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Inclusion Properties of 1,4-(Triorganostannyl and -silyl)buta-1,3-diynes: Thermal, Structural, and NMR Spectroscopic Aspects

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The tin-containing diyne $Ph_3SnC\equiv CC\equiv CSnPh_3$ (**4**) forms 1:1 host−guest complexes with a large variety of organic molecules. These complexes have been characterized by ^1H NMR spectroscopy, thermogravimetry (TGA), and differential scanning calorimetry (DSC). Weak interactions between the host and guest molecules are observed with toluene, tetrachloroethane, and *p*-xylene (the latter gives a 2:1 complex). Strong interactions are found with dichloromethane, chloroform, tetrahydrofuran, and dioxane. An intermediate behavior is observed with acetone, benzene, and pyridine. Guest-selectivity studies have been carried out on some of these complexes that confirm the results obtained from the TGA measurements. A single-crystal X-ray diffraction analysis of **4**:dioxane shows that it has a true clathrate (cage) structure with the guest molecule being surrounded by 12 phenyl groups from 6 Ph_3Sn moieties. Inclusion compounds do not form when the length of the spacer is shortened, i.e. with $Ph_3SnC\equiv CSnPh_3$, or when the $SnPh_3$ groups of **4** are replaced by $SnMe_3$ moieties. On going from $Ph_3SnC\equiv CC\equiv CSnPh_3$ to $Ph_3Sn(CH_2)_4SnPh_3$, i.e. when the rigid diacetylene fragment is replaced by the flexible butanediyl group, formation of a clathrate is observed only in the case of dioxane. When $Ph_2PC\equiv CC\equiv CPPh_2$ or $Ph_3SiC\equiv CC\equiv CSiPh_3$ is used as host instead of $Ph_3SnC\equiv CC\equiv CSnPh_3$, there is no evidence for clathrate formation. However, in the case of $Ph_3SiC\equiv CC\equiv CSi^*MePhNp$ (**5**: Np = 1-naphthyl), a 1:1 clathrate is obtained with dioxane. A single-crystal X-ray diffraction analysis of the **5**:dioxane inclusion compound shows that the guest molecule lies exclusively in channels formed by phenyl substituents from the Ph_3Si groups. Solid-state ^{13}C, ^{119}Sn, and ^{29}Si NMR and X-ray powder diffraction analyses have been carried out on **4**:$CHCl_3$, **4**:dioxane and **5**:dioxane prior to and after removal of the guest molecules, and the results demonstrate the structure-stabilizing ability of these molecules. It has been possible to obtain single crystals of **4** with no included solvent, and the X-ray crystal structure of this material shows that the organization of the diacetylenic compound is such that it leads to a more compact packing as compared to that found in **4**:dioxane.

Introduction

Diacetylenic compounds with bulky end groups, commonly called wheel-and-axle molecules, can act as hosts in clathrate structures.[1−4] The diacetylenic moiety is a rigid spacer that keeps the bulky groups apart and inhibits close packing of the molecules. Voids are created where solvent molecules can nest.

Diynes **1**, in which no strongly polar groups are present, have been found to give host−guest complexes with benzene, toluene, xylenes, and chloroform.[5]

$$Ar_3CC\equiv CC\equiv CCAr_3$$

1

Ar_3 = Ph_3, Ph_2(*p*-biphenyl), Ph(*p*-biphenyl)$_2$, (*p*-biphenyl)$_3$

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A structural study of the 1:1 complex between (*p*-biphenyl)$Ph_2CC{\equiv}CC{\equiv}CCPh_2$(*p*-biphenyl) and *p*-xylene indicates that CH···π interactions are the predominant interactions in these clathrates: such contacts may be found between the guest molecule and the aryl groups from the host and, also, are the way by which aryl groups from neighboring host molecules interact with one another.[5,6]

The distance between the bulky end groups of the host may be increased. For instance, $Ph_3C(C{\equiv}C)_3CPh_3$ forms a stable 1:1 complex with *p*-xylene and somewhat less stable complexes with benzene, toluene, *o*-xylene, and chlorobenzene.[5]

To analyze the influence of the rigid molecular axis on clathrate formation, sp^2- and sp^3-hybridized carbons were incorporated in the structure and it was found that the new compounds still functioned as hosts toward toluene and xylenes. For instance, the following clathrates were obtained:[5]

$$Ph_3CCH{=}CHCH{=}CHCPh_3\text{:toluene (3:1)}$$

$$Ph_3CCH_2CH{=}CHCH_2CPh_3\text{:toluene (1:1)}$$

$$Ph_3C(CH_2)_4CPh_3\text{:toluene (1:1)}$$

In this series of compounds, all of those that were characterized by crystallography were of the channel type, meaning that, to some degree, the nature of the central part of the host and the type of guest have only little impact on the structure of the clathrate. The key feature seems to be the bulkiness of the end groups and the way they interact with one another. The organization of the clathrate is also dependent on interactions that exist between the guest molecule and the host: it was observed that the plane of the toluene ring in the channel was not random but was involved in CH···π interactions with phenyl substituents from the host.[5,6] These interactions undoubtedly contribute to the stability of the host−guest complexes.

CH···π contacts may be found with groups other than aromatics. Thus, such interactions have recently been observed by Müller et al. in the case of the 1:2 host−guest complex bis[(naphthyldiphenylphosphino)gold]-acetylene−chloroform;[7] these involve the weakly acidic hydrogen of the chloroform molecule and the electron-rich triple bond.

Replacement of an aryl group with an hydroxyl functionality leads to clathrates where hydrogen bonding is present:[2]

$$Ar_2C(OH)C{\equiv}CC{\equiv}C(OH)Ar_2$$

2

Molecules such as **2** form host−guest complexes that have found applications in the resolution of racemates.[8] Using the optically active host *l*-1,6-diphenyl-1,6-bis(*o*-chlorophenyl)hexa-2,4-diyne-1,6-diol (**3**), and *dl*-3-methylcyclohexanone, Toda et al. have obtained the clathrate **3**:*d*-3-methylcyclohexanone (1:2), which liberates *d*-3-methylcyclohexanone upon heating.

On the basis of these results, we decided to investigate the inclusion properties of diacetylene compounds possessing heteroelement-containing groups such as SiR_3, SnR_3, and PPh_2. These heteroelements are larger than carbon and may favor the creation of voids in the crystal, possibly leading to novel structural types. Furthermore, the differences that exist in their electronic properties and the panel of substituents available with these heteroelements make these derivatives attractive.

Only one short paper has appeared in the literature concerning the structure of a tin-containing clathrate, namely 1,4-bis(triphenylstannyl)buta-1,3-diyne (**4**):chloroform (1:1), which was determined by single-crystal X-ray diffraction.[9] The lead analogue of **4** gives an inclusion complex with dichloromethane.[9]

In this paper we generalize the inclusion properties of **4**; i.e., we study clathrate formation from it and determine the stability of the host−guest complexes via thermogravimetric analysis (TGA) and selectivity studies. A study of the relationship between ^{13}C and ^{119}Sn solid-state NMR results and X-ray powder diffraction data is presented that demonstrates the templating effect of the guest molecule. The solid-state structure of **4**:dioxane is also reported, and it is compared with that of the unsolvated material. Steric and electronic factors are evaluated by changing (i) the substituents attached to the heteroelement (aryl or methyl), (ii) the nature of the heteroelement (Si, Sn, P), and (iii) the length and rigidity of the spacer between the two heteroelements.

Results and Discussion

1. Formation, Characterization and Stability of the Host−Guest Complexes. $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ (**4**) was dissolved in various organic solvents (benzene, dioxane, chloroform, etc.) and allowed to crystallize (see Experimental Section). Compound **4** does not come out of solution when *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) are used to dissolve it, even though it is only sparingly soluble in these solvents. A ^{119}Sn NMR spectroscopic study of the DMF and DMSO solutions indicates that the structure of **4** is unchanged in these solvents ($\delta(^{119}Sn(DMF))$ −185.6 and $\delta(^{119}Sn(DMSO))$ −205.4 ppm). Diyne **4** is not soluble in ethanol. With mesitylene, the crystals that formed showed no inclusion of solvent. In all of the other cases, the crystals that were obtained corresponded to clathrates which were analyzed by ^1H NMR spectroscopy and TGA. The results are summarized in Table 1.

Compound **4** is capable of including a large variety of molecules, e.g. halogenated hydrocarbons (dichloromethane, chloroform, 1,1′,2,2′-tetrachloroethane, and 2-chloropropane), polar molecules (acetone, tetrahydrofuran, dioxane, and acetonitrile), and aromatic solvents (benzene, toluene, *p*-xylene, and pyridine).

