The molecular dynamics and cycloaddition chemistry of tris(1-indenyl)allylsilane

Part 1 Generation of the first crystallographically characterized tris(benzonorbornyl)silane†

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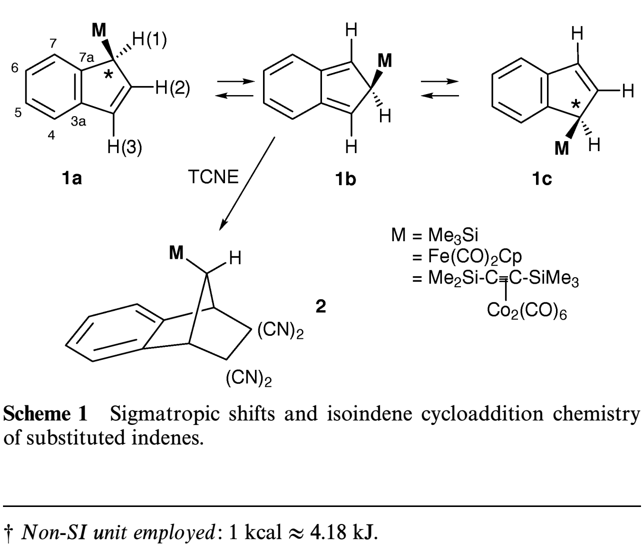
The preparation, characterization and molecular dynamics of tris(1-indenyl)allylsilane, **5**, are presented. Data obtained from single selective inversion and ^1H–^1H EXSY NMR experiments demonstrate that **5** is indeed fluxional ($\Delta G^{\neq} \sim 25$ kcal mol^{-1}). Moreover, a solution of **5** stirred with three equivalents of tetracyanoethylene yields tris(5,6-benzo-2,2,3,3-tetracyanobicyclo[2.2.1]heptan-7-yl)allylsilane, **7**, an observation that is consistent with the sequential generation and trapping of isoindene intermediates in a [1,5]-silatropic shift mechanism. The triple cycloadduct, **7**, represents what is believed to be the first crystallographically characterized tris(benzonorbornyl)silane.

While the capacity of σ-bonded molecular fragments to migrate over a variety of polyenyl organic surfaces has been recognized for over two decades,[1–10] the increasingly important role of poly(indenyl)-substituted main-group compounds as ligands in the synthesis of *ansa*-bridged metallocenes[11–17] has brought about renewed interest in their dynamic behaviour. The dominant migratory pathway for such stereochemically non-rigid indenyl compounds can be rationalized in terms of two successive [1,5]-sigmatropic shifts, which interconvert the enantiomers **1a** and **1c**, according to the orbital symmetry rules defined by Woodward and Hoffmann (Scheme 1).[18] In several cases, Diels-Alder trapping with reactive dienophiles such as tetracyanoethylene (yielding adducts analogous to **2**) has been put forth as evidence for the existence of transient isoindenes (**1b**);[19,20] the crystallographic characterization of such cycloadducts derived from metallo-isoindenes bearing silicon, iron, and cobalt substituents has been the focus of recent reports from our laboratory.[21–23]

In the case of fluxional poly(1-indenyl) precursors, such as bis(1-indenyl)dimethylsilane, **3**, the stereogenic character of the C(1) carbons results in the formation of interconverting diastereomers (**3-D,L** and **3-*meso***) (Scheme 2), each of which, after incorporation of a group 4 metal, gives rise to an *ansa*-bridged catalyst possessing unique structure, molecular symmetry and polymerization activity. As such, the diastereoselective synthesis of an *ansa*-bridged catalyst necessitates that a diastereomerically pure poly(indenyl) ligand be employed, and that the stereochemical integrity of this precursor be maintained throughout the metallation procedure.[24] Any process that leads to a change in configuration in such poly(indenyl) compounds is therefore worthy of examination at a rather fundamental level.



Scheme 1 Sigmatropic shifts and isoindene cycloaddition chemistry of substituted indenes.

With the ultimate objective of gaining insight into the sequential nature of silicon migrations about the periphery of indenyl rings, and in continuation of our investigation of the factors that influence these migrations,[25,26] we have reported on the molecular dynamics of bis(1-indenyl)dimethylsilane, **3**,[27] and more recently, tris(1-indenyl)methylsilane, **4**.[21] As an extension of these studies, we describe herein the synthesis and characterization of tris(1-indenyl)allylsilane, **5**, and the corresponding triple cycloadduct, **7**; the latter represents the first crystallographically characterized tris(benzonorbornyl)silane of which we are aware.

