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Supporting Information

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Supporting Information
for
"Self-Assembled Monolayer of Compact Phosphane with Alkanethiolate Pendant: Remarkable Reusability and Substrate Selectivity in Rh Catalysis"

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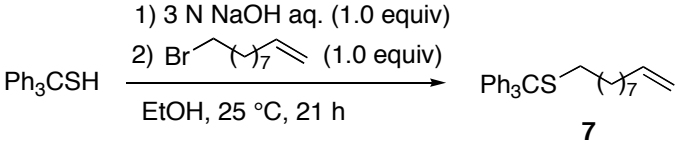
General

All reactions were performed in oven-dried glassware under argon or nitrogen atmosphere, unless otherwise noted. Commercial reagents were purified by distillation or recrystallization prior to use. A xylenes solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) (Aldrich), trifluoromethanesulfonic acid, trifluoroacetic acid (Junsei Chemical Co., Ltd.), hexachlorodisilane, diphenylphosphane (Tokyo Chemical Industry Co., Ltd.), sodium hydride (Wako Pure Chemical Industries, Ltd.) and an ether solution of methyllithium (Kanto Chemical Co., Inc.) were used as received. Anhydrous hexane, toluene, dichlromethane (Kanto) and benzene (Aldrich) were used as received, unless otherwise specified. For the procedure using phosphane or Rh complex, all solvents were deaerated by iterative freeze-pump-thaw cycles. 10-bromodecene,[1] 4-hydro-1-phospha-4-silabicyclo[2.2.2]octane-1-sulfide (**6**),[2] 4-phenyl-1-phospha-4-silabicyclo[2.2.2]octane (Ph-SMAP, **5**)[3] and $[RhCl(C_2H_4)_2]_2$[4] were prepared according to the literatures. Column chromatography was performed using silica gel 60N (Kanto, 40-100 μm mesh).

NMR spectra were recorded on Varian Gemini 2000 (^{1}H: 300 MHz; ^{13}C: 75.4 MHz; ^{31}P: 121 MHz) at 25°C. Spectra are referenced to tetramethylsilane (^{1}H), residual chloroform (^{13}C), residual benzene (^{1}H, ^{13}C) or phosphoric acid (^{31}P). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet) and m (multiplet). Coupling constants, *J*, are reported in Hz. Gas chromatographic analyses were conducted using 1,4-diisopropylbenzene as an internal standard on a Shimazu GC-14B equipped with a capillary column HR-1 (I.D. 0.25 mm × 25 m) and a flame ionization detector. XPS measurements were performed on a Rigaku XPS7000 spectrometer using Al Kα X-ray source with 15 eV pass energy and 300 W electron-beam power under resolution of 0.1 eV. All binding energies were calibrated with Au $4f_{7/2}$ peak at 83.8 eV. ICP-MS measurements were carried out on Perkin-Elmer ELAN DRC II or ELAN DRC-e. A standard solution of Rh was purchased from Wako or from Kanto, and those of Au and Ti were purchased from Kanto.

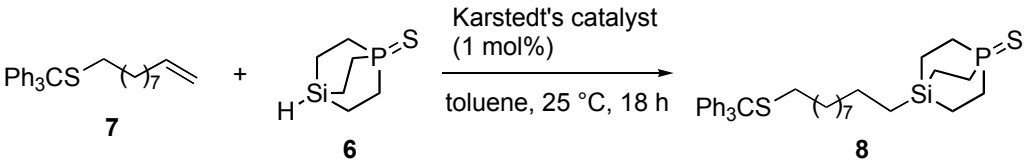
Synthesis of 10-(*S*-trityl)mercaptodec-1-ene (7).



7

Triphenylmethanethiol (990 mg, 3.60 mmol) and aqueous solution of NaOH (3 N, 1.20 mL, 3.60 mmol) were dissolved in ethanol (8.0 mL). The mixture was stirred for 10 minutes, followed by the addition of 10-bromodec-1-ene (788 mg, 3.60 mmol). After stirring for 21 h at 25°C, the reaction was quenched by the addition of saturated aqueous NH_4Cl solution (5 mL). The organic phase was separated, and the aqueous layer was extract with CH_2Cl_2 (5 mL×3). The combined organic phase was dried over $MgSO_4$ and concentrated under a reduced pressure. The residue was purified by silica gel column chromatography (5% ethyl acetate in hexane) to give the titled compound as white solid (1.34 g, 90%): ^{1}H NMR ($CDCl_3$) δ 7.43-7.40 (m, 6H), 7.30-7.26 (m, 6H), 7.23-7.18 (m, 3H), 5.87-5.73 (tdd, J = 17.1, 10.2, 6.9, 1H), 5.02-4.91 (m, 2H), 2.13 (t, J = 7.2, 2H), 2.00 (q, J = 6.9, 2H), 1.40-1.10 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 154.2 (3C), 139.2, 129.7 (6C), 127.8 (6C), 126.5 (3C), 114.2, 66.3, 33.7, 31.9, 29.1, 29.0, 28.9, 28.8, 28.7, 28.4.

