The molecular dynamics and reactivity of tris(inden-1-yl)silane: an NMR spectroscopic and X-ray crystallographic study †

PERKIN 2

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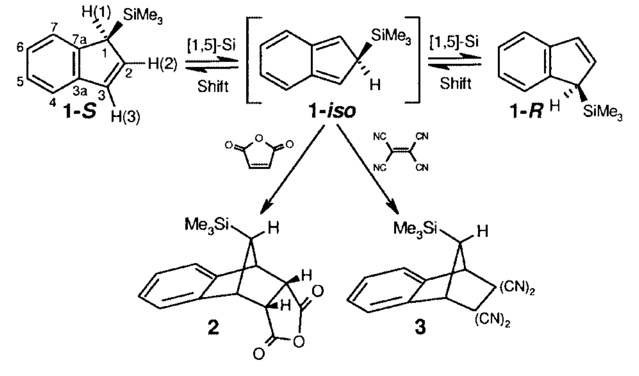
Received (in Cambridge, UK) 17th January 2000, Accepted 3rd February 2000

The synthesis, structural characterisation (NMR, X-ray), molecular dynamics and reactivity of tris(inden-1-yl)silane, **9**, are discussed. Spectroscopic data obtained from 2D-EXSY NMR experiments clearly demonstrate that the title compound is stereochemically non-rigid, even at temperatures where line broadening is not evident ($\Delta G^{\ddagger} \approx 24$ kcal mol^{-1}). The dynamic behaviour of **9** is rationalised in terms of successive [1,5]-silicon shifts; indeed, the isoindene intermediates generated in this process have been sequentially trapped by tetracyanoethylene, yielding tris(5,6-benzo-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-en-7-yl)silane,‡ **14**. The silane, **9**, has been transformed into tris(inden-1-yl)hexylsilane, **19**, *via* hydrosilylation with hex-1-ene in the presence of Wilkinson's catalyst. Compound **14** was quantitatively converted into the crystallographically characterised tris(5,6-benzo-2,2,3,3-tetracyanobicyclo-[2.2.1]hept-5-en-7-yl)silanol, **17**, by treatment with water, or into tris(5,6-benzo-2,2,3,3-tetracyanobicyclo[2.2.1]-hept-5-en-7-yl)fluorosilane, **22**, by the addition of either HBF_4 or $Ph_3C^+PF_6^-$.

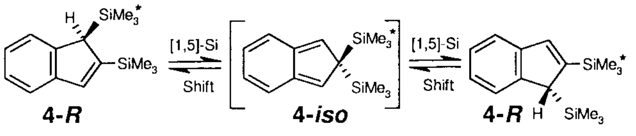
Introduction

Although the stereochemically non-rigid[1] nature of inden-1-ylsilanes has been recognised for over three decades,[2,3] the utility of these species as ligands in the preparation of chiral metallocene precatalysts[4] has brought about renewed interest in their dynamics and reactivity. For mono(inden-1-yl)silanes, including 1-(trimethylsilyl)indene, **1**, the operation of a symmetry-allowed,[5] suprafacial [1,5]-silicon shift process results in the interconversion of enantiomeric pairs (**1-*S*** and **1-*R***) *via* the corresponding isoindene intermediate, **1-*iso*** (Scheme 1). In 1970, Larrabee[6] and Ashe[7] independently reported the trapping of **1-*iso*** as the corresponding [4 + 2] cycloadduct with maleic anhydride and tetracyanoethylene, respectively, yielding **2** and **3**; more recently, we provided corroborating X-ray crystallographic characterisation for **3**,[8] and related chromium-,[9] iron-[10] and cobalt-containing[11] derivatives.



Scheme 1 Sigmatropic shifts and isoindene cycloaddition chemistry of **1**.

Compelling evidence in support of such a stepwise [1,5] shift mechanism (rather than the direct, but symmetry-forbidden [1,3] pathway) was advanced by Davison and Rakita[12] in their examination of the dynamic behaviour of 1,2-bis(trimethylsilyl)indene, **4**. These workers recognised that while suprafacial [1,3]-silicon shifts in **4** would interconvert the *R* and *S* enantiomers of this compound (thus equilibrating the two halves of the indenyl framework), the trimethylsilyl groups in **4** would retain their chemical and magnetic non-equivalence. In contrast, a mechanism involving sequential [1,5] shifts would proceed *via* the symmetric isoindene intermediate, **4-*iso***, leading both to a permutation of the related indenyl environments and to chemical exchange of the trimethylsilyl groups. During the course of a variable-temperature NMR study, these authors noted that the silicon fragments in **4** were equilibrated on the NMR time scale with the same barrier ($E_a \approx 26$ kcal mol^{-1}) as that associated with exchange between the H(1) and H(3) protons. This observation pointed to a [1,5]-silicon shift process, in which both silyl groups reside temporarily at C(2) in **4-*iso***, as depicted in Scheme 2.



Scheme 2 Scrambling of the trimethylsilyl groups in **4**, as a result of [1,5]-silicon shifts. One silicon group is arbitrarily marked with an asterisk (*) to aid in monitoring its position throughout the migratory process.

In the case of poly(inden-1-yl)silanes, the situation is considerably more complex since the presence of more than one indenyl moiety permits diastereotopism; for these species, [1,5] silatropic shifts not only interconvert enantiomers, but also diastereomers of differing molecular symmetry. Perhaps the most prominent example of this class of molecules is the commercially available compound, bis(inden-1-yl)dimethylsilane, **5**.[13] Following a report by Rausch and co-workers[14] in which it is claimed that **5** undergoes symmetry-forbidden [1,3]-silicon shifts, we demonstrated by use of 2D-EXSY (EXchange SpectroscopY) and single selective inversion NMR techniques that the molecular dynamics of this compound can instead be rationalised in terms of [1,5]-silicon shifts, which permute the C_s (**5-*meso***) and the C_2 isomers (**5-*d,l***) of this species.[15] Moreover, support for the sequential generation of isoindenes in this process was obtained *via* treatment of **5** with two equivalents

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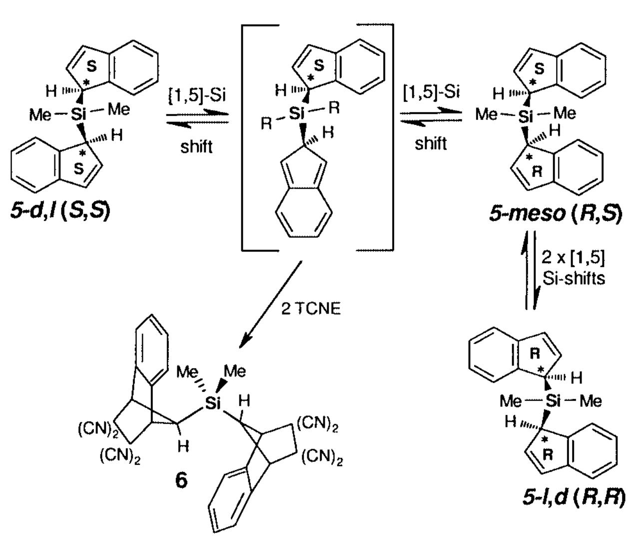
† Non-SI units employed: 1 kcal ≈ 4.18 kJ.

‡ The IUPAC name for the structure named in this paper as 5,6-benzobicyclo[2.2.1]hept-5-ene is tricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene.

DOI: 10.1039/b000458h



Scheme 3 Interconversion of the C_2 and C_S isomers of **5**, and isoindene trapping with tetracyanoethylene, yielding the double Diels–Alder adduct, **6**.