Results and discussion

Using the methodology that we previously described for the preparation of tris(1-indenyl)methylsilane, **4**, the target compound, **5**, was readily synthesized by the quenching of allyltrichlorosilane with an excess of indenyllithium, generating the anticipated statistical (1 : 3) mixture of interconverting *RRR*/*SSS* and *RRS*/*SSR* diastereomers (Scheme 3). As was observed for **4**, the ^1H NMR spectrum of **5** contains four equal-intensity resonances in each of the H(1), H(2) and H(3) regions, while in the ^{29}Si NMR spectrum of **5**, two resonances (∼1 : 3) are observed. These data are entirely consistent with the concepts discussed by Stobart and coworkers who, in studying complexes of the type $(1\text{-indenyl})_3SnR$, recognized that while the indenyl ring environments in the *RRR*/*SSS* isomers of such molecules are homotopic, three unique ring

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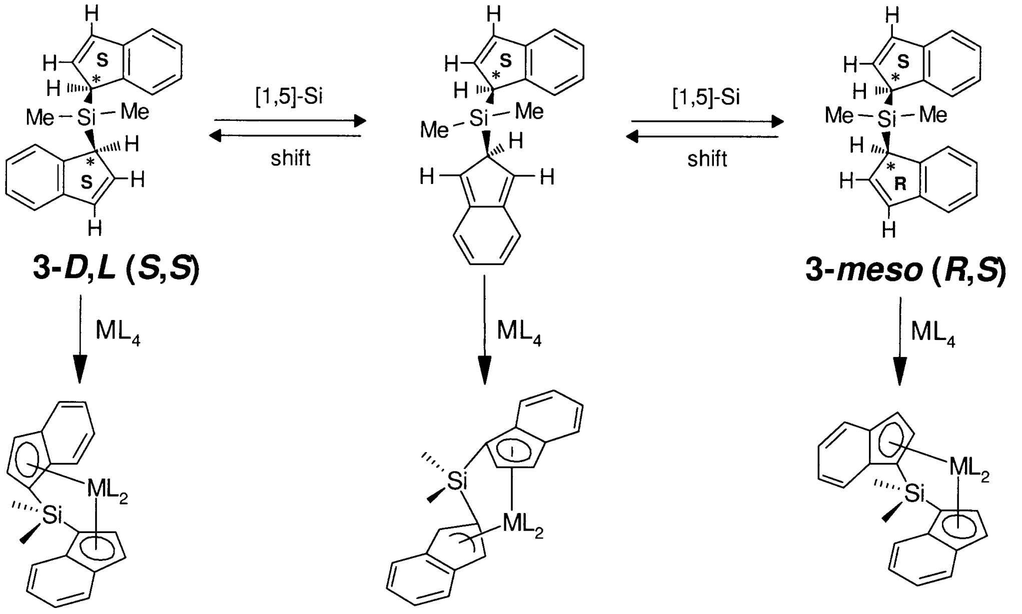
† *Non-SI unit employed*: 1 kcal ≈ 4.18 kJ.



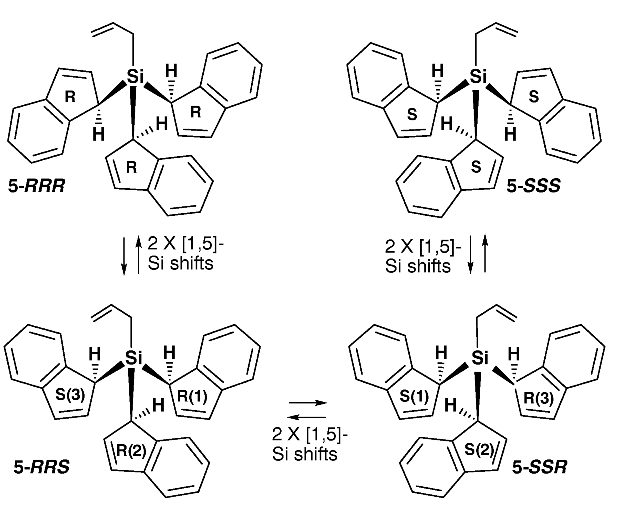
Scheme 2 Isomerization of 3-D,L to 3-*meso*, *via* [1,5]-silatropic shifts.

