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THE CHEMICAL RECORD

Chemistry of Sumanene

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ABSTRACT: Sumanene ($C_{21}H_{12}$) is a bowl-shaped π-conjugated molecule with C_{3v} symmetry, consisting of alternating benzene rings and cyclopentadiene rings around the central benzene ring. The structure corresponds to the smallest C_{3v}-symmetric fragment for the structural motifs of fullerenes or end-caps of carbon nanotubes. The presence of three sp^3-hybridized benzylic sites is one of the most characteristic structural features in sumanene, which allows the different chemistry from that of corannulene. Since our first synthesis in 2003, we have engaged in the study of sumanene. This article summarizes our continuous study, including the synthesis, structure, dynamics, derivatization, complexation with transition metals, charge carrier mobility, and conversion to nitrogen-doped graphitic carbon, of sumanene.

Keywords: arenes, fused-ring systems, isomerization, π bowls, sumanene

1. Introduction

Sumanene (**1**, $C_{21}H_{12}$) is a bowl-shaped, π-conjugated molecule with C_{3v} symmetry, consisting of alternating benzene rings and cyclopentadiene rings around the central benzene ring (Figure 1). The name sumanene comes from “suman”, which means flower in Hindi and Sanskrit, due to its shape; the ring edges on the rim resemble petals and it is reminiscent of a flower.[1] The name according to IUPAC is 4,7-dihydro-1*H*-tricyclopenta[*def,jkl,pqr*]triphenylene. The structure corresponds to the smallest C_{3v}-symmetric fragment for the structural motifs of fullerenes or end-caps of carbon nanotubes. In the C_{5v}-symmetric fragment molecules, the smallest one is called corannulene (**2**, $C_{20}H_{10}$; Figure 1), which is the most famous one in the family of the bowl-shaped π-conjugated molecules (the term “π bowls” is used for bowl-shaped π-conjugated molecules herein, although they have also been called open geodesic polyarenes[2] or buckybowls.[3]). Their unique open-end structures and dynamic behavior (bowl-to-bowl inversion), as well as the strained π conjugation, make π bowls attractive to study.[4]

The chemistry of π bowls commenced with the synthesis of **2** in 1966.[5] Subsequent development of a more practical synthetic method using flash vacuum pyrolysis (FVP) for **2** in 1991 led to a breakthrough in this area, which resulted in a number of π bowls.[4c,6] However, the synthetic birth of **1** was left behind in the development, although there are some reports of studies using theoretical calculations.[7] One of the reasons includes that FVP did not work for the synthesis of **1**.[1] The presence of three sp^3-hybridized benzylic sites, which is the most important difference from **2**, may make the synthesis difficult. On the other hand, this feature allows different

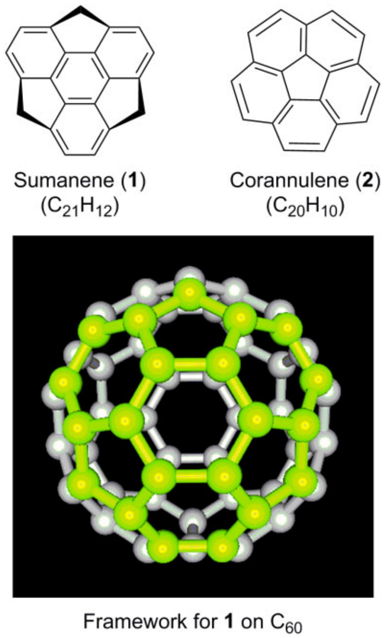

Fig. 1. Sumanene (**1**), corannulene (**2**), and the image of the framework for **1** on C_{60}.

chemistry from that of **2**. For example, active species, such as radicals, cations, anions, and carbenes, can be stabilized at the benzylic position, and their generation will lead to the derivatization of **1**. In 2003, our group achieved the synthesis of **1** without using the FVP method (details are given in Section 2.1).[8] Since then, we have engaged in the study of **1**. A question frequently asked about aesthetically pleasing molecules concerns whether they have functional importance. We believed from the very beginning that the beautiful molecule **1** would have a functional role, which prompted us to study its chemistry in detail. Herein, we summarize our continuous research on **1**.

2. Synthesis and Structure of 1

2.1. Synthesis of 1

Attempts to synthesize **1** based on an approach involving the construction of three five-membered rings using a planar precursor with a triphenylene skeleton have failed.[1] Other approaches using trindane or trindene derivatives as precursors have also been proposed,[9] but the synthesis of **1** has not been achieved. The construction of a three-dimensional framework followed by oxidative aromatization provided a solution.[8] The aromatization energy compensates for the disadvantage of strain. Scheme 1 shows the synthetic scheme. The synthesis started with the trimerization of 2,5-norbornadiene to give **3**. This was conducted through the copper-mediated cyclization of (3-bromobicyclo[2.2.1]hepta-2,5-dien-2-yl)potassium (or lithium) species (Scheme 1a). Trapping of the anion species with Bu_3SnCl gave (3-bromobicyclo[2.2.1]hepta-2,5-dien-2-yl)tributylstannane, followed by copper-mediated cyclization,

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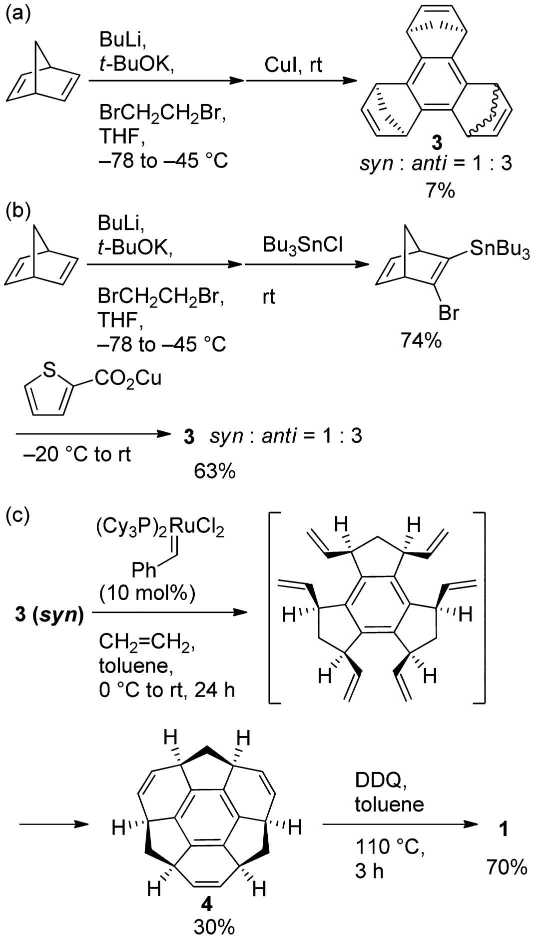
Toshikazu Hirao graduated from Kyoto University in 1973, where he obtained his doctorate in 1978. He became Assistant Professor at Osaka University and was a postdoctoral fellow at the University of Wisconsin with Professor Barry M. Trost (1981–1982). Dr. Hirao was promoted to Associate Professor in 1992 and Professor in 1994. His current research interests lie in the area of the construction of an efficient system for electron transfer, which allows the development of new methods in organic synthesis, and novel redox-active systems consisting of transition-metal complexes and/or planar and nonplanar π-conjugated compounds. This research is correlated to the development of bioorganometallic conjugate systems. He was the Director of the University Library (2003–2011) and Vice President of the Chemical Society of Japan (2010–2012). He received some international awards, as exemplified by an “Award for Outstanding Achievements in Bioorganometallic Chemistry” and a “Vanadis Award” in 2008.



