Multidimensional NMR Study of Tris(indenyl)methylsilane: Molecular Dynamics Mapped onto a Hypercube

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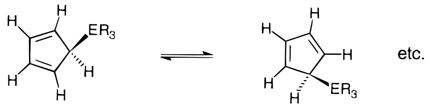
Received July 25, 1996[⊗]

(Trimethylsilyl)indene exists as a pair of enantiomers which interconvert by means of Me$_3$Si migrations. The mechanism involves successive [1,5]-suprafacial sigmatropic shifts via the corresponding isoindene, which can be trapped with tetracyanoethylene as the Diels−Alder adduct, **7**. The X-ray crystal structure of **7** reveals that the TCNE approaches from the opposite face to the Me$_3$Si substituent. Tris(indenyl)methylsilane, **5**, also undergoes a series of [1,5]-silatropic shifts which interconvert the *RRR*, *RRS*, *RSS*, and *SSS* isomers, where the *R* and *S* labels refer to the absolute configuration of C(1) in each indenyl ring. By use of ^{1}H−^{1}H COSY, ^{1}H−^{13}C and ^{1}H−^{29}Si shift-correlated NMR spectra, the proton and carbon-13 nuclei in all four different indenyl ring environments can be unequivocally assigned. The molecular dynamics of **5** have been elucidated by means of 1D-selective inversion experiments together with 2D-EXSY data, and the exchange pathways between indenyl sites can be conveniently mapped onto a hypercube. Moreover, **5** yields a triple Diels−Alder adduct, **12**, with TCNE; the Si-CH$_3$ ^{1}H NMR resonance in **12** is found at −1.8 ppm suggesting that this methyl lies inside a cavity formed by the three phenyls.

Introduction

While migrations of main group fragments, for example R$_3$E (E = Si, Ge, Sn), have been studied for many years,[1] the catalytic importance of *ansa*-bridged metallocenes has recently brought about renewed interest in these systems.[2] In particular, the preparation of chiral catalysts requires that the stereochemical integrity of the ligands be maintained. It is known that metallotropic shifts around cyclopentadiene rings, as in **1**, are more facile than are the analogous migrations in indenes; [1,5]-shifts in these latter molecules are assumed to proceed via isoindenes, **2**, with concomitant reduction of aromaticity (and inversion of stereochemistry at the migration terminus).[3]



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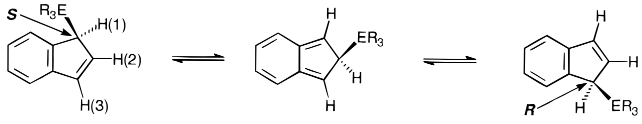

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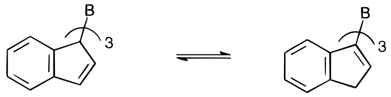
While most of the published data relate to migrations of group 14 elements, there are reports on tris(indenyl)borane and tris(indenyl)phosphine. In the former case, rapid hydrogen migration occurs to yield (3-indenyl)$_3$B, **3**, in which the boron occupies a vinylic site, presumably so that conjugation with the double bonds can help to alleviate the electron deficiency at boron.[4] Surprisingly perhaps, it has been reported that the attempted synthesis of tris(1-indenyl)phosphine gave instead (3-indenyl)$_3$P, **4**. Moreover, X-ray crystallographic data on the complex [(indenyl)$_3$P]$_2$PtCl$_2$ indicated that it possessed a mixture of 1-indenyl and 3-indenyl fragments.[5]



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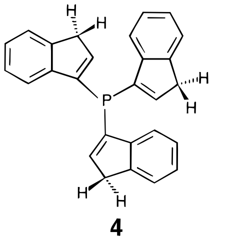

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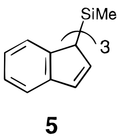

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

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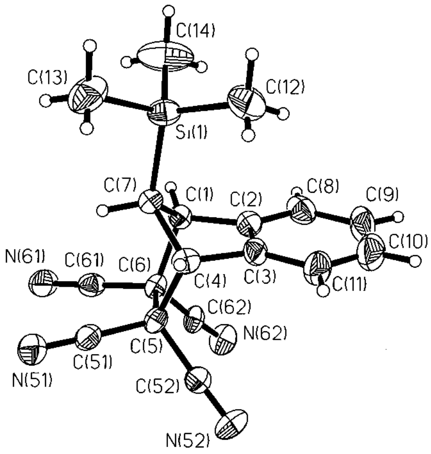
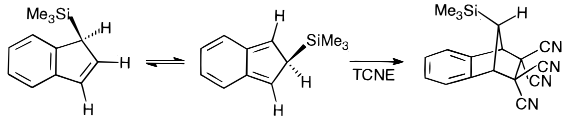


Figure 1. View of the TMS−isoindene/TCNE Diels−Alder adduct **7**, showing the atom numbering scheme.

We here describe a complete ^{1}H, ^{13}C, and ^{29}Si one- and two-dimensional NMR study of tris(1-indenyl)methylsilane, **5**. This system exhibits a rich stereochemical complexity, and a full analysis of the molecular dynamics provides considerable insight into the sequential nature of the silatropic shifts.

Results and Discussion

The [1,5]-Shift Mechanism. The variable-temperature ^{1}H NMR spectra of (trimethylsilyl)indene, **6**, reveal that the Me_3Si moiety migrates so as to interconvert the H(1) and H(3) environments. The barrier toward this fluxional process is ≈25 kcal mol^{-1}, but it falls to approximately 15 kcal mol^{-1} in the analogous trimethyltin system.[1,3] Orbital symmetry considerations suggest that this process should occur via successive [1,5]-suprafacial sigmatropic shifts. Ashe has claimed that the intermediate isoindene can be trapped by tetracyanoethylene (TCNE) as its Diels−Alder adduct, **7**, for which spectroscopic data were reported.[6]