The stoichiometry observed in these clathrates is typically 1:1. One exception is the **4**:*p*-xylene complex, for which the host−guest ratio is 2:1. As the steric demand of the guest molecule increases, as in the case

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Table 1. Stoichiometry and Thermal Stability of the 4:solvent Clathrates As Determined by ^{1}H NMR Spectroscopy and TGA Measurements

solvent	host−guest ratio (^{1}H NMR)	TGA[a]			T_b of solvent, °C	$T_f - T_b$,[e] °C
		Δm_{obs},[b] %	Δm_{th},[c] %	ΔT,[d] °C		
dichloromethane	1:1	10.2	10.2	50−110	40	70
chloroform	1:1	13.7	13.8	55−110	61	50
tetrachloroethane	1:1	18.5	18.3	50−95	147	−50
isopropyl chloride	1:1	*f*			35	
acetone	1:1	5.7	7.2	room temp−65	56	10
tetrahydrofuran	1:1	8.8	8.8	70−135	66	70
dioxane	1:1	10.6	10.5	80−160	101	60
acetonitrile	1:1	*f*			81	
benzene	1:1	9.1	9.5	45−100	80	20
toluene	1:1	7.1	11.0	room temp−60	110	−50
pyridine	1:1	9.6	9.5	65−110	115	−5
p-xylene	2:1	6.6	6.6	70−95	138	−40

[a] Thermogravimetric analyses were carried out under argon between 20 and 350 °C with a heating rate of 5 °C/min. [b] Observed weight losses. [c] Expected weight losses. [d] Temperature domain for the weight loss. [e] Difference between the final temperature of the weight loss (T_f) and the boiling point of the guest molecule (T_b). [f] The solubility of **4** in these solvents is too low, and so enough clathrate could not be obtained to carry out TGA measurements.

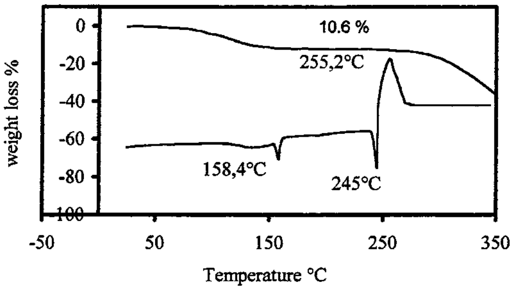

Figure 1. DSC and TGA curves of **4**:dioxane.

of mesitylene, crystals of **4** are obtained without inclusion of a guest.

TGA measurements confirm the stoichiometries determined by ^{1}H NMR analysis (Table 1). The observed weight losses correspond to the departure of the included solvent and take place before the melting of **4** (245 °C). As an example, Figure 1 shows the differential scanning calorimetry (DSC) and TGA curves of the **4**:dioxane complex.

The TGA curve of **4**:dioxane shows a weight loss of 10.6% between 80 and 160 °C; the calculated value for the complete loss of dioxane is 10.5%. The first endotherm of the DSC curve indicates that the loss of the guest molecule occurs in a single step (between 80 and 160 °C), while the second endotherm corresponds to the melting of the host compound. The exothermic peak observed at higher temperatures corresponds to the polymerization of the diacetylene units.

Elemental analyses were carried out on two of the most stable **4**:solvent clathrates, and the results are in good agreement with the compositions determined by ^{1}H NMR and TGA measurements (see Experimental Section).

The thermal stability of the host−guest complexes may be assessed from the DSC and TGA curves.[10] The ΔT values (Table 1) corresponding to the temperature range in which the solvent is lost depends on the boiling point of the guest molecule and the interactions with the host. It gives an estimation of the stability of the clathrates. The stability may also be related to the difference $T_f - T_b$ between the final temperature of the weight loss (T_f) and the boiling point of the guest (T_b). These values are given in Table 1 and agree well with the order of stability determined from ΔT values.

The **4:**solvent clathrates may be divided into three classes according to their stability.

(i) Weak interactions ($-50 \leq T_f - T_b \leq -40$) are observed for the inclusion compounds prepared from **4** and toluene or tetrachloroethane. The release of the guest occurs in a temperature range that is much lower than the boiling point of the solvent. Furthermore, the weight loss observed by TGA for the **4**:toluene inclusion compound is smaller than that expected from ^{1}H NMR measurements; this is due to partial loss of the solvent during sample preparation.

(ii) Strong interactions ($50 \leq T_f - T_b \leq 70$) are observed when the weight loss occurs in a large temperature domain that is higher than or barely includes the boiling point of the solvent. Strong interactions are observed for the clathrates prepared from dichloromethane, chloroform, tetrahydrofuran, and dioxane.

(iii) An intermediate behavior ($-5 \leq T_f - T_b \leq 20$) is observed with acetone, benzene, and pyridine. In this case, the weight loss occurs just below the boiling point of the solvent or the final temperature is close to that boiling point.

The **4**:*p*-xylene complex is different from the other clathrates analyzed in this study, as the host−guest ratio is 2:1. However, on the basis of the ΔT and $T_f - T_b$ values, it is clear that this complex belongs to the first class of compounds, i.e. those with weak host−guest interactions.

The size of the guest is important. This is illustrated in the case of the aromatic solvents: with benzene, the clathrate that is formed is fairly stable but, with toluene, the stability is much lower. When two methyl groups are present on the aromatic ring, i.e. in the case of *p*-xylene, the nesting of the guest becomes more difficult and the stoichiometry (and the structure) of the clathrate changes. Finally, when mesitylene is used, crystals are formed that do not include a guest. The same holds true for the halogenated hydrocarbons used in this study: it is indeed observed that the stability of the **4**:solvent clathrates decreases in the order $CH_2Cl_2 > CHCl_3 > CHCl_2CHCl_2$.

Isopropyl chloride and acetonitrile behave differently (Table 1); they are very poor solvents of $Ph_3SnC{\equiv}CC{\equiv}$

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Table 2. Guest-Selectivity Properties of Host 4

solvent mixture 50:50 (v/v)	guest	stoichiometry
pentane−chloroform	chloroform	1:1
benzene−acetone	benzene	1:1
dioxane−*p*-xylene	dioxane	1:1

Table 3. Solid-State ^{13}C and ^{119}Sn NMR Data of the 4:CHCl$_3$ and 4:dioxane Clathrates

	$\delta(^{13}C)$ (ppm) and $^nJ_{SnC}$ (Hz)				$\delta(^{119}$ Sn)
clathrate	C^1, C^4	C^2, C^3	Ph	guest^a	(ppm)
4:CHCl$_3$	82.0 $^1J = 463$	94.3 $^2J = 102$	C^{ipso} 135.0 $^1J = 600$ C^{3,5} 130.0 C^{2,6} 137.7 C^4 131.2	76.8	−165.2
4:dioxane	82.5 $^1J = 460$	94.8 $^2J = 97$	C^{ipso} 135.1 $^1J(^{119}Sn) = 628$ $^1J(^{117}Sn) = 604$ C^{3,5} 130.3 C^{2,6} 137.9 C^4 131.5	67.2	−164.6

[a] In solution: CHCl$_3$, 77.2 ppm; dioxane, 66.7 ppm.

Table 4. ^{13}C and ^{119}Sn NMR Data of the 4:dioxane Clathrate in CDCl$_3$

$\delta(^{13}C)$ (ppm) and $^nJ_{SnC}$ (Hz)				
C^1, C^4	C^2, C^3	Ph	guest^a	$\delta(^{119}Sn)$ (ppm)
82.9 $^1J = 492$ $^4J = 7$	95.0 $^2J = 97$ $^3J = 20$	C^{ipso} 136.5 $^1J(^{119}Sn) = 628$ $^1J(^{117}Sn) = 601$ C^{3,5} 129.3 $^3J(^{119}Sn) = 61$ $^3J(^{117}Sn) = 58$ C^{2,6} 137.2 $^2J(^{119}Sn) = 44$ $^2J(^{117}Sn) = 43$ C^4 130.2 $^4J(^{117/119}Sn) = 13$	67.5	−170.1

[a] In solution: dioxane, 66.7 ppm.

CSnPh$_3$, and so we were unable to obtain enough material to carry out TGA measurements on the corresponding clathrates.

To determine if clathrate formation was selective, we have used mixtures of guest molecules (Table 2).

As shown in Table 2, only one of the two solvents forms a host−guest complex. The clathrate that is formed is always the more stable one on the basis of the results from Table 1: chloroform over pentane, which is a nonsolvent for **4**, benzene over acetone, and dioxane over *p*-xylene.

2. Solid-State NMR and X-ray Powder Diffraction Studies. The interactions that exist in the solid state between **4** and the guest molecules dioxane and chloroform were analyzed by solid-state NMR methods. Indeed, strong interactions between the host and guest molecules are expected to affect the chemical shifts and coupling constants of the concerned atoms.[11] The clathrates were also studied by X-ray powder diffraction.

The solid-state ^{119}Sn and ^{13}C NMR data of **4**:dioxane and **4**:CHCl$_3$ are listed in Table 3, and Table 4 gives the values observed in CDCl$_3$ solution. The ^{119}Sn and ^{13}C NMR spectra of the **4**: dioxane complex are shown in Figures 2a and 3a.

