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Heterogeneous Catalysis

Self-Assembled Monolayers of Compact Phosphanes with Alkanethiolate Pendant Groups: Remarkable Reusability and Substrate Selectivity in Rh Catalysis**

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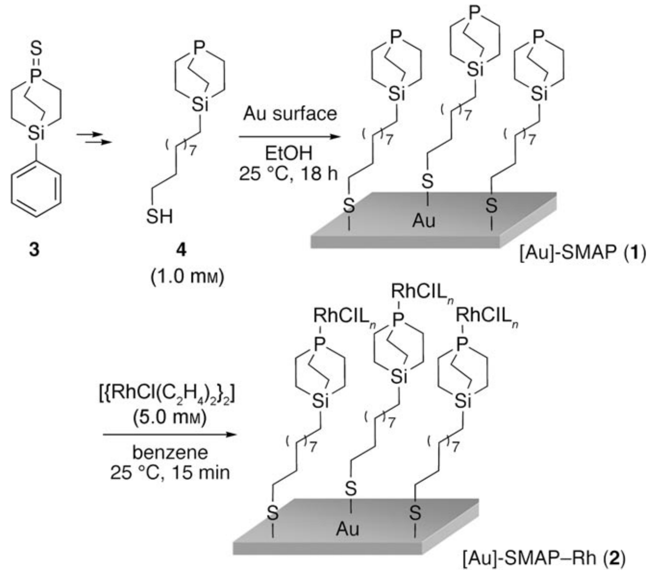
Building-up an assembly of designed molecules on a well-defined surface would be an interesting approach towards the development of highly efficient catalysts. Numerous studies have reported on the modification of a gold surface with alkanethiolate molecules to afford self-assembled monolayers (SAMs) with functions that depend on the design of the terminal moiety.[1,2] However, attempts to utilize the SAM-modified gold surface to prepare catalysts for organic synthesis have not been fully established.[3–6]

Herein, we report the modification of gold surfaces with a caged, compact trialkylphosphane (SMAP)[7] which bears an alkanethiolate pendant group. These surfaces ([Au]-SMAP, **1**) were utilized in a chip form for rhodium-catalyzed dehydrogenative alcohol silylation. Compared with the corresponding surface catalyst bearing the conventional Ph_2P-type coordinating groups[5,6] and with homogeneous Rh catalysts, the Rh catalyst [Au]-SMAP-Rh (**2**) prepared from **1** was extremely robust and highly efficient in terms of reusability.[8]

The preparation of the phosphane monolayer **1** and its complexation with rhodium is illustrated in Scheme 1.



Scheme 1. Preparation of [Au]-SMAP (**1**) and [Au]-SMAP-Rh (**2**).

Accordingly, Ph-SMAP sulfide (**3**) was transformed in five steps into the phosphane **4** with a decanethiol pendant group. Immersion of the gold surface (evaporated on glass) in a 1.0 mM solution of **4** in EtOH for 18 h, followed by washing with EtOH, afforded [Au]-SMAP (**1**; 130.1 eV in the P 2p region of the X-ray photoelectron spectrum). Complexation of **1** with rhodium to obtain [Au]-SMAP-Rh (**2**) was carried out by immersion of the phosphanated chip **1** into a 5.0 mM solution of $[\{RhCl(C_2H_4)_2\}_2]$ in benzene for 15 minutes followed by washing with EtOH.

Attachment of the Rh atoms was confirmed by surface analysis of **2** by XPS, which showed a signal at 307.6 eV in the Rh $3d_{5/2}$ region and a signal at 198.6 eV in the Cl 2p region. Analysis in the P 2p region showed a signal at 131.4 eV, which is significantly higher in energy than that of the P atom of **1** (at 130.1 eV), thus suggesting the coordination of the P atom to the Rh center. The P/S/Rh/Cl elemental ratio of **2** was calculated to be 1:1:0.8:0.7. Accordingly, **2** is considered to exist in the mono(phosphane)–rhodium form (P/Rh 1:1).[9]

The concentration of Rh atoms (per geometric surface area) in **2** was determined to be (0.63 ± 0.02) nmol cm^{-2} by inductively coupled plasma mass spectrometry (ICP-MS).