6 **7**

Since it is known that indene itself undergoes [2+2] cycloadditions and/or “ene” reactions with electron-poor double-bonded systems,[7] we chose to confirm the identity of the Diels−Alder adduct **7** by means of a single-crystal X-ray diffraction experiment. The product is indeed the Diels−Alder adduct described by Ashe, and the resulting structure appears as Figure 1. Relevant crystallographic data and atomic coordinates are listed in Table 1 and the Supporting Information. It is apparent that TCNE approaches the less hindered face of the isoindene such that the bulky trimethylsilyl substituent lies directly over the aromatic ring in **7**. In comparison with other structurally characterized benzannulated norbornene systems,[8] the C(1)−C(6) and C(4)−C(5) bonds (1.582(8) and 1.593(8) Å, respectively) are rather long; these linkages are the ones made in the Diels−Alder reaction, and their bond distances suggest that they are relatively weak. We note, however, that the C(5)−C(6) bond (1.608(8) Å) is even longer; nevertheless, it is difficult to decide whether such a distance is typical since, although many TCNE Diels−Alder adducts are known, few have been structurally characterized.[8]

Table 1. Crystal Data and Structure Refinement Summary for 7

empirical formula	$C_{18}H_{16}N_4Si_1$
fw	316.44
dimens (mm)	0.2 × 0.2 × 0.2
cryst system	triclinic
space group	$P\bar{1}$
a, Å	8.0200(8)
b, Å	8.4380(6)
c, Å	13.6010(12)
α, deg	80.644(8)
β, deg	81.245(9)
γ, deg	79.100(7)
V, Å^3	884.75(13)
$F(000)$	332.0
Z	2
ρ_{calc}, Mg/m^3	1.188
radiation	Cu Kα (λ = 1.541 78 Å)
temp (K)	293(2)
monochromator	highly oriented graphite crystal
μ, mm^{-1}	1.20
scan type	$2\theta-\omega$
scan speed, °/min. in ω	8.00
2θ range, deg	6.64−110.0
index ranges	$-9 \le h \le 8$, $-9 \le k \le 0$, $-15 \le l \le 15$
no. of measd reflns	2420
no. of indepdt reflns	2232 (R_{int} = 16.19%)
no. of obsd reflns	1141 ($F \ge 2.0\sigma(I)$)
abs corr	ψ-scan
quantity minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000F^2$
no. of params refined	209
R, %	7.07
R_w, %	16.84
GOF	1.191
data-to-param ratio	10.4:1
largest diff peak, e Å^{-3}	0.266
largest diff hole, e Å^{-3}	−0.249

These structural data correlate with observations we have made on the benzindenes **9** and **10** whose isoindene/TCNE adducts undergo facile retro-Diels−Alder reactions.[9] Indeed, we find that the incorporation of additional rings, in positions that augment the aromatic character of the intermediate isoindene, not only lowers the barrier toward [1,5]-silatropic shifts but also destabilizes their Diels−Alder adducts with TCNE.[10] Overall, we note that there is excellent agreement between the calculated and experimental barriers for silatropic shifts in the linear and angular benzindenes **8**−**10** shown in Scheme 1.[9]

Stereochemical Considerations. Successive [1,5]-suprafacial silatropic shifts not only interconvert the

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[6] Ashe, A. J., III. *Tetrahedron Lett.* **1970**, 2105.

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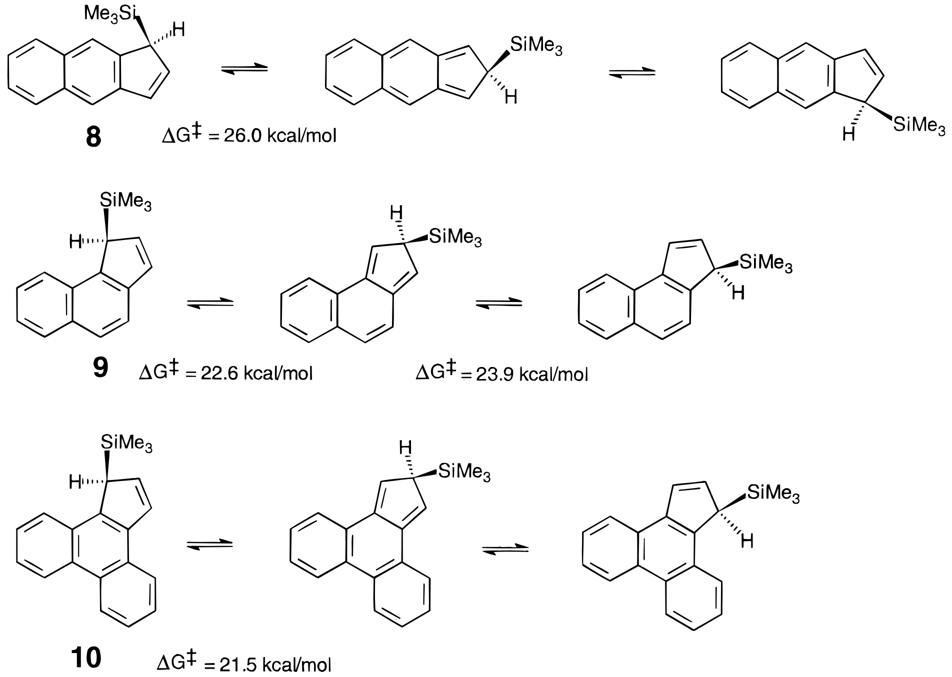
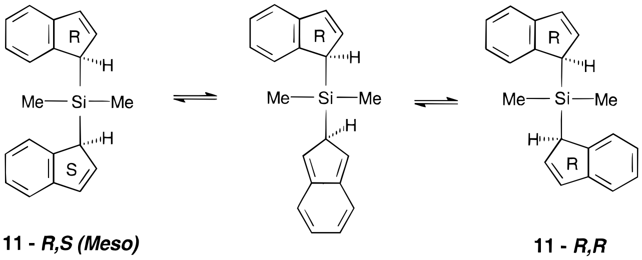
[9] Rigby, S. S.; Gupta, H. K.; Werstiuk, N. H.; Bain, A. D.; McGlinchey, M. J. *Inorg. Chim. Acta*, in press.

[10] Rigby, S. S.; Gupta, H. K.; Werstiuk, N. H.; Bain, A. D.; McGlinchey, M. J. *Polyhedron* **1995**, *14*, 2787.

