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THE BARRIERS TO TRIMETHYLSILYL MIGRATIONS IN INDENES AND BENZINDENES: SILATROPIC SHIFTS VIA AROMATIC TRANSITION STATES*

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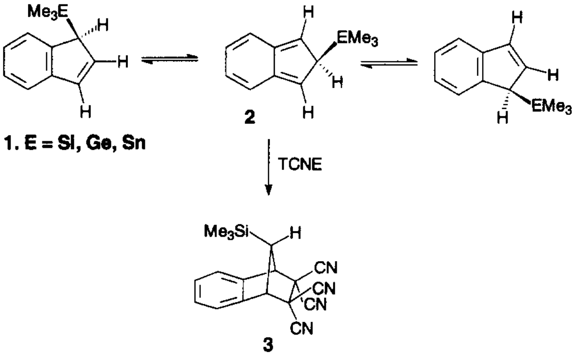
Abstract—The barriers to migration of a trimethylsilyl group around the five-membered ring of indene, and of linear and angular benzindenes, have been calculated at the unrestricted Hartree–Fock (UHF) level of theory by using AMPAC and MOPAC. It is found that the retention of aromatic character in the transition state and in the intermediate iso-indene lowers the barrier for the silatropic shifts. A preliminary experimental study on a trimethysilyl derivative of angular benzindene reveals that Me_3Si migration is indeed a facile process. However, in the corresponding bis-trimethylsilyl systems, rearrangements which require the intermediacy of geminal Me_3Si groups have rather high barriers.

The ability of organosilyl groups to migrate over molecular surfaces continues to attract attention.[1] In particular, molecules of the type L_2ZrX_2, where L = cyclopentadienyl, indenyl or fluorenyl, are important because of their relevance to stereospecific polymerizations of alkenes.[2] Moreover, when the metallocene rings are linked via alkyl or silyl bridges, the resulting complexes can be chiral catalysts. Thus, any process which might bring about loss of stereochemical integrity in the catalytic species needs to be understood at a rather fundamental level.

For a number of years, it has been known that the migration of an R_3E group (where E = Si, Ge, Sn) round a cyclopentadienyl ring proceeds via successive [1,5]-metallotropic shifts with retention of configuration at the migrating Group 14 centre;[3] the barriers for such migrations have been reported as 15 kcal mol^{-1} (for Me_3Si), falling to 13 and 7 kcal mol^{-1} for Me_3Ge and Me_3Sn, respectively.[4] In the corresponding indenyl systems (**1**), the activation energies increase to ≈24 (Si), 22 (Ge) and 15 (Sn) kcal mol^{-1}.[5] The pathway requires the generation of an iso-indene intermediate (**2**), which has been trapped by tetracyanoethylene as the Diels–Alder adduct (**3**).[6] It is evident that the loss of aromatic character in the iso-indene is a major factor in raising the barrier for the silatropic shift.



More recently, it has been proposed[1] that in bis(indenyl)$SiMe_2$ (**4**), the rearrangement occurs via [1,3]-silatropic shifts; however, this hypothesis has since been disproven, and the [1,5]-shift mechanism has been established by trapping the intermediate iso-indene **5** as shown in Scheme 1.[7]

The [1,5]-silatropic shift in **4** has an activation

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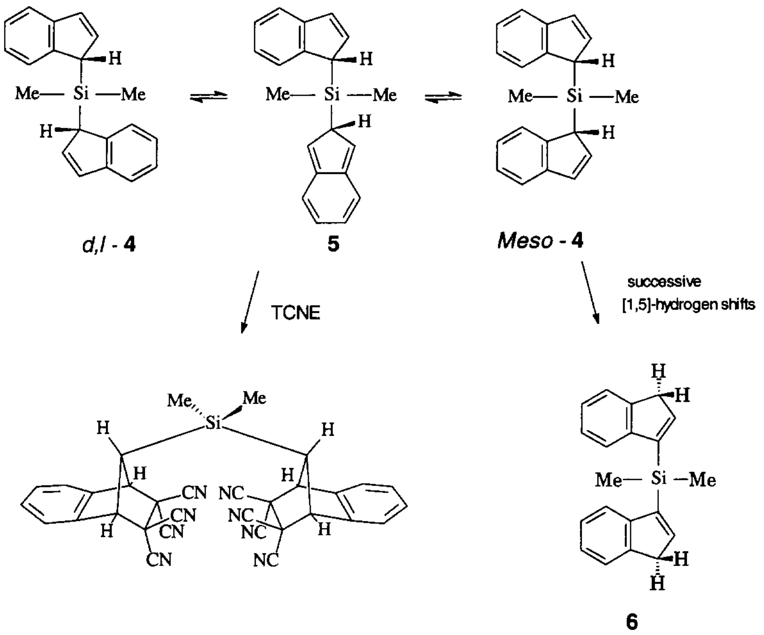
* Dedicated to Prof. E. W. Abel on the occasion of his retirement.

† Authors to whom correspondence should be addressed.



