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Highlight Review

Synthesis of Sumanene and Related Buckybowls

Shuhei Higashibayashi* and Hidehiro Sakurai

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Abstract

Sumanene ($C_{21}H_{12}$) is a C_{3v} symmetric buckybowl, which corresponds to a partial fullerene structure. Recent advances in the syntheses of sumanene and its derivatives, including heterasumanenes, are summarized in this review. Their chemical reactivities and derivatizations are also presented.

◆ Introduction

Buckybowls are bowl-shaped aromatic hydrocarbons corresponding to a partial fullerene structure or a cap structure of carbon nanotubes. Since the discovery of C_{60} fullerene in 1985, buckybowls have attracted much attention due to their physical properties, not only as model compounds for fullerenes, but also as unique bowl-shaped aromatic compounds. In order to elucidate their attractive physical properties, gas-phase syntheses (flash vacuum pyrolysis, FVP) and solution-phase syntheses of various buckybowls, especially C_{5v} symmetric corannulene ($C_{20}H_{10}$) and related buckybowls, have been developed since the 1990s.[1] Sumanene (**1**) is a C_{3v} symmetric buckybowl (Figure 1), which Mehta et al. named after "suman," the Hindi and Sanskrit word for a type of flower.[2] They first reported their attempts to synthesize **1** by a FVP technique in 1993. However, it failed to construct the strained bowl structure. The synthesis of **1** in solution-phase was achieved by Sakurai et al. in 2003.[3a] This synthesis enabled the interesting physical properties of sumanene to be studied, such as its bowl-shaped structure, bowl inversion, columnar crystal packing, electron conductivity, metal complexes, and bowl chirality. Recent advances in buckybowl chemistry have also led to the application of buckybowls to novel materials. This review summarizes the recent developments in the synthesis of sumanene (**1**) and its derivatives, including heterasumanenes, focusing especially on solution-phase syntheses. The synthetic strategies for the construction of sumanene and heterasumanene skeletons are presented in the first chapter and the functionalization and derivatization of sumanenes are discussed in the second chapter.

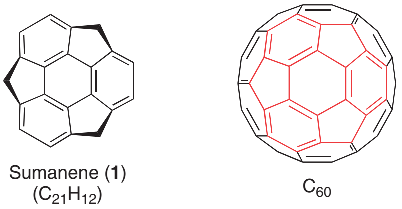
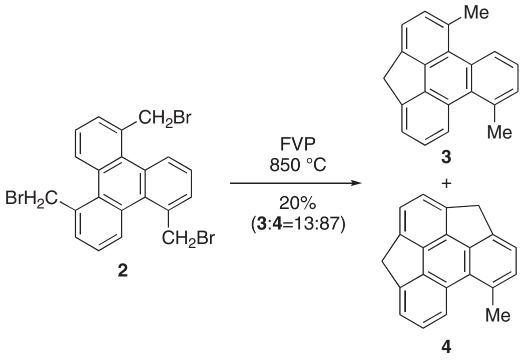


Figure 1.

◆ Synthesis of Sumanene Skeleton

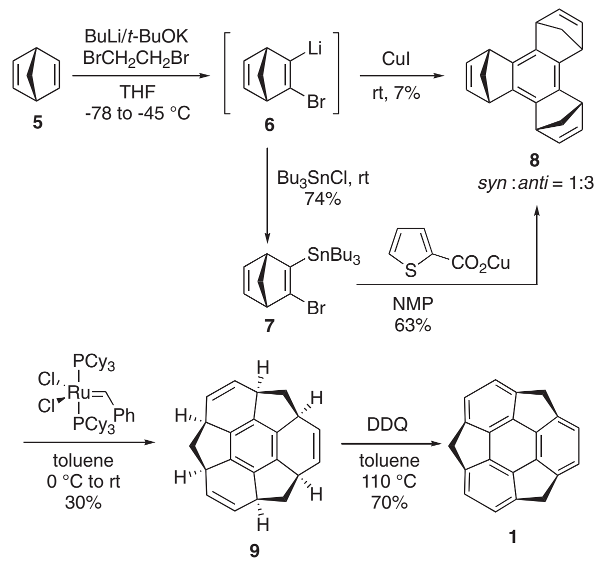
In 1993, Mehta et al. reported that tris(bromomethyl)triphenylene **2** does not undergo cyclization to give sumanene (**1**) under FVP conditions, giving only a mixture of **3** and **4** (Scheme 1).[2] Although FVP has been successful in preparing many kinds of buckybowls, only fully aromatic buckybowls without any substituents have been synthesized to date.[1b,1e] Fully aromatic buckybowls containing the sumanene structure, such as C_3 symmetric hemifullerene, have been prepared by FVP.[4] Since **1** possesses three benzylic sp^3 carbons, the structure would not tolerate the harsh FVP conditions. However, under milder conditions, it would also be very difficult to bend and cyclize a planar aromatic precursor such as a triphenylene derivative directly into the strained bowl-shaped aromatic structure of **1**.