Scheme 1. Barriers to Trimethylsilyl Migration in a Series of Benzindenes



Scheme 2. Interconversions of Diastereomers of Bis(indenyl)dimethylsilane, 11



C(1) and C(3) positions within an indenyl moiety, they also invert the configuration of the stereocenter within the five-membered ring. This phenomenon has been noted previously with respect to the interconversion of the *R*- and *S*-enantiomers of Me_3E–indene that proceeds via the isoindene **2**. Such a scenario also accounts for the recently reported interconversion of the *meso*- and *d*,*l*-isomers of bis(indenyl)dimethylsilane, **11**, shown in Scheme 2.[2,11]

The stereochemical features of the $(indenyl)_3ER$ and $(indenyl)_4E$ systems were originally investigated by McMaster and Stobart.[12] They drew attention to the stereochemical correspondence of $(indenyl)_3SnPh$ and the propeller-shaped[13] triarylboranes; moreover, they noted the homotopic character of the indenyl rings in the *RRR*/*SSS* isomers of such molecules but pointed out that in the *RRS*/*SSR* enantiomorphs all three indenyl environments are different. Experimental verification of these ideas was provided by the *n*-butyltris(η^1-indenyl)tin system for which the expected 1:3 statistical ratio of *RRR*/*SSS* to *RRS*/*SSR* stereoisomers was observed. Ideally, this system should exhibit four equally intense ^1H and ^{13}C NMR resonances for each of the C(1), C(2), and C(3) positions. Indeed, four peaks are discernible for the C(1) and H(1) sites but, with the limited magnetic fields accessible at that time, no detailed assignments were possible. Nevertheless, the existence of interconverting diastereomers of *n*-BuSn(indenyl)$_3$ was definitively proven.[12]

NMR Spectra of Tris(1-indenyl)methylsilane. The power and versatility of the 2-dimensional techniques currently available on modern high-field spectrometers allow a complete analysis of the molecular dynamics of these fluxional systems. As anticipated for a statistical mixture of *RRR*/*SSS* to *RRS*/*SSR* stereoisomers, the ^{29}Si NMR spectrum of **5** exhibits two peaks in a 1:3 intensity ratio. The 500 MHz ^1H NMR spectrum of tris(1-indenyl)methylsilane, **5**, shows four clearly separated absorptions for each of the H(1), H(2), and H(3) sites. The connectivity of the three protons within the five-membered ring of each of the four individual types of indenyl fragment is easily ascertained by careful scrutiny of the $^1H-^1H$ COSY spectrum, and these assignments are collected in Table 2. Likewise, the C(1), C(2), and C(3) assignments within each indenyl environment were made by means of the $^1H-^{13}C$ shift-correlated spectrum. At this point, it was necessary to identify (a) the set of indenyl proton resonances that are assignable to the *RRR*/*SSS* silatropomers[14] and (b) the three sets of H(1), H(2), and H(3) peaks attributable to the three indenyl environments in the *RRS*/*SSR* molecules. This was readily accomplished via a $^1H-^{29}Si$ shift-correlated experiment, as illustrated in Figure 2. The ^{29}Si resonance at 5.04 ppm (intensity 1) couples to only one proton in each of the H(1), H(2), and H(3) environments, while its coun-

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(13) (a) For a detailed analysis of such systems, see: Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26. (b) Blount, J. F.; Finocchiaro, P.; Gust, D.; Mislow, K, *J. Am. Chem. Soc.* **1973**, *95*, 7019. (c) Willem, R.; Gielen, M.; Hoogzand, C.; Pepermans, H. In *Advances in Dynamic Stereochemistry*; Freund Publishing House: London, 1985; p 207. (d) Yet another stereochemical analogue is the tris(α-isopropyltropolonato)cobalt(III) system: Eaton, S. S.; Hutchison, J. R.; Holm, R. H.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 6411.

(14) *Silatropomers* are isomers related by sigmatropic shifts of silyl substituents.

Table 2. ^{1}H and ^{13}C NMR Data (ppm) for Tris(indenyl)methylsilane[a–c]

		H-1	H-2	H-3
		SSS/RRR isomers		
S/R				
	^{1}H	3.51 (3H)	6.30 (3H)	6.88 (3H)
		t 1.8 Hz	d (5.4 Hz) of d (1.8 Hz)	d (5.4 Hz) of d (1.8 Hz)
	^{13}C	43.1	134.8	130.1
Si-CH$_3$			^{1}H -0.20 (3H)	^{13}C -7.5
		SSR/RRS isomers		
		H-1	H-2	H-3
S(1)/R(1)				
	^{1}H	3.89 (1H)	6.49 (1H)	7.02 (1H)
		t 1.8 Hz	d (5.4 Hz) of d (1.8 Hz)	d (5.4 Hz) of d (1.8 Hz)
	^{13}C	44.1	134.9	130.4
S(2)/R(2)				
	^{1}H	3.27 (1H)	5.90 (1H)	6.73 (1H)
		t 1.8 Hz	d (5.4 Hz) of d (1.8 Hz)	d (5.4 Hz) of d (1.8 Hz)
	^{13}C	41.9	134.6	129.6
R(3)/S(3)				
	^{1}H	3.40 (1H)	5.72 (1H)	6.80 (1H)
		t 1.8 Hz	d (5.4 Hz) of d (1.8 Hz)	d (5.4 Hz) of d (1.8 Hz)
	^{13}C	42.7	134.9	129.7
Si-CH$_3$			^{1}H -0.22 (3H)	^{13}C -7.5

[a] All data obtained at 30 °C in CDCl$_3$. [b] ^{29}Si chemical shifts: *SSS*/*RRR* at 5.04 ppm; *SSR*/*RRS* at 5.96 ppm. [c] Aromatic chemical shifts: ^{1}H (4,5,6,7) 7.61–7.14 ppm; ^{13}C, (4,5,6,7) 125.7–121.3 ppm and (3a,7a) 144.6–144.2 ppm.

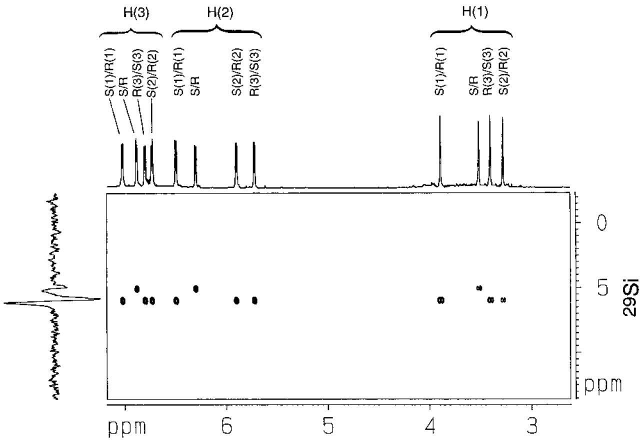


Figure 2. ^{1}H–^{29}Si shift-correlated NMR spectrum of tris(indenyl)methylsilane, **5**.

terpart at 5.96 ppm (intensity 3) correlates to the other three hydrogens in each set.