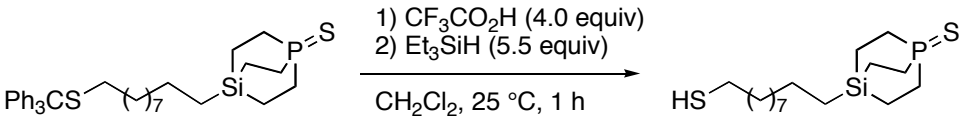
Synthesis of 4-(10-(*S*-trityl)mercaptodecyl)-1-phospha-4-silabicyclo[2.2.2]octane-1-sufide (8).



7 **6** **8**

To a mixture of alkene **7** (125 mg, 0.300 mmol) and SMAP sulfide (**6)** (35.2 mg, 0.200 mmol) in anhydrous toluene (2.0 mL), Karstedt's catalyst (2 wt% Pt in xylenes, 50 μL, 2 μmol) was added. After stirring for 18 h at 25°C, the reaction mixture was concentrated under a reduced pressure. Purification by silica gel column chromatography (5% ethyl acetate in hexane) afforded the titled compound as colorless oil (108 mg, 91%): ^{1}H NMR ($CDCl_3$) δ 7.40-7.30 (m, 6H), 7.30-7.25 (m, 6H) 7.23-7.18 (m, 3H), 2.42-2.32 (m, 6H), 2.13 (t, J = 7.5, 2H), 1.36 (br qn, J = 7.5, 2H), 1.25-1.08 (m, 20H), 0.59 (t, J = 7.5, 2H); ^{13}C NMR ($CDCl_3$) δ 154.2 (3C), 129.6 (6C), 127.8 (6C), 126.5 (3C), 66.2, 32.9, 31.8, 29.2, 29.1, 28.9 (2C), 28.7, 28.4, 28.1 (d, $J_{p\text{-}c}$ = 50.7, 3C), 23.1, 10.7 (d, $J_{p\text{-}c}$ = 3.0), 5.6 (d, $J_{p\text{-}c}$ = 3.8, 3C); ^{31}P NMR ($CDCl_3$) δ 26.9.

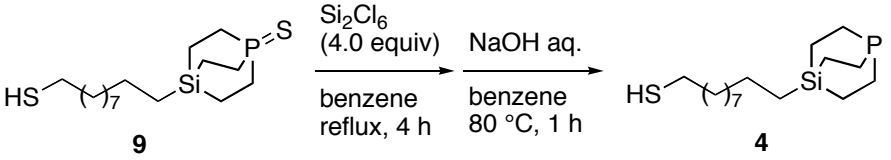
Synthesis of 4-(10-mercaptodecyl)-1-phospha-4-silabicyclo[2.2.2]octane-1-sufide (9).



8 **9**

A solution of thioether **8** (108 mg, 0.182 mmol) and trifluoroacetic acid (83.0 mg, 0.728 mmol) in CH_2Cl_2 (3.6 mL) was stirred for 10 minutes at 25°C, followed by the addition of triethylsilane (116 mg, 1.00 mmol). The reaction mixture was stirred for 1 h at 25°C, and then quenched by the addition of saturated aqueous $NaHCO_3$ solution. The organic phase was separated, and the aqueous layer was extract with CH_2Cl_2 (5 mL×3). The combined organic phase was dried over $MgSO_4$ and concentrated under a reduced pressure. The residue was purified by silica gel column chromatography (5% ethyl acetate in hexane), which afforded the titled compound as white solid (61.0 mg, 96%): ^{1}H NMR ($CDCl_3$) δ 2.52 (q, J = 7.2, 2H), 2.42-2.33 (m, 6H), 1.60 (qn, J = 7.2, 2H), 1.36-1.25 (m, 14H), 1.19-1.09 (m, 6H), 0.60 (t, J = 7.4, 2H); ^{13}C NMR ($CDCl_3$) δ 33.9, 33.0, 29.4 (d, $J_{p\text{-}c}$ = 50.7, 3C), 29.3, 29.0, 28.9, 28.2, 28.1, 24.5, 23.2, 10.8 (d, $J_{p\text{-}c}$ = 2.2), 5.7 (d, $J_{p\text{-}c}$ = 3.8, 3C); ^{31}P NMR ($CDCl_3$) δ 26.6.