Scheme 1. (a) Trimerization of 2,5-norbornadiene. (b) Trimerization of (3-bromobicyclo[2.2.1]hepta-2,5-dien-2-yl)tributylstannane. (c) Synthesis of **1** by ring-opening metathesis and ring-closing metathesis reactions of **3** (***syn***). Cy = cyclohexyl, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

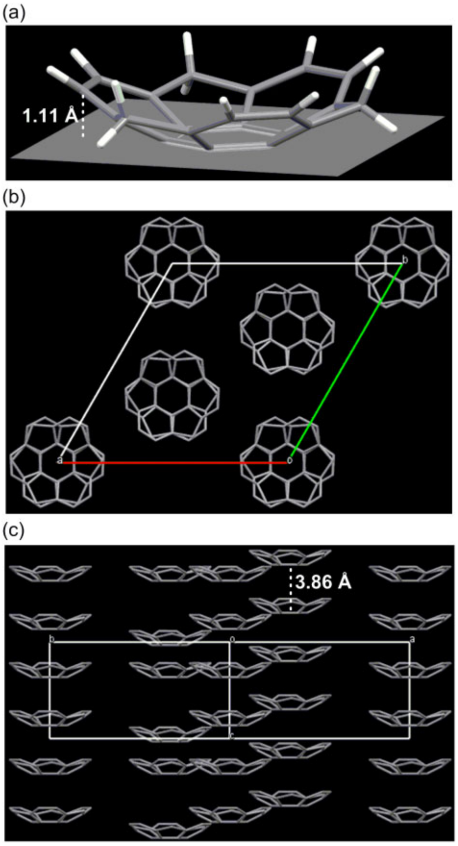


Fig. 2. (a) X-ray crystal structure of **1**; (b) top and (c) side views of the packing structure.

affording trimer **3** (Scheme 1b). The resulting trimer **3** includes *syn* and *anti* isomers. The double bonds in the *syn* isomer were formally reorganized by ruthenium-catalyzed tandem ring-opening metathesis and ring-closing metathesis reactions under an ethylene atmosphere to give hexahydrosumanene **4**. Its oxidative aromatization with DDQ resulted in **1** (Scheme 1c).[8]

2.2. Structure and Dynamics of 1

The bowl-shaped structure of **1** was clearly shown by X-ray crystallographic analysis (Figure 2a). The bowl depth, defined as the distance between a plane of a central benzene ring and a rim aromatic carbon atom, was 1.11 Å.[10] This value is larger than that of **2** (0.87 Å).[11] In the crystal structure, sumanene (**1**) stacked in a concave–convex fashion to form the columns (Figure 2b and c). Each layer of the column was fixed in a staggered fashion. The intermolecular stacking distance from the centroids of the central six-membered rings is approximately 3.86 Å (Figure 2c),[10] which is larger than that for ordinary π stacking. The stacking directions of every column were the same, resulting in a polar crystal. Such polar bowl-in-bowl stacking has also been found in crystals of hemifullerene[12] and circumtrindene.[13] Solid-state NMR spectroscopy of **1** was also studied.[14]

Bowl-to-bowl inversion is characteristic behavior for some flexible π bowls.[15] The activation energy of **1** for bowl-to-bowl inversion was measured by variable-temperature ^{1}H NMR spectroscopy experiments. The obtained value was approximately 20 kcal mol^{-1} (Figure 3a).[8] The 2D exchange spectroscopy (EXSY) experiments of trideuteriosumanene compound **5** also indicated a similar value for the activation energy.[16] This value is consistent with the estimate obtained using theoretical calculations.[17] The activation energy of **1** is much higher than that of corannulene derivative **6** (10.2 kcal mol^{-1}; Figure 3b).[15a] Sumanenyl monoanion **7** and dianion **8** showed slightly larger activation barriers (21.8 and 21.5 kcal mol^{-1} in [D$_8$]THF, respectively) for bowl-to-bowl inversion, relative to that of **1** (Figure 3c).[16]

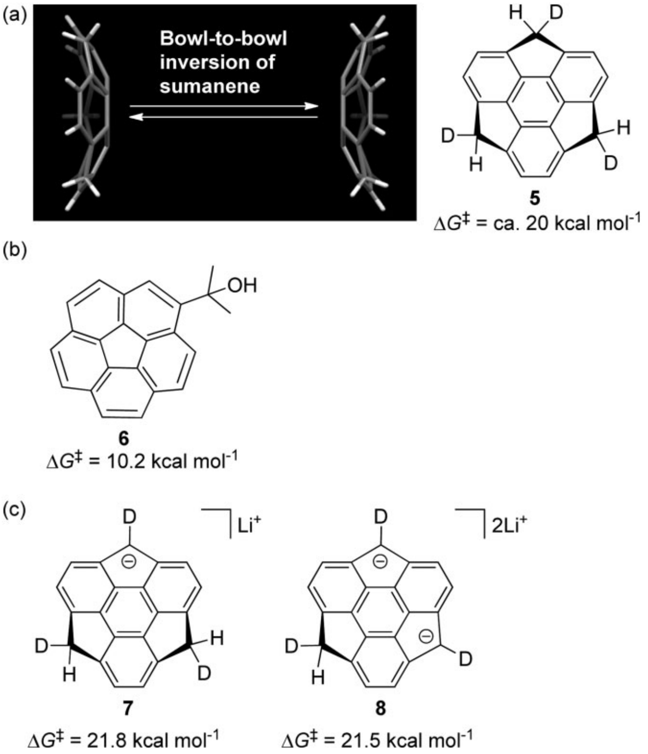
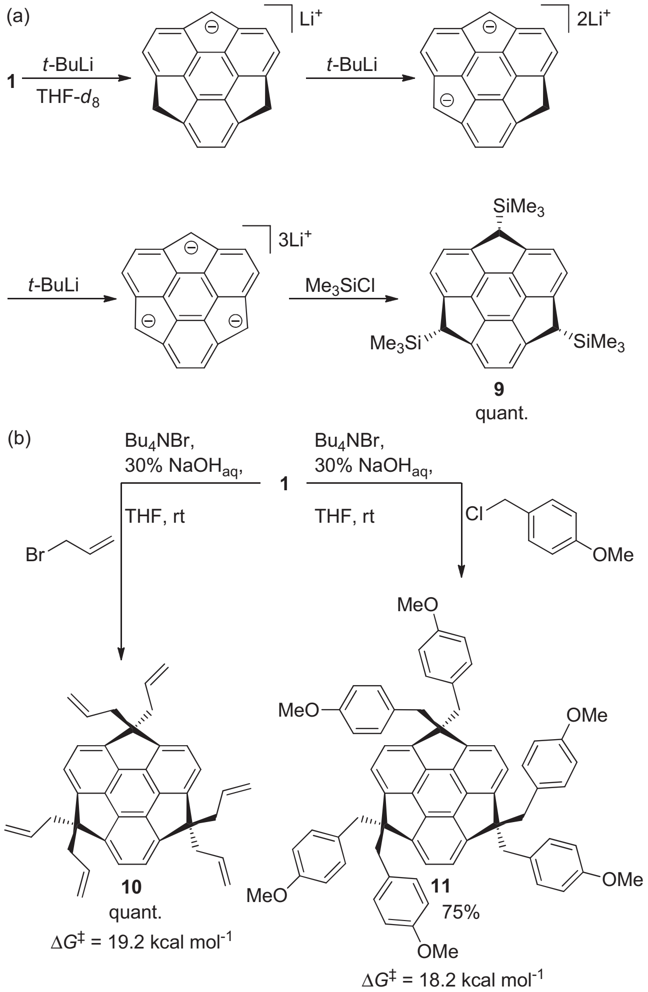


Fig. 3. (a) Bowl-to-bowl inversion of **1,** and activation energy, $\Delta G^{\ddagger}$, for bowl-to-bowl inversion of **5**, (b) **6**, (c) **7**, and **8**.