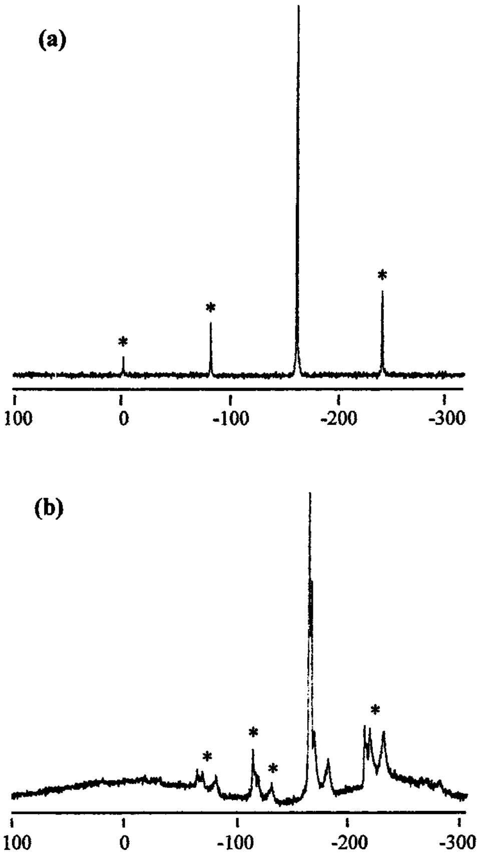

Figure 2. Solid-state ^{119}Sn MAS NMR spectra of **4**: (a) with included dioxane, observation frequency 149.2 MHz, number of transients 8008, recycle delay time 10 s, 0 Hz line broadening, spinning rate 12 kHz; (b) without included dioxane, observation frequency 74.6 MHz, number of transients 8736, recycle delay time 10 s, 0 Hz line broadening, spinning rate 3.7 kHz. Asterisks denote spinning sidebands.

In the solid-state ^{119}Sn NMR spectra (Table 3), only one signal is observed, meaning that, in both cases, the tin atoms are crystallographically equivalent. The observed chemical shifts, −164.6 ppm (**4**:dioxane) and −165.2 ppm (**4**:CHCl$_3$) are close together and differ only slightly from the value measured in CDCl$_3$ (−170.1 ppm) (Table 4). This slight difference indicates that there are no significant structural changes within the host molecule on passing from the solid to the dissolved state; i.e., the tin atoms of the host do not interact with the guest molecules in the inclusion compounds. Similar observations have been made in the case of Me$_3$SnC≡CC≡CSnMe$_3$ that reinforce this presumption: the ^{119}Sn chemical shift in CDCl$_3$ solution, −59.0 ppm, is close to those found in the solid state, −61.5 and −62.7 ppm, and we have established (vide infra) that Me$_3$SnC≡CC≡CSnMe$_3$ does not give host−guest complexes with common laboratory solvents.

The solid-state ^{13}C NMR spectra of **4**:dioxane and **4**:chloroform display sharp lines with nearly the same chemical shifts for the acetylenic carbons. These chemical shifts are close to the values observed in solution, meaning that, if some interactions exist between the solvent and the host, they are the same in solution and in the solid state or that these interactions are weak.

The X-ray powder patterns of **4**:dioxane (Figure 4) and **4**:CHCl$_3$ are identical and show sharp lines indicative of good crystallinity and similar structures for the two clathrates.

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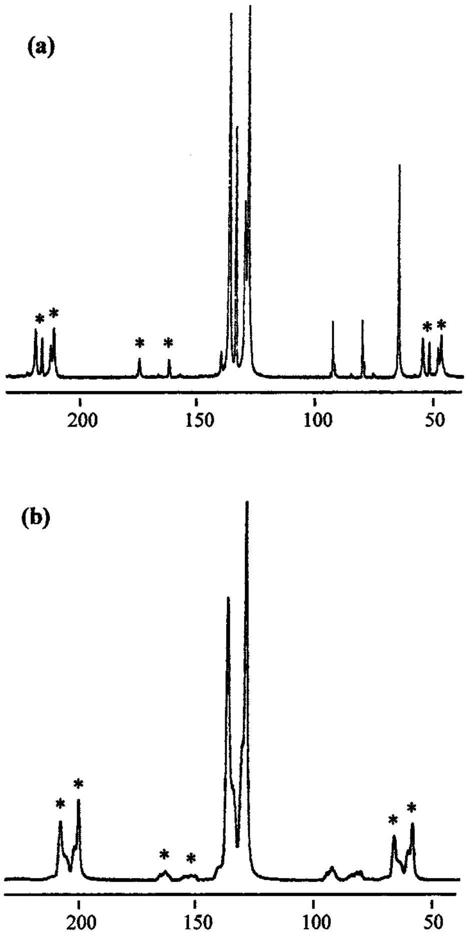

Figure 3. Solid-state ^{13}C CP/MAS NMR spectra of **4**: (a) with included dioxane, observation frequency 50.3 MHz, number of transients 15 184, recycle delay time 5 s, contact time 5 ms, 0 Hz line broadening, spinning rate 4.0 kHz; (b) without included dioxane, observation frequency 50.3 MHz, number of transients 18 056, recycle delay time 5 s, contact time 5 ms, 0 Hz line broadening, spinning rate 3.5 kHz. Asterisks denote spinning sidebands.

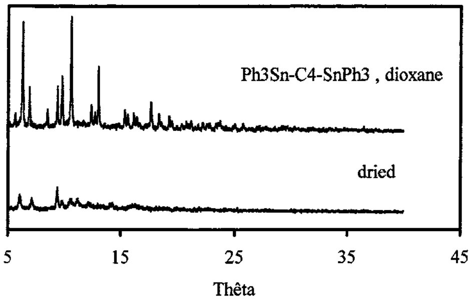

Figure 4. X-ray powder patterns of **4**:dioxane before and after removal of the included solvent molecule.

Table 5. Solid-State ^{13}C and ^{119}Sn NMR Data for the 4:CHCl$_3$ and 4:dioxane Clathrates after Removal of the Guest Molecules

	$\delta(^{13}C)$ (ppm) and $^{n}J_{SnC}$ (Hz)			$\delta(^{119}Sn)$ (ppm) and rel intens
clathrate	C^1, C^4	C^2, C^3	Ph	
4:CHCl$_3$	80.2	91.3	C^{ipso} 133.6	−158.7 (10)
	81.7	92.5	$^1J = 605$	−160.8 (8)
	82.5	93.4	$C^{3,5}$ 128.9	−163.0 (2)
	83.6	94.6	$C^{2,6}$ 136.4	−175.9 (1)
	84.6	*a*	C^4 130.8	
4:dioxane	81.4	93.6	C^{ipso} 135.4	−159.1 (10)
	82.8	94.6	$^1J = 610$	−161.3 (6)
	83.7	95.7	$C^{3,5}$ 129.8	−163.4 (2)
	84.9	*a*	$C^{2,6}$ 137.3	−176.1 (1)
	85.9		C^4 131.3	

[a] Additional ill-defined resonances are observed in the spectrum.

To assess the structuring ability of the guest molecule, clathrates **4**:dioxane and **4**:CHCl$_3$ were heated at 40−50 °C under vacuum to remove the included solvent molecules. The residues were analyzed by solid-state ^{119}Sn and ^{13}C NMR spectroscopy and X-ray powder diffraction. Figures 2b and 3b show the solid-state ^{119}Sn MAS and ^{13}C CP/MAS NMR spectra of the **4**:dioxane inclusion compound after removal of the guest molecule, and Table 5 summarizes the NMR results.

The solid-state ^{119}Sn NMR spectra of the dried samples display four resonances with different intensities, suggestive of tin atoms in four different types of environments instead of just one as observed in the case of the clathrates. This complexity is also evident in the solid-state ^{13}C NMR spectra: a minimum of three well-defined resonances are observed for each acetylenic carbon. The symmetry of the molecule is completely lost after removal of the guest molecule from the clathrate. This is confirmed by an X-ray diffraction analysis of the dried material (Figure 4) that shows the loss of crystallinity of the sample. These results demonstrate that the guest molecule acts as a "template" in the crystal structure; its removal destroys the organization of the crystal lattice. This is in sharp contrast with what is observed in the case of clathrasils.[12] These data also show how powerful solid-state NMR is in providing information about the organization and the structure of inclusion compounds.[13] This conclusion is further exemplified in the case of Ph$_3$SiC≡CC≡CSi*MePhNp: dioxane (**5**; Np = 1-naphthyl) (vide infra).

3. Single-Crystal X-ray Diffraction Analysis of Ph$_3$SnC≡CC≡CSnPh$_3$:dioxane. The ZORTEP[14] drawing of the host part of the **4**:dioxane complex is shown in the Supporting Information, and the corresponding crystal data are summarized in Table 6. The crystal structure of **4**:dioxane is centrosymmetric with inversion centers located at the center of the diacetylene unit, i.e. between C_8 and C_8', and at the center of the dioxane molecule. It also has 3-fold symmetry with the C_3 axis passing through the four acetylenic carbons and the two tin atoms. The SnPh$_3$ moieties are propeller-shaped.