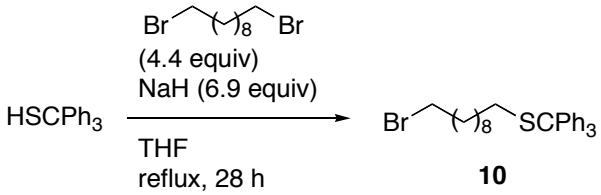
Synthesis of 4-(10-mercaptodecyl)-1-phospha-4-silabicyclo[2.2.2]octane (4).



9 **4**

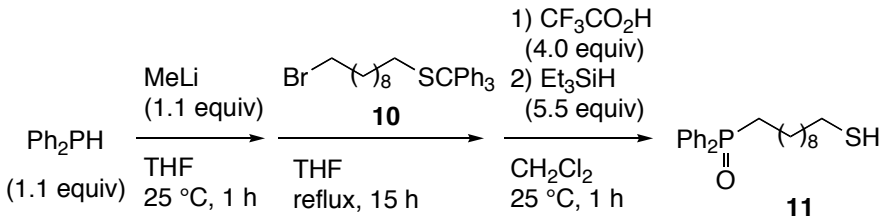
To a solution of SMAP sulfide derivative **9** (115 mg, 0.330 mmol) in deaerated benzene (0.33 mL), hexachlrodisilane (355 mg, 1.32 mmol) was added. The mixture was refluxed for 3 h at 80°C. Deaerated aqueous NaOH solution (1 N, 1 mL) was added to the reaction mixture followed by further stirring for 1 h at 80°C. The organic phase was separated, and the aqueous layer was extract with dearated benzene (1 mL×3). The combined organic phase was dried over $MgSO_4$ and concentrated under a reduced pressure. The residue was purified by silica gel column chromatography (benzene) to afford the titled compound as white soild (75.3 mg, 72%): ^{1}H NMR (C_6D_6) δ 2.22 (q, J = 7.4, 2H), 1.95-1.88 (m, 6H), 1.40-1.20 (m, 16H), 0.76-0.70 (m, 6H), 0.47 (m, 2H); ^{13}C NMR (C_6D_6) δ 34.1, 33.6, 29.7, 29.7, 29.5, 29.2, 28.4, 24.4, 23.8, 18.0 (d, $J_{p\text{-}c}$ = 15.4, 3C), 12.4 (d, $J_{p\text{-}c}$ = 4.1), 4.1 (3C); ^{31}P NMR (C_6D_6) δ -59.1.

Synthesis of 1-bromo-10-(*S*-trityl)mercaptodecane (10).



A suspension of 1,10-dibromodecane (25.0 g, 83.3 mmol), triphenylmethanethiol (5.06 g, 18.9 mmol) and sodium hydride (60% in mineral oil, 52.3 g, 131 mmol) in THF (104 mL) was refluxed for 28 h. The suspension was filtered and the filtrate was concentrated *in vacuo*. The residue was dissolved in Et_2O (100 mL) and washed with water (100 mL×5). The organic phase was dried over $MgSO_4$ and concentrated under a reduced pressure. The residue was purified by recrystallization from hexane to afford the titled compound as white solid (4.63 g, 49%): ^{1}H NMR ($CDCl_3$) δ 7.43-7.40 (m, 6H), 7.30-7.17 (m, 9H), 3.40 (t, J = 6.9, 2H), 2.13 (t, J = 7.2, 2H), 1.84 (qn, J = 7.2, 2H), 1.39-1.18 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 145.2 (3C), 129.7 (6C), 127.9 (6C), 126.6 (3C), 66.3, 33.9, 32.8, 31.9, 29.2, 29.1, 29.0, 28.9, 28.6, 28.5, 28.1.

