Intermolecular C−H···O and C−H···π Interactions in the Chloroform Solvate $(CH_3)_3Si{-}C{\equiv}C{-}C{\equiv}C{-}Si(OCH_2CH_2)_3N{\cdot}2CHCl_3$: Crystallographic, Spectroscopic, and DFT Studies

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$(CH_3)_3Si{-}C{\equiv}C{-}C{\equiv}C{-}Si(OCH_2CH_2)_3N{\cdot}2CHCl_3$ (**3**·$2CHCl_3$) was analyzed crystallographically. Each chloroform molecule interacts with diacetylene **3** through one C−H···O contact and one C−H···π contact. Based on distances and angles, these interactions are found to be weaker than those encountered in compounds containing only C−H···O interactions or C−H···π interactions. A comparison between the infrared, ^{13}C, and ^{29}Si NMR data of **3** obtained in $CHCl_3$ or $CDCl_3$ solutions with data obtained in the solid state for the unsolvated material gives further evidence that the chloroform molecules are only weakly bonded to the diacetylenic silatrane. Density functional theory (DFT) calculations have been carried out at the B3LYP level that confirm these findings.

Introduction

Hydrogen bonds are key interactions that hold together supramolecular assemblies and biological systems.[1−3] There exists a wide range of hydrogen bonds with strengths ranging from near 50 kcal mol^{-1} (in KHF_2) down to less than 1 kcal mol^{-1}.[3,4] C−H···O hydrogen bonds belong to the latter category, and it is accepted that their energies are typically ≤ 2 kcal mol^{-1}.[5] These interactions have been studied extensively on the basis of geometric considerations, spectroscopic data, and reduction in thermal vibration of the atoms involved in the C−H···O bond.[5−9] One major conclusion was that the strength of C−H···O interactions depends strongly on carbon acidity and O acceptor basicity.[5,10−12]

C−H···π interactions represent another structural motif that is commonly encountered in supramolecular and bioorganic chemistry. The π-systems that have been found to give rise to such interactions include aromatics, alkenes, and alkynes.[13−16] Of particular interest to us are C−H···π interactions involving chloroform molecules

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(1) Desiraju, G. R. In *Solid-state Supramolecular Chemistry: Crystal Engineering*; *Comprehensive Supramolecular Chemistry Vol. 6*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Elsevier: Oxford, UK, 1996; p 1.

(2) Nangia, A.; Desiraju, G. R. In *Design of Organic Solids*; *Topics in Current Chemistry 198*; Weber, E., Ed.; Springer-Verlag: Berlin, 1998; p 57.

(3) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.

(4) Glusker, J. P. In *Design of Organic Solids*; *Topics in Current Chemistry 198*; Weber, E., Ed.; Springer-Verlag: Berlin, 1998; p 1.

(5) Steiner, T. *Chem. Commun.* **1997**, 727.

(6) (a) Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1989**, 179. (b) Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1990**, 454.

(7) (a) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290. (b) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441.

(8) Steiner, T.; Desiraju, G. R. *Chem. Commun.* **1998**, 891.

(9) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1994**, 101.

(10) Pedireddi, V. R.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1992**, 988.

(11) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2341.

(12) Steiner, T. *New J. Chem.* **1998**, *22*, 1099.

(13) (a) Cox, E. G.; Cruickshank, D. W. J.; Smith, J. A. S. *Proc. R. Soc. A (London)* **1958**, *247*, 1. (b) Burley, S. K.; Petsko, G. A. *Science (Washington, D.C.)* **1985**, *229*, 23. (c) Burley, S. K.; Petsko, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 7995. (d) 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. (e) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768. (f) Hunter, C. A. *Chem. Soc. Rev.* **1994**, *23*, 101.

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and acetylenic systems. Mingos et al. reported recently the X-ray crystal structures of $NpPh_2P-Au-C\equiv C-Au-PNpPh_2\cdot 2CHCl_3$ (**1**·$2CHCl_3$) (Np = 1-naphthyl) and $Np_2PhP-Au-C\equiv C-Au-PNp_2Ph\cdot 6CHCl_3$ (**2**·$6CHCl_3$), in which the chloroform molecules interact with the central triple bonds through $C-H\cdots\pi$ contacts.[17] In **1**·$2CHCl_3$, the two chloroform molecules are coordinated to the triple bond in a T-shaped fashion; in **2**·$6CHCl_3$, four chloroform molecules interact in the same way with the triple bond. Furthermore, the same group has carried out ab initio and density functional calculations on the solvate $H_3PAuC\equiv CAuPH_3\cdots CHCl_3$ that indicate that the energy of interaction between the triple bond and the chloroform molecule is ca. 6 kcal mol^{-1}.[18]

Diacetylenes such as $Ph_3C-C\equiv C-C\equiv C-CPh_3$ and $Ph_3Sn-C\equiv C-C\equiv C-SnPh_3$ are known to give inclusion compounds with chloroform, and in the case of $Ph_3Sn-C\equiv C-C\equiv C-SnPh_3$, X-ray crystallography has shown that the included solvent molecule does not interact with the triple bonds.[19,20] Interestingly, however, the silicon-containing analogue $Ph_3Si-C\equiv C-C\equiv C-SiPh_3$ does not give inclusion compounds with chloroform or any other solvent.[21]

We describe herein the X-ray crystal structure of $(CH_3)_3Si-C\equiv C-C\equiv C-Si(OCH_2CH_2)_3N\cdot 2CHCl_3$ (**3**·$2CHCl_3$) and present the results of our investigations on the bonding of the chloroform molecules to **3** based on crystallographic data, infrared and NMR measurements, and density functional theory (DFT) calculations.

Results and Discussion

Single-Crystal X-ray Diffraction Study of $(CH_3)_3Si-C\equiv C-C\equiv C-Si(OCH_2CH_2)_3N\cdot 2CHCl_3$ (3·2CHCl$_3$). Diacetylene **3** is an air-stable compound that is prepared from (*Z*)-$CH_3O-CH=CH-C\equiv C-Si(OCH_2CH_2)_3N$.[22] Slow concentration of a chloroform solution containing **3** gave colorless plates that became opaque upon staying in air at room temperature or upon drying in vacuo. X-ray crystallography (vide infra) showed the crystals to be **3**·$2CHCl_3$, and the presence of the included solvent molecules is consistent with the poor stability of these crystals.

