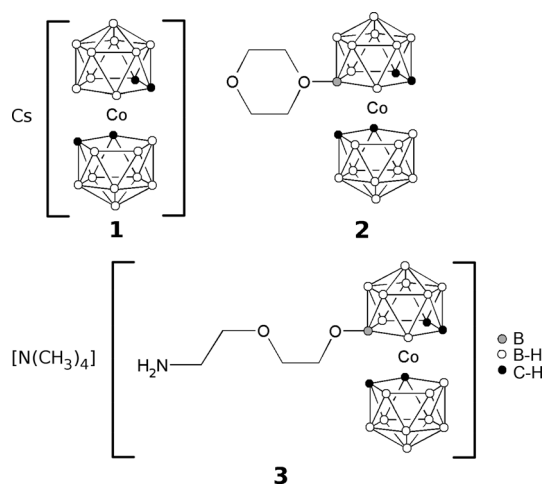


## Grafting of Metallocarboranes onto Self-Assembled Monolayers Deposited on Silicon Wafers

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The recent emergence of applications of carboranes as materials for nanotechnology and pharmacophores in drug design has greatly expanded the potential use of boron clusters.<sup>[1]</sup> The cobaltabisdicarbollide anion  $[3,3\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  (**1**) is a sandwich complex characterized by an extraordinary chemical and thermal stability (Scheme 1).<sup>[2]</sup> The cobaltabisdicarbollide is a hydrophobic<sup>[3]</sup> and weakly



Scheme 1. Structures of compounds **1**, **2**, and **3**.

nucleophilic anion.<sup>[4]</sup> Recently, Teixidor and co-workers reported that this cosane presented an amphiphilic character that led to the formation of monolayer vesicles at low concentration in water and small micelles at higher concentrations.<sup>[5]</sup> All these properties make it suitable for the stabilization of transient complex cation particles in catalysis and

for use as a strong non-oxidizing acid<sup>[1a]</sup> or as a solid electrolyte.<sup>[1a]</sup> It has also been proposed as a doping agent in conducting polymers<sup>[4,6]</sup> and as an extractant of radionuclides.<sup>[1h,7]</sup> The cobaltabisdicarbollide and its derivatives have several applications in medicine, for instance as specific inhibitors of HIV protease<sup>[8]</sup> and for boron neutron capture therapy of cancer (BNCT).<sup>[9]</sup> The use of cobaltabisdicarbollide in ion-selective poly(vinyl chloride) membrane electrodes for chiral amino acids and tuberculosis drug analysis has been recently published.<sup>[10]</sup> Great expectations have risen from these promising pharmaceutical tectons, and studies about their type of binding in the solid state, or association in solution, are being developed in order to understand the behavior of these borane compounds and their influence on biological mechanisms.<sup>[11]</sup>

The modification of surfaces with boron clusters to obtain new materials with specific properties and applications resulting from the presence of these compounds has recently attracted much attention.<sup>[12]</sup> The functionalization of gold, silver, and magnetic nanoparticle surfaces with charge-neutral *ortho*-carborane derivatives has been reported.<sup>[12]</sup> Nevertheless, to our knowledge very few examples of surface functionalization with the cobaltabisdicarbollide anion have been described. Recently, we reported the surface functionalization of TiO<sub>2</sub> nanoparticles with the cobaltabisdicarbollide anion, in which two phosphorous-containing cobaltabisdicarbollide derivatives Cs[1,1'- $\mu$ -(HO)(O)P-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>], and Cs[8,8'- $\mu$ -(OH)(O)-P(O)<sub>2</sub>-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] were grafted to the nanoparticles.<sup>[13]</sup>

In the course of our work dealing with the functionalization of surfaces, we have looked for a convenient method to chemically attach the cobaltabisdicarbollide anion to oxidized silicon surfaces, which actually are by far the most studied inorganic surfaces. Two different substitutions can be carried out on the cobaltabisdicarbollide, either on carbon or on boron atoms. Few examples have been reported concerning direct substitutions on carbon atoms.<sup>[14]</sup> In contrast, cobaltabisdicarbollide derivatives have been prepared by substitution at boron under Friedel-Crafts conditions<sup>[15]</sup> or with strong alkylating agents.<sup>[16]</sup> The high-yield synthesis and easy preparation of the zwitterionic 8-dioxanate derivative  $[3,3'\text{-Co}(8\text{-C}_4\text{H}_8\text{O}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$  (**2**) has been reported (see Scheme 1).<sup>[17]</sup> Compound **2** has been shown to be susceptible to nucleophilic attack on the positively charged oxygen atom, for example,