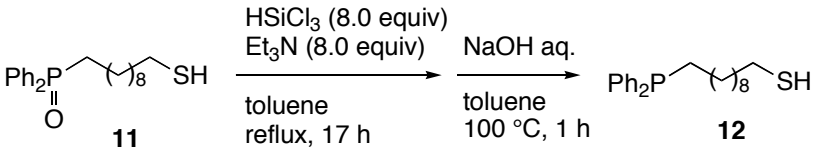
Synthesis of (10-mercaptodecyl)diphenylphosphane oxide (11).



To a solution of diphenylphosphane (102 mg, 0.550 mmol) in THF (4.0 mL), MeLi (1.04 M in Et_2O, 0.530 mL, 0.551 mmol) was added and the mixture was stirred for 1 h at 25°C. A solution of bromide **10** (248 mg, 0.500 mmol) in THF (1.0 mL) was then added over a period of 15 min. The mixture was refluxed for 15 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl solution. The organic phase was separated, and the aqueous layer was extract with Et_2O (5 mL×3). The combined organic phase was dried over $MgSO_4$ and concentrated under a reduced pressure. The residue was dissolved in CH_2Cl_2 (5.0 mL), followed by the addition of trifluoroacetic acid (228 mg, 2.00 mmol) and triethylsilane (290 mg, 2.50 mmol). The mixture was stirred for 1 h at 25°C in the air, and then quenched by the addition of saturated aqueous $NaHCO_3$ solution. The aqueous layer was extract with CH_2Cl_2 (5 mL×3). The combined organic phase was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography (10% MeOH in CH_2Cl_2), which afforded the titled compound as white solid (101 mg, 64%): ^{1}H NMR ($CDCl_3$) δ 7.77-7.70 (m, 4H), 7.52-7.44 (m, 6H), 2.51 (q, J = 6.9, 2H), 2.30-2.21 (m, 2H), 1.59 (m, 2H), 1.42-1.23 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 133.3 (d, $J_{p\text{-}c}$ = 98.0, 2C),

131.7 (d, $J_{p\text{-}c}$ = 3.0, 2C), 130.9 (d, $J_{p\text{-}c}$ = 9.0, 4C), 128.7 (d, $J_{p\text{-}c}$ = 11.3, 4C), 33.9, 30.8 (d, $J_{p\text{-}c}$ = 15.1), 29.5 (d, $J_{p\text{-}c}$ = 81.4), 29.3, 29.2, 28.9 (2C), 28.2, 24.5, 21.3 (d, $J_{p\text{-}c}$ = 4.0); ^{31}P NMR ($CDCl_3$) δ 33.0.

Synthesis of 10-diphenylphosphano-1-mercaptodecane (12).



A solution of phosphane oxide **11** (90.0 mg, 0.240 mmol), trichlorosilane (259 mg, 1.92 mmol) and triethylamine (194 mg, 1.92 mmol) in deaerated toluene (5.0 mL) was refluxed for 17 h. Deaerated aqueous NaOH solution (1 N, 1 mL) was added to the reaction mixture, and the mixture was stirred for 1 h at 100 °C. The organic layer was separated, and the aqueous layer was extracted with dearated toluene (1 mL×3). The combined organic phase was dried over $MgSO_4$ and concentrated under a reduced pressure. The residue was purified by silica gel column chromatography (toluene) to afford the titled compound as colorless oil (68.9 mg, 80%): ^{1}H NMR (C_6D_6) δ 7.55-7.49 (m, 4H), 7.17-7.07(m, 6H), 2.21 (q, J = 7.4, 2H), 2.06-2.00 (m, 2H), 1.55-1.10 (m, 16H); ^{13}C NMR (C_6D_6) δ 140.0 (d, $J_{p\text{-}c}$ = 15.1, 2C), 133.1 (d, $J_{p\text{-}c}$ = 18.1, 4C), 128.7(d, $J_{p\text{-}c}$ = 6.0, 4C), 128.6 (2C), 34.1, 31.3 (d, $J_{p\text{-}c}$ = 12.8), 29.7 (2C), 29.4, 29.2, 28.5 (d, $J_{p\text{-}c}$ = 12.1), 28.4, 26.2 (d, $J_{p\text{-}c}$ = 16.6), 24.4; ^{31}P NMR (C_6D_6) δ -15.8.

Preparation of evaporated gold surface and [Au]-SMAP (1).

