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Preparation of Platinum(II) Sulfide Complexes Immobilized on Silica

D. A. de Vekki and M. A. Il'ina

St. Petersburg State Technological Institute, Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: ilina_masha@list.ru

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Abstract—We report on preparation of silica-immobilized platinum(II) complexes of the $[\{SiO_2\}O_2Si(CH_3)\cdot(CH_2)_3SR]_2PtCl_2$ type (R = Bu, Hex, or Bn; $\{SiO_2\}$ = silica surface).

Keywords: platinum, immobilized complex, silica, sulfide, hydrosilylation

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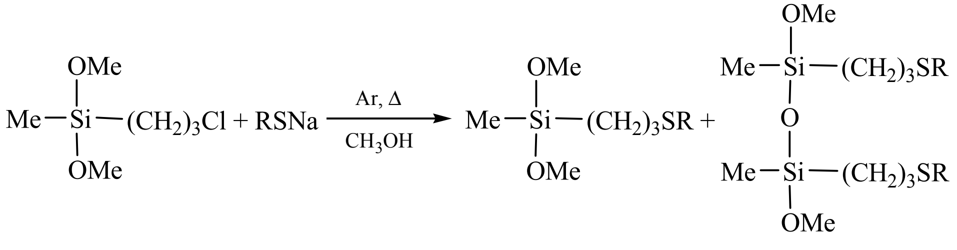
Sulfur-containing platinum(II) complexes are known as efficient catalysts of homogeneous hydrosilylation [1–10]. However, application of anchored metal complexes as catalysts of this reaction has been scarcely studied so far [11] despite their promising performance in other reactions [12–18]. Herein we report on simple preparation of novel silica-anchored platinum(II) complexes of the $[\{SiO_2\}O_2Si(CH_3)\cdot(CH_2)_3SR]_2PtCl_2$ type, R being Bu, Hex, or Bn.

Preparation of sulfides. Interaction of γ-chloropropylmethyldimethoxysilane (**I**) with sodium alkylthiolates in methanol led to corresponding silyl sulfides (**IIa**–**IIc**) and disiloxanes (**IIIa**–**IIIc**). The reaction rate was practically independent of the nature of substituent R; however, yield of the side product, disiloxane, decreased in the case of bulky substituent. In particular, ratio of the silyl sulfide to the disiloxane was of 2.3 : 1 (R = Bu), 25.2 : 1 (R = Hex), and 89.9 : 1 (R = Bn) (chromatography data). Moreover, in the R = Bu case the reaction mixture contained trisiloxane $CH_3[OSi(CH_3)(CH_2)_3SBu]_3OCH_3$ (**IV**), the **IIIa** : **IV** ratio being of 71 : 10 when the reaction was complete (Scheme 1).

The so prepared sulfides (**IIa**–**IIc**) and siloxanes (**IIIa**–**IIIc**) were readily soluble in chloroform, acetone, diethyl ether, methanol, pentane, toluene, and DMF; they were poorly soluble in acetonitrile. The sulfides were relatively stable in air; however, in the course of prolonged incubation they were gradually converted into the corresponding siloxanes. For example, after 10 months storage at room temperature the **IIa** : **IIIa** : **IV** ratio was of 2.1 : 3.3 : 1 (chromatography data).

^{1}H NMR spectra of the sulfides **IIa**–**IIc** contained multiplet signals of methyl and methylene groups adjacent to silicon atom at 0.05–0.12 ppm (CH_3) and 0.60–0.76 ppm (CH_2) along with methoxy groups multiplets at 3.44–3.52 ppm. Signals of methylene

Scheme 1.



I **IIa–IIc** **IIIa–IIIc**

R = Bu (**a**), Hex (**b**), Bn (**c**).

groups adjacent to sulfur atom were partially overlapping in the cases of **IIa** [2.50 ppm, t, (2H, CH_2SBu, *J* 7.5 Hz) and 2.53 ppm, t, (2H, $CH_2SC\underline{H}_2$, *J* 7.3 Hz)] and **IIb**, [2.47 ppm, t, (2H, CH_2SHex, *J* 7.4 Hz) and 2.49 ppm, t (2H, $CH_2SC\underline{H}_2$, *J* 6.9 Hz)]. Due to the influence of benzene ring, those signals were well separated in the spectrum of **IIc** [2.44 ppm, t (2H, $C\underline{H}_2SBn$, *J* 7.4 Hz) and 3.70 ppm, m (2H, $SC\underline{H}_2C_6H_5$)]. In the spectrum of **IIb**, methylene groups remote from sulfur atom resonated as quintets at 1.35 ppm (2H, $SCH_2CH_2C\underline{H}_2$, *J* 6.8 Hz), 1.55 ppm (2H, $SCH_2C\underline{H}_2CH_2$, *J* 7.4 Hz), and 1.62 ppm (2H, $SiCH_2C\underline{H}_2$, *J* 8.4 Hz)] or as multiplet at 1.25–1.33 ppm (4H, $C\underline{H}_2C\underline{H}_2CH_3$). Aromatic part of **IIc** molecule gave rise to the signals at 7.23–7.26 ppm (m, 3H, $C^{\alpha+\gamma}H$) and 7.31 ppm (t, 2H, $C^{\beta}H$, *J* 2.2 Hz). ^{13}C NMR spectra of sulfides **IIa**–**IIc** contained the following signals: of the groups adjacent to silicon atom at –6 ppm (CH_3), 13 ppm (CH_2), and 50 ppm (OCH_3) as well as of methyl and methylene groups remote from silicon atom at 13–36 ppm; signals of aromatic carbon atoms appeared at 127–137 ppm.