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by pyrrolyl,<sup>[18]</sup> imide, cyanide or amines,<sup>[19]</sup> phenolate, dialkyl or diaryl phosphite,<sup>[20]</sup> alkoxides,<sup>[21]</sup> among others;<sup>[22]</sup> resulting in anionic species formed by the opening of the dioxane ring. As a consequence, compound **2** has been attached to different groups, such as nucleosides,<sup>[23]</sup> porphyrins,<sup>[24]</sup> calixarenes,<sup>[21]</sup> and dendrimers.<sup>[25]</sup>

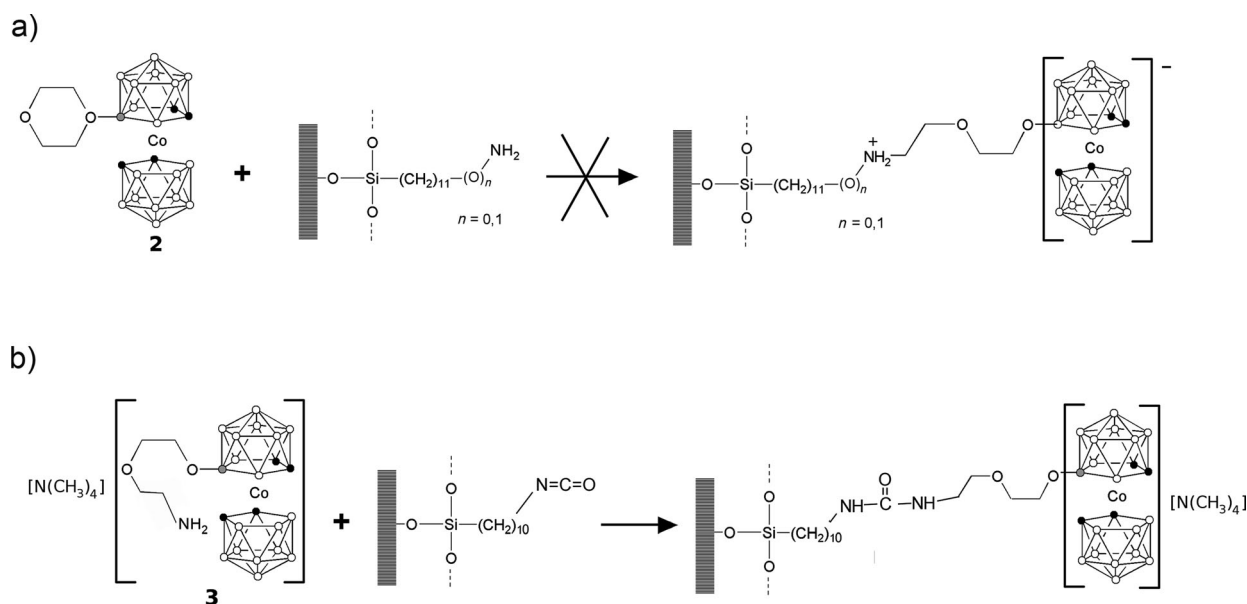
Herein, two approaches were investigated for the anchoring of cobaltabisdicarbollide to oxidized silicon surfaces (Scheme 2): a) in situ opening of the dioxane ring in **2** by reaction with an amine- or an oxyamine-terminated monolayer deposited on the oxidized silicon wafer surface and b) pre-opening of the dioxane ring of **2** by NH<sub>3</sub> to form compound **3** (see Scheme 1) and further reaction of **3** with an isocyanate-terminated monolayer deposited on the oxidized silicon wafer surface.

