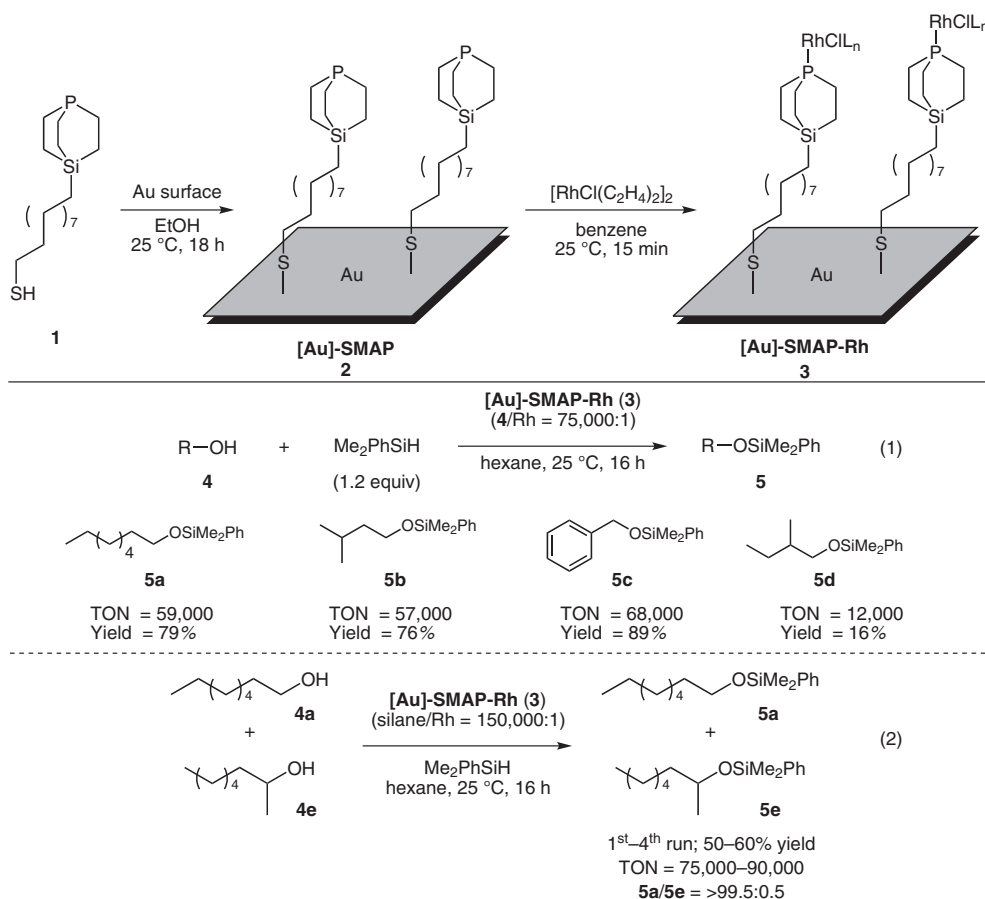


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Self-Assembled Monolayers of Compact Phosphanes with Alkanethiolate Pendant Groups: Remarkable Reusability and Substrate Selectivity in Rh Catalysis

*Angew. Chem. Int. Ed.* **2008**, *47*, 5627-5630.

## Dehydrogenative Silylation of Primary Alcohols Catalyzed by [Au]-SMAP-Rh



**Significance:** Immersion of the gold surface in a solution of phosphine **1** in EtOH afforded [Au]-SMAP **2**. [Au]-SMAP **2** was treated with a solution of  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  in benzene to give [Au]-SMAP-Rh **3**. ICP-MS measurement of **3** revealed that rhodium was incorporated at a concentration of 0.63 nmol/cm<sup>2</sup>. [Au]-SMAP-Rh **3** was found to promote the dehydrogenative silylation of primary alcohols **4** to afford the corresponding silyl ether **5a-d** with high TON up to 68,000 (eq. 1).

**Comment:** The silylation reaction of a mixture of primary alcohol **4a** and secondary alcohol **4e** with [Au]-SMAP-Rh gave silyl ether **5a**, exclusively, without the formation of **5e** (eq. 2). Catalyst **3** was reused three times in the dehydrogenative silylation of EtOH through which a total TON of 235,000 was achieved.

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Synfacts 2008, 10, 1111-1111 Published online: 22.09.2008  
DOI: 10.1055/s-2008-1078196; Reg-No.: Y10108SF