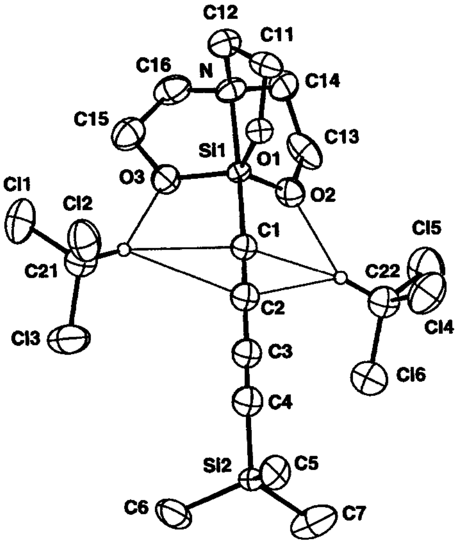

Figure 1. ZORTEP drawing of **3**·$2CHCl_3$ showing 50% probability ellipsoids.

Table 1. Crystal Data and Experimental Details for 3·2CHCl$_3$[a]

formula	$C_{15}H_{23}Cl_6NO_3Si_2$
fw	534.22
cryst color, habit	colorless plate
cryst size, mm	0.50 × 0.20 × 0.15
cryst syst	monoclinic
space group	$P2_1/n$ (no. 14)
a, Å	12.2897(12)
b, Å	13.2598(10)
c, Å	15.514(2)
β, deg	90.062(10)
V, Å^3	2528.2(4)
Z	4
ρ_{calc}, g cm^{-3}	1.404
$F(000)$	1096
μ(Mo Kα), mm^{-1}	0.790
2θ range, deg	2.9−48.4
no. of reflns collected	16 091
no. of unique reflns	3982
R_{int} (on I)	0.0345
no. of obsd reflns ($F_o > 4\sigma(F_o)$)	2593
no. of variable params	252
goodness-of-fit on F_o^2 (all reflns)	0.821
w^b	$[\sigma^2(F_o^2) + (0.0113P)^2]^{-1}$
max and mean shift/esd	0.002, 0.000
R,^{c} $R_w{}^d$ (obsd reflns)	0.030, 0.050
R,^{c} $R_w{}^d$ (all reflns)	0.053, 0.058
largest diff peak and hole, e Å^{-3}	0.20, −0.17

[a] Data collected at $T = 160$ K on a Stoe-IPDS diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). [b] $P = (F_o^2 + 2F_c^2)/3$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $R_w = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Owing to the ready loss of the included solvent, measurements of the intensity data were carried out at 160 K. A ZORTEP[23] drawing of **3**·$2CHCl_3$ is shown in Figure 1, and the corresponding crystal data have been summarized in Table 1.

The solid state structure shows that the chloroform molecules do not simply fill voids present in the lattice but that these molecules are coordinated to **3**. Each solvent molecule interacts with the C(1)−C(2) triple bond and one oxygen of the silatrane moiety. The chloroform molecules lie far apart from one another as

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(14) (a) Steiner, T.; Starikov, E. B.; Amado, A. M.; Teixeira-Dias, J. J. C. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1321. (b) Steiner, T.; Starikov, E. B.; Tamm, M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 67.

(15) Lutz, B.; Kanters, J. A.; van der Maas, J.; Kroon, J.; Steiner, T. *J. Mol. Struct.* **1998**, *440*, 81.

(16) (a) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1995**, 95. (b) Weiss, H.-C.; Bläser, D.; Boese, R.; Doughan, B. M.; Haley, M. M. *Chem. Commun.* **1997**, 1703. (c) Weiss, H.-C.; Boese, R.; Smith, H. L.; Haley, M. M. *Chem. Commun.* **1997**, 2403. (d) Robinson, J. M. A.; Kariuki, B. M.; Gough, R. J.; Harris, K. D. M.; Philp, D. *J. Solid State Chem.* **1997**, *134*, 203. (e) Steiner, T.; Tamm, M. *J. Organomet. Chem.* **1998**, *570*, 235. (f) Galoppini, E.; Gilardi, R. *Chem. Commun.* **1999**, 173. (g) Madhavi, N. N. L.; Bilton, C.; Howard, J. A. K.; Allen, F. H.; Nangia, A.; Desiraju, G. R. *New J. Chem.* **2000**, *24*, 1.

(17) (a) Müller, T. E.; Mingos, D. M. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1787. (b) Müller, T. E.; Wing-Kin Choi, S.; Mingos, D. M. P.; Murphy, D.; Williams, D. J.; Wing-Wah Yam, V. *J. Organomet. Chem.* **1994**, *484*, 209.

(18) Fan, M.-F.; Lin, Z.; McGrady, J. E.; Mingos, D. M. P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 563.

(19) Hart, H.; Lin, L.-T. W.; Ward, D. L. *J. Am. Chem. Soc.* **1984**, *106*, 4043.

(20) Brouty, C.; Spinat, P.; Whuler, A. *Acta Crystallogr.* **1980**, *B36*, 2624.

(21) Carré, F.; Dutremez, S. G.; Guérin, C.; Henner, B. J. L.; Jolivet, A.; Tomberli, V.; Dahan, F. *Organometallics* **1999**, *18*, 770.

(22) Brunel, L.; Chaplais, G.; Dutremez, S. G.; Guérin, C.; Henner, B. J. L.; Tomberli, V. *Organometallics* **2000**, *19*, 2516.

(23) Zsolnai, L.; Pritzkow, H.; Huttner, G. *ZORTEP*: *Ortep for PC, Program for Molecular Graphics*; University of Heidelberg: Heidelberg, Germany, 1996.

Table 2. Hydrogen Bonds and Contacts between $CHCl_3$ and $(CH_3)_3Si{-}C{\equiv}C{-}C{\equiv}C{-}Si(OCH_2CH_2)_3N$ in $3{\cdot}2CHCl_3$[a]

D	H	D−H	A	H···A	D···A	D−H···A
C(21)	H(21)	1.06(3)	O(3)	2.38(3)	3.249(3)	138(2)
			C(1)	2.63(3)	3.636(4)	158(2)
			C(2)	2.82(3)	3.648(4)	135(2)
			M(12)[b]	2.65(3)	3.591(4)	147(2)
C(22)	H(22)	1.08(3)	O(2)	2.29(3)	3.205(3)	141(2)
			C(1)	2.54(3)	3.541(4)	153(2)
			C(2)	2.78(3)	3.574(4)	130(2)
			M(12)[b]	2.59(3)	3.505(4)	141(2)

[a] Distances are in angstroms and angles in degrees. [b] M(12) is the midpoint of the C(1)−C(2) bond.