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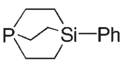
Although we have not been successful in direct quantification of the density of P atoms in **1** and **2**, the density of the Au(111) single crystal surface modified with the phosphane sulfide derivative of **4** was accurately determined by electrochemical reductive desorption of the attached thiolate molecules.[10] The analysis indicated that the surface density of the thiolates, which should be identical to the density of P atoms, is 0.69 nmol cm^{-2} (4.2 molecules nm^{-2}; the corresponding density for the linear alkanethiolate SAM on Au(111) is 4.6 molecules nm^{-2}), which strongly suggests the formation of a monolayer in the closest packing arrangement (see the Supporting Information).

Surface modification of a decanethiol derivative bearing a conventional Ph_2P-type coordinating group to afford [Au]-Ph_2P-Rh was also conducted for comparison. ICP-MS analysis showed a density of Rh atoms (per geometric surface area) of (0.71 ± 0.06) nmol cm^{-2}, which is almost identical to the value (0.63 nmol cm^{-2}) for **2**.

We first examined [Au]-SMAP-Rh (**2**) for its catalytic activity towards the hydrosilylation of ketones. Upon reaction with cyclohexanone and Me_2PhSiH (1.1 equiv) in hexane (ketone/Rh 75 000:1), **2** showed exceptionally high catalytic activity, with a turnover number (TON) of 9800 over 30 h at 25 °C.[11] In contrast, the corresponding homogeneous conditions, consisting of a mixture of $[\{RhCl(C_2H_4)_2\}_2]$ and Ph-SMAP (**5**) (Rh/P 1:1) in CH_2Cl_2 (ketone/Rh 100:1), afforded a TON of 51 under otherwise identical conditions. Moreover, **2** showed good reusability (TON of 25 000 over three successive runs). However, its applicability to other ketones was very limited. This result was in sharp contrast with that of the related silica-supported SMAP ligand [silica]-SMAP,[12] which was applicable to a broad range of sterically hindered ketones. The narrow substrate scope of the hydrosilylation catalyzed by **2** suggests a severely crowded catalytic environment.


Ph-SMAP (**5**)

Thus, we turned our attention to the dehydrogenative silylation of alcohols with a hydrosilane,[13,14] with the expectation that this reaction would be less sterically demanding (Table 1). Accordingly, a single chip of [Au]-SMAP-Rh (**2**; 5 × 5 mm^2) was placed at the bottom of a glass screw-capped test tube containing a solution of Me_2PhSiH (12 μmol) and EtOH (1.2 equiv) in hexane (0.12 mL). The substrate/catalyst ratio (S/C) under these conditions was 75 000:1, based on the surface density of Rh atoms. The reaction was conducted at 25 °C without stirring. After 16 h, 80 % of the Me_2PhSiH was converted into the silyl ether. This conversion corresponds to a TON of 60 000 (Table 1, entry 1).

The platelike shape of the catalyst means that recycling can be readily achieved by physically transferring the used catalyst chip into the reaction vessel for the next run. The TON over four successive runs reached a total of 235 000 (Table 1, entries 1–4). The activity of **2** was maintained during repeated uses, thus indicating that the active species was not released into the solution phase, but remained on the catalyst surface without significant loss of activity. ICP-MS analysis of the solution phase after a catalytic reaction indicated that only less than 0.5 % of the Rh atoms had leached out from the Au surface.

Table 1: Rhodium-catalyzed dehydrogenative silylation of EtOH.[a]

$$\mathrm{EtOH + Me_2PhSiH \xrightarrow[\text{hexane, 25 °C}]{\text{catalyst (silane/Rh 75 000:1)}} EtOSiMe_2Ph + H_2}$$

Entry	Catalyst	*t* [h]	Yield [%]	TON[b]	Total TON
1	[Au]-SMAP-Rh (**2**)[c]	16	80	60 000	
2	2nd run	16	81	61 000	121 000
3	3rd run	16	78	59 000	180 000
4	4th run	16	73	55 000	235 000
5[d]	$[\{RhCl(C_2H_4)_2\}_2]$	16	36	15 000	
6[d]	$[\{RhCl(C_2H_4)_2\}_2]$	30	37	16 000	
7[d]	**5**/$[\{RhCl(C_2H_4)_2\}_2]$ (P/Rh 1:1)	16	9	3900	
8[d]	**5**/$[\{RhCl(C_2H_4)_2\}_2]$ (P/Rh 1:1)	30	9	3900	
9[e]	[Au]-Ph_2P-Rh[c]	16	45	30 000	
10[e]	2nd run	16	7	4700	34 700

[a] The reaction was carried out with Me_2PhSiH (12 mmol), EtOH (1.2 equiv), and catalyst (Me_2PhSiH/Rh 75 000:1) in hexane (0.12 mL) at 25 °C. [b] Catalyst turnover number. [c] A gold surface with dimensions of 5 × 5 mm^2 was used. [d] The reaction was carried out in CH_2Cl_2. Me_2PhSiH/Rh 43 000:1. [e] Me_2PhSiH/Rh 67 000:1.

