

Creation of Hoop- and Bowl-Shaped Benzenoid Systems by Selective Detraction of [60]Fullerene Conjugation. [10]Cyclophenacene and Fused Corannulene Derivatives

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Abstract: Selective penta-addition of a methylcopper reagent followed by addition of a phenylcopper reagent to a suitably modified synthetic intermediate results in creation of 40π -electron systems—hoop- and bowlshaped cyclic benzenoid compounds, [10]cyclophenacene, and dibenzo-fused corannulene derivatives. The 40π -electron cyclophenacene derivatives have been found to be chemically stable, yellow-colored, luminescent (560 nm), and EPR-silent. X-ray crystallographic analysis provided precision structural data sets. The dibenzo-fused corannulene derivatives exhibit blue-green (460 nm) to red (649 nm) fluorescence.

Introduction

Among numerous ways to look at [60]fullerene,¹ there is a structural chemists' view to identify various unconventional aromatic systems in this spherical molecule. For instance, one may remove the "north pole" and the "south pole" of the fullerene molecule to generate the polyene structure of a hoopshaped 40π -electron cyclic benzenoid A, [10]cyclophenacene (Figure 1a).^{2–4} Having thus far remained hypothetical,^{5–7} such hoop-shaped benzenoid compounds have attracted the interest of chemists for half a century⁸ because of a questions about their aromaticity,⁹ their potential utilities in materials science,⁵ and their structures that have challenged synthetic chemists for a number of years.⁶ They have recently become the subject of interest of the broader scientific community because they comprise a part of carbon nanotubes (CNT).^{10–12} An alternative

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Figure 1. [10]Cyclophenacene, fused corannulene, and its carbonsubstituted derivatives. (a) Hoop-shaped molecule C40H20 (A, D5d symmetry). (b) Bowl-shaped molecule, fused corannulene $C_{30}H_{12}$ (**B**, $C_{2\nu}$ symmetry). (c) Dibenzo-fused corannulene $C_{38}H_{16}$ (C, $C_{2\nu}$ symmetry) and *p*-phenylene-bridged dibenzo-fused corannulene $C_{44}H_{20}$ (**D**, C_s symmetry). (d) [10]Cyclophenacene embedded in a fullerene framework $C_{60}R^{1}_{5}R^{2}_{5}H_{2}$ (1 and E). (e) p-Phenylene-bridged dibenzo-fused corannulene in a fullerene framework (3 and F). (f) Dibenzo-fused corannulene in a fullerene framework (4 and G).

view of [60]fullerene may generate hemispherical bowl-shaped aromatic systems.^{13,14} For instance, a bowl-shaped aromatic system, fused corannulene B (C₃₀H₁₂, Figure 1b), can be identified as a half of fullerene.¹⁵ In this article, we describe

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Figure 2. Synthesis of [10]cyclophenacene derivatives and fused corannulene derivatives. Reaction conditions: a, (1) MeMgBr (30 equiv), CuBr·SMe₂ (30 equiv), DMI (30 equiv) in THF/o-dichlorobenzene, (2) NH₄Cl/H₂O; b, (1) 'BuOK (1.1 equiv) in THF, (2) TsCN (1.2 equiv) in PhCN; c, (1) PhMgBr (30 equiv), CuBr·SMe₂ (30 equiv), DMI (30 equiv) in THF, (2) NH₄Cl/H₂O; d, (1) Li⁺[C₁₀H₁₀]⁻ (30 equiv) in PhCN, (2) NH₄Cl/H₂O; e, (1) PhMgBr (30 equiv), CuBr·SMe₂ (30 equiv), 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene (30 equiv) in THF/o-dichlorobenzene, (2) HCl/H₂O; f, (1) KH in THF, (2) under air in THF; g, (1) 'BuOK (1.1 equiv) in THF, (2) [PdCl(π -allyl)]₂; h, (1) 'BuOK (1.1 equiv) in THF, (2) [RhCl(cod)]₂; i, (1) Li⁺[C₁₀H₁₀]⁻ (30 equiv) in PhCN, (2) EtOH, (3) NH₄Cl/H₂O. For 1, 2, 3, 4, 7, 9, 10, and 11, isomers always formed with respect to the relative stereochemistry of the top and the bottom pentagons (only one isomer is shown in this figure).

the full details of our recent communication on the creation of the first hoop-shaped, [10]cyclophenacene conjugated structure **1** (Figure 1d) by selective detraction of the fullerene conjugation,³ as well as on the isolation of **3** and **4** (Figure 1e,f) that possess a dibenzo-fused corannulene conjugation **C** and its *p*-phenylene derivative **D** (Figure 1c).

Results and Discussion

Synthetic Strategy. Our approach shown in Figure 2 relies on our own synthetic method that converts [60]fullerene exclusively and quantitatively into a cyclopentadiene compound, **5**, by the reaction of [60]fullerene with a methylcopper reagent derived from MeMgBr and CuBr·SMe₂.¹⁶ Repetition of the reaction on the bottom 50π -electron part of **5** should directly produce the desired cyclic 40π -electron system in three overall steps from [60]fullerene. However, it did not take place at all; the copper reagent deprotonates **5** to generate the corresponding cyclopentadienyl anion, which is entirely unreactive toward further addition reactions (because of the homoconjugation between the cyclopentadienide and the bottom 50π -electron system).¹⁷ To circumvent this problem, we temporarily protected the acidic hydrogen atom in **5** with a cyano group, which was later removed after the second penta-addition was achieved. The second penta-addition to the nitrile **6** was successful with a phenylcopper reagent to give, in 18% yield, the first hoop-shaped aromatic compound, **2**, as a mixture of three isomers, owing to the relative position of the cyano group and the bottom hydrogen atoms. The reaction of methylcopper to cyanide **6** was much less clean than we hoped it would be. The cyano group was removed by lithium naphthalenide reduction to give the di-protio compound **1**. Oxidation of its di-potassium compound with air afforded the oxidized product **7**. X-ray crystallographic analysis of **7** and a palladium derivative, **8**, gave the information on the structure of the first hoop-shaped aromatics (vide infra).

The poor yield (18%) of **2** was due to formation of numerous side products, resulting largely from the formation of two sideway adducts **3** and **4**, each of which comprises many isomers due to the relative location of the hydrogen atoms attached to the fullerene core. Careful product identification and optimization of the reaction conditions allowed us to isolate **3** in 32% yield and to convert it to **4** in high yield. The structure determination of this side-way adduct was achieved by conversion to rhodium complex **9** followed by X-ray crystallographic analysis. Alternatively, we could optimize the conditions to obtain the dibenzo-fused corannulene conjugation system, **4**,

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Figure 3. Crystal structure of $6 \cdot (CH_2Cl_2)_{0.5}$. (a) ORTEP drawing. CH_2Cl_2 molecules found in the unit cell and disordered carbon and nitrogen atoms of the cyano group are omitted for clarity. (b) Top view of CPK model. (c) Side view of CPK model.

directly from **6**. The formation of two products, **2** and **4**, is obviously due to the presence of six radialene-type pentagons in **6**, all of which can react with the organocopper reagent. The details of the synthesis and the properties of the [10]cyclophenacene and the dibenzo-fused corannulene are described below.