environments are present in the *RRS*/*SSR* enantiomorphs.[28–30] Nevertheless, experimental verification of these ideas had to await the advent of high-field spectrometers with multi-pulse capability.[21]

With the connectivity between the various H(1), H(2) and H(3) protons (within the five-membered ring of each of the four individual indenyl ring environments) established, based on ^1H–^1H COSY spectral data, the set of indenyl proton resonances assignable to the homochiral *RRR*/*SSS* isomers and the three sets of H(1), H(2) and H(3) peaks attributable to the three indenyl environments in the *RRS*/*SSR* diastereomers were unequivocally assigned by careful scrutiny of the ^1H–^{29}Si shift correlated spectrum, a portion of which is presented as Fig. 1. Correlation between the ^{29}Si resonance at 2.1 ppm (intensity 1, **5-*RRR*/*SSS***) and a single proton in each of the H(1), H(2) and H(3) regions is readily observable, while the ^{29}Si resonance at 3.4 ppm (intensity 3, **5-*RRS*/*SSR***) shows coupling to the other hydrogens in each set. Similarly, the ^{13}C NMR chemical shift assignments within each indenyl ring environment were determined based on data obtained from a combination of ^1H–^{13}C shift-correlated experiments.

It is evident that the suprafacial migration of a (1-indenyl)$_2$-Si(CH$_2$CH=CH$_2$) fragment about the periphery of the remaining indenyl ring in **5-*RRR*** would proceed with inversion of stereochemistry at the migration terminus, converting a molecule of configuration *RRR* (**5-*RRR***) into the corresponding **5-*RRS*** diastereomer. This rearrangement process takes three equivalent H(2) protons of the **5-*RRR*** isomer (in which the 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 **5-*RRS*** and **5-*SSR*** molecules, and a third pair of [1,5]-silicon shifts regenerates the homotopic molecule, **5-*SSS***, in which all three indenyl ring environments are identically "S." These exchange pathways have been verified experimentally based on proton ^1H–^1H EXSY (exchange spectroscopy) data. Single selective inversion NMR experiments yield a $\Delta G^{\neq}$ value of 25 ± 2 kcal mol^{-1} for the silatropic shifts in **5**, a value that is comparable to those previously determined for [1,5]-silicon shifts in related species.[21,23,27] As previously described for **4**,[31] the exchange pathways between indenyl sites and environments in **5** can be conveniently mapped onto a hypercube.[32,33]

While indenes primarily undergo [2 + 2] cycloadditions with tetracyanoethylene,[34,35] (1-indenyl)silanes yield adducts apparently derived from [4 + 2] cycloaddition processes involving the corresponding silyl-isoindene. Since the complex dynamic behaviour of tris(1-indenyl)allylsilane may be completely rationalized in terms of successive [1,5]-silicon shifts, we sought to intercept the transient isoindenes as they are sequentially generated, by *in situ* reaction with tetra-



Scheme 3 Interconversions of the eight different indenyl ring environments in the **5-*RRR***, **5-*RRS***, **5-*SSR*** and **5-*SSS*** isomers of the tris(indenyl)allylsilane. The ***R*** or ***S*** designations refer to the absolute configuration at C(1) in each indenyl ring environment.

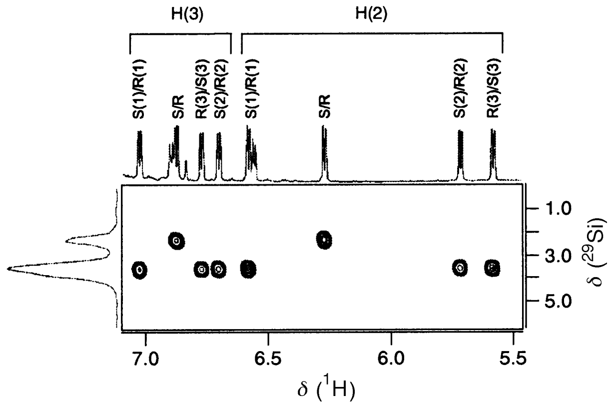
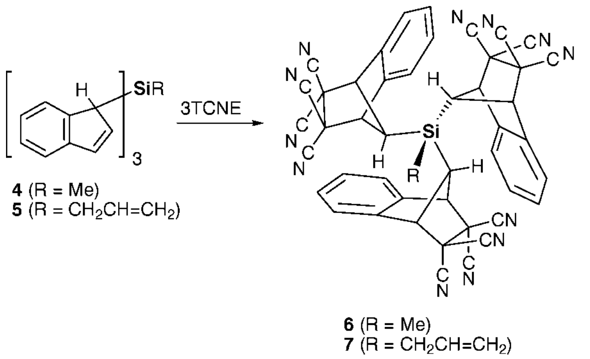


Fig. 1 ^1H–^{29}Si shift-correlated spectrum of tris(indenyl)allylsilane, **5**.