Full lists of bond lengths and angles are given in the Supporting Information. The lengths of the triple bonds (1.186(4) Å) and the single bond (1.417(6) Å) are close to those found in related diacetylenic molecules.[9,15,16]

The unit cell consists of four Ph$_3$SnC≡CC≡CSnPh$_3$ units and four dioxane molecules. The origin of the cell was chosen so as to place the center of one of the dioxane

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Table 6. Crystal Data for $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$:dioxane, $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$, and $Ph_3SiC{\equiv}CC{\equiv}CSi^*MePhNp$:dioxane

	4:dioxane	**4**	**5**:dioxane
formula	$C_{44}H_{38}O_2Sn_2$	$C_{40}H_{30}Sn_2$	$C_{43}H_{38}O_2Si_2$
mol wt	836.12	748.02	642.95
cryst color	colorless	colorless	colorless
cryst size, mm	0.50 × 0.30 × 0.20	0.40 × 0.30 × 0.30	0.4 × 0.4 × 0.2
cryst syst	cubic	triclinic	monoclinic
space group	$Pa\bar{3}$ (No. 205)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)
a, Å	15.6723(7)	13.5023(19)	9.423(2)
b, Å		22.231(3)	8.973(2)
c, Å		9.5759(15)	20.728(3)
α, deg		91.785(18)	
β, deg		103.526(18)	95.31(1)
γ, deg		75.570(18)	
V, Å^3	3849.4(3)	2503.0(7)	1745.1(6)
Z	4	3	2
d_{calcd}, g cm^{-3}	1.443	1.488	1.224
$F(000)$	1672	1110	680
μ, mm^{-1}	1.332	1.521	0.132
temp of data collctn, K	293	180	155
radiation, graphite-monochromated	Mo Kα	Mo Kα	Mo Kα
$2\theta_{max}$, deg	50	48.4	50
no. of unique rflns	1135	7313	3044
no. of obsd rflns	781 ($F_o > 4\sigma(F_o)$)	6422 ($F_o > 4\sigma(F_o)$)	2136 ($F > 6.0\sigma(F)$)
no. of variables	76	568	204
R	0.0249[a]	0.0194[a]	0.0575[a]
R_w	0.0686[b]	0.0398[b]	0.0629[c]
residual electron dens, e Å^{-3}	0.18	0.39	0.45
goodness of fit, S	1.070	0.981	0.997

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o{}^2|^2]^{1/2}$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

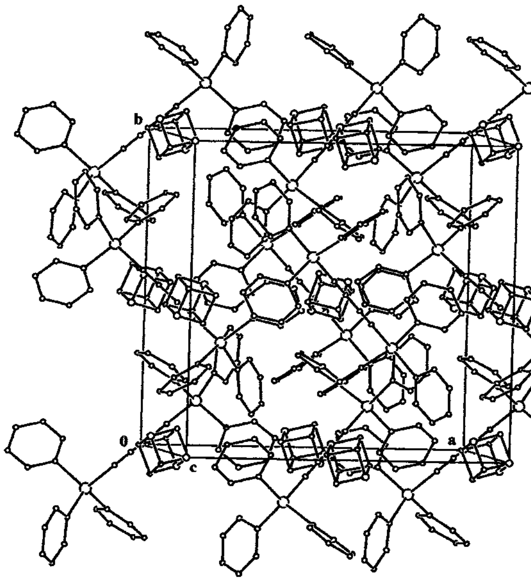

Figure 5. Packing diagram of **4**:dioxane.

molecules at the coordinate 1/2, 1/2, 1/2. By doing so, the packing around the cell center is made of eight half-molecules of compound **4**. The remaining dioxane molecules are located in the middle of each edge of the cell (Figure 5).

The best fit to the diffraction data is achieved when the dioxane molecule is disordered between three positions, each of them accounting for one-third occupation. This model respects the 3-fold rotation axis which passes through the oxygen atoms of the latter molecule. The guest is located in a cavity formed by 12 phenyl groups from 6 different molecules of **4**. A simplified representation of this arrangement is shown in Figure 6. The shortest distances between the guest molecule and the host are as follows: 3.404 Å for O(dioxane)···H(phenyl), 3.319−3.687 Å for C(dioxane)···H(phenyl), 2.953−3.594 Å for H(dioxane)···C(phenyl), and 2.378−2.798 Å for H(dioxane)···H(phenyl). No diacetylene fragment appears to delimit the cavity.

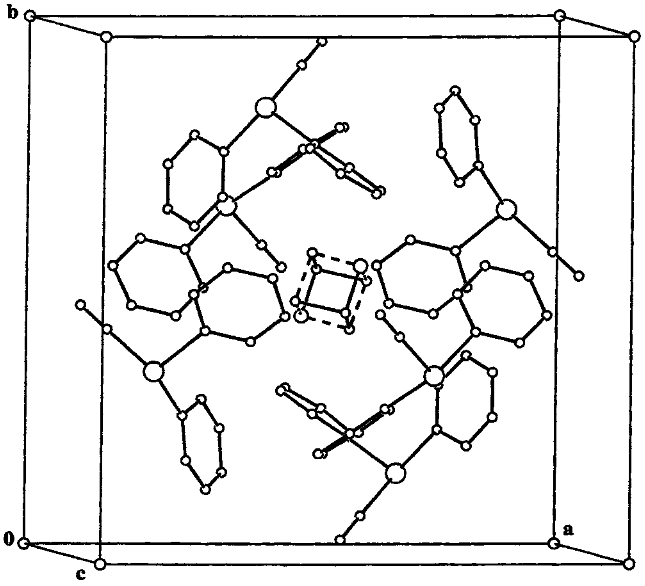

Figure 6. Arrangement of the diphenyltin moieties around the dioxane molecule in **4**:dioxane.

It is clear from these data that the interactions between the host and the guest are weak, and so it is not surprising to find that the guest molecule is disordered. Similar observations were made in the case of the **4**:$CHCl_3$ clathrate.[9] However, these results are in sharp contrast with those found for Hart's complexes, for which fairly strong CH···π interactions between the host and guest molecules were observed, thus preventing any disorder of the guest from occurring.[5,6] An analysis of the packing of the (p-biphenyl)$Ph_2CC{\equiv}CC{\equiv}CCPh_2$($p$-biphenyl):$p$-xylene inclusion compound reveals that one hydrogen from a phenyl ring from the host, H(65), interacts strongly with all of the aromatic carbon atoms from a nearby p-xylene molecule: the six H(65)···C_{arom} contacts range from 2.923 to 3.366 Å.[6] There is also one short (2.809 Å) H(biphenyl)···C_{arom}(p-xylene) distance. In our case, the dioxane molecule simply fills the empty spaces that are in the structure.

It may be thought that the cavity in **4**:dioxane arises from strong interactions between phenyl groups from the host. These interactions do exist, but they do not appear to be extremely strong: there is only one intermolecular distance smaller than 2.97 Å, i.e. 2.961 Å between H(4) and C(3), and there are four intermolecular H···C contacts between phenyl groups close to 3.1 Å. These interactions are of the edge-to-face type[17] with, however, some variations: the interaction between the H(2)−C(2)−C(3)−H(3) fragment and carbon atoms from a neighboring phenyl ring is similar to the tilted T structure reported by Jorgensen and Severance.[17f] The interaction between H(4) and all of the carbon atoms

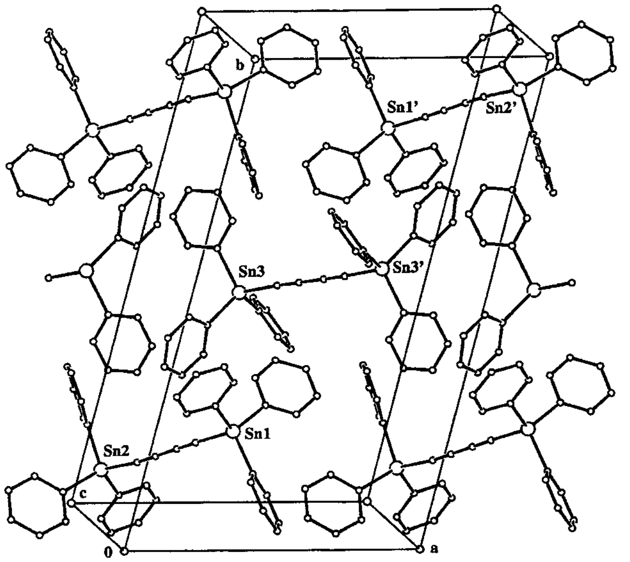

Figure 7. Packing diagram of **4**.

from a nearby phenyl ring (the six H(4)···C_{arom} distances range from 2.961 to 3.814 Å) resembles the "T-stacked" configuration described in Burley's paper.[17d] H(5) is in close contact with only two carbon atoms from a neighboring phenyl ring (H(5)···C(5) = 3.171 Å and H(5)···C(6) = 3.092 Å), and the same is true for H(6) (H(6)···C(4) = 3.747 Å and H(6)···C(5) = 3.248 Å). These interactions are weaker than those encountered in **4**:$CHCl_3$, $Ph_3PbC{\equiv}CC{\equiv}CPbPh_3$:$CH_2Cl_2$ and (*p*-biphenyl)-$Ph_2CC{\equiv}CC{\equiv}CCPh_2$(*p*-biphenyl):*p*-xylene.[6] In the case of **4**:$CHCl_3$, one phenyl hydrogen, H(4), interacts strongly in a "T-stacked" fashion with all of the carbon atoms from a nearby phenyl ring (the six H(4)···C_{arom} distances range from 2.633 to 3.357 Å). A similar edge-to-face interaction is observed in the case of $Ph_3PbC{\equiv}CC{\equiv}CPbPh_3$:$CH_2Cl_2$: the six H(3)···$C_{arom}$ contacts range from 2.822 to 3.224 Å. In the case of (*p*-biphenyl)$Ph_2CC{\equiv}CC{\equiv}CCPh_2$(*p*-biphenyl):*p*-xylene, there are two H(phenyl)···C(biphenyl) distances smaller than 2.97 Å, i.e. H(15)···C(32) = 2.906 Å and H(15)···C(33) = 2.959 Å.