Scheme 2. (a) Stepwise anion generation from **1**, and synthesis of **9**. (b) Synthesis of hexaalkylated compounds **10** and **11**, and their activation energy, $\Delta G^{\ddagger}$, for bowl-to-bowl inversion.

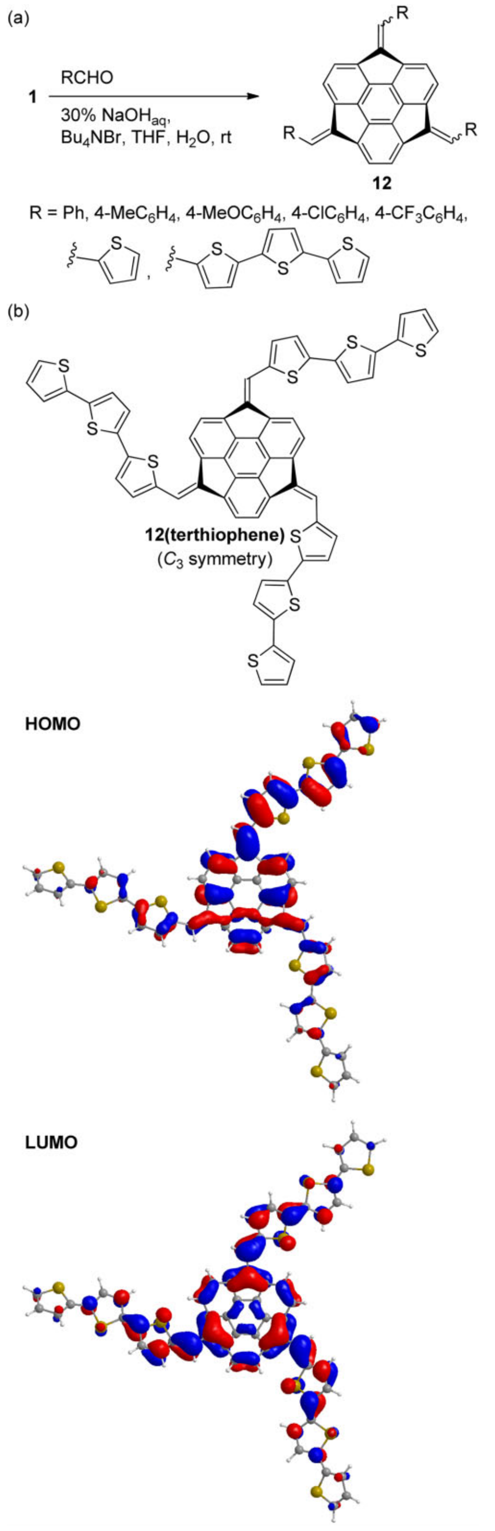
2.2. Derivatization of 1

Anions can be stabilized at the benzylic positions. Treatment of **1** with a strong base generates sumanenyl anions. A carefully controlled amount of *t*BuLi to **1** afforded the corresponding mono-, di-, and tribenzylic anions, selectively (Scheme 2a).[10] Trapping of the trianion with Me_3SiCl took place from outside of the bowl to give tris(trimethylsilyl) compound **9** (Scheme 2a).[10] On the other hand, hexaalkylation was carried out by using a 30% aqueous solution of NaOH as a base (Scheme 2b).[16] The hexaallylated and hexa-*p*-methoxybenzylated sumanenes **10** and **11** underwent bowl-to-bowl inversion. Their activation energies are 19.2 and 18.2 kcal mol-1, respectively.[16]

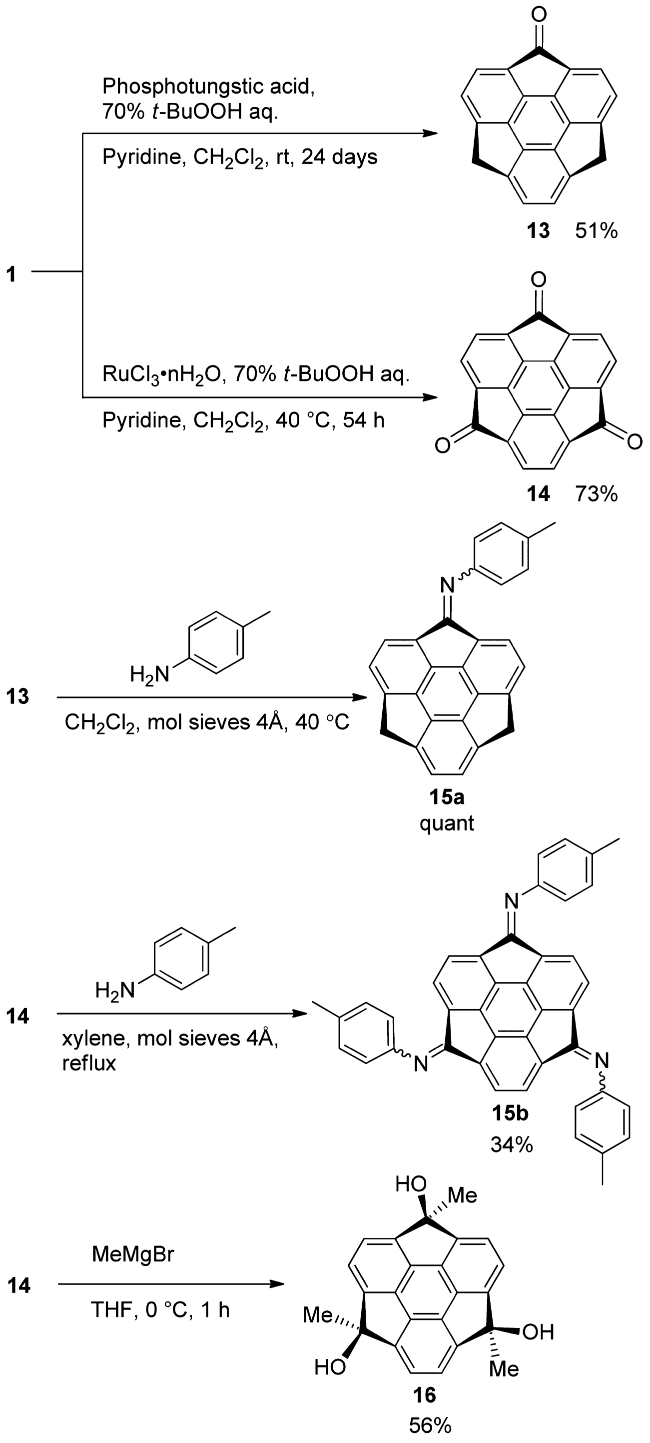
Extension of π conjugation at the benzylic position of **1** is considered to be the most efficient method to synthesize π-conjugation-extended sumanenes. As mentioned above, benzyl anions are available for derivatization. Condensation of **1** with various aldehydes afforded the corresponding π-conjugation-extended sumanenes **12** in the presence of a 30% aqueous solution of NaOH as a base (Scheme 3a).[18] The obtained products **12** have absorptions in a longer wavelength region than that of **1**, especially for the compound with terthiophene moieties. Orbital diagrams for the HOMO and LUMO of **12(terthiophene)** (C_3 symmetry) obtained by DFT calculations at the B3LYP6-31G(d,p)//B3LYP6-31G(d,p) level shows efficient π conjugation (Scheme 3b).[18]