In the first approach we wanted to take advantage of the well-documented ring-opening reaction of compound **2** by a nucleophile.<sup>[18–25]</sup> For that purpose, NH<sub>2</sub> and ONH<sub>2</sub> terminated monolayers were deposited on oxidized silicon wafers by reaction with (11-amino)undecyltrimethoxysilane or (11-aminoxy)undecyltrimethoxysilane, as described in the Experimental Section. In both cases, the thickness determined by ellipsometry was consistent with the formation of a monolayer.<sup>[26]</sup> Then, these monolayers were further reacted with compound **2** in the hope that nucleophilic attack of the amine or oxyamine would open the dioxane ring (Scheme 2a). After the surfaces were washed and sonicated, they were characterized by X-ray photoelectron spectroscopy (XPS). However, in both cases the peak at approximately 780 eV corresponding to Co 2p<sub>3/2</sub> electrons could barely be detected. The peak corresponding to B 1s electrons is expected at about 188 eV,<sup>[27]</sup> but in this region only a weak and very broad peak between 195 and 180 eV was observed, indicating strong interference by silicon plasmon peaks, which prevented quantification. These results indicated that the in

situ dioxane ring opening approach was not successful, and the samples were not further characterized.<sup>[28]</sup> The poor reactivity is probably due to the mild conditions used as well as to steric hindrance.<sup>[29]</sup> Flink et al. investigated the reactivity of amino-terminated SAMs toward different functional groups, concluding that if the reactant was very bulky, the conversion was low.<sup>[29]</sup> Thus, although in solution these reactions go to completion, and the ring-opening reaction has been a very useful way for anchoring cobaltabisdicarbollide units to different platforms,<sup>[23–25]</sup> in our case this reaction did not allow significant anchoring of anionic metallacarboranes to the substrate. This result led us to look for an alternative strategy.

In the second approach, the dioxane ring was opened with an adequate nucleophile in solution prior to reaction with an isocyanate-terminated monolayer. Thus, [NMe<sub>4</sub>][8-NH<sub>2</sub>-C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>-3,3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] (**3**) was obtained by the reaction of **2** with aqueous ammonia (28%), using the procedure described by Semioshkin et al. for oxonium derivatives of [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup>.<sup>[30]</sup> Compound **3** was isolated as a tetramethylammonium salt by adding a saturated solution of [NMe<sub>4</sub>]Cl. The structure of **3** (see Scheme 1) was corroborated by IR and <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy data, which agreed well with those described by Sivaev et al.<sup>[19]</sup> Then, an isocyanate-terminated monolayer surface was prepared by reaction of the oxidized silicon Si(100) wafer with a solution of 10-isocyanatodecyltrichlorosilane in trichloroethylene in the presence of diisopropylethylamine. AFM and ellipsometry measurements indicated the formation of a homogeneous monolayer.<sup>[26]</sup> This isocyanate-terminated SAM was reacted with **3** to form urea bridges (NH–C=O–NH) between the surface and the cobaltabisdicarbollide derivative (Scheme 2b).

After rinsing and sonication, the modified wafers were characterized by XPS, attenuated total reflectance Fourier



Scheme 2. Approaches used for the grafting of cobaltabisdicarbollide species to self-assembled monolayers (SAMs).

transform infrared (ATR-FTIR) spectroscopy, ellipsometry, water contact angle measurements, and AFM. XPS confirmed the efficiency of this approach. Indeed, the survey scan showed the presence of both B and Co besides the C, N, Si, and O (Figure 1). Quantification of the different ele-

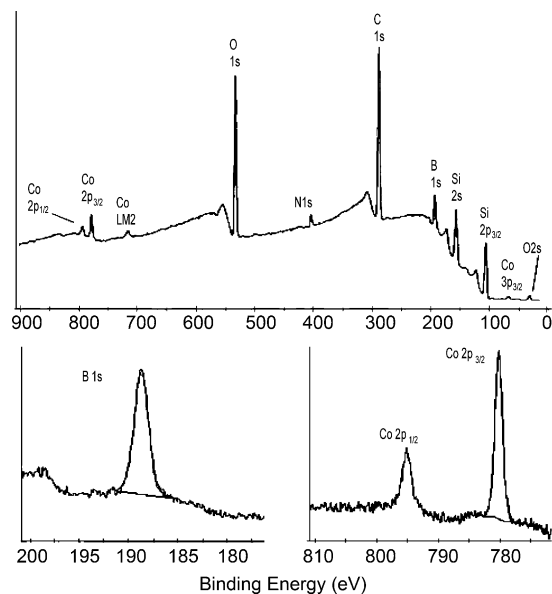


Figure 1. XPS wide-scan survey spectrum and B 1s and Co 2p XPS peaks of the cobaltabisdicarbollide **3** anchored by reaction with an isocyanate-terminated monolayer on a Si wafer.