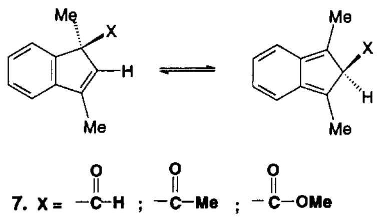
Scheme 1. Inconversion of *meso*- and D, L-bis(indenyl)dimethylsilanes (**4**) via the iso-indene **5**.

energy of ≈ 24 kcal mol^{-1}, and this $\Delta G^{\ddagger}$ value is too high to be reliably obtained by means of conventional NMR line-broadening methods. However, it has been rather straightforwardly evaluated by using single selective inversion techniques in which magnetization transfer between exchanging sites is monitored over a range of temperature.[7,8]

The more fundamental question, perhaps, involves the relative ease of silatropic shifts versus the corresponding prototropic shifts. In the bis(indenyl)dimethylsilyl case, the latter process leads to isomer **6**, but only occurs at temperatures in excess of 150°C. Moreover, the facility with which the iso-indenes **2** and **5** can be trapped suggests that the organosilyl moiety plays a significant role in stabilizing these non-aromatic intermediates. Of course, the possible role of silicon 3*d* orbitals has long been a contentious issue,[9] but the majority of recent commentators have rejected the use of the 3*d* orbitals, at least in rationalizing the bonding in Si—O—Si systems.[10]

In the dimethylindene system **7**, the migration aptitudes of a variety of substituents have been studied by Jones *et al.*[11] It was found that the formyl group migrates 10^3 times more rapidly than does the acetyl group, which in turn migrates 10^4 times more rapidly than does the carbomethoxy group. These results were rationalized in terms of the electron-accepting ability of the migrating group (in a resonance sense, rather than purely inductively). Moreover, it was proposed that the intermediate iso-indene is stabilized by donation of electron density from the HOMO of the bicyclic framework into the LUMO of the formyl substituent, as shown in Fig. 1.

However, Epiotis and Shaik[12] chose to interpret the data in a different manner. They suggested that these sigmatropic shifts were controlled by the donor and acceptor character of the migrating group, and of the cyclic framework over which the rearrangement occurred. Thus, they viewed the cyclopentadienyl moiety in $C_5H_5SiMe_3$ as being "an intrinsic acceptor" because of the aromatic nature of $C_5H_5^-$; in contrast, the cycloheptatrienyl frag-



7. $X = -\overset{O}{\overset{\|}{C}}-H\ ;\ -\overset{O}{\overset{\|}{C}}-Me\ ;\ -\overset{O}{\overset{\|}{C}}-OMe$

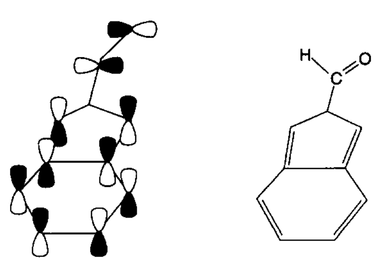
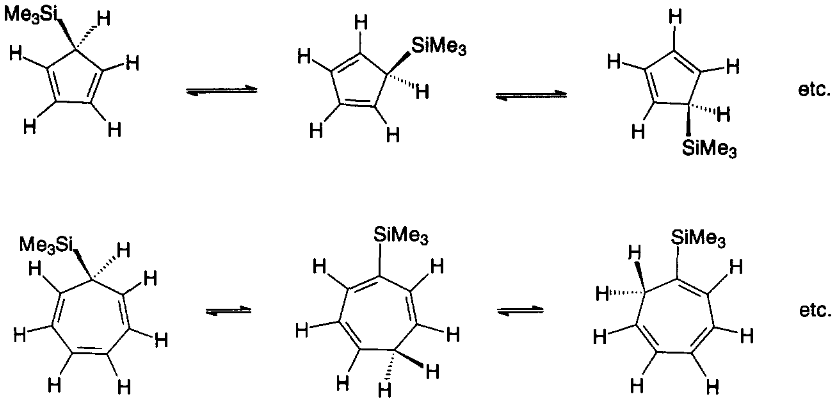


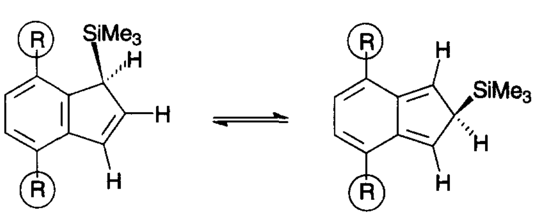
Fig. 1. Stabilization of 2-formyl-iso-indene by overlap of the HOMO of the indenyl fragment with the vacant π^* orbital of the carbonyl group.



Scheme 2. [1,5]-Shifts in trimethylsilyl-cyclopentadiene and in trimethylsilyl-cyclohexatriene.

