($n = $constant) decreases in the order $(SiH)_n$, $(GeH)_n$, $(SnH)_n$, $(PbH)_n$; it is, however, about 250 kJ mol^{-1} even for $(PbH)_8$.

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[10] According to our detailed studies the insoluble tin compound is not the tetrahedrane **3c** and the soluble tin compound is not a zwitterionic distannene $R^*_2Sn \rightarrow SnR^*_2$, as proposed by others (M. Weidenbruch, A. Stilter, H. Marsmann, K. Peters, H. G. von Schnering, *Eur. J. Inorg. Chem.* **1998**, 1333).

[11] According to X-ray structure analyses,[9] in tristannallenes $R^*_4Sn_3$ the Sn–Sn bond lengths and the Sn-Sn-Sn bond angles are 2.68 Å and 156°, respectively, in the isomeric cyclotristannenes $R^*_4Sn_3$ the lengths of the Sn–Sn single and double bonds are 2.86 and 2.61 Å, respectively.[9]

[12] Crystal structure analysis of $(tBu_3Si)_6Sn_6 \cdot 0.4\,(tBu_3Si)_2 \cdot 2\,tBuOMe$: Siemens P4 diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator, CCD area detector, crystal dimensions $0.03 \times 0.15 \times 0.14$ mm^3. The crystal was mounted in perfluoroether oil, $T = 163(2)$ K, $C_{90.6}H_{204.6}O_2Si_{6.8}Sn_6$, $M_r = 2229.54$, black-red prisms, triclinic, $a = 16.86(1)$, $b = 17.229(9)$, $c = 21.64(1)$ Å, $\alpha = 89.17(1)$, $\beta = 67.15(2)$, $\gamma = 84.25(2)°$, $V = 5764(6)$ Å^3, $Z = 2$; space group $P\bar{1}$, $\rho_{calcd} = 1.287$ Mg m^{-3}, $\mu = 1.391$ mm^{-1}, $F(000) = 2280$. Data collection: 2θ from 2.38 to 58.26° in $-20 \leq h \leq 20$, $-22 \leq k \leq 22$, $-24 \leq l \leq 26$, 32656 measured reflections, 18048 of which are independent and 11502 observed ($F > 4\sigma(F)$), semiempirical absorption correction with SADABS (max/min transmission 1.000/0.928), $R_1 = 0.0618$, $wR_2 = 0.1185$ ($F > 4\sigma(F)$), $GOF(F^2) = 1.042$; maximum residual electron density 1.287 e Å^{-3}. The weighting factor is $w^{-1} = \sigma^2 F_o^2 + (P)^2 + P$ with $P = (F_o^2 + 2F_c^2)/3$. The structure was solved by direct methods (SHELXL; G. M. Sheldrick **1997**). All non-hydrogen atoms of the prismane were refined anisotropically. The hydrogen atoms were introduced in calculated positions and included in the refinement with a riding model and fixed isotropic U_i values. The unit cell contains in addition to the nondisordered molecules $(tBu_3Si)_6Sn_6$ strongly disordered molecules $(tBu_3Si)_2$ with an occupancy factor of 0.8 and four molecules of *tert*-butyl methyl ether. The disorder could only be approximately resolved. The *t*Bu groups of the disilane and the atoms of the ether molecules were refined with isotropic thermal parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-113897. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[16] In fact thermolysis of the tristannacyclopropene $(tBu_3Si)_4Sn_3$ did not give $(tBu_3Si)_8Sn_8$ but rather the supersilyl-poorer $(tBu_3Si)_6Sn_8$ with an Sn_8 cubane framework.[9] N. Wiberg, H.-W. Lerner, S. Wagner, H. Nöth, T. Seifert, unpublished results.