Synthesis of [10]Cyclophenacenes and Dibenzo-Fused Corannulenes. The synthesis started with penta-methylated [60]fullerene 5,^{16b} which was synthesized in 92% isolated yield from [60]fullerene. It was treated first with 'BuOK and then with *p*-toluenesulfonyl cyanide (TsCN) in benzonitrile to obtain the cyano fullerene 6 in 81% yield. The structure of this compound was confirmed by X-ray crystallographic analysis (Figure 3). In this synthetic sequence, the electronegative cyano protective group also acts to increase the electrophilicity of the 50π -electron system (the first reduction potential of 6 is -1.35 V (Fc/Fc⁺) in tetrahydrofuran (THF); those of 5 and [60]fullerene are -1.48 V (Fc/Fc⁺) in THF and -0.98 V in toluene/acetonitrile, respectively).¹⁸

Treatment of **6** with a phenylcopper reagent in the presence of *N*,*N'*-dimethylimidazolidinone (DMI) afforded the [10]cyclophenacene C₆₀(CN)Me₅Ph₅H (**2**) in 14% isolated yield as a mixture of three isomers.¹⁹ The cyanide group in **2** was reductively removed by treatment with lithium naphthalenide in benzonitrile to obtain C₆₀Me₅Ph₅H₂ (**1**) in 82% yield. This compound was found not to give any EPR signals (solid, at 4 K). In agreement with its closed-shell, aromatic (vide infra) character, the 40 π -electron system was found to be chemically stable.

Conversion of the sp² carbon atoms in the polar cyclopentadiene moieties into sp³ hybridization was then examined. Treatment of **1** with potassium hydride followed by exposure to molecular oxygen afforded the penta-oxygenated product $C_{60}Me_5Ph_5O_3(OH)_2$ (**7**). High-resolution APCI-TOF MS of **7** showed that five oxygen atoms attached to the fullerene core. X-ray structural analysis of **7** revealed the molecular structure (Figure 4). In the north pole of **7**, the cyclopentadienyl anion was oxidized into a hydroxy bis(epoxide) (Figure 5, I). A similar part structure has been reported by Taylor et al.²⁰ on $C_{60}Me_5O_2$ -(OH), obtained by a reaction of $C_{60}Cl_6^{21}$ with excess MeLi. The



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Figure 4. Crystal structure of $7 \cdot (C_6H_5Cl)_{1.5}$. (a) ORTEP drawing. C_6H_5Cl molecules found in the unit cell and disordered oxygen atoms are omitted for clarity. (b) Top view of CPK model. (c) Side view of CPK model.



Figure 5. Oxidation product of the [60]fullerene pentagon.



Figure 6. Crystal structure of $8 \cdot C_6H_5Cl$. (a) ORTEP drawing of one of the two crystallographically independent molecules of $8 \cdot C_6H_5Cl$ molecules found in the unit cell and disordered cyano groups are omitted for clarity. (b) Side view of CPK model. (c) Bottom view of CPK model.

south pole cyclopentadienyl anion was oxidized into a hydroxy mono-epoxide (Figure 5, II). Our oxidation procedure, via a dianion compound, cleanly gives the epoxide of the pentaphenyl derivative II, but none of the benzo-furan compound III reported previously.²² Bis-epoxidation giving I-type product did not take place on the south pole, likely because of both steric and electronic effects of the five phenyl groups. The hoop-shaped 40π -electron system was not oxidized at all under these conditions (or any other conditions so far).

Deprotonation of the cyclopentadiene in **2** with 'BuOK in THF afforded an anion $[K(THF)_n][C_{60}(CN)Me_5Ph_5]$, which reacted with $[PdCl(\pi-allyl)]_2$ to give a palladium complex, Pd- $[C_{60}(CN)Me_5Ph_5](\pi-allyl)$ (**8**),²³ as a single isomer in 57% yield. The ¹³C NMR data showed the C_s symmetric structure of **8**, whose signals due to the cyclophenacene carbon atoms appeared at 144–158 ppm. The crystal structure of **8** is shown in Figure 6. The metrical data of **7** and **8** will be discussed in detail in the following section.

Thorough analysis and separation of a product mixture of the reaction of cyanide 6 and phenylcopper reagents allowed

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For other nickel, palladium, and platinum complexes of the penta(organo)-[60]fullerenes, Pd(C₆₀R₅)(π-allyl) (R = Me, Ph), see: Kuninobu, Y.; Matsuo, Y.; Toganoh, M.; Sawamura, M.; Nakamura, E. Organometallics 2004, 23, 3259-3266.



Figure 7. Crystal structure of 9. (THF)3. (a) ORTEP drawing. THF molecules found in the unit cell and disordered cyano group due to a mixture of three regioisomers are omitted for clarity. (b) Top view of CPK model. (c) Side view of CPK model.

us to identify the dibenzo-fused corannulene, C₆₀(CN)Me₅Ph₃H (3), and its phenylene derivative, $C_{60}(CN)Me_5Ph_5H$ (4), as a mixture of isomers with respect to the position of the cyano group and the hydrogen atom attached to the fullerene core. Optimization of the conditions by the use of DMI as an additive led to the production and isolation (silica gel column chromatography with CS₂/toluene elution) of the triphenyl compound 3 in 32% yield as a mixture of five isomers. While 3 was found not to react further with the phenylcopper reagent under the same conditions, it reacted smoothly in the presence of 1,4dicyclohexyl-1,4-diaza-1,3-butadiene to afford the dibenzo-fused corannulene (4) in 91% isolated yield (an inseparable mixture of 13 regioisomers). Alternatively, treatment of 6 with the phenylcopper reagent in the presence of the diazabutadiene directly afforded 4 in 32% yield and 2 in 18% yield. The cyano group in 3 and 4 was removed by lithium naphthalenide reduction in benzonitrile to give di-protio products 10 and 11, respectively. Rigorous structural identification of 3 and 4 was hampered by the presence of many isomers, but it was finally achieved for 3 through the synthesis and crystallographic analysis of a rhodium derivative (Figure 7). Compound **3** was converted to the corresponding potassium salt, which was treated with [RhCl(cod)]₂ to afford a rhodium 1,5-cyclooctadiene complex Rh[C₆₀(CN)Me₅Ph₃](cod) (9) in 88% yield. The complex, 9, is an η^5 -indenylmetal complex, similar to the one reported for a [70]fullerene derivative,²⁴ and consisted of a mixture of three regioisomers with respect to the location of the cyano group. The structural features of the bowl-shaped aromatic system are described in the following section. On the basis of the product ratio (18% for 2 and 32% for 4), the carbon atom on the south pole pentagon appears to be slightly more reactive than those on the remaining five pentagons in the "southern hemisphere".

Structure and Properties of [10]Cyclophenacene. (a) Structural Analysis. X-ray crystallographic structures were determined for [10]cyclophenacene derivatives 7 and 8 (Table 1; refer to Figure 8 for the location of bonds a-g). Whereas the double bonds on the edge are quite short (bonds a and g are 1.36(2) and 1.37(2) Å for 7 and 1.36(1) and 1.37(2) Å for 8, respectively), bond alternation in the "equator" region is very small (c, e = 1.43(1) and d = 1.40(2) Å for 7, and c = 1.43(1), e = 1.44(2), and d = 1.40(2) Å for 8, respectively). The unsymmetrical substitution (methyl vs phenyl groups) and the coordination of the palladium atom have little effect on the



Figure 8. NICS values in $C_{40}H_{20}$ (A, D_{5d} symmetric constant) and C60H12 (E, C2h symmetric constant). Color coding shows NICS-based aromaticity of the rings (red, aromatic, NICS < -4.0; blue, nonaromatic, NICS > -4.0). The NICS calculations were performed at the GIAO-SCF/ 6-31G*//HF/6-31G* level for the B3LYP/6-31G* geometry.