Let us consider the consequences of successive [1,5]-silatropic shifts across the surface of a single indenyl moiety. It is evident from Figure 3 that such a process would invert the chirality of one indenyl ring and take a molecule of configuration *RRR* into its *RRS* stereoisomer. This rearrangement process takes the three equivalent H(2) protons of the *RRR* isomer (in which all three indenyl ring environments can be designated **R**) and moves them into three new indenyl ring environments, labeled **R(1)**, **R(2)**, and **S(3)**. A second ring inversion interconverts the enantiomorphic *RRS* and *RSS* molecules; this takes the indenyl rings labeled **R(1)**, **R(2)**, and **S(3)** into **R(3)**, **S(2)**, and **S(1)** environments, respectively. Finally, the third step regenerates a homotopic molecule, *SSS*, in which all three indenyl ring environments are identically **S**. [We emphasize that the ring labels **R**, **S(2)**, etc. are related to the absolute configuration of the C(1) stereocenter of the particular indenyl environment; *RRS* refers to one of four diastereomeric (indenyl)$_3$SiMe molecules.]

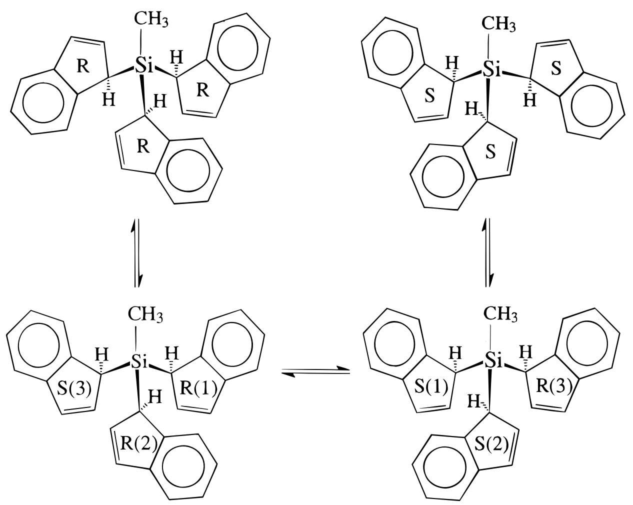


Figure 3. Interconversions of the eight different indenyl ring environments in the *RRR*, *RRS*, *RSS*, and *SSS* isomers of tris(indenyl)methylsilane, **5**. The configurational inversion of a single indenyl ring requires two [1,5]-suprafacial sigmatropic shifts.

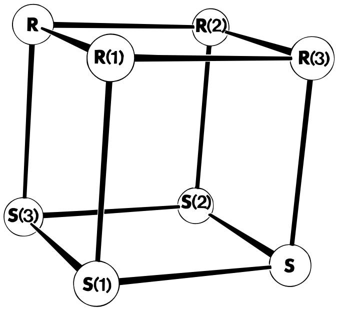


Figure 4. Cube vertices representing the eight indenyl-H(2) environments in **5** and the edges mapping out the exchange pathways.

Figure 4 depicts a cube onto which can be mapped all the permitted exchange pathways for the H(2) environments. Each exchange along a cube edge requires two successive [1,5]-shifts of a Me(indenyl)$_2$Si moiety across the surface of the remaining indenyl ring; the net result is equivalent to a single [1,3]-shift. We emphasize that (i) the **R(1)** → **S(1)** and **R(2)** → **S(2)** transformations are invisible since they involve isochronous sites, (ii) the **R(1)** → **R(2)** or **S(1)** → **S(2)** exchanges require that one traverse two adjacent edges of the cube (*i.e.* the configurational inversion of two indenyl rings), and (iii) the interconversion of the **R** and **S** environments (corresponding to transformation of *RRR* into *SSS*) inevitably must proceed via silatropic shifts across all three indenyl fragments.

Unlike the previously studied *n*-butyltris(η^1-indenyl)tin system, where the barrier toward R$_3$Sn migration is rather low and peak coalescence is evident even at room temperature,[12] the activation energies for silatropic shifts in **5** are high and the exchange pathways are most conveniently followed by 2D-EXSY experiments.[15] Fluxional behavior in tris(1-indenyl)methylsilane, **5**, is readily detectable at temperatures in excess

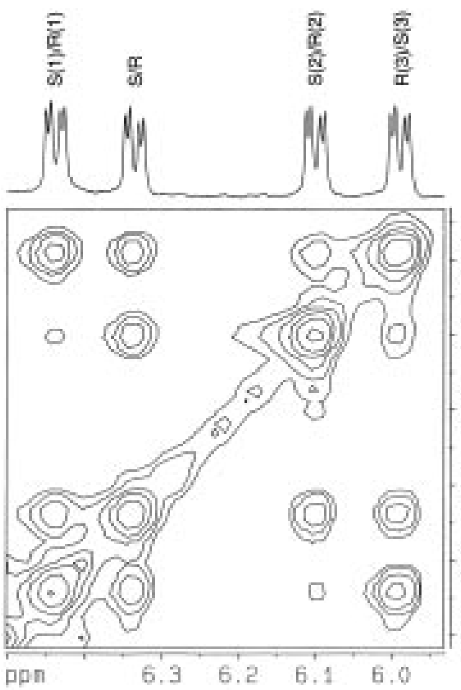


Figure 5. Portion of the 2D-EXSY spectrum of tris(indenyl)methylsilane, **5**. The large cross-peaks indicate the indenyl-H(2) environments that undergo direct exchange. Data were acquired at 105 °C in toluene-d_8.

of 100 °C, and Figure 5 shows the exchange pattern for the indenyl protons at position H(2). In keeping with the mechanism depicted graphically in Figure 4, one can see that the unique **R/S** environment (previously identified from the ^{1}H$-^{29}$Si spectrum) exchanges directly with the other three sites. Likewise, one other resonance shows off-diagonal correlations with the other three H(2) peaks; this can be assigned to the H(2) absorption in the **R(3)/S(3)** indenyl environment. It is apparent that there is no direct interconversion of the two remaining H(2) sites, and these must be situated in the **R(1)/S(1)** and **R(2)/S(2)** indenyl rings. The 2D-EXSY spectrum shown in Figure 5 was acquired with a relatively long delay time of 1.5 s at which point the development of small cross-peaks for the **R(1)** → **R(2)** interconversion becomes apparent. This corresponds to sequential configurational inversion of two indenyl rings (or traversal of two adjacent edges of the cube shown in Figure 4).

