

Chemistry of Bowl-Shaped Aromatic Compounds and Metal Nanocluster Catalysts

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems



SAKURAI, Hidehiro
Associate Professor

SUGIISHI, Tsuyuka
MORITA, Yuki
KUMAR, Selva
PANDIT, Palash
MAITY, Prasenjit
DHITAL, Raghu Nath
KAMONSATIKUL, Choavarit
JINASAN, Atchaleeya
TSAL, I-Chang



HIGASHIBAYASHI, Shuhei
Assistant Professor

IMS Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow
Post-Doctoral Fellow
Visiting Scientist
Visiting Scientist
Visiting Scientist

MANNA, Sudipta Kumar
PONGPIPATT, Paweena
SINGH, Priyanka
AGRAWAL, Meghdeep
THONGPAEN, Jompol
ONOGI, Satoru
KAEWMATI, Patcharin
KARANJIT, Sangita
SHRESTHA, Binod Babu
HAESUWANNAKIJ, Setsiri
OKABE, Yuki
SASAKI, Tokiyo
HAZAMA, Kozue

Visiting Scientist
Visiting Scientist
Visiting Scientist
Visiting Scientist
Graduate Student
Graduate Student
Graduate Student
Graduate Student
Graduate Student
Secretary
Secretary

Bowl-shaped π -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. 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. Very few buckybowls has been achieved for preparation mainly due to their strained structure, and no report on the preparation of chiral bowls has appeared. In this project, we develop the rational route to the various buckybowls 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.

1. Stereoelectronic Effect of Curved Aromatic Structure Favouring the Unexpected *Endo* Conformation of Benzylic Substituted Sumanene¹⁾

Since the discovery of fullerene and carbon nanotubes, curved aromatic compounds including bowl-shaped buckybowls have elicited much attention in science and industry. One prin-

cipal question in these curved aromatic compounds is the difference between the concave face and the convex face. The curvature affects the nature between the two faces, resulting in differences of the through-space and through-bond effects. The latter would appear as a stereoelectronic effect between the curved aromatic structure and a connected functional group. In general, the stereoelectronic effect is reflected in the conformational stability and chemical reactivity of a molecule. Therefore, it is important to understand such conformations or chemical reactivities as a consequence of stereoelectronic effects. The interpretation of the stereoelectronic effect of curved aromatic compounds would lead to understanding the difference in nature between the two faces. However, no example of stereoelectronic effects of curved aromatic compounds have been found and studied to date. We have found a first example of the stereoelectronic effect of a curved aromatic structure, which dominates the *endo/exo*-R conformational stability of benzylic substituted sumanenes (**1**) (Figure 1).

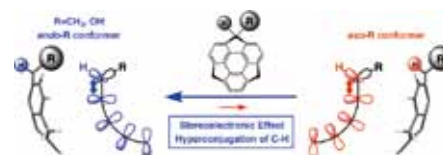


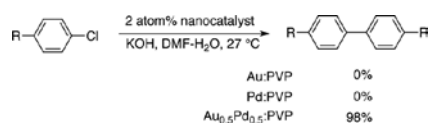
Figure 1. Schematic diagram of the stereoelectronic effect and through-space effects between the bowl and the C-H/C-R of benzylic substituted sumanene.

2. Low-Temperature Carbon–Chlorine Bond Activation by Bimetallic Gold/Palladium Alloy Nanoclusters: An Application to Ullmann Coupling²⁾

In the past decade, nanoclusters (NCs) of bimetallic alloys have attracted considerable research interest because of their unique catalytic properties, which differ substantially from those of single-phase monometallic counterparts. Among the various bimetallic NCs that have been fabricated to date, gold/palladium alloy NCs are particularly fascinating because of their high catalytic activities.

Because of the relatively high dissociation energy of C–Cl bond in comparison with C–Br or C–I, it is difficult to activate chloroarenes by undergoing oxidative addition on Pd without ligation by nucleophilic ligands. Here we demonstrate a new method for activation of C–Cl bonds at low temperature as a result of bimetallic Au/Pd synergy and we report the successful examples of the Ullmann coupling of chloroarenes under ambient conditions. Ullmann coupling, which was first reported in 1901, is a conventional method for the synthesis of symmetrical biaryls. Initially, aryl iodides were used in coupling reactions that were promoted by excess amount of copper at high temperatures. Recent developments in the Ullmann coupling reaction has permitted the use of aryl bromides or chlorides as reactants in the presence of a co-reductant such as Zn powder, formic acid, and dihydrogen under mild conditions. Such reactions can be catalyzed by many types of homogenous or heterogeneous transition-metal catalysts, such as Ni, Pd or Au. However, to the best of our knowledge, there are no reports of any successful examples of Ullmann coupling reactions of chloroarenes under ambient conditions. It is because of relative difficulty in the activation a C–Cl bond, which needs to occur twice within a single catalytic cycle, and because all C–M intermediates need to resist hydrogenation by external co-reductant.