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Syntheses and Ligating Properties of Molybdocene Alkoxides—The First Heterodimetallic Alkoxide Containing Molybdenum and Bismuth**

Marc Hunger, Christian Limberg,* and Peter Kircher

The unique property of $[Bi_2MoO_6]$ to act as a heterogeneous catalyst for the technical propene oxidation[1a] remains a subject of intense discussion.[1b] According to recent investigations, the oxygenation occurs at Bi-μ-O-Mo moieties,[1c] which encourages research aimed at preparing molecular species containing both Mo and Bi in oxo environments. In this context bismuth–molybdenum heterometallic alkoxides are of particular interest, as studies on metal alkoxides have clearly shown their potential to simulate the properties and structures of metal oxides.[2] There is, however, a dearth of information about even the homometallic alkoxides of bismuth.[3] While several groups have claimed the existence of a bismuth/transition metal precursor in their sol–gel processes,[4] only two heterometallic alkoxide complexes containing Bi and a transition metal (V[3] and Ti[5]) have been isolated and structurally characterized. This is particulary surprising as an increasing number of advanced oxide materials based on bismuth appear to display attractive properties,[5] and mixed-metal alkoxides could act as single-source precursors for such oxides. In an extension of our studies on the synthesis and formation of novel molybdenum alkoxides[6] we present here the first mixed Bi/Mo alkoxide, which to our knowledge is also the first structurally characterized example of a molecular compound with a discrete oxo linkage of any type between Bi and Mo.

All initial attempts to prepare the aforementioned type of species by methods established for the synthesis of other heterometallic alkoxides[7] such as Lewis acid–base reactions of certain alkoxides, or by applying the principles of the nonhydrolytic gel formation process,[8] yielded—in agreement with observations described in the literature[4]—insoluble, intractable solids. Since this is almost certainly a result of high aggregation levels, we decided to employ organomolybdenum compounds in which a part of the coordination sphere at the Mo center is protected by tightly bound organic ligands. For several reasons $[Cp_2Mo(OR)_2]$ compounds seemed to be ideally suited for our purpose, but—despite the vast literature on species bearing the Cp_2Mo fragment[9]—these alkoxides have not been described yet. This is probably due to the electron richness of the Cp_2Mo unit, which accordingly does not accept any strong π-donor ligands (note that the corresponding thiolates[9] are readily made!). Consequently $[Cp_2Mo{=}O]$ was chosen as an alternative reagent to treat bismuth alkoxides, since its oxo functionality possesses

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nucleophilic character[10] due to substantial negative charge accumulation and may therefore be capable of displacing weakly bound ligands at Bi centers. As already pointed out, the choice of employable bismuth alkoxides is narrow. $[\{Bi(OCH(CF_3)_2)_3(thf)\}_2]$ is one of the few showing a relatively low degree of aggregation and possessing labile ligands in form of coordinated THF molecules (according to the solid-state structure).[11] The reaction with $[Cp_2Mo{=}O]$ in THF yields after appropriate workup an insoluble amorphous material and a red-brown solid, which can be recrystallized from toluene. Spectroscopic and single-crystal X-ray analyses[12] of the red-brown crystals (Figure 1) revealed that not a Bi-containing Mo alkoxide but $[Cp_2Mo\{OCH(CF_3)_2\}_2]$ **1** had been obtained—the first representative of the elusive $[Cp_2Mo(OR)_2]$ class of complexes.[13] This is probably a consequence of the comparatively poor π-donor properties of the $OCH(CF_3)_2$ group (vide supra). As anticipated the Mo–O bonds are rather long (2.065(5) and 2.101(5) Å, cf. 1.880(1) Å in $[Mo_2[OCMe(CF_3)_2]_6]$[14]), while the O-Mo-O angle (78.8(2)°) lies within the usual range found for Cp_2MoX_2 (X = singly bonded ligand) compounds.

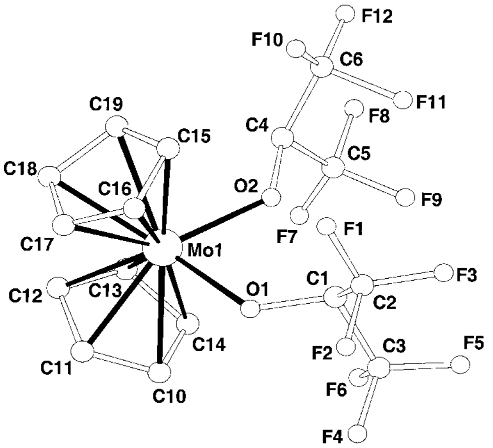
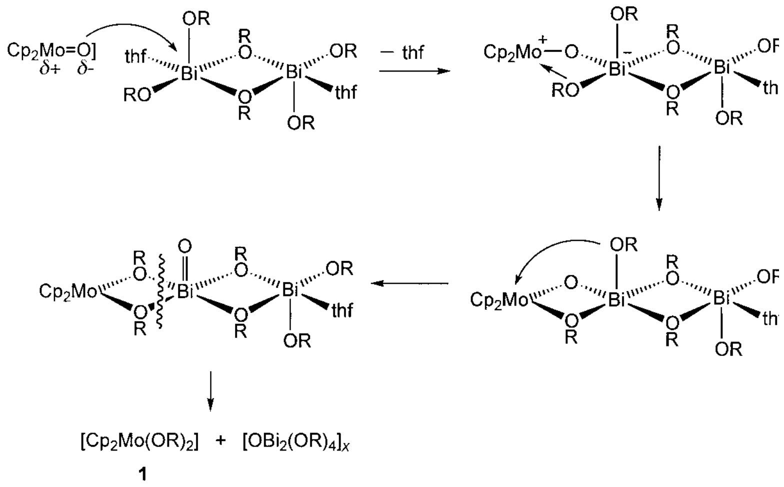