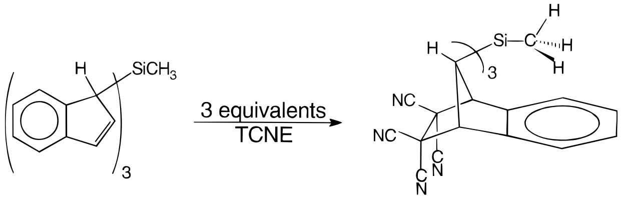
The situation for the exchange between the various H(1) and H(3) environments is slightly more complicated. As illustrated in Figure 6, two successive [1,5]-silatropic shifts within an indenyl moiety not only bring about inversion of the configuration of the ring but they also interconvert the H(1) and H(3) sites. Specifically, the three homotopic H(1)-**R** protons in the *RRR* isomer become H(1)-**R(1)**, H(1)-**R(2)**, and H(3)-**S(3′)** in the *RRS* molecule. That is, two of the three sp^3-carbons retain their absolute configuration but now find themselves in magnetically different environments, as do their attached hydrogens; after the departure of the silyl group, the third carbon is now sp^2-hybridized and occupies the C(3) site *in an indenyl ring whose configuration has been inverted*.

This set of exchange pathways is conveniently represented by a hypercube[16] (see Figure 7) in which the *inner* cube corresponds to the eight sp^3-bonded H(1) environments (labeled **S**, **R(3)**, etc.); the vinylic H(3) protons are mapped onto the *outer* cube and designated as **R′**, **S(1′)**, etc.

We reiterate that direct interchange between the inner and outer cubes must occur with inversion of configuration of an indenyl ring environment. Moreover, the three-step interconversion of the *RRR* and *SSS* enantiomers requires that all three sp^3-bonded H(1) protons in the former molecule occupy vinylic H(3) environments in the latter isomer. The net result is that the **R** and **S′** cube vertices are connected, but the **R** → **R′** and **S** → **S′** transformations are not possible. The hypercube depicted in Figure 7 shows that there are two noninterconverting manifolds into which enantiomorphic environments are separated. Of course, in tris(1-indenyl)methylsilane, **5**, only four H(1) and four H(3) resonances are observed. However, if the methyl group in **5** were to be replaced by a chiral substituent, *e.g.* menthyl, then one should see a total of 16 resonances for the H(1) and H(3) environments, but the 2D-EXSY spectrum should exhibit off-diagonal correlations only within the two groups of 8.

Mechanistic Conclusions. The experimental 2D-EXSY data for exchange between the H(1) and H(3) environments in tris(1-indenyl)methylsilane, **5**, are shown in Figure 8 and confirm in all respects the mechanistic model represented graphically by the hypercube in Figure 7. Thus, each H(1) proton shows clear and unambiguous off-diagonal correlations with two other H(1) environments and with a single H(3) site. The central portion of Figure 8 (between 6.50 and 5.75 ppm) shows exchange only between H(2) sites; Figure 5 presents an enlarged view of this section.

To demonstrate unequivocally that the fluxional behavior of **5** is rationalizable in terms of successive formation of intermediate isoindenes, tris(1-indenyl)methylsilane was allowed to react with TCNE with the aim of isolating the triple Diels−Alder adduct, **12**. The product obtained was readily characterized by mass spectrometry and by a series of 1D- and 2D-NMR experiments as the 1:3 adduct; moreover, the simplicity of the NMR spectra clearly indicate that **12** possesses 3-fold symmetry. An energy-minimized model of **12** was generated by use of the molecular modeling programs *ALCHEMY*[17] and *HYPERCHEM*.[18] These programs yielded essentially identical results. In *ALCHEMY*, the initial structure was built up from the X-ray crystal-



12

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(15) (a) Meier, B. H.; Ernst, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 6441. (b) Huang, Y.; Macura, S.; Ernst, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 5327. (c) Derome, A. E. *Modern NMR Techniques for Chemical Research*; Pergamon Press: Oxford, U.K., 1987; p 241.

(16) In a hypercube (or *tesseract*) all cube edges are of equal length and all internal angles are 90°; it is difficult to represent such a 4-dimensional figure in 2-dimensions, but an intriguing photograph merits examination: MacKay, D. M. *Electronic Engin.* **1960**, *32*, 344.

(17) *ALCHEMY*: Available from Tripos Associates, St. Louis, MO.

(18) *HYPERCHEM*: Available from Hypercube Inc., Waterloo, Ontario.

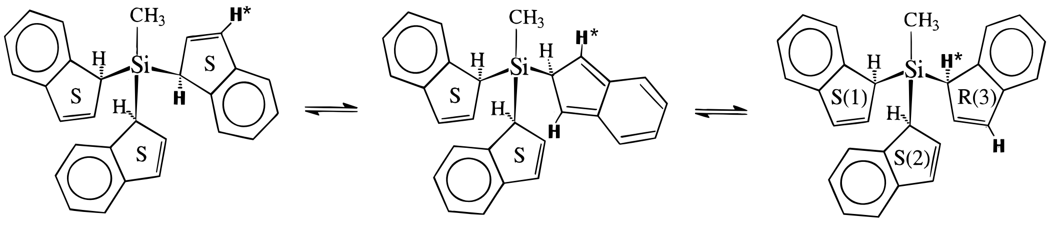

Figure 6. Interconversion of the *SSS* and *SSR* isomers of tris(indenyl)methylsilane, **5**, showing how the H(1) and H(3) environments are exchanged during the course of configurational inversion of a single indenyl ring.