Table 3. Selected Bond Lengths and Angles for $3{\cdot}2CHCl_3$

Bond Lengths (Å)

Si(1)−O(1)	1.645(2)	O(1)−C(11)	1.440(3)	C(3)−C(4)	1.192(3)
Si(1)−O(2)	1.657(2)	O(2)−C(13)	1.443(3)	C(11)−C(12)	1.532(3)
Si(1)−O(3)	1.640(2)	O(3)−C(15)	1.431(3)	C(21)−Cl(1)	1.736(3)
Si(1)−N	2.042(2)	N−C(12)	1.465(3)	C(21)−H(21)	1.06(3)
Si(1)−C(1)	1.859(2)	C(1)−C(2)	1.219(3)	C(22)−Cl(4)	1.746(3)
Si(2)−C(4)	1.847(3)	C(2)−C(3)	1.404(3)	C(22)−H(22)	1.08(3)
Si(2)−C(5)	1.863(2)				

Angles (deg)

O(1)−Si(1)−O(2)	120.71(8)	Si(1)−O(3)−C(15)	125.6(2)
O(1)−Si(1)−O(3)	119.35(8)	Si(1)−N−C(12)	105.7(2)
O(1)−Si(1)−N	85.89(7)	C(12)−N−C(14)	117.7(2)
O(1)−Si(1)−C(1)	95.61(9)	Si(1)−C(1)−C(2)	176.8(2)
O(2)−Si(1)−O(3)	118.41(8)	C(1)−C(2)−C(3)	177.8(3)
O(2)−Si(1)−N	87.85(8)	C(2)−C(3)−C(4)	179.2(3)
O(2)−Si(1)−C(1)	92.60(9)	Si(2)−C(4)−C(3)	174.3(2)
O(3)−Si(1)−N	83.91(8)	O(1)−C(11)−C(12)	107.2(2)
O(3)−Si(1)−C(1)	94.09(9)	N−C(12)−C(11)	105.2(2)
N−Si(1)−C(1)	177.92(9)	Cl(1)−C(21)−Cl(2)	108.7(2)
C(4)−Si(2)−C(5)	107.4(1)	Cl(1)−C(21)−H(21)	111.9(14)
C(5)−Si(2)−C(6)	116.5(1)	Cl(4)−C(22)−Cl(5)	107.7(2)
Si(1)−O(1)−C(11)	121.0(2)	Cl(4)−C(22)−H(22)	109.9(14)
Si(1)−O(2)−C(13)	119.7(2)		

indicated by the 150.4° dihedral angle between the H(21)−C(1)−C(2) and C(1)−C(2)−H(22) planes. The positions of these molecules are intermediate between those found in C−H···O interactions and those encountered in C−H···π interactions. In other words, the structure may be regarded as consisting of C−H···O hydrogen bonds bifurcated by C−H···π interactions. In agreement with this, the H···O and C···O distances found in **3**·$2CHCl_3$ are slightly longer than the mean values given in the literature.[24] The H(21)···O(3), H(22)···O(2), C(21)···O(3), and C(22)···O(2) distances are respectively 2.38(3), 2.29(3), 3.249(3), and 3.205(3) Å (see Table 2). The mean H···O and C···O distances reported by Steiner[5,11] are 2.22(3) and 3.16(2) Å; the mean C···O distance reported by Pedireddi and Desiraju[10] is 3.21(3) Å. Our H···O values are actually similar to the H···O(atrane) distance found in the chloroform solvate of (−)-1-menthoxygermatrane (2.35(9) Å), in which a second H···O interaction is present between the hydrogen of the chloroform molecule and the oxygen of the menthoxy group.[25]

Directionality is another important aspect to consider when studying hydrogen bonding.[5,8] The mean value for the $Cl_3C{-}H{\cdots}O$ angle is 147(4)°.[10] In our case, the C(21)−H(21)···O(3) and C(22)−H(22)···O(2) angles are respectively 138(2)° and 141(2)° (see Table 2). The slightly more bent angles observed for **3**·$2CHCl_3$ are suggestive of weaker hydrogen bonds.

Due to the presence of the C−H···O interactions, H(21) and H(22) do not interact in a symmetrical fashion with C(1) and C(2): the H(21)···C(1), H(21)···C(2), H(22)···C(1), and H(22)···C(2) distances are respectively 2.63(3), 2.82(3), 2.54(3), and 2.78(3) Å. The H(21)···M(12) (M(12) = midpoint of the C(1)−C(2) bond) and H(22)···M(12) distances are respectively 2.65(3) and 2.59(3) Å. These latter distances are slightly longer than those reported by Mingos and co-workers, i.e., 2.42 Å in the case of **1**·$2CHCl_3$ and 2.50 and 2.58 Å in the case of **2**·$6CHCl_3$.[17] These results are suggestive of weaker C−H···π contacts in **3**·$2CHCl_3$.

The low values observed for the C(21)−H(21)···M(12) and C(22)−H(22)···M(12) angles, 147(2)° and 141(2)°, are additional supports of the presence of weaker C−H···π interactions in **3**·$2CHCl_3$. These values differ significantly from the 174.3° angle reported in the case of **1**·$2CHCl_3$ and the 166.6° and 172.7° angles found in **2**·$6CHCl_3$.[17]

Coordination of the chloroform molecules to the oxygens of the silatrane moiety does not have much effect on the Si−O and O−C bond lengths. The Si−O distances are all very similar (see Table 3), and the same is true for the O−C bond lengths. Furthermore, these distances are close to those reported in the literature for other silatranes.[26] Curiously, however, the Si−N distance in **3**·$2CHCl_3$, 2.042(2) Å, is significantly shorter than the distance typically found in 1-hydrocarbylsilatranes (2.1−2.2 Å).[26,27] In fact, it is similar to that found in 1-halosilatranes (2.023 and 2.042 Å).[28] It is not clear whether the short Si−N distance in **3**·$2CHCl_3$ originates from coordination of the chloroform molecules to the silatrane cage or from electronic effects brought about by the $Me_3Si{-}C{\equiv}C{-}C{\equiv}C$ fragment *trans* to the nitrogen atom.[29] A survey of the Cambridge Structural Database[30] indicates that, apart from **3**·$2CHCl_3$, no 1-alkynylsilatrane has yet been characterized crystal-

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(24) In contrast with the often observed significant shortening of bond distances involving hydrogen, our X-ray-derived C−H distances for chloroform are very near the typical internuclear C−H distance, i.e., 1.08 Å. See: Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(25) Zaitseva, G. S.; Nasim, M.; Livantsova, L. I.; Tafeenko, V. A.; Aslanov, L. A.; Petrosyan, V. S. *Heteroat. Chem.* **1990**, *1*, 439.