IR spectra of sulfides **IIa**–**IIc** contained the absorption bands assigned to vibrations of C–H (2921–2958 and 771–796 cm^{-1}), C–S (2830–2873 and 1453–1493 cm^{-1}), Si–C (1259 cm^{-1}), and Si–O (1092–1094 cm^{-1}) bonds.

Mass spectra (electron impact) of all the sulfides **IIa**–**IIc** contained peaks of the corresponding molecular ions $[M]^+$ with *m*/*z* of 236 (R = Bu), 264 (R = Hex), and 270 (R = Bn). The base peak in all the cases was assigned to the $[CH_3Si(OCH_3)_2]^+$ ion (*m*/*z* 105). The following common peaks were found in the spectra of all the sulfides: $[M - CH_3]^+$ [*m*/*z* 221 (R = Bu), 249 (R = Hex), and 255 (R = Bn)], $[M - SR]^+$ (*m*/*z* 147), $[M - CH_2SR]^+$ and/or $[M - R - OCH_3 - CH_3]^+$ (*m*/*z* 133), $[M - R - (OCH_3)_2]^+$ (*m*/*z* 117), $[CH_3Si(OCH_3)_2 - 2CH_3]^+$ (*m*/*z* 75), $[SiOCH_3]^+$ (*m*/*z* 59), $[S]^+$ (*m*/*z* 32), and $[CH_3]^+$ (*m*/*z* 15). Fragmentation of compounds **IIa** and **IIb** was accompanied with elimination of various alkyl ions: $[M - (CH_2)_2CH_3]^+$ with *m*/*z* of 193 (R = Bu) and 221 (R = Hex) and $[M - (CH_2)_3CH_3]^+$ with *m*/*z* of 179 (R = Bu) and 207 (R = Hex) as well as elimination of alkyl and methoxy groups to give $[M - (CH_2)_2CH_3 - OCH_3]^+$ (*m*/*z* 190), $[M - (CH_2)_2CH_3 - OCH_3 - CH_3]^+$ (*m*/*z* 175), and $[M - (CH_2)_3CH_3 - OCH_3 - CH_3]^+$ (*m*/*z* 161) ions. The spectrum of **IIc** contained additional signals of $[CH_2C_6H_5]^+$ (81% of the base peak, *m*/*z* 91), $[M - 3CH_3]^+$ (*m*/*z* 225), and $[M - CH_3Si(OCH_3)_2]^+$ (*m*/*z* 165).

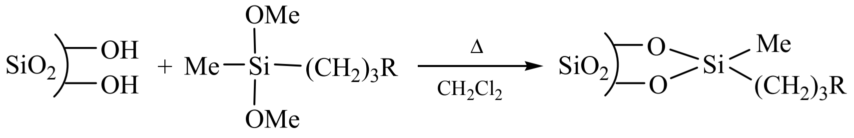
Signals in ^1H NMR spectra of siloxanes **IIIa**–**IIIc** and **IV** were practically identical to those in the spectra of sulfides **IIa**–**IIc**, whereas ^{13}C NMR spectra of siloxanes were somewhat different. In particular, signals of methyl and methylene groups adjacent to silicon atom as well as of methyl of alkyl fragment in the spectra of siloxanes and disiloxane were shifted downfield as compared to those in the sulfides spectra. For example, in the case of R = Bu: $\delta_C(SiCH_3) = -5.80$ (**IIa**), –3.19 (**IIIa**), and –0.46 (**IV**) ppm; $\delta_C(SiCH_2) =$ 12.62 (**IIa**), 13.69 (**IIIa**), and 14.72 (**IV**) ppm; δ_C $(C\underline{C}H_3) = 13.67$ (**IIa**), 14.77 (**IIIa**), and 16.67 (**IV**) ppm.