The size of the nearly spherical cavity of **4**:dioxane was calculated from the hydrogen atoms nearest to the center of the cell. The lower and upper limits for the diameter are respectively 6.37 and 6.42 Å, and these values take into account the van der Waals radii of the hydrogens as defined by Bondi.[18]

4. Single-Crystal X-ray Diffraction Analysis of $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ without Included Solvent Molecule. To determine the changes brought about to the solid-state structure of **4** by the solvent molecule, a single-crystal X-ray diffraction study was conducted on the material containing no included solvent. Crystals suitable for the diffraction experiment were grown from mesitylene. In this case we find that compound **4** crystallizes in the low-symmetry space group $P\bar{1}$ with three molecules per unit cell: one molecule occupies a general position, and the other one lies on a center of inversion (Figure 7).

At the molecular level, **4** no longer has the $\bar{3}$ symmetry observed in the **4**:dioxane inclusion compound: for both types of molecules present in the cell of **4**, it is found that the tin atoms are not aligned with the four acetylenic carbons (see the Supporting Information). The angles formed by three adjacent C_{sp} carbons deviate slightly from 180°; a more significant deviation is observed for the $SnC{\equiv}C$ fragments of the molecule. The length of the central C−C bond in **4**, ca. 1.38 Å, is shorter than that found in **4**:dioxane by about 0.04 Å, and this seems to compensate for the fact that the C≡C bonds in the former compound are longer, i.e. about 1.20 Å versus 1.186 Å. No major differences are observed between the two structures concerning the lengths of the Sn−C bonds. They all range from 2.11 to 2.13 Å.

As far as the packing of the cell is concerned, we find that a major change in the organization of the diacetylenic molecules has occurred, as compared to that observed in **4**:dioxane, so as to minimize the size of the voids between the chains. In fact, sizable voids are not present in the structure, as indicated by the many short intermolecular carbon···carbon distances: there are eight C(phenyl)···C(phenyl) distances between 3.391 and 3.794 Å and three C(acetylenic)···C(phenyl) distances between 3.797 and 3.950 Å.

We also find that there are a great many more intermolecular contacts between phenyl groups than are observed in the **4**:dioxane structure, and these interactions are stronger. There are 10 distances H(phenyl)···C(phenyl) smaller than 2.97 Å, with the smallest one being 2.803 Å between H(53) and C(56).

5. Extension to Other Clathrates. To determine the main factors controlling the formation and stability of the clathrates, the structure of the host molecule has been modified in three different ways: (i) modification of the end groups, (ii) change in the nature of the heteroelement, and (iii) modification of the length and rigidity of the bridge between the bulky end groups.

(i) Hart et al. have shown that the bulkiness of the end groups in wheel-and-axle-type compounds was involved in the creation of cavities in which the guest molecule could nest.[5] We have prepared $Me_3SnC{\equiv}CC{\equiv}CSnMe_3$, which corresponds to the replacement of all of the phenyl groups in **4** by methyl groups. This tin derivative crystallizes easily from acetone, toluene, and chloroform, but no inclusion of solvent is observed. Most likely, the cavities are too small to allow the formation of a clathrate. Steric arguments are obviously important when trying to rationalize these results. However, removal of all of the aromatic substituents on tin also induces a change in the electronic factors of the host molecule and modifies the packing ability due to the aromatic groups: CH···π interactions are no longer possible in the case of $Me_3SnC{\equiv}CC{\equiv}CSnMe_3$.

(ii) The $SnPh_3$ groups of $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ (**4**) have been replaced by $SiPh_3$ and PPh_2 moieties. The

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(17) (a) Cox, E. G.; Cruickshank, D. W. J.; Smith, J. A. S. *Proc. R. Soc., Ser. A (London)* **1958**, *247*, 1. (b) Burley, S. K.; Petsko, G. A. *Science (Washington, D.C.)* **1985**, *229*, 23. (c) Perutz, M. F.; Fermi, G.; Abraham, D. J.; Poyart, C.; Bursaux, E. *J. Am. Chem. Soc.* **1986**, *108*, 1064. (d) Burley, S. K.; Petsko, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 7995. (e) Askew, B.; Ballester, P.; Buhr, C.; Jeong, K. S.; Jones, S.; Parris, K.; Williams, K.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 1082. (f) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768. (g) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525. (h) Hunter, C. A. *Chem. Soc. Rev.* **1994**, 101. (i) Dougherty, D. A. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 2; Chapter 6, pp 195−209. (j) Weiss, H.-C.; Bläser, D.; Boese, R.; Doughan, B. M.; Haley, M. M. *Chem. Commun.* **1997**, 1703.

(18) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

heteroelement is expected to modify the ability of the molecule to form host−guest complexes by its size and coordination number. 1,4-Bis(diphenylphosphino)buta-1,3-diyne crystallizes from acetone, toluene, and chloroform, but no inclusion of solvent is observed. This result can be explained by the coordination number of 3 for phosphorus instead of 4 for tin, which must diminish the potential formation of cavities large enough to accommodate solvent molecules in the crystalline state. In agreement with this, $Ph_2P(Se)(CH_2)_2(Se)PPh_2$ is known to be a host toward various aromatic solvents.[19] Nonetheless, electronic effects due to the presence of a lone pair on phosphorus in $Ph_2PC{\equiv}CC{\equiv}CPPh_2$ cannot be completely ruled out.

When the tin atoms of compound **4** are replaced by silicon atoms, namely in the case of $Ph_3SiC{\equiv}CC{\equiv}CSiPh_3$, no inclusion complex forms upon crystallization from the same solvents as those used in the case of **4**, e.g. THF, dioxane, chloroform, dichloromethane, toluene, *p*-xylene, and pyridine, as determined by ^1H NMR spectroscopy. This result is somewhat unexpected, as $Ph_3CC{\equiv}CC{\equiv}CCPh_3$ is known to give a 1:1 inclusion compound with chloroform.[5] The difference that exists between $Ph_3SiC{\equiv}CC{\equiv}CSiPh_3$ and $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ can easily be rationalized on the basis of the fact that silicon and tin have very different atomic radii, i.e. 1.17 Å for silicon and 1.40 Å for tin.[20] However, effects due to the size of the heteroelement cannot account for the difference that exists between $Ph_3SiC{\equiv}CC{\equiv}CSiPh_3$ and $Ph_3CC{\equiv}CC{\equiv}CCPh_3$, as carbon has a much smaller atomic radius than silicon.[20] This difference is believed to arise from electronic effects, due to the fact that carbon has a much higher Pauling electronegativity than silicon: i.e. 2.5 for carbon and 1.8 for silicon.[20] Nonetheless, electronic effects can be overpowered by crystal packing forces; this is suggested by the observation that a 1:1 inclusion complex forms between $Ph_3SiC{\equiv}CC{\equiv}CSi^*MePhNp$ (**5**) and dioxane. The X-ray crystal structure of this clathrate indicates that the guest molecule sits in channels formed by Ph_3Si groups from the host (vide infra).

(iii) The role of the bridging carbon chain was studied by changing its length and rigidity. The formation of inclusion compounds was tested with $Ph_3SnC{\equiv}CSnPh_3$. This derivative only has one triple bond instead of two in **4**. $Ph_3SnC{\equiv}CSnPh_3$ crystallizes from chloroform, dioxane, THF, toluene, pyridine, chlorobenzene, and trichloroethylene without the inclusion of a solvent molecule. Solvent−metal interactions appear to be absent in solution, as evidenced by the closeness between the solid-state and solution ^{119}Sn NMR data. The chemical shifts of the resonances observed in the ^{119}Sn CP/MAS NMR spectrum of $Ph_3SnC{\equiv}CSnPh_3$ are −184.6 and −198.3 ppm. The values found in solution are as follows: −176.1 ppm ($CDCl_3$),[21] −174.0 ppm (toluene), −177.1 ppm (pyridine), and −179.6 ppm (dioxane).

To change the flexibility of the carbon chain, without changing drastically the distance between the two bulky triphenyltin groups, we have replaced the 1,3-butadiyne-1,4-diyl spacer by the saturated 1,4-butanediyl group. $Ph_3Sn(CH_2)_4SnPh_3$ was allowed to crystallize from chloroform, dioxane, THF, toluene, chlorobenzene, and pyridine; inclusion of solvent in the crystal was observed only in the case of dioxane. The stoichiometry of the inclusion compound is 1:1, as determined by ^1H NMR spectroscopy and TGA measurements. Thus, clathrate formation occurs only with the solvent giving the most stable complex with **4**. Furthermore, the temperature range for the weight loss (between 40 and 90 °C) shows that the clathrate $Ph_3Sn(CH_2)_4SnPh_3$:dioxane is less stable than the clathrate with the rigid diacetylene spacer **4**:dioxane (see Table 1).