Table 1. Experimental Data (Standard Deviation in Parentheses) from X-ray Crystallographic Analysis and Theoretical Optimized Structures of Model Compounds A (C40H20) and E (C60H12)

	bond length (Å) ^{a,b}									
compounds	а	b	С	d	е	f	g			
7 (X-ray)	1.37(2)	1.44(2)	1.43(1)	1.40(2)	1.43(1)	1.45(1)	1.36(1)			
8 (X-ray)	1.36(1)	1.45(1)	1.43(1)	1.40(2)	1.44(2)	1.44(2)	1.37(2)			
A (HF)	1.35	1.44	1.43	1.38						
A (B3LYP)	1.37	1.44	1.45	1.42						
A (PM3)	1.36	1.43	1.44	1.40						
E (HF)	1.35	1.44	1.43	1.38						
E (B3LYP)	1.37	1.45	1.44	1.39						
E (PM3)	1.37	1.44	1.44	1.40						

^a a, b, c, d, average lengths of five equivalent bonds; e, f, g, average lengths of 10 equivalent bonds. Calculated data for A and E refer to the geometry optimized structures (D_{5d} symmetry and C_{2h} symmetry, respectively) obtained by the hybrid density functional method (B3LYP), the Hartree-Fock ab initio method (HF) using the 6-31G* basis set, and the semiempirical PM3 method. ^b Bond coding (a-g) is shown in Figure 8.

structure. This experimental structure obviously does not conform to the "ideal graphitic structure", which was assumed in most of the previous theoretical studies of CNTs.25 The geometries of the model compounds $C_{40}H_{20}$ (A) and $C_{60}H_{12}$ (E) (Figures 1 and 8) were optimized with quantum mechanical calculations at various levels of theory (semiempirical, Hartree-Fock, and hybrid density functional methods)²⁶ and were found to reproduce the experimental data very well (Table 1). Note that, in contrast to the [10]cyclophenacenes, there is distinctive bond alternation in [60]fullerene (1.36 vs 1.47 Å),²⁷ in 1,3butadiene (1.35 vs 1.47 Å),²⁸ and in 20π cyclic *cis*-polyacetylene (1.36 vs 1.46 Å, B3LYP/6-31G*-optimized, see Supporting Information).

(b) Aromaticity of [10]Cyclophenacenes. Nucleus independent chemical shift (NICS)²⁹ is a useful measure of the magnetic

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Table 2. Bond Lengths of the Dibenzo-Fused Corannulene Moiety in 9, C, D, F, and G

	bond length (Å) a														
compounds	а	b	С	d	е	f	g	h	i	j	k	I	m	n	0
9 ^b (X-ray)	1.44(2)	1.43(1)	1.40(2)	1.44(2)	1.40(1)	1.37(1)	1.44(2)	1.46(1)	1.43(2)	1.40(2)	1.44(1)	1.42(1)	1.42(2)	1.37(1)	1.44(2)
C (PM3)	1.432	1.464	1.396	1.445	1.353	1.380	1.430	1.452	1.430	1.376	1.461	1.403	1.391	1.383	1.397
C (B3LYP)	1.436	1.486	1.409	1.431	1.351	1.393	1.420	1.446	1.435	1.383	1.472	1.407	1.447	1.388	1.400
C (HF)	1.435	1.487	1.385	1.426	1.328	1.374	1.413	1.448	1.435	1.359	1.476	1.400	1.427	1.375	1.392
D ^c (PM3)	1.442	1.451	1.394	1.446	1.370	1.368	1.445	1.445	1.442	1.381	1.451	1.419	1.393	1.380	1.420
D ^c (B3LYP)	1.442	1.471	1.405	1.4.37	1.374	1.379	1.437	1.440	1.442	1.390	1.467	1.421	1.434	1.388	1.423
F ^c (PM3)	1.444	1.451	1.388	1.458	1.381	1.368	1.446	1.461	1.444	1.384	1.454	1.432	1.393	1.375	1.436
\mathbf{F}^{c} (B3LYP)	1.438	1.447	1.402	1.451	1.396	1.377	1.438	1.454	1.439	1.397	1.452	1.422	1.408	1.384	1.433
G (PM3)	1.445	1.449	1.388	1.458	1.381	1.366	1.445	1.460	1.443	1.384	1.453	1.430	1.391	1.375	1.428
G (B3LYP)	1.438	1.446	1.402	1.450	1.397	1.375	1.438	1.455	1.439	1.397	1.451	1.422	1.407	1.383	1.425
G (HF)	1.435	1.441	1.379	1.445	1.374	1.355	1.432	1.452	1.437	1.373	1.448	1.415	1.386	1.364	1.419

^{*a*} Bond coding (a–o) is shown in Figure 9 **C**. Bond coding in other geometries is similar to the bond coding of **C** in dizenzo-fused corannulene part structure. Calculated data for **C**, **D**, **F**, and **G** refer to the geometry optimized structures (C_{2h} symmetry for **C** and **G**, C_s symmetry for **D**, and C_1 symmetry for **F**, respectively) obtained by the hybrid density functional method (B3LYP), the Hartree–Fock ab initio method (HF) using 6-31G* basis set, and the semiempirical PM3 method. ^{*b*} Average bond lengths from X-ray single-crystal analysis (standard deviation in parentheses). ^{*c*} Average bond lengths from optimized geometry.

shielding effect of aromatic ring current. Analysis of the NICS values for six-membered rings of cyclophenacene in the model compounds **A** and **E** indicates that the hoop-like 40π -electron system is aromatic (Figure 8, NICS = -8.62 and NICS = -11.46 to -11.99, respectively) and the other rings in **E** are nonaromatic (NICS = -1.27 to 0.30). The center of gravity (CG; NICS = -7.25 and NICS = -11.58) is predicted to be subject to an aromatic shielding effect (a value experimentally provable by ³He NMR experiments).³⁰ We ascribe the difference in the NICS values between **A** and **E** to the effect of the σ skeleton.³¹

Since Heilbronner proposed hypothetical hoop-shaped benzenoid "cyclacene" in 1954,8a the aromaticity of cyclic benzenoids has attracted much interest, and chemists have attempted in vain to synthesize such molecules in the past half century. Houk et al.9b and Kim et al.9a predicted that "cycloanthracene" has a double "trannulene" structure and a small HOMO-LUMO gap, making it rather unstable. On the other hand, "cyclophenacene" was suggested by Aihara et al.^{9d} and Türker et al. to enjoy a large degree of conjugative stabilization.^{9c} The 40π electron conjugated system in compounds 1 and 7 showed low chemical reactivity and was EPR-silent. In addition, delocalized benzenoid structures were found by the X-ray single-crystal analysis of 7 and 8. This class of compounds has rather large HOMO-LUMO gaps,¹¹ and the NICS values of model compounds A and E also revealed large aromatic shielding effects at all hexagons in the 40 π -electron system. We thus conclude that the 40π -electron cyclic benzenoid molecules stabilize themselves by conjugative stabilization, as has been predicted.

Subsequently, a theoretical study on a series of [5,5] and [6,6] armchair nanotubes up to the carbon number of 200¹¹ showed that the present cyclophenacene represents the first compound in a series of finite CNTs, whose chemical properties are predicted to change periodically as the tube is elongated by a layer-by-layer addition of carbon atoms. This prediction based on the frontier molecular orbital energies was recently confirmed by the theoretical study on the reactivity of CNTs toward fluorine atom and a carbene-reactive intermediate.^{12,32}



Figure 9. NICS values of the model compounds **B**, **C**, **D**, **F**, and **G** (GIAO–SCF/6-31G*//HF/6-31G* for the B3LYP/6-31G* geometry). Color coding shows NICS-based aromaticity of the rings (red, aromatic, NICS < -4.0; blue, nonaromatic, NICS > -4.0). Refer also to Figure 1 for whole structures of **F** and **G**.

Structure and Properties of Dibenzo-Fused Corannulene. (a) Structural Analysis. The X-ray crystallographic analysis of 9 provided the experimental structural data of this intriguing aromatic system, a dibenzo-fused corannulene embedded in a fullerene skeleton (Table 2). The bond alternation found in the crystal structure is as shown in Figure 9 and closely follows the pattern found in [60]fullerene. The bond lengths obtained from the experimental structure of 9 agrees within 1.1% error with the calculated structures of the two model fullerene-derived compounds F and G and shows a bond alternation pattern similar to those of corannulene and tetramethyl-fused corannulene.^{15e} Such agreement of bond lengths indicates that the fullerene framework and the dibenzo-conjugation added to the parent corannulene structure have a rather small structural effect despite a rather large difference of hybridization of the carbon atoms.33

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⁽³¹⁾ Dihedral angles between the two planes including the bonds [a and b] and [d and e] on the 10 hexagons = 22.9° (A) and $2.9(4)^{\circ}$ (E).