The activity increased markedly for a bimetallic catalyst containing 50% of Pd, giving the coupling product in 98% yield with 100% conversion. The coupling reaction occurred smoothly even when the reaction temperature was decreased to 35 °C or to 27 °C (room temperature) quantitatively for 6 h and 24 h, respectively. To the best of our knowledge, this is the first example of Ullmann coupling of chloroarenes under ambient conditions.



An essential step, which determines the characteristics difference in the catalytic activities of Au, Au/Pd, and Pd NCs is the oxidative addition of chloroarene followed by the spill over of Cl, and we therefore intensively studied only this step at present. Our previous report demonstrated that Au_{20}^- , a negatively charged homogeneous Au NCs, is a suitable model for simulating reaction on the surface of Au:PVP. We therefore examined the model systems Au_{20}^- , $\text{Au}_{16}\text{Pd}_4^-$, $\text{Au}_{10}\text{Pd}_{10}^-$, and Pd_{20} to compare the reaction pathway for oxidative additions

on Au, Pd, and Au/Pd alloy clusters. Fundamental consideration of these models and the computational details are given in supporting information. The calculations were performed by the Gaussian09 suite of programs. The energy diagram of the oxidative addition of chlorobenzene (**1b**) on Au_{20}^- and $\text{Au}_{10}\text{Pd}_{10}^-$ is shown in Figure 2 where the energies are shown by taking those of adsorption complexes being the same for these clusters.

In the case of the Au_{20}^- system, **1b** is adsorbed on the facet site and a local minimum is obtained for the dissociative chemisorption (Int_B1). However, the calculated activation energy barrier for this (C–Cl) dissociative chemisorption is very high at 137.9 kJ/mol. In $\text{Au}_{10}\text{Pd}_{10}^-$ bimetallic cluster which simulates $\text{Au}_{0.5}\text{Pd}_{0.5}$ alloy, we found two types of intermediates for chemisorption. The adsorption was calculated to proceed with low activation energy barrier of 63.1 kJ/mol to give adsorption intermediate (Int_A2) in which both the phenyl group and the Cl atom are attached to the same Pd site. The other intermediate for dissociative chemisorption (Int_B2) is also stable as the adsorbed complex (Ads) or Int_A2. The calculated activation energy barrier from Int_A2 is 56.0 kJ/mol. The reaction pathway, which directly provides Int_B2 from the adsorption complex is also possible and has a moderate energy barrier of 52.6 kJ/mol. Note that an intermediate corresponding to Int_A2 was not obtained in the case of Au_{20}^- system. These results clearly show that the inclusion of Pd has an effect of stabilizing the dissociative adsorption and reducing activation energy, which is not possible in pure Au cluster.

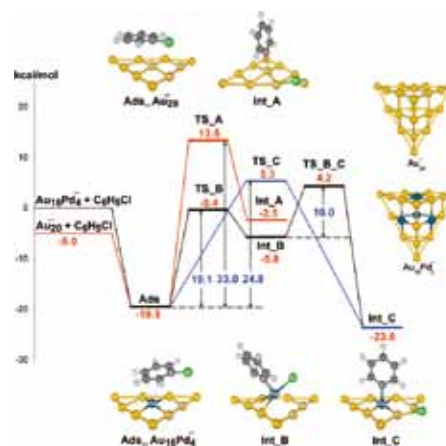


Figure 2. Energy profile diagram of oxidative addition of chlorobenzene on Au_{20}^- and $\text{Au}_{10}\text{Pd}_{10}^-$ NCs.

References

- 1) S. Higashibayashi, S. Onogi, H. K. Srivastava, G. N. Sastry, Y.-T. Wu and H. Sakurai, *Angew. Chem., Int. Ed.* **52**, 7314–7316 (2013).
- 2) R. N. Dhital, C. Kamonsatikul, E. Somsook, K. Bobuatong, M. Ehara, S. Karanjit and H. Sakurai, *J. Am. Chem. Soc.* **134**, 20250–20253 (2012).

Awards

HIGASHIBAYASHI, Shuhei; Incentive Award in Synthetic Organic Chemistry (2012).
 HIGASHIBAYASHI, Shuhei; Sumitomo Chemical Award in Synthetic Organic Chemistry (2012).
 HAESUWANNAKIJ, Setsiri; Best Poster Presentation, PERCH-CIC Congress VIII (2013).