4 (R = Me)
5 (R = $CH_2CH{=}CH_2$)

6 (R = Me)
7 (R = $CH_2CH{=}CH_2$)

Scheme 4 The triple Diels-Alder reactions of **4** and **5** with tetracyanoethylene, producing **6** and **7**, respectively.

cyanoethylene (TCNE, as in Scheme 4). Gratifyingly, the product isolated gave NMR spectroscopic and mass spectrometric data consistent with the formation of the triple Diels-Alder cycloadduct, **7**. Kerber *et al.* have noted that [3 + 2] cycloadditions (involving the corresponding metallo-indene, **1a**) could lead sequentially through rearrangement to the same products as derived from a one-step [4 + 2] process (*via* the metallo-isoindene, **1b**).[36] Although the [3 + 2] mechanism appears mandatory for η^1-allyl systems,[37] the corresponding η^1-cyclopentadienyl complexes are known to react in a Diels-Alder fashion.[38] Moreover, dibenzoisoindene, which is generated by a thermally promoted [1,5]-hydrogen shift in the parent dibenzo[*e*,*g*]indene (cyclopenta[*l*]phenanthrene), is sufficiently long-lived so as to undergo a [4 + 2] cyclodimerization with its progenitor.[35]

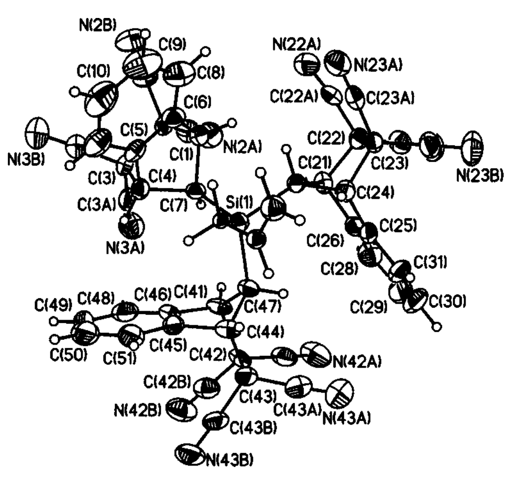


Fig. 2 X-Ray structure of **7**, showing the atomic numbering scheme. Thermal ellipsoids are shown at the 40% probability level.

Table 1 Selected bond lengths (Å) and angles (deg) for **7**

Si(1)—C(7)	1.903(7)	C(1)—C(7)—Si(1)	116.6(5)
Si(1)—C(27)	1.878(7)	C(4)—C(7)—Si(1)	120.6(5)
Si(1)—C(47)	1.908(7)	C(24)—C(27)—Si(1)	121.9(5)
C(1)—C(2)	1.58(1)	C(21)—C(27)—Si(1)	122.3(5)
C(21)—C(22)	1.58(1)	C(41)—C(47)—Si(1)	119.7(5)
C(41)—C(42)	1.59(1)	C(44)—C(47)—Si(1)	115.1(5)
C(4)—C(3)	1.58(1)	C(7)—Si(1)—C(27)	101.4(3)
C(24)—C(23)	1.57(1)	C(7)—Si(1)—C(47)	110.5(3)
C(44)—C(43)	1.58(1)	C(27)—Si(1)—C(47)	113.2(3)
C(3)—C(2)	1.60(1)	C(7)—Si(1)—C(60A)	115.8(6)
C(23)—C(22)	1.60(1)	C(27)—Si(1)—C(60A)	107.2(7)
C(43)—C(42)	1.61(1)	C(47)—Si(1)—C(60A)	108.7(6)

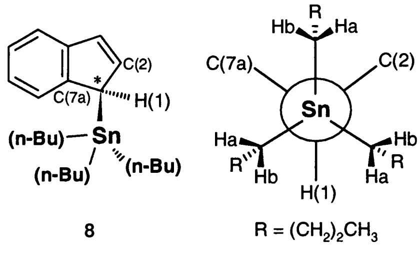


Chart 1 Newman projection along the Sn—C(1) bond of **8**, showing the local C_3 symmetry that equilibrates only the Ha and only the Hb proton environments, but does not interconvert these sites.