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Figure 10. Absorption and emission spectra of [10]cyclophenacene derivatives and dibenzo-fused corannulene derivatives. (a) C₆₀Me₅Ph₅H₂ (1, 1.0 \times 10⁻⁵ M in cyclohexane) and C₆₀Me₅Ph₅O₃(OH)₂ (7, 1.0×10^{-5} M in cyclohexane). (b) C_{60}Me_5Ph_5H_2 (1, 1.0×10^{-5} M in cyclohexane), $C_{60}(CN)Me_5Ph_3H$ (3, 1.0 × 10⁻⁵ M in cyclohexane), and $C_{60}(CN)Me_5Ph_5H$ (4, 1.0 × 10⁻⁵ M in cyclohexane). The intensities of emission spectra of 3 and 4 are magnified $\times 8$ and $\times 2$, respectively.

(b) Aromaticity of Dibenzo-Fused Corannulenes. In light of good agreement of the calculated and experimental geometry (vide supra), we studied the aromaticity NICS calculations. The NICS data for various compounds are summarized by red/blue color coding in Figure 9. All hexagons are aromatic (colored in red, NICS = -14.26 to -4.04), and the two five-membered rings are nonaromatic (blue, NICS = -1.94 to 7.12). These results agree with the pattern of bond alternation found by experiment and by theory.

Absorption and Emission Spectra of [10]Cyclophenacenes and Dibenzo-Fused Corannulenes. The absorption spectra of the [10]cyclophenacene molecules (1 and 7 in cyclohexane) are similar to each other, showing a maximum at ca. 260 nm, with broad absorption that extends to ca. 500 nm (Figure 10a). The [10]cyclophenacene derivatives 1 and 7 emit bright yellow light ($\lambda_{\text{max}} = \sim 560 \text{ nm}$ and $\sim 620 \text{ nm}$) with quantum efficiency (Φ) of 0.10 in cyclohexane (irradiation at 366 nm, rhodamin B as standard, see Experimental Section). The dibenzo-fused corannulene 4 exhibits blue-green fluorescence, with a maximum at 460 nm ($\Phi = 0.028$, Figure 10b), and the *p*-phenylenebridged compound 3 emits red light, with a maximum at 649 nm ($\Phi = 0.012$). The maximum wavelength of **3** is redshifted ca. 100 nm and that of 4 is blue-shifted ca. 100 nm, as compared with 1, respectively. The large shift of the maximum wavelength between 3 and 4 indicates that cyclic conjugation in the p-phenylene-bridge compound 3 greatly affects the photoluminescent property. The wavelengths of the luminescence

are in qualitative agreement with the HOMO-LUMO gap calculated for simplified model compounds E, F, and G.³⁴ We expect that the photophysical properties of the compounds can also be modified by changing the R^{1}/R^{2} organic groups.^{35–37} Metal complexes 8 and 9, however, are not luminescent, probably because of quenching of the excited state by the transition metals.

Summary

In summary, we have accomplished the first synthesis of a hoop-shaped cyclic benzenoid system, [10]cyclophenacene, by selective removal of conjugation out of the [60]fullerene π -electron array and have also found an effective synthetic route to corannulene-type π -electron conjugated systems. The experimental data on the [10]cyclophenacenes provided the first information on the precision structure and chemical and physical properties of a class of hoop-shaped cyclic benzenoid, which enjoys a high degree of conjugative stabilization. The present route offers flexibility of installation of functional groups to these new benzenoid systems $^{35-38}$ so that, for instance, we can control the solubility, synthesize metal complexes, and make composite materials out of these functionalized molecules. The syntheses of palladium complex 8 and rhodium complex 9 suggest that the compounds 1, 10, and 11 can be used as starting materials for the synthesis of previously unavailable classes of organometallics.³⁹ Finally, we expect that similar multipleaddition reactions would also be possible for higher fullerenes to provide an access to other classes of novel aromatic compounds.

Experimental Section

General. All manipulations involving air- and moisture-sensitive compounds were carried out using the standard Schlenk technique under nitrogen or argon. Hexane and THF were distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation before use. Toluene was distilled from Na and thoroughly degassed by trap-to-trap distillation. Chloroform-d was distilled from CaH2 and thoroughly degassed by trap-to-trap distillation. THF-d₈ was distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation. o-Dichlorobenzene was distilled from CaH2 under nitrogen and stored over molecular sieves. Benzonitrile was distilled from P2O5 under nitrogen and stored over molecular sieves. All commercially available reagents were distilled or recrystallized before use. 'BuOK in THF was purchased from Aldrich Inc. and used as received. 1,4-Dicyclohexyl-1,4-diaza-1,3-butadiene was prepared according to the literature.⁴⁰

 $^1\mathrm{H}$ (400 MHz, 500 MHz) and $^{13}\mathrm{C}$ (100 MHz, 125 MHz) NMR spectra were measured on JEOL EX 400 and ECA 500 spectrometers.

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⁽³³⁾ Compounds 9, F, and G show larger p-orbital axis vector (POAV) angles (8.0–12.8°) than C (0.0–11.0°). For the POAV angle, see: (a) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137–142. (b) Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243–249. (c) Haddon, R. C. *Science* **1993**, *261*, 1545–1550.

⁽³⁴⁾ HOMO-LUMO gaps of model compounds E, F, and G obtained from

^{432 - 433}

Table 3.	Crystal [Data and	Structure	Analysis	Results	for (6, 7	7,8	, and	9
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	6-(CH ₂ Cl ₂) _{0.5}	7-(C ₆ H ₅ Cl) _{1.5}	8•C ₆ H₅CI	9 •(C ₄ H ₈ O) ₃
formula	C _{68.5} H ₁₆ N ₁ Cl ₁	C104H46Cl1.5O4	C105H50Cl1N1Pd1	C100H66N1Rh1
crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	Fdd2 (No. 43)	$P 2_1/a$ (No. 14)	$P 2_1/n$ (No. 14)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)
$R, R_w (I > 2\sigma(I))$	0.033, -	0.145, 0.365	0.105, 0.270	0.079, 0.198
R1, $wR2$ (all data)	$-, 0.036^{a}$	0.243, 0.427	0.180, 0.324	0.096, 0.216
GOF on F^2	3.112	1.265	0.993	1.040
a (Å)	29.7502(4)	19.7450(15)	14.9920(17)	14.3460(7)
$b(\mathbf{A})$	24.2689(7)	16.5410(20)	27.5470(20)	14.5830(14)
c (Å)	20.0769(7)	20.0340(30)	32.7300(14)	32.1220(3)
α (deg)	90	90	90	90
β (deg)	90	91.6750(60)	97.044(5)	90
γ (deg)	90	90	90	90
$V(Å^3)$	14495.6(7)	6540.4(13)	13415(5)	6720.2(9)
Z	8	4	8	4
$T(\mathbf{K})$	293(2)	153(2)	173(2)	173(2)
crystal size (mm)	0.50, 0.33, 0.25	0.20, 0.05, 0.05	0.25, 0.21, 0.20	0.50, 0.20, 0.15
D_{calcd} (g/cm ³)	1.58	1.435	1.453	1.463
$2\theta_{\min}, 2\theta_{\max}$ (deg)	4.58, 51.22	4.54, 51.3	4.12, 51.5	4.72, 51.24
no. refln measured (unique)	12396	9281	21958	6563
no. refln measured $(I > 2\sigma(I))$	4267	3456	9462	5385
no. parameters	654	1433	1944	910
$\Delta (e \dot{A}^{-3})$	0.25, -0.33	1.29, -1.58	2.696, -1.773	0.182, -0.831

^{*a*} A final *R* index is calculated with $I > 3\sigma(I)$.

