

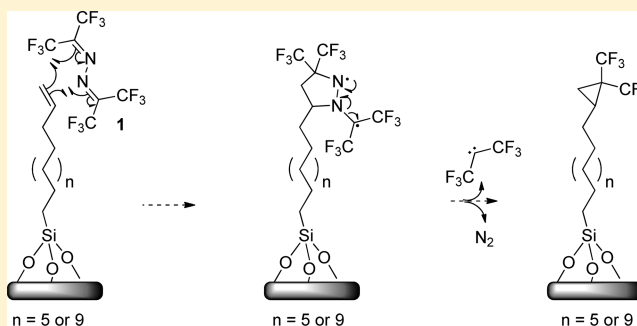
Bis(trifluoromethyl)methylene Addition to Vinyl-Terminated SAMs: A Gas-Phase C–C Bond-Forming Reaction on a Surface

Malgorzata Adamkiewicz, David O'Hagan,* and Georg Hähner*

EaStCHEM School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, U.K.

Supporting Information

ABSTRACT: Vinyl-terminated self-assembled monolayers (SAMs) on silicon oxide substrates were chemically modified by the addition of a bis(trifluoromethyl)methylene group in a rare gas-phase C–C bond-forming reaction to directly generate films carrying terminal CF_3 groups. The vinyl-terminated films were treated with hexafluoroacetone azine (HFAA) for modification. The films were characterized with ellipsometry, contact angle measurements, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). In this study, we find that for optimized conditions clean reactions occur on a surface between SAMs with terminal olefins and HFAA, and the product is consistent with bis(trifluoromethyl)cyclopropanation formation after nitrogen extrusion.



INTRODUCTION

Silane-based self-assembled monolayers (SAMs) with long organic chains play an important role in surface chemistry as they establish physically,^{1,2} thermally,^{3,4} and chemically stable films⁵ on substrates such as silicon oxide and glass. In addition, varying the functionality of the organic chain offers the potential to tailor surface properties in a controllable fashion.⁶ While there are many options to deposit a SAM from solution or to chemically modify a preformed SAM in solution (see, for example, refs 6–10), direct gas-phase modification is much more limited.^{11,12} In organic chemistry, C–C bond-forming reactions that occur entirely in the gas phase and without an added catalyst are extremely rare, thus there are few options for direct C–C bond gas-phase surface modification. Despite the limited reactions in the gas phase, solventless reactions are attractive as they are potentially less disruptive to film integrity than dipping a preformed SAM into a reaction solution. Immersion can reduce the quality of the resultant films, and the penetration and homogeneity are compromised if a solution cannot wet all parts of a (sub)microstructure substrate, for example, in the case of microelectromechanical systems (MEMS), due to microscopic gas bubbles. On the other hand, vapor-phase deposition has been used to form SAMs on silica¹³ and graphite, and we have recently shown that high-quality vinyl-terminated films can be achieved by this approach.¹⁴ The present study aimed to chemically modify the SAM in a second gas-phase process by a C–C bond-forming reaction. In this context, hexafluoroacetone azine (HFAA) **1** emerged as an appropriate reagent as it has been reported to generate cyclopropanes **2** with olefins such as but-2-ene without any catalyst or coadditive on heating as illustrated in Figure 1.^{15,16}

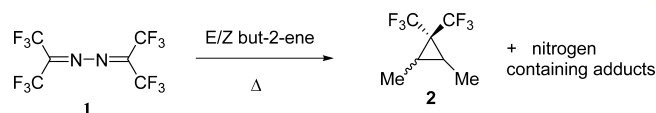


Figure 1. Hexafluoroacetone azine **1** generates di(trifluoro-methyl)-cyclopropanes on heating with olefins.^{15,16}

The reaction also gave rise to some nitrogen-containing cycloadducts when performed in the gas phase and does not appear to proceed via a discrete $(\text{CF}_3)_2\text{C}:$ carbene, but rather the cyclopropane arises from decomposition and nitrogen (N_2) extrusion after the addition of **1** to the olefin. Clearly, if **1** is activated and long-lived enough in the vapor phase, then it may react directly in the gas phase with the olefinic residues of the vinyl-terminated silanes of preformed SAMs.

The goal of the present study was to demonstrate the potential of vinyl-terminated films for direct chemical modification in the gas phase. Such an approach offers cleaner reaction conditions than solution-based techniques and would be preferable in many high-end applications. In addition, the selectivity of the reaction would have a clear advantage over the gas-phase plasma treatment of hydrocarbons (e.g., ref 17). In the present study, fluorine was employed as an XPS marker to track the C–C bond-forming reaction, rather than a substituent to modify surface properties per se.

