

Densely Packed Alkanethiolate Monolayer of Rh- and Ir-Phosphine Complexes on Gold Surface —Preparation and Catalysis—

Kenji Hara^{1*}, Ryuto Akiyama², Kohei Uosaki², Atsushi Fukuoka¹ and Masaya Sawamura²

¹Catalysis Research Center, Hokkaido University, Sapporo 001-0021 (Japan)

²Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810 (Japan)

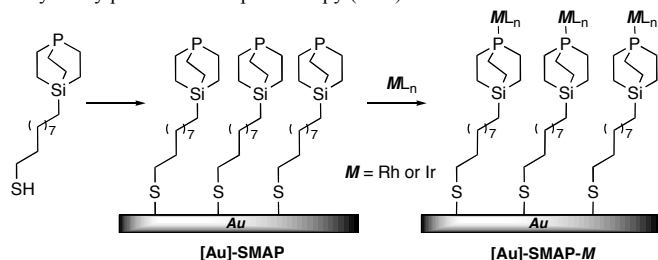
*hara@cat.hokudai.ac.jp

Introduction

The building-up of an assembly of designed molecules on a well-defined surface would be an interesting approach towards the development of highly efficient catalysts. However, attempts to utilize such defined monolayer catalysts for organic synthesis have not been fully established [1,2]. We recently reported the modification of gold surface with a caged, compact trialkylphosphane (SMAP) [3] bearing an alkanethiolate pendant in a form of self-assembled monolayer (SAM) and its application to a rhodium-catalyzed dehydrogenative alcohol silylation [4]. We herein present further results and discussion on the origin of the high selectivity and application to hydrosilylation of terminal alkenes and various alkynes. We also report an iridium-catalyzed hydroboration of terminal alkenes.

Materials and Methods

The phosphine-terminated monolayer surface ([Au]-SMAP) was prepared by immersion of gold surface (evaporated on glass) in a solution of the thiol in EtOH (Scheme.1). The surface density of the phosphine-terminated thiolate molecules was found to be 0.69 nmol/cm² (4.2 molecules/nm²) by electrochemical desorption method, strongly suggesting the formation of a monolayer with high *P*-density. Complexation with rhodium or iridium was conducted by immersion of [Au]-SMAP in a solution of [RhCl(C₂H₄)₂]₂ or [IrCl(cod)]₂ in CH₂Cl₂. The elemental analyses of [Au]-SMAP, [Au]-SMAP-Rh and [Au]-SMAP-Ir were conducted by X-ray photoelectron spectroscopy (XPS).

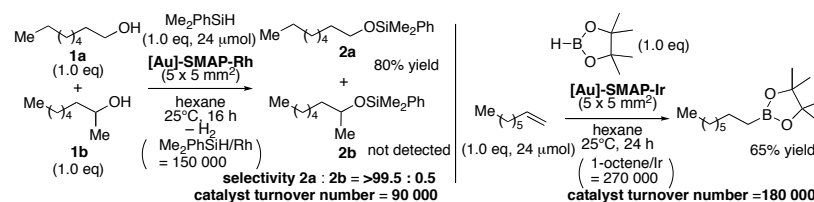


Scheme 1. Preparation of densely packed alkanethiolate monolayer of Rh- and Ir-phosphine complexes on gold surface.

Results and Discussion

Rh-complexed surface ([Au]-SMAP-Rh) (Rh: 0.63 nmol cm⁻²) showed high catalytic activity and reusability in dehydrogenative silylation of primary alcohol. Compared with the corresponding surface catalyst bearing the conventional Ph₂P-type coordinating group and with homogeneous Rh catalysts, [Au]-SMAP-Rh exhibited robustness and efficient reusability. In addition, [Au]-SMAP-Rh showed extremely high selectivity (>99.5%) toward primary alcohols in the presence of secondary alcohols (left part in Scheme 2). Our trial to elucidate the high selectivity by preparation of mixed monolayer of the Rh-phosphine active component and normal alkanethiolates will be reported. Its unique substrate selectivity in hydrosilylation of alkynes will be also presented in this paper.

Ir-complexed surface ([Au]-SMAP-Ir) (Ir: 0.34 nmol cm⁻²) showed high catalytic activity and reusability in hydroboration of terminal alkenes (right part in Scheme 2).



Scheme 2. Preparation of densely packed alkanethiolate monolayer of Rh- and Ir-phosphine monolayer on gold surface.

Significance

In this study, we created the catalytically active structures in forms of monolayer on defined flat surface. Our demonstration with mixed monolayer will increase the applicability and significance of still underdeveloped research field of the monolayer catalyst.

References

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