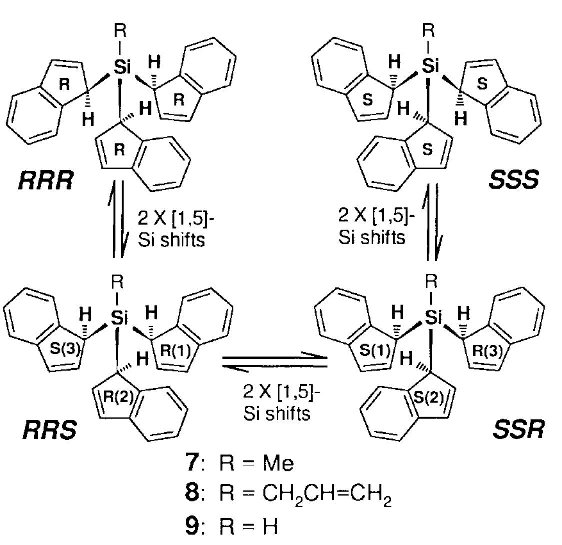
of tetracyanoethylene, which yielded the anticipated double [4 + 2] cycloadduct, **6** (Scheme 3).

In continuation of our studies pertaining to the dynamics of poly(inden-1-yl)silanes, we have reported on the operation of [1,5]-silicon shifts in tris(inden-1-yl)methylsilane, **7**,[8] and tris(inden-1-yl)allylsilane, **8**.[16] Despite the potential utility of this class of molecules as ligands in the preparation of chiral *ansa*-metallocene *bimetallic* precatalysts, to date, **7** and **8** represent the only examples of tris(inden-1-yl)silanes of which we are aware. Moreover, we have demonstrated that these molecules serve as precursors to tris(benzonorbornyl)silanes, a rare class of sterically demanding organosilicon compounds.[8,16] Herein we describe the synthesis, characterisation and molecular dynamics of tris(inden-1-yl)silane, **9**, its cycloaddition chemistry, and some preliminary silicon-based reactivity studies involving tris(inden-1-yl)silanes and their corresponding triple Diels–Alder cycloadducts.

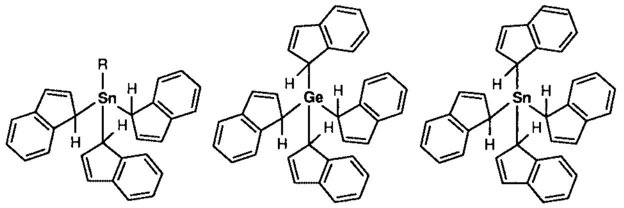
Results and discussion

The title compound, **9**, was readily prepared *via* quenching of trichlorosilane with an excess of indenyllithium, followed by chromatographic purification on silica. This reaction proved to be much more efficient (64% yield) than the corresponding reactions involving alkyltrichlorosilanes (42%[8] and 13%[16] for **7** and **8**, respectively), likely owing to the reduced congestion in **9**. As has been observed previously for **7** and **8**, compound **9** exists in solution as a statistical (1 : 3 : 3 : 1) mixture of interconverting isomers (Scheme 4). The ^{1}H and ^{13}C NMR spectra of **9** contain four equally intense resonances in each of the C(1)–H(1), C(2)–H(2) and C(3)–H(3) regions; two silicon hydride resonances (1 : 3) are also observed in both the ^{1}H and ^{29}Si NMR spectra of **9**. The connectivity between the various ^{1}H, ^{13}C and ^{29}Si NMR signals within each of the four individual indenyl ring environments in **9** was ascertained by use of ^{1}H, ^{13}C and ^{29}Si one- and two-dimensional NMR spectroscopic techniques, in a manner directly analogous to that utilised in assigning the NMR spectra of **7**.[8]

The NMR spectroscopic features observed for compounds **7**, **8** and **9** parallel those observed by McMaster and Stobart, who qualitatively examined the dynamic behaviour of poly(η^1-indenyl) complexes of germanium and tin (**10** to **13**).[17] In an attempt to rationalise the observed number of signals in the low temperature NMR spectra of these heavier Group 14 poly(inden-1-yl) complexes, McMaster and Stobart systematically evaluated the (inden-1-yl)$_n$MR$_{4-n}$ (R = achiral substituent) series by use of group theory. For (inden-1-yl)$_3$MR complexes, the existence of two pairs of diastereomers is viable, one possessing C_3 symmetry (*RRR*/*SSS*), and another of C_1 symmetry in which the absolute configurations of the C(1) carbon in the three indenyl rings are not identical (*RRS*/*SSR*). These workers reasoned that while the C_1 isomer of (inden-1-yl)$_3$MR compounds gives rise to three magnetically non-equivalent indenyl ring environments, the indenyl environments of the C_3 isomer[18] are identical. Such a scenario results in the expectation of four unique indenyl ^{1}H and ^{13}C NMR signals for this class of compounds. When statistical weighting is considered, the systematic approach of McMaster and Stobart provides a rationale for the observation of four equal intensity indenyl sp^3-CH signals in the ^{1}H and ^{13}C NMR spectra of compound **9**, as described above. In the case of the (inden-1-yl)$_4$M complexes, such as **12** and **13**, three isomers of D_2, C_1 and S_4 symmetry are predicted *a priori*. Although no Group 14 compounds of the type (inden-1-yl)$_3$MR have been crystallographically characterised to date, single crystal X-ray data for the S_4-symmetric isomers of both **12** and **13** were provided in a subsequent publication by Stobart and co-workers.[19]



Scheme 4 Interconversion of the eight different indenyl ring environments in the *RRR*, *RRS*, *SSR* and *SSS* isomers of tris(inden-1-yl)silanes.



10: R = *n*Bu
11: R = Ph
12
13

The conceptual model used in rationalising the NMR spectral features of Group 14 tris(inden-1-yl) complexes, such as **9**, is underpinned by the assumption that all three ligands are actually bonded to the silicon centre through the indenyl C(1) carbon, though crystallographic evidence for such a bonding configuration has yet to be reported. As a complement to the NMR spectroscopic data detailed above, a crystalline sample of **9** was subjected to a single crystal X-ray diffraction analysis. The molecular structure of **9-*SSR*** appears as Fig. 1, while salient crystallographic data and metrical parameters are collected in Tables 1 and 2, respectively. In the crystalline lattice, **9-*SSR*** and **9-*RRS*** pack as two crystallographically independent molecules per asymmetric unit, between which no unusually close intermolecular contacts exist (see Experimental section). Given the structural similarity between these two enantiomers, commentary on specific geometric details is limited to only one of the independent molecules (**9-*SSR***). The molecular geom-

Table 1 Crystal data and structure refinement parameters for **9** and **17·(CH$_3$COCH$_3$)$_2$**

	9	**17·(CH$_3$COCH$_3$)$_2$**
Chemical formula	$C_{27}H_{22}Si_1$	$C_{51}H_{34}O_3N_{12}Si_1$
Formula weight (*M*)	374.54	890.99
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a/Å	9.6561(1)	14.0079(5)
b/Å	20.5988(3)	14.7086(4)
c/Å	20.9879(3)	23.3079(7)
β/°	90	102.395(1)
Volume/Å^3	4174.6(1)	4690.3(3)
Temperature/K	302(2)	302(2)
Z	8	4
Abs. coeff. (μ)/mm^{-1}	0.122	0.107
No. reflections collected	30 305	27 620
No. independent reflections	7347	6518
R(int)	0.1132	0.0906
Final *R* indices ($I > 2\sigma(I)$)*		
*R*1	0.0683	0.0628
*wR*2	0.1002	0.1445
R indices (all data)*		
*R*1	0.1524	0.1177
*wR*2	0.1280	0.1816