ments indicated a large amount of carbon (45.9 at %) arising in part from contamination. The B content ( $14.4 \pm 0.6$  at %) and Co content ( $0.6 \pm 0.2$  at %) confirmed the presence of the cobaltabisdicarbollide anion. The binding energies for the B 1s and Co 2p<sub>3/2</sub> peaks were 188.7 and 780.2 eV, respectively, in good agreement with those reported in the literature for Cs[3,3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>].<sup>[4,27]</sup>

The AFM image (Figure 2) showed that the reaction of the NCO-terminated monolayer with **3** led to an increase of the root mean square (rms) roughness from 0.33 to 1.6 nm (1  $\mu\text{m}^2$  images). Similarly, ellipsometry indicated an increase

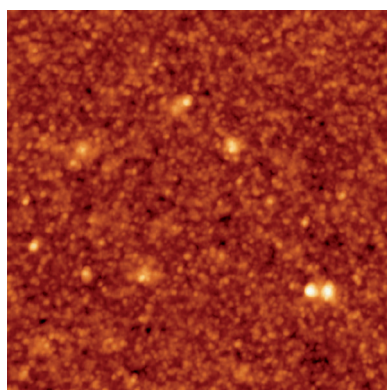


Figure 2. AFM image of the cobaltabisdicarbollide **3** anchored by reaction with an isocyanate-terminated monolayer on a Si wafer.

of the average layer thickness from  $1.5 \pm 0.3$  to  $2.2 \pm 0.3$  nm. The water contact angle for the functionalized surface was  $75.2 \pm 2.0^\circ$ . The increase of the contact angle corroborates the grafting of the surface with the hydrophobic species [3,3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>]<sup>-</sup>.

The ATR-FTIR spectra of the NCO-terminated monolayer after reaction with **3** (Figure 3) showed a band at

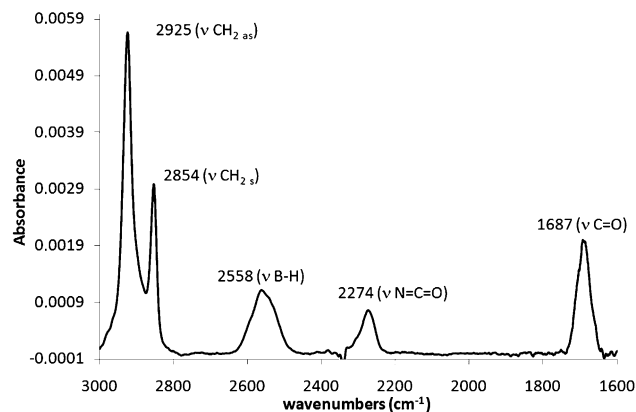


Figure 3. ATR-FTIR spectrum of the NCO-terminated monolayer after reaction with compound **3**.

$2558 \text{ cm}^{-1}$ , characteristic of the  $\nu(\text{B-H})$  vibrations in the cobaltabisdicarbollide. A band at  $2274 \text{ cm}^{-1}$  indicated the presence of residual isocyanate groups. The band at  $1687 \text{ cm}^{-1}$  was ascribed to urea groups, resulting from the reaction between the isocyanate function and the amine group from compound **3**.

These results indicate that the reaction of the amino-cobaltabisdicarbollide derivative [NMe<sub>4</sub>][8-NH<sub>2</sub>-C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>-3,3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] with a NCO-terminated monolayer was successful for grafting metallocarborane units to a silicon oxide surface. To our knowledge, this is one of the few examples<sup>[4b,31]</sup> evidencing the reactivity of a derivative of compound **2** obtained by ring-opening reaction. Furthermore, this method confirms the interest of isocyanatotrchlorosilane as a coupling agent for the modification of oxidized silicon substrates.<sup>[26]</sup>