Analysis of mass spectrum of disiloxane **IIIa** revealed that the fragmentation path was similar to that of sulfide **IIa**, as the following ions were detected: $[M]^+$ (*m*/*z* 426), $[M - CH_3]^+$ (*m*/*z* 411), $[M - Bu]^+$ (*m*/*z* 369), $[M - (CH_2)_3SBu]^+$ (*m*/*z* 295), $[M - CH_3 - Bu - OCH_3]^+$ (*m*/*z* 323), $[CH_3Si(OCH_3)_2]^+$ (*m*/*z* 105), etc; the peak at *m*/*z* 305 being the base one. Presence of two sulfide groups and the siloxane scaffold in the molecule led to appearance of other fragments, for instance, $[M - CH_3 - Bu - SBu]^+$ (*m*/*z* 265). Fragmentation of trisiloxane **IV** revealed simultaneous elimination of three butyl or butyl sulfide fragments, reflected in appearance of the following ions: $[M - CH_3 - 3Bu]^+$ (*m*/*z* 430), $[M - CH_3 - OCH_3 - 3Bu]^+$ (*m*/*z* 399), $[M - 3(CH_2)_3SBu]^+$ (*m*/*z* 223), $[M - OCH_3 - 3(CH_2)_3SBu]^+$ (*m*/*z* 192), $[M - 2OCH_3 - 3(CH_2)_3SBu]^+$ (*m*/*z* 161), etc. Molecular ion peak was not observed in the spectrum of **IV**; the highest *m*/*z* value corresponded to the $[M - 3Bu]^+$ ion (*m*/*z* 445), the base peak being that of $[M - CH_3 - OCH_3 - 3(CH_2)_3SBu]^+$ ion (*m*/*z* 177). In contrast to disiloxane **IIIa**, in the case of trisiloxane **IV** the fragmentation was accompanied by destruction of the siloxane scaffold, giving rise to such ions as $[M - Bu - OSi(OCH_3)(CH_3)(CH_2)_3SBu]^+$ (*m*/*z* 207) and $[CH_3SiOSi(OCH_3)CH_3 - CH_3]^+$ (*m*/*z* 118).

Modification of silica. Heating of porous silica with silyl sulfides **IIa**–**IIc** led to immobilization of the latter via interaction of the sulfides methoxy groups and silica surface hydroxyl groups (the modified silica **Va**–**Vc** was formed) (Scheme 2).

That reaction was accompanied with expected changes of silica IR spectrum. In particular, the bands assigned to Si–O–H bands vibration (stretching at 3453 cm^{-1} and deformation at ≈805 cm^{-1}) were weakened; and new bands appeared, assigned to vibrations of the attached sulfide: C–H (2925–2968 cm^{-1}), Si–OH (954–960 cm^{-1}), C–S (1430–1432 cm^{-1}), and Si–C (1204–1209 cm^{-1}). The reaction

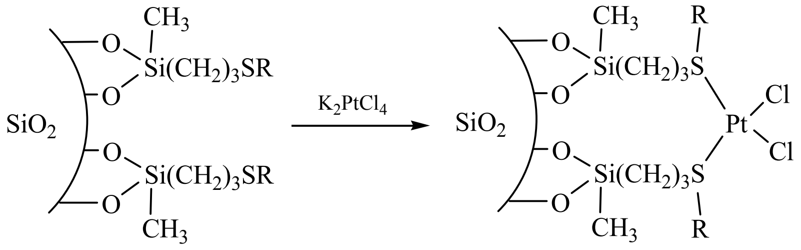
Scheme 2.



I, IIa–IIc **Va–Vd**

R = SBu (**a**), SHex (**b**), SBn (в), Cl (**d**).

Scheme 3.



Va–Vc **VIa–VIc**

R = Bu (**a**), Hex (**b**), Bn (**c**).

rate and silica modification degree increased in the following series (55°C): **IIa** (conversion of 28%, surface concentration of immobilized sulfide c = 0.93 μmol/m^2) < **IIb** (43%, c = 1.05 μmol/m^2) < **IIc** (54%, c = 1.20 μmol/m^2).

The observed trend was in line with the above-discussed tendency of the sulfides **IIa** and **IIb** to undergo side transformations, for instance, to form compounds **IIIa**(**b**) and **IV**, thus embarrassing the target reaction.

Alternatively, silica particles could be modified via addition of γ-chloropropylmethyldimethoxysilane **I** followed by the conversion of the immobilized fragment into corresponding sulfides. The first stage of the process was relatively efficient: the silane conversion was of 69% after 35 h at 55°C, yielding the surface concentration of the immobilized modifier (**Vd**) 1.28 μmol/m^2, somewhat higher than in the case of direct modification with sulfides. However, substantial amount of various siloxanes was formed as side products; furthermore, subsequent conversion of **Vd** into the sulfides **Va**–**Vc** via chlorine substitution with thiolate in alkaline medium was accompanied with detachment of the modifier from silica surface. Hence, that pathway to **Va**–**c** was considered less promising.