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EXPERIMENTAL SECTION

Chemicals. Commercially available n-type, one-side-polished silicon (100) wafers (Wacker Chemie AG, Munich, Germany) were used as substrates.

Vinyl-terminated trichlorosilanes with alkyl chain lengths of 11 carbon atoms (10-undecenyltrichlorosilane, $\text{CH}_2=\text{CH}-(\text{CH}_2)_9-\text{SiCl}_3$) and 15 carbon atoms (14-pentadecenyltrichlorosilane, $\text{CH}_2=\text{CH}-(\text{CH}_2)_{13}-\text{SiCl}_3$), referred to as molecules 3 and 4 (Figure 2),

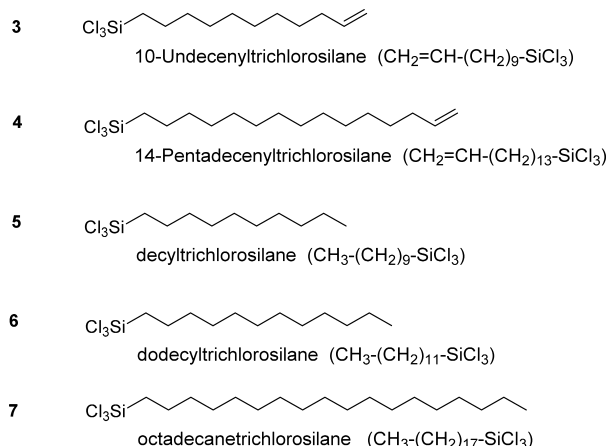


Figure 2. Molecules used for the formation of SAMs on silicon oxide substrates.

were prepared according to the literature.¹⁸ Details are also given in the Supporting Information (SI). The purity of the newly synthesized compounds was similar to values reported in the literature (see SI).¹⁹

The methyl-terminated species (referred to as 5, 6, and 7, see Figure 2) were obtained from Alfa Aesar (Lancashire, U.K.): decyltrichlorosilane ($\text{CH}_3(\text{CH}_2)_9\text{SiCl}_3$ - 97%), dodecyltrichlorosilane ($\text{CH}_3(\text{CH}_2)_{11}\text{SiCl}_3$ - 95%), and octadecyltrichlorosilane ($\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ - 95%). HPLC-grade toluene (99.9%) was obtained from Sigma-Aldrich (Dorset, U.K.). HPLC-grade dichloromethane was obtained from VWR International (Leicestershire, U.K.). Hydrogen peroxide (30%), ammonium hydroxide (35%), sulfuric acid (95%), and hydrochloric acid (36%) were all obtained from Fisher Scientific (Leicestershire, U.K.). Hexafluoroacetone azine (HFAA - 99%) was obtained from Sigma-Aldrich. All chemicals were used without further purification.

All experimental steps were performed in a fume hood under an inert atmosphere of nitrogen or argon using oven-dried glassware.

Precleaning of the Silicon Substrates. The silicon substrates were cleaned before the deposition of the self-assembling monolayers as described in ref 14. Details of the cleaning procedure are also given in the SI. Once precleaned, the substrates were immediately coated with an organic (silane) film.

Vinyl- and Methyl-Terminated Films. At the outset, we prepared good-quality methyl- and vinyl-terminated SAMs on silicon oxide substrates.¹⁴ The methyl-terminated SAMs served as nonreactive reference substrates, devoid of olefinic groups.

Chemical Modification of Alkyl- and Alkenyltrichlorosilane SAMs. Freshly prepared, SAM-coated silicon substrates were placed in a Schott Duran bottle (100 mL capacity) equipped with a PTFE sealed cap. The bottle was purged three times with nitrogen before a certain amount of reactive intermediate precursor material HFAA (boiling point: 67–68 °C) was added to the bottle in a separate, smaller, open-topped vessel (see Figure 3).

There was no direct contact between the liquid HFAA 1 reservoir and the organically precoated substrates during the reaction. The vessel was held at fixed temperatures (80, 120, and 160 °C) and for defined periods of time (10, 20, and 30 min and 1, 2, 5, and 48 h). After each reaction, the samples were sonicated (15 min) sequentially in toluene, dichloromethane, and then deionized water.

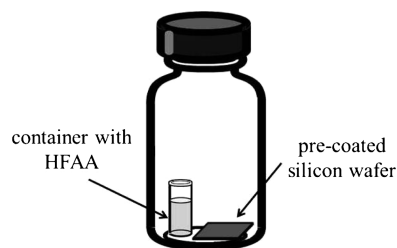


Figure 3. Schematic of the setup used for the chemical gas-phase modification of the SAMs.