In summary, the results described above show that one triple bond is not sufficiently long to allow the formation of cavities capable of including guest molecules. With a spacer of four carbons, the main factor controlling the formation of host−guest complexes seems to be the bulkiness of the end groups: inclusion complexes are obtained when the tin atom possesses phenyl substituents and not when methyl groups are present. However, the replacement of the phenyl groups by methyl substituents modifies the Lewis acidity of the tin atom and also prevents $CH{\cdots}\pi$ interactions from occurring, and these phenomena most likely contribute to the fact that clathrates do not form when $SnMe_3$ fragments are present. The crystal structure of **4**:dioxane shows that the guest molecule is surrounded only by phenyl groups; no interaction between the solvent molecule and the diacetylene unit is observed, nor is one observed between the solvent molecule and the tin atoms. This latter result suggests that the tin atoms in **4** are not sufficiently Lewis acidic to interact with the solvent molecule. Such interactions are known to occur in compounds where the tin atom is bonded to electron-withdrawing groups.[22] Finally, it should be emphasized that the rigidity of the C_4 bridge is also important, since **4** forms inclusion complexes with a large variety of solvents; only one such complex was obtained with $Ph_3Sn(CH_2)_4SnPh_3$.

6. Solid-State NMR and X-ray Crystallographic Studies of $Ph_3SiC{\equiv}CC{\equiv}CSi^*MePhNp$ (5):dioxane.

The complex **5**:dioxane has been characterized by solid-state ^{13}C and ^{29}Si NMR spectroscopy and X-ray crystallography. In the room-temperature ^{13}C NMR spectrum, the acetylenic carbons of the clathrate appear as four lines at 82.9, 86.2, 92.0, and 92.7 ppm, as expected for four magnetically different carbon atoms. The carbon signal of the guest is observed at 66.5 ppm. It is worth pointing out that more than one resonance might have been expected for the methylene carbons of the dioxane molecule, as they are crystallographically nonequivalent and, furthermore, diastereotopic. The fact that only one signal is observed may be purely accidental. Another possibility is that the higher thermal motion of the dioxane molecule at room temperature renders the methylene carbons magnetically equivalent. If this hypothesis is correct, it means that, even though there are some strong interactions between the host and the guest at low temperature, preventing the guest from being disordered (vide infra), these interactions are overpowered at room temperature by thermal motion. The fact that the ^{13}C resonance of the dioxane molecule

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[20] Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, U.K., 1984; p 431.

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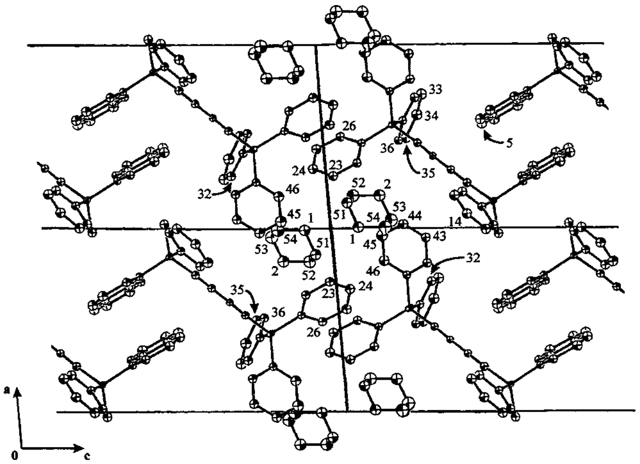

Figure 8. View along the *b* axis of the cell of **5**:dioxane showing the dioxane molecule surrounded by the $SiPh_3$ groups of $Ph_3SiC{\equiv}CC{\equiv}CSi^*MePhNp$.

is broad and the fact that the host−guest complex easily loses its guest at room temperature (see below) appear to agree with this interpretation. The solid-state ^{29}Si NMR spectrum displays two sharp lines with chemical shifts close to those found in solution (−24.8 and −28.5 ppm).

When crystalline **5**:dioxane is left in air at room temperature, it loses the dioxane molecule, as confirmed by the disappearance of the ^{13}C resonance at 66.5 ppm. The solid-state NMR spectra of the unsolvated sample display more lines than are observed for the solvated material (vide supra): the ^{29}Si NMR spectrum shows a main signal at −25.6 ppm (relative intensity 1) along with four smaller signals at δ −28.5, −29.7, −30.2, and −30.7 ppm (each signal with a relative intensity of 0.2). The acetylenic carbons give rise to nine signals in the range 83−93 ppm in the solid-state ^{13}C NMR spectrum, confirming the loss of crystallinity of the material.

Crystal data for the **5**:dioxane complex are listed in Table 6. The crystal system is monoclinic, and the space group is $P2_1$. Full lists of bond lengths and angles and a ZORTEP drawing of the $Ph_3SiC{\equiv}CC{\equiv}CSi^*MePhNp$ part of the clathrate are given in the Supporting Information. Figure 8 shows the crystal packing of the unit cell. The cell contains two molecules of $Ph_3SiC{\equiv}CC{\equiv}CSi^*MePhNp$ and two molecules of dioxane.

The lengths of the triple bonds and the single bond of the butadiynyl unit (respectively 1.219(9), 1.195(10), and 1.375(9) Å) are close to the values observed for other diacetylenic compounds.[9,15,16] The four acetylenic carbons and the two silicon atoms are nearly aligned with bond angles ranging from 176.2 to 178.7°.

The refinement of the structure allowed the determination of the absolute configuration at silicon: it is *R* (see Experimental Section).

There are some sizable van der Waals interactions between the dioxane molecule and the triphenylsilyl groups from surrounding hosts, and most likely this is the reason the guest molecule is not disordered. Table 7 gives the shortest distances between the phenyl groups of the Ph_3Si moiety and the dioxane molecule. There is no interaction between the guest and the methylphenylnaphthylsilyl part of the host, nor is there one between the former and the diacetylene unit. Two adjacent naphthyl groups do not interact with one another, but there are two short intermolecular contacts between the H(5) hydrogen of a naphthyl group and the C(33) and C(34) carbons from a neighboring Ph_3Si moiety: the H(5)···C(33) and H(5)···C(34) distances are respectively 2.956 and 2.856 Å. A fairly short distance (2.776 Å) is also observed between the H(14) hydrogen of the phenyl group bound to the stereogenic silicon center and the C(43) carbon from a nearby Ph_3Si fragment.

Table 7. Shortest Host−Guest Contacts in the Case of 5:dioxane

atoms[a]	dist (Å)[b]	atoms[a]	dist (Å)[b]
H(51a)···C(45)	2.77(1)	H(54b)···C(32)	2.65(1)
H(51a)···C(46)	2.93(1)	H(54b)···C(46)	2.91(1)
H(51b)···C(26)	2.95(1)	O(1)···H(23)	2.42(1)
H(51b)···H(36)	2.36(1)	O(2)···H(35)	2.57(1)
H(53a)···H(24)	2.35(1)	O(2)···H(36)	2.67(1)

[a] Ha and Hb are located on the same carbon atom of the dioxane molecule. [b] van der Waals contacts: 2.97 Å between hydrogen and an aromatic carbon, 2.40 Å between two hydrogens, and 2.72 Å between hydrogen and oxygen.[18]

Finally, a comparison between the structure of $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$:dioxane and that of $Ph_3SiC{\equiv}CC{\equiv}CSi^*MePhNp$:dioxane allows for the following comment to be made: in the tin derivative, the dioxane molecule is confined in cavities formed by phenyl groups (it is a true clathrate), whereas in the case of $Ph_3SiC{\equiv}CC{\equiv}CSi^*MePhNp$:dioxane, the guest molecule lies in zigzag-shaped channels built by phenyl substituents from the Ph_3Si groups. The cavities in these channels roughly resemble compressed spheres: a spacing of about 4.2 Å is found along the direction going through the oxygen atoms of the dioxane molecule, and it is 6.2 and 7.0 Å in directions perpendicular to that axis. These values take into account the van der Waals radii of the atoms delimiting the cavity.[18]

Conclusion

The work presented here shows that $Ph_3SnC{\equiv}CC{\equiv}CSnPh_3$ (**4**) forms 1:1 inclusion compounds with a wide range of organic molecules. The stability of these clathrates has been determined by TGA measurements and guest selectivity studies. The first important structural feature that the host must possess in order to form stable host−guest compounds is the presence of bulky Ph_3M (M = C, Si, Sn) groups. This is supported by the fact that, in the crystal structures of **4**:dioxane and $Ph_3SiC{\equiv}CC{\equiv}CSi^*MePhNp$ (**5**):dioxane, the dioxane molecule is located in the vicinity of the Ph_3M groups. No clathrate is obtained when the end group is Ph_2P. **4**:dioxane has a true clathrate (cage) structure, whereas that of **5**:dioxane is of the channel type. The second requirement for the host is to have a chain with at least four carbon atoms between the two end groups. Stable complexes are obtained when the carbon chain between the bulky groups is rigid, and less stable ones are obtained when the carbon chain is flexible. A combination of multinuclear solid-state NMR and X-ray powder diffraction analyses performed on **4**:dioxane and **5**:dioxane shows that the presence of the solvent molecule is essential in that it maintains the cohesion of the crystal lattice; its removal disorganizes the structure of the host in the solid. It is possible to prepare single crystals of **4** with no included solvent. In this case, it is found that a change in the organization of the diacetylenic molecule in the solid state has occurred, as compared to that observed in **4**:dioxane, so as to minimize the size of the voids between the chains.

Experimental Section

General Considerations. All of the reactions were carried out under nitrogen or argon using standard Schlenk-line techniques. Solvents were dried and distilled prior to use. Tetrahydrofuran (THF) was distilled over sodium−benzophenone ketyl. The solvents used as guests were utilized without purification.