In 2003, Sakurai et al. solved these problems by adopting a synthetic strategy to construct a nonconjugated three-dimensional bowl structure containing tetrahedral sp^3 carbons leading to the conjugated bowl structure of **1**.[3a] The key intermediates are non-conjugated bowl-shaped hexahydrosumanene **9** and the precursor, *syn*-tris(norbornadieno)benzene **8** (Scheme 2). *syn*-Tris(norbornadieno)benzene **8** is easily obtained as a *syn* and *anti* mixture (1:3) in 7% yield by Cu-mediated cyclotrimerization of **6**, which is generated in situ from **5**. Alternatively, transmetallation to **7** in 74% yield, followed by Cu-mediated cyclotrimerization, improves the cyclotrimerization yield to 63%. Since **8** possesses strained norbornadiene structures, *syn*-**8** is transformed to the thermodynamically more stable **9** in 30% yield by tandem ring-opening and -closing metathesis reaction



Scheme 1.

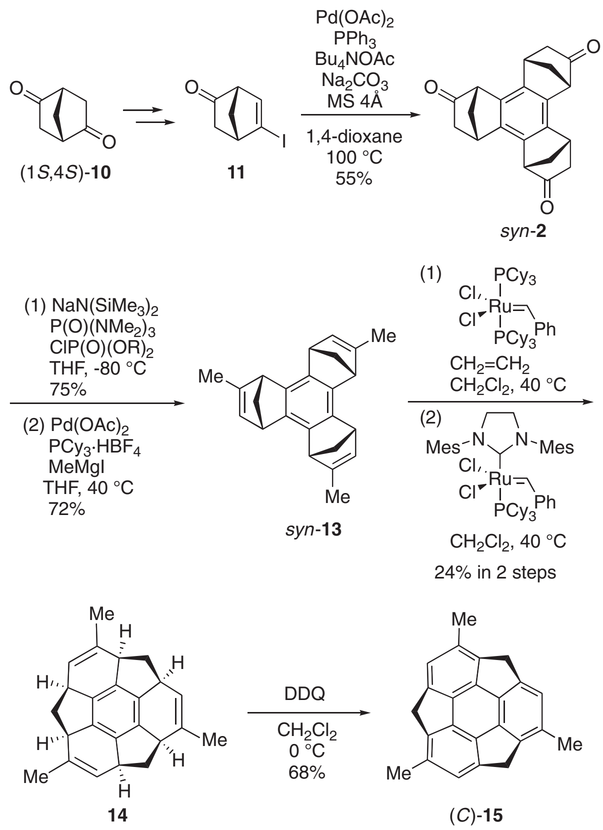
Dr. Shuhei Higashibayashi* and Prof. Hidehiro Sakurai
Institute for Molecular Science, 5-1 Higashiyama, Myodaiji, Okazaki, Aichi 444-8787
E-mail: higashi@ims.ac.jp



Scheme 2.

with $[Cl_2(PCy_3)_2Ru{=}CHPh]$ catalyst under ethylene atmosphere. Finally, **9** is easily aromatized by DDQ oxidation, giving sumanene (**1**) in 70% yield. In contrast to FVP syntheses of buckybowls, every reaction of this synthetic sequence is performed under very mild conditions. X-ray crystallographic analysis of **1** revealed that it possesses a bowl depth of 1.11 Å and a columnar stacking structure in a convex-to-concave fashion.[3b] Amaya et al. reported that a single crystal of **1** shows anisotropic electron mobility ($0.75\,cm^2\,V^{-1}\,s^{-1}$, time-resolved microwave conductivity) along the stacking column axis.[3c]