Surface Analytical Characterization. The chemically modified silicon substrates were analyzed using contact angle measurements to determine their hydrophilicity/hydrophobicity, ellipsometry to determine the thickness of the (modified) coating, X-ray photoelectron spectroscopy (XPS) to determine the chemical composition of the (modified) coating, and atomic force microscopy (AFM) to investigate the homogeneity and roughness of the (modified) coating. All reported results and values are based on at least two independent measurements.

Contact Angle Measurements. Water contact angles (DI water) were measured with a G10 goniometer microscope (Krüss GmbH, Hamburg, Germany) under ambient conditions at room temperature. Droplets of $\sim 3 \mu\text{L}$ were dispensed from a microburet. All reported values are the average of three measurements taken from different places on the surface.

Ellipsometry. The thickness of the SAMs was measured with an M-2000DI spectroscopic ellipsometer (J. A. Woollam Co., Inc., USA). Thickness values were extracted from fits to the data taken at 45, 50, 55, 60, 65, and 70° over wavelengths from 200 to 1000 nm. The sample surface was modeled as a Si substrate with an oxide layer and a Cauchy layer. The thickness of the silicon oxide after the oxidative cleaning treatment was $16 \pm 1 \text{ \AA}$ (average of three samples). The thickness of the monolayer films was calculated with an index of refraction of 1.45.^{20,21} Film thickness values are averages of at least three measurements. The observed variability of the thickness of organic films prepared under identical conditions was $\sim 2 \text{ \AA}$, i.e., the variation of chemically identical films which were prepared at different times (not the same "batch"). In some cases, we prepared a batch of samples (10 to 15) with the C_{11} vinyl-terminated film. We determined the film thickness for several samples (typically three to five) rather than for each sample individually. Values between 14.5 and 15.5 Å are reported as $\sim 15 \text{ \AA}$ (mean value) for all samples from the same batch in the following. The reproducibility (standard deviation) of the thickness for a single film was $\sim 0.2 \text{ \AA}$ (measured on at least three different spots on the same surface).

XPS. X-ray photoelectron spectroscopy spectra were obtained using a VG Sigma Probe (VG Scientific Ltd., U.K.) and Al $K\alpha$ radiation (1486.6 eV). During the analysis, the pressure in the test chamber was kept at around 1×10^{-8} Torr. The XPS spectra were corrected for charging by referencing the aliphatic C 1s peak of hydrocarbon to 285.0 eV. Elemental compositions of the various surfaces were determined from the area under individual elemental peaks using sensitivity factors provided with the software as well as taking the transmission function of the analyzer into account. CasaXPS (Casa Software Ltd., U.K.) was used for the analysis. The spectra were fitted using Gaussian peak shapes. A Shirley background was subtracted for the quantitative analysis. Quantitative data is reported assuming a model where all constituents are homogeneously and isotropically distributed in the analyzed volume.

Atomic Force Microscopy. The atomic force microscope used was a PicoSPM II (Molecular Imaging, USA) with an interchangeable nose scanner. The nominal spring constant of the V-shaped cantilevers used was 0.06–0.12 N/m (Veeco, USA). Images were recorded under ambient conditions at a scanning speed of ~ 0.8 lines/s and with a nominal contact force on the order of 10 nN.

Synthesis of 2,6-Dioctyl-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazobicyclo[3,3,0]octane. Hexafluoroacetone azine (1.0 g,

3.1 mmol, 1 equiv) and 1-decene (0.9 g, 6.2 mmol, 2 equiv) were placed in an autoclave and held at 160 °C for 48 h. The reaction mixture was purified by silica gel chromatography (hexane) to give the “criss-cross” adduct shown in Figure 4 as a colorless oil (278 mg,

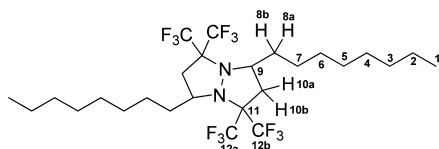


Figure 4. Schematic of criss-cross adduct $C_{26}H_{41}F_{12}N_2$.