^{1}H NMR spectra were obtained on Bruker AW 80, AC 250, and Avance DPX 200 spectrometers and ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra on Bruker WP 200 SY and AC 250 instruments. Solid-state ^{13}C, ^{119}Sn, and ^{29}Si magic-angle spinning (MAS) and cross-polarization magic-angle spinning (CP/MAS) NMR spectra were recorded on Bruker ASX 200 and ASX 400 spectrometers using 4 or 7 mm zirconia rotors. Spinning rates ranged from 3.5 to 12 kHz. The chemical shifts, δ, are relative to tetramethylsilane (TMS) for ^{1}H, ^{13}C, and ^{29}Si and tetramethylstannane for ^{119}Sn. Mass spectra were recorded on a JEOL JMS-DX300 spectrometer. Thermogravimetric analyses (TGA) were carried out under flowing argon (50 mL/min) with a NETZSCH STA 409 thermobalance and a heating rate of 5 °C/min. DSC experiments were carried out under nitrogen on a Mettler 30 instrument with a heating rate of 5 °C/min. X-ray powder patterns were obtained using Cu Kα radiation on a Philips diffractometer interfaced with a multiacquisition computerized system developed by Prof. R. Fourcade (Université Montpellier II).[23]

Materials. Chlorosilanes, chlorostannanes, diphenylchlorophosphane, organolithium derivatives, and 1,4-dibromobutane were purchased from Aldrich, Fluka, and Janssen. The following compounds were prepared according to published methods: $Me_3SiC\equiv CC\equiv CSiMe_3$,[24] $LiC\equiv CC\equiv CLi$,[25,26] $Ph_3SiC\equiv CC\equiv CSiPh_3$,[25] $Ph_2PC\equiv CC\equiv CPPh_2$,[27] $Ph_3SnC\equiv CSnPh_3$,[28] and $Ph_3SnC\equiv CC\equiv CSnPh_3$.[25]

Syntheses. $Me_3SnC\equiv CC\equiv CSnMe_3$. $Me_3SnC\equiv CC\equiv CSnMe_3$[28] is a known compound that is more conveniently prepared by the procedure described by Corriu et al.[25] Yield: 78%. ^{1}H NMR (CDCl$_3$; δ, ppm): 0.2 (s, $^2J(^1H,^{119}Sn) = 61$ Hz, $^2J(^1H,^{117}Sn) = 58$ Hz). ^{13}C NMR (CDCl$_3$; δ, ppm): −7.3 ($^1J(^{13}C,^{119}Sn) = 407$ Hz, $^1J(^{13}C,^{117}Sn) = 389$ Hz, Sn(CH_3)$_3$), 85.0 ($^1J(^{13}C,^{119}Sn) = 369$ Hz, $^1J(^{13}C,^{117}Sn) = 353$ Hz, Sn$C\equiv$), 91.9 ($^2J(^{13}C,^{117/119}Sn) = 81$ Hz, $^3J(^{13}C,^{117/119}Sn) = 18$ Hz, Sn$C\equiv C$). ^{119}Sn NMR (CDCl$_3$; δ, ppm): −59.0. MS (EI): *m*/*z* (assignment, relative intensity) 361 ($[M - CH_3]^+$, 100).

$Ph_3Sn(CH_2)_4SnPh_3$. $Ph_3Sn(CH_2)_4SnPh_3$ was prepared according to the method reported by Holtkamp et al.[29] Yield: 45%. Mp: 155.5−156.2 °C. ^{1}H NMR (CDCl$_3$; δ, ppm): 1.7 and 2.1 (two multiplets, 8H, CH_2), 7.5−7.7 (multiple signals, 30H, aromatics). ^{13}C NMR (CDCl$_3$; δ, ppm): 11.2 ($^1J(^{13}C,^{119}Sn) = 393$ Hz, $^1J(^{13}C,^{117}Sn) = 375$ Hz, SnCH_2), 31.9 ($^2J(^{13}C,^{119}Sn) = 66$ Hz, $^2J(^{13}C,^{117}Sn) = 64$ Hz, $^3J(^{13}C,^{117/119}Sn) = 21$ Hz, SnCH$_2$$CH_2$), 129.1 ($^3J(^{13}C,^{119}Sn) = 49$ Hz, $^3J(^{13}C,^{117}Sn) = 47$ Hz, $C^{3,5}$), 129.4 ($^4J(^{13}C,^{117/119}Sn) = 11$ Hz, C^4), 137.6 ($^2J(^{13}C,^{119}Sn) = 36$ Hz, $^2J(^{13}C,^{117}Sn) = 34$ Hz, $C^{2,6}$), 139.6 ($^1J(^{13}C,^{119}Sn) = 483$ Hz, $^1J(^{13}C,^{117}Sn) = 461$ Hz, C^{ipso}).

(*S*)-(−)-MePhNpSiCl. (*S*)-(−)-Chloromethylphenylnaphthylsilane is prepared from phenyltrichlorosilane by following a five-step procedure.

(i) Phenyltrimethoxysilane is obtained from the reaction between phenyltrichlorosilane and methanol in the presence of triethylamine.[30]

(ii) Dimethoxyphenylnaphthylsilane results from the reaction between phenyltrimethoxysilane and naphthylmagnesium bromide.[30]

(iii) The reduction of dimethoxyphenylnaphthylsilane with lithium aluminum hydride gives phenylnaphthylsilane, as described below.

(iv) Phenylnaphthylsilane is allowed to react first with (1*R*,2*S*)-(−)-ephedrine in the presence of Wilkinson's catalyst, $ClRh(PPh_3)_3$, and then with methylmagnesium bromide to produce (*R*)-(+)-methylphenylnaphthylsilane according to a reported method.[31]

(v) In the last step, (*S*)-(−)-chloromethylphenylnaphthylsilane is obtained via chlorination of (*R*)-(+)-methylphenylnaphthylsilane with chlorine gas, in CCl$_4$, at 0 °C.[32]

$PhNpSiH_2$. A solution of $PhNpSi(OMe)_2$ (93 g, 0.32 mol) in diethyl ether (500 mL) is added dropwise to a suspension of $LiAlH_4$ (12 g, 0.32 mol) in diethyl ether (500 mL). The mixture is stirred at room temperature for 16 h and then refluxed for 30 min. It is hydrolyzed with a chilled dilute solution of HCl and extracted with diethyl ether. The organic layer is dried over MgSO$_4$. The volatiles are removed using a rotary evaporator. The residual oil is distilled under reduced pressure. $PhNpSiH_2$ is obtained as a yellow liquid with a 91% yield (67 g, 0.29 mol). Bp$_{0.01}$: 110−115 °C. ^{1}H NMR (CCl$_4$; δ, ppm): 5.4 (s, 2H, SiH_2), 7.6−8.2 (m, 12H, aromatics). IR (neat): 2139 vs (Si−H) cm^{-1}.

(*R*)-(+)-$Ph_3SiC\equiv CC\equiv CSiMePhNp$ (5). A 2.20 M solution of *n*-BuLi (4.94 mL, 10.86 mmol) is added dropwise to a cold (−78 °C) solution of $Ph_3SiC\equiv CC\equiv CH$[33] (3.35 g, 10.86 mmol) in diethyl ether (60 mL). After it is stirred for 15 min at −78 °C, the mixture containing $LiC\equiv CC\equiv CSiPh_3$ turns into a red suspension. At −78 °C, a solution of (*S*)-(−)-MePhNpSiCl (3.43 g, 12.14 mmol; $[\alpha]_D = -5.37°$ (pentane)) in diethyl ether (40 mL) is added to the suspension. The mixture is stirred for 12 h, during which time it is warmed to room temperature. After hydrolysis with a saturated solution of NH$_4$Cl and extraction with diethyl ether, the organic layer is dried over MgSO$_4$. The volatiles are removed under reduced pressure. The solid residue is dissolved in a CH$_2$Cl$_2$−hexane mixture (40:60 v/v) and the solution cooled at −18 °C. (*R*)-(+)-$Ph_3SiC\equiv CC\equiv CSiMePhNp$ (**5**) is obtained as a white powder in 82% yield (4.97 g, 8.96 mmol). Mp: 169.1−170.4 °C. $[\alpha]_D = +10.9°$ (CH$_2$Cl$_2$). ^{1}H NMR (CCl$_4$; δ, ppm): 0.9 (s, 3H, CH_3), 7.3−8.0 (m, 27H, aromatics). ^{13}C NMR (CDCl$_3$; δ, ppm): −0.8 (s, CH_3), 82.5 (s, $Ph_3SiC\equiv C$), 84.5 (s, $C\equiv CSiMePhNp$), 91.9 (s, $C\equiv CSiMePhNp$), 92.5 (s, $Ph_3SiC\equiv C$), 125.6−136.3 (17 signals, aromatics). ^{29}Si NMR (CDCl$_3$; δ, ppm): −24.4 (s, SiMePhNp), −28.3 (s, SiPh$_3$). IR (CCl$_4$): 3071 m, 3054 m (C−H arom), 2961 w (C−H aliph), 2069 vs (C≡C), 1590 w, 1429 vs (aromatics), 1255 w (Si−C$_{sp^3}$), 1113 vs (Si−C$_{sp^2}$) cm^{-1}. MS (EI, 70 eV): *m*/*z* (assignment, relative intensity) 555 (M$^+$, 57), 539 ($[M - Me - H]^+$, 39), 476 ($[M - Ph - 2H]^+$, 56), 461 ([M − Ph − Me −

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$2H]^+$, 23), 398 ($[M - 2Ph - 3H]^+$, 9), 333 ($[M - Np - Ph - Me - 3H]^+$, 39), 283 ($[Ph_3SiC{\equiv}C]^+$, 34), 259 ($Ph_3Si^+$, 54), 247 ($MePhNpSi^+$, 30), 231 ($[PhNpSi - H]^+$, 56), 181 ($[Ph_2Si - H]^+$, 79), 155 ($NpSi^+$, 31), 105 ($PhSi^+$, 89), 77 ($Ph^+$, 14). Anal. Calcd for $C_{39}H_{30}Si_2$: C, 84.45; H, 5.45; Si, 10.12. Found: C, 84.3; H, 5.2; Si, 10.0.

