

# 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.

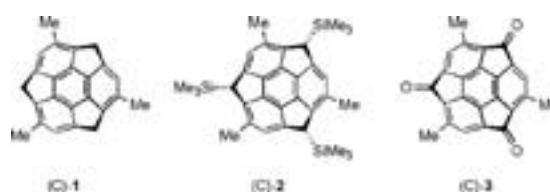
We also investigate to develop novel catalytic properties of metal nanoclusters. We focus on the following projects: Preparation of size-selective gold nanoclusters supported by hydrophilic polymers and its application to aerobic oxidation catalysts: Synthetic application using metal nanocluster catalyst: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

## 1. Optical Resolution of Chiral Buckybowls by Chiral HPLC<sup>1)</sup>

Buckybowls have been a focus of recent attention because of their interesting physical properties derived from the bowl-shaped  $\pi$ -conjugated aromatic structure. One of the interesting

features of the structure is the chirality of these spherical aromatic compounds unlike planer ones, named *Bowl chirality*. The bowl chirality is expected to provide fascinating characters for their applicability not only for asymmetric molecular recognition and chiral ligands for transition metals, but also for precursors of chiral fullerenes and carbon nanotubes in chemical synthesis. Enantiopure or -enriched chiral buckybowls could be obtained by either asymmetric synthesis or optical resolution of racemate. As an example of the former, we have recently achieved the first enantioselective synthesis of chiral trimethylsumanene (**1**) (Figure 1) by converting chirality based on  $sp^3$  carbon to bowl chirality. In contrast, the latter approach has not been reported, although those of related chiral fullerenes and carbon nanotubes have been reported. We focus on optical resolution of chiral buckybowls, trimethyltris(trimethylsilyl)sumanene (**2**) and trimethylsumanenetrione (**3**) (Figure 1), by chiral HPLC, and determination of bowl inversion energy barrier of **3** by CD spectra.

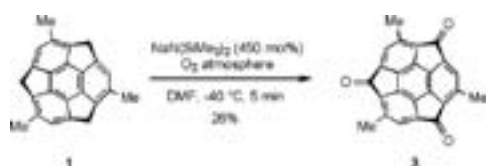
Optical resolution of racemic trimethyltris(trimethylsilyl)sumanene (**2**) was initially investigated for the following reasons. The ee of enantioselectively prepared substituted sumanenes would be easily determined by the chiral HPLC analysis of the tris(trimethylsilyl)-derivatives as well. Chiral column DAICEL CHIRALPAK® IA, which is composed of



**Figure 1.** Structures of (C)-8,13,18-trimethylsumanene (**1**), (C)-(8*R*,13*R*,18*R*)-10,15,20-trimethyl-8,13,18-tris(trimethylsilyl)sumanene (**2**), and (C)-10,15,20-trimethylsumanene-8,13,18-trione (**3**).

amylose tris(3,5-dimethylphenylcarbamate), realized the desired optical resolution.

Next, we investigated the optical resolution of racemic **3**. The racemization energy barrier of **3** was estimated to be ca. 23.5 kcal/mol, which corresponds to ca. 44 h half-life at 10 °C. This could be sufficiently high to obtain enantioenriched **3** in HPLC time-scale. Racemic **3** was prepared by aerobic oxidation of racemic **1** (Scheme 1). Reaction of **1** with sodium hexamethyldisilazide and molecular oxygen in DMF at low temperature for 5 min gave the desired product in 26% yield. As expected, optical resolution of **3** was attained at 9 °C and afforded each enantioenriched sample of **3**. Absolute configuration of each enantiomer was assigned as (A)-**3** ( $t^R$  = 17 min) and (C)-**3** ( $t^R$  = 18 min) by the fact that enantioenriched sample prepared from (C)-**1** possessed  $t^R$  = 18 min.



Scheme 1. Synthesis of trimethylsumanenetrone (**3**).