(26) (a) Turley, J. W.; Boer, F. P. *J. Am. Chem. Soc.* **1968**, *90*, 4026. (b) Turley, J. W.; Boer, F. P. *J. Am. Chem. Soc.* **1969**, *91*, 4129. (c) Párkányi, L.; Nagy, J.; Simon, K. *J. Organomet. Chem.* **1975**, *101*, 11. (d) Párkányi, L.; Hencsei, P.; Bihátsi, L.; Kovács, I.; Szöllösy, Á. *Polyhedron* **1985**, *4*, 243. (e) Hencsei, P.; Kovács, I.; Fülöp, V. *J. Organomet. Chem.* **1989**, *377*, 19. (f) Nasim, M.; Petrosyan, V. S.; Zaitseva, G. S.; Lorberth, J.; Wocadlo, S.; Massa, W. *J. Organomet. Chem.* **1992**, *441*, 27. (g) Zaitseva, G. S.; Karlov, S. S.; Churakov, A. V.; Avtomonov, E. V.; Lorberth, J.; Hertel, D. *J. Organomet. Chem.* **1996**, *523*, 221. (h) Calhorda, M. J.; Lopes, P. E. M.; Schier, A.; Herrmann, R. *J. Organomet. Chem.* **1997**, *543*, 93. (i) Pedersen, B.; Wagner, G.; Herrmann, R.; Scherer, W.; Meerholz, K.; Schmälzlin, E.; Bräuchle, C. *J. Organomet. Chem.* **1999**, *590*, 129.

(27) Pestunovich, V.; Kirpichenko, S.; Voronkov, M. In *The Chemistry of Organic Silicon Compounds Vol. 2 Part 2*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Chapter 24, p 1447.

(28) (a) Kemme, A. A.; Bleidelis, J. J.; Pestunovich, V. A.; Baryshok, V. P.; Voronkov, M. G. *Dokl. Akad. Nauk SSSR* **1978**, *243*, 688. Cited in: Voronkov, M. G.; Baryshok, V. P.; Petukhov, L. P.; Rakhlin, V. I.; Mirskov, R. G.; Pestunovich, V. A. *J. Organomet. Chem.* **1988**, *358*, 39. (b) Párkányi, L.; Hencsei, P.; Bihátsi, L.; Müller, T. *J. Organomet. Chem.* **1984**, *269*, 1.

(29) The electronegative character of the phenylacetylenic substituent has been postulated as being responsible for the short Ge−N distance in $N(CH_2CH_2O)_3GeC{\equiv}CC_6H_5{\cdot}CHCl_3$. See: Zaitseva, G. S.; Karlov, S. S.; Churakov, A. V.; Howard, J. A. K.; Avtomonov, E. V.; Lorberth, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1144.

(30) Cambridge Structural Database. Release version 5.19. 215 403 entries.

lographically, and so a meaningful comparison with known structural data is not possible. But great care must be exercised when trying to rationalize the Si−N distance of silatranes, as this bond is known to be quite sensitive to substituent effects and also very easily distorted by crystal packing forces.[26h,31−33]

A slight deviation from linearity similar to that found in the Si−C≡C−C≡C−Si fragment of **3**·2$CHCl_3$ (see Table 3) has been observed previously in the X-ray crystal structure of Ph_3Si−C≡C−C≡C−Si*MePhNp·dioxane, and so this phenomenon cannot be ascribed to coordination of the chloroform molecules to **3**.[21] Also, the Si−C distances are similar to those found in Ph_3Si−C≡C−C≡C−Si*MePhNp·dioxane, and the same is true for the C−C triple bonds and the central C−C single bond.[21] The slight difference that exists between the C(1)−C(2) distance and the C(3)−C(4) distance does not originate from coordination of the chloroform molecules to **3**, as a similar difference has been observed in Ph_3Si−C≡C−C≡C−Si*MePhNp·dioxane.[21]

The O−Si(1)−C(1) angles of **3**·2$CHCl_3$, 92.60(9)−95.61(9)° (see Table 3), are a bit smaller than those typically found in 1-hydrocarbylsilatranes (95−99°),[26] and this observation is in line with the short Si−N distance noted previously. Although the origin of this phenomenon is unclear (vide supra), it is worth pointing out that the O(2)−Si(1)−C(1) and O(3)−Si(1)−C(1) angles are smaller than the O(1)−Si(1)−C(1) angle, and this difference may well originate from coordination of chloroform to these former two fragments. Interestingly, the difference in the O−Si(1)−C(1) angles between the solvated and unsolvated parts of **3**·2$CHCl_3$ is a lot smaller than that observed in the O(germatrane)−Ge−O(menthoxy) angles of the chloroform solvate of (−)-1-menthoxygermatrane: the fragment interacting with the chloroform molecule has a O(germatrane)−Ge−O(menthoxy) angle of 90.7(3)°, and these angles are 97.6(3)° and 99.0(3)° for the free fragments.[25]

Attempts to Detect the C−H···O and C−H···π Interactions Present in 3·2CHCl$_3$ by Infrared and NMR Measurements. The infrared spectrum of **3** in KBr displays a strong absorption band at 2065 cm^{-1} corresponding to ν(C≡C) and two very strong bands at 1117 and 1087 cm^{-1} assigned to ν(C−O) and ν_{as}(Si−OC).[22] In $CHCl_3$ solution, these bands are observed at 2070, 1126, and 1098 cm^{-1}. Furthermore, an additional band is observed at 1148 cm^{-1}. Thus, coordination of chloroform to **3** does not affect noticeably the positions of the ν(C≡C) and ν(C−O) bands. The slight shift in the position of the ν_{as}(Si−OC) band and the presence of the additional band at 1148 cm^{-1} could be thought to arise from the interaction of **3** with chloroform, but this seems unlikely, as the same bands are observed in the infrared spectrum of **3** in CCl_4 solution.

In $CDCl_3$ solution, the NMR signals corresponding to the acetylenic carbons of **3** are observed at 80.3, 82.8, 88.2, and 89.7 ppm.[22] In the same solvent, the ^{29}Si NMR spectrum displays two signals at −16.7 ppm ($Si(CH_3)_3$) and −96.4 ppm ($Si(OCH_2CH_2)_3N$).[22] In the CP/MAS ^{13}C NMR spectrum, the signals corresponding to the acetylenic carbons are observed at 78.9, 83.6, 90.1, and 93.3 ppm. The CP/MAS ^{29}Si NMR spectrum shows two signals at −15.8 and −97.1 ppm. Thus, the chemical shifts found in the solid state are close to those measured in $CDCl_3$ solution, and the differences that are observed are similar to those typically encountered when going from the solution to the solid state.[21]

In conclusion, X-ray crystallography indicates that the C−H···O and C−H···π interactions observed in **3**·2$CHCl_3$ are weak, and this is confirmed by infrared and NMR measurements. To better understand the interaction of **3** with chloroform, DFT calculations have been carried out.