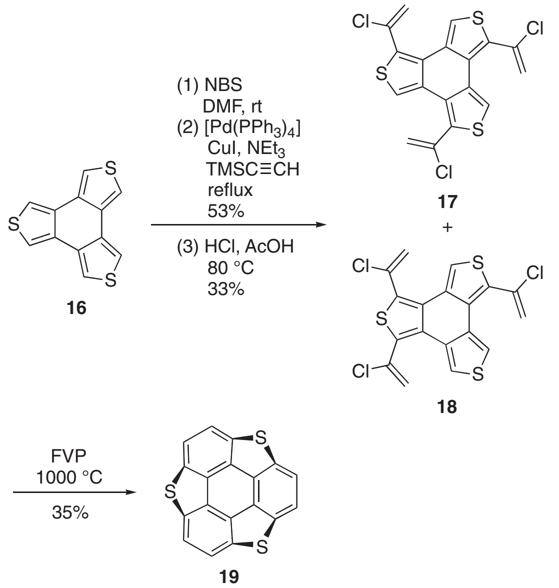
Higashibayashi et al. further advanced this synthetic strategy in 2008 to generate a selective synthesis of C_3 symmetric trisubstituted sumanene, as well as the first enantioselective synthesis of a chiral buckybowl.[5] As mentioned in the next chapter, in the preparation of C_3 symmetric derivatives, the contamination by regioisomers is difficult to avoid in the selective introduction of substituents at aromatic positions of sumanene (**1**). The synthesis of these derivatives is based on the transformation of a C_3 symmetric *syn*-tris(norborneno)benzene with functional groups that enable introduction of substituents (Scheme 3). C_3 symmetric substituted sumanenes possess inherent chirality derived from the three-dimensional bowl structure. The bowl chirality can be controlled by the transmission from sp^3 stereogenic centers of the precursor to bowl chirality. The synthesis starts from enantiopure norbornandione **10**, which is converted to iodonorbornanone **11**. Newly developed Pd-catalyzed *syn*-selective cyclotrimerization of **11** yields C_3 symmetric *syn*-tris(norborneno)benzene **12** in 55% yield.[6] In contrast to the non-selective Cu-mediated cyclotrimerization of norbornene derivatives, the Pd-catalyzed cyclotrimerization reaction improves this step to afford *syn*-selectivity. After introduction of methyl substituents, ring-opening and -closing metathesis reaction of **13** gives hexahydrotrimethylsumanene **14**. The chiral transmission from the sp^3 stereogenic centers of **14** to the bowl chirality of **15** occurs in the final oxidative aromatization step. Since (*C*)-**15** has a low bowl inversion energy ($\Delta G =$ ca. $21\,kcal\,mol^{-1}$) leading to its fast racemization (half life = 9 min at 20 °C), the aromatization of **14** is performed at 0 °C in 1 min to afford (*C*)-**15**. The bowl chirality of (*C*)-**15** was confirmed by CD spectral measurements and the enantiomeric excess was determined to be 89% ee after derivatization (Scheme 8). Time-dependent CD spectral measurements of (*C*)-**15** enabled the determination of the bowl inversion energy of $21.6\,kcal\,mol^{-1}$, which is higher than that of sumanene (**1**) (ca. $20\,kcal\,mol^{-1}$). The synthetic strategy for **15** is amenable to the synthesis of other C_3 symmetric substituted sumanenes by introduction of other substituents or further derivatization.



Scheme 3.

Heterasumanenes are sumanene analogs containing heteroatoms in the skeleton. Replacement of carbons by heteroatoms induces significant structural and electronic changes.[7] Imamura et al. reported the FVP synthesis of trithiasumanene **19**, the first synthetic heterabuckybowl, in 1999 (Scheme 4).[8] The precursor in the FVP is a mixture of tris(chloroethenyl)benzotrithiophenes **17** and **18** prepared from benzotrithiophene **16**. Under FVP conditions at 1000 °C, **17** and **18** are converted to trithiasumanene **19**. In contrast to the unsuccessful synthesis of sumanene (**1**) by the FVP method, trithiasumanene is tolerant to the harsh conditions of FVP, possibly owing to the replacement of the reactive benzylic carbons by sulfur atoms and the shallower bowl structure. X-ray crystallographic analysis of **19** indicates a shallower bowl depth (0.79 Å) compared to that of **1** (1.11 Å). The molecules are stacked in a convex-to-concave fashion but alternatively slipped from side to side with intermolecular S–S contacts.