Interaction of the sulfide-modified silica **Va**–**Vc** with potassium tetrachloroplatinite(II) gave surface-anchored platinum complexes **VIa**–**VIc**; the reaction was accompanied with decrease of Pt(II) concentration in the solution, but no changes in IR spectra of the modified silica were detected. Incorporation of platinum was confirmed by X-ray photoelectron spectroscopy data. In particular, the spectrum of **Va** contained the signals of Si (E $2p_{3/2}$ = 103.5 eV) and O (E $1s$ = 532.8 eV); the **Va**→**VIa** transformation led to appearance of additional signals of S (E $2p_{3/2}$ = 163.6 eV), C (E $1s$ = 285.0 and 286.3 eV)], O (E $1s$ = 534.1 eV), Si (E $2p_{3/2}$ = 101.9 eV), Pt (E $4f_{7/2}$ = 72.9 eV), and Cl (E $2p_{3/2}$ = 200.3 eV); the Pt : Cl : S molar ratio in **VIa** was of 1 : 2 : 14. The above-listed signals of platinum and sulfur corresponded to the bonding energy of Pt^{2+} ($4f_{7/2}$) and of coordinated S ($2p_{3/2}$) [15, 19, 20], thus confirming formation of sulfide complexes of Pt(II). Platinum concentration at the silica carrier was of 2.81×10^{-5} (**VIa**), 3.85×10^{-5} (**VIb**), and 4.10×10^{-5} (**VIc**) mol/g, being equivalent to surface concentration of sulfide groups in **Va**–**Vc** (Scheme 3).

Catalytic properties. Preliminary tests of catalytic activity of the prepared anchored metal complexes **Va**–**c** were performed using hydrosilylation of allyl butyl ether with 1,1,3,3-tetramethyldisiloxane as the indicative reaction. All the complexes favored formation of the anti-Markovnikov addition product. The interaction occurred under milder conditions (60–

80°C, $c = 1.8 \times 10^{-4}$ mol/L) as compared to the reaction in the presence of a known sulfur-containing catalyst, Pt(II) complex immobilized at polymethylene sulfide [21] (80–120°C, $c = 3.0 \times 10^{-3}$ mol/L).

To conclude, we have developed a procedure for facile preparation of the platinum complexes **VIa**–**VIc** anchored at silica surface and confirmed their potential for catalytic applications.

EXPERIMENTAL

^{1}H and ^{13}C spectra of the solutions in $CDCl_3$ were recorded using the Bruker AC-200 and WM-400 instruments at 400.13 MHz (^{1}H) and 50.33 (^{13}C) MHz with TMS as reference. IR spectra were recorded using the Shimadzu FTIR-8400S (4000–400 cm^{-1}, KBr) spectrometer and the Lumex InfraLyum FT-02 instrument equipped with ATR attachment (4000–500 cm^{-1}, thin layer). Elemental analysis was performed with the Leco CHN-932 C,H,N-analyzer. Atom emission spectra were registered using the iCAP 6300 (Thermo Electron) inductively coupled plasma spectrometer. X-ray photoelectron spectra were recorded with the Kratos Axis Ultra instrument equipped with the monochromatic radiation source (AlK_α at power of 180 V). The measurements were performed at 3×10^{-7} Pa; the surface charge was compensated with slow electrons bombardment. The spectra were referenced to C (1*s*) energy taken equal to 285 eV. Accuracy of the bonding energy determination was of ±0.2 eV. Mass spectra were recorded taking advantage of the Agilent 6890N chromatograph equipped with the Agilent 5973N mass-selective detector (ionization at 70 eV). Other conditions were as follows: the DB Petro 100 capillary column (100 m × 0.25 mm, the film thickness of 5 nm); vaporizer temperature of 280°C, interface temperature 290°C, helium as carrier gas, stream splitting of 1 : 200; specimen volume of 1 μL; column temperature program: R = Bu or Hex, 100°C during 11 min followed by heating to 290°C at 10 deg/min, R = Bn, 100°C during 10 min followed by heating to 290°C at 10 deg/min.

The following chemicals were used as received: 1,1,3,3-tetramethyldisiloxane and allyl butyl ether (Aldrich), K_2PtCl_4 (Alfa Aesar), and porous silica with specific surface area at 600 m^2/g (0.125–0.160 mm fraction) (Lachema Chemapol); butanethiol, hexanethiol, and benzylthiol (all of “chemical pure” grade) were distilled before use.

Hydrosilylation was performed as described elsewhere [22].

Preparation of sulfides was performed under argon atmosphere at room temperature. 36 mmol of metal sodium was added to 20 mL of CH_3OH upon stirring; after complete dissolution of sodium, 36 mmol of the corresponding thiol RSH (R = Bu, Hex, or Bn) was added dropwise, and finally 36 mmol of γ-chloropropylmethyldimethoxysilane was added. The mixture was refluxed during 4 h and then quenched with 30 mL of water. The product was extracted with Et_2O (3 × 20 mL), the extract was dried over $CaCl_2$. The sulfide was isolated via distillation after removal of the ether.