Synthesis of monooxosumanene **13** and trioxosumanene **14** was achieved through the oxidation of the benzylic positions of **1** (Scheme 4).[19] The oxosumanenes have an extended π conjugation relative to that of **1**. Imination of **13** and **14** afforded **15a** and **15b**,[20] respectively, exhibiting further π extension (Scheme 4).[21] The crystal structure of **13** shows the bowl-shaped structure and columnar packing (Figure 4).[19] In contrast to **1**, the columnar packing in the crystal of **13** is nonpolar. The crystal structure of **14** was recently reported by Higashibayashi et al.[22] In the reaction of **14** with methyl magnesium bromide, methyl magnesium bromide selectively attacked from outside of the bowl to give triol **16** (Scheme 4).[19]

Bridging of π-conjugated functional units by a π-conjugated spacer, such as an electron- or hole-conducting



Scheme 3. (a) Synthesis of π-conjugation-extended sumanenes **12**. (b) Orbital diagrams for the HOMO and LUMO of **12(terthiophene)** (*C*$_3$ symmetry) obtained by DFT calculations at the B3LYP6-31G(d,p)// B3LYP6-31G(d,p) level.



Scheme 4. Synthesis of monooxosumanene **13** and trioxosumanene **14**. Imination of **13** and **14**, and the addition of MeMgBr to **14**.

molecular wire, is considered to lead to the creation of novel organic functional molecules and materials. On the other hand, the redox behavior of conducting polymer polyanilines depends on the interconversion between 1,4-

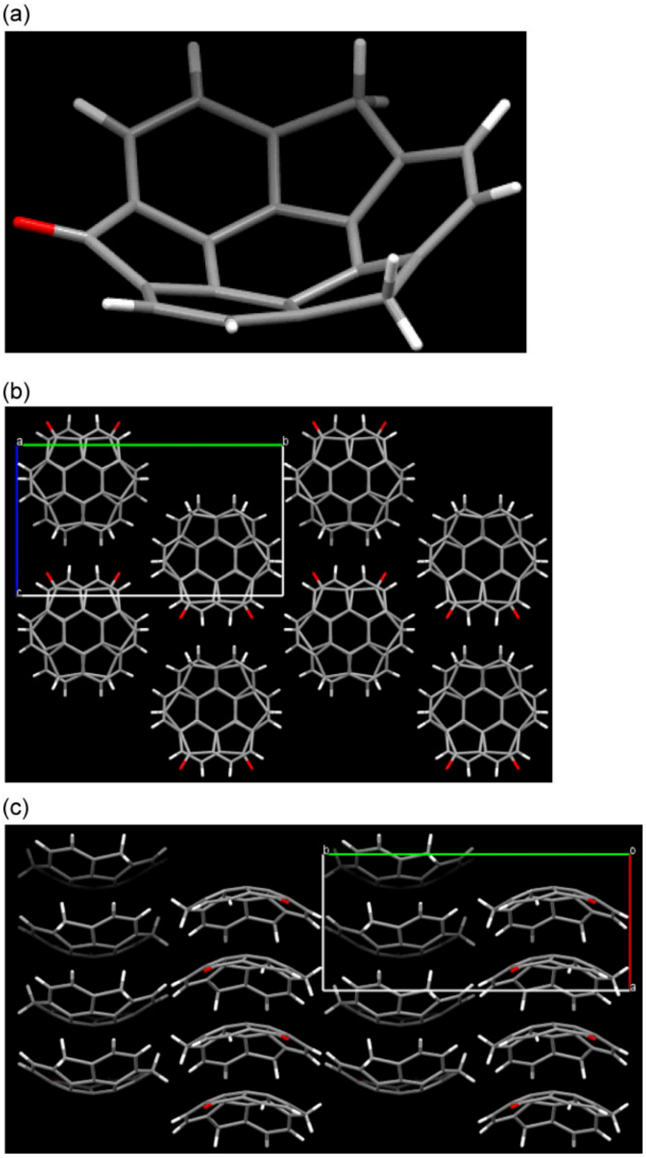
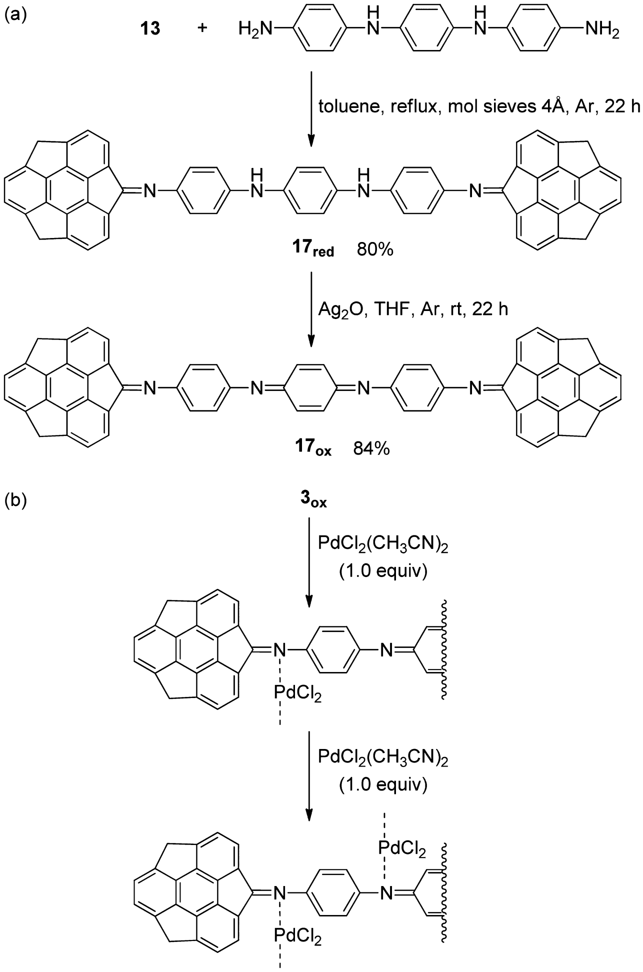


Fig. 4. (a) X-ray crystal structure of **13**, and (b) top and (c) side views of the packing structure.