Solution-phase syntheses of heterasumanenes have also been achieved recently. Furukawa et al. reported the synthesis

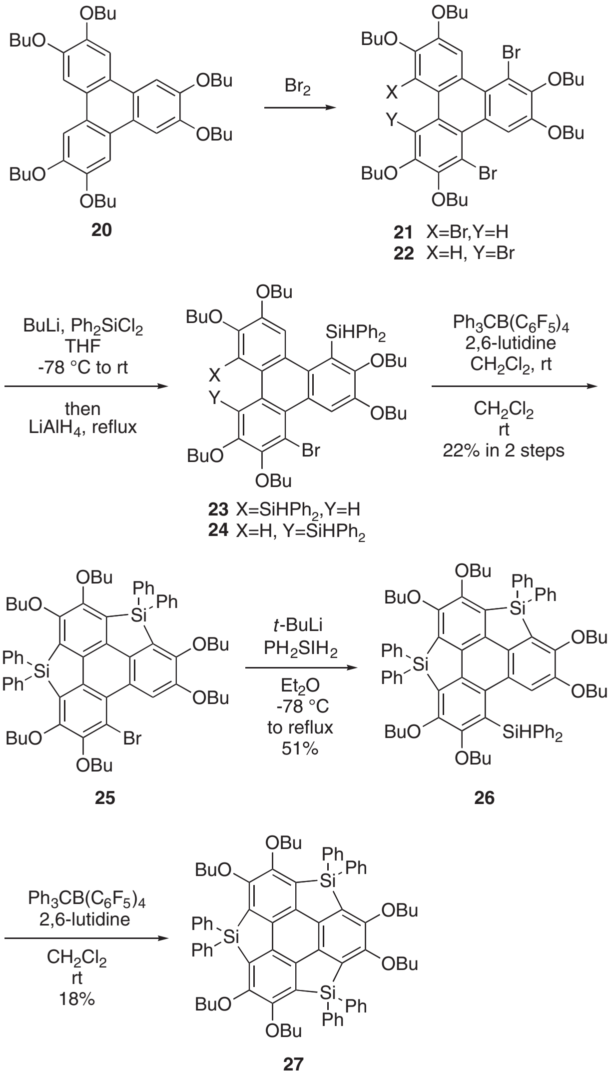


Scheme 4.

of trisilasumanene **27** in 2009 (Scheme 5).[9] The synthesis is achieved by a novel sila-Friedel–Crafts reaction to construct dibenzosilole moieties from a triphenylene derivative. A mixture of tribromotriphenylene **21** and **22** is prepared from hexabutoxytriphenylene **20**. Two Ph_2HSi-groups are introduced by lithiation of **21** and **22** followed by the addition of Ph_2SiCl_2 and reduction, giving **23** and **24**. Treatment of **23** and **24** with $Ph_3CB(C_6F_5)_4$ generates silicenium ions, which undergo double intramolecular sila-Friedel–Crafts cyclizations to afford **25** in 22% yield. By repeating the introduction of the Ph_2HSi-group and sila-Friedel–Crafts reaction on **25**, trisilasumanene **27** is synthesized in 9% yield from **25**. X-ray crystallographic analysis of **27** indicates that it has an almost planar structure because of the larger covalent radius of the silicon atoms.

In 2010, Saito et al. succeeded in achieving the syntheses of heterasumanenes containing two or three kinds of heteroatoms by stepwise introduction of heteroatoms to triphenylene (Scheme 6).[10] Triphenylenothiophene **29** is prepared from triphenylene **28**. First, the more reactive α-positions of the dibenzothiophene moiety are capped by trimethylsilyl groups to give **30** in 71% yield. Treatment of **30** with BuLi generates a dilithio species at the bay positions of **30**, which is trapped by dichlorodimethylsilane to afford **31** in 27% yield. The next treatment of **31** with BuLi causes dilithiation at the bay positions as well as the replacement of two methyl groups of the dimethylsilole moiety by butyl groups. Addition of Me_2SiCl_2 or Me_2SnCl_2 furnishes heterasumanene **32** in 3% yield or **33** in 0.4% yield, respectively. X-ray crystallographic analysis of **32** revealed that it possesses a very shallow bowl structure (bowl depth = 0.23 Å) in the crystal packing.

The shallow or planar structures of these heterasumanenes facilitate the introduction of the heteroatoms onto the triphenylene precursor to construct the sumanene skeleton. This approach would be useful to prepare heterasumanenes containing other heteroatoms with shallower or more planar structures. Although these heterasumanenes do not have a significant bowl-shape, the effects caused by heteroatoms on the electronic properties will help us to expand the chemistry of sumanene more widely.