Interaction of sulfides with silica was performed in glass ampoule at 40–55°C. 2 mL of the sulfide **IIa**–**IIc** (3.7–4.2 mol/L in methylene chloride) and 0.5 mL of toluene (internal reference for the sulfide conversion measurement) were added to 1 g of calcined porous silica, and the mixture was stirred during 15–30 h. The mixture was then filtered, washed with methylene chloride (3 × 10 mL) and diethyl ether (3 × 10 mL), and dried at 40°C.

Concentration of the grafted sulfide was determined from elemental analysis data:

$$c = 10^6 \times P_C/(1200n_C - P_C M')S^0,$$

where P_C, content of carbon, %; n_C, number of carbon atoms in the grafted fragment; S^0, specific surface area of the initial silica, m^2/g; M', molar mass (g/mol) calculated as follows:

$$M' = M - M_X$$

from M, molar mass of the compound **IIa**–**IIc** and M_X, molar mass of the eliminated group [2H + 2(OCH_3)].

Application of platinum at the modified silica. 1.2 mL of K_2PtCl_4 in water (0.07 mol/L) was added to 300 mL of porous silica, and the mixture was stirred during 2 days at room temperature. Them the mixture was filtered, washed with distilled water (3 × 5 mL), and dried during 12 h at 40°C. Platinum concentration at the carrier was determined from residual concentration of K_2PtCl_4 in the mother liquor and rinsing water (atom emission spectrometry) and confirmed by X-ray photoelectron spectroscopy of the product.

(3-Butylsulfanylpropyl)dimethoxymethylsilane (IIa). Yield 57%, bp 101°C (4 mmHg), n_D^{20} 1.453, d^{20}

0.977 g/mL. IR spectrum, ν, cm^{-1}: 2958, 2934 [ν_{as}(C–H)]; 2873 [ν_s(C–H)]; 2835 [ν_{as}(C–S)]; 1457 [δ(C–S)]; 1416, 1379, 1340 (C–H); 1259, 1190 [δ_s(Si–C)]; 1093, 999 (Si–O); 796 [γ(C–H)]. ^{1}H NMR spectrum, δ, ppm: 0.11 t (3H, $SiCH_3$, J_{SiH} 3.3 Hz), 0.71–0.76 m (2H, $SiCH_2$), 0.91 t (3H, $CH_2C\underline{H}_3$, *J* 7.4 Hz), 1.41 sextet (2H, $C\underline{H}_2CH_3$, *J* 7.5 Hz), 1.56 quintet (2H, $SCH_2C\underline{H}_2$, *J* 7.5 Hz), 1.66 quintet (2H, $SiCH_2C\underline{H}_2$, *J* 7.5 Hz), 2.50 t (2H, CH_2SBu, *J* 7.5 Hz), 2.53 t (2H, $CH_2SC\underline{H}_2$, *J* 7.3 Hz), 3.51 s (6H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: –5.80 ($SiCH_3$), 12.62 ($SiCH_2$), 13.67 ($CH_2\underline{C}H_3$), 22.00 ($\underline{C}H_2CH_3$), 23.17 ($SCH_2\underline{C}H_2$), 31.69 ($CH_2S\underline{C}H_2$), 31.84 ($\underline{C}H_2SBu$), 35.31 ($SiCH_2\underline{C}H_2$), 50.17 (OCH_3). Mass spectrum, *m/z* (I_{rel}, %): 236 (9) $[M]^+$, 221 (3) $[M - CH_3]^+$, 204 (5), 193 (5) $[M - (CH_2)_2CH_3]^+$, 179 (1) $[M - (CH_2)_3CH_3]^+$, 147 (34) $[M - S(CH_2)_3CH_3]^+$, 133 (11) $[M - CH_2S(CH_2)_3CH_3]^+$ and/or $[M - (CH_2)_3CH_3 - OCH_3 - CH_3]^+$, 117 (7) $[M - (CH_2)_3CH_3 - 2(OCH_3)]^+$, 105 (100) $[M - (CH_2)_3S\cdot(CH_2)_3CH_3]^+$, 90 (1) $[(CH_3O)_2Si]^+$, 75 (19) $[CH_3Si\cdot(OCH_3)_2 - 2CH_3]^+$, 59 (5) $[CH_3OSi]^+$, 32 (2) $[S]^+$, 29 (3) $[CH_2CH_3]^+$, 15 (1) $[CH_3]^+$.