With enantioenriched **3** in hand by chiral HPLC separation, the bowl inversion energy barrier of **3** can be determined by CD spectra measurement. Bowl inversion is a characteristic feature of buckybowls and has been extensively studied by experimental and theoretical methods. A limitation of commonly used NMR methods for experimental determination of the energies is that those of buckybowls without diastereotopic protons cannot be determined by the technique. In contrast, the energies of enantiopure or -enriched chiral buckybowls even without diastereotopic protons such as **3** can be determined by CD spectra measurement because they are racemized through bowl inversion. By time-dependent decay of the intensity of CD spectra of **3** at 255 nm at 30 °C (Figure 2), the energy barrier was determined to be 23.4 and 23.3 kcal/mol in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub>, respectively. These experimental values showed good agreement with predicted values.

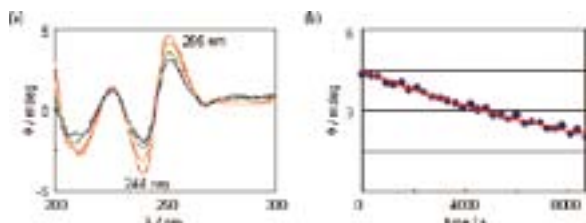


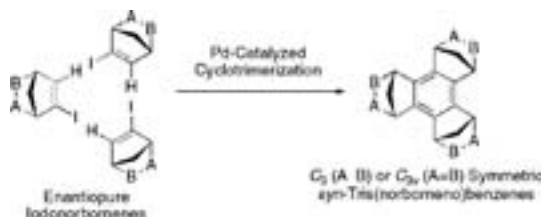
Figure 2. (a) Time-dependent decay of intensity of CD spectra of (A)-**3** in CH<sub>3</sub>CN at 30 °C (red: 0 h, orange: 1 h, green: 2 h, blue: 3 h). (b) Decay of ellipse  $\theta$  and their fitting curve at 255 nm in CH<sub>3</sub>CN at 30 °C.

#### Award

HIGASHIBAYASHI, Shuhei; The 24<sup>th</sup> Young Scholar Lectures in the 90<sup>th</sup> Annual Meeting of CSJ.

## 2. Stereoselective Cyclotrimerization of Enantiopure Iodonorbornenes Catalyzed by Pd Nanoclusters for C<sub>3</sub> Symmetric *syn*-Tris(norborneno)benzenes<sup>2)</sup>

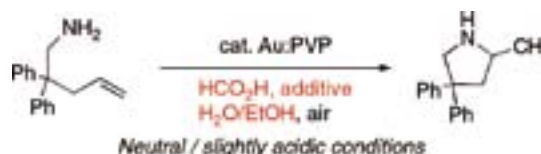
C<sub>3</sub> or C<sub>3v</sub> symmetric enantiopure *syn*-tris(norborneno)benzenes with various functional groups were synthesized through Pd-catalyzed cyclotrimerization of enantiopure iodonorbornenes. The generality of Pd-catalyzed cyclotrimerization for *syn*-tris(norborneno)benzenes were well-demonstrated.



Scheme 2. Pd-catalyzed cyclotrimerization of iodonorbornenes.

## 3. Gold Nanocluster as a Catalyst for Intramolecular Addition of Primary Amines to Unactivated Alkenes under Aerobic Conditions<sup>3)</sup>

Gold nanoclusters stabilized by hydrophilic polymer, poly(*N*-vinyl-2-pyrrolidone) (Au:PVP), catalyzed the intramolecular addition of primary amines to unactivated alkenes in good yield in the presence of formic acid derivatives under aerobic conditions. Since Au:PVP also promotes the cycloaddition of toluenesulfonamides under basic conditions, Au:PVP catalyst is expected to be a versatile and easy-to-handle catalyst for hydroamination reactions.



Scheme 3. Au:PVP-catalyzed Hydroamination.

#### References

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