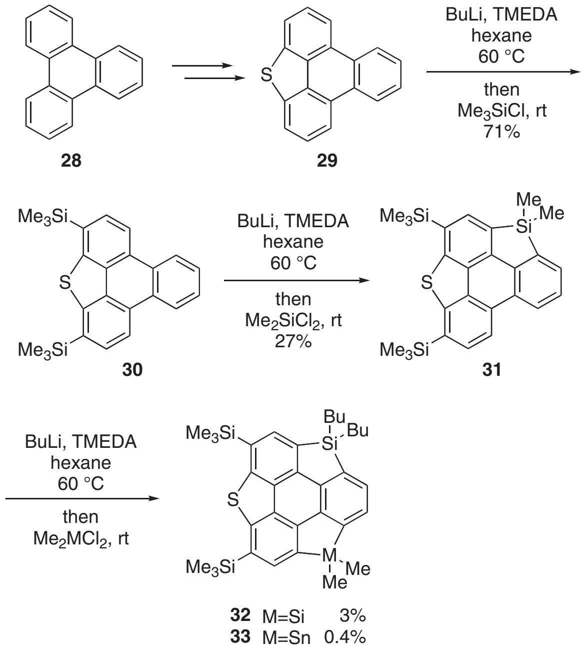


Scheme 5.

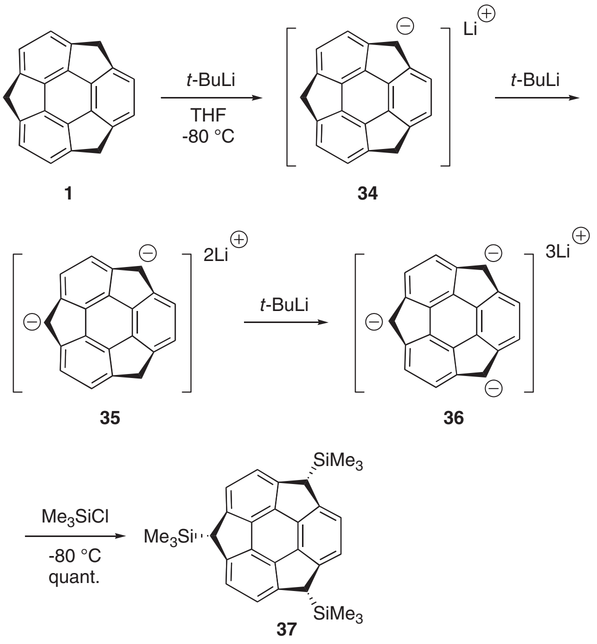
◆ Functionalization and Derivatization of Sumanenes

Chemical reactivities of buckybowls are of interest in regards to the strained bowl-shaped aromatic structure. The convex or concave faces are expected to exhibit different chemical reactivities from each other. The chemical reactivities also help us to understand the nature of buckybowls as well as those of related fullerenes and carbon nanotubes. Functionalization and derivatization of the sumanene skeleton lead to modification of the physical properties, which can be advanced to application in material science. In this chapter, the chemical reactivities and derivatization of sumenenes reported to date are summarized.

Sumanene (**1**) possesses three benzylic positions in its structure which can be easily functionalized through generation of anions. Sakurai et al. reported face-selective functionalization



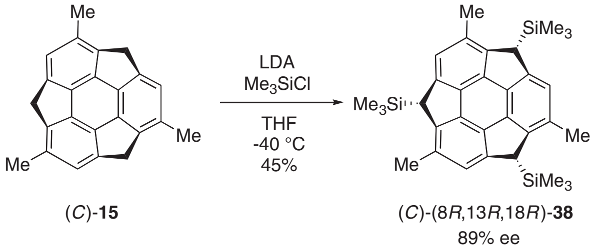
Scheme 6.



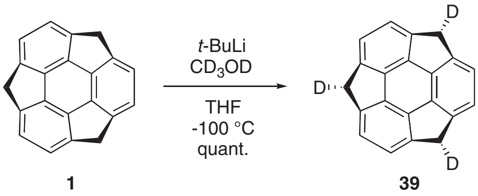
Scheme 7.

at the benzylic positions.[3b] Treatment of **1** with 100 mol% of *t*-BuLi generates mono-anion **34** (Scheme 7). Successive additions of *t*-BuLi afford di-anion **35** and tri-anion **36**. These anions are trapped by chlorotrimethylsilane, furnishing tris(trimethylsilyl)-derivative **37**. The trimethylsilyl groups are directed to the less-hindered convex face at the *exo*-positions, which prevents bowl inversion of **37** to the less stable conformer with *endo*-directed trimethylsilyl groups.