Figure 1. Molecular structure of **1**; all hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo1–O2 2.065(5), Mo1–O2 2.101(5), O1–C1 1.384(8), O2–C4 1.376(9), O2-Mo1-O1 78.84(18), C1-O1-Mo1 126.5(4), C4-O2-Mo1 129.4(5).

How can the formation of **1** be rationalized? Under the assumption that $[Cp_2Mo{=}O]$ attacks one Bi center under expulsion of THF (Scheme 1), the resulting intermediate Mo-O-Bi unit would surely be stabilized by alkoxide bridging, which in turn could initiate its decomposition to yield **1** and an oxo-containing Bi compound. The latter is expected to aggregate and display a solubility as observed. The mechanism proposed in Scheme 1 implies that—in contrast to the corresponding thiolates $[Cp_2Mo(SR)_2]$, which act as ligands for transition metal halides or organometallic fragments—**1** cannot serve as a kind of "tweezer" for Lewis acidic BiL_x fragments. This apprehension proved true in many experiments in which bismuth alkoxides and chlorides were allowed to react with **1**: The donor capacity of the $(CF_3)_2CHO$ ligands in **1** is not sufficient to stabilize a second metal fragment between them. Recourse had to be made to "classical" alkoxides but apart from $[Bi(OtBu)_3]_\infty$, which is too bulky to be employed, these are poorly characterized and display low solubilities.[15] The in situ preparation of $[Bi(OEt)_3]$ by ethanolysis of $[\{Bi(OtBu)_3\}_\infty]$ was reported to proceed quantitatively[16] but a reaction with $[Cp_2Mo{=}O]$ is not reasonable as the latter decomposes in the presence of EtOH, so that a different Cp_2Mo-containing starting material had to be employed. Reactions of metal chlorides with metal alkoxides have proved to be applicable for the synthesis of a large number of heterometallic alkoxides, which form after rapid ligand site exchanges as the thermodynamically most stable products, and consequently $[Cp_2MoCl_2]$ was treated with in situ prepared $[Bi(OEt)_3]$ at 70 °C. After appropriate workup brown crystals were obtained, which were very sensitive to moisture. An X-ray crystal structure analysis[12] (Figure 2) identified the corresponding compound as $[Cp_2Mo(\mu\text{-}OEt)_2\text{-}Bi(OEt)_2Cl]$ (**2**), where indeed a Mo and a Bi center are bridged by two ethanolate ligands. The coordination sphere of



Scheme 1. Possible mechanism for the formation of **1**, R = $CH(CF_3)$.

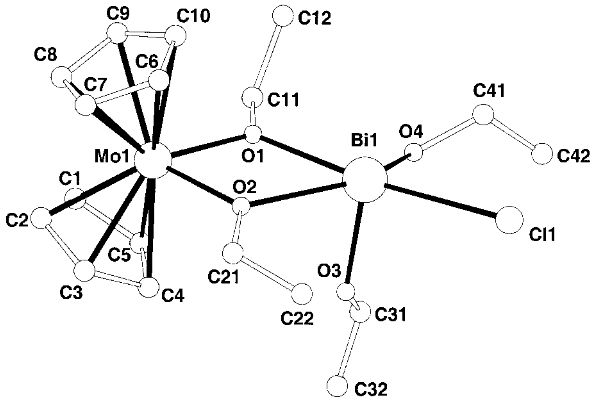


Figure 2. Molecular structure of **2**; all hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi1–O3 2.093(10), Bi1–O4 2.095(10), Bi1–O2 2.323(8), Bi1–O1 2.537(8), Bi1–Cl1 2.918(4), Mo1–O2 2.041(9), Mo1–O1 2.116(8), O3-Bi1-O4 88.9(5), O4-Bi1-O1 85.1(4), O1-Bi1-O2 61.6(3), O2-Bi1-Cl1 119.3(2), O1-Mo1-O2 73.7(3).