Theoretical Studies. $(CH_3)_3Si$−C≡C−C≡C−Si$(OCH_2CH_2)_3N$·$CHCl_3$ (**3**·$CHCl_3$) was calculated for direct comparison with the experimental system (**exp3**·2$CHCl_3$). Several simplified models that include H_3Si−C≡C−C≡C−Si$(OCH_2CH_2)_3N$·$CHCl_3$ (**3SiH$_3$**·$CHCl_3$), H−C≡C−Si$(OCH_2CH_2)_3N$·$CHCl_3$ (**4O**·$CHCl_3$), H−C≡C−Si$(OCH_2CH_2)_3N$·2$CHCl_3$ (**4O**·2 $CHCl_3$), H−C≡C−Si$(CH_2CH_2CH_2)_3N$·$CHCl_3$ (**4CH$_2$**·$CHCl_3$), H−Si$(OCH_2CH_2)_3N$·$CHCl_3$ (**5O**·$CHCl_3$), H−C≡C−$SiMe_3$·$CHCl_3$ (**6**·$CHCl_3$), H−C≡C−H·$CHCl_3$ (**7**·$CHCl_3$), and H_2O·$CHCl_3$ were also calculated to gain insight into the bonding of the chloroform molecule. Each solvate system consisting of one substrate molecule and one molecule of chloroform (or two in the case of **4O**) was fully optimized. The dissociation energy (E_d) corresponds to the difference between the energy of the solvate system and the sum of the energies of each isolated partner in the geometry of the solvate system. The geometries of all of the systems are shown in Figures 2, 3, and 4.

Optimization of **3**·$CHCl_3$ places the chloroform molecule near **3** with an overall geometry that is similar to that found in the solid state (compare **3**·$CHCl_3$ with **exp3**·2$CHCl_3$ in Figure 2). The H···C(1) and H···O distances are calculated to be 3.027 and 2.189 Å, respectively, and these values are reasonably close to the average experimental distances, 2.59 and 2.34 Å. The directionality of the solvent molecule is also similar to that found in the solid state: the Cl_3C−H···O angle is found to be 151.3° against 140° experimentally. The calculated geometrical parameters of **3** agree fairly well with the X-ray data except that the Si−N distance is much too long (2.370 Å found by calculations against 2.042 Å experimentally). This too long Si−N distance is accompanied by noticeable differences in the angles around silicon as compared with the experimental values: the average O−Si−C angle is calculated to be 99.7°, whereas it is 94.1° in the crystal structure. The dissociation energy of chloroform is 4.2 kcal mol^{-1}; this energy is lower than that found by Mingos and coworkers in the case of H_3PAuC≡$CAuPH_3$···$CHCl_3$, where only C−H···π interactions are present (ca. 6 kcal mol^{-1}).[18]

Difficulties to adequately represent the trigonal bipyramidal geometry at silicon and accurately reproduce the axial Si−N bond length have been encountered in previous ab initio and DFT studies.[26h,31−36] Indeed, the

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(31) Gordon, M. S.; Carroll, M. T.; Jensen, J. H.; Davis, L. P.; Burggraf, L. W.; Guidry, R. M. *Organometallics* **1991**, *10*, 2657.

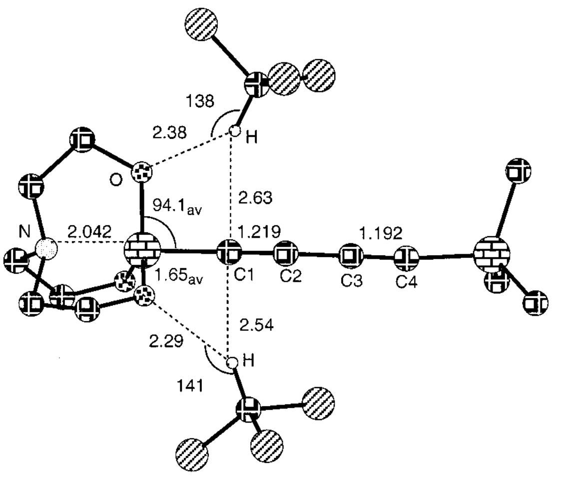
(32) Schmidt, M. W.; Windus, T. L.; Gordon, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 7480.

(33) Anglada, J. M.; Bo, C.; Bofill, J. M.; Crehuet, R.; Poblet, J. M. *Organometallics* **1999**, *18*, 5584.

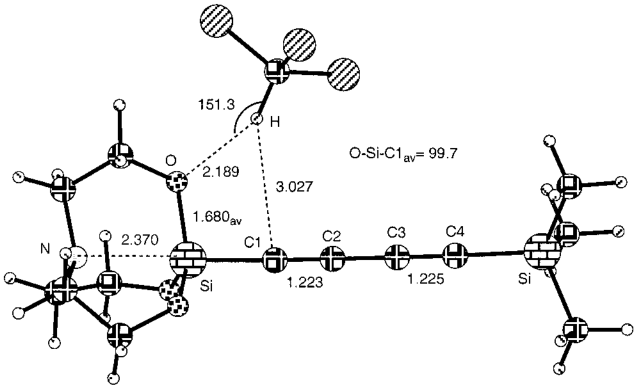
(34) Greenberg, A.; Plant, C.; Venanzi, C. A. *J. Mol. Struct. (THEOCHEM)* **1991**, *234*, 291.

(35) Csonka, G. I.; Hencsei, P. *J. Mol. Struct. (THEOCHEM)* **1996**, *362*, 199.

(36) Sidorkin, V. F.; Balakhchi, G. K.; Voronkov, M. G.; Pestunovich, V. A. *Dokl. Chem. (Engl. Trans.)* **1987**, *296*, 400.

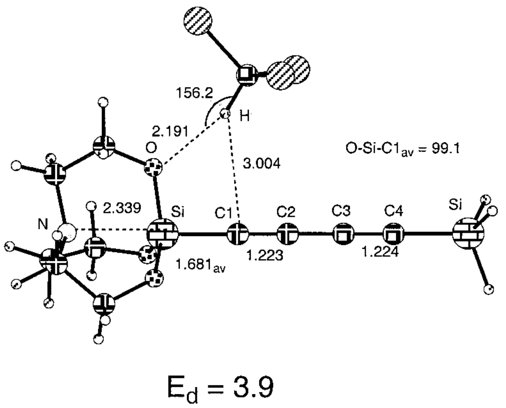


exp3·2 $CHCl_3$



$E_d = 4.2$

3·$CHCl_3$



$E_d = 3.9$

3SiH₃·$CHCl_3$

Figure 2. Optimized structures (DFT at the B3LYP level) of **3**·$CHCl_3$ and **3SiH₃**·$CHCl_3$. The experimental structure **exp3**·2$CHCl_3$ is also shown for comparison with the calculations. Distances are in angstroms and angles in degrees. The dissociation energy (E_d) of chloroform is in kcal mol^{-1}.