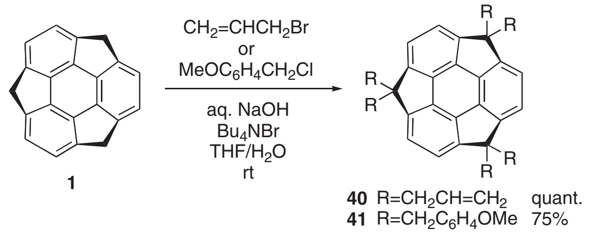
Higashibayashi et al. reported a chiral tris(trimethylsilyl)-derivative of chiral trimethylsumanene (*C*)-**15** (Scheme 8).[5] (*C*)-**15** is prepared at low temperature to prevent its racemization (Scheme 3). After purification at low temperature, trimethylsilyl groups are face-selectively introduced by treatment with LDA and chlorotrimethylsilane at −40 °C, giving (*C*)-(8*R*,13*R*,18*R*)-**38**. The introduction of trimethylsilyl groups generates new sp^3 stereogenic centers at the benzylic positions owing to the C_3 symmetry of the molecule. Although (*C*)-**15** is easily racemized at room temperature through bowl inversion, (*C*)-(8*R*,13*R*,18*R*)-**38** is not racemized because of the newly induced sp^3 stereogenic centers. Chiral HPLC analysis of (*C*)-(8*R*,13*R*,18*R*)-**38** at room temperature enabled the determination of the enantiomeric excess of **38** (89% ee).[11]



Scheme 8.



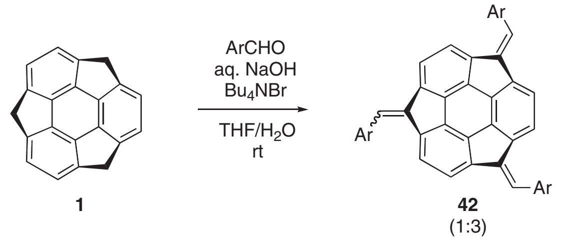
Scheme 9.

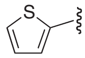
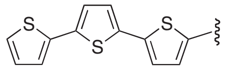


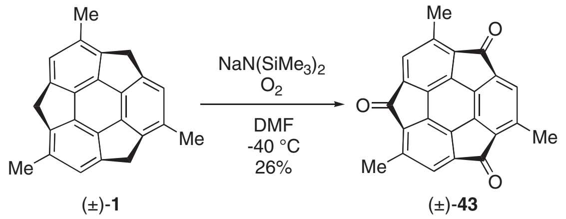
Scheme 10.

Amaya et al. reported the preparation of trideuterated sumanene **39** by quenching with CD_3OD (Scheme 9).[12] Chemical exchange NMR spectroscopy (EXSY) of **39** allowed the determination of the bowl inversion energy (ca. 21 kcal mol^{-1}). These researchers also reported hexa-alkylated sumanene derivatives (Scheme 10).[12] Under conditions using aqueous NaOH and Bu_4NBr with allyl bromide or 4-methoxybenzyl chloride, hexaallylsumanene **40** or hexakis(4-methoxybenzyl)sumanene **41** is prepared (Scheme 10). These derivatives show lower bowl inversion energies (19.2–18.2 kcal mol^{-1}) than sumanene. Under similar conditions, condensation of various aldehydes takes place, giving π-extended derivatives **42**, although they are mixtures of *cis*- and *trans*-isomers (Table 1).[13] Since sumanene (**1**) is a C_{3v} symmetric molecule, control of the stereoisomerism during derivatization at the benzylic positions toward C_3 symmetric π-conjugated compounds is a general problem.