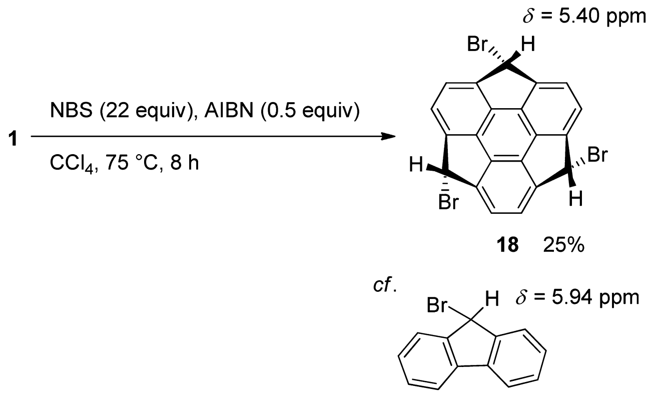


Scheme 5. (a) Synthesis of sumanene monoketimine compounds $\mathbf{17_{red}}$ and $\mathbf{17_{ox}}$. (b) Stepwise coordination of the imino groups to Pd^{II} in $\mathbf{17_{ox}}$.

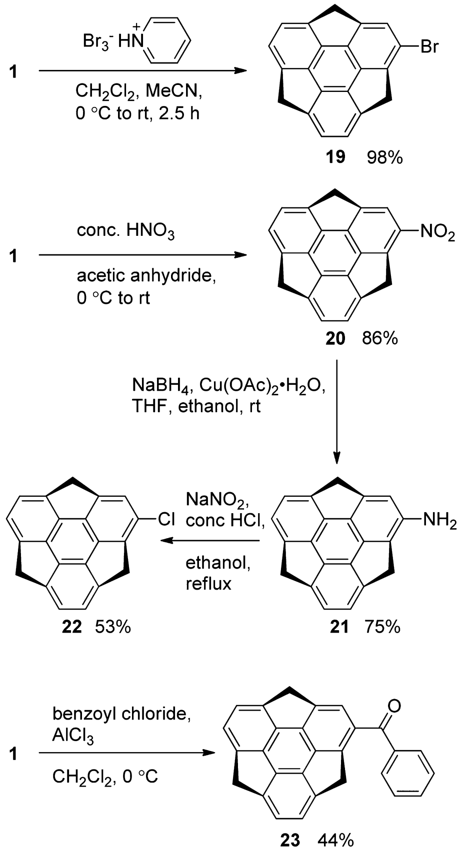
benzoquinonediimine and 1,4-phenylenediamine structures. Therefore, employing an oligoaniline as a spacer to bridge the functional moieties can lead to a function switching system based on redox interconversion. Furthermore, imino nitrogen atoms of the 1,4-benzoquinonediimine can coordinate to transition metals, which permits the construction of the d,π-conjugated redox systems. Our previous study demonstrated the construction of such redox systems.[23] Sumanene monoketimine compounds $\mathbf{17_{red}}$ and $\mathbf{17_{ox}}$ bridged by a redox-active π-conjugated unit based on the conversion between 1,4-phenylenediamine and 1,4-benzoquinonediimine were synthesized (Scheme 5a).[24] The stepwise coordination of the imino groups to Pd(II) in the presence of sumanene monoketimine compound $\mathbf{17_{ox}}$ was indicated by titration experiments (Scheme 5b).[24]

Radical bromination of **1** also gave the corresponding tribromide **18** (Scheme 6).[25] The isolated compound was a single isomer. The chemical shift for the benzylic position of **18** was observed 0.54 ppm lower than that of 9-bromo-9*H*-fluorene, which suggests *exo* substitution.

The development of aromatic substitution methods for the introduction of functional groups and benzylic derivatization is considered to be important to construct a nonplanar π-conjugated system based on **1**. Bromination of **1** using pyridinium hydrobromide perbromide gave bromide **19** in good yield (Scheme 7).[26] A typical nitration reaction and Friedel–Crafts acylation of **1** afforded nitro compound **20** and benzoyl compound **23**, respectively.[27] Thus-obtained **20** was reduced to amino compound **21** by $NaBH_4$ and $Cu(OAc)_2 \bullet H_2O$. The introduced amino group would be useful



Scheme 6. Synthesis of tribromosumanene **18**. NBS = *N*-bromosuccinimide, AIBN = 2,2'-azobisisobutyronitrile.



Scheme 7. Aromatic substitution reactions of **1**.

for a variety of transformations, such as diazo coupling or the Sandmeyer reaction. The Sandmeyer reaction was demonstrated to provide the corresponding chloride **22**.[27] Related aromatic substitution methods for **1** were also reported.[28]

The synthesis of naphthosumanenes, which have a larger ring-fused structure, was carried out. The synthetic scheme includes the following three steps from **1**: 1) bromination of the arene periphery (the degree of the bromination is controlled by a reagent and/or amount of reagent), 2) introduction of the 2-formylphenyl moiety by Suzuki–Miyaura coupling, and 3) intramolecular condensation in the presence of base. Mono-, di-, and trinaphthosumanenes **24**–**26** were synthesized based on the strategy outlined in Scheme 8a.[29] Bowl-to-bowl inversion of dideuteriomononaphthosumanene derivative **27** (32.2 kcal mol^{-1}) was much slower than that of **1** (Scheme 8b).[29] Structural optimization of the naphthosumanenes shows deeper bowl structures.[17,29] The bowl depth of trinaphthosumanene **26** was 1.36 Å (measured as shown in Scheme 8c).[17,29]

Bisumanenyl **28**, the aryl–aryl-coupled sumanene dimer, was synthesized through one-pot borylation and Suzuki–Miyaura coupling of bromosumanene **19** (Scheme 9a).[30] Despite the inherent rich isomerism based on the relative bowl direction and bond rotation, the selective formation of one isomer was suggested by variable-temperature NMR spectroscopy experiments. The optimized structure of the most stable conformer is shown in Scheme 9a. Ethynylation of **19** and subsequent desilylation gave ethynylsumanene **29** (Scheme 9b).[31] Oxidative homocoupling of **29** gave dimer **30**. The absorption and emission spectra for **28**–**30** show the extension of π conjugation, especially in **30** (Scheme 9b).[31] The benzyl–benzyl-coupled sumanene dimer **31** was also synthesized by oxidative dimerization of the sumanenyl monoanion (Scheme 9c).[32]