15%). 1H NMR (300 MHz, $CDCl_3$): δ_H 3.62–3.48 (2H, m, $CH(CH_2)_7CH_3$), 2.75 (2H, dd, J 13.8, 6.1 Hz, $(CF_3)_2CH_2$ 10a), 2.45 (2H, dd, J 13.8, 9.7 Hz, $(CF_3)_2CCH_2$ 10b), 1.89–1.75 (2H, m, $CH_2(CH_2)_6CH_3$ 8a), 1.37–1.14 (26H, m, $CH_2(CH_2)_6CH_3$ 8b), 0.88 (6H, t, J 6.5 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 123.7 (q, J 2.8 Hz, CF_3 12a), 123.5 (q, J 2.9 Hz, CF_3 12b), 69.0 (m, $(CF_3)_2C$), 56.6 (CH: C9), 41.1 ($(CF_3)_2CCH_2$: C10), 33.0 ($CH_2(CH_2)_6CH_3$: C8), 32.0, 29.7, 29.6, 29.3, 25.9, 22.8 (CH_2 , C2–C7), 14.2 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ_F –67.6 (6F, q, J 18.0, 8.6 Hz, CF_3 a), –73.6 (6F, q, J 18.0, 8.6 Hz, CF_3 b). HRMS m/z (CI): calculated for $C_{26}H_{41}F_{12}N_2$ $[M + H]^+$, 609.3073; found, 609.3064.

RESULTS

Methyl- and Vinyl-Terminated SAMs. The XPS survey spectra of all samples with methyl- and vinyl-terminated SAMs (not shown) showed the presence of Si (2s 150.4 eV, 2p 99.2 eV), C (1s 285.0 eV), and O (1s 533.0 eV) as expected. The spectra distinguish between the bulk Si (Si 2s 150.4 eV, Si 2p 99.2 eV) and the silicon oxide (Si 2s 154.3 eV, Si 2p 102.8 eV). No Cl peak was observable for any of the films. Contact angle measurements and the film thickness determination with ellipsometry confirmed densely packed monolayers. The results are summarized in Tables 1 and 2.

Methyl- and Vinyl-Terminated SAMs after Reaction with HFAA. In the first step, the best preparation conditions for the reaction between HFAA and the vinyl-terminated films

were determined by testing a range of different temperatures (80, 120, and 160 °C) at several defined periods (10, 20, and 30 min and 1, 2, 5, and 48 h). In addition, different amounts of HFAA (50, 100, 150, 200, 300, and 400 μ L) were employed for modification. The water contact angle values as well as the film thicknesses, before and after the reaction of the vinyl-terminated SAMs, are listed in Table 1. If the evaluation indicated a significant decrease (>5 Å) in film thickness after the reaction, then we interpreted this as an indication of degradation. Those thickness values are reported as <10 Å and were not investigated further.

For the vinyl-terminated surfaces derived from 3 and 4, organic fluorine on the surface became obvious in the XPS spectra at reaction temperatures above 120 °C (see Figure 5).

Figure 6 displays survey spectra recorded for samples with different reaction periods. Samples that reacted for times greater than 1 h showed the strongest F signal by XPS.

The results reported in Table 1 and the XPS spectra in Figure 6 indicate that degradation of the vinyl-terminated SAMs occurs for reaction periods of more than 30 min. Therefore, different amounts of HFAA were tested in combination with a reaction period of 20 min and a temperature of 160 °C. Figure 7 shows the corresponding XPS survey spectra.

Although a reservoir volume of 400 μ L of HFAA resulted in a higher F signal than a volume of 200 μ L, Table 1 indicates that 400 μ L also caused a slight decrease in both the film thickness and contact angle value. We interpret this as a sign of degradation. Since a volume of 300 μ L appeared to give very similar results to that of 200 μ L, without a further increase in the contact angle value, we decided to use a volume of 200 μ L as the optimum for the preparation of nondegraded modified films.

On the basis of the results above a temperature of 160 °C, a reaction period of 20 min and a volume of 200 μ L of HFAA gave the optimum conditions for the modification of the vinyl-terminated SAMs. The F 1s single-region scan of the films

