

# Chemistry of Bowl-Shaped Aromatic Compounds and Metal Nanocluster Catalysts

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Bowl-shaped  $\pi$ -conjugated compounds including partial structures of the fullerenes, which are called “buckybowls,” are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. Heteroatom-containing buckybowls (heterobuckybowls) have also been expected to exhibit unique physical characters. For example, in solution they show the characteristic dynamic behavior such as bowl-to-bowl inversion. On the other hand, they sometimes favor stacking structure in a concave-convex fashion in the solid state, giving excellent electron conductivity. Furthermore, some buckybowls are conceivable to possess the bowl-chirality if the racemization process, as equal as bowl-to-bowl inversion, is slow enough to be isolated. However, very few buckybowls/heterobuckybowls has been achieved for preparation mainly due to their strained structure, and no report on the preparation of chiralbowls has appeared. In the present project, we develop the rational route to the various kinds of buckybowls/heterobuckybowls with perfect chirality control using the organic synthesis approach.

We also investigate to develop novel catalytic properties of metal nanoclusters. We focus on the following projects: Preparation of size-selective gold nanoclusters supported by hydrophilic polymers and its application to aerobic oxidation catalysts: Synthetic application using metal nanocluster catalyst: Development of designer metal nanocluster catalyst using the highly-functionalized protective polymers: Catalytic activity of metal nanoclusters under the laser-irradiated conditions.

## 1. Synthesis of an Enantiopure *syn*-Benzocyclotrimer through Regio-Selective Cyclotrimerization of Halonorbornenes under Palladium Nanocluster Conditions<sup>1)</sup>

An enantiopure *syn*-benzocyclotrimer (**1**) was selectively synthesized from an enantiopure halonorbornene (**2**) through

regio-selective cyclotrimerization catalyzed by palladium nanoclusters. The yield of **1** was dependent on the stability of the palladium clusters, which was ascertained from the appearance and TEM images of the reaction mixtures. The thus-prepared enantiopure benzocyclotrimer will serve as a key intermediate for the synthesis of  $C_{3v}$  symmetric chiral buckybowls.

Table 1.

Entry	Bu <sub>4</sub> NX	Base	Solvent	Yield of <b>1</b>
1	Bu <sub>4</sub> NBr 100 mol %	NEt <sub>3</sub> 250 mol %	DMF	trace
2	Bu <sub>4</sub> NOAc 100 mol %	Na <sub>2</sub> CO <sub>3</sub> 1000 mol %	1,4-dioxane	34%
3	Bu <sub>4</sub> NOAc 300 mol %	Na <sub>2</sub> CO <sub>3</sub> 1000 mol %	1,4-dioxane	42%
4	Bu <sub>4</sub> NOAc 500 mol %	Na <sub>2</sub> CO <sub>3</sub> 1000 mol %	1,4-dioxane	47%
5	Bu <sub>4</sub> NOAc 1000 mol %	Na <sub>2</sub> CO <sub>3</sub> 1000 mol %	1,4-dioxane	53%

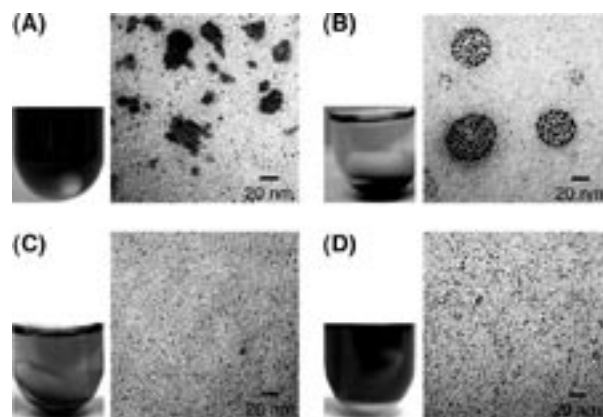
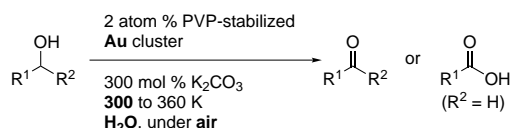


Figure 1.

Photographs and typical TEM images of the reaction mixtures under the conditions listed in entries 1, 2, 4, and 5 in Table 1 are shown in Figure 1. Judging from the appearance of the reaction mixtures, the Pd nanoclusters were well dispersed in the order of (B) < (C) < (D) which was consistent with the amount of Bu<sub>4</sub>NOAc. The amount of precipitation of Pd black was observed in the opposite order, (B) > (C) > (D). The TEM images supported these observations. In Table 1, we show the result using the conditions which are considered typical reaction conditions for generation of Pd nanoclusters (Entry 1; Figure 1A). Indeed, the appearance of (A) was similar to that of (D), indicating the formation of nanoclusters. However, a considerable degree of aggregation of clusters was observed in the TEM images as well as in those of (B). Although both clusters in (C) and (D) were well dispersed judging from the TEM images, the concentration of clusters was much higher in (D), consistent with their appearance. These observations strongly suggest that the generation of Pd nanoclusters in appropriate conditions might be very important and that an excess amount of Bu<sub>4</sub>NOAc could realize well-dispersed nanoclusters.

