with $I > 2\sigma(I)$, Lp correction ($\mu = 7.120$ mm^{-1}), 247 refined parameters with $R = 0.074$, residual electron density (max/min): 2.747/ -1.984 e Å^{-3} (caused by the data collection at room temperature and the stereoactive lone pair of electrons at Bi); $Mo_{K\alpha}$ radiation, $\lambda =$ 0.71073 Å, was used in both cases and the structures were solved by direct methods (program: SHELXS-97), refined versus F^2 (program: SHELXL-97) with anisotropic temperature factors for all non-hydrogen atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112043 and CCDC-112044. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] In situ characterization showed that **1** also forms in the reaction of $[Cp_2MoCl_2]$ with $NaOCH(CF_3)_2$.

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A Spreader-Bar Approach to Molecular Architecture: Formation of Stable Artificial Chemoreceptors**

Vladimir M. Mirsky,* Thomas Hirsch, Sergey A. Piletsky, and Otto S. Wolfbeis

A struggle between chaos and order is especially hardened in the nano-world, where local concentration gradients are very high and diffusion processes extremely fast. Moreover, as is typical for many systems ordered on the nanometer scale, even small structural changes can lead to a total loss of function of the whole system. Major progress in these systems led to the concept of molecular architecture and chemical nanotechnology.[1, 2] Introduction of self-assembly, which allowed the formation of molecularly organized multilayer systems with relatively slow diffusion between different molecular layers. We describe herein a spreader-bar approach that allows for the first time noncross-linked monolayers to be obtained, whose structure can not be distorted by lateral diffusion.

The most effective technique to form artificial receptors for small molecules is based on molecular imprinting,[3–8] which comprises the formation of a three-dimensional porous polymer whose cavities match the molecular structure of the analyte of interest. Only a few attempts to apply this principle to form two-dimensional chemical receptors have been reported (Figure 1a)[9–11], but lateral diffusion of molecules in the noncross-linked monolayers distorts the receptor structure (Figure 1b). We describe herein a novel approach for the preparation of stable artificial interfaces with predefined affinity in which the stability against lateral diffusion was achieved by means of a molecular spreader-bar (Figure 1c).

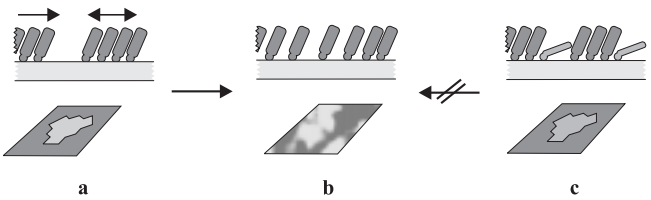

Figure 1. Schematic representation of the possibilities of building artificial receptors on a surface as viewed from above (below) and in cross section (above). By two-dimensional molecular imprinting the binding sites (a) can be distorted by lateral diffusion (b). The binding sites can be stabilized—as shown here for the first time—by using a template (c) in the monolayer.

An artificial interface with a high affinity for barbituric acid (a starting material for many pharmaceuticals) was created by co-adsorption of thiobarbituric acid **1** (the template) and dodecanethiol **2** (the matrix) onto a gold substrate (Figure 2). This process leads to the formation of binding sites with a structure complementary to that of thiobarbituric acid. Binding of barbituric acid **3** and of other species to the respective surface was detected by capacitance measurements: an increase in the dielectric thickness decreases the electrode capacitance.[12] A high selectivity of this artificial chemoreceptor for barbituric acid was observed (Figure 3): while there is a considerable response to the addition of barbituric acid, the addition of diethylbarbituric acid caused no effect. Moreover, the effects that arise from additions of barbituric acid in the presence of a high concentration of diethylbarbituric acid were exactly the same as in its absence. The capacitance response to pyridine was also much lower than to barbituric acid. The response of such a receptor is shown in Figure 4.