When chloroform-*d* and THF- d_8 were used as solvent, the spectra were referenced to residual solvent protons in the ¹H NMR spectra (7.26 and 3.58 ppm, respectively) and to solvent carbons in the ¹³C NMR spectra (77.0 and 67.4 ppm, respectively). Other spectra were recorded by the use of the following instruments: IR spectra, JASCO IR-420 and ReactIR 1000; UV/vis spectra, Hitachi U3500; fluorescence spectra, Hitachi F4010; and mass spectra, Shimadzu LCMS-QP8000 and JEOL JMS SX102.

X-ray Crystallographic Analysis. Single crystals of 6, 7, 8, and 9 suitable for X-ray diffraction study were grown and subjected to data collection. The data sets were collected on a MacScience DIP2030 imaging plate diffractometer using Mo Ka (graphite monochromated, $\lambda = 0.71069$ Å) radiation. Crystal data and data statistics are summarized in Table 3. The structure of 6 was solved by the directed method (SIR97).41 The positional and thermal parameters of nonhydrogen atoms were refined anisotropically on F^2 by the fullmatrix least-squares method, using SHELXL-97.42 Hydrogen atoms were placed at calculated positions and refined "riding" on their corresponding carbon atoms. In the subsequent refinement, the function $\sum \omega (F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \sum (||F_0| - |F_c||) / \sum |F_0|$ and wR2 = $[\sum \omega (F_o^2 - F_c^2)^2 / \sum (\omega F_o^4)]^{1/2}$. The crystal of **8** contains two crystallographically independent molecules. While both compounds 6 and 8 consist of single isomers, crystallographic disorder of the cyano groups was observed. The crystal of 9 consists of a mixture of three regioisomers with respect to the cyano group. It could not be determined whether compound 7 (obtained as five regioisomers) crystallizes into a single isomer or not, since the structure of 7, except for disordered oxygen atoms, has pseudo- C_5 symmetry.

Theoretical Calculations. All theoretical calculations were performed with the Gaussian 98 package.⁴³ The PM3, the Hartree–Fock, and the B3LYP calculations with the 6-31G* basis sets were used for the geometry optimization of model compounds (**A**, **B**, **C**, **D**, **E**, **F**, and **G**). The nucleus-independent chemical shift (NICS) at the ring centers was calculated at the GIAO–SCF/6-31G*//HF/6-31G* level for the B3LYP/6-31G* geometries. **Electrochemical Measurements.** Cyclic voltammetry (CV) was performed using a BAS CV-50W voltammetric analyzer and threeelectrode cell, with a glassy carbon working electrode and a platinum wire counter electrode. All potentials were recorded vs a Ag/Ag⁺ reference electrode and corrected against Fc/Fc⁺. CV was measured at a scan rate of 100 mV/s.

UV–Vis Absorption and Fluorescence Measurements. Fluorescence spectra were measured on the HITACHI F4010 spectrometer using a 1.0×10^{-5} M solution of 1, 3, 4, and 7. All solutions were prepared in spectrograde cyclohexane that was purged with argon prior to the measurements. Fluorescence quantum yields were determined using recrystallized rhodamin B ($\Phi = 0.71$ in ethanol) as a standard.⁴⁴

Preparation of C_{60}Me_5H (5). A white suspension of CuBr·SMe₂ (4.28 g, 20.8 mmol) in THF (30 mL) was treated at 23 °C with a solution of MeMgBr (1.0 M, 20.8 mL, 20.8 mmol) in THF and with DMI (2.25 mL, 20.8 mmol). To the resulting yellow suspension, a solution of C₆₀ (500 mg, 0.694 mmol) in *o*-dichlorobenzene (50 mL) was added. After being stirred for 1 h at 23 °C, the reaction was quenched with NH₄Cl (aqueous, 0.5 mL). The mixture was diluted with toluene (250 mL) and filtered through a pad of silica gel. A red-colored eluent was concentrated to a small volume and then precipitated with Et₂O (300 mL). The precipitate was washed with EtOH and ether and dried in vacuo to obtain 1 (507 mg, 92% yield, 95% purity determined by HPLC). IR (KBr) 2957, 2918, 2856, 1575, 1548, 1521, 1444, 1417, 1370, 1343, 1324, 1285, 1262, 1235, 1200, 1170, 1146, 1127, 1092, 1054, 1034, 1011, 953, 830, 807, 745, 683 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.30 (s, 6H, CH₃), 2.32 (s, 6H, CH₃), 2.42 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 26.91 (2C, CH₃), 27.26 (2C, CH₃), 32.86 (1C, CH₃), 50.98 (2C, C₆₀), 51.12 (1C, C₆₀), 53.13 (2C, C₆₀), 59.22 $(1C, C_{60}), 142.89 (2C, C_{60}), 143.52 (2C, C_{60}), 143.74 (2C, C_{60}), 144.04$ (2C, C₆₀), 144.08 (2C, C₆₀), 144.28 (2C, C₆₀), 144.64 (2C, C₆₀), 144.82

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(2C, C₆₀), 145.27 (2C, C₆₀), 145.37 (2C, C₆₀), 146.39 (1C, C₆₀), 146.55 (2C, C₆₀), 146.66 (2C, C₆₀), 147.49 (2C, C₆₀), 147.53 (2C, C₆₀), 147.69 (2C, C₆₀), 147.76 (1C, C₆₀), 147.93 (2C, C₆₀), 148.00 (2C, C₆₀), 148.26 (2C, C₆₀), 148.32 (2C, C₆₀), 148.38 (2C, C₆₀), 149.57 (2C, C₆₀), 153.70 (2C, C₆₀), 153.74 (2C, C₆₀), 154.02 (2C, C₆₀), 157.17 (2C, C₆₀); APCI-MS (+) m/z = 796 [M⁺].

Synthesis of C₆₀Me₅CN (6). A solution of 'BuOK (0.69 mL, 0.69 mmol, 1.0 M in THF) was added to a suspension of C₆₀Me₅H (500 mg, 0.63 mmol, 94% purity) in PhCN (10 mL) at 23 °C. The color of the reaction mixture changed from red to black. A solution of TsCN (3.0 mL, 0.25 M in PhCN, 0.75 mmol) was added to the mixture. After it was stirred for 10 min, the reaction was quenched with HCl (aqueous, 0.20 mL). The solvent was removed, and the resulting red-colored solid was dissolved with CS₂. Purification on a pad of silica gel (CS₂ and toluene as eluent) afforded the fractions containing 6. The fractions were evaporated to a small volume. Precipitation with EtOH and then washing with Et2O and hexane afforded 6 (416 mg, 81% yield, 99% HPLC purity). Slow diffusion of ethanol to a methylene chloride solution of 6 gave a single crystal suitable for X-ray analysis. IR (KBr) 2963, 2920, 2860, 2229 (CN), 1641, 1547, 1445, 1418, 1374, 1264, 1239, 1200, 1106, 684, 658, 552, 522 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.38 (s, 6H, CH₃), 2.39 (s, 6H, CH₃), 2.64 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 25.36 (2C, CH₃), 26.80 (2C, CH₃), 32.35 (1C, CH₃), 51.12 (2C, C₆₀), 51.37 (1C, C₆₀), 52.62 (2C, C₆₀), 55.46 (1C, C₆₀), 118.08 (1C, CN), 143.02 (2C, C₆₀), 143.07 (2C, C₆₀), 143.93 (2C, C₆₀), 144.03 (2C, C₆₀), 144.10 (4C, C₆₀), 144.31 (2C, C₆₀), 144.35 (2C, C₆₀), 144.50 (2C, C₆₀), 145.10 (2C, C₆₀), 145.27 (2C, C₆₀), 146.71 (1C, C₆₀), 146.83 (2C, C₆₀), 146.85 (2C, C₆₀), 147.77 (2C, C₆₀), 147.91 (2C, C₆₀), 147.98 (1C, C₆₀), 148.03 (2C, C₆₀), 148.15 (2C, C₆₀), 148.31 (2C, C₆₀), 148.33 (2C, C₆₀), 148.50 (2C, C₆₀), 148.56 (2C, C₆₀), 148.68 (2C, C₆₀), 151.75 (2C, C₆₀), 152.24 (2C, C₆₀), 152.98 (2C, C₆₀), 156.37 (2C, C₆₀); HRMS (APCI-TOF, negative) m/z calcd for C₆₆H₁₅N₁ (M⁻), 821.12045; found, 821.12261.