In summary, two different approaches have been attempted for the anchoring of cobaltabisdicarbollide units to oxidized silicon surfaces. The first approach was the in situ ring opening of the dioxane in [3,3'-Co(8-C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] by reaction with an amine- or an oxyamine-terminated self-assembled monolayer that had been previously deposited on the silicon wafer. The second strategy was the pre-opening of the dioxane ring of [3,3'-Co(8-C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1',2'-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] to obtain the amino derivative [NMe<sub>4</sub>][8-NH<sub>2</sub>-C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>-3,3-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]], which reacted with an isocyanate-terminated SAM. Although the first approach was not successful, probably owing to steric hindrance, homogeneous monolayers of cobaltabisdicarbollide covalently linked to the silicon wafer surface were obtained using the second

strategy. Work is in progress to explore potential applications of these grafted cobaltabisdicarbollide species.

## Experimental Section

**Instrumentation:** ATR IR spectra of modified surfaces were recorded on an FTIR Perkin–Elmer 2000 spectrometer equipped with a narrow band liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector and a thermoregulated ATR flow cell using a trapezoidal Si single crystal cut from a two-sides polished p-type (1,0,0) silicon wafer ( $45^\circ$ ,  $72 \times 10 \times 1 \text{ mm}^3$ ) as internal reflection element. The sample compartment was purged with dry air. All the spectra were recorded at a resolution of  $1 \text{ cm}^{-1}$ , and 128 scans were accumulated. Surface composition was studied by XPS using an ESCALAB 250 (Thermo Electron) instrument equipped with a monochromatic  $\text{Al}_{K\alpha}$  (1486.6 eV) source. The analyzed surface had a  $400 \mu\text{m}$  diameter. The background signal was removed using the Shirley method.<sup>[32]</sup> Surface atomic concentrations were determined from photoelectron peak areas using the atomic sensitivity factors reported by Scofield.<sup>[33]</sup> The C 1s component at 285.6 eV was used for calibration of binding energy. Ellipsometric measurements were made on a Plasmos SD 2300 ellipsometer with a rotating analyzer as modulating element. The laser source was a helium/neon laser with a wavelength of 632.8 nm. The angle of incidence was  $70^\circ$  and the spot size was about 2 mm. The substrate was silica which has grown on silicon. The refractive index is 1.46 for silica and 3.83 for silicon. A refractive index of 1.45 was used for the silane layers. An atomic force microscope (Dimension 3100 with Nanoscope IIIa Digital Instruments) was used for roughness analysis. Measurements were performed in the tapping mode, and commercial silicon cantilever probes with a nominal radius of 5–10 nm and a spring constant in the range of  $20\text{--}70 \text{ N m}^{-1}$  were used. Data were acquired on  $1 \mu\text{m} \times 1 \mu\text{m}$  frames, and the images were flattened and no other filtering was done before analyzing roughness. A Digidrop-GBX contact angle meter G1 goniometer was used to determine the chemical properties of the surfaces (such as hydrophobic character). The measurements were performed by using HPLC water (Acros organics). About six drops were deposited onto the surface using a microsyringe, and the reading was taken 6 s after deposition.

**Materials:** All manipulations were carried out under an argon atmosphere using standard Schlenk techniques at room temperature unless otherwise mentioned. Solvents were reagent grade and were purified by distillation over appropriate drying agents before use.  $\text{Cs}[3\text{-Co-1,2-(C}_2\text{B}_9\text{H}_{11})_2]$  (**1**) (Katchem Ltd., Prague) was used as received. (11-amino)undecyltrimethoxysilane, (11-aminooxy)undecyltrimethoxysilane and 10-isocyanatodecyltrichlorosilane were purchased from Sikemia company.  $[3,3'\text{-Co}(8\text{-C}_4\text{H}_8\text{O}_2\text{-1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]$  (**2**)<sup>[17]</sup> and  $[\text{NMe}_4][8\text{-NH}_2\text{-C}_4\text{H}_8\text{O}_2\text{-3,3'-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]$  (**3**)<sup>[30]</sup> were prepared according to the literature procedures.