Table 1. Vinyl-Terminated SAM-Coated Silicon Substrates

precursor molecule	reaction temperature (°C)	HFAA (μ L)	time	film thickness (Å)		film contact angle (deg)	
				before	after	before	after
C_{11} -vinyl (3)	160	150	48 h	~15	<10	101	55
C_{11} -vinyl (3)	160	50	48 h	~15	<10	101	50
C_{11} -vinyl (3)	160	50	5 h	~15	<10	101	83
C_{11} -vinyl (3)	160	50	2 h	~15	<10	101	97
C_{11} -vinyl (3)	160	50	1 h	~15	<10	101	95
C_{11} -vinyl (3)	160	50	30 min	~15	<10	101	99
C_{11} -vinyl (3)	160	50	20 min	~15	13.1	101	106
C_{11} -vinyl (3)	160	50	10 min	~15	13.1	101	104
C_{11} -vinyl (3)	120	50	20 min	14.9	12.4	101	101
C_{11} -vinyl (3)	120	100	20 min	15.3	15.3	101	101
C_{11} -vinyl (3)	80	50	20 min	13.6	12.4	101	101
C_{11} -vinyl (3)	80	100	20 min	14.7	15.3	101	101
C_{11} -vinyl (3)	160	100	20 min	~15	16.1	101	106
C_{11} -vinyl (3)	160	150	20 min	14.6	15.2	101	106
C_{11} -vinyl (3)	160	200	20 min	14.9	15.3	101	106
C_{11} -vinyl (1)	160	300	20 min	15.1	16.7	101	106
C_{11} -vinyl (3)	160	400	20 min	15.4	13.1	101	100
C_{15} -vinyl (4)	160	200	20 min	19.1	20.4	101	106
C_{15} -vinyl (4)	160	300	20 min	19.1	21.7	101	106
C_{15} -vinyl (4)	160	400	20 min	20.2	18.1	101	103

Table 2. Methyl-Terminated SAM-Coated Silicon Substrates

precursor molecule	reaction temperature (°C)	HFAA (μL)	time	film thickness (\AA)		film contact angle (deg)	
				before	after	before	after
C ₁₀ -methyl (5)	160	100	20 min	15.2	10.9	105	103
C ₁₀ -methyl (5)	120	50	20 min			105	105
C ₁₀ -methyl (5)	120	100	20 min			105	105
C ₁₀ -methyl (5)	80	50	20 min			105	105
C ₁₀ -methyl (5)	80	100	20 min			105	105
C ₁₀ -methyl (5)	160	200	20 min	13.2	15.3	105	105
C ₁₈ -methyl (7)	160	200	20 min	27.1	26.2	109	109
C ₁₈ -methyl (7)	160	50	5 h	26.2	19.1	109	104
C ₁₈ -methyl (7)	160	50	2 h	26.3	25.4	109	109
C ₁₂ -methyl (6)	160	200	20 min	13.9	15.5	106	106

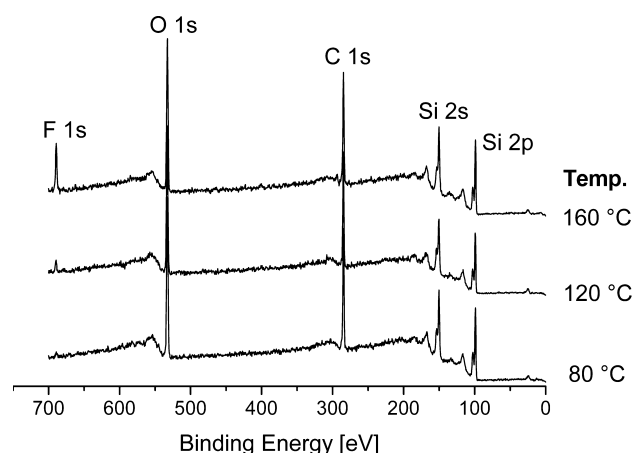


Figure 5. XPS survey scans of vinyl-terminated SAMs prepared from 3 after the reaction (20 min) with 1, performed at 80, 120, and 160 °C.

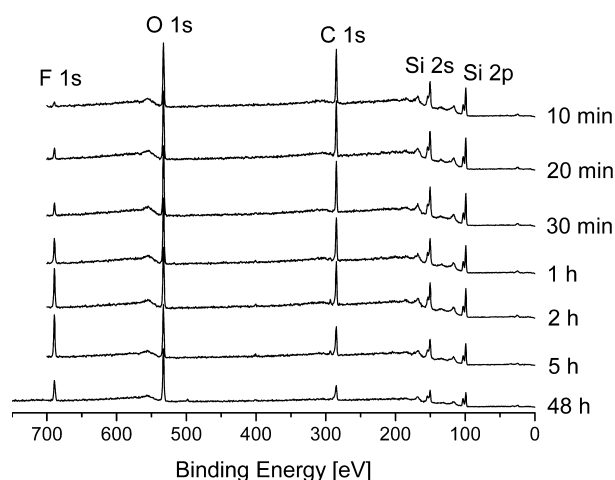


Figure 6. XPS scans of vinyl-terminated SAMs prepared from 3 after the reaction with 1, at 160 °C for various time periods.

treated with HFAA under these conditions showed one symmetric peak (not shown). In the C 1s single-region scan of HFAA-treated vinyl-terminated films, four different carbon species were observed (Figure 8).