Evaporated gold surfaces were prepared by successive vapor deposition of 5 nm thickness of titanium (99.5%, Nilaco) and 100 nm thickness of gold (99.99%, Tanaka Precious Metal) onto glass slides in a vacuum evaporator apparatus (ULVAC, EBH-6). The pressure was maintained below 1×10^{-6} Torr and the temperature was kept at 300 °C. Deposition was carried out at constant rate of 0.01 nm/s. The gold surfaces thus obtained were stored in hexane and annealed in a hydrogen-flame before use. The monolayer formation was carried out by immersing the gold surface in a 1.0 mM solution of phosphane-terminated thiol **4** in ethanol for 18 h at 25°C. The modified gold surface was sufficiently rinsed with ethanol (1 mL×3), immersed in ethanol for 5 min and dried by Ar purge. The gold surface modified with thiol **12** was carried out following the same procedure.

Preparation of [Au]-SMAP-Rh (2).

[Au]-SMAP (**1**) was immersed in a 5.0 mM benzene solution of $[RhCl(C_2H_4)_2]_2$ for 15 min at 25°C. The surface was sufficiently rinsed with benzene (1 mL×3), immersed in benzene for 5 min and dried by Ar purge. [Au]-Ph_2P-Rh was prepared in the same procedure but with the gold surface modified with thiol **12**.

Electrochemical measurements.

Electrochemical measurements were performed with a conventional three-compartment cell. An Ag/AgCl, and a Pt wire were used as a reference and a counter electrode, respectively. An Au(111) electrode was prepared from gold wire (99.99% Tanaka Precious Metal) by the Clavilier method and was then cut and mechanically polished. The Au(111) surface was then placed to contact the surface of a 1.0 mM solution of thiol **9** in ethanol for 18 h at 25°C, followed by sufficient rinse with ethanol. The electrochemical desorption of the formed monolayer was carried out in 0.5 N KOH aqueous solution with a scan rate of 50 mV/s. The cathodic peak corresponding to the reductive desorption of the adsorbed thiolate was observed at –0.95 V, and the density of the thiolate **9** was estimated to be 0.69 nmol/cm^2 (4.2 molecules/nm^2) from the cathodic charge of the desorption peak.

ICP-MS measurements.

A Rh-immobilized gold surface ([Au]-SMAP-Rh (**2**) or [Au]-Ph_2P-Rh (dimension; 8 × 8 mm^2)) was dissolved into aqua regia. The solution thus obtained was evaporated by heating to afford the residue, which was then dissolved in 100 mL of 0.5 % nitric acid (Ultratrace Analysis grade, Kanto) diluted with Milli-Q® water. The Rh concentration in the sample was determined with an ICP-MS (ELAN DRC II or ELAN DRC-e, Perkin Elmer Co. Ltd.) calibrated using a set of the Rh standard solutions containing the expected concentrations of Au and Ti as matrix components.

Typical procedure for dehydrogenative silylation of alcohols catalyzed by [Au]-phospine-Rh monolayer.

A solution of dimethylphenylsilane (1.63 mg, 12.0 μmol) and ethanol (0.662 mg, 14.4 μmol) in hexane (0.120 mL) was placed in a glass screw-capped test tube (NN-13, Maruemu Corporation, I.D. 10 mm × 100 mm). [Au]-SMAP-Rh (**2**) (5 × 5 mm^2) was then placed in the reaction mixture, which was allowed to stand without stirring for 16 h at 25°C (See, Figure S-1 (a), (b), (c)). For a larger scale experiment using **2** with 25 × 25 nm^2 dimension, a reaction vial (SV-50A, Nichiden-rika Glass Co., Ltd.,

I.D. 36 mm × 75 mm) was used (See, Figure S-1 (d)). The solution phase was analyzed by gas chromatography to determine the yield of the product.