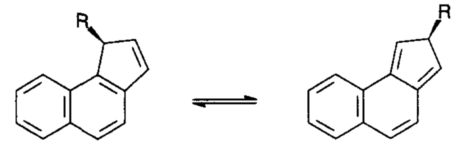
ment in $C_7H_7SiMe_3$ behaves as "an intrinsic donor" owing to the aromatic nature of $C_7H_7^+$. As shown in Scheme 2, the trimethylsilyl substituent undergoes facile rearrangement over the five-membered ring, while the prototropic shift has a very high barrier. In the seven-membered ring, it is the hydrogen which undergoes the [1,5]-suprafacial shift, while the $SiMe_3$ group is much more reluctant to migrate.[13] However, we note that in $C_7H_7SnMe_3$, the trimethyltin moiety is apparently fluxional.[14]

We consider here the possibility of disturbing the equilibrium between an organosilylindene and its corresponding silyl-iso-indene, by modifying steric or electronic factors. It is well known that *ortho*-xylylenes and iso-indenes can be readily stabilized as $Fe(CO)_3$ complexes,[15] but that is not the approach we are advocating in this case. For example, one might envisage putting extremely bulky substituents at the 4- and 7-positions of the aromatic ring, as in **8**, so as to favour the iso-indene **9**.



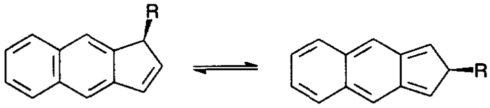
8 **9**

A second approach would involve the incorporation of another six-membered ring so as to maintain some aromatic character even in the iso-indene. For such purposes, one would expect the angular molecules **10a** and **10b** to be more effective than the linear systems **12a** and **12b**; in the iso-benzindene **12b**, one cannot draw a conventional aromatic structure. The relatively enhanced stability of the iso-benzindene **10b** over the linear isomer **12b** could also be reflected in lower barriers for the [1,5]-silatropic shifts in the analogous silylated derivatives **11** and **13**, respectively.



10a: R = H
11a: R = SiMe3

10b: R = H
11b: R = SiMe3



12a: R = H
13a: R = SiMe3

12b: R = H
13b: R = SiMe3

We describe here a preliminary synthetic and NMR study of a bis(trimethylsilyl)benzindene, together with some semi-empirical molecular orbital calculations and molecular modelling studies which illustrate these concepts.

RESULTS AND DISCUSSION

To test the viability of the combined calculatory and experimental approach, the energy-minimized structure of 1-trimethylsilylindene (**1**), the iso-indene **2** and the transition state which connects them were computed at the unrestricted Hartree–Fock (UHF) level with the programs AMPAC[16] and MOPAC.[17] These calculated geometries are depicted in Fig. 2, which also shows that the transition state lies 26.0 kcal mol^{-1} above the energy of the starting configuration (**1**), while the iso-indene **2** lies in a potential well 7.9 kcal mol^{-1} above the ground state. These results are in excellent accord with the experimental NMR data, which yielded an

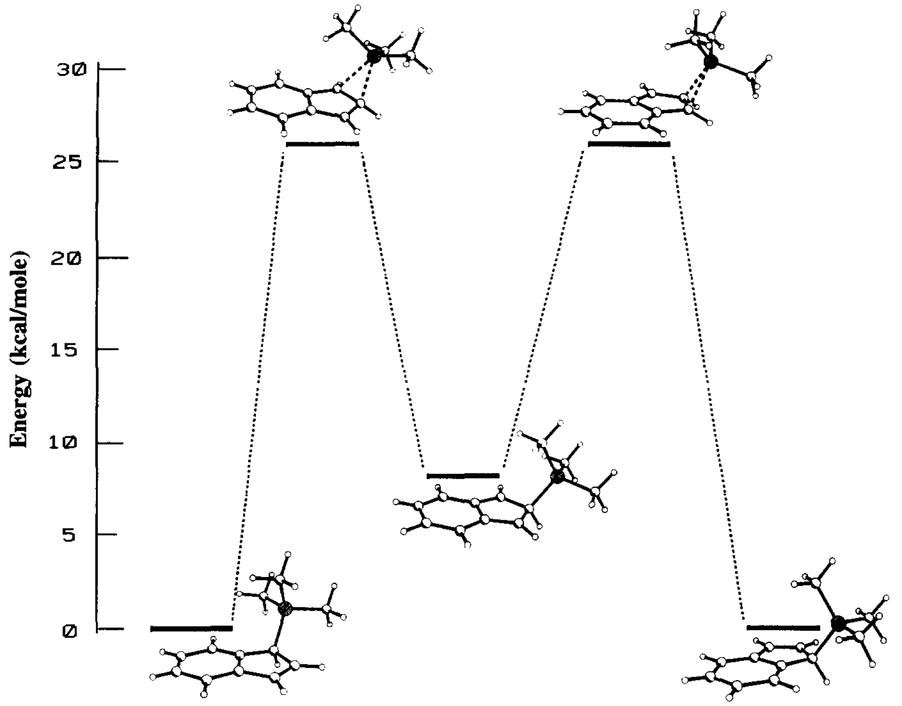


Fig. 2. Energy profile for the [1,5]-$SiMe_3$ shifts in trimethylsilylindene (**1**).