Si−N distance is very sensitive to the nature of the other ligands attached to silicon (inductive effects) and to medium effects. For instance, for the fluoro- and methylsilatranes, the Si−N bond has been shown to be longer by 0.28 Å in the gas phase than in the solid state.[27,37,38] Calculations of pentacoordinated silicon compounds at the MP2 level give geometrical results that are in better agreement with the experimental values.[33] Although DFT calculations are of poorer quality, especially when trying to reproduce the Si←N bond length, the size of the model systems optimized in this study requires the use of this method. Thus, our results are in line with data obtained by other groups, and the difference of about 0.3 Å in the Si−N distance that is observed may, to a large extent, be attributed to solid state effects. While the focus of this work is not on the geometry of the silatrane moiety, the position and dissociation energy of the chloroform molecule are not totally independent from this problem. This will be apparent later in this study.

Going to simplified models of **3** does not change much the overall shape of the solvate system. In **3SiH₃**·$CHCl_3$ (Figure 2), the H···C(1) and H···O distances are calculated to be 3.004 and 2.191 Å, respectively, and the $Cl_3C−H···O$ angle is equal to 156.2°. The Si−N distance is shortened (2.339 Å) and the average O−Si−C angle is equal to 99.1°. The dissociation energy of chloroform is 3.9 kcal mol^{-1}, which is marginally smaller than that found for **3**·$CHCl_3$.

In **4O**·$CHCl_3$ (Figure 3), the chloroform molecule is located closer to the π-system (H···C(1) = 2.706 Å, H···O = 2.310 Å, and ∠$Cl_3C−H···O$ = 135.1°). The Si−N distance, 2.358 Å, is lengthened as compared with that found in **3SiH₃**·$CHCl_3$, and the average O−Si−C angle is equal to 99.4°. The dissociation energy of chloroform is 4.6 kcal mol^{-1}. The fact of having two molecules of chloroform interacting with the substrate results in only minor changes in the position of each solvent molecule (see **4O**·2$CHCl_3$ in Figure 3). However, a shortening of the Si−N bond is observed (2.315 Å) with an average O−Si−C angle of 98.7°. This observation illustrates the sensitivity of the Si−N distance to medium effects as previously noted by others.[26h,31,32,34−36] The dissociation energy for the two chloroform molecules is twice that of a single molecule, indicating the absence of any cooperative effects.

Removal of the alkyne group from the model system (**5O**·$CHCl_3$ in Figure 3) leads to drastic changes in the coordination of the solvent molecule. The H···O distance is significantly shortened (2.092 Å), and the C−H···O vector is almost linear (∠C−H···O = 166.2°). The Si−N distance is the longest (2.379 Å), with an average H−Si−O angle of 100.0°. The dissociation energy of chloroform is 4.5 kcal mol^{-1}. Evidently, the triple bond has an influence on the position of the chloroform molecule since removing this group from the substrate leads to a geometry that is very close to that typically observed for a C−H bond interacting with an oxygen atom.[5]

To complete this study, a system analogous to **4O**·$CHCl_3$ in which the three oxygen atoms have been replaced by CH_2 groups has been calculated (**4CH₂**·$CHCl_3$ in Figure 3). In this case, the C−H bond of $CHCl_3$ points at the midpoint of the triple bond (H···midpoint = 2.474 Å); the Si−N distance is 2.520 Å and the average C−Si−C angle is equal to 101.0°. Also, the

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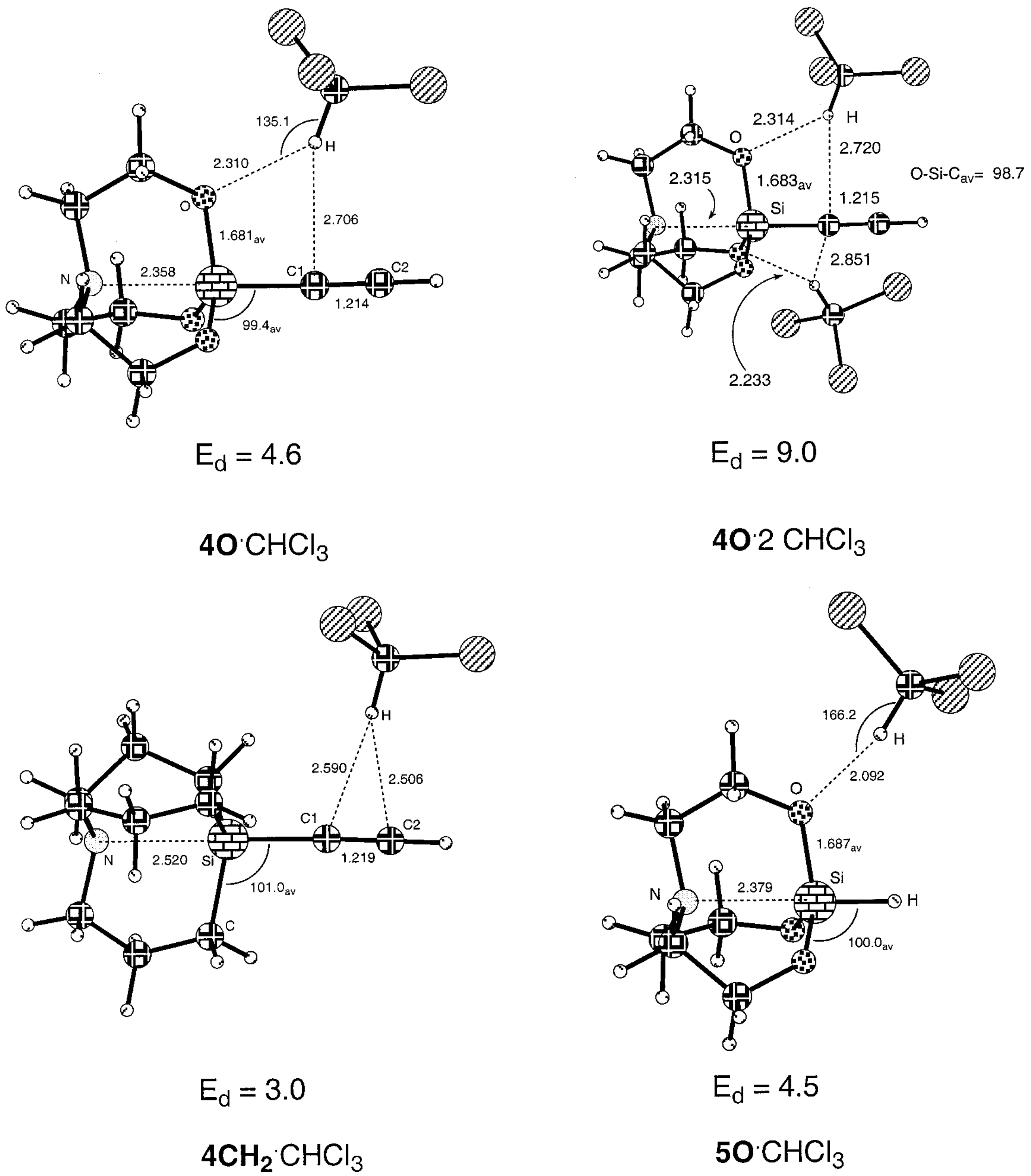
(37) Forgács, G.; Kolonits, M.; Hargittai, I. *Struct. Chem.* **1990**, *1*, 245.