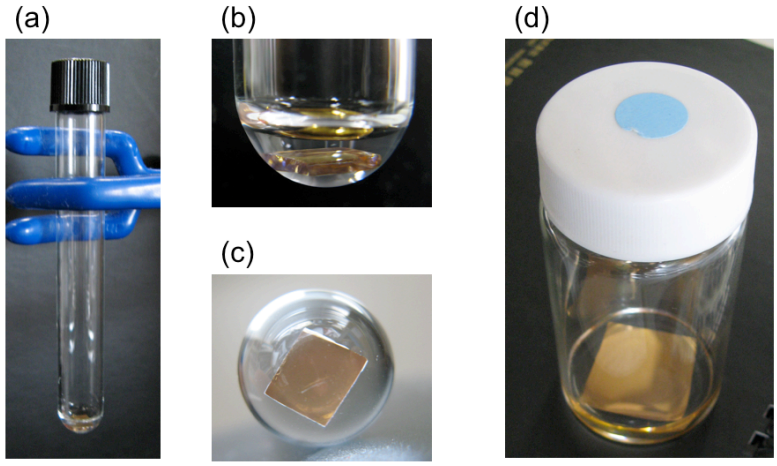


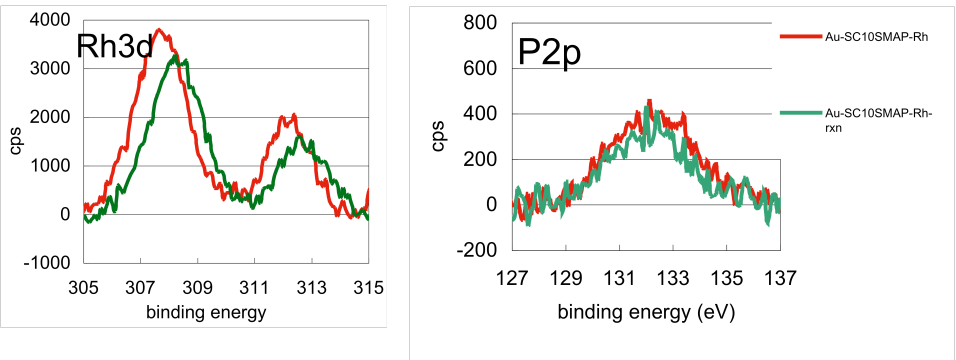
Figure S-1. The Reaction Tubes for the Catalytic Reaction with [Au]-SMAP-Rh (**2**). (a) Entire, (b) side and (c) bottom views of the reaction tube for a 5 × 5 mm^2 catalyst chip. (d) The reaction tube for a 25 × 25 mm^2 catalyst chip.

Reuse of the surface catalyst.

After the first reaction, the catalyst tip was picked up with tweezers and washed with hexane (1 mL×3). The catalyst tip was dried under nitrogen atmosphere, and was then transferred to the reaction tube for the next catalytic reaction.

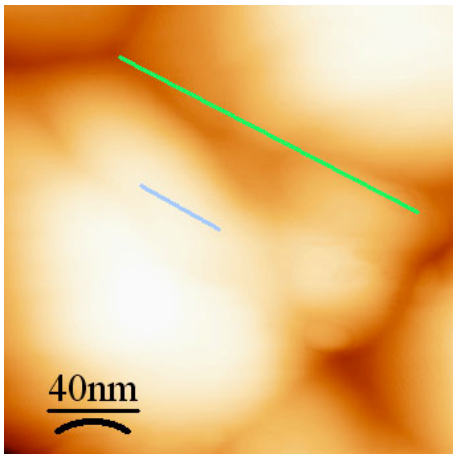
XPS measurements.

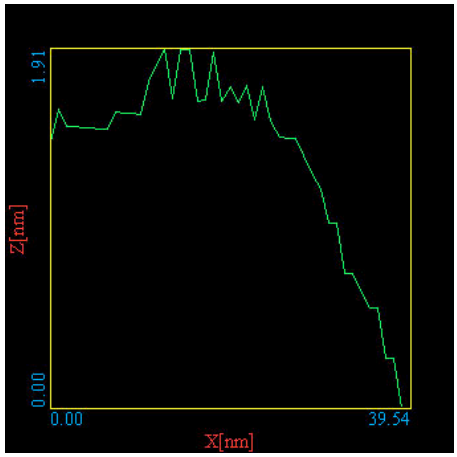
The Rh 3d and P2p regions of XP spectra of [Au]-SMAP-Rh (**2**) before (in red) and after (in green) the catalytic reaction are shown below.



AFM measurements.

AFM observation of the catalyst surface ([Au]-SMAP-Rh (**2**), dimension: 8 × 8 mm^2) at the end of the first catalytic reaction was conducted. A typical image and its cross-section are shown below. The flatness of the AFM image was same as that of the bare gold surface. We could not find any particle under a noise level of 0.3 nm.





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