Atomic Force Microscopy. AFM images of the vinyl-terminated films before and after modification with carbene showed very smooth surfaces with RMS values for roughness of ~ 75 – 120 pm averaged over an area of $5 \mu\text{m} \times 5 \mu\text{m}$, in agreement with monolayer coverage.¹⁴

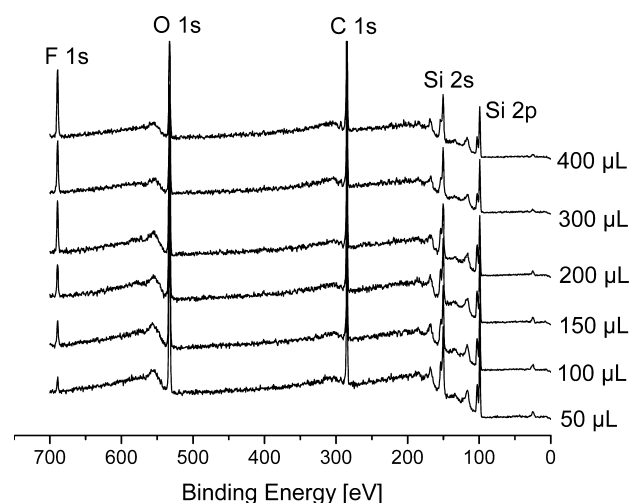


Figure 7. XPS results obtained from reactions of SAMs derived from 3 and treated for 20 min at 160 °C, varying the levels of 1.

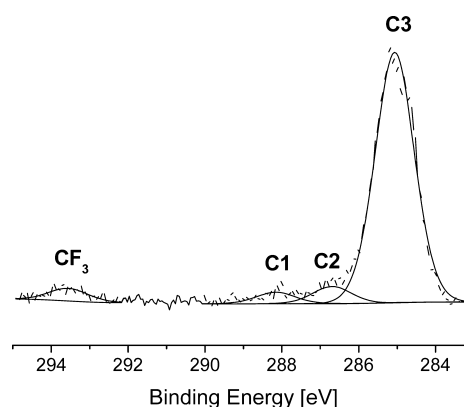


Figure 8. XPS C 1s single-region scan of the modified film of 3.

To explore the degree of selective reactivity of HFAA with the C=C double bond versus direct CH₂ insertion, several experiments were also performed with methyl-terminated SAMs of 5 and 7 as an unreactive control. A batch of C₁₀-methyl-terminated films (5) was prepared, and film thickness values were determined in selected cases. The water contact angle values as well as the film thicknesses, before and after exposure of the methyl-terminated SAMs to HFAA, are listed in Table 2.

Methyl-terminated samples exposed to HFAA under the optimum preparation conditions were further investigated with

XPS. After their exposure to HFAA, no changes were observed, consistent with their lack of reactivity (see Figure 9).

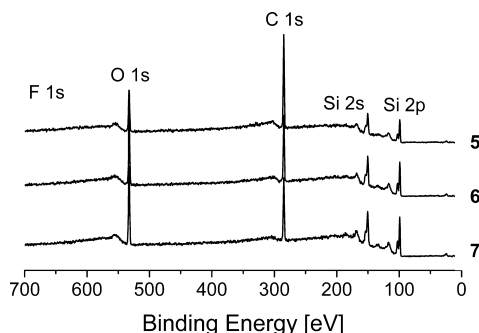


Figure 9. XPS survey scans of methyl-terminated SAMs prepared from 5, 6, and 7 after the reaction with HFAA. The spectra showed the presence of Si, C, and O. No F signal was observed (reaction conditions: 20 min, 160 °C, 200 μ L HFAA).

Gas-Phase Reaction between HFAA and 1-Decene. A control vapor-phase reaction between HFAA and 1-decene was performed under similar reaction conditions to those described above with the vinyl-terminated SAMs. In the reaction mixture, the “criss-cross” adduct shown in Figure 4 was formed.

DISCUSSION

The methyl-terminated surfaces prepared from 5–7 remained unmodified for reaction periods of less than 5 h. This is obvious by the absence of any signal in the XPS spectra corresponding to the presence of fluorine on the surface. This lack of reaction was also confirmed by film thickness measurements with ellipsometry and water contact angle measurements both before and after the reaction of the precoated substrates. The contact angle values as well as the film thicknesses remained approximately constant before and after exposure to HFAA (Table 2).

For the vinyl-terminated SAMs, the optimum reaction conditions produced surfaces with slightly higher contact angles and similar film thickness values to those of the unmodified vinyl-terminated SAMs (Table 1). The reactivity of HFAA and the intermediates formed during reaction and the mechanism of the reaction with a double bond have been a source of discussion for some time.^{22,23} Figure 10 illustrates a putative mechanism for the formation of bis(trifluoromethyl)methylene-terminated SAMs in the vapor phase.