(38) Shen, Q.; Hilderbrandt, R. L. *J. Mol. Struct.* **1980**, *64*, 257.



$E_d = 4.6$ **4O**·$CHCl_3$

$E_d = 9.0$ **4O**·2 $CHCl_3$

$E_d = 3.0$ **4CH₂**·$CHCl_3$

$E_d = 4.5$ **5O**·$CHCl_3$

Figure 3. Optimized structures (DFT at the B3LYP level) of **4O**·$CHCl_3$, **4O**·2$CHCl_3$, **4CH$_2$**·$CHCl_3$, and **5O**·$CHCl_3$. Distances are in angstroms and angles in degrees. The dissociation energy (E_d) of chloroform is in kcal mol^{-1}.

$H(CHCl_3)\cdots C(1)$ bond is staggered with the two adjacent Si–CH_2 bonds, whereas it is eclipsed with one Si–O bond in the case of **4O**·$CHCl_3$. Finally, it appears that the replacement of the oxygen atoms by less electronegative CH_2 groups diminishes the tendency of silicon to become pentacoordinated (Si–N = 2.520 Å in **4CH$_2$**·$CHCl_3$ vs 2.358 Å in **4O**·$CHCl_3$). This observation is in line with the accepted idea that electronegative groups favor pentacoordination,[33,39] although difficulties to represent this effect at the RHF level have been reported.[32] The dissociation energy of chloroform is 3.0 kcal mol^{-1}.

The influence of the nitrogen atom in the substrate on the position of chloroform has been assessed by calculating **6**·$CHCl_3$ (Figure 4). The C–H bond of the solvent molecule still points at the triple bond of the substrate, but the distance between the hydrogen and the C≡C midpoint is longer (2.528 Å). The dissociation energy of chloroform is greatly diminished (2.1 kcal mol^{-1}) as compared to the system in which the silane cage is present, with or without oxygen atoms. The presence of the silyl group increases the energy of interaction, as it is only 1.7 kcal mol^{-1} in the case of H–C≡C–H·$CHCl_3$ (**7**·$CHCl_3$ in Figure 4). This last value is similar to that calculated by Mingos et al. with a different DFT method and a different basis set (1.01 kcal mol^{-1}).[18] These workers also found that MP2 gives slightly larger interaction energies (E_d) as compared to DFT.[18] We have made the same observation: our E_d(MP2) value for **7**·$CHCl_3$ is 2.2 kcal mol^{-1}, and that reported in the literature[18] is 1.82 kcal mol^{-1}. DFT calculated E_d is thus likely to be a lower limit of the true interaction energy. Nonetheless, comparisons between systems are probably correctly reproduced with

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(39) Voronkov, M. G.; Dyakov, V. M.; Kirpichenko, S. V. *J. Organomet. Chem.* **1982**, *233*, 1.

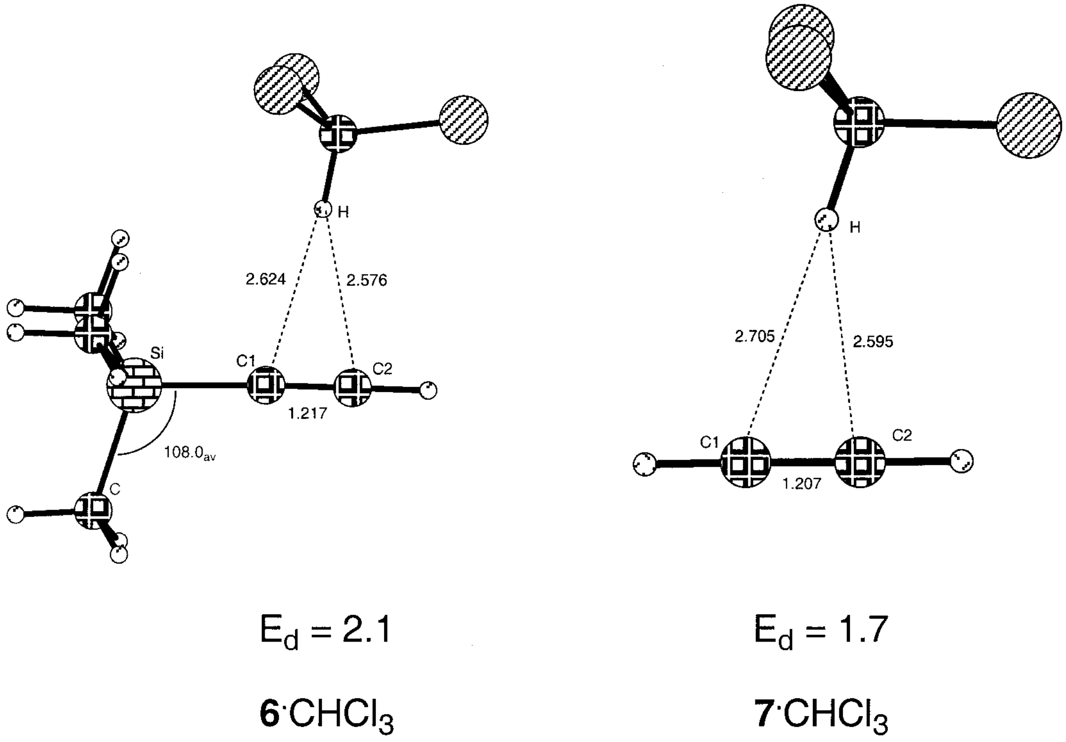

Figure 4. Optimized structures (DFT at the B3LYP level) of **6**·$CHCl_3$ and **7**·$CHCl_3$. Distances are in angstroms and angles in degrees. The dissociation energy (E_d) of chloroform is in kcal mol^{-1}.