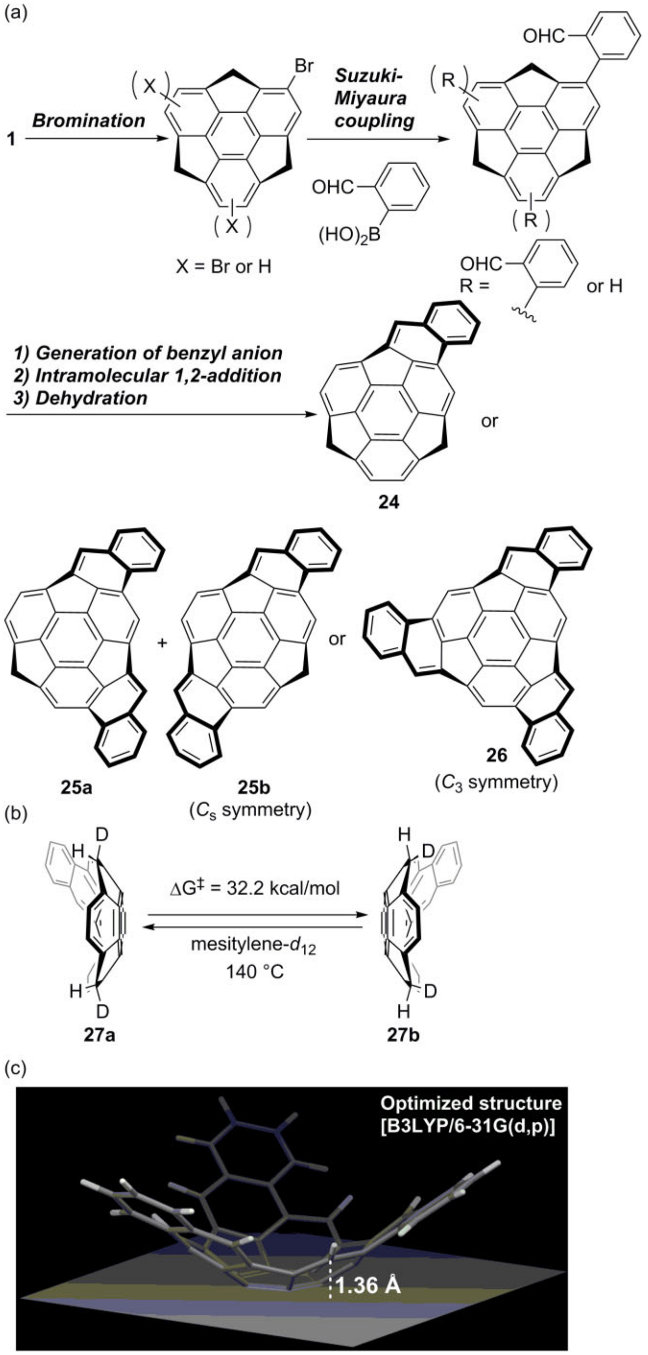
Bisumanenylidene **32**, consisting of two sumanene components connected by a double bond, was synthesized by McMurry coupling of monooxosumanene **13** (Scheme 10).[33] The calculation and low-temperature ^{1}H NMR spectroscopy experiments suggest that bisumanenylidene is likely to be predominantly present as a C_{2h}-symmetric structure (the bowls pointing to opposite sides) rather than as a C_2-symmetric one (the two bowls facing each other with some torsion along the C–C axis; Scheme 10). The extension of π conjugation of bisumanenylidene was also shown from the absorption and emission spectra.

Hydrogenation of **1** was carried out in the presence of Pd/C (Scheme 11).[34] As a result, $C_{21}H_{24}$ (**33**; a benzene ring remained) was indicated by NMR spectroscopy and MS experiments.

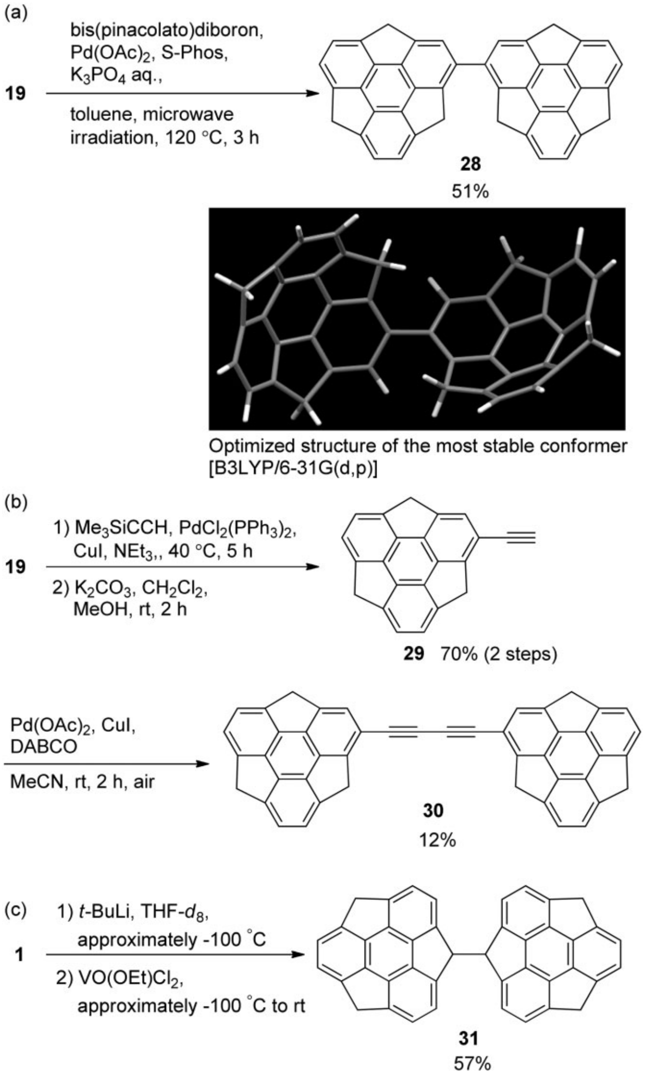
2.3. Complexation of 1

In the coordination chemistry of π bowls, there is an intriguing issue on the preference for metal binding to a concave surface versus that of a convex one. Convex binding of transition metals has been found to be favorable so far, especially for **2**.[35]

The selective synthesis of the concave-bound complex [CpFe(**1**)]PF_6 (**34**; Cp = cyclopentadienyl) was achieved by



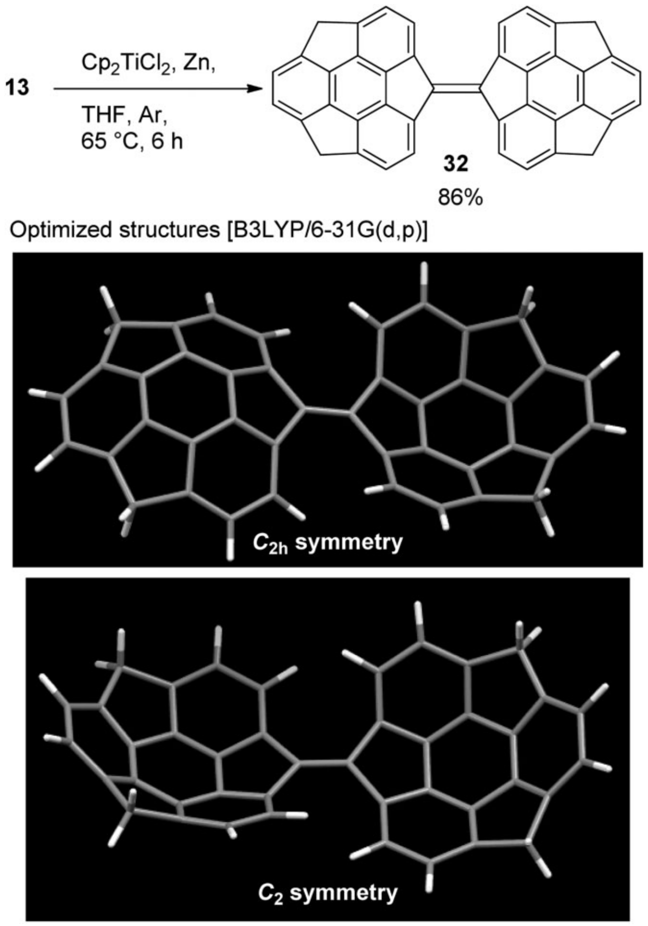
Scheme 8. (a) Synthesis of naphthosumanenes **24**–**26**. (b) Bowl-to-bowl inversion of **27**. (c) Optimized structure of **26** by DFT calculations at the B3LYP6-31G(d,p) level.