## 2. Synthetic Application of PVP-Stabilized Au Nanocluster Catalyst to Aerobic Oxidation of Alcohols in Aqueous Solution under Ambient Conditions<sup>2)</sup>

Gold nanoclusters ( $\phi = 1.3$  nm) stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP) were found to show a high catalytic activity toward the aerobic oxidation of alcohols. Various kinds of primary and secondary alcohols were converted to the corresponding carboxylic acids and ketones, respectively, in basic aqueous media at 300–360 K under air.



## 3. Lewis Acid Character of Zero-Valent Gold Nanoclusters under Aerobic Conditions: Intramolecular Hydroalkoxylation of Alkenes<sup>3)</sup>

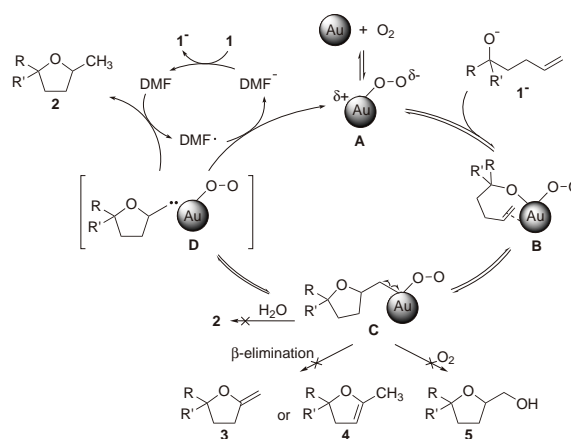
Gold nanoclusters stabilized by poly(*N*-vinyl-2-pyrrolidone) (Au:PVP NCs,  $\phi = 1.3$  nm) behave as Lewis acid catalyst in aqueous media under aerobic conditions, to promote the intramolecular hydroalkoxylation of unactivated alkenes. Molecular oxygen generates a reaction center having

the Lewis acidic character on the surface of Au NCs in which constituent gold atoms are formally in zero-valence state.

**Table 2.** The role of molecular oxygen in the cyclization of **1a**.

$\text{Ph-C(Ph)(OH)-CH}_2\text{CH=CH}_2 \xrightarrow[\text{H}_2\text{O/DMF, 50 } ^\circ\text{C, 16 h}]{\begin{array}{c} 10 \text{ atom \% Au:PVP} \\ 200 \text{ mol \% DBU} \end{array}} \text{Ph-C(Ph)(O-CH}_2\text{CH}_2\text{CH}_3\text{)-CH}_3$			
entry	catalyst	conditions	yield, %
1	Au:PVP(1.3)	under air	87
2	Au:PVP(1.3)	under degassed conditions	0
3	Au:PVP(9.5)	under air	0

A possible mechanism is shown in Scheme 1. The reaction is initiated by formation of key intermediate **A**, which possesses an electron-deficient site generated by adsorption of O<sub>2</sub> onto the surface of the Au NCs. **A** acts as a Lewis acid, activating both the alkoxide and alkene by adsorption onto the surface (**B**), and giving **C** by the insertion of an alkene into the O–Au bond. From **C**, neither  $\beta$ -elimination, O<sub>2</sub> insertion, nor protonation proceeds; only homolytic dissociation takes place, generating the radical intermediate **D**, which afforded **2** via hydrogen abstraction from DMF accompanied by the regeneration of free Au NCs. Judging from the decrease in the reaction rate in DMF-*d*<sub>7</sub>, all the steps between **A** and **D** may be in equilibrium.



**Scheme 1.** A possible mechanism for Au(0):PVP-catalyzed hydroalkoxylation.

## References

- 1) S. Higashibayashi and H. Sakurai, *Chem. Lett.* **36**, 18–19 (2007).
- 2) H. Tsunoyama, T. Tsukuda and H. Sakurai, *Chem. Lett.* **36**, 212–213 (2007).
- 3) I. Kamiya, H. Tsunoyama, T. Tsukuda and H. Sakurai, *Chem. Lett.* **36**, 646–647 (2007).

## Awards

KAMIYA, Ikuyo; Best Poster Presentation Award, The 3<sup>rd</sup> Organic Chemistry Young Researchers' Workshop, Nagoya University.  
 HIGASHIBAYASHI, Shuhei; Best Presentation Award, The 87<sup>th</sup> Spring Meeting, Chemical Society of Japan.  
 HIGASHIBAYASHI, Shuhei; Best Poster Presentation Award, Symposium on Molecular Chirality 2007.  
 HIGASHIBAYASHI, Shuhei; Best Poster Presentation Award, The 17<sup>th</sup> International Symposium on Olefin Metathesis.