DFT calculations, as it appears from a recent review on this subject.[40]

The above results suggest that the chloroform molecule interacts with **3** through one C−H···π contact and one C−H···O contact. What seems to be paradoxical at first is that the magnitude of the interaction does not become larger when both contacts are present at the same time in a single system (compare **4CH₂**·$CHCl_3$ with **5O**·$CHCl_3$). To confirm these findings, the energy of interaction of $CHCl_3$ with H_2O (not shown) was calculated and found to be 4.9 kcal mol^{-1} (H···O = 1.996 Å and ∠C−H···O = 171.9°). A comparison of this last system with **4CH₂**·$CHCl_3$, for which the dissociation energy was calculated to be 3.0 kcal mol^{-1}, suggests that the interaction with an oxygen lone pair is greater than that with a π-bond. However, these interactions are sufficiently important to be competitive in a system where they both are present. For this reason, the chloroform molecule tries to interact with both groups at the expense of having a geometry that is suited to each one. Individual interactions are thus diminished, but the overall sum remains approximately constant.

In summary, all of the calculations indicate that the interaction between **3** and $CHCl_3$ detected in the solid state is weak and, thus, the latter does not survive in solution (entropy factors favoring dissociation have been neglected in the computational study). However, the E_d values calculated here are probably a lower limit of the real values. The interaction is increased by the presence of a pentacoordinated silicon atom, which makes the triple bond more electron-rich due to a greater accumulation of electron density on the apical ligands.[41] Our calculations underestimate this phenomenon since the Si−N bond is systematically too long. This explains why our calculated C−H···π distances are longer than the experimental values, whereas the C−H···O distances are better represented. An increase in the strength of the Si←N interaction would result in the following: the O−Si−C(1) average angle would decrease and more electron density would be transferred to the C(1)−C(2) triple bond and to the oxygens of the silatrane moiety. A combination of these geometrical and electronic effects should lead to a stronger interaction with chloroform as the latter molecule would be closer to both O and C(1) and, thus, would interact better with each center. Finally, DFT calculated energy values are smaller than MP2 values. Although it is not possible to give a more accurate value of E_d, the reality of these interactions is safely established.

Conclusion

The X-ray crystal structure of $(CH_3)_3Si-C\equiv C-C\equiv C-Si(OCH_2CH_2)_3N\cdot 2CHCl_3$ (**3**·$2CHCl_3$) has been solved. It shows that each chloroform molecule interacts with diacetylenic silatrane **3** through one C−H···O contact and one C−H···π contact. A careful examination of the distances and angles between the solvent molecules and the silatrane indicates that these interactions are weak, and spectroscopic measurements have been carried out in solution and in the solid state that confirm this. DFT calculations at the B3LYP level indicate that these interactions are real and the importance of each factor responsible for them (presence of oxygens in the silatrane cage, presence of the triple bond, pentacoordina-

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[40] Calhorda, M. J. *Chem. Commun.* **2000**, 801.

[41] (a) Frolov, Yu. L.; Shevchenko, S. G.; Voronkov, M. G. *J. Organomet. Chem.* **1985**, *292*, 159. (b) Gordon, M. S.; Windus, T. L.; Burggraf, L. W.; Davis, L. P. *J. Am. Chem. Soc.* **1990**, *112*, 7167. (c) Carroll, M. T.; Gordon, M. S.; Windus, T. L. *Inorg. Chem.* **1992**, *31*, 825.

tion at silicon) has been assessed. A value of 4.2 kcal mol^{-1} has been calculated for the interaction energy between chloroform and silatrane **3**. This energy is probably underestimated because of the limitations of the computational method that we have used and also because pentacoordination at silicon is not fully taken into account due to the weak Si←N bond.

Experimental Section

General Comments. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer with a 4 cm^{-1} resolution. Cross-polarization magic angle spinning (CP/MAS) ^{13}C and ^{29}Si NMR spectra were obtained on a Bruker AM 300 instrument operating at 7.1 T (^{13}C at 75.5 MHz and ^{29}Si at 59.6 MHz) using high-power proton-decoupling. Samples were spun at 5 kHz in 7 mm zirconia rotors. Carbon and silicon chemical shifts were referenced with an external sample of tetramethylsilane (TMS).

Synthesis of $(CH_3)_3Si-C\equiv C-C\equiv C-Si(OCH_2CH_2)_3N$ (3). Compound **3** was prepared as described in a previous study.[22]

Crystallography. Data were collected on a Stoe imaging plate diffraction system (IPDS) equipped with an Oxford Cryostream cooling device. The crystal-to-detector distance was 80 mm; 125 exposures (4 min per exposure) were taken with $0° < \varphi < 200°$ and crystal oscillations of 1.6° in φ.[42] Coverage of the unique set was over 99.7% complete to at least 24.2°. Owing to the low value of μ, no absorption correction was made.

The structure was solved by direct methods (SHELXS-86).[43] The SHELXL-93 program was used for full-matrix least-squares refinement against F_o^2 using 3982 independent reflections.[44] Atomic scattering factors were taken from a standard source.[45] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a difference Fourier map. The hydrogens of the chloroform molecules were allowed to vary. The other ones were introduced in the calculations with the riding model (d(C−H) = 0.97 Å for CH_2, d(C−H) = 0.96 Å for CH_3) with isotropic thermal parameters equal to 1.1 times that of the atom of attachment. Final R values and relevant crystallographic data are given in Table 1. Hydrogen bonds and contacts between $CHCl_3$ and $(CH_3)_3Si-C\equiv C-C\equiv C-Si-(OCH_2CH_2)_3N$ are listed in Table 2. Selected bond lengths and angles are given in Table 3.

Computational Details. All calculations were carried out using the Gaussian 94 set of programs[46] within the framework of DFT at the B3LYP level of theory.[47] Cl and Si were represented with the LANL2DZ ECPs,[48] and their associated double ζ augmented by a d polarization function.[49] A 6-31G(d,p) basis set was used for all other atoms.[50] Full optimizations were carried without symmetry constraints.

Supporting Information Available: For **3**·2$CHCl_3$, tables of crystal data and experimental details, positional and thermal parameters, full lists of interatomic distances, bond angles, and final hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(42) *Stoe IPDS Manual: Version 2.87*; Stoe & Cie: Darmstadt, Germany, 1997.

(43) Sheldrick, G. M. *SHELXS-86*: *Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.

(44) Sheldrick, G. M. *SHELXL-93*: *Program for the Refinement of Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1993.

(45) *International Tables for Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1992; Vol. C.

(46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision D.2*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(47) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(48) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(49) Höllwarth, A. H.; Böhme M. B.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237.

(50) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.