Organic chemistry on surfaces: Direct cyclopropanation by dihalocarbene addition to vinyl terminated self-assembled monolayers (SAMs)

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Abstract
C11-Vinyl-terminated self-assembled monolayers (SAMs) on silica surfaces are successfully modified in C–C bond forming reactions with dihalocarbenes to generate SAMs, terminated with dihalo- (fluoro, chloro, bromo) cyclopropane motifs with about 30% surface coverage.

Introduction
Self-assembled monolayers (SAMs) are increasingly being used as a means of surface modification to alter properties in a tuneable manner [1-3]. The major classes of SAMs are those with adsorbed long chain alkyl thiols on gold surfaces/nanoparticles [4,5], or long chain alkylsilanes on silica surfaces [6,7]. Two general approaches are taken to achieve surface modification as illustrated in Figure 1. The first involves incorporating pre-functionalised alkylsilanes/alkylthiols carrying functional groups (FG) to generate the SAM directly, whereas the second approach involves chemical modification of a pre-assembled monolayer carrying reactive groups (RG), as a means to introduce the SAM carrying the FGs [8]. Both approaches present challenges. In the former the desired functionality (FG) requires to be robust and orthogonal in reactivity to the chemistry involved in securing the substrate to the organic film (e.g., FG-Alkyl-SiCl3 and silicon substrate). In the latter chemical modification of the reactive groups of the pre-coated SAM has to be efficient enough such that a reasonable conversion can be obtained, with chemical specificity and lack of surface degradation. In this respect ‘click’ reactions have become attractive including azide–alkyne cycloadditions [9,10], Diels–Alder reactions [11,12], maleimide–thiol reactions [13], thiol–ene additions [14], and imine/oxime conjugations [15]. In this article we demonstrate that dihalocarbenes can be used to generate dihalocyclopropanes on olefin terminated SAMs.

We recently reported the formation of high quality vinyl-terminated SAMs generated from the vapour phase by adsorption of...
Figure 1: General strategies for incorporating functional groups (FGs) on the surface of self-assembled monolayers (SAMs), illustrated for alkylsilanes onto silica.

Figure 2a represents a surface after chemical modification with \( \text{CBr}_2 \) generated from CHBr\(_3\). New peaks appeared at binding energies of 71 and 182 eV in all of the samples. These were assigned to Br 3d and Br 3p signals, respectively [24,25]. Figure 2b shows the results obtained from SAMs after modification with \( \text{CCl}_2 \) generated from CHCl\(_3\). New signals at binding energies of 201 and 270 eV were detected. These were assigned to Cl 2p and Cl 2s [26]. Finally Figure 2c represents the surface after chemical modification with \( \text{CF}_2 \) generated from TMSCF\(_3\). A new signal at binding energy of 688.7 eV was detected and assigned to F 1s, consistent with a CF\(_2\) group present on the surface [27].

It was anticipated that gem-dibromo-, gem-dichloro- and gem-difluorocyclopropane-terminated SAMs will be formed, following the usual transformations of these carbones with double bonds. To add further support to this expectation, model reactions were carried out under each of the reaction conditions with dec-1-ene (1, Scheme 1). All of the cyclopropane products 2a-c were obtained cleanly and in moderate yields (see...
Figure 2: XPS scans after reactions with a) :CBr₂; b) :CCl₂ and c) :CF₂. In each case the upper traces are scans of C₁₁-vinyl SAMs, and the lower traces are C₁₈-Me-terminated SAMs each treated with the relevant carbene reaction solution. The expanded regions on the right hand side, associated with each C₁₁-vinyl SAM spectrum, show the key halide specific XPS signals.

Scheme 1: Model reactions of dec-1-ene (1) with dihalocarbenes in the liquid phase. a) and b) NaOH, BTEAC, CHX₃, DCM, 8 h, 25 °C; c) TMSCF₃, THF, NaI, 3 h, 65 °C.
Supporting Information File 1). The results of the model reactions demonstrate that formation of the dihalocyclopropane rings is a relatively clean process for this long chain terminal vinyl substrate. The absence of any side products gives confidence that only dihalocyclopropanes will be formed in the surface reactions.