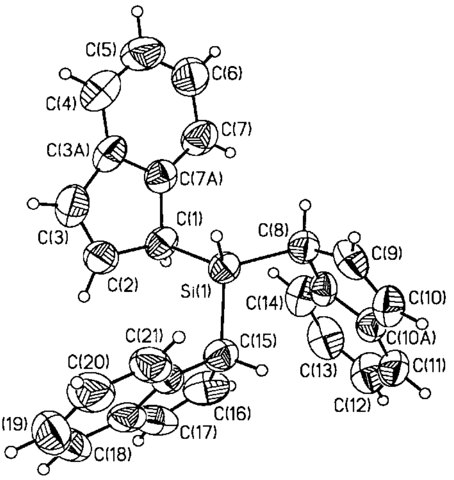


Fig. 1 X-Ray structure of one of the two independent molecules of **9**, showing the atomic numbering scheme. Thermal ellipsoids are shown at the 50% probability level. The absolute configurations at C(1), C(8) and C(15) are *S*, *S* and *R*, respectively.

Table 2 Selected bond lengths [Å] and angles [°] for **9** and **17·(CH$_3$COCH$_3$)$_2$**

9			
Si(1)–C(8)	1.889(4)	C(9)–C(10)	1.327(6)
Si(1)–C(15)	1.895(5)	C(15)–C(16)	1.517(7)
Si(1)–C(1)	1.896(5)	C(16)–C(17)	1.326(7)
Si(2)–C(29)	1.894(5)	C(22)–C(23)	1.497(6)
Si(2)–C(36)	1.898(5)	C(23)–C(24)	1.331(6)
Si(2)–C(22)	1.911(4)	C(29)–C(30)	1.505(6)
C(1)–C(2)	1.486(6)	C(30)–C(31)	1.324(6)
C(2)–C(3)	1.339(6)	C(36)–C(37)	1.508(7)
C(8)–C(9)	1.499(6)	C(37)–C(38)	1.346(7)
C(8)–Si(1)–C(15)	108.9(2)	C(29)–Si(2)–C(36)	112.2(2)
C(8)–Si(1)–C(1)	113.6(2)	C(29)–Si(2)–C(22)	112.8(2)
C(15)–Si(1)–C(1)	111.1(2)	C(36)–Si(2)–C(22)	108.7(2)
17·(CH$_3$COCH$_3$)$_2$			
Si(1)–O(1)	1.603(3)	C(21)–C(22)	1.590(5)
Si(1)–C(7)	1.895(4)	C(23)–C(24)	1.582(5)
Si(1)–C(27)	1.894(4)	C(22)–C(23)	1.617(6)
Si(1)–C(47)	1.884(4)	C(43)–C(44)	1.597(5)
C(3)–C(4)	1.589(6)	C(41)–C(42)	1.595(5)
C(1)–C(2)	1.587(5)	C(42)–C(43)	1.615(6)
C(2)–C(3)	1.612(5)		
C(2)–C(1)–C(7)	99.7(3)	Si(1)–C(27)–C(21)	113.9(3)
Si(1)–C(7)–C(4)	117.5(3)	Si(1)–C(47)–C(44)	121.0(3)
Si(1)–C(7)–C(1)	119.7(3)	Si(1)–C(47)–C(41)	121.6(3)
Si(1)–C(27)–C(24)	120.7(3)		

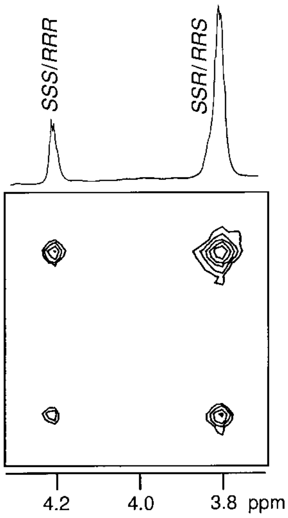
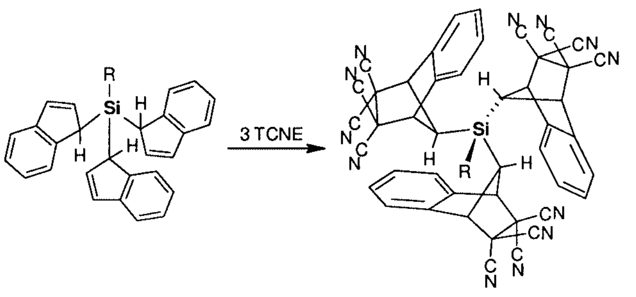


Fig. 2 The Si–H region of the ^{1}H–^{1}H EXSY spectrum of tris(inden-1-yl)silane, **9**, showing chemical exchange between diastereomers.

etry of **9-*SSR*** contains no unusual features and can be compared to other crystallographically characterised *sp*^{3}-bonded Group 14 inden-1-yl complexes.[8,11,19,20] Indeed, the crystal structure of **9-*SSR*** is entirely consistent with the NMR spectral data presented above, in that all three of the indenyl fragments are connected to the silicon centre through *sp*^{3}-hybridised carbons. The silicon environment deviates only modestly from ideal tetrahedral geometry and is characterised by normal Si–C bond lengths,[21] while the carbocyclic units are essentially planar and possess distinct 'allylic' (C(1)–C(2)=C(3), *etc.*) linkages. Attempts to characterise **9-*RRR*** and **9-*SSS*** in the solid state are ongoing.

The stereochemical consequences associated with the occurrence of sequential [1,5]-silicon shifts in tris(inden-1-yl)methylsilane, **7**, were described in a previous report,[8] and the molecular dynamics of **9** can be rationalised analogously. The suprafacial migration of an (inden-1-yl)$_2$SiH fragment about the periphery of the remaining indenyl ring in **9-*RRR*** proceeds with inversion of stereochemistry at the migration terminus, transforming a molecule of configuration *RRR* (**9-*RRR***) into the corresponding **9-*RRS*** diastereomer. This rearrangement process takes three equivalent H(2) protons of the **9-*RRR*** isomer (in which the three indenyl ring environments can be designated "R") and moves them into three new indenyl ring environments, labelled "R(1)", "R(2)" and "S(3)" (Scheme 4). A second ring inversion interconverts the enantiomorphic **9-*RRS*** and **9-*SSR*** molecules, while a third pair of [1,5]-silicon shifts regenerates the homotopic molecule, **9-*SSS***, in which all three indenyl ring environments are identically "S". Moreover, these molecular rearrangements permute the Si–*H* environments in the diastereomeric pairs of molecules (**9-*RRR*/*SSS*** and **9-*RRS*/*SSR***). We have previously demonstrated that the exchange pathways between indenyl sites and environments in tris(inden-1-yl)silanes, which are determined experimentally based on 2D-EXSY data, can be conveniently mapped onto a hypercube;[8] a portion of a ^{1}H–^{1}H EXSY spectrum acquired for **9** appears as Fig. 2. The stereochemically non-rigid nature of **9** is manifested in the development of off-diagonal cross-peaks between the silicon hydride signals associated with **9-*RRR*/*SSS*** and **9-*RRS*/*SSR***, attributable to chemical exchange involving these sites. Single selective inversion NMR experiments yielded a $\Delta G^{\ddagger}$ value of 24 ± 1 kcal mol^{-1} for the silatropic shifts in **9**, a value which is consistent with data previously reported for [1,5]-silicon shifts in related inden-1-ylsilanes.[7–11,15,16]