To study the structure of the binding sites the affinity properties of several other types of interface were compared (Table 1). No binding of barbituric acid to the surface formed by a pure monolayer of dodecanethiol or by a pure monolayer of thiobarbituric acid was observed.[13] Therefore, the barbituric acid binding sites on the interface formed by the co-adsorption of dodecanethiol and thiobarbituric acid must include both types of molecules and one can exclude binding mechanisms based on the formation of hydrogen bonds or other interactions between barbituric acid and thiobarbituric acid only. Also, no binding of barbituric acid on gold electrodes covered by a mixed monolayer of thiobarbituric acid and short-chain alkylthiols (butanethiol and 2-methyl-2-propanethiol) was observed. Therefore, for a strong specific interaction with the template, the matrix is required to form a sufficiently thick monolayer.

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[**] We are grateful to Dr. V. Tvarozek, Dr. I. Novotny, and Dr. V. Rehacek (University of Technology, Bratislava, Slovakia) for providing us with gold electrodes. This work was supported by the Deutsche Forschungsgemeinschaft and a NATO-Linkage Grant.

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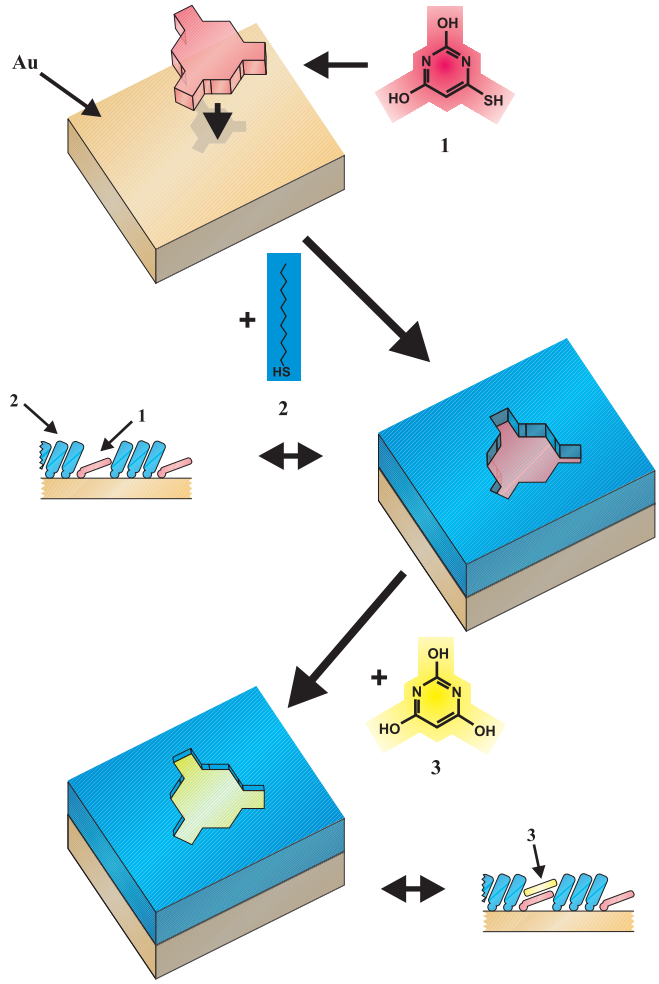

Figure 2. Preparation and operation of artificial chemoreceptors. The binding sites are formed by co-adsorption of the template and matrix molecules. The template should have a shape similar to that of the analyte, and both the template and the matrix molecules must be able to bind strongly to the surface. As an example, co-adsorption of thiobarbituric acid **1** (template) and dodecanethiol **2** (matrix) on the gold surface results in the formation of binding sites for barbituric acid **3**.

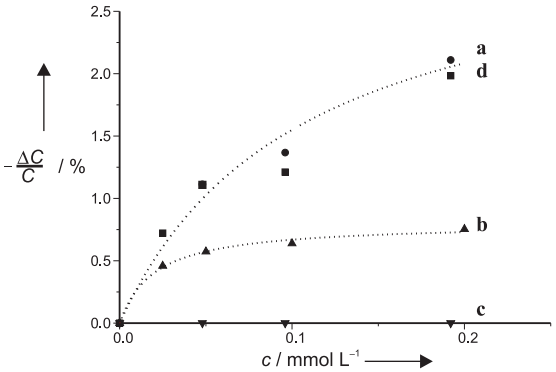

Figure 3. Detection of binding by measuring the capacitance changes of the artificial receptors: a: barbituric acid, b: pyridine, c: diethylbarbituric acid, d: barbituric acid in the presence of 1 mmol L^{-1} diethylbarbituric acid. Template: thiobarbituric acid, matrix: dodecanethiol. Electrolyte: 5 mmol L^{-1} phosphate buffer, 100 mmol L^{-1} KCl, pH 5.5.