In the absence of reported structural data for tris(benzonorbornyl)silanes such as **6** or **7**, we sought to obtain definitive crystallographic characterization for **7**; the structure appears in Fig. 2 and selected metrical parameters are collected in Table 1. The X-ray structure of **7** serves unequivocally to confirm its identity as the desired triple cycloadduct, and reveals that in all three cases the dieneophilic attack by TCNE on the silicon-substituted isoindene occurs on the less-hindered face, opposite to that occupied by the $R_2Si(CH_2CH{=}CH_2)$ unit. So as to relieve unfavourable steric interactions, the bulky benzonorbornyl units in **7** rotate with respect to one another,[39] and in doing so produce a molecular geometry that deviates significantly from the C_3 symmetric structure previously anticipated for **6**. It is also apparent from the structure of **7** that, while the allyl fragment appears to be accessible to incoming reagents, the orientation of the benzonorbornyl units places the allyl methylene group directly over an arene ring [containing C(8)–C(11)]; such a scenario should bring about noticeable aromatic ring-current effects on these allyl protons. This prediction is verified by the marked shielding of nearly 1.3 ppm for the methylene protons in **7**, relative to the tris(1-indenyl) precursor, **5**. It is interesting to note that in **6**, a similar but more dramatic (~1.9 ppm) shielding of the methyl protons was observed, possibly resulting from the additive ring-current anisotropy of more than one arene ring in a C_3 or C_{3v} "pseudo-calixarene" type structure. It remains to be seen whether the structure of **7** is typical of tris(benzonorbornyl)silanes, or whether the allyl substituent is sufficiently large so as to effect perturbations that result in a reduction in the solid state molecular symmetry of these novel, sterically demanding molecules. Our investigations into the utility of **5** and **7** as sterically demanding organometallic ligands will be the subject of future reports.

In closing, we note that misconceptions concerning the dynamic behaviour of indenyl systems still persist—even in the current literature. For example, it has been claimed that tris(1-indenyl)arsine exists in three diastereomeric forms; in fact, the two supposed *meso* forms are merely enantiomers, as shown for $(1\text{-indenyl})_3SiR$ in Scheme 3.[17] Moreover, it has been repeatedly stated that the Bu_3Sn group in 1-(tri-*n*-butylstannyl)indene, **8**, undergoes a [1,3]-migration, rather than successive [1,5]-shifts.[40] Even more curiously, whereas it is claimed that the broadening of the methylene ^1H NMR signals of the butyl chains indicates slowed rotation about the C(1)—Sn axis, the authors failed to recognise the diastereotopic character of these methylene protons when the Bu_3Sn group is attached to a stereogenic carbon centre (Chart 1). It is evident that poly(indenyl) systems will continue to provide fascinating synthetic, spectroscopic and structural challenges.

Experimental

General

All preparations were carried out under an atmosphere of dry nitrogen, using freshly distilled solvents. Trichloroallylsilane (Aldrich) and tetracyanoethylene (Aldrich) were used as received, while indene (Aldrich) was distilled prior to use. 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 acquired on a Bruker Avance DRX-500 spectrometer, equipped with an 11.74 T superconducting magnet. These experiments consisted of 1-D ^{1}H, ^{13}C and ^{29}Si NMR spectra as well as 2-D ^{1}H–^{1}H COSY, ^{1}H–^{1}H EXSY, ^{1}H–^{13}C shift-correlated and ^{1}H–^{29}Si long-range shift-correlated spectra. Except during the acquisition of 2-D data, NMR spectra were recorded on spinning samples, locked to a solvent signal. ^{1}H–^{1}H EXSY[41] spectra were recorded at 102 °C, with mixing times of 0.5, 1.5 and 2.5 s; f_1 was 512 words, while f_2 was 1024 words, and four scans were collected for each spectrum. Free induction decays (FIDs) 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 1.0 s, and the initial value for the 2-D evolution was set to 10 μs. Single selective inversion experiments[42–44] were carried out using previously detailed methods.[21]