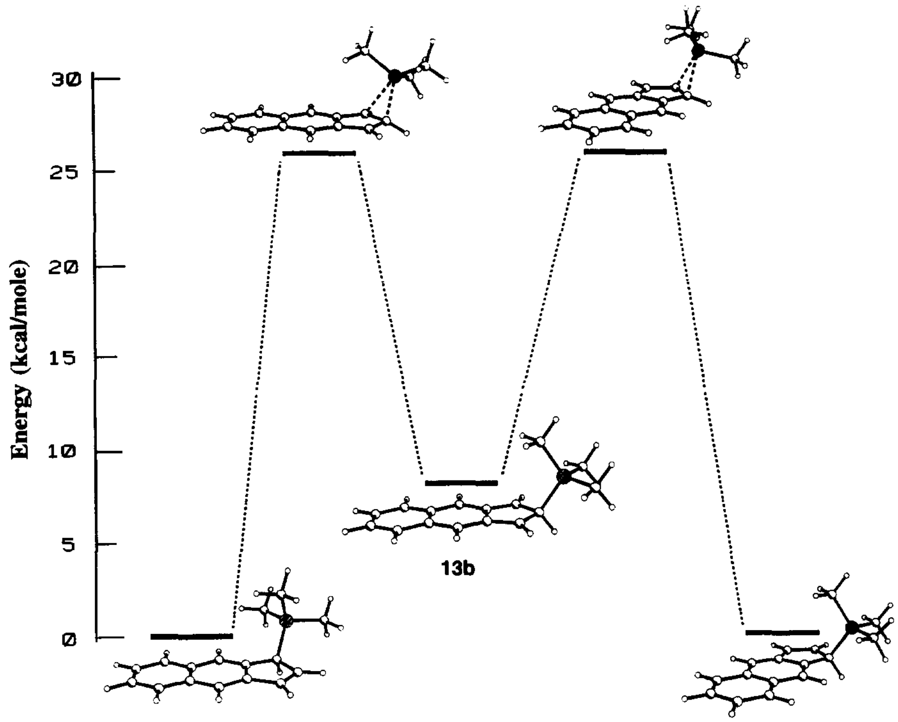
activation energy barrier of 24 kcal mol^{-1}.[5] Moreover, the intermediate iso-indene should be sufficiently long-lived for Diels–Alder trapping reactions to be competitive with a second [1,5]-silatropic shift which regenerates 1-trimethylsilylindene. The analogous calculations for a [1,5]-hydrogen shift yield a much larger barrier of 43.0 kcal mol^{-1}.

Subsequently, AMPAC computations were carried out on the angular and linear trimethylsilylbenzindenes **11a** and **13a**, respectively; the results of these calculations are illustrated in Figs 3 and 4. It is evident that in the linear benzindene system **13**, the activation parameters—the transition state lies 26.8 kcal mol^{-1} above **13a**—closely resemble those found both theoretically and experimentally for silatropic shifts over the indene framework. In contrast, for the angular benzindene **11a**, the calculated transition state energy lies only 22.9 kcal mol^{-1} above the ground states. In **11**, of course, we must consider two isomeric starting structures which can interconvert through the same iso-benzindene intermediate, but via different transition states. These five configurations are shown in Fig. 4. The transition state for the rearrangement of angular benzindene **11a′** to **11b** lies 23.9 kcal mol^{-1} above **11a′**.

With these data in hand, we chose to synthesize the angular benzindene **10a** with the intent of monitoring the barrier to migration of a trimethylsilyl group around the five-membered ring. As depicted in Scheme 3, this ring system is accessible starting with the Friedel–Crafts addition of maleic anhydride to naphthalene.[18] Subsequent cyclization and decarboxylation, followed by reduction of the ketone and elimination of water, gave the benzindene **10a** together with **10a′**. No separation of these isomers was attempted since their trimethylsilyl derivatives **11a** and **11a′** should readily interconvert.