The electrodes covered by the dodecanethiol/thiobarbituric acid mixture have a specific capacitance of $4.4 \pm 0.4\ \mu F\,cm^{-2}$. From comparison with specific capacitances of the electrodes

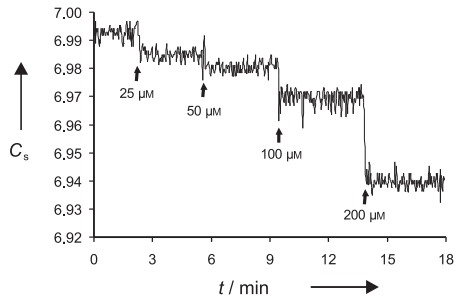

Figure 4. Response time of the artificial receptors as measured by the changes in capacitance C_s [$\mu F\,cm^{-2}$] on binding barbituric acid to an electrolyte coated with thiobarbituric acid and hexanethiol.

covered by matrix or template molecules only and assuming independent contributions of both species to the capacitance of the electrode covered by mixed monolayers, one can estimate that about 48% of the electrode area is covered by thiobarbituric acids. A modification of the alkanethiol/thiobarbituric acid ratio at the interface, achieved by varying this ratio in the solution used for electrode coating or by varying the adsorption time, resulted in a decrease or even total loss of the sensor response to barbituric acid.

The requirement that both types of molecules should be present at the interface at a definite ratio implies that the binding sites have a definite structure. This structure can be assumed to consist of cavities in the monolayer of the matrix with a cross-section exactly defined by the shape of the template molecules. These binding sites cannot be distorted by the lateral diffusion of molecules in the monolayer: like a boat in the ocean, they can conserve their definite shape anywhere at the interface and are independent of any movements of the surrounding molecules.

A comparative study of the temporal stability of the binding sites to barbituric acid that were formed by the two-dimensional molecular imprinting[9] and by the novel spreader-bar technique was performed. The two-dimensional molecular imprinting technique also resulted in a formation of selective binding sites, however, a total loss of these receptor properties was observed already after the first adsorption/desorption cycle. On the contrary, the binding sites formed by the molecular spreader-bar technique display receptor properties during many adsorption/desorption cycles with only a slight loss of the affinity for every next cycle.

Table 1. Formation of artificial binding sites.[13]

Monolayer composition		Capacitance increase after addition of		
matrix	template	barbituric acid	5,5-diethyl-barbituric acid	pyridine
1-dodecanthiol	–	none		none
–	2-thiobarbituric acid	none	none	none
1-dodecanthiol	2-thiobarbituric acid	high	none	low
1-hexanthiol	2-thiobarbituric acid	high	none	low
1-butanthiol	2-thiobarbituric acid	none	none	–
2-methyl-2-propanthiol	2-thiobarbituric acid	none	none	–

Two mechanisms for the selective capacitive response can be considered: a) different binding constants for different species and b) a sievelike effect, namely, there are steric

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limitations for large molecules. In this case, the molecules smaller than the cavities provide lower capacitive effects than the molecules whose shape allows them to fill the cavities.

The new spreader-bar technique provides a simple way of forming stable nanostructures without chemical polymerization. One can suggest possible applications of this principle in the preparation of artificial receptors (for chemosensors, active phases for chromatography, stereoselective catalysis, and membrane filtration), molecular electronic devices, or other nanostructures.

Experimental Section

The interface with artificial binding sites for barbituric acid was prepared on the gold surface by firstly cleaning it with a hot solution of concentrated H_2SO_4 (3 mL) and 30% H_2O_2 (1 mL), then rinsing with water, and drying.