Table 1. Condensation of **1** with aldehydes



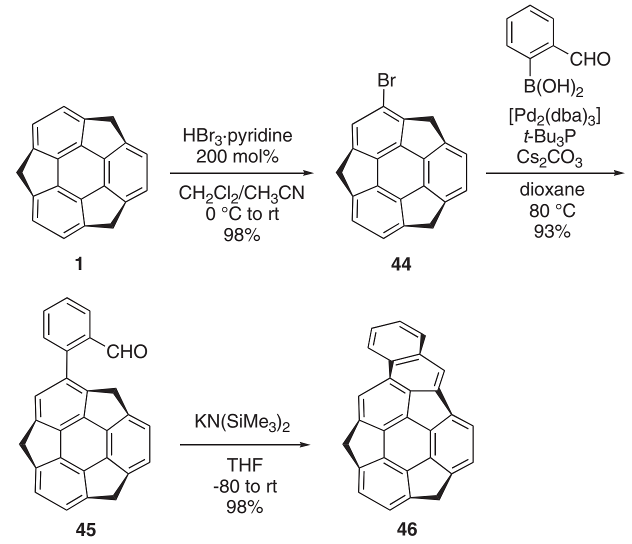
Ar	Yield/%
Ph	quant.
$4\text{-}MeC_6H_4$	quant.
$4\text{-}MeOC_6H_4$	quant.
$4\text{-}ClC_6H_4$	88
$4\text{-}CF_3C_6H_4$	68
$3,4,5\text{-}(MeO)_3C_6H_2$	79
	85
	57



Scheme 11.

Tsuruoka et al. reported trimethylsumanenetrione **43**.[11] By treatment with $NaN(SiMe_3)_2$ under O_2 atmosphere, (±)-**1** is oxidized to trione (±)-**43** (Scheme 11). **43** possesses a deeper bowl depth and a higher bowl inversion energy (23.4 kcal mol^{-1}) than **1**, resulting in slow racemization through bowl inversion. The racemization is slow enough to resolve (±)-**43** by chiral HPLC to furnish the enantioenriched **43**.

Functionalization of the benzene rings of **1** was achieved through electrophilic bromination by Amaya et al.[3c,14] Treatment of **1** with HBr_3•pyridine complex causes selective monobromination to afford bromosumanene **44** in 98% yield (Scheme 12). The conversion of **44** to naphthosumanene **46** was also achieved through cross-coupling and benzannulation reactions. The Suzuki–Miyaura coupling between **44** and 2-formylphenylboronic acid, followed by benzannulation using $KN(SiMe_3)_2$, affords naphthosumanene **46** having an extended π-conjugated bowl shape (Scheme 12). This strategy was further applied to the syntheses of dinaphthosumanene and trinaphthosumanene (Scheme 13). Bromination of **1** using Br_2 gives an inseparable mixture of dibromosumanenes **47a**/**47b** and tribromosumanenes **48a**/**48b**. The Suzuki–Miyaura coupling of the mixture with 2-formylphenylboronic acid affords **49a**/**49b** (1.2:1) and **50a**/**50b** (5:1) in 45% and 41% yields, respectively. **49** and **50** are separable at this stage. Both **49a** and **49b** undergo double benzannulation by treatment with $KN(SiMe_3)_2$, giving a mixture



Scheme 12.

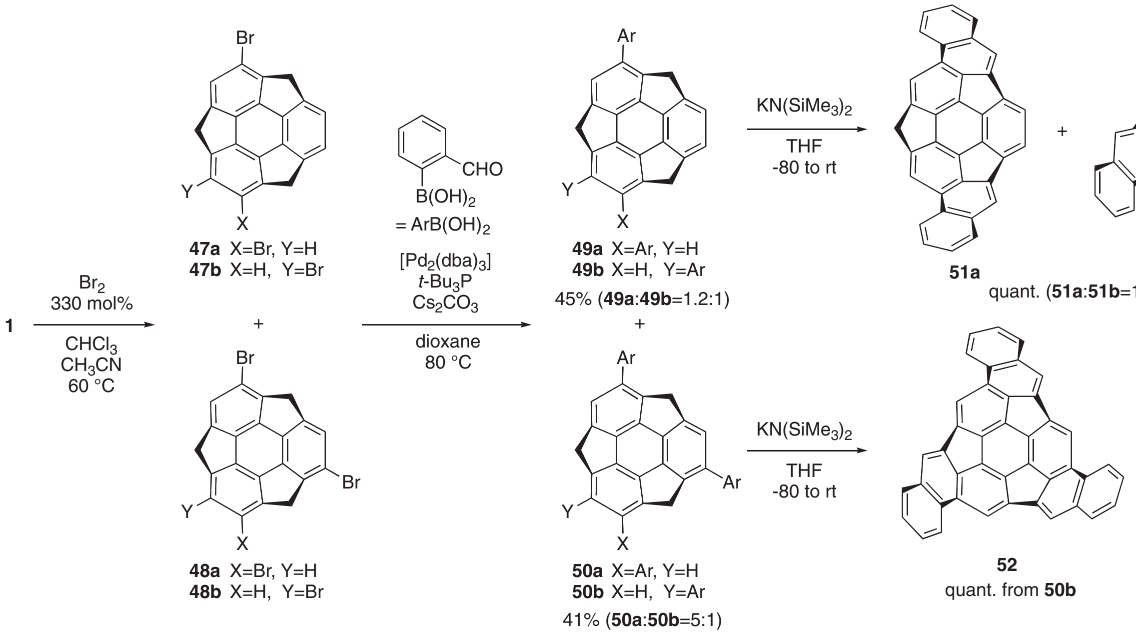
of dinaphthosumanenes **51a**/**51b** (1.2:1). In contrast, only **50b** undergoes triple benzannulation to afford trinaphthosumanene **52** by treatment of a mixture of **50a**/**50b**, which makes the isolation of **52** easier. Although the bromination is still not selective and the separation of isomers is difficult, subsequent transformation can aid in the separation.