Syntheses

Tris(1-indenyl)allylsilane, 5. Indene (4.0 g, 34.5 mmol) in freshly distilled ether (100 mL) was cooled to -78 °C, and *n*-butyllithium (21.6 mL of a 1.6 M hexane solution, 35 mmol) was added dropwise over a one-hour period. The solution was stirred at -78 °C for an additional 2 h after which time allyltrichlorosilane (1.2 g, 6.90 mmol) was added dropwise over a two-hour 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 hexanes–CH_2Cl_2 (80:20) gave **5** as a viscous yellow oil (0.36 g, 0.88 mmol, 13%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64–7.11 (m, 48H, aromatic), 7.02 [dd, $J = 5.4$ and 1.9 Hz, 3H, H(3) in S(1)/R(1)], 6.86 [dd, $J = 5.4$ and 1.9 Hz, 3H, H(3) in S/R], 6.76 [dd, $J = 5.4$ and 1.9 Hz, 3H, H(3) in R(3)/S(3)], 6.69 [dd, $J = 5.4$ and 1.9 Hz, 3H, H(3) in S(2)/R(2)], 6.57 [dd, $J = 5.4$ and 1.9 Hz, 3H, H(2) in S(1)/R(1)], 6.26 [dd, $J = 5.4$ and 1.9 Hz, 3H, H(2) in S/R), 5.70 [dd, $J = 5.4$ and 1.9 Hz, 3H, H(2) in S(2)/R(2)], 5.57 [dd, $J = 5.4$ and 1.9 Hz, 3H, H(2) in R(3)/S(3)], 4.77–4.59 (m, 12H, $SiCH_2CHCH_2$), 4.00 [d, $J = 1.9$ Hz, 3H, H(1) in S(1)/R(1)], 3.61 [d, $J = 1.9$ Hz, 3H, H(1) in S/R], 3.40 [d, $J = 1.9$ Hz, 3H, H(1) in R(3)/S(3)], 3.38 [d, $J = 1.9$ Hz, 3H, H(1) in S(2)/R(2)], 1.49 (m, 6H, $SiCH_2$ in **5-*RRS*** *and* **5-*SSR***), 1.39 (m, 2H, $SiCH_2$ in **5-*RRR*** and **5-*SSS***). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.0–143.6 [C(3a), C(7a)], 134.9 [C(2) in R(3)/S(3)], 134.7 [C(2) in S(1)/R(1)], 134.4 [C(2) in S/R], 134.3 [C(2) in S(2)/R(2)], 133.3 ($SiCH_2CHCH_2$ in **5-*RRR*** and **5-*SSS***), 133.2 ($SiCH_2CHCH_2$ in **5-*RRS*** and **5-*SSR***), 130.6 [C(3) in S(1)/R(1)], 130.4 [C(3) in S/R], 129.9 [C(3) in S(2)/R(2)], 129.9 [C(3) in R(3)/S(3)], 126.2–120.9 [C(4), C(5), C(6) and C(7)], 42.3 [C(1) in S(1)/R(1)], 42.1 [C(1) in S/R], 41.8 [C(1) in R(3)/S(3)], 41.7 [C(1) in S(2)/R(2)], 19.8 ($SiCH_2$ in **5-*RRR*** and **5-*SSS***), 18.9 ($SiCH_2$ in **5-*RRS*** and **5-*SSR***). ^{29}Si NMR ($CDCl_3$, 99.35 MHz): δ 3.41 (**5-*RRS*** and **5-*SSR***), 2.11 (**5-*RRR*** and **5-*SSS***). IR ($CDCl_3$, cm^{-1}): 3048m, 2952s, 2929m, 1448s, 1259s. Mass spectra: [DEI, *m*/*z* (%)]: 414 (4) $[M]^+$, 299 (36) $[M - C_9H_7]^+$, 256 (100) $[M - (C_9H_7) - C_3H_5]^+$, 115 (95) $[C_9H_7]^+$; (high resolution, DEI): calcd for $^{12}C_{30}H_{26}Si$ (M^+), 414.1804 amu; obsd, 414.1801 amu.