(3-Hexylsulfanylpropyl)dimethoxymethylsilane (IIb). Yield 67%, bp 138–140°C (4 mmHg). IR spectrum, ν, cm^{-1}: 2921 (C–H), 2830 [ν_{as}(C–S)]; 1493 (C–H), 1453 [δ(C–S)]; 1259, 1236 [δ_s(Si–C)]; 1172; 1092, 1071 (Si–O); 771, 701 [γ(C–H)]. ^{1}H NMR spectrum, δ, ppm: 0.05–0.12 m (3H, $SiCH_3$), 0.63–0.73 m (2H, $SiCH_2$), 0.86 t (3H, $CH_2C\underline{H}_3$, *J* 6.9 Hz), 1.25–1.33 m (4H, $C\underline{H}_2C\underline{H}_2CH_3$), 1.35 quintet (2H, $SCH_2CH_2C\underline{H}_2$, *J* 6.8 Hz), 1.55 quintet (2H, $SCH_2C\underline{H}_2$, *J* 7.4 Hz), 1.62 quintet (2H, $SiCH_2C\underline{H}_2$, *J* 8.4 Hz), 2.47 t (2H, CH_2SHex, *J* 7.4 Hz), 2.49 t (2H, $CH_2SC\underline{H}_2$, *J* 6.9 Hz), 3.46–3.51 m (6H, OCH_3). Mass spectrum, *m/z* (I_{rel}, %): 264 (9) $[M]^+$, 249 (3) $[M - CH_3]^+$, 234 (1) $[M - 2CH_3]^+$, 232 (5), 221 (5) $[M - (CH_2)_2CH_3]^+$, 207 (1) $[M - (CH_2)_3CH_3]^+$, 190 (2) $[M - (CH_2)_2CH_3 - OCH_3]^+$, 175 (1) $[M - (CH_2)_2CH_3 - OCH_3 - CH_3]^+$, 161 (4) $[M - (CH_2)_4CH_3 - OCH_3 - CH_3]^+$, 147 (38) $[M - S(CH_2)_5CH_3]^+$, 133 (10) $[M - CH_2S(CH_2)_5CH_3]^+$ and/or $[M - (CH_2)_5CH_3 - OCH_3 - CH_3]^+$, 119 (8) $[M - (CH_2)_2S(CH_2)_5CH_3]^+$, 117 (3) $[M - (CH_2)_5CH_3 - 2(OCH_3)]^+$, 105 (100) $[M - (CH_2)_3S(CH_2)_5CH_3]^+$, 90 (1) $[(CH_3O)_2Si]^+$, 75 (19) $[CH_3Si(OCH_3)_2 - 2CH_3]^+$, 59 (5) $[CH_3OSi]^+$, 32 (3) $[S]^+$, 29 (3) $[CH_2CH_3]^+$, 15 (1) $[CH_3]^+$.

(3-Benzylsulfanylpropyl)dimethoxymethylsilane (IIc). Yield 89%. IR spectrum, ν, cm^{-1}: 3062, 3028 (C–H); 1413, 1376 (C–H$_{arom}$); 2956, 2927 (C–H); 2857 [ν_{as}(C–S)], 1458 [δ(C–S)], 1259 [δ_s(Si–C)], 1094 (Si–O), 794 [γ(C–H)]. ^{1}H NMR spectrum, δ, ppm: 0.07–0.15 m (3H, $SiCH_3$), 0.60–0.72 m (2H, $SiCH_2$), 1.61–1.67 m (2H, $SiCH_2C\underline{H}_2$), 2.44 t (2H, $\underline{CH_2}SCH_2C_6H_5$, *J* 7.4 Hz), 3.44–3.52 m (6H, OCH_3), 3.70 m (2H, $SC\underline{H}_2C_6H_5$), 7.23–7.26 m (3H, 2C$^{\alpha+\gamma}$H), 7.31 t (2H, C$^{\beta}$H, *J* 2.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 270 (1) $[M]^+$, 255 (1) $[M - CH_3]^+$, 238 (59), 225 (2) $[M - 3CH_3]^+$, 204 (28), 189 (3), 172 (3), 165 (1) $[M - CH_3Si(OCH_3)_2]^+$, 147 (41) $[M - SCH_2C_6H_5]^+$, 133 (4) $[M - CH_2SCH_2C_6H_5]^+$ and/or $[M - CH_2C_6H_5 - OCH_3 - CH_3]^+$, 117 (9) $[M - CH_2C_6H_5 - 2(OCH_3)]^+$, 105 (100) $[M - (CH_2)_3SCH_2C_6H_5]^+$, 91 (81) $[CH_2C_6H_5]^+$, 75 (29) $[CH_3Si(OCH_3)_2 - 2CH_3]^+$, 59 (9) $[CH_3OSi]^+$, 32 (1) $[S]^+$, 15 (1) $[CH_3]^+$.