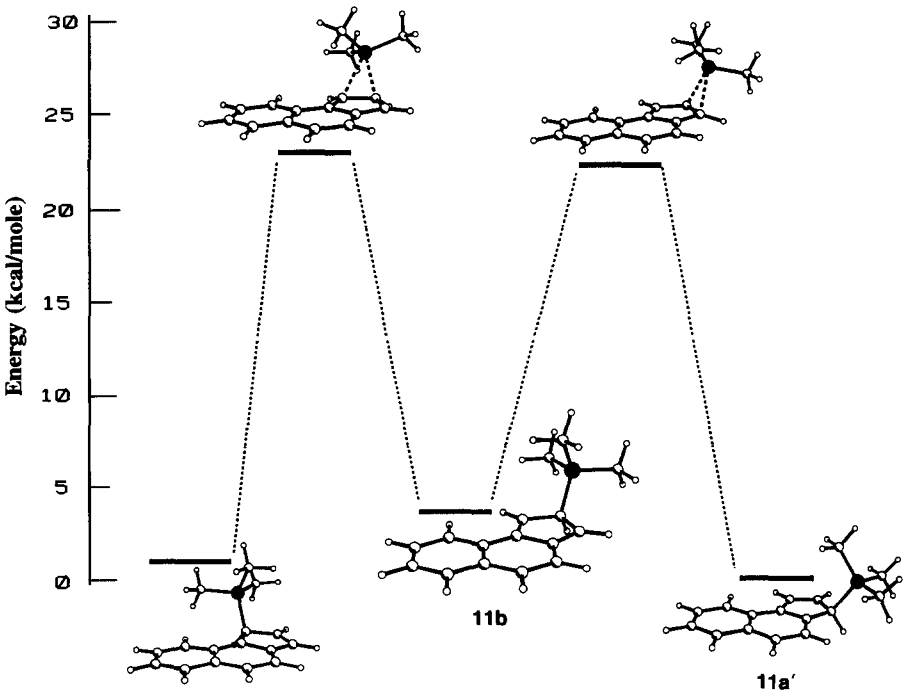
At the end of this multi-stage synthesis, the benzindenes **10** and **10a′** were obtained in small quantities. Lithiation at low temperature, followed by addition of Me_3SiCl, gave the bis(trimethylsilyl)benzindene **16** (see Scheme 4), which was characterized by mass spectrometry and by its one- and two-dimensional NMR spectra. Presumably, the initially formed molecule **14**, with its two geminal $SiMe_3$ groups, is sterically crowded and so undergoes silatropic migration, via the iso-benzindene **15**, to give the favoured 1,3-bis(trimethylsilyl) isomer **16**, in which the interaction between the Me_3Si substituent at C(3) with the in-plane hydrogens is minimized.

The alternative geminal isomer **17** would yield **18**, which has been shown by molecular modelling to lead to severe steric hindrance with an aromatic hydrogen in the terminal six-membered ring. Space-



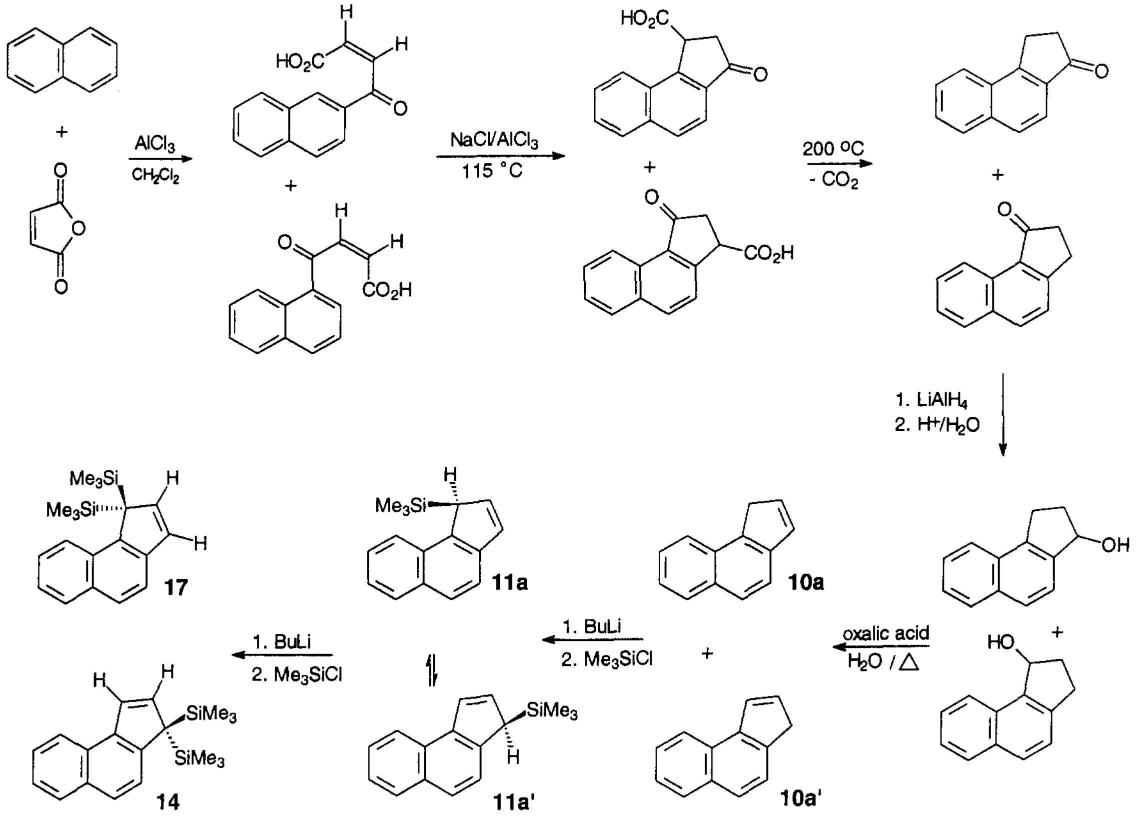
13a

Fig. 3. Energy profile for the [1,5]-SiMe$_3$ shifts in the linear trimethylsilyl-benzindene 13.