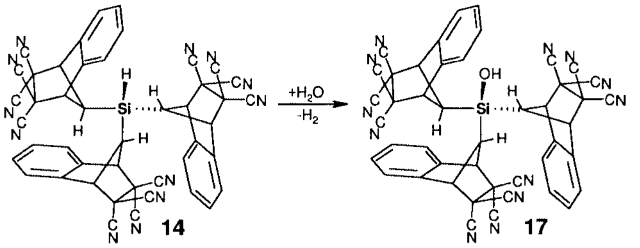
With the goal of further substantiating our claim that the dynamic behaviour of tris(inden-1-yl)silanes can be rationalised in terms of successive [1,5]-silicon shifts, an attempt was made to intercept the transient isoindenes in a manner similar to that reported by Ashe.[7] The product obtained after allowing **9** to react with three equivalents of tetracyanoethylene yielded NMR spectroscopic and mass spectrometric data consistent with the formation of the anticipated triple [4 + 2] Diels–Alder cycloadduct, **14** (Scheme 5).



14: R = H
15: R = Me
16: R = $CH_2CH=CH_2$

Scheme 5 The triple Diels–Alder reactions involving tris(inden-1-yl)silanes and tetracyanoethylene.

The triple cycloadduct, **14**, represents only the third such compound derived from a tris(inden-1-yl)silane to be isolated. Whereas in the case of **15**, preliminary computational results suggested a C_3 symmetric structure,[8] crystallographic data obtained for **16** revealed a molecular geometry of C_1 symmetry.[16] Although we were unable to isolate an appropriate sample of **14** for X-ray crystallographic studies, the corresponding silanol provided suitable crystals. As depicted in Scheme 6, **14** is quantitatively converted to the tris(benzonorbornyl)silanol, **17**, by treatment with wet acetone; the X-ray crystal structure of **17** appears as Fig. 3, while crystallographic data and selected metrical parameters are collected in Tables 1 and 2, respectively.



Scheme 6 Conversion of the silane, **14**, into the tris(benzonorbornyl)silanol, **17**.

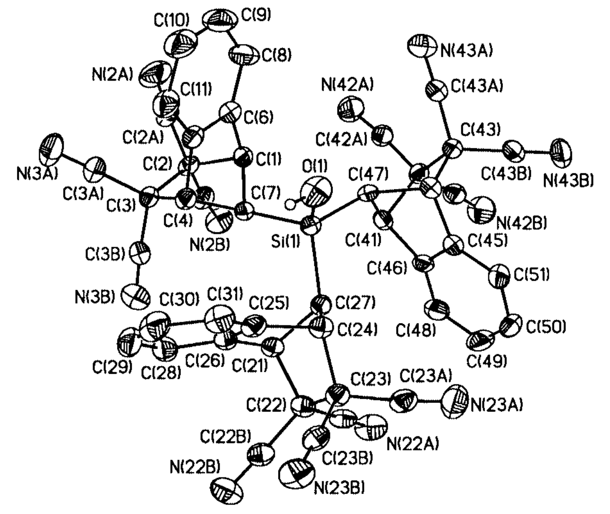


Fig. 3 X-Ray structure of **17**, showing the atomic numbering scheme. Thermal ellipsoids are shown at the 40% probability level. The solvated acetone molecules and selected hydrogen atoms have been omitted for clarity.

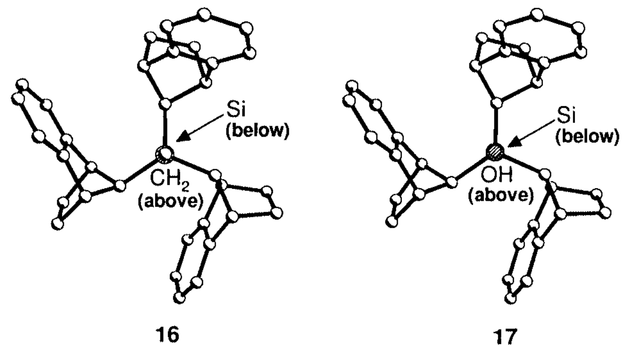
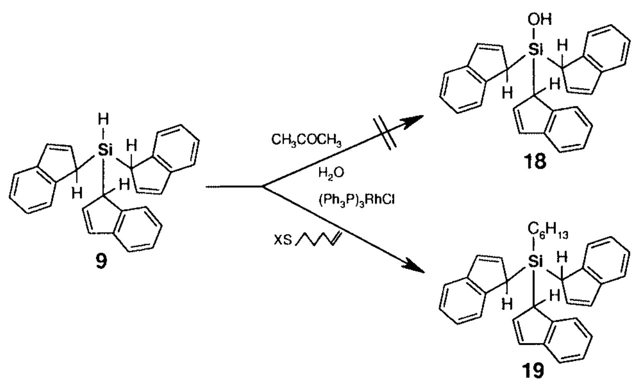


Fig. 4 Comparing the solid-state geometries of the crystallographically characterised tris(benzonorbornyl)silanes, **16** and **17**. Selected atoms have been omitted for clarity.

The X-ray structure of **17** serves to unequivocally confirm its identity as the product resulting from the hydrolysis of **14**, and reveals that in all three cases the addition of tetracyanoethylene to the silicon-functionalised isoindene (derived from **9**) occurs on the face opposite to that occupied by the R_2SiH unit. The overall geometric features of the benzonorbornyl frameworks in **17** are comparable to related cycloadducts derived from metallo-isoindenes for which we have provided crystallographic characterisation.[8–10,16] The steric demands of the (benzonorbornyl)$_2$SiOH fragments in **17** result in observation of carbon centres which are distorted from ideal tetrahedral geometry. This phenomenon is especially evident in the expansion of the Si(1)–C(47)–C(41) and Si(1)–C(47)–C(44) angles to 121.0 and 121.3°, respectively. As previously noted for **16**,[16] the non-uniform orientation of the benzonorbornyl units in **17** leads to the observation of C_1 molecular symmetry for this compound.[22] In fact, a comparison of the benzonorbornyl torsion angles (defined by H–C(n)–Si(1)–O(1), where n = 7, 27, 47) in **16** and **17** reveals that in the solid state, the orientations of the ligands in these two compounds are strikingly similar (Fig. 4); in the case of **16**, torsion angles of 156.4, 109.0, and 69.2° are observed (for n = 7, 27, 47, respectively),[16] while for **17** the corresponding angles are 157.1, 111.8 and 71.1°. The apparent duplication of the structural features in **16** and **17** suggests that these do, in fact, represent an 'energy-minimised' structural motif for this class of tris(benzonorbornyl)silanes. It is also noteworthy that, despite the sterically demanding nature of the substituents in **16** and **17**, and the apparent preference for an asymmetric C_1 geometry in the solid state, negligible NMR line broadening is observed for these compounds, even at temperatures as low as −80 °C. Indeed, the simplicity of the ^1H and ^{13}C NMR spectra obtained from samples of **16** and **17** suggests a time-averaged C_{3v} molecular geometry in solution, resulting from rapid rotation about the Si–C(benzonorbornyl) bond.