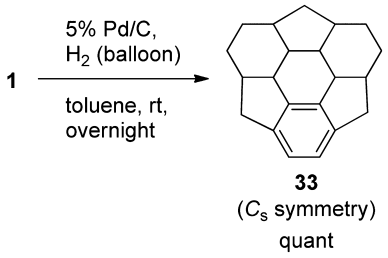
Scheme 9. Synthesis of sumanene dimers (a) **28**, (b) **30**, and (c) **31**. DABCO = 1,4-diazabicyclo[2.2.2]octane.

ligand exchange of ferrocene with **1** (Scheme 12a).[36] The structure was confirmed in both solution and solid states. The X-ray crystal structure of **34** is shown in Scheme 12a. This is the first report for the selective synthesis of concave-bound π-bowl complexes.[36,37] The curved concave π surface serves as an η^6 ligand. The selectivity of complexation is theoretically discussed.[38] The redox properties of the complex were investigated through an electrochemical study. The complex exhibited Fe^{II}/Fe^{I} reduction, which displayed features of partial chemical reversibility, coupled to the fragmentation of the corresponding Fe^{I} species to ferrocene.[39]

The methyl-substituted complex [MeCpFe(**1**)]PF$_6$ (**35**) was also synthesized (Scheme 12a).[40] The complex showed the concave binding of MeCpFe. The ^{1}H NMR spectroscopy experiments suggest that the methyl group is directed out of the bowl with restricted rotation. Iron atom dynamics of MeCpFe ligated to a concave face in **1** were investigated using temperature-dependent Mössbauer spectroscopy.[41] MeCpFe in the complex with **1** was revealed to be bound more tightly than that in the corresponding fluorene complex.

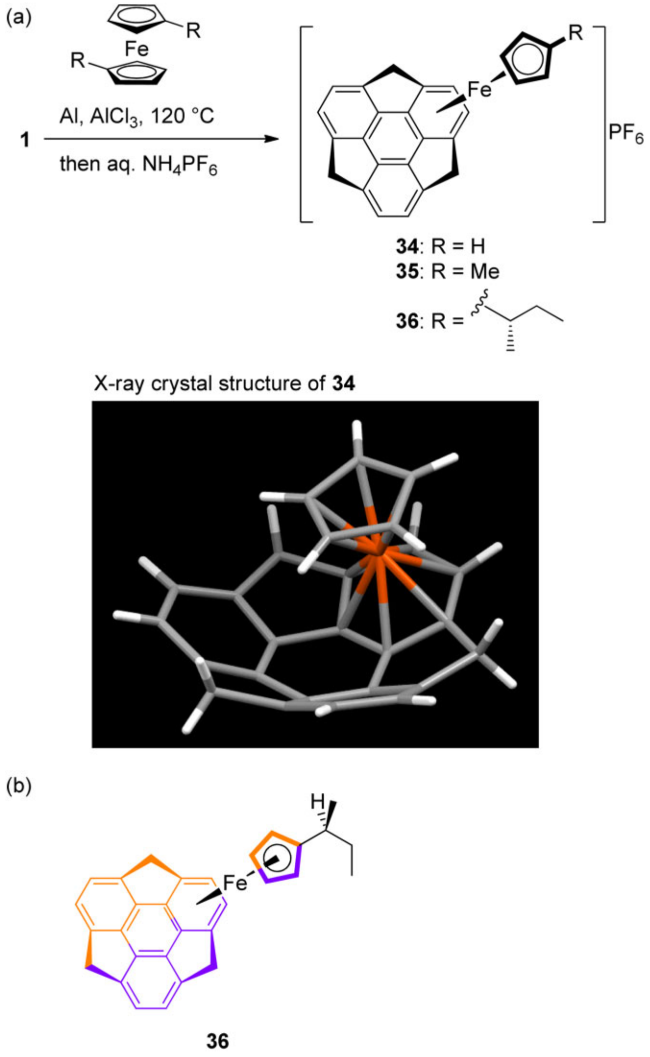


Scheme 10. Synthesis of bisumanenylidene **32**.



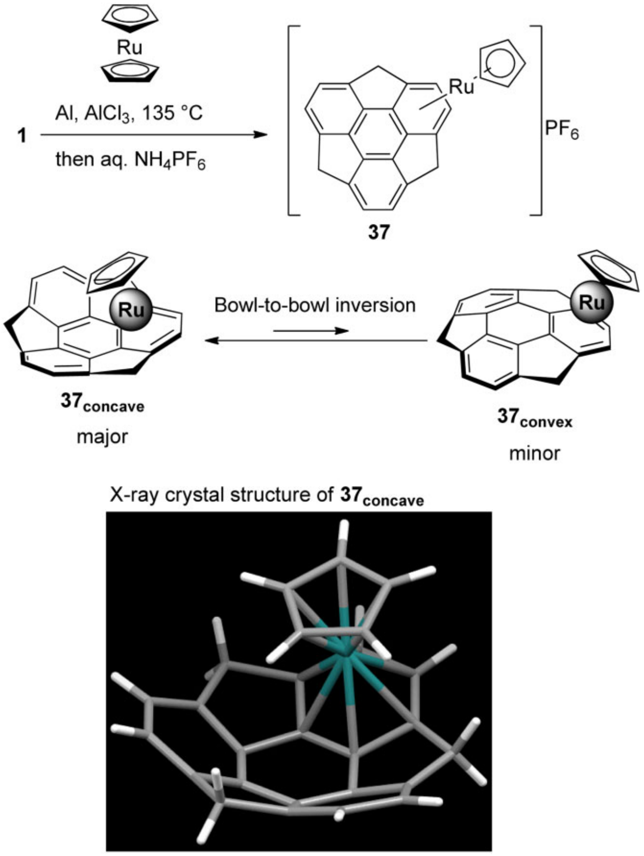
Scheme 11. Hydrogenation of **1**.

Synthesis of Fe^{II} complex **36**, with a Cp ligand attached to a chiral *s*-butyl group, was performed in a similar manner to the preparation of **34** (Scheme 12a).[40] Complex **36** also shows concave face selective coordination in solution, in which rotation of the Cp ring was restricted. Magnetic and optical desymmetrization in **1** was found in the complex (Scheme 12b).[40] This is the first optically active complex with a π-bowl ligand.



Scheme 12. (a) Synthesis of the concave-bound complexes [RCpFe(**1**)]PF$_6$ **34**–**36**. (b) Dissymmetric image of **36**.

[CpRu(**1**)]PF$_6$ (**37**) was synthesized in the similar way as **34**.[42] However, the resulting complex **37** was a mixture of concave and convex binding of CpRu, in which concave binding was preferable. Dynamic isomerization through bowl-to-bowl inversion was observed in solution (Scheme 13).[42] This preference can be accounted for by the thermodynamic stability. The activation barrier between **37**$_{\textbf{concave}}$ and **37**$_{\textbf{convex}}$ for bowl-to-bowl inversion is 17.3 kcal mol^{-1} in CD$_2$Cl$_2$, which is smaller than that of **1**. The X-ray crystal structure of **37**$_{\textbf{concave}}$, a major isomer, was obtained, and shows the concave binding structure and slight flattening of the bowl structure, which is likely to cause lowering of the activation barrier for bowl-to-bowl inversion relative to that of **1** (Scheme 13).[42] When the crystal of **37**$_{\textbf{concave}}$ was re-dissolved in a solvent, both isomers were observed.