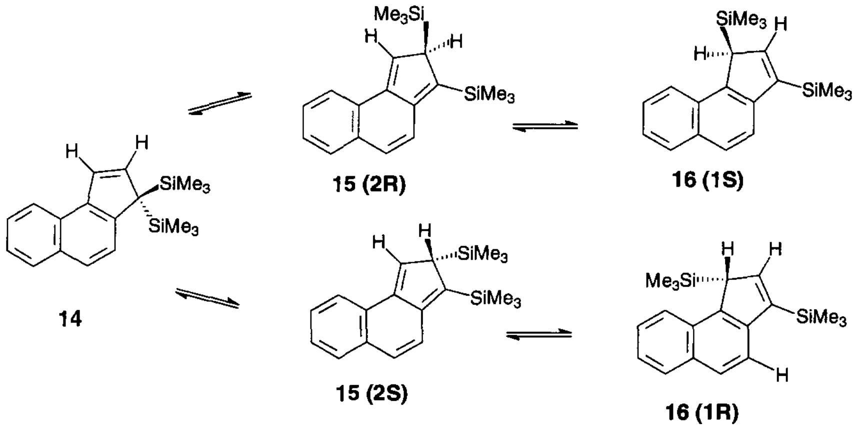


11a

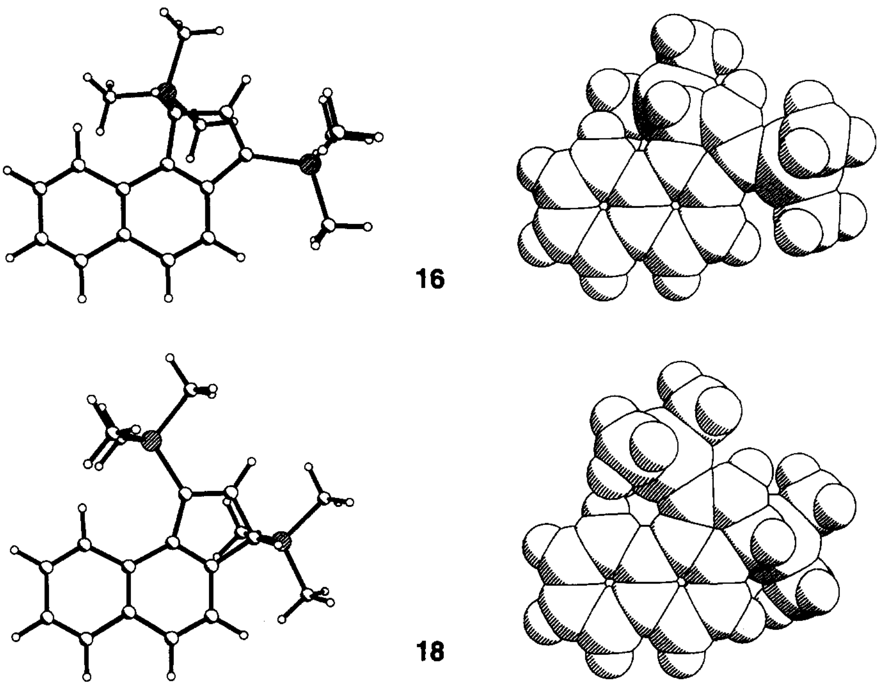
Fig. 4. Energy profile for the [1,5]-SiMe$_3$ shifts in the angular trimethylsilyl-benzindene 11.



Scheme 3. Synthetic route to angular benzindene **10**.



Scheme 4. Migrations in angular bis(trimethylsilyl)benzindenes; the absolute configuration of the trimethylsilyl-substituted sp^3-hybridized carbon is indicated in each case.

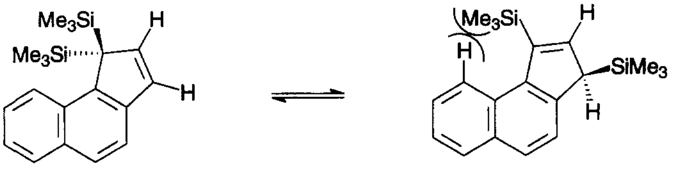


16

18

Fig. 5. Space-filling models of the bis(trimethylsilyl)benzindenes **16** and **18**.

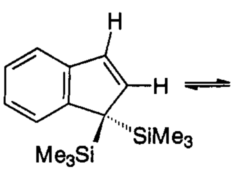
filling models of the bis-trimethylsilyl-benzindenes **16** and **18** are shown in Fig. 5.



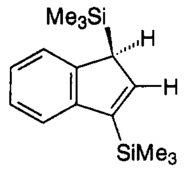
17 **18**

Complex **16** exhibits ^{1}H NMR resonances at δ -0.03 and δ 0.10 for the two Me_3Si moieties, and even at 140°C these peaks retain their sharp character; since the coalescence temperature must be higher than 413 K, the Gutowsky–Holm approximation[19] yields a minimum activation energy of 21 kcal mol^{-1} for the equilibration of the trimethylsilyl environments. In an attempt to evaluate the barrier, we carried out a series of single selective inversion experiments in which one of the Me_3Si signals was inverted and the return of that peak to equilibrium, and also that of the other Me_3Si peak, was monitored. However, at the temperatures accessible, it was not possible to detect exchange between the Me_3Si sites; thus, we are unable to give a reliable barrier for the interconversion of the two trimethylsilyl environments which can only occur via the formation of the sterically crowded geminal bis-Me_3Si complex **14**. We note an earlier report that the attempted synthesis of 1,1-bis(trimethylsilyl)indene (**19a**) actually yields an appreciable amount of the 1,3-isomer **19b**. However, these molecules showed no evidence of interconversion, even at 206°C.[5a] In the same vein, the Me_3Si groups in 1,2-bis(trimethylsilyl)indene (**20**) only show evidence of fluxional behaviour at ≈ 140°C, and the reported barrier is ≈ 26 kcal mol^{-1}.[5a]