Sommer[34] and Corriu[35] have reported that nucleophilic attack of (phenylethynyl)lithium on (*S*)-(−)-alkylchloronaphthylphenylsilanes takes place with inversion of configuration at silicon and is stereospecific. On the basis of these results, it can be anticipated that the attack of $LiC{\equiv}CC{\equiv}CSiPh_3$ on (*S*)-(−)-MePhNpSiCl will lead to a silane (**5**) in which the absolute configuration of the silicon center is *R*. This is confirmed by a single-crystal X-ray diffraction analysis of the **5**:dioxane inclusion compound (vide infra). An analysis of a bulk sample of **5** using a chiral HPLC column (the column used was a CHIRALPAK AD, the eluent an hexane−2-propanol mixture (99:1 v/v), and the flow rate 1 mL/min) confirms that the reaction is stereospecific, as an enantiomeric excess greater than 99.9% is calculated from the chromatogram.

Preparation of the Clathrates. Between 50 and 100 mg of host was dissolved in a minimum amount of boiling solvent (typically 2−5 mL), and the solution was allowed to crystallize at room temperature or at −20 °C. Crystals were quickly dried and crushed just before carrying out TGA and NMR measurements. Elemental analyses of two of the most stable **4**:solvent clathrates gave the following results. Anal. Calcd for **4**:dioxane, $C_{44}H_{38}O_2Sn_2$: C, 63.20; H, 4.58; O, 3.83. Found: C, 63.08; H, 4.59; O, 3.68. Calcd for **4**:$CHCl_3$, $C_{41}H_{31}Cl_3Sn_2$: C, 56.77; H, 3.60; Cl, 12.26. Found: C, 56.76; H, 3.35; Cl, 13.23.

Crystal Structure of 4:dioxane. Sample Preparation. X-ray-quality crystals were grown from a concentrated solution of **4** in dioxane at room temperature. A small colorless block of dimensions 0.50 × 0.30 × 0.20 mm was glued on a glass fiber that was subsequently mounted on an Enraf-Nonius CAD4 automated diffractometer.

Data Collection. Data were collected at 293 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The lattice parameters (Table 6) were determined from a least-squares fit to 25 reflections measured in the range $26.0 < 2\theta < 37.0°$. The intensities of three standard reflections were monitored at intervals of 120 min; no significant change in these intensities occurred during data collection. The systematic absences ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$) indicated the cubic space group $Pa\bar{3}$. The calculated Z value is 4. Reduction to $F_o{}^2$ and $\sigma(F_o{}^2)$ and corrections for background and Lorentz and polarization were performed in the usual manner,[36] and absorption corrections were made from ψ scans.[37] A total of 3385 reflections were collected, of which 1135 were unique ($R_{int} = 0.0218$); 781 were considered to be observed ($F_o > 4\sigma(F_o)$).

Structure Determination and Refinement. The Patterson method using SHELXS-97[38] succeeded in locating the Sn atom. The SHELXL-97 program[39] was used for the full-matrix least-squares refinement against $F_o{}^2$ with all non-hydrogen atoms anisotropic. Phenyl hydrogens were introduced in the calculations with the riding model with U_{iso} equal to 1.1 times that of the atom of attachment. Hydrogen atoms of the disordered dioxane molecule were not included in the calculations. The atomic scattering factors for all atoms were taken from the literature.[40] All of the reflections (3385) were taken into account in the refinement on $F_o{}^2$. The last cycle of refinement gave $R(\text{obs}) = 0.0249$ and $R_w(\text{obs}) = 0.0686$ with 76 variable parameters and a maximum residual peak of 0.18 e Å^{-3}. The labeling scheme of the host part of the **4**:dioxane clathrate is shown in the Supporting Information, and bond lengths and angles are listed.

Crystal Structure of 4 without Included Solvent Molecule. Sample Preparation. Suitable crystals were grown from a concentrated solution of **4** in mesitylene at room temperature. A small colorless block of dimensions 0.40 × 0.30 × 0.30 mm was glued on a glass fiber that was subsequently mounted on a IPDS−Stoe diffractometer equipped with an Oxford Cryostream cooling device.

Data Collection. Data were collected at 180 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). A total of 19 635 reflections were measured in ϕ movement rotation from 0 to 249.6°.[41] The cell parameters (Table 6) were refined from 5000 reflections. Two hundred control reflections were measured; neither decay nor absorption corrections were made to the data. The absence of systematic absences indicated the triclinic space group $P1$ or $P\bar{1}$. The merge program in $P\bar{1}$ gave 7313 unique reflections ($R_{int} = 0.0215$).[41] Of these reflections, 6422 were considered to be observed ($F_o > 4\sigma(F_o)$). The calculated Z value is 3.

Structure Determination and Refinement. The Patterson method using SHELXS-97[38] succeeded in locating the Sn atoms. The SHELXL-97 program[39] was used for the full-matrix least-squares refinement against $F_o{}^2$ with all non-hydrogen atoms anisotropic. Hydrogen atoms were introduced in the calculations with the riding model with U_{iso} values equal to 1.1 times that of the atom of attachment. The atomic scattering factors for all atoms were taken from the literature.[40] All of the reflections (7313) were taken into account in the refinement on $F_o{}^2$. The last cycle of refinement gave $R(\text{obs}) = 0.0194$ and $R_w(\text{obs}) = 0.0398$ with 568 variable parameters and a maximum residual peak of 0.39 e Å^{-3}. ZORTEP drawings of the one and a half independent molecules of **4** present in the unit cell along with the corresponding labeling schemes may be found in the Supporting Information. Tables of bond lengths and angles are also given.

Crystal Structure of 5:dioxane. Sample Preparation. Crystals of the **5**:dioxane clathrate were grown from a dioxane solution at room temperature. A small plate of dimensions 0.40 × 0.40 × 0.20 mm was stuck on a glass fiber with mineral oil and immersed in a stream of cold nitrogen on an Enraf-Nonius CAD4 automated diffractometer.

Data Collection. Two sets of data were collected. The first set was collected at 155 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). Lattice constants (Table 6) result from the least-squares refinement of 25 reflections measured in the range $15.3 < 2\theta < 46.6°$. The intensities of three standard reflections were monitored at intervals of 60 min; no significant change in these intensities was observed. The systematic absence ($0k0$, $k = 2n + 1$) is in agreement with space groups $P2_1$ and $P2_1/m$. The structure factor amplitudes were obtained after the usual Lorentz and polarization corrections ($R_{int} = 0.0287$). Only the reflections with $F > 6.0\sigma(F)$ were considered to be observed. No absorption correction was made.

This set of data proved to be of good quality to solve the structure and led to a conventional R value of 0.0575. However, only nonsignificant differences were observed in the R and R_w values upon changing the configuration of the silicon atom. For a reliable determination of the absolute configuration, another set of data was collected at 158 K on a smaller crystal using Cu Kα radiation ($\lambda = 1.5418$ Å) (see below).

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Structure Determination and Refinement. The noncentrosymmetric space group $P2_1$ was assumed in view of the chirality of compound **5**. Direct methods (SHELXS-86 program[42]) succeeded in locating all of the non-hydrogen atoms, except those of the dioxane molecule. These atoms were located in a subsequent difference Fourier map. The silicon atoms were refined anisotropically. The positions of the hydrogen atoms were calculated (SHELX-76 program[43]) and taken into account in the refinement on F_o. The atomic scattering factors for all atoms were taken from the literature.[44] The refinement based on the data obtained with Mo Kα radiation converged to R and R_w values of 0.0575 and 0.0629, respectively. The labeling scheme of the host part of the **5**:dioxane inclusion compound along with full lists of bond lengths and angles may be found in the Supporting Information.

Two distinct refinements were conducted in identical ways for each possible configuration at silicon using the data set (1347 observed reflections) measured with the Cu Kα radiation. The displayed absolute configuration (R) (see the Supporting Information) gave the final residuals $R = 0.0798$ and $R_w = 0.0850$, whereas the opposite configuration led to $R = 0.0803$ and $R_w = 0.0857$. Calculation of the R index[45] for the 0.01 level gives 1.0036.

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Supporting Information Available: Tables of crystal data and experimental details, positional and thermal parameters, and all interatomic distances, bond angles, and final hydrogen coordinates and ZORTEP drawings for **4**, **4**:dioxane, and **5**:dioxane (31 pages). Ordering information is given on any current masthead page.

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