Tris(5,6-benzo-2,2,3,3-tetracyanobicyclo[2.2.1]heptan-7-yl)-allylsilane, 7. Upon adding TCNE (0.216 g, 1.69 mmol) to a solution of **5** (0.200 g, 0.483 mmol) in ethyl acetate (75 mL) the solution turned dark blue; after stirring under ambient conditions for 72 h, the dark colouration subsided. Removal of the ethyl acetate left a solid residue, which was washed with hexanes to remove any residual tris(1-indenyl)allylsilane, and then dissolved in boiling diethyl ether (30 mL). Upon cooling, the desired compound, **7**, precipitated as a white powder (162 mg, 0.203 mmol, 42%). ^{1}H NMR (CD_3CN, 500 MHz): δ 7.62 [m, 6H, H(9) and H(10)], 7.56 [m, 6H, H(8) and H(11)], 4.77 (m, 2H, $SiCH_2CHCH_2$), 4.21 [d, $^3J = 1.0$ Hz, 6H, H(1) and H(4)], 4.18 (m, 1H, $SiCH_2CHCH_2$), 1.97 [t, $^3J = 1.0$ Hz, 3H, H(7)], 0.10 (m, 2H, $SiCH_2CHCH_2$). ^{13}C NMR (CD_3CN, 125 MHz): δ 139.5 [C(5) and C(6)], 132.2 [C(9) and C(10)], 130.1 ($SiCH_2CHCH_2$), 127.1 [C(8) and C(11)], 119.8 ($SiCH_2CHCH_2$), 113.4 (pseudo-equatorial nitriles), 111.8 (pseudo-axial nitriles), 59.7 [C(1) and C(4)], 50.6 [C(2) and C(3)], 48.2 [C(7)], 19.4 ($SiCH_2CHCH_2$). ^{29}Si NMR (CD_3CN, 99.35 MHz): δ − 3.6. Mass spectrum [DEI, *m*/*z* (%)]: 670 (4) $[M - (TCNE)]^+$, 542 (6) $[M - 2(TCNE)]^+$, 299 (100) $[(C_9H_7)_2SiCH_2CHCH_2]^+$, 143 (55) $[C_9H_7Si]^+$, 115 (14) $[C_9H_7]^+$. [CI, NH_3, *m*/*z* (%)]: 799 (5) $[M + 1]^+$, 688 (6) $[M - (TCNE) + 18]^+$, 560 (100) $[M - 2(TCNE) + 18]^+$, 432 (57) $[M - 3(TCNE) + 18]^+$. A crystalline sample (0.36 mm × 0.06 mm × 0.03 mm) suitable for structural determination by single-crystal X-ray diffraction was grown from acetonitrile.

X-Ray crystallography

Data for **7** were collected from a sample mounted on a glass fiber, using a P4 Siemens diffractometer equipped with a Siemens SMART 1K CCD area detector (using the program SMART)[45] and a rotating anode using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data processing was carried out by use of the program SAINT,[46] while the program SADABS[47] was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structure was solved by using the direct methods procedure in the Siemens SHELXTL[48] program library, and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms, with the exception of the disordered allyl fragment described below. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded. The final refined structure was based on a disordered model in which the allyl group could exist in one of two conformations. From the observed thermal displacement ellipsoids it was apparent that only the positions of the three allyl carbon atoms were affected by this disorder. The occupancy of the two conformations was allowed to refine as a free variable (final ratio of approximately 60 : 40) and then hydrogen atoms for each unique component of the disorder were added at calculated positions, and allowed to refine based on the carbon atoms to which they were attached. Selected crystallographic data: chemical formula $C_{48}H_{26}N_{12}Si_1$, $M = 798.90$, $T = 302(2)$ K, space group $P2_1/c$, monoclinic, $a = 13.9562(3)$, $b = 15.0799(4)$, $c = 23.1845(2)$ Å, $\beta = 102.979(1)°$, $U = 4754.7(2)$ Å^3, $Z = 4$, linear absorption coefficient 0.094 mm^{-1}, θ range for collection = 1.50°–20.00° ($-15 \leqslant h \leqslant 15$; $-16 \leqslant k \leqslant 16$; $-25 \leqslant l \leqslant 25$), no. reflections collected = 20188, no. indep. reflections = 4448, data/restraints/parameters = 4405/0/549, final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0777$; $wR_2 = 0.2053$; R indices (all data) $R_1 = 0.1334$, $wR_2 = 0.2477$.

CCDC reference number 440/092. See http://www.rsc.org/suppdata/nj/1999/317/ for crystallographic data files in .cif format.

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