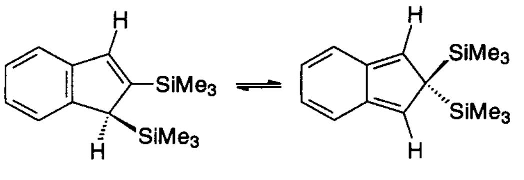
Even though we are, as yet, unable to provide a reliable estimate of the barrier to the interconversion of the enantiomers of **16**, nevertheless, these preliminary experimental results do provide some insight into the chemical behaviour of this system. The very ready incorporation of a second Me_3Si substituent to form the bis(trimethylsilyl)benzindene **14** is in accord with previous observations that carbanionic centres adjacent to Me_3Si substituents are particularly fav-



19a



19b



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oured.[20] The facile migration of a trimethylsilyl group, as in **14** via **15** to **16**, even at room temperature, is indicative of a lowered barrier for silatropic shifts. The fact that **16** is observed, and that the alternative structure **18** is apparently not formed, again lends credence to the idea of a relatively rapid interconversion of the mono-silylated benzindenes **11a** and **11a′**. Currently, we are directing our efforts towards obtaining these latter molecules in sufficient quantities so as to allow a full study of their molecular dynamics, and these will be the focus of a future report.

The results of these calculations, together with the preliminary experimental data, indicate that the incorporation of an extra six-membered ring to the indenyl system lowers the barrier to iso-indene formation, with a consequent enhancement of the rate of silatropic shifts over the benzindene molecular framework. The possibility of stabilizing a transition state by allowing the development (or retention) of aromatic character is reminiscent of the "indenyl effect" whereby the rate of ligand substitution at a metal centre is enormously enhanced in (indenyl)ML$_n$ systems (**21**) relative to their (cyclopentadienyl)ML$_n$ analogues.[21] Similarly, η^6- to η^5-haptotropic shifts in (cyclopentanophenanthrenyl)ML$_n$ complexes, such as **22**, proceed much more rapidly than they do to their fluorenyl analogues because of the "napththalene-type" character of the transition state.[22]

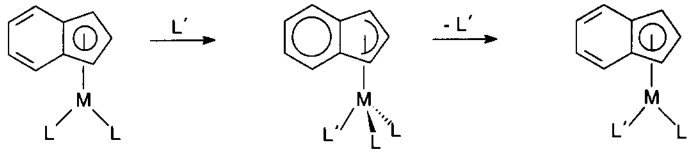
EXPERIMENTAL

Reagents and general techniques

All preparations involving n-butyl lithium were carried out under an atmosphere of dry nitrogen. Solvents were dried according to standard procedures, and aluminium chloride was sublimed before use. Benzindenes **10a** and **12a** were prepared by published procedures.[18] ^{1}H and ^{13}C NMR spectra were acquired on Bruker AC 200 or AC 300 spectrometers, and the chemical shifts are reported relative to TMS. Mass spectra (DEI) were obtained on a VG Analytical ZAB-SE spectrometer with an accelerating potential of 8 kV and a resolving power of 10,000.

Bis(trimethylsilyl)benzindene (16)

Over a 30 min period, n-butyl lithium (1.25 cm^3 of a 1.6 M hexane solution; 2 mmol) was added dropwise to a solution of benzindenes **10a** and **12a** (0.166 g, 1 mmol) in THF (10 cm^3) at −78°C, and the cold mixture was stirred for 1 h. Tri-



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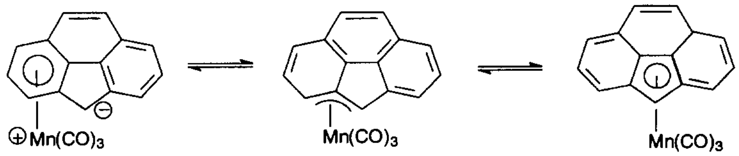
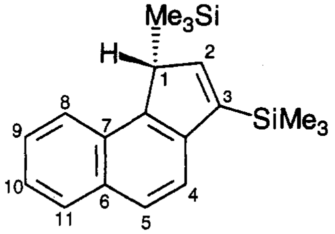