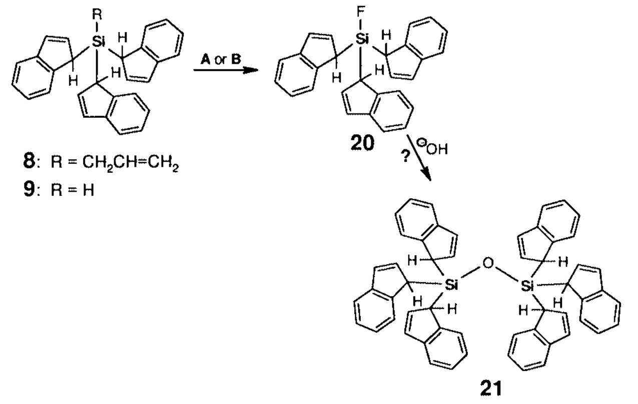
In an effort to survey the utility of tris(inden-1-yl)silane, **9**, as a synthetic precursor to other tris(inden-1-yl)silanes, the conversion of this compound into the corresponding tris(inden-1-yl)silanol, **18**, was attempted by allowing the former to react with wet acetone (Scheme 7). However, in direct contrast to the successful conversion of **14** to **17**, when this methodology was employed using **9**, hydrolysis of the Si–indenyl linkage (rather than the Si–H bond) was observed, as evinced by the generation of indene. Alternatively, the functionalisation of **9** and its triple Diels–Alder adduct, **14**, *via* hydrosilylation was undertaken. In neat hex-1-ene, and in the presence of Wilkinson's catalyst ($(Ph_3P)_3RhCl$), **9** was converted to tris(inden-1-yl)hexylsilane, **19**, in moderate yield (34%) (Scheme 7). Unfortunately, **14**



Scheme 7 Attempted hydrolysis and hydrosilylation reactions involving **9**.

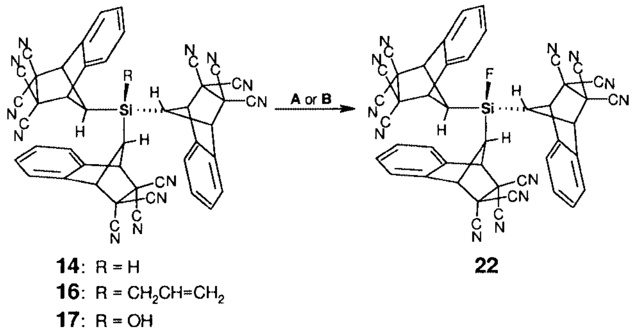
did not participate in hydrosilylation reactions under similar experimental conditions, presumably because of unfavourable steric interactions between the bulky benzonorbornyl substituents and the ligands present on the rhodium catalyst.

Although *prima facie* the steric demands of the benzonorbornyl ligands in **16** and **17** would be expected to impede reactivity at the silicon centre in these molecules, a careful inspection of their crystal structures reveals that the allyl and hydroxy moieties in these compounds should be accessible to incoming chemical reagents. As such, the reactivity of the tris(inden-1-yl)silanes, **8** and **9**, and the tris(benzonorbornyl)silanes, **14**, **16** and **17**, with electrophiles was examined. The NMR spectral data obtained immediately after adding either HBF_4 or $Ph_3C^+PF_6^-$ to a CD_2Cl_2 solution of tris(inden-1-yl)allylsilane, **8**, or tris(inden-1-yl)silane, **9**, suggested the formation of the anticipated product, tris(inden-1-yl)fluorosilane, **20** (Scheme 8), based on the loss of ^{29}Si NMR signals attributable



Scheme 8 Reactions involving tris(inden-1-yl)silanes (**8** or **9**) and electrophiles (H^+ or Ph_3C^+). **A** = $HBF_4{\cdot}O(C_2H_5)_2$ and **B** = $Ph_3C^+PF_6^-$.

to the starting material (**8** or **9**) and the appearance of two overlapping doublets at approximately 12.2 ppm ($^1J_{SiF} = 277$ Hz, presumably corresponding to the *RRR*/*SSS* and *RRS*/*SSR* diastereomers).[23,24] In contrast to the previously characterised tris(inden-1-yl)silanes (**7**, **8** or **9**) the complexity of the ^1H and ^{13}C NMR spectra of tris(inden-1-yl)fluorosilane, **20**, did not allow conclusive chemical shift assignments to be made. When measures were not taken to exhaustively remove moisture from the NMR solvents, samples re-examined after approximately 24 h at −20 °C showed nearly complete deterioration of the ^{29}Si NMR peaks near 12 ppm, and the formation of a new, broad signal centred at −15.5 ppm. This new resonance was tentatively assigned to hexa(inden-1-yl)disiloxane, **21**, which may have arisen because of adventitious moisture in the NMR solvent; solutions of the fluorosilane, **20**, generated and stored under rigorously anhydrous conditions showed little decomposition, even after six weeks. Analogous reactions carried out using either **14**, **16** or **17** in CD_3CN similarly gave rise to the corresponding fluorosilane, **22**, which was unambiguously characterised by use of ^1H, ^{13}C, ^{19}F and ^{29}Si NMR spectroscopic techniques (Scheme 9). Particularly diagnostic was the observation of spin–spin coupling between the fluorine nucleus and both the silicon centre and the three magnetically equivalent Si–C–*H* hydrogen nuclei in **22**.



Scheme 9 Reactions involving tris(benzonorbornyl)silanes (**14**, **16** or **17**) and electrophiles (H^+ or Ph_3C^+). **A** = $HBF_4{\cdot}O(C_2H_5)_2$ and **B** = $Ph_3C^+PF_6^-$.

Concluding remarks

In this report we have outlined the synthesis, characterisation and molecular dynamics of tris(inden-1-yl)silane, **9**, which undergoes successive [1,5]-silicon shifts with a barrier of ~24 kcal mol^{-1}. The isoindene intermediates generated in this migratory process can be sequentially trapped by tetracyanoethylene, yielding the corresponding tris(benzonorbornyl)silane, **14**. Preliminary reactivity studies suggest that, despite the bulky nature of the benzonorbornyl substituents in this unique class of compounds, the silicon centre is still accessible by chemical reagents. The use of these sterically loaded silanes, both as protecting groups and as ligands in the preparation of organometallic complexes, will be the subject of future reports.

Experimental

General

All preparations were carried out under an atmosphere of dry nitrogen using freshly distilled solvents. Tris(inden-1-yl)allylsilane, **8**, and tris(5,6-benzo-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-en-7-yl)allylsilane, **16**, were prepared using published methods,[16] while trichlorosilane, hex-1-ene, $HBF_4{\cdot}O(C_2H_5)_2$, $Ph_3C^+PF_6^-$, and $(Ph_3P)_3RhCl$ (Wilkinson's catalyst) were obtained from Aldrich and used as received. All deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA). Mass spectrometric data were obtained using a Finnigan 4500 spectrometer by direct electron impact (DEI) or by chemical ionization (CI) with NH_3. Infrared spectra were obtained on a Bio-Rad FTS-40 FT-IR spectrometer. Melting points were measured in open glass capillaries using a Thomas Hoover Unimelt capillary melting point apparatus, and were not corrected. Microanalyses were performed by Guelph Chemical Laboratories (Guelph, Ontario, Canada). One-dimensional NMR spectroscopic data were recorded using either a Bruker AC-300 (^1H and ^{19}F NMR) or Bruker Avance DRX-500 spectrometer (^1H, ^{13}C and ^{29}Si NMR). In all cases, NMR spectra were obtained from samples dissolved in deuterated solvents, with NMR signals referenced internally to tetramethylsilane (^1H, ^{13}C and ^{29}Si NMR) or externally to $CFCl_3$ (^{19}F NMR). Two-dimensional NMR experiments were conducted on the DRX-500 instrument, equipped with an 11.74 T superconducting magnet, a Bruker B-VT 2000 temperature controller, and a 5 mm multinuclear inverse probe possessing 3-axis gradient capabilities. These consisted of ^1H–^1H COSY, ^1H–^{13}C HSQC, ^1H–^{13}C HMBC, ^1H–^1H

EXSY and ^{1}H–^{29}Si HMBC experiments. Sample temperatures were set and maintained throughout the course of these studies by use of the temperature controller, and externally calibrated by placing a copper–constantan thermocouple, contained within an NMR tube, inside the probe. Using this procedure, absolute temperatures were measured and maintained to within ±0.5 °C.