Synthesis of [10]Cyclophenacene C₆₀(CN)Me₅Ph₅H (2) and p-Phenylene-Bridged Dibenzo-Fused Corannulene C₆₀(CN)Me₅Ph₃H (3). To a white suspension of CuBr·SMe2 (3.75 g, 18.3 mmol) in THF (31 mL) was added a solution of PhMgBr (0.93 M in THF, 20.0 mL, 18.6 mmol) at 23 °C, and then N,N'-dimethylimidazolidinone (2.05 mL, 25.4 mmol) was added immediately. To the resulting dark yellow solution, a solution of C₆₀(CN)Me₅ (515 mg, 0.608 mmol) in odichlorobenzene (50 mL) was transferred though a cannula. After being stirred for 24 h at 23 °C, the reaction was stopped with an addition of saturated NH₄Cl (aqueous, 0.20 mL). The mixture was diluted with toluene (200 mL) and filtered though a pad of silica gel. The solvent of an orange-colored eluent was evaporated, and the orange residue was purified by silica gel column chromatography (toluene/ CS_2 , 3:97). The fractions containing 2 were collected, and the solvent was evaporated to a small volume. Precipitation with MeOH afforded 2 (111 mg, 14% isolated yield) as a mixture of three stereoisomers. The fractions containing 3 were collected, and the solvent was evaporated to a small volume. Precipitation with MeOH afforded 3 (205 mg, 32% isolated yield) as a mixture of five stereoisomers. NMR and IR spectra were measured for the mixture of the stereoisomers.

2: IR (ReactIR, diamond prove) 3056, 3026, 2963, 2922, 2860, 2229 (CN), 1600, 1493, 1445, 1316, 1210, 1116, 1032, 1003, 950, 913, 684, 658 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.44–2.49 (s, 12H, CH₃), 2.66–2.68 (s, 3H, CH₃), 5.421, 5.424 and 5.448 (s, 1H, three signals of C₆₀-*H*), 7.12–7.27, 7.32–7.38, 7.43–7.47, 7.61–7.70 and 7.82–7.89 (m, 25H, C₆H₅); HRMS (FAB-MS, positive) *m*/*z* calcd for C₉₆H₄₁N₁ [M]⁺, 1207.3230; found, 1207.3236.

3: IR (ReactIR, diamond prove) 3059, 3027, 2962, 2923, 2863, 2229, 1593, 1583, 1493, 1445, 1375, 1297, 1243, 1156, 1031, 922, 759, 692, 676 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.03–2.19, 2.38–2.50, 2.68–2.76 and 3.02 (s, 15H, CH₃), 5.04, 5.07, 5.08, 5.09 and 5.12 (s, 1H, five signals of C₆₀-*H*), 7.16–7.38, 7.42–7.52, 7.57–7.82 and 8.12–8.16 (m, 15H, C₆H₅); ¹³C NMR (125 MHz, CDCl₃) δ 24.99–27.32,

31.58–33.22, 50.62–53.22, 54.82–54.84, 55.53–55.83, 57.45–57.65, 59.97–60.88, 118.65–118.70, 127.16–129.07, 134.01–160.33; HRMS (APCI-TOF, negative) m/z calcd for $C_{84}H_{30}N_1$ [M–H][–], 1052.2378; found, 1052.2396.

Synthesis of [10]Cyclophenacene $C_{60}Me_5Ph_5H_2$ (1). To a solution of C₆₀(CN)Me₅Ph₅H (80 mg, 66 mmol) in PhCN (20 mL) in a Schlenk tube was added a solution of lithium naphthalenide (2.6 mL, 0.76 M in THF, 2.0 mmol). The color of the solution changed immediately from yellow to dark red, indicating decyanation and formation of a bis-cyclopentadienyl dianion. After it was stirred for 1 h at 23 °C, the reaction mixture was quenched by the addition of saturated NH₄Cl (aqueous, 0.10 mL). The color of the resulting solution changed immediately from dark red to light red, indicating the protonation of the bis-cyclopentadienyl dianion took place. The mixture was diluted with toluene (100 mL) and filtered though a pad of silica gel. A redcolored eluent was evaporated to a small volume, and precipitation with MeOH afforded a crude product. This mixture was purified by HPLC (Nacalai Tesque, Buckyprep, 250 mm, toluene/2-propanol, 7:3). The fractions containing C60Me5Ph5H2 were collected and evaporated to a small volume. Precipitation with MeOH afforded C₆₀Me₅Ph₅H₂ (65 mg, 82% yield) of 98% purity by HPLC as a mixture of three isomers. NMR and IR spectra were measured for the mixture of the stereoisomers. IR (ReactIR, diamond prove) 3064, 3024, 2959, 2918, 2857, 1599, 1521, 1492, 1445, 1370, 1345, 1318, 1262, 1210, 1185, 1158, 1076, 1031, 950, 922, 812, 789, 752, 727, 682, 660 cm⁻¹; ¹H NMR (400 MHz, THF-d₈) δ 2.37-2.50 (s, 15H, CH₃), 4.847, 4.853 and 4.868 (s, 1H, three signals of C₆₀-H), 5.527 and 5.545 (s, 1H, three signals of C₆₀-H), 7.00-7.20, 7.30-7.33, 7.45-7.50, 7.60-7.70 and 7.89–7.91 (m, 25H, C₆H₅); UV-vis spectra (cyclohexane, ϵ) 261 (33 400), 278 (32 600), 334 (10 900), 380 (2500), 425 (2000), 454 (2900), 460 (3000) nm; HRMS (FAB, positive) m/z calcd for C₉₅H₄₂ (M⁺), 1182.3356; found, 1182.3320.

Synthesis of Dibenzo-Fused Corannulene (4). Method A: Synthesis from 6. To a brown suspension of CuBr·SMe₂ (150 mg, 0.73 mmol) and 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene (161 mg, 0.73 mmol) in THF (2.0 mL) was added a solution of PhMgBr (0.97 M in THF, 0.75 mL, 0.73 mmol) at 23 °C. To the resulting yellow suspension, a solution of 6 (20 mg, 23 μ mol) in *o*-dichlorobenzene (2.0 mL) was transferred though a cannula. After it was stirred for 40 h at 40 °C, the reaction was stopped by the addition of an aqueous HCl. The mixture was diluted with toluene (20 mL) and filtered though a pad of silica gel. An orange-colored eluent was concentrated and purified by HPLC (Nomura Chemical, RPFullerene, 250 mm, toluene/acetonitrile, 2:3). The fractions containing 4 were collected, and the solvent was evaporated to a small volume. Precipitation with MeOH afforded 4 (9.5 mg, 32% isolated yield with 98% HPLC purity) as a mixture of stereoisomers. NMR and IR spectra were measured for the mixture of the stereoisomers. IR (ReactIR, diamond prove) 3056, 3024, 2962, 2921, 2863, 2227 (CN), 1598, 1582, 1492, 1445, 1374, 1262, 1096, 1075, 1030, 753, 694 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.05-1.30, 1.47-1.77, 2.02-2.25, 2.36-2.67 and 2.82 (s, 15H, CH₃), 4.303, 4.343, 4.349, 4.414, 4.559, 4.618, 4.670, 4.719, 4.713, 4.723, 4.741 and 4.778 (s, 1H, C₆₀-H),⁴⁵ 6.85-8.00 (m, 25H, C₆H₅); HRMS (APCI-TOF, negative) m/z calcd for C₉₆H₄₀N₁ [M - H]⁻, 1206.3161; found, 1206.3142.