Caution: this solution reacts violently with most organic materials and must be handled with extreme care. For the preparation of the artificial receptors by the spreader-bar technique, the electrodes were placed into a solution of dodecanethiol ($10\ \mu mol\,L^{-1}$) and thiobarbituric acid ($10\ mmol\,L^{-1}$) in methanol/water (1/9) for 70 h at 22 °C, then rinsed with chloroform, and dried under nitrogen. The electrodes were further investigated during the following few days; no systematic effect on the surface properties was observed with storage. A coating of the electrodes by other species were performed using the same conditions and with the same concentrations of template and matrix compounds. A mixture of dodecanethiol ($10\ \mu mol\,L^{-1}$) and barbituric acid ($14\ mmol\,L^{-1}$) in the same solvent and coating conditions was used for the preparation of the artificial receptors according to two-dimensional molecular imprinting.

All adsorption measurements were performed at room temperature in the electrolyte consisting of phosphate buffer ($5\ mmol\,L^{-1}$) and KCl ($100\ mmol\,L^{-1}$) at pH 5.5. The capacitive method used to study adsorption, as well as essential experimental details, are described in reference [12].

Received: November 23, 1998 [Z12693IE]
German version: *Angew. Chem.* **1999**, *111*, 1179 – 1181

Keywords: molecular architecture · molecular recognition · monolayers · nanostructures · sensors

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Synthesis and Structures of *cis*- and *trans*-[Os(Bcat)(aryl)(CO)$_2$(PPh$_3$)$_2$]: Compounds of Relevance to the Metal-Catalyzed Hydroboration Reaction and the Metal-Mediated Borylation of Arenes**

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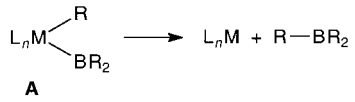
Alex Williamson, and L. James Wright*

Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

In some discussions of the mechanism of the metal-catalyzed hydroboration of unsaturated hydrocarbons[1, 2] the final step is the reductive elimination of an organoborane from a postulated intermediate **A**, which has both a boryl ligand and a σ-bound carbon ligand (Scheme 1). Theoretical



A

Scheme 1. Reductive elimination of RBR_2 from postulated alkyl, boryl intermediate **A**.

studies of this reaction support the intermediacy of such a metal complex.[3] In related studies arenes and alkenes have been borylated with the metal complexes [CpFe(Bcat)(CO)$_2$], [Mn(Bcat)(CO)$_5$], and [Re(Bcat)(CO)$_5$] (H_2cat = catechol, 1,2-$(HO)_2C_6H_4$) under photolytic conditions.[4] Even alkanes can be functionalized in a similar way with [(C_5Me_5)M(Bcat′)(CO)$_n$] (M = Fe, Ru, $n = 2$; M = W, $n = 3$; H_2cat′ = 1,2-$(HO)_2C_6H_2$-3,5-Me_2).[5] Although the mechanism of these borylation reactions is not known with certainty, an intermediate of type **A** has been suggested as a reasonable possibility.[5] Despite the obvious significance of characterizing stable examples of metal boryl complexes that also contain a σ-bound carbon ligand, only two rather special examples of such complexes have been described more recently. The first of these is an iridium(IV) complex in which both the boryl and aryl donor atoms are part of a complex chelating ligand system[6] and the second is [Ir(Bcat)(C{CO_2CH_3}=CH{CO_2CH_3})Cl(PMe_3)$_3$] in which the vinyl function arises from insertion of dimethyl acetylenedicarboxylate into an iridium – hydrogen bond.[7]

Herein we describe 1) the first stable examples of both coordinatively unsaturated and saturated metal complexes containing boryl and simple σ-bound aryl ligands, 2) structure determinations of both *cis* and *trans* isomers of the coordinatively saturated octahedral examples with implications for the bonding characteristics of the Bcat ligand, and 3) the facile

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[**] This work was supported by the Marsden Fund.

  1433-7851/99/3808-1110 $ 17.50+.50/0