^{1}H–^{1}H EXSY (EXchange SpectroscopY) experiments

Two-dimensional ^{1}H–^{1}H EXSY[25] spectra were recorded in the phase-sensitive mode, using the gradient implementation of the NOESY (90°–t_1–90°–t_m–90°–ACQ) pulse sequence. In a typical experiment, 512 FID's were recorded in the f_2 dimension, with each FID acquired in 16 scans. These FID data were subsequently Fourier transformed using Gaussian window functions in both f_1 and f_2, with line broadening set to 3.0 Hz. All experiments were carried out in perdeuterated toluene between 102 and 108 °C, with mixing times ranging from 0.5 to 2.7 s, the initial value of the 2D evolution set to 10 μs, and the relaxation delay set to 2.7 s.

Single selective inversion NMR experiments

All kinetic data were obtained in the slow exchange regime by use of ^{1}H selective inversion NMR experiments,[26–29] in which one resonance in the spectrum was perturbed using a 90–τ–90 pulse sequence ($\tau = 1/2\Delta\nu$), and then the return to equilibrium of this and the other signals involved in the chemical exchange process was monitored as a function of time, as in an inversion-recovery T_1 experiment. These experiments were conducted on a Bruker AC-300 spectrometer, equipped with a 7.65 T superconducting magnet, a Bruker B-VT 2000 temperature controller and a 5 mm QNP probe; spectral data were obtained between 95 and 110 °C. Non-linear least-squares fitting of the experimental data was performed using a C-programming language version of the SIFIT program provided by McClung,[28] and permitted the extraction of rate data. Analysis of these temperature-dependent rates using Eyring theory allowed for an estimate of the free energy of activation, $\Delta G^{\ddagger}$ (reported at 303 K), associated with the dynamic process.

X-Ray crystallography §

X-Ray crystallographic data for **9** and **17·(CH$_3$COCH$_3$)$_2$** were collected from single crystal samples, each mounted on a glass fibre. Data were collected using a P4 Siemens diffractometer, equipped with a Siemens SMART 1K Charge-Coupled Device (CCD) Area Detector (using the program SMART[30]) and a rotating anode using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal-to-detector distance was 3.991 cm, and the data collection was carried out in 512 × 512 pixel mode, utilising 2 × 2 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected by a 4.5° scan in 15 frames over three different parts of reciprocal space (45 frames total). One complete hemisphere of data was collected, to better than 0.8 Å resolution. Upon completion of the data collection, the first 50 frames were recollected in order to improve the decay corrections analysis. Processing was carried out by use of the program SAINT,[31] which applied Lorentz and polarisation corrections to three-dimensionally integrated diffraction spots. The program SADABS[32] was utilised 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[33] program library. Refinement was carried out by using full-matrix least squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Unless stated, hydrogen atoms were added at calculated positions and refined using a riding model with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of their attached carbon. In the case of **9**, two independent molecules (of absolute configuration *RRS* and *SSR*) were found in the asymmetric unit. That these two enantiomers were truly independent and not related by a crystallographic inversion centre was verified externally by sending the crystallographic information file (CIF) through the automated checking program, CHECKCIF, made available by the International Union of Crystallography; this program failed to detect any missing crystallographic inversion centre and the refined value of the absolute structure parameter (0.2) supports the absolute configurations chosen. The hydrogens bound directly to the silicon atoms were found in the electron difference map and refined isotropically. In the case of **17·(CH$_3$COCH$_3$)$_2$**, no close contacts exist between the **17** and the solvated acetone molecules, suggesting an absence of hydrogen bonding in the crystal.

Tris(inden-1-yl)silane, 9

Indene (4.0 g, 34.5 mmol) in freshly distilled diethyl 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 1 h. The mixture was stirred for an additional 2 h at −78 °C, and then trichlorosilane (1.6 g, 11.5 mmol) was added dropwise over 2 h. When the addition was complete, the mixture was allowed to warm to room temperature and stirred for an additional 18 h. The product was then extracted with water (3 × 100 mL), and the organic phase dried over anhydrous MgSO$_4$. The residue obtained after removal of the solvent was subjected to flash chromatography on silica gel. Elution with a mixture of hexanes and CH$_2$Cl$_2$ (80 : 20) yielded a viscous yellow oil, which solidified after several hours under vacuum at ambient temperature. Recrystallisation from hexanes yielded **9** as a yellow powder, mp 91–92 °C (2.75 g, 7.36 mmol, 64%). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.36–7.07 (m, 48H, aromatic), 6.77 (m, 3H, H(3) in S/R), 6.71 (m, 3H, H(3) in R(3)/S(3)), 6.62 (m, 3H, H(3) in S(2)/R(2)), 6.60 (m, 3H, H(3) in S(1)/R(1)), 6.57 (m, 3H, H(2) in R(3)/S(3)), 6.18 (m, 3H, H(2) in S/R), 5.87 (m, 3H, H(2) in S(1)/R(1)), 5.60 (m, 3H, H(2) in S(2)/R(2)), 4.24 (m, 1H, Si*H* in 11-*SSS*/*RRR*), 3.83 (m, 3H, Si*H* in 11-*SSR*/*RRS*), 3.36 (m, 3H, H(1) in R(3)/S(3)), 3.14 (m, 3H, H(1) in S(2)/R(2)), 3.06 (m, 3H, H(1) in S/R), 2.91 (m, 3H, H(1) in S(1)/R(1)); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 144.9–143.7 (C(3a), C(7a)), 135.2 (C(2) in S(1)/R(1)), 134.9 (C(2) in R(3)/S(3)), 134.7 (C(2) in S(1)/R(1)), 134.7 (C(2) in S(2)/R(2)), 130.9 (C(3) in R(3)/S(3)), 130.3 (C(3) in S(1)/R(1)), 130.2 (C(3) in S(2)/R(2)), 130.0 (C(3) in S/R), 126.5–121.2 (C(4), C(5), C(6) and C(7)), 42.4 (C(1) in R(3)/S(3)), 40.8 (C(1) in S/R), 40.8 (C(1) in S(2)/R(2)), 39.9 (C(1) in S(1)/R(1)); ^{29}Si NMR (CDCl$_3$, 99.35 MHz): δ −2.2 (11-*RRR* and 11-*SSS*), −3.4 (11-*RRS* and 11-*SSR*); IR (CDCl$_3$): $\nu_{\text{Si–H}}$ 2120 cm^{-1}; Mass spectra: (DEI, *m*/*z* (%)): 374 (17, [M]$^+$), 259 (42, [M − C$_9$H$_7$]$^+$), 143 (46, [M − 2(C$_9$H$_7$)]$^+$), 115 (100, [C$_9$H$_7$]$^+$); (high resolution, DEI): calculated for mass ^{12}C$_{27}$H$_{22}$-Si$_1$, 374.1491 amu; observed, 374.1497 amu; Anal.: Calcd. for C$_{27}$H$_{22}$Si$_1$: C 86.58; H 5.92. Found: C 86.64; H 5.85%. A sample suitable for structural determination by single-crystal X-ray diffraction studies (yellow plate; 0.3 × 0.3 × 0.1 mm^3) was obtained by recrystallisation from a mixture of dichloromethane and hexanes (1 : 1).