1,3-Di(3-butylsulfanylpropyl)-1,3-dimethoxy-1,3-dimethyldisiloxane (IIIa). Yield 28%, bp 192°C (4 mmHg), n_D^{20} 1.466, d^{20} 0.999 g/mL. ^{1}H NMR spectrum, δ, ppm: 0.13 s (3H, $SiCH_3$), 0.69–0.73 m (2H, $SiCH_2$), 0.93 t (3H, $CH_2C\underline{H}_3$, *J* 7.3 Hz), 1.42 sextet (2H, $C\underline{H}_2CH_3$, *J* 7.5 Hz), 1.58 quintet (2H, $SCH_2C\underline{H}_2$, *J* 7.5 Hz), 1.66 quintet (2H, $SiCH_2C\underline{H}_2$, *J* 7.9 Hz), 2.52 t (2H, CH_2SBu, *J* 7.8 Hz), 2.54 t (2H, $CH_2SC\underline{H}_2$, *J* 7.7 Hz), 3.51 s (6H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: –3.19 ($SiCH_3$), 13.69 ($SiCH_2$), 14.77 ($CH_2\underline{C}H_3$), 22.03 ($\underline{C}H_2CH_3$), 23.30 ($SCH_2\underline{C}H_2$), 31.73 ($CH_2S\underline{C}H_2$), 31.86 ($\underline{C}H_2SBu$), 35.39 ($SiCH_2\underline{C}H_2$), 49.95 (OCH_3). Mass spectrum, *m/z* (I_{rel}, %): 426 (4) $[M]^+$, 411 (1) $[M - CH_3]^+$, 394 (9), 369 (3) $[M - (CH_2)_3CH_3]^+$, 354 (1) $[M - CH_3 - (CH_2)_3CH_3]^+$, 323 (1) $[M - CH_3 - (CH_2)_3CH_3 - OCH_3]^+$, 305 (100), 295 (93) $[M - (CH_2)_3S(CH_2)_3CH_3]^+$, 291 (6) $[M - CH_3 - 2(OCH_3) - (CH_2)_2CH_3 + H]^+$, 265 (5) $[M - 2CH_3 - (CH_2)_3S(CH_2)_3CH_3]^+$ and/or $[M - CH_3 - S(CH_2)_3CH_3 - (CH_2)_3CH_3]^+$, 263 (5) $[M - CH_3 - OCH_3 - (CH_2)_2S\cdot(CH_2)_3CH_3]^+$, 249 (1) $[M - CH_3 - OCH_3 - (CH_2)_3S\cdot(CH_2)_3CH_3]^+$, 207 (94) $[M - OCH_3 - (CH_2)_3CH_3 - (CH_2)_2S(CH_2)_3CH_3]^+$, 197 (10), 181 (7), 165 (36) $[M - 2(CH_2)_3S(CH_2)_3CH_3 + H]^+$, 143 (7), 141 (7), 135 (16), 105 (5) $[CH_3Si(OCH_3)_2]^+$, 57 (7) $[(CH_2)_3CH_3]^+$, 32 (1) $[S]^+$, 29 (5) $[CH_2CH_3]^+$.

1,3,5-Tri(3-butylsulfanylpropyl)-1,5-dimethoxy-1,3,5-trimethyltrisiloxane (IV). ^{1}H NMR spectrum, δ, ppm: 0.10 s (3H, $SiCH_3$), 0.63–0.71 m (2H, $SiCH_2$), 0.90 t (3H, $CH_2C\underline{H}_3$, *J* 7.3 Hz), 1.40 sextet (2H, $C\underline{H}_2CH_3$, *J* 7.2 Hz), 1.55 quintet (2H, $SCH_2C\underline{H}_2$, *J* 7.3 Hz), 1.60–1.70 m (2H, $SiCH_2C\underline{H}_2$), 2.49 t (2H, CH_2SBu, *J* 7.3 Hz), 2.51 t (2H, $CH_2SC\underline{H}_2$, *J* 7.0 Hz), 3.45–3.49 m (6H, OCH_3). ^{13}C NMR spectrum, δ_C, ppm: –0.46 ($SiCH_3$), 14.72 ($SiCH_2$), 16.67 ($CH_2\underline{C}H_3$), 22.99 ($\underline{C}H_2CH_3$), 23.32 ($SCH_2\underline{C}H_2$), 31.65 ($CH_2S\underline{C}H_2$), 31.85