Method B: Synthesis from *p*-Phenylene-Bridged Dibenzo-Fused Corannulene (3). To a brown suspension of CuBr·SMe₂ (64 mg, 0.31 mmol) and 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene (69 mg, 0.31 mmol) in THF (2.0 mL) was added PhMgBr (0.97 M in THF, 0.32 mL, 0.31 mmol) at 24 °C. A solution of C₆₀(CN)Me₅Ph₃H (11 mg, 10 μ mol) in *o*-dichlorobenzene (2.0 mL) was transferred to the yellow phenylcopper reagent though a cannula. After being stirred for 14 h at

⁽⁴⁵⁾ Although the reaction may give 13 isomers due to the stereochemistry of the cyano group and the hydrogen atom on the C₆₀ exterior, 12 signals due to the C₆₀-H were observed in the ¹H NMR measurement. One C₆₀-H signal was missing because of overlap with other C₆₀-H signals.

40 °C, the reaction was quenched with saturated HCl (aqueous, 10 μ L). The mixture was diluted with toluene (20 mL) and filtered though a pad of silica gel. A yellow-colored eluent was evaporated to a small volume. Precipitation with MeOH afforded C₆₀(CN)Me₅Ph₅H (**4**) (12 mg, 91% isolated yield with 100% HPLC purity) as a mixture of stereoisomers.

Synthesis of Penta-oxygenated Compound (7). C₆₀Me₅Ph₅H₂ (1, 10 mg, 8.5 mmol) and KH (3.2 mg, 80 mmol) were dissolved in THF (5.0 mL) in a Schlenk tube. The color of the solution changed immediately from yellow to blackish-brown, indicating the formation of a bis-cyclopentadienyl dianion, [K]₂[C₆₀Me₅Ph₅]. The dianion was allowed to react with oxygen in air to afford oxidized products. This mixture was purified by column chromatography on silica gel (30-70% toluene in hexane) to obtain $C_{60}Me_5Ph_5O_3(OH)_2$ (4.5 mg, 42% yield) as a mixture of isomers. Single crystals suitable for X-ray structure analysis were obtained by slow diffusion of MeOH to a saturated chlorobenzene solution of C60Me5Ph5O3(OH)2. IR (ReactIR, diamond prove) 3501 (OH), 3484 (OH), 3084, 3058, 3031, 3025, 2963, 2923, 2860, 1598, 1583, 1494, 1446, 1373, 1365, 1345, 1323, 1224, 1070, 1019, 927, 807, 752, 723, 685 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.14-2.46 (s, 15H, CH₃), 3.86-3.91 (s, 1H, OH), 4.59-4.60 (s, OH), 7.13-7.17 7.26-7.35, 7.42-7.48, 7.55-7.57, 7.78-7.80, 7.86-7.90 and 8.09-8.12 (m, 25H, C_6H_5); UV-vis spectra (cyclohexane, ϵ) 256 (32 600), 282 (22 000), 335 (9600), 414 (1000), 424 (1600), 452 (3300) nm; HRMS (APCI-TOF, positive) m/z calcd for $C_{95}H_{41}O_5$ (M - 1)⁺, 1261.2954; found, 1261.29370.

Synthesis of [K(THF)_{*n*}][C₆₀(CN)Me₅Ph₅]. To a THF-*d*₈ (0.50 mL) solution of C₆₀(CN)Me₅Ph₅H (2, 27 mg, 22 µmol) in a NMR tube was added a THF solution of 'BuOK (30 µL, 1.0 M in THF, 30 µmol) at room temperature. The color of the solution changed immediately from yellow to black, indicating the formation of cyclopentadienyl anion. ¹H NMR (400 MHz, THF-*d*₈) δ 2.36 (s, 12H, CH₃), 2.52 (s, 3H, CH₃), 7.00-7.07 (m, 15H, m- and p-C₆H₅), 7.90-7.98 (m, 10H, o-C₆H₅); ¹³C NMR (100 MHz) δ 26.06 (2C, CH₃), 27.22 (2C, CH₃), 32.09 (1C, CH₃), 51.13 (1C, C₆₀), 51.56 (2C, C₆₀), 53.09 (1C, C₆₀), 56.34 (1C, C₆₀), 62.58 (2C, C₆₀), 62.68 (2C, C₆₀), 62.73 (1C, C₆₀), 119.75 (1C, CN), 125.69 (2C, p-C₆H₅), 125.70 (3C, p-C₆H₅), 125.81 (1C, C₆₀) 126.03 (2C, C₆₀) 127.03 (2C, C₆₀), 127.98 (10C, three signals of m-C₆H₅), 129.50 (8C, two signals of o-C₆H₅), 129.54 (2C, o-C₆H₅), 143.49 (2C, C₆₀), 143.78 (2C, C₆₀), 144.03 (2C, C₆₀), 144.46 (2C, C₆₀), 145.65 (2C, C₆₀), 147.10 (2C, C₆₀), 147.55 (3C, two signals of ipso-C₆H₅), 147. 63 (2C, *ipso*-C₆H₅), 148.54 (2C, C₆₀), 149.31 (2C, C₆₀), 149.56 (4C, two signals of C₆₀), 149.77 (2C, C₆₀), 151.01 (2C, C₆₀), 152.37 (2C, C₆₀), 153.45 (2C, C₆₀), 154.70 (2C, C₆₀), 156.40 (2C, C₆₀), 158.15 (2C, C₆₀), 159.33 (2C, C₆₀), 159.53 (2C, C₆₀), 160.15 (2C, C₆₀), 160.80 (2C, C₆₀), 160.90 (2C, C₆₀).

Synthesis of Pd[C₆₀(CN)Me₅Ph₅](*π*-allyl) (8). A THF solution of 'BuOK (0.50 M, 73 μ L, 36 μ mol) was added to a solution of C₆₀(CN)Me₅Ph₅H (2, 40 mg, 33 µmol) in THF (4.0 mL). The color of the solution changed from yellow to black, indicating formation of $[K(THF)_n][C_{60}(CN)Me_5Ph_5]$. $[Pd(\pi-allyl)Cl]_2$ (7.3 mg, 20 μ mol) was added to the solution. After it was stirred at 26 °C for 10 min, the reaction was quenched with saturated NH₄Cl (aqueous, 0.10 mL). The crude mixture was diluted with toluene (10 mL), and the organic layer was collected. After being dryed over MgSO₄, the solution was concentrated in vacuo. The resulting orange solid was purified by HPLC (Nacalai Tesque, Buckyprep, 250 mm, toluene/hexane, 3:7). The fractions containing 8 were collected and evaporated to a small volume. Precipitation with MeOH afforded 8 (26.0 mg 57% yield). Recrystallization from a two-layered solution of chlorobenzene and ethanol gave a single crystal of 8. ¹H NMR (400 MHz, CDCl₃) δ 2.17 (d, J_{H-H} = 12.0 Hz, 2H, allyl-CH₂(anti)), 2.41 (s, 6H, CH₃), 2.44 (s, 6H, CH₃), 2.66 (s, 3H, CH₃), 3.14 (d, $J_{H-H} = 6.4$ Hz, 2H, allyl-CH₂(syn)), 4.78 (ddt, 1H, allyl-CH), 7.16-7.30 (m, 10H + 5H, o,m-C₆H₅), 7.84-7.86 (m, 10H, *p*-C₆H₅,); ¹³C NMR (100 MHz, CDCl₃) δ 25.46 (2C, CH₃), 26.70 (2C, CH₃), 31.55 (1C, CH₃), 50.99 (1C, C₆₀), 51.41 (2C, C₆₀), 52.92 (1C, C₆₀), 55.42 (1C, C₆₀), 57.12 (2C, CH_2CH), 59.28 (2C, C₆₀), 59.36 (1C, C₆₀), 59.39 (2C, C₆₀), 99.87 (1C, $CHCH_2$), 118.96 (1C, CN), 121.28 (1C, C₆₀), 121.45 (2C, C₆₀), 122.32 (2C, C₆₀) 127.00 (5C, p-C₆H₅) 127.63 (10C, m-C₆H₅), 128.24 (10C, o-C₆H₅), 143.90 (2C, C₆₀), 144.16 (2C, C₆₀), 144.27 (2C, C₆₀), 144.34 (1C, *ipso*-C₆H₅), 144.38 (2C, C₆₀), 144.46 (2C, C₆₀), 144.93 (2C, C₆₀), 145.52 (2C, C₆₀), 146.02 (2C, C₆₀), 146.41 (2C, C₆₀), 146.63 (2C, C₆₀), 146.66 (2C, C₆₀), 146.88 (2C, C₆₀), 147.76 (2C, C₆₀), 151.09 (2C, C₆₀), 151.27 (2C, C₆₀), 153.37 (2C, C₆₀), 153.40 (2C, C₆₀), 156.41 (2C, C₆₀), 158.04 (2C, C₆₀), 154.59 (2C, C₆₀), 155.07 (2C, C₆₀), 156.41 (2C, C₆₀), 158.04 (2C, C₆₀); HRMS (APCI-TOF, positive) m/z calcd for C₉₉H₄₅N₁¹⁰⁵Pd₁ (M⁺), 1352.26028; found, 1206.25577.