To obtain further information on the Rh species after the catalytic reaction we analyzed **2** by XPS. The binding energy of Rh 3d was 308.0 eV, which is much higher than that of metallic Rh (typically, at 306.0–307.5 eV). The binding energy of P 2p after the reaction was similar to that before the reaction and much higher than free, noncoordinating phosphane (at 130.1 eV). The P/Rh elemental ratio was calculated to be 1:0.8. On the basis of these XPS results, it is unlikely that the major component of the Rh species consists of nanoparticles.[9,15] It is probable that the P–Rh bond is maintained in [Au]-SMAP-Rh (**2**) during the catalysis.

The use of $[\{RhCl(C_2H_4)_2\}_2]$ in the solution phase (a homogeneous control) showed a TON of 15 000, which was only a quarter of that obtained with **2** (Table 1, entry 5). The addition of SMAP **5** to the Rh complex (P/Rh 1:1) caused a further decrease in the activity (Table 1, entry 7). In addition to the moderate effect of the immobilization on activity enhancement, a more pronounced effect was observed in terms of the catalyst lifetime and reusability. In fact, the homogeneous catalyst systems completely lost their activities within 16 h, and afforded no further conversion after prolonged reaction times (Table 1, entries 6 and 8).

The same reaction was also catalyzed by [Au]-Ph_2P-Rh, which resulted in a yield of 45 % and a TON of 30 000 for the first use. Interestingly, the yield for the second use of [Au]-Ph_2P-Rh dropped to 7 %, which indicates that the SMAP structure was critically important for the robustness and reusability of the catalytically active surfaces. Furthermore, [Au]-Ph_2P-Rh was found to be unstable under the reaction conditions. XPS analysis of the [Au]-Ph_2P-Rh after a catalytic reaction showed significant decomposition of the catalyst monolayer. Although the signal intensity of the S atom remained unchanged, only a trace amount of P atoms was detected.

The range of substrates compatible with the dehydrogenative silylation catalyzed by **2** (5 × 5 mm^2, S/C 75 000:1, 25 °C, 16 h) is shown in Table 2. The catalyst promoted the reaction of the longer linear aliphatic alcohol **6a** with a TON of 59000 (Table 2, entry 1). The silylation of γ-branched alcohol **6b** and benzyl alcohol (**6c**) also proceeded smoothly to afford the corresponding silyl ethers (Table 2, entries 2 and 3). In the reaction with β-branched alcohol **6d**, however, the reaction rate was slightly retarded, and gave a TON of 12000 (Table 2, entry 4).

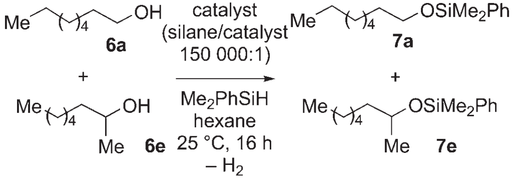
Table 2: Dehydrogenative silylation of primary alcohols with Me_2PhSiH catalyzed by [Au]-SMAP-Rh (**2**).[a]

Entry	Alcohol	Yield [%]	TON[b]
1	$CH_3(CH_2)_7OH$ (**6a**)	79	59000
2	$(CH_3)_2CHCH_2CH_2OH$ (**6b**)	76	57000
3	$PhCH_2OH$ (**6c**)	89	68000
4	$CH_3CH_2CH(CH_3)CH_2OH$ (**6d**)	16	12000

[a] The reaction was carried out with alcohol (12 μmol), Me_2PhSiH (1.2 equiv), and **2** (5×5 mm²; alcohol/Rh 75000:1) in hexane (0.12 mL) at 25 °C for 16 h. [b] Catalyst turnover number.