22

methylchlorosilane (0.25 cm^3, 0.217 g, 2 mmol) in THF (5 cm^3) was added dropwise at −78°C and stirred at this temperature for 1 h. The reaction mixture was allowed to warm to room temperature, stirred for 2 h and the solvent removed *in vacuo*. The residue was washed with distilled water (10 cm^3) to dissolve the lithium chloride, and the silyl compound was extracted with 15 cm^3 of ether. After drying the ethereal solution over anhydrous magnesium sulphate, the ether was evaporated under reduced pressure to leave **16** as a yellow oil (0.186 g, 6 mmol; 60%). Mass spectrum (DEI), m/z (%): 310 $[M]^+$ (35%), 295 $[M-Me]^+$ (15%), 222 $[M-Me-Me_3Si]^+$ (83%), 159 $[Me_6Si_2CH]^+$ (60%), 73 $[Me_3Si]^+$ (100%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.23 [d of d, 1H, H(9)], 8.02 [d, 1H, H(8)], 7.83 [d, 1H, H(11), 7.69 [d, 1H, H(4)], 7.49 [d of d, 1H, H(10)], 6.90 [d, 1H, H(5)], 3.86 [d, 1H, H(2)], 1.85 [d, 1H, H(1)], 0.10 (s, 9H, $SiMe_3$), −0.03 (s, 9H, $SiMe_3$). [The assignments of H(8) and H(11) can be interchanged; likewise for H(9) with H(10) and H(4) with H(5).] The numbering system for **16** is shown below:



Calculations

Optimized equilibrium geometries and transition states were calculated with AM1 of AMPAC[16] (version 2.1) and MOPAC[17] (version 6.0) at the UHF level of theory. The keyword PRECISE was used to tighten the convergence criteria. Molecular mechanics calculations with the MMX force-field of PCMODEL[23] provided the optimized geometries used as input for the AM1 calculations, which gave optimized equilibrium geometries and the heats of formation for **1a**, **11a**, **13a**, and for their isoindene analogues **2**, **11b** and **13b**, respectively.

To locate the transition state for the rearrangement of **1** into **2**, the C(1)—$SiMe_3$ bond was stretched to 2.3 Å, then the Si—C(1)—C(2) bond angle was decreased from 108.8° to 65° in 5° increments while the C(1)—$SiMe_3$ bond length was fixed at 2.3 Å. The geometry with a C(1)—$SiMe_3$ bond length of 2.3 Å and Si—C(1)—C(2) bond angle of 70° was used as input to calculate the transition state. SIGMA or NLLSQ calculations* were used in the case of the AMPAC calculation; in the case of the MOPAC calculation, the eigenvector following (EF) method, which is invoked with the keyword TS, was used to locate the transition state.

The AMPAC and MOPAC calculations gave identical geometries and heats of formation for the transition state. The calculated Me_3Si—C(1) and Me_3Si—C(2) bond distances for the transition state were 2.368 and 2.305 Å, respectively, significantly longer than the value of 1.860 Å obtained in the calculation for **1**; the C(1)—C(2) bond length in the transition state was 1.473 Å. A force calculation with AMPAC or MOPAC—the keyword FORCE is used—gave one negative force constant (frequency), as is required for a transition state.

To locate the transition state for the [1,5]-shift of hydrogen from C(1) to C(2) in **1**, the C(1)—H bond was lengthened to 1.5 Å, the H—C(1)—C(2) bond angle was decreased from 110.3° to 75° in 5° increments, and the 1.5 Å/75° geometry was used as the input geometry in a MOPAC EF calculation. The calculated H—C(1) and H—C(2) bond distances for the transition state were 1.417 and 1.368 Å, respectively, significantly longer than the value of 1.121 Å calculated for **1**; the C(1)—C(2) bond length in the transition state was 1.493 Å. A force calculation with AMPAC or MOPAC, as was the case for the Me_3Si shift, gave one negative force constant (frequency), as is required for a transition state.

To ensure that the vibrations with the negative frequencies connected the reactants and products (both for the Me_3Si- and H-shifts), the system was viewed with CHEMSTAT, which animates normal modes of vibration calculated with semi-empirical and *ab initio* quantum chemistry programs. This computer software package was run on an IBM RS/6000 Model 530 workstation equipped with a 24-bit graphics adapter.

Calculations on the [1,5]-silatropic shifts in **11** and **13** were carried out in the manner described for **1**. In the transition state for the rearrangement of **11a** to **11b**, the calculated distances were found to be: $Me_3Si \cdots C(1)$ 2.364 Å, $Me_3Si \cdots C(2)$ 2.318 Å, C(1)—C(2) 1.473 Å; for the transformation of **11a′** into **11b**, the calculated distances were found to be: $Me_3Si \cdots C(1)$ 2.359 Å, $Me_3Si \cdots C(2)$ 2.316 Å, C(1)—C(2) 1.472 Å. In the transition state that connects **13a** with **13b**, the calculated distances were found to be: $Me_3Si \cdots C(1)$ 2.368 Å, $Me_3Si \cdots C(2)$

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* The keyword SIGMA invokes the McIver–Komornicki gradient norm minimization routines. The keywork NLLSQ invokes L, Bartel's non-linear least-squares gradient norm minimization method.

2.309 Å, C(1)—C(2) 1.472 Å. In each case, the transition state exhibited one negative frequency.

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