-indacene (1.5 mmol) prepared as before in THF was cooled to −60 °C and added to an excess of trimethylchlorosilane (1 ml, 7.9 mmol) in 5 ml THF at 20 °C. The reaction mixture, treated as before, was analyzed by GC and GC/MS, showing a change in the proportions of the diastereoisomers (meso **P$_4$**, 73% and threo **P$_3$**, 27%) with traces of the monosilylated derivative. Three successive recrystallizations in hexane afforded 0.38 g of meso

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compound $\mathbf{P_4}$ (yield 62%), which was further recrystallized in chloroform to give crystals suitable for X-ray analysis.
m.p.: 172 °C. ^{1}H NMR ($CDCl_3$) δ ppm: -0.05 (s, 18H, Me_3^{Si}); 1.16 (t, 6H, CH_3^{Et}, ^3J $CH_2CH_3 = 7.5$ Hz); 2.28 (m, 2H, CH_2^{Et}); 2.72 (m, 2H, CH_2^{Et}); 2.29 (s, 6H, 3, 7-Me); 2.57 (s, 6H, Me^{Ph}); 3.58 (s, 2H, CH^{Si}). ^{13}C NMR ($CDCl_3$) δ ppm: -0.53 (Me_3^{Si}), 14.50 (CH_3^{Et}), 18.63 (Me^{Ph}); 21.85 (CH_2^{Et}); 44.57 (CH^{Si}); 121.24 (C2, C6); 131.49 (C3, C7); 140.11, 142.64, 145.22 (aromatic C_{IV}). Mass (EI): $M^{+\bullet} = 410$ (61%); $M^{+\bullet} - Me_3Si = 337$ (26%). Anal. found: C 75.96; H 10.13. Calcd for $C_{26}H_{42}Si_2$: C 76.20; H 10.31%.

Third experimental conditions: starting from the monosilylated derivative of 2,6-diethyl-3,4,7,8-tetramethyl-1,5-dihydro-s-indacene

1-Trimethylsilyl-2, 6-diethyl-3, 4, 7, 8-tetramethyl-5-dihydro-s-indacene[1] (1.06 g, 3.16 mmol) in 10 ml THF, was lithiated by addition of nBuLi (2 ml, 1.6 M in hexane, 3.2 mmol) at -60 °C. The lithiated compound was kept at 20 °C for 30 min, and then silylated by Me_3SiCl (0.6 ml, 5 mmol). The mixture was kept for 1 h at 20 °C, then refluxed for 1 h. The solvent was replaced by toluene to eliminate LiCl by filtration and then analyzed by GC and GC/MS yielding meso $\mathbf{P_4}$: 50% (±2%), and threo $\mathbf{P_3}$: 50% (±2%) isomers. After several crystallizations from hexane to eliminate $\mathbf{P_4}$ (the solid isomer), followed by GC analysis of the liquid phase, the remaining solution of crude $\mathbf{P_3}$ was microdistilled under reduced pressure, leading to 0.37 g of pure $\mathbf{P_3}$. Yield 29%.
b.p.: 150 °C/4×10^{-2} mmHg. ^{1}H NMR ($CDCl_3$) δ ppm: -0.12 (s, 18H, Me_3^{Si}); 1.10 (t, 6H, CH_3^{Et}, ^3J $CH_2CH_3 = 7.5$ Hz); 2.32 (m, 2H, CH_2^{Et}); 2.72 (m, 2H, CH_2^{Et}); 2.30 (s, 6H, 3,7-Me); 2.58 (s, 6H, Me^{Ph}); 3.61 (s, 2H, CH^{Si}). ^{13}C NMR ($CDCl_3$) δ ppm: -1.01 (Me_3^{Si}), 14.18 (CH_3^{Et}), 18.15 (Me^{Ph}); 21.97 (CH_2^{Et}); 44.75 (CH^{Si}); 120.89 (C2, C6); 130.80 (C3, C7); 139.28, 142.85, 145.55 (aromatic C_{IV}). Mass (EI): $M^{+\bullet} = 410$ (95%); $M^{+\bullet} - Me_3Si = 337$ (23%). Anal. found. C 75.75; H 10.23. Calcd for $C_{26}H_{42}Si_2$: C 76.20; H 10.31%.

Crystal structure determination of $\mathbf{P_4}$

$C_{13}H_{21}Si$, $M = 205.39$, triclinic, $P\bar{1}$, $a = 7.147(2)$ Å, $b = 8.662(3)$ Å, $c = 10.560(3)$ Å, $\alpha = 92.935(4)°$, $\beta = 101.090(4)°$, $\gamma = 105.523(4)°$, $V = 614.5(3)$ Å^3, $Z = 2.3726$ reflections (2053 independent, $R_{int} = 0.040$) were collected at 173(2) K using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with MoKα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct-methods (SHELXS-97)[13] and all nonhydrogen atoms were refined anisotropically using a least-squares method based on F^2.[14] R[1800 reflections with $I > 2\sigma(I)$] = 0.052 and $wR_2 = 0.138$ (all data). CCDC deposition no.: 610551.

Acknowledgments

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REFERENCES

1. Dahrouch M, Jara P, Mendez L, Portilla Y, Abril D, Alfonso G, Chavez I, Manriquez JM, Rivière-Baudet M, Rivière P, Castel A, Rouzaud J, Gornitzka H. *Organometallics* 2001; **20**: 5591.
2. Ceccon A, Bisello A, Crociani L, Gambarro A, Ganis P. Manoli F, Santi S, Venzo A. *J. Organomet. Chem.* 2000; **600**: 94.
3. Bisello A, Ceccon A, Gambarro A, Ganis P, Manoli F, Santi S, Venzo A. *J. Organomet. Chem.* 2000; **593–594**: 315.
4. Esponda E, Adams C, Burgos F, Chavez I, Manriquez JM, Delpech F, Castel A, Gornitzka H, Rivière-Baudet M, Rivière P. *J. Organomet. Chem.* 2006; **691**: 3011.
5. Kawai H, Katoono R, Nishimura K, Matsuda S, Fujiwara K, Tsuji T, Suzuki T. *J. Am. Chem. Soc.* 2004; **126**: 5034.
6. Kawai H, Katoono R, Fujiwara K, Tsuji T, Suzuki T. *Chem Eur. J.* 2005; **11**: 815.
7. Stezowski JJ, Hoier H, Wilhelm D, Clark T, Von Ragué Schleyer P. *J. Chem. Soc. Chem. Com.* 1985; 1263.
8. Sygula A, Lipkowitz K, Rabideau PW. *J. Am. Chem. Soc.* 1987; **109**: 6602.
9. Hiermeier J, Köhler FH, Müller G *Organometallics* 1991; **10**: 1787.
10. Moene W, Vos M, Schakel M, de Kanter FJJ, Schmitz RF, Klumpp GW. *Chem. Eur. J.* 2000; **6**: 225.
11. Sorger K, Von Ragué Schleyer P, Fleischer R, Stalke D. *J. Am. Chem. Soc.* 1996; **118**: 6924.
12. Bassindale AR, Glynn SJ, Taylor PG. *The Chemistry of Organic Silicon Compounds*, Vol. 2, Part. 1, Chap. 9, Patai S, Rappoport Z, Apeloig Y (eds). Wiley: New York, 1998.
13. Sheldrick GM. *Acta Crystallogr.* 1990; **A46**: 467.
14. SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen, 1997.