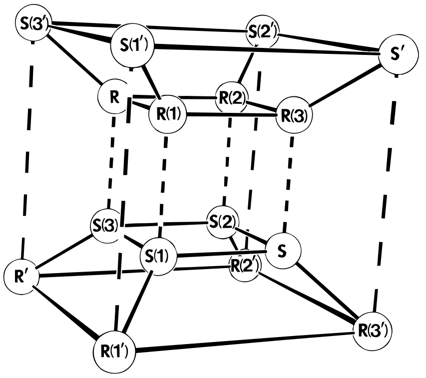

Figure 7. Vertices of the inner cube representing the eight sp^3-bonded indenyl-H(1) environments and those of the outer cube corresponding to the eight sp^2-bonded indenyl-H(3) environments. Edges connected by solid lines represent observed exchange processes, while dashed lines connect sites that do not interconvert.

lographic data for the (trimethylsilyl)isoindene/TCNE adduct **7**; replacement of two of the methyl groups in **7** by two Diels–Alder fragments gave an initial geometry which was then allowed to energy-minimize. The resulting structure is shown in Figure 9, and the 3-fold symmetry is evident. [Interestingly, the calculated structure has C_3 rather than C_{3v} symmetry.] Particularly striking are the orientations of the three phenyl moieties of the indenyl rings. These arene rings form a "pseudo-calixarene" within which is situated the single Si–CH$_3$ group. In similar fashion, the molecular structure of **12** was drawn in *HYPERCHEM* and was then allowed to energy-minimize. Again, the resulting structure placed the silyl methyl inside the cavity of phenyls. Such a model receives strong experimental support from the ^{1}H NMR spectrum of **12** in which the methyl resonance is found at −1.88 ppm; this assignment was confirmed by means of a ^{1}H–^{29}Si shift-correlated experiment. One might infer that these methyl protons are experiencing a very large shielding attributable to arene ring currents. Moreover, calculations based on the Waugh–Fessenden–Johnson–Bovey ring current model[19] predict an incremental shielding of 2.2 ppm for these protons. Assuming an inherent chemical shift for the Si–CH$_3$ protons in **12** to be similar to those in tetramethylsilane, then the observed resonance at −1.88 ppm seems eminently reasonable. Attempts to obtain a sample of **12** suitable for a single-crystal X-ray study are continuing.

These results allow one to draw a number of conclusions concerning the mechanisms of diastereomerization via silatropic shifts. First, the suprafacial [1,5]-shift

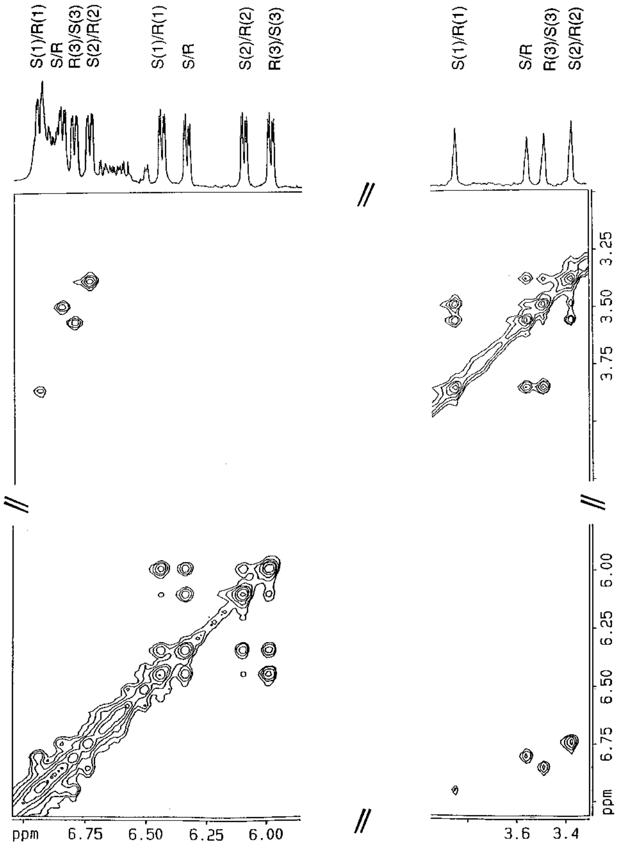

Figure 8. Sections of the 2D-EXSY spectrum of tris(indenyl)methylsilane, **5**, showing exchange *within* H(1) and H(3) environments and also exchange *between* H(1) and H(3) sites. Note how H(2) peaks exchange only among themselves. Data were acquired at 105 °C in toluene-d_8.

character of the migrations has been abundantly demonstrated; second, the sequential nature of the inversion of configuration of the indenyl rings mandates that the (indenyl)$_2$SiMe fragment retain its stereochemical integrity during the course of the migration;[20] third, the sigmatropic shifts by silicon over the three indenyl units are uncorrelated since only those sites directly connected by edges of the cube in Figure 4 (or the hypercube in Figure 7) exhibit large cross-peaks in the EXSY spectra. If migrations were to occur over two, or more, rings simultaneously, one would see direct exchange across the cube diagonals.

Relative Rates of Enantiomerization and Diastereomerization. The statistically expected 3:1 ratio of *RRS*/*RSS* to *RRR*/*SSS* molecules tells us that the free energies of these pairs of enantiomers are essentially identical, but this does not provide data on the

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(19) (a) Waugh, J. S.; Fessenden, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 846; **1958**, *80*, 6697. (b) Johnson, C. E., Jr.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012.

(20) This result is in accord with Stobart's observation on the chiral (η^1-C$_5$Me$_5$)SnMe(i-Pr)Ph system: McMaster, A. D.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2275.