The mechanism is obtained from previous studies on the addition of **1** to organic olefins^{15,16} in reactions carried out in sealed tubes. In those reactions, cyclopropanes were formed, as

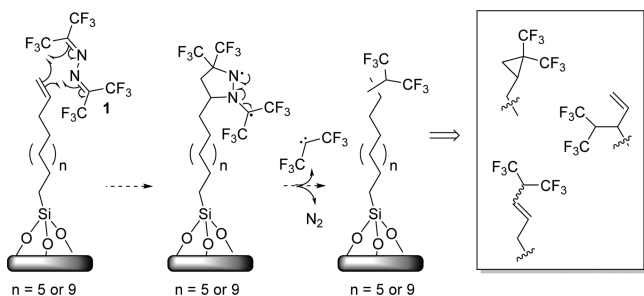


Figure 10. Putative minimal mechanism^{15,16} for the formation of bis(trifluoromethyl)methylene-terminated SAMs in the vapor phase.

were dimeric adducts where two molecules of the olefin substrate had reacted with **1** to generate nitrogen-containing heterocyclic products. We did not find any XPS evidence for nitrogen-containing products in the surface reactions between vinyl-terminated SAMs of 3 and 4 and azine **1** for reaction periods of less than 30 min. Only after 1 h of reaction with vinyl-terminated films was a small amount of nitrogen detected by XPS (see SI). The presence of nitrogen might suggest the formation of the criss-cross adduct, but this was apparent only when the SAM had undergone degradation, and presumably the steric constraints of the surface became less of a constraint.

The control vapor-phase reaction between HFAA and 1-decene showed the criss-cross adduct and some unidentified compounds in the reaction mixture. Since reaction on the surface has unique conformational constraints in bringing two olefin groups together, the preferred mode of breakdown of the initial adduct appears to result in products where nitrogen (N_2) is extruded and the C_3 fragment adds to the double bond (see Figure 10).

The fact that the XPS F 1s single-region scan of the films treated with HFAA showed one symmetric peak suggests a single fluorine environment on the surface, which is assigned to the CF_3 group. The carbon region has four different species (Figure 8) and is consistent with a bis(trifluoromethyl)methylene cyclopropyl motif as illustrated in Figure 11.



Figure 11. Schematic of the proposed reaction product of the vinyl-terminated SAMs with HFAA, a bis(trifluoromethyl)methylene cyclopropyl motif. The XPS C 1s scans indicate four different carbon species.

The carbon peak, showing the largest shift toward higher binding energies from the region of 282.5–288.5 eV, was assigned to carbon C1 (288.1 eV).²⁴

According to the proposed structure, this corresponds to the $-C(CF_3)_2$ species. A second carbon peak, with a binding energy of ~ 286.6 eV, was assigned to the C2 carbon species (two carbons of the cyclopropane ring). The most intense signal, C3, was assigned to the carbons from the alkyl chain (285.0 eV). The XPS spectrum in Figure 8 indicates a close to 2:1 ratio of the carbon C2 and C1 species. Because of the low intensity of the C1 and C2 signals, their ratio entails some uncertainty. Note, however, that these signals should be viewed in combination with the clearly observable $-CF_3$ signal. The correlation of the three carbon signals supports the assignment and the quantification of the ratios. The ratios are consistent with a predominant cyclopropanation product at the chain terminus. Other C_3 addition products may also be relevant as illustrated in the box in Figure 10; however, they fit much less

well into the integrated carbon ratios from XPS as their carbon C2 to C1 ratio is 1:1. The corresponding ratios obtained from the C₁₁-vinyl **3** and the C₁₅-vinyl **4** SAMs based on the C 1s and F 1s single-region scans are presented in Table 3.

Table 3. Theoretical and Experimental Ratios between F and C XPS Peak Intensities of **3 and **4****

		ratios		
		F/CF ₃	CF ₃ /C1	CF ₃ /C2
theoretical	C ₁₁ -vinyl 3	3:1	2:1	1:1
	C ₁₅ -vinyl 4	3:1	2:1	1:1
experimental	C ₁₁ -vinyl 3	3.1:1	1.8:1	1.0:1
	C ₁₅ -vinyl 4	3.1:1	2.1:1	1.0:1

Figure 8 also demonstrates that the experimentally observed ratio of the aliphatic C 1s to the –CF₃ signal is as high as ~20:1, while the theoretical ratio is ~7:1 if all vinyl groups of the SAM derived from **3** react. On the basis of the intensity of the F 1s signal and the sum of intensities of the C 1s signals and taking into account the attenuation of the latter, the reaction conversions of HFAA with C₁₁-vinyl **3** and C₁₅-vinyl **4** can be estimated to be 27 and 23%, respectively.