**Preparation of the samples:** 1) Preparation of oxidized silicon Si(100). The native oxide layer was removed from the Si(100) by immersion in aqueous HF (40%) until total dewetting of the surface was achieved (about 10 s). The substrates were cleaned by rinsing them with HPLC water. The substrates were then treated for 30 min in a homebuilt UV/ozone chamber to eliminate organic impurities from the surface and to oxidize the silicon surface. The wafers were placed at a maximum distance of 5 mm from a two-wavelength low-pressure mercury lamp ( $\lambda = 185$  and  $254 \text{ nm}$ ) under an  $\text{O}_2$  stream. After 30 min of exposition, a hydrophilic silica surface free of organic pollution (contact angle  $\theta$  ca  $10^\circ$ ) was obtained. The thickness of the silica layer, measured by ellipsometry, was about 1.8–2.0 nm and its rms roughness, measured by tapping mode atomic force microscopy ( $1 \mu\text{m}^2$  image), was about 0.15 nm.<sup>[26]</sup>

2) Grafting of (11-amino)undecyltrimethoxysilane to the oxidized silicon surface. The oxidized silicon wafer was placed into a Schlenk tube under a nitrogen atmosphere. The grafting solution contained (11-aminooxy)undecyltrimethoxysilane ( $10^{-2} \text{ M}$ ) in trichloroethylene (10 mL). The wafer was treated with the solution at  $0^\circ\text{C}$  for 24 h under a nitrogen atmosphere without stirring. The modified wafer was then washed with trichloroethylene, THF, and  $\text{CHCl}_3$ . The layer thickness measured by ellipsometry was  $1.5 \pm 0.2 \text{ nm}$ . The rms roughness, measured by tapping mode atomic force microscopy ( $1 \mu\text{m}^2$  image), was about 0.24 nm.<sup>[26]</sup>

3) Grafting of (11-aminooxy)undecyltrimethoxysilane to the oxidized silicon surface. The oxidized silicon wafer was placed into a Schlenk tube under a nitrogen atmosphere. The grafting solution contained (11-aminooxy)undecyltrimethoxysilane ( $10^{-2} \text{ M}$ ) in trichloroethylene (10 mL). The wafer was treated with the solution at  $0^\circ\text{C}$  for 24 h under a nitrogen atmosphere without stirring. The modified wafer was then washed with trichloroethylene, THF, and  $\text{CHCl}_3$ . The rms roughness determined by AFM was 0.15 nm ( $1 \mu\text{m}^2$  images) and the layer thickness measured by ellipsometry was  $1.9 \pm 0.2 \text{ nm}$ .

4) Deposition of 10-isocyanatodecyltrichlorosilane monolayer onto the oxidized silicon surface. The oxidized silicon wafer was placed into a Schlenk tube under a nitrogen atmosphere. The grafting solution containing 10-isocyanatodecyltrichlorosilane ( $10^{-2} \text{ M}$ ) and diisopropylethylamine ( $2 \times 10^{-1} \text{ M}$ ) in trichloroethylene (15 mL) was introduced into the tube. The wafer was treated with the solution at  $0^\circ\text{C}$  for 45 min under a nitrogen atmosphere without stirring. Then, the solution was removed, and the modified wafer was washed with trichloroethylene, THF, and  $\text{CHCl}_3$ . The rms roughness determined by AFM was 0.33 nm ( $1 \mu\text{m}^2$  images) and the layer thickness measured by ellipsometry was  $1.5 \pm 0.3 \text{ nm}$ .

5) Reaction of the immobilized amine or oxyamine groups with **2**. The wafers modified by the amine-terminated or the oxyamine-terminated monolayer were immersed in a solution of **2** (205 mg, 0.5 mmol) in acetonitrile (5 mL). After 48 h reaction at room temperature under argon the wafer was washed with acetonitrile, THF, and chloroform under sonication.

6) Reaction of the immobilized isocyanate with **3**. A solution containing **3** (64 mg,  $10^{-2} \text{ M}$ ) in acetonitrile (15 mL) was introduced into a Schlenk tube. The wafer modified with NCO-terminated monolayers was treated with this solution at  $0^\circ\text{C}$  for 2 h under an argon atmosphere. Then the wafer was rinsed under sonication with acetonitrile (5 min), methanol (5 min), THF (5 min), and  $\text{CHCl}_3$  (5 min) and dried in a stream of nitrogen.

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**Keywords:** cluster compounds • metallocarboranes • self-assembly • silicon oxide modification • surface chemistry

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