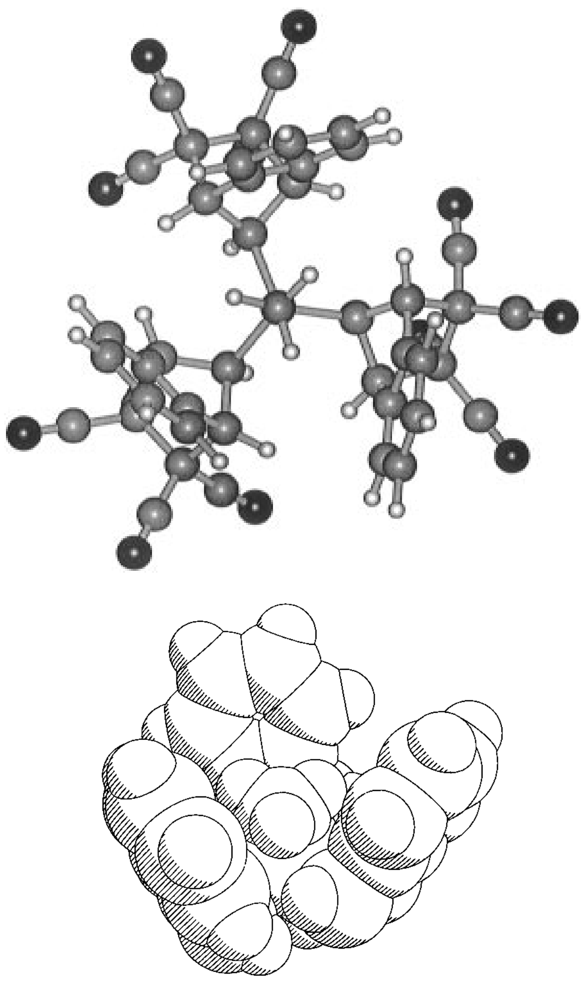

Figure 9. (a) Top: Energy-minimized structure of the tris(isoindenyl)methylsilane−TCNE triple Diels−Alder adduct, **12**. (b) Bottom: Space-filling model of **12**. The three TCNE units have been deleted for clarity.

relative exchange rates between the four isomers. That is, the rate of interconversion between enantiomers (*RRS* to *RSS*) is not necessarily the same as between diastereomers (*RRR* to *RRS* or *SSS* to *SSR*). However, we see from the foregoing mechanistic analysis that it is possible to monitor both processes simultaneously. For example, one could evaluate the rates of interconversion among the various H(2) environments. Typically, the transition **R(1)** → **R** probes the *RRS* to *RRR* process, while **R(1)** → **R(3)** measures the *RRS* to *RSS* enantiomerization.

In recent years, extensive use has been made of single selective inversion experiments[11,21−24] to obtain rate data for processes which have such high activation energies that conventional peak coalescence measurements are not viable.[25] 2D-EXSY methods are excellent for qualitative mechanistic studies, but selective inversions provide quantitative rate data much more efficiently. In the case at hand, the H(2)-**R(1)** resonance was selectively inverted, and the rates of recovery of this nucleus and also of the H(2)-**R** and H(2)-**R(3)** sites were monitored. The temperature dependence of these rate constants yielded activation energies of 24 ± 0.5 kcal mol^{-1} in both cases, suggesting that the configuration at the silicon atom has little influence on the migration process. The barriers found here for tris(indenyl)methylsilane, **5**, are in excellent accord with values previously reported for silatropic shifts showing that no unusual steric effects come into play in this system.

Extension of the concepts outlined here to related stereochemical systems, such as $(indenyl)_4E$, $(indenyl)_3$-SiR* (where R* is a chiral group), or molecules in which the polycyclic ligands bear π-complexed organometallic fragments, will be the subject of future reports.

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen, using freshly dried solvents. Mass spectra were obtained on a VG Analytical ZAB-E double-focusing mass spectrometer. Infrared spectra were obtained on a Bio-Rad FTS-40 spectrometer using NaCl windows.

NMR spectra were recorded on a Bruker DRX 500 spectrometer with an 11.74 T superconducting magnet, equipped with a Bruker B-VT 2000 temperature controller, and a 5 mm multinuclear inverse probe, equipped with 3-axis gradients. ^{1}H, ^{29}Si, and ^{13}C data were obtained at 500.13, 99.36, and 125.76 MHz, respectively. All spectra, except for 2D experiments on the DRX 500 were recorded on spinning samples. Peaks were referenced to a residual proton signal of the solvent or to a ^{13}C solvent signal.

^{1}H EXSY and ^{1}H selective inversion NMR spectra were recorded on a Bruker AC 300 spectrometer with a 7.65 T superconducting magnet, equipped with a Bruker B-VT 2000 temperature controller, and a 5 mm QNP probe. ^{1}H and ^{13}C data were obtained at 300.13 and 75.47 MHz, respectively.

Selective Inversion Measurements. The exchange rates in the slow exchange limit were measured by selective inversion relaxation experiments.[21−23] One signal in the spectrum was perturbed using a $90-\tau-90$ pulse sequence,[24] and then the return to equilibrium was monitored as a function of time, as in an inversion-recovery T_1 experiment. Measurements were made at 99 and 108 °C, giving rates of 0.02 and 0.05 s^{-1}, respectively. Each temperature was measured by placing a copper−constantan thermocouple, contained in an NMR tube, into the probe. All FID's were transferred to an IBM PC using the program NMRLINK. Spectra were Fourier transformed using the program NMR286. A C programming language version of McClung's program SIFIT[23] was used to do a nonlinear least-squares fit to the experimental results and to extract values for the rates. Typical errors in the rates are ±10%.

^{1}H EXSY spectra were recorded at 108.1 °C, with mixing times of 0.5, 1.5, and 2.7 s; f_1 was 512 words, while f_2 was 1024 words, and the sweep width was 2192.982 Hz. Four scans were collected for each spectrum. FID's were processed with a Gaussian window function in both f_1 and f_2 and a line broadening of 4.4 Hz. The relaxation delay was set to 2.7 s, and the initial value for the 2D evolution was set to 10 μs.

^{1}H-Detected ^{29}Si Multiple-Bond (HMBC) Correlation Experiment. The ^{29}Si spectral width was 5531.0 Hz with 2048 data points, zero filled to 4096. The ^{1}H spectral width was 5952.4 Hz with 256 time increments and 64 scans per increment. A relaxation delay of 2 s between scans was used. Values of $^{1}J_{Si-H} = 224$ Hz and $^{2}J_{Si-H} = 6.7$ Hz were used to calculate Δ_1 and Δ_2 [where $\Delta_1 = 1/[2(^{1}J_{Si-H})]$ and $\Delta_2 = 1/[2(^{2}J_{Si-H})]$.