the Bi center, which is completed by two terminal ethanolate ligands and a chloro ligand, can be described as square pyramidal with the stereoactive lone pair of electrons occupying the ligand site missing for an octahedron. The terminal Bi–OEt distances (2.09(1) and 2.09(1) Å) are quite normal for such ligands in bismuth alkoxides. Due to the different *trans* ligands of each μ-OEt group, the Bi–μ-OEt bond lengths differ quite significantly (2.537(8) (O2) and 2.323(8) Å (O1)) but are comparable with the Bi–O_μ distances in the two other known heterometallic bismuth alkoxides,[3, 5] while the Bi–Cl bond of 2.918(4) Å is rather long (in comparison with the average value of 2.532 Å in a $Cl_3Bi(\mu\text{-}OR)_3$ moiety[3]). The Mo–O distances (2.041(9) (O2) and 2.116(8) Å (O1)) can be described as normal for $Mo(\mu\text{-}OEt)_2$ moieties,[6a] and the fact that the distances of the terminal ligands in **1** are comparable yet again stresses that the Cp_2Mo centers reject the donor capacity the terminal alkoxide ligands have on offer.

Apparently, in agreement with above arguments the electron-donating character of the ethyl group allows μ-OR bridging between the Cp_2Mo fragment and the Bi center, while synergetically the electron-withdrawal by the Bi center ensures that the π-electron density at the Cp_2Mo fragment is not too high (this role is played by the F atoms in **1**). According to the solid-state structure the diamagnetic compound **2** should show signal sets for four different CH_3CH_2 groups in the ^1H NMR spectrum. Only two sets are found for solutions of the compound in CD_2Cl_2, but lowering of the temperature leads to a broadening of all signals,[17] which further split at about −40 °C to give the complex spectrum expected for **2**. Consequently, at room temperature the compound shows dynamic behavior in solution involving site exchanges of the terminal ligands at Bi, which make the two bridging and the two terminal EtO ligands equivalent.

The formation of **2** can be assumed to proceed by μ-Cl bridging of $[Cp_2MoCl_2]$ to in situ generated, coordinatively unsaturated $[Bi(OEt)_3]$ molecules, which initiates ligand exchange reactions. The bridging positions are finally occupied by EtO ligands, which possess the more favorable properties for this purpose.[6a] However, only one of the two original Cl ligands binds at the Bi center in **2**, the second one is replaced by external EtO^-.

In conclusion, the results presented suggest that alkoxides of Cp_2Mo can only be isolated if the π-donor strength of the alkoxide ligands is decreased by electron-withdrawing groups or by their complexation to a Lewis acidic center. This principle was used to prepare the first Bi/Mo alkoxide, which represents the first step towards molecular Bi/Mo alkoxides or even oxides suitable to serve as structural or functional models for fragments of the $[Bi_2MoO_6]$ surface. Moreover, the first representative of the $[Cp_2Mo(OR)_2]$ class of compounds was isolated by employing a fluorinated alkoxide ligand. In view of the antitumor activity of $[Cp_2MoCl_2]$, the origin of which is under current investigation,[18] compounds like **1** may be suitable alternatives.