An additional characteristic feature of the silylation catalyzed by **2** is the extremely high selectivity for primary over secondary alcohols: no conversion was observed in the reaction of secondary alcohols such as 2-octanol, cyclohexanol, and 1-phenylethanol. The intrinsic selectivity was further examined under competitive reaction conditions (Table 3). [Au]-SMAP-Rh (**2**) catalyzed the conversion of primary alcohol **6a** into silyl ether **7a** without the formation of the silylated product **7e** from the secondary alcohol (Table 3, entry 1). This selectivity is higher than that observed for the highly selective homogeneous catalyst DTBM-xantphos-Cu(O-*t*Bu) (Table 3, entry 8).[14] Three successive runs were catalyzed without any decrease in the selectivity, and afforded a total TON of 335000 with greater than 99.5% selectivity (Table 3, entries 2–4).

Table 3: Catalytic dehydrogenative silylation of primary alcohols in the presence of secondary alcohols.[a]



Entry	Catalyst	Yield [%]	TON[b]	Total TON	**7a/7e**
1	[Au]-SMAP-Rh (**2**)[c]	60	90000		>99.5:0.5
2	2nd run	58	87000	177000	>99.5:0.5
3	3rd run	55	83000	260000	>99.5:0.5
4	4th run	50	75000	335000	>99.5:0.5
5[d]	$[\{RhCl(C_2H_4)_2\}_2]$	7	6000		71:29
6[d]	**5**/$[\{RhCl(C_2H_4)_2\}_2]$ (P/Rh 1:1)	3	2600		72:28
7	[Au]-Ph_2P-Rh[c,e]	43	58000		81:19
8[f]	DTBM-xantphos-Cu	92	46		98:2

[a] The reaction was carried out with Me_2PhSiH (24 μmol), **6a** (1.0 equiv), **6e** (1.0 equiv), and catalyst in hexane (0.24 mL) at 25 °C for 16 h. Me_2PhSiH/catalyst 150000:1. [b] Catalyst turnover number. [c] A gold surface with dimensions of 5×5 mm² was used. [d] The reaction was carried out in CH_2Cl_2. Me_2PhSiH/catalyst 86000:1. [e] Me_2PhSiH/catalyst 130000:1. [f] The reaction was carried out with a copper complex of a xanthene-based diphosphane. Reaction conditions: 1-decanol, 2-decanol, Me_2PhSiH, Me_2PhSiH/Cu 50:1, in toluene, 22 °C, 7 h; see reference [14]. DTBM-xantphos = 4,5-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-9,9-dimethylxanthene.

In contrast, the homogeneous counterparts using either $[\{RhCl(C_2H_4)_2\}_2]$ alone or a mixture of $[\{RhCl(C_2H_4)_2\}_2]$ and Ph-SMAP (**5**; Rh/P 1:1) catalyzed the competitive reaction with fairly low selectivities (Table 3, entries 5 and 6). The same reaction using [Au]-Ph_2P-Rh, also resulted in low selectivity (Table 3, entry 7). The highly selective nature of [Au]-SMAP-Rh (**2**) is attributable to the steric congestion of the catalytic environment, which exists in a densely packed rhodium–phosphane assembly.

Enlargement of the catalyst chip was expected to allow for a larger scale reaction. Thus, in the presence of a [Au]-SMAP-Rh (**2**) chip of dimensions 25×25 mm² (3.9 nmol Rh), the reaction of 39 mg (0.30 mmol) of 1-octanol, 39 mg (0.30 mmol) of 2-octanol, and 41 mg (0.30 mmol) of Me_2PhSiH gave the primary silyl ether **6a** with greater than 99.5% selectivity and in 81% yield after 16 h, which corresponds to a TON of 62000. For practical purposes, chemical engineering methodologies, such as microfluidic systems, are expected to enhance the efficiency of our catalytic system.[16] Another option for a scale-up technique would be immobilization of the rhodium–phosphane monolayer on gold particles.[3,6]

In summary, the phosphane-functionalized gold surface [Au]-SMAP (**1**), which consists of a caged, compact trialkylphosphane (SMAP) with an alkanethiolate pendant group, was developed. The rhodium-complexed surface [Au]-SMAP-Rh (**2**) showed high catalytic activity and reusability, as well as a unique selectivity in the dehydrogenative silylation of alkanols. The application of this system to other transition-metal-catalyzed reactions is under investigation.

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