Tris(5,6-benzo-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-en-7-yl)-silane, 14

Upon addition of tetracyanoethylene (2.8 g, 22 mmol) to a solution of tris(inden-1-yl)silane, **9**, (2.8 g, 7.5 mmol) in ethyl acetate (100 mL) the solution turned dark blue; the dark coloration subsided after 72 h. The residual solid obtained after removal of the solvent was washed with hexanes (2 × 50 mL),

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§ CCDC reference number 188/228.

and then purified by recrystallisation from dichloromethane, yielding **14** as a beige powder, mp (with decomposition) 217–219 °C (2.7 g, 3.6 mmol, 47%). ^{1}H NMR (acetone-d_6, 99.35 MHz): δ 7.64 (apparent d (5.4 Hz) of d (3.1 Hz), 6H, H(8) and H(11)), 7.52 (apparent d (5.4 Hz) of d (3.1 Hz), 6H, H(9) and H(10)), 4.35 (d, $^3J = 1.1$ Hz, 6H, H(1) and H(4)), 2.54 (d ($^3J_{\text{Si–H}} = 3.1$ Hz) of t ($^3J = 1.1$ Hz), 3H, H(7)), 2.12 (quart., 1H, SiH); ^{13}C NMR (CD_3CN, 125 MHz): δ 139.4 (C(5) and C(6)), 131.3 (C(9) and C(10)), 126.7 (C(8) and C(11)), 113.4 (pseudo-equatorial nitriles), 111.5 (pseudo-axial nitriles), 60.5 (C(1) and C(4)), 50.5 (C(2) and C(3)), 49.6 (C(7)); ^{29}Si NMR (CD_3CN, 99.35 MHz): δ −10.3; IR (cm^{-1}): 2256, 2221, 2112, 1937; Mass spectrum: (CI, NH_3, *m*/*z* (%)): 724 (7, $[M - 2(CN) + 18]^+$), 648 (61, $[M - (TCNE) + 18]^+$), 520 (100, $[M - 2(TCNE) + 18]^+$), 392 (92, $[M - 3(TCNE) + 18]^+$); Anal.: Calcd. for $C_{45}H_{22}N_{12}Si_1$: C 71.22; H 2.92; N 22.16. Found: C 70.84; H 3.02; N 21.91%.

Tris(5,6-benzo-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-en-7-yl)silanol, 17

A sample of **14** in wet acetone (approximately 3% water added) was quantitatively converted to the corresponding silanol, **17**, after stirring for 24 h at room temperature. Slow evaporation of the solvent yielded **17·(CH$_3$COCH$_3$)$_2$** as a white powder. ^{1}H NMR (acetone-d_6, 99.35 MHz): δ 7.59 (apparent d (5.4 Hz) of d (3.1 Hz), 6H, H(8) and H(11)), 7.48 (apparent d (5.4 Hz) of d (3.1 Hz), 6H, H(9) and H(10)), 5.16 (s, 1H, SiO*H*), 4.39 (d, $^3J = 1.1$ Hz, 6H, H(1) and H(4)), 2.39 (t, $^3J = 1.1$ Hz, 3H, H(7)); ^{13}C NMR (acetone-d_6, 125 MHz): δ 139.5 (C(5) and C(6)), 131.0 (C(9) and C(10)), 126.4 (C(8) and C(11)), 113.5 (pseudo-equatorial nitriles), 111.6 (pseudo-axial nitriles), 60.0 (C(1) and C(4)), 50.6 (C(2) and C(3)), 49.5 (C(7)); ^{29}Si NMR (acetone-d_6, 99.35 MHz): δ −4.7. The presence of the SiOH functionality was verified by a D_2O exchange experiment, and by data obtained from a ^{1}H–^{29}Si HMBC shift-correlated NMR experiment. Anal.: Calcd. for $C_{51}H_{34}N_{12}O_3Si_1$: C 68.75; H 3.85; N 18.86. Found: C 68.62; H 3.77; N 19.03%. A single crystal of **17·(CH$_3$COCH$_3$)$_2$** (colourless prism; 0.16 mm × 0.15 mm × 0.12 mm) grown from acetone was studied by use of X-ray crystallographic techniques, which verified the presence of two molecules of acetone per asymmetric unit, as initially suggested by the elemental analyses data.

Tris(inden-1-yl)hexylsilane, 19

Based on synthetic methods previously described in the literature,[34,35] tris(inden-1-yl)silane, **9**, (210 mg, 0.56 mmol), hex-1-ene (300 mg, 3.6 mmol) and a catalytic amount of Wilkinson's catalyst ($(Ph_3P)_3RhCl$) were sealed in an evacuated tube and kept at 60 °C for 7 d. The resulting solid obtained after removal of the residual olefin *in vacuo* was subjected to flash chromatography on silica gel. Elution with a mixture of hexanes and CH_2Cl_2 (90 : 10) yielded **19**, as a viscous oil (88 mg, 0.19 mmol, 34%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.56–6.99 (m, 48H, aromatic), 6.96 (d of d, $J = 5.4$ Hz and 1.9 Hz, 3H, H(3) in S(1)/R(1)), 6.83 (d of d, $J = 5.4$ Hz and 1.9 Hz, 3H, H(3) in S/R), 6.75 (d of d, $J = 5.4$ Hz and 1.9 Hz, 3H, H(3) in R(3)/S(3)), 6.67 (d of d, $J = 5.4$ Hz and 1.9 Hz, 3H, H(3) in S(2)/R(2)), 6.51 (d of d, $J = 5.4$ Hz and 1.9 Hz, 3H, H(2) in S(1)/R(1)), 6.26 (d of d, $J = 5.4$ Hz and 1.9 Hz, 3H, H(2) in S/R), 5.79 (d of d, $J = 5.4$ Hz and 1.9 Hz, 3H, H(2) in S(2)/R(2)), 5.62 (d of d, $J = 5.4$ Hz and 1.9 Hz, 3H, H(2) in R(3)/S(3)), 3.98 (d, $J = 1.9$ Hz, 3H, H(1) in S(1)/R(1)), 3.56 (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)), 3.25 (d, $J = 1.9$ Hz, 3H, H(1) in S(2)/R(2)), 1.51–0.84 (m, 52H, hexyl); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.7–143.4 (C(3a), C(7a)), 135.3 (C(2) in S(1)/R(1)), 135.0 (C(2) in S/R), 134.9 (C(2) in S(2)/R(2)), 134.9 (C(2) in R(3)/S(3)), 130.4 (C(3) in S(1)/R(1)), 130.1 (C(3) in S/R), 129.6 (C(3) in R(3)/S(3)), 129.5 (C(3) in S(2)/R(2)), 126.0–121.3 (C(4), C(5), C(6) and C(7)), 42.7 (C(1) in S(1)/R(1)), 42.4 (C(1) in S/R), 42.2 (C(1) in R(3)/S(3)), 41.9 (C(1) in S(2)/R(2)), 34.6–11.4 (hexyl). Some ^{1}H and ^{13}C NMR signal assignments were made by comparison with data obtained for tris(inden-1-yl)methylsilane, **7**. Mass spectra: (DEI, *m*/*z* (%)): 458 (8, $[M]^+$), 401 (7, $[M - C_4H_9]^+$), 343 (74, $[M - C_9H_7]^+$), 258 (86, $[Si(C_9H_7)_2]^+$), 143 (100, $[Si(C_9H_7)]^+$), 115 (22, $[C_9H_7]^+$); (high resolution, DEI): calculated for mass $^{12}C_{33}H_{34}Si_1$, 458.2430 amu; observed, 458.2426 amu; Anal.: Calcd. for $C_{33}H_{34}Si_1$: C 86.41; H 7.47. Found: C 86.55; H 7.52%.