For temperatures above 120 °C, surface degradation competed with chemical modification over the time period of 30 min to 48 h, as was evident from a reduced carbon signal in XPS (see Figure 6), a reduced film thickness, and the decrease in water contact angle values (see Table 1). A comparison of the vinyl- and the methyl-terminated films (Tables 1 and 2) suggests that entire surfactant molecules are most likely removed, i.e., cleavage at the Si–O interface occurs because otherwise the methyl-terminated films should also show signs of degradation under these conditions.

The F signals in the survey scans of the vinyl-terminated films indicate that some F-containing species are present, which might be expected to lead to an increase in the contact angle (Figure 6). However, this will depend on the overall coverage. The vinyl-terminated films are less well packed than their methyl-terminated counterparts,¹⁴ which makes it easier for hydroxyl or potentially fluoride species to access the surfactant substrate interface and to attack the Si–O bond. A possible route for degradation is then via cleavage of the Si–O bond.

It therefore appears that the C–C addition reaction is competing with the removal of entire molecules, which is reflected by the increasing F signal but decreasing C signal in the XPS survey spectra for periods of between 30 min and 5 h (Figure 6). From a certain point on, however, all remaining surfactants are modified and further removal of surfactants will then lead to a decrease in the F signal (Figure 6, spectrum for 48 h). This is also supported by the appearance of a nitrogen signal in the XPS spectra for periods of between 1 and 5 h (see SI), indicating the establishment of the criss-cross product followed by a decrease in the N signal if modified molecules are removed by further degradation. It has been suggested that similar films decompose via C–C bond cleavage;²³ however, this is inconsistent with our observations. Elucidating the mechanism of degradation was not a focus of the present study and remains somewhat speculative.

We observed indications of degradation in methyl-terminated films only after a reaction period of 5 h (see Table 2). At this time, the intensity of the carbon signal decreased. This observation is consistent with that reported in ref 23 that HFAA is stable at elevated temperatures. However, after 5 h at

160 °C HFAA may start to decompose, and the various species formed from its decomposition may initiate SAM degradation. After this time, heating of the methyl-terminated films to 160 °C led to a degradation in control experiments.

For a reaction period of 20 min there was no degradation if less than 300 μL of HFAA was used, while the presence of fluorine atoms at the surface was clearly evident from XPS. At a constant reaction time of 20 min and a temperature of 160 °C the amount of HFAA **1** precursor in the reservoir evaporated completely from the liquid reservoir. There is a clear correlation between the amount of HFAA **1** precursor in the vapor phase and the level of conversion. At this relatively short reaction time, there was no obvious film deterioration observable. The resulting films were smooth when analyzed by AFM (the RMS roughness varied from ~75 to ~120 pm over a scan area of 5 μm × 5 μm) and showed no significant change in the film thickness and a slight increase in the contact angle value, supporting the integrity of high-quality films. The modified films are likely to be slightly more disordered than the vinyl-terminated layers due to the bulky bis(trifluoromethyl)-cyclopropane group. With a reaction yield of around 25%, no significant change in the contact angle value is expected or observed.

No reaction was observed for temperatures below 120 °C (Table 1). This indicates that the processes that occur are complex and depend on several parameters such as exposure dose and temperature. It appears that the chemical modification is determined by an activation energy and the kinetics of the competing reactions that are involved.

CONCLUSIONS

In this article, we describe a gas-phase surface modification reaction that is performed by heating in standard glassware under standard conditions, and there is no need for a mixed monolayer to ensure that the functional groups are particularly exposed.^{8,26} The reaction of HFAA with terminal olefins generates a bis(trifluoromethyl)cyclopropyl product, which constitutes a rare C–C bond-forming reaction in the gas phase. Bis(trifluoromethyl)cyclopropane-terminated SAMs are consistent with our results. A future challenge will be to extend the range of precursors that can generate suitable reactive species for such modification. It is also a challenge to offset the chemically induced thermal degradation of the surface layer for longer reaction periods.

ASSOCIATED CONTENT

Supporting Information

Syntheses of vinyl trichlorosilanes **3** and **4**. Cleaning procedure for the silicon oxide substrates. Nitrogen XPS spectra indicating the presence of the criss-cross product and film degradation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: do1@st-andrews.ac.uk.

*E-mail: gh23@st-andrews.ac.uk.

Notes

The authors declare no competing financial interest.

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