Scheme 13. Synthesis of [CpRu(**1**)]PF$_6$ (**37**), bowl-to-bowl inversion between **37$_{concave}$** and **37$_{convex}$**, and the X-ray crystal structure of **37$_{concave}$**.

Cyclopentadienyl-like anions of **1**, shown in Scheme 2a, are considered to provide mono and even multinuclear metallocene-type complexes. The syntheses of mono- and trinuclear sumanenyl zirconocene complexes were demonstrated.[43]

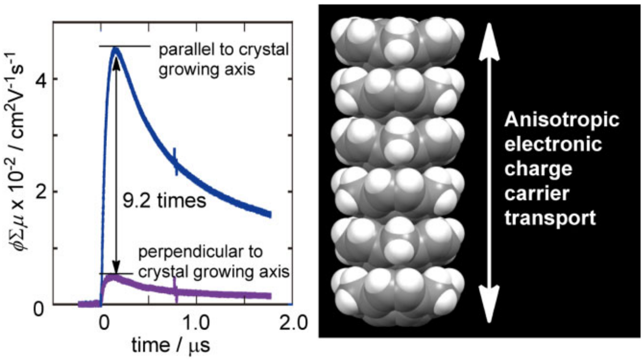


Fig. 5. Conductivity transients and packing structure of **1**.

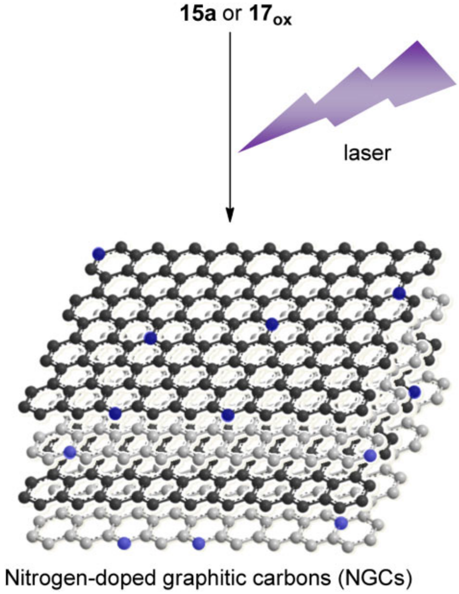


Fig. 6. Laser-induced formation of NGCs.

2.4. Function of 1

As described in the previous section, the packing structure of **1** in the crystal is columnar (Figures 2 and 5).[10,26] Such stacking is considered to be effective for anisotropic charge carrier transportation, which was investigated by the time-resolved microwave conductivity (TRMC) method. This method allows one to evaluate intrinsic intramolecular conductivity by minimizing the effect of impurity, defects, and interfaces, that is, compared with conventional methods, such as time-of-flight and field-effect transistors because the nanometer-scale mobility of charge carriers generated by laser pulse irradiation is quantified under oscillating microwaves without electrodes.[44] The charge carrier mobility of a needle-like crystal of **1** along the stacking axis was larger than that along the perpendicular direction to the stacking axis. The anisotropic difference of conductivity reached 9.2 times, as shown in the graph for conductivity transients (Figure 5).[26] The mobility along the stacking axis was estimated to be $>7.5 \times 10^{-1}$ cm^2 V^{-1} s^{-1} by the TRMC method and photocurrent integration measurements, in which the charge carrier is mainly the electron.[26]

Research on graphitic carbons is now one of the most active fields in materials chemistry.[45] Among graphitic carbons, nitrogen-doped graphitic carbons (NGCs) have attracted much interest due to their electrical and catalytic properties.[46] Laser annealing induced the transformation of sumanene derivatives **15a** and **17$_{ox}$**, bearing the imine moiety, into NGCs (Figure 6).[21,24] Notably, the nitrogen/carbon ratios were almost retained in the resulting NGCs, although most nitrogen atoms are generally known to become lost during the carbonization process when it is conducted above 600–800 °C.

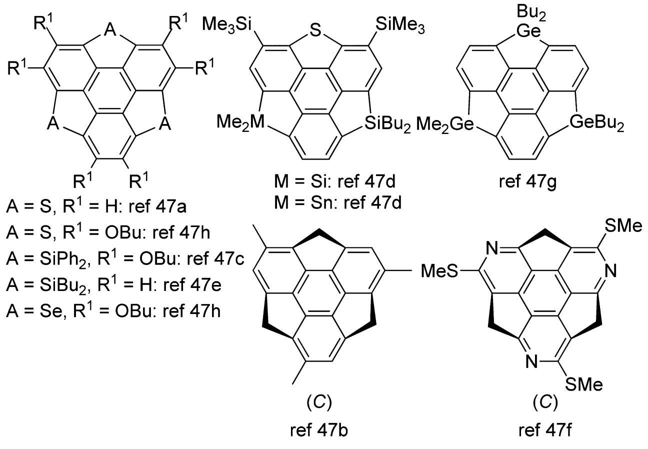


Fig. 7. Heterasumanenes and chiral sumanenes.

Conductivity (up to 4 S cm^{-1}) of the NGCs was demonstrated.[21]

3. Summary and Perspectives

We summarized the chemistry of **1**, including the synthesis, structure, dynamics, derivatization, complexation with transition metals, charge carrier mobility, and conversion to NGCs, based on our continuous study. The study of sumanenes in other research groups includes that of heterasumanenes and chiral sumanenes,[47] as shown in Figure 7. Most studies were reported from Japan, which may be triggered by the fact that **1** was first synthesized in Japan. In the future, π bowls based on **1** may lead to the development of novel electrical materials, organometallic catalysts, and other applications. For these applications, a next-generation synthetic procedure that allows more practical and low-cost synthesis is required, as in the preceding case for **2**.[48]

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[20] T. Amaya, M. Okada, Y. Inada, T. Hirao, unpublished results. **15b**: ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.65$ (d, $J = 7.8$ Hz, 1H), 7.63 (d, $J = 7.8$ Hz, 1H), 7.29–7.21 (m, 6H), 7.19–7.12 (m, 6H), 7.09 (d, $J = 8.2$ Hz, 2H), 7.04 (d, $J = 8.2$ Hz, 2H),

6.99 (d, $J = 8.2$ Hz, 2H), 6.50 (d, $J = 5.7$ Hz, 1H), 6.48 (d, $J = 5.7$ Hz, 1H), 6.15 (d, $J = 8.0$ Hz, 1H), 6.12 (d, $J = 8.0$ Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 2.37 (s, 3H), 2.35 ppm (s, 3H). The molar ratio of C_3-symmetric and unsymmetric isomers is approximately 1:3, as determined by the integral ratio. The number of protons is based on the unsymmetric isomer. HRMS (MALDI-TOF): *m*/*z* calcd for $C_{42}H_{28}N_3^+$ $[M\text{+H}]^+$: 574.2278; found: 574.2275.

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[32] T. Amaya, M. Okada, K. Kobayashi, T. Hirao, unpublished results. **31**: ^{1}H NMR (600 MHz, CD_2Cl_2): $\delta = 7.22$ (d, $J = 7.8$ Hz, 4H), 7.17 (d, $J = 7.8$ Hz, 4H), 7.14 (s, 4H), 4.74 (d, $J = 19.2$ Hz, 4H), 4.43 (s, 2H), 3.47 ppm (d, $J = 19.2$ Hz, 4H).

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