Turning to the C₁₁-vinyl-terminated SAMs products. In each case the presence of gem-dihalocyclopropane groups on the surface is supported by the ratios of the C 1s signals to the Br 3d, Cl 2p or F 1s signal, respectively. The theoretical and experimental ratios between the carbon and halogen XPS signals are summarised in Table 1. In all cases the ratios are consistent with a modification coverage of ~30%, with a slightly lower conversion rate in case of F, which might be due to its higher electronegativity and an associated higher repulsion between the terminal groups after cyclopropanation. Conversion rates were determined by correcting the experimental C₃/(C₁ + C₂) ratios from Table 1 with a factor of \(d/(\lambda(1 - \exp(-d/\lambda)))\), where \(d\) is the film thickness (determined with ellipsometry) and \(\lambda\) the mean free path of the electrons. This accounts for the partial attenuation of the C₃ XPS carbon signal. The water contact angles (CAs) of Br, Cl and F carbene treated surfaces were recorded and the CA values obtained of 80°, 85° and 104°, respectively, are in good agreement with the literature [28-30]. Notably the fluorinated SAM has the largest contact angle as expected, however, the increase and the final contact angle values are clearly lower than that for a pure CF₃ terminated film (~118–120°) [31], but this is not surprising given that the halogen functional group density is lower.

Finally AFM images were recorded for the three dihalocyclopropane modified surfaces and they are shown in Figure 3a–c. In all cases the images are smooth and defect free. There was no excess of material observed from reagents after washing, and in each case the RMS surface roughness values did not exceed 150 pm. It is clear that there is no detectable change observed in

| Ratios | X:C₁ | X:C₂ | C₁:C₂ | C₃:(C₁+C₂) |
|--------|------|------|-------|------------|
| Theor. | .CX₂ | 2:1  | 1:1   | 1:2        | 3:1        |
| Exp.   | :CBr₂| 1.9:1| 0.9:1 | 1:2       | 7:6:1      |
| Exp.   | :CCl₂| 2.2:1| 1.1:1 | 1:2       | 7:4:1      |
| Exp.   | :CF₂ | 2.1:1| 1:1   | 1:2       | 8:5:1      |

Figure 3: AFM images of 5 μm × 5 μm area of C₁₁-vinyl SAMs modified with a) :CBr₂ carbene, RMS 93 pm; b) :CCl₂ carbene, RMS 101 pm; c) TMSCF₃, RMS 79 pm.
the film after each modification, and that the films are of good integrity.

An alternative approach, also illustrated in Figure 1 is to prepare SAMs using pure samples of pre-halogenated cyclopropyl chains, with deposition directly onto the surface. This presents the obvious challenge of obtaining highly ordered films after direct deposition. The current approach establishes films of good integrity, which then become chemically modified. There is good evidence that this is less straightforward with functionalised surfactants [32].

Conclusion
In summary we have been able to demonstrate that vinyl-terminated SAMs can be chemically modified by a range of dihalocarbenes to generate surfaces carrying the corresponding dihalocyclopropane motifs. The reactions demonstrate that these organic chemical transformations, which have been relatively widely used in solution reactions of olefins, can be extended to surface reactions of SAMs. This opens up prospects too of modifying surfaces in this manner with carbenes carrying more elaborate functional groups, and thus a more dramatic change to the surface properties.

Experimental
Bromoform (CHBr₃), chloroform (CHCl₃) and the Ruppert–Prakash reagent (CF₃Si(CH₃)₂) [33,34] were used as the carbene precursors for surface modification, with the resultant carbenes generated in solution. For dibromo- and dichlorocarbene generation a solution of NaOH with CHBr₃ or CHCl₃ was stirred with a solution of benzyltriethylammonium chloride (BTEAC, 0.1 mmol) in dichloromethane for 10 min at 0 °C. Pre-coated silicon wafers (1 cm × 1.5 cm) were immersed in the reaction mixture and the liquids were stirred at room temperature for fixed periods of time (see Supporting Information File 1). SAMs on silicon substrates form stable films [6,7], however, they can be vulnerable to chemical degradation particularly in aqueous base [28,35,36]. For this reason the NaOH concentration and reaction time required to be optimised. The reaction temperature was kept at 25 °C and the phase-transfer catalyst, benzyltriethylammonium chloride (BTEAC) was chosen to generate the :CX₂ carbenes, and minimise exposure of the wafers to the base.

The Ruppert–Prakash reagent (TMSCF₃) was used to prepare the gem-difluorocyclopropane-terminated SAMs by generating difluorocarbene, following the procedure of Wang et al. [22] for small molecule transformations. This involved stirring a solution of NaI (0.2 equiv) and TMSCF₃ in THF (2 mL), and then immersing the silicon wafers (1 cm × 1.5 cm) into the reaction mixture at 65 °C for a fixed period of time (see Supporting Information File 1). The experimental set-up for the surface modification with the three different carbenes is shown in Figure 4. Details of the surface analytical techniques used are given in the Supporting Information File 1.

Supporting Information
Supporting Information File 1
Synthesis protocols and additional surface analysis data. [http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-10-307-S1.pdf]

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Figure 4: The experimental set-up for the dibromo-, dichloro- and difluorocarbene reactions performed on C₁₁-vinyl SAMs.