$(\underline{C}H_2SBu)$, 35.35 $(SiCH_2\underline{C}H_2)$, 50.66 (OCH_3). Mass spectrum, m/z (I_{rel}, %): 445 (1) $[M - 3(CH_2)_3CH_3]^+$, 430 (1) $[M - CH_3 - 3(CH_2)_3CH_3]^+$, 399 (2) $[M - CH_3 - OCH_3 - 3(CH_2)_3CH_3]^+$, 357 (1), 343 (1), 339 (1) $[M - CH_3 - OCH_3 - 2(CH_2)_3CH_3 - (CH_2)_2S(CH_2)_3CH_3]^+$, 311 (1) $[M - (CH_2)_2CH_3 - 2(CH_2)_3S(CH_2)_3CH_3]^+$, 279 (4) $[M - S(CH_2)_3CH_3 - (CH_2)_2S(CH_2)_3CH_3 - (CH_2)_3S\cdot(CH_2)_3CH_3]^+$, 251 (1) $[M - CH_2S(CH_2)_3CH_3 - 2(CH_2)_3\cdot S(CH_2)_3CH_3]^+$, 223 (1) $[M - 3(CH_2)_3S(CH_2)_3CH_3]^+$, 207 (23) $[M - (CH_2)_3CH_3 - OSi(OCH_3)(CH_3)(CH_2)_3S\cdot(CH_2)_3CH_3]^+$, 192 (9) $[M - OCH_3 - 3(CH_2)_3S(CH_2)_3CH_3]^+$, 177 (100) $[M - CH_3 - OCH_3 - 3(CH_2)_3S(CH_2)_3CH_3]^+$, 161 (4) $[M - 2OCH_3 - 3(CH_2)_3S(CH_2)_3CH_3]^+$, 135 (88) $[M - 2CH_3 - OCH_3 - 3(CH_2)_3S(CH_2)_3CH_3 + H]^+$, 118 (2) $[CH_3SiOSi(OCH_3)CH_3 - CH_3]^+$, 105 (6) $[CH_3Si\cdot(OCH_3)_2]^+$, 73 (21), 59 (4) $[CH_3OSi]^+$, 16 (2).

Compound Va. Concentration of grafted sulfide 0.93 μmol/m^2. IR spectrum, ν, cm^{-1}: 3438 (O–H); 2961, 2925 (C–H); 2850 [ν_{as}(C–S)], 1636; 1096 (Si–O), 958 [δ(O–H)], 804 [δ(O–H)]; 470. Found, %: C 4.87; H 1.57.

Compound Vb. Concentration of grafted sulfide 1.05 μmol/m^2. IR spectrum, ν, cm^{-1}: 3445 (O–H); 2968, 2934 (C–H); 1627; 1432 [δ(C–S)], 1204 [δ_s(Si–C)], 1097 (Si–O), 960 [δ(O–H)], 807 [δ(O–H)]. Found, %: C 8.04; H 1.74.

Compound Vc. Concentration of grafted sulfide 1.20 μmol/m^2. IR spectrum, ν, cm^{-1}: 3639; 3419 (O–H), 2929 (C–H); 1630; 1430 [δ(C–S)], 1209 [δ_s(Si–C)], 1090 (Si–O), 954 [δ(O–H)], 805 [δ(O–H)], 702 [γ(C–H)], 567, 465. Found, %: C 9.78; H 1.59.

Compound Vd was prepared using the same procedure as in the cases of sulfides **Va**–**c**. Concentration of grafted fragment 1.28 μmol/m^2. IR spectrum, ν, cm^{-1}: 3435 (O–H), 1630; 1220 [δ_s(Si–C)], 1098 (Si–O), 964 [δ(O–H)], 803 [δ(O–H)], 470. Found, %: C 3.38; H 1.27.

Complex VIa. c_{Pt} $2.81\cdot10^{-5}$ mol/g. IR spectrum, ν, cm^{-1}: 3433 (O–H); 2966, 2931 (C–H); 2858 [ν_{as}(C–S)], 1630; 1096 (Si–O), 960 [δ(O–H)], 803 [δ(O–H)], 473, 463. XPS: Pt (E $4f_{7/2}$ = 72.9 eV), Si (E $2p_{3/2}$ = 101.9, 103.5 eV), O (E $1s$ = 532.8, 534.1 eV), S (E $2p_{3/2}$ = 163.6 eV), C (E $1s$ = 285.0, 286.3 eV)], Cl (E $2p_{3/2}$ = 200.3 eV).

Complex VIb. c_{Pt} $3.85\cdot10^{-5}$ mol/g. IR spectrum, ν, cm^{-1}: 3445 (O–H); 2961, 2930 (C–H), 2858, 1630; 1443 [δ(C–S)], 1095 (Si–O), 960 [δ(O–H)], 804 [δ(O–H)], 472. XPS: Pt (E $4f_{7/2}$ = 73.0 eV), Si (E $2p_{3/2}$ = 102.1, 103.4 eV), O (E $1s$ = 532.7, 534.0 eV), S (E $2p_{3/2}$ = 163.5 eV), C (E $1s$ = 285.0, 286.9 eV)], Cl (E $2p_{3/2}$ = 200.2 eV).

Complex VIc. c_{Pt} 4.10×10^{-5} mol/g. IR spectrum, ν, cm^{-1}: 3448 (O–H), 2960; 2929 (C–H), 2858, 1630; 1438 [δ(C–S)], 1095 (Si–O), 956 [δ(O–H)]; 801 [δ(O–H)], 703 [γ(C–H)], 474. XPS: Pt (E $4f_{7/2}$ 73.0 eV), Si (E $2p_{3/2}$ = 102.0, 103.6 eV), O (E $1s$ = 532.9, 534.2 eV), S (E $2p_{3/2}$ = 163.7 eV), C (E $1s$ = 285.1, 286.5 eV)], Cl (E $2p_{3/2}$ = 200.3 eV).

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