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Tris(1-indenyl)methylsilane (5). Indene (4.5 g, 38.8 mmol) in freshly distilled ether (100 mL) was cooled to −78 °C, and *n*-butyllithium (24.24 mL of a 1.6 M hexane solution, 39 mmol) was added dropwise over a 1 h period. The solution was stirred at −78 °C for an additional 2 h after which time methyltrichlorosilane (1.3 g, 8.70 mmol) was added dropwise over a 2 h period. When the addition was complete, the mixture was allowed to warm to room temperature and stirred for an additional 18 h. The product was extracted by using water (3 × 100 mL), and the organic phase was dried over anhydrous $MgSO_4$. After removal of ether, the residue was subjected to flash chromatography on silica gel. Elution with hexane/CH_2Cl_2 (70:30) gave **5** as a yellow waxy solid (1.41 g, 3.63 mmol, 42%). IR ($CDCl_3$, cm^{-1}): 3068 m, 2960 s, 2927 m, 2873 w, 1452 s, 1257 s. Mass spectrum (DEI, *m/z* (%)): 388 (9) ($[M]^+$), 273 (34) ($[M - C_9H_7]^+$), 143 (27) ($[M - 2(C_9H_7) - CH_3]^+$), 115 (100) ($[C_9H_7]^+$). Mass spectrum (high resolution, DEI): calculated for mass $^{12}C_{28}H_{24}Si$, 388.1648 amu; observed, 388.1650 amu. ^1H, ^{13}C, and ^{29}Si NMR data are collected in Table 2.

Trapping of (Trimethylsilyl)isoindene with Tetracyanoethylene. Following the method previously described by Ashe and co-workers,[2] tetracyanoethylene (1.53 g, 11.95 mmol) was added to a solution of (trimethylsilyl)indene (2.25 g, 11.95 mmol) in ethyl acetate (200 mL) and stirred at ambient temperature for 72 h. After removal of the ethyl acetate, the residue was washed with hexane (1 × 25 mL) ether (3 × 15 mL) and then dried to give **7** as a beige powder, mp 193−194 °C (3.35 g, 10.60 mmol, 89%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.53−7.48 (m, 2H, H-8,11), 7.47−7.42 (m, 2H, H-9,10), 4.29 (d, $^3J = 1.05$ Hz, 2H, H-1,4), 2.09 (t, $^3J = 1.05$ Hz, 1H, H-7), −0.21 (s, $^1J_{C-H} = 119.2$ Hz, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.4 (C-2,3), 130.6 (C-9,10), 124.9 (C-8,11), 110.2, 112.3 (*exo* and *endo* nitriles), 60.5 (C-1,4), 50.3 (C-5,6), 49.8 (C-7), −2.0 ($SiMe_3$). ^{29}Si NMR (CH_2Cl_2, 59.63 MHz): δ 1.89. IR ($CDCl_3$, cm^{-1}): 3085 w, 3032 m, 2959 vs, 2901 m, 2860 sh, 1984 m, 1943 m. Mass spectrum (DEI, *m/z* (%)): 301 (11) ($[M - CH_3]^+$), 188 (20) ($[C_{12}H_{16}Si]^+$), 173 (13) ($[C_{11}H_{15}Si]^+$), 115 (17) ($[C_9H_7]^+$), 73 (100) ($[Si(CH_3)_3]^+$). Mass spectrum (high resolution, DEI): calculated for mass $^{12}C_{17}H_{13}SiN_4$ ($[M - CH_3]^+$), 301.0909 amu; observed, 301.0926 amu. A sample suitable for structural determination by single-crystal x-ray diffraction was obtained by crystallization from dichloromethane.

Trapping of Tris(isoindenyl)methylsilane with Tetracyanoethylene. Tetracyanoethylene (0.093 g, 0.73 mmol) was added to a solution of tris(1-indenyl)methylsilane (0.08 g, 0.21 mmol) in ethyl acetate (75 mL) and stirred at ambient temperature for 2 weeks. After removal of the ethyl acetate, the residue was subjected to flash chromatography on silica gel. Elution with diethyl ether/ hexane (30:70) gave **12** as a white powder (59 mg, 0.076 mmol, 33%). ^1H NMR (CD_3CN, 500 MHz): δ 7.52 (apparent d (5.6 Hz) of d (3.2 Hz), 6H, H-9,-10), 7.47 (apparent d (5.6 Hz) of d (3.2 Hz), 6H, H-8,11), 4.26 (d, $^3J = 1.0$ Hz, 6H, H-1,4), 2.28 (t, $^3J = 1.0$ Hz, 3H, H-7), −1.88 (s, 3H, $SiCH_3$). ^{13}C NMR (CD_3CN, 125 MHz): δ 139.6 (C-2,3), 131.7 (C-9,10), 126.6 (C-8,11), 113.5 (pseudo-equatorial nitriles), 111.9 (pseudo-axial nitriles), 60.2 (C-1,4), 50.8 (C-5,6), 48.5 (C-7), −4.4 ($SiCH_3$). ^{29}Si NMR (CD_3CN, 99.35 MHz): δ 1.3. The ring junction carbons and the nitriles were assigned by means of an HMBC experiment. Mass spectrum: (DEI, *m/z* (%)) 644 (3) ($[M - (TCNE)]^+$), 516 (8) ($[M - 2(TCNE)]^+$), 388 (12) ($[M - 3(TCNE)]^+$), 273 (100) ($[C_{19}H_{17}Si]^+$), 143 (22) ($[C_9H_7Si]^+$), 115 (45) ($[C_9H_7]^+$).

X-ray Crystallography. X-ray crystallographic data for **7** were collected on a Rigaku AFC6R diffractometer with a rotating anode and graphite-monochromated Cu Kα radiation ($\lambda = 1.541\,78$ Å). Three standard reflections that were measured after every 97 reflections showed neither instrument instability nor crystal decay. The structure was solved by using the direct methods procedure in the SHELXTL-PLUS program library.[26] The method of refinement was full-matrix least-squares. All H atoms were included by using a riding model with isotropic thermal parameters fixed at 0.08 Å^2. Crystal data collection parameters and atom coordinates are collected in Table 1 and the Supporting Information, respectively.

Ring current calculations were carried out by using the program *LARC*.[27]

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada and also from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank Dr. J. F. Britten for advice on X-ray crystallography.

Supporting Information Available: Tables of thermal parameters, bond lengths, bond angles, and complete atom coordinates for **7** (5 pages). Ordering information is given on any current masthead page.

OM960617I

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