Experimental Section

1: A solution of $[\{Bi(OCH(CF_3)_2)_3(thf)\}_2]$[11] (0.64 g (0.4 mmol) in THF (20 mL) was added dropwise to a solution of $[Cp_2MoO]$[10] (0.20 g, 0.82 mmol) in THF (40 mL). After the mixture had been stirred for 1 h, all volatiles were removed from the resulting brown solution and the solid brown residue was extracted with toluene. The filtrate was reduced to about 20 mL and stored at −40 °C to afford analytically pure **1** (0.32 g, 0.58 mmol; 70% yield). ^1H NMR ($[D_8]THF$): $\delta = 5.69$ (s, 10 H, H_{Cp}), 4.54 (sept, 1 H, $^3J(H,F) = 6.83$ Hz, CH); ^{13}C NMR: $\delta = 124.1$ (q, 2 C, $^1J(C,F) = 287.7$ Hz, CF_3), 103.0 (s, 10 C, Cp), 73.6 (sept, $^3J(C,F) = 28.5$ Hz, CH); ^{19}F NMR: $\delta = 75.56$ (d, 6 F, CF_3); MS (EI): *m*/*z* (%): 563 (100) $[(\mathbf{1}+H)^+]$, 498 (8) $[(\mathbf{1}+H-Cp)^+]$, 396 (51) $[(\mathbf{1}+H-OCH(CF_3)_2)^+]$, 366 (50) $[(Cp_2Mo(CF_3)_2)^+]$, 228 (44) $[Cp_2Mo^+]$, 198 (38) $[(MoOCH(CF_3))^+]$.

2: $[Cp_2MoCl_2]$[10] (0.74 g, 2.5 mmol) was suspended in EtOH (30 mL) and the mixture was added to $[Bi(OtBu)_3]_\infty$ (2.15 g, 5.0 mmol) dissolved in EtOH (30 mL). All $[Cp_2MoCl_2]$ was taken up into the brown solution after stirring for 2 h, and the mixture was subsequently heated for 40 min to 70 °C. All volatiles were removed and the residue was extracted with THF (15 mL). Cooling of the solution to −80 °C afforded analytically pure **2** (0.60 g, 0.9 mmol; 37% yield). ^1H NMR (CD_2Cl_2): see ref. [17]; ^{13}C NMR (CD_2Cl_2): $\delta = 101.6$ (Cp), 73.8 (t-OCH_2), 59.9 (μ-OCH_2), 26.0 (t-OCH_2CH_3), 19.9 (μ-OCH_2CH_3).

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[12] **1:** $C_{16}H_{12}F_{12}MoO_2$, $M_r = 560.19$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 13.905(3)$, $b = 10.138(2)$, $c = 13.887(3)$ Å, $\beta = 105.14(3)$, $V = 1889.80$ Å^3, $3.0 < 2\theta < 52.1°$, o-scan, $T = 200$ K, $\delta_{calcd} = 1.962$ g cm^{-3}, 10057 measured, 3553 independent, and 2141 observed reflections with $I > 2\sigma(I)$, Lp correction ($\mu = 0.820$ mm^{-1}), 283 refined parameters with $R = 0.068$, residual electron density (max/min): 0.484/−0.589 e Å^{-3}; due to the low quality of the crystal the anisotropic temperature factors of the F atoms are relatively high. **2:** $C_{18}H_{30}BiClMoO_4 \cdot 0.25\,EtOH$, $M_r = 662.310$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 12.549(3)$, $b = 13.796(3)$, $c = 16.112(3)$ Å, $\alpha = \beta = 105.48(3)$, $V = 2688.20$ Å^3, $3.9 < 2\theta < 51.9°$, o-scan, $T = 298$ K, $\delta_{calcd} = 1.636$ g cm^{-3}, 39626 measured, 5222 independent, and 3261 observed reflections

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$_2$MoCl$_2$] with NaOCH(CF$_3$)$_2$.

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[17] One set ($\delta = 1.06$ (t)/4.66 (q) belonging to the terminal EtO ligands) broadened more pronouncedly than the other one ($\delta = 1.23$ (t)/3.50 (q) for μ-OEt); δ(Cp) $= 5.74$.

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

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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 1 a)[9–11], but lateral diffusion of molecules in the noncross-linked monolayers distorts the receptor structure (Figure 1 b). 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 1 c).

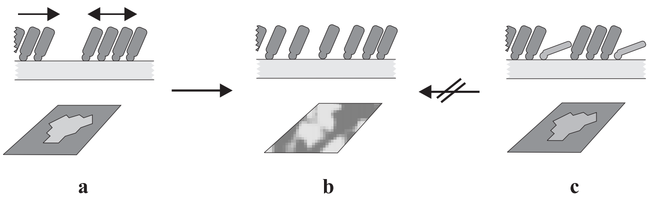

Figure 1. Schematic representation of the possibilities of building artificial receptors on a surface as viewed from above (below) and in cross section (above). By two-dimensional molecular imprinting the binding sites (a) can be distorted by lateral diffusion (b). The binding sites can be stabilized—as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