Coordination of buckybowls to transition metals is an interesting topic in this field.[1a,1c,1f,1g] Buckybowls have multiple coordination sites in regards to the convex or concave face and the position in the polycyclic structure. Reported 1:1 η^2- or η^6-corannulene–metal complexes show *exo*-selective coordination at the convex face of corannulene. In contrast, Amaya et al. reported a Fe(η^6-sumanene) complex as the first example of an *endo*-coordinated metal complex at a concave face (Scheme 14).[15] In the presence of Al powder and $AlCl_3$, heating of sumanene (**1**) and ferrocene at 120 °C without solvent, followed by exchange of the counter anion with NH_4PF_6, gives [CpFe(η^6-*endo*-sumanene)]PF_6 **53a** in 91% yield. X-ray crystallographic analysis of **53a** shows that iron is bound on the side benzene ring at the concave face. Iron complexes **53b** and **53c** with a substituted Cp are prepared as well (Scheme 14). Under similar conditions, a Ru complex, [CpRu(η^6-sumanene)]PF_6 **54**, is also successfully prepared[16] (Scheme 15). Interestingly, both *endo*-**54** and *exo*-**54** are observed in solution, and dynamic bowl inversion is exhibited between *endo*-**54** and *exo*-**54**. *endo*-**54** is thermodynamically more stable than *exo*-**54**. The ratio of *endo*/*exo*-**54** is dependent on solvent and temperature.

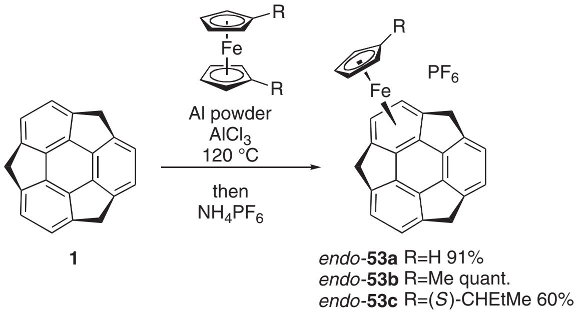
It is very striking that structural differences in buckybowls (corannulene or sumanene) alter the coordination face to a transition metal and the stability and dynamic behavior of the complexes are highly dependent on the transition metal. These findings contribute to the elucidation of properties of metal complexes of nonplanar polyaromatics and their applications.

◆ Outlook

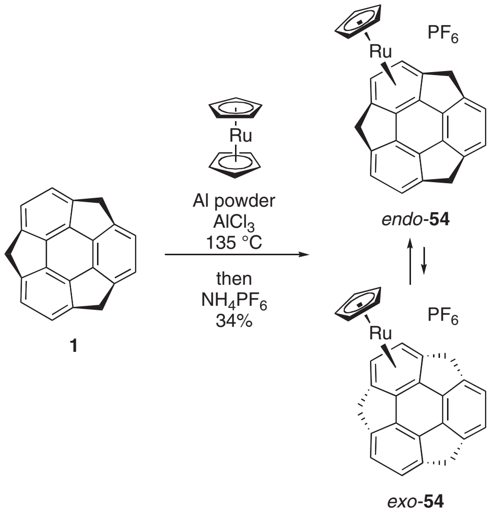
Development of synthetic methodology for sumanene has opened up new attractive chemistry of bowl-shaped aromatic



Scheme 13.



Scheme 14.



Scheme 15.

hydrocarbons. Interesting unique physical properties and chemical reactivities already have been reported. Further experimental and theoretical studies are expected to fully characterize them. Functionalization and derivatization modify the physical properties, leading to applications in material science. Recent synthetic advances of heterasumanenes will expand the range of properties of sumanene as well.

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