Reactions involving HBF$_4$ or Ph$_3$C$^+$PF$_6^-$

To a solution of the silane (0.05 mmol) in CD_2Cl_2 (**8** or **9**) or CD_3CN (**14**, **16** or **17**) was added either $HBF_4{\cdot}O(C_2H_5)_2$ or $Ph_3C^+PF_6^-$ (~0.07 mmol) at −78 °C under nitrogen in an NMR sample tube. In the case of **8** or **9**, the identities of the products (**20** and **21**) were determined based on multidimensional NMR spectral data obtained from the mixture (at −50 °C) immediately thereafter. For **14**, **16** or **17**, the sample was allowed to warm to −30 °C, and the quantitative formation of the corresponding tris(5,6-benzo-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-en-7-yl)fluorosilane, **22**, verified *in situ* by use of NMR spectroscopy. Numerous attempts to isolate analytically pure samples of either **20**, **21** or **22** were unsuccessful.

Tris(5,6-benzo-2,2,3,3-tetracyanobicyclo[2.2.1]hept-5-en-7-yl)fluorosilane, 22

^{1}H NMR (CD_3CN, 500 MHz): δ 7.65 (apparent d (5.7 Hz) of d (3.4 Hz), 6H, H-8,11), 7.56 (apparent d (5.7 Hz) of d (3.4 Hz), 6H, H(9) and H(10)), 3.95 (d, $^3J = 1.0$ Hz, 6H, H(1) and H(4)), 2.11(d ($^3J_{HF} = 4.5$ Hz) of t ($^3J_{HH} = 1.1$ Hz), 3H, H(7)); ^{13}C NMR (CD_3CN, 125 MHz): δ 139.0 (C(5) and C(6)), 131.7 (C(9) and C(10)), 126.3 (C(8) and C(11)), 113.2 (pseudo-equatorial nitriles), 111.7 (pseudo-axial nitriles), 58.9 (C(1) and C(4)), 50.1 (C(2) and C(3)), 48.9 (d, $^2J_{FC} = 12$ Hz, C(7)); ^{19}F NMR (CD_3CN, 282.4 MHz): δ −148.4 (quart., $^3J_{HF} = 4.5$ Hz); ^{29}Si NMR (CD_3CN, 99.35 MHz): δ −8.89 (d, $^1J_{SiF} = 278$ Hz).

Acknowledgements

Financial support from the Natural Sciences and Engineering Research Council (NSERC) of Canada, and from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. M. S. thanks NSERC for a postgraduate fellowship, and McMaster University for a Centennial Scholarship. Mass spectrometric data were obtained courtesy of Dr Kirk Green of the McMaster Regional Center for Mass Spectrometry.

References

1 E. L. Muetterties, *Inorg. Chem.*, 1965, **4**, 769.
2 P. E. Rakita and A. Davison, *Inorg. Chem.*, 1969, **8**, 1164.
3 C. W. Spangler, *Chem. Rev.*, 1976, **76**, 187.
4 R. L. Halterman, *Chem. Rev.*, 1992, **92**, 965.
5 R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 1965, **87**, 2511.
6 R. B. Larrabee and B. F. Dowden, *Tetrahedron Lett.*, 1970, **12**, 915.
7 A. J. Ashe, III, *Tetrahedron Lett.*, 1970, **24**, 2105.
8 M. Stradiotto, S. S. Rigby, D. W. Hughes, M. A. Brook, A. D. Bain and M. J. McGlinchey, *Organometallics*, 1996, **15**, 5645.
9 M. Stradiotto, P. Hazendonk, A. D. Bain, M. A. Brook and M. J. McGlinchey, *Organometallics*, 2000, **19**, 590.
10 M. Stradiotto, D. W. Hughes, M. A. Brook, A. D. Bain and M. J. McGlinchey, *Organometallics*, 1997, **16**, 5563.
11 M. Stradiotto, M. A. Brook and M. J. McGlinchey, *Inorg. Chem. Commun.*, 1998, **1**, 105.
12 A. Davison and P. E. Rakita, *J. Organomet. Chem.*, 1970, **23**, 407.
13 L. H. Sommer and N. S. Marans, *J. Am. Chem. Soc.*, 1951, **73**, 5135.
14 Y. Chen, M. D. Rausch and J. C. W. Chien, *Organometallics*, 1993, **12**, 4607.
15 S. S. Rigby, L. Girard, A. D. Bain and M. J. McGlinchey, *Organometallics*, 1995, **14**, 3798.

16 M. Stradiotto, M. A. Brook and M. J. McGlinchey, *New J. Chem.*, 1999, 317.

17 A. D. McMaster and S. R. Stobart, *J. Am. Chem. Soc.*, 1982, **104**, 2109.

18 Strictly speaking, a C_3 isomer exists for (inden-1-yl)$_3$MR complexes only when the "R" fragment is either linear or possesses three-fold symmetry about the Si–R molecular axis.

19 J. L. Atwood, A. D. McMaster, R. D. Rogers and S. R. Stobart, *Organometallics*, 1984, **3**, 1500.

20 B. Thiyagarajan, R. F. Jordan and V. G. Young, *Organometallics*, 1998, **17**, 281.

21 G. Klebe, *J. Organomet. Chem.*, 1985, **293**, 147.

22 If the position of the hydroxyl hydrogen atom is ignored, **17** could, in principle, adopt a geometry with C_3 or even C_{3V} symmetry.

23 R. Ruffolo, S. Kainz, H. K. Gupta, M. A. Brook and M. J. McGlinchey, *J. Organomet. Chem.*, 1997, **547**, 217.

24 R. J. P. Corriu, J. J. E. Moreau and H. Praet, *Organometallics*, 1989, **8**, 2779.

25 C. L. Perrin and T. J. Dwyer, *Chem. Rev.*, 1990, **90**, 935.

26 M. Grassi, B. M. Mann, B. T. Pickup and C. M. Spencer, *J. Magn. Reson.*, 1986, **69**, 92.

27 J. J. Led and H. Gesmar, *J. Magn. Reson.*, 1982, **49**, 444.

28 D. R. Muhandiram and R. E. D. McClung, *J. Magn. Reson.*, 1987, **71**, 187.

29 A. D. Bain and J. A. Cramer, *J. Magn. Reson.*, 1996, **A 118**, 21.

30 G. M. Sheldrick, SMART (1996), Release 4.05; Siemens Energy and Automation Inc., Madison, WI 53719.

31 G. M. Sheldrick, SAINT (1996), Release 4.05; Siemens Energy and Automation Inc., Madison, WI 53719.

32 G. M. Sheldrick, SADABS (Siemens Area Detector Absorption Corrections) (1996).

33 G. M. Sheldrick, Siemens SHELXTL (1994), Version 5.03; Siemens Crystallographic Research Systems, Madison, WI 53719.

34 R. N. Haszeldine, R. V. Parish and R. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1974, 2311.

35 R. N. Haszeldine, R. V. Parish and D. J. Parry, *J. Chem. Soc. (A)*. 1969, 683.

Paper b000458h