Synthesis of [K(THF)_n][C₆₀(CN)Me₅Ph₃]. To a THF- d_8 (0.50 mL) solution of C₆₀(CN)Me₅Ph₃H (**3**, 7.0 mg, 6.6 μ mol) in an NMR tube, a 'BuOK solution (13 μ L, 1.0 M in THF, 13 μ mol) was added at room temperature. The color of the solution changed immediately from orange to black, indicating the formation of the cyclopentadienyl anion with three structural isomers of [K(THF)_n][C₆₀(CN)Me₅Ph₃]. 'H NMR (400 MHz, THF- d_8) δ 2.08–2.10, 2.36–2.42, 2.62–2.64 and 2.92 (m, 15H, CH₃), 7.00–7.35, 7.85–7.97 and 8.41–8.48 (m, 15H, C₆H₅).

Synthesis of Rh[C60(CN)Me5Ph5](cod) (9). To a solution of $C_{60}(CN)Me_5Ph_3H$ (3, 15 mg, 14 μ mol) in THF (2.0 mL) was added a solution of 'BuOK (17 µL, 1.0 M in THF, 17 µmol). The color of the solution changed from orange to black, indicating formation of [K(THF)_n][C₆₀(CN)Me₅Ph₃]. To the reaction mixture was added $[RhCl(cod)]_2$ (21 mg, 43 μ mol), and the mixture was stirred for 10 min at 26 °C. Precipitation with MeOH afforded Rh[C₆₀(CN)Me₅Ph₃]-(cod) (16 mg, 88% yield) as a mixture of three isomers. Single crystals suitable for X-ray structure analysis were obtained by slow diffusion of methanol to a THF solution of 9. NMR and IR spectra were measured for the mixture of the stereoisomers. IR (ReactIR, diamond prove) 3058, 3028, 2961, 2921, 2864, 2831, 2227, 1599, 1494, 1445, 1373, 1297, 1243, 1155, 1033, 1004, 963, 921, 861, 745, 733, 695, 678 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.74–1.77 (m, 8H, cod), 1.78–1.80 (m, 2H, cod), 2.22-2.32, 2.45-2.54, 2.67-2.77 and 2.92 (s, 15H, CH₃), 3.42 (br, 2H, cod), 7.12-7.32, 7.47-7.67, 7.75-7.79 and 9.28-9.35 (m, 15H, C₆H₅); HRMS (APCI-TOF, positive) m/z calcd for C₉₂H₄₂N₁¹⁰³Rh₁ (M⁺), 1263.23723; found, 1263.23883.

Synthesis of *p*-Phenylene-Bridged Dibenzo-Fused Corannulene C₆₀Me₅Ph₃H₂ (10). To a solution of C₆₀Me₅CNPh₃H (3, 40 mg, 38 μ mol) in PhCN (10 mL) in a Schlenk tube was added a solution of lithium naphthalenide (1.5 mL, 0.76 M in THF, 1.1 mmol) under an argon atmosphere. The color of the solution changed immediately from yellow to blackish-red, indicating the decyanation and formation of bis-cyclopentadienide had occurred. After it was stirred for 1 h at 23 °C, the reaction was quenched by the addition of EtOH (0.10 mL) and saturated NH₄Cl (aqueous, 0.05 mL). The color of the solution changed immediately from dark red to light red. The mixture was diluted with toluene (50 mL) and filtered though a pad of silica gel, which was done with a small amount of MeOH. A red-colored eluent was evaporated to a small volume, and precipitation with MeOH afforded a crude product. This mixture was purified by HPLC (Nacalai Tesque, Buckyprep, 250 mm, toluene/2-propanol, 5:5) under an argon atmosphere. The fractions containing 10 were collected and concentrated to a small volume. Precipitation with MeOH afforded 10 (23 mg, 59% yield), with 98% HPLC purity, as a mixture of five isomers. IR (ReactIR 1000, diamond prove) 3059, 3030, 2960, 2918, 2859, 1598, 1493, 1445, 1241, 1155, 1072, 1031, 921, 911, 748, 731, 714, 685, 660 cm⁻¹; ¹H NMR (400 MHz CDCl₃) δ 1.80-2.04, 2.34-2.39, 2.46-2.49, 2.60-2.61 and 2.74 (s, 15H, CH₃), 4.445, 4.458, 4.591, 4.615 and 4.686 (s, 1H, C₆₀-H), 4.991, 5.108, 5.029, 5.034 and 5.063 (s, 1H, C₆₀-H), 7.00-7.43, 7.45-7.52, 7.62-7.73, 7.75-7.79 and 8.12-8.15 (m, 15H, C₆H₅); APCI-MS (-) $m/z = 1027 [(M - 1)^{-}].$

Synthesis of Dibenzo-Fused Corannulene $C_{60}Me_5Ph_5H_2$ (11). To a solution of $C_{60}(CN)Me_5Ph_5H$ (4, 15 mg, 12 µmol) in PhCN (4.0 mL) in a Schlenk tube was added a solution of lithium naphthalenide (0.74 mL, 0.50 M in THF, 0.37 mmol). The color of the solution changed immediately from yellow to dark red, indicating decyanation and formation of a bis-cyclopentadienide. After being stirred for 1 h at 23 °C, the reaction mixture was quenched by the addition of EtOH and then saturated NH₄Cl (aqueous, 0.10 mL). The color of the resulting solution changed immediately from dark red to light red, indicating that the protonation of the bis-cyclopentadienyl dianion took place. The mixture was diluted with toluene (20 mL) and filtered though a pad of silica gel. A red-colored eluent was evaporated to a small volume, and precipitation with MeOH afforded a crude product. This mixture was purified by HPLC (Nacalai Tesque, Buckyprep, 250 mm, toluene/ 2-propanol, 7:3). The fractions containing 11 were collected and concentrated to a small volume. Precipitation with MeOH afforded 11 (9.1 mg, 63% yield), with 95% HPLC purity, as a mixture of isomers. IR (ReactIR, diamond prove) 3085, 3058, 3027, 2958, 2919, 2861, 1600, 1584, 1493, 1445, 1372, 1181, 1156, 1136, 1078, 1032, 1003, 928, 754, 694, 675 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.14-1.27, 1.37-1.64 and 2.04-2.68 (s, 15H, CH₃), 3.946, 3.974, 3.986, 4.103,

4.126, 4.313, 4.320, 4.557, 4.593 and 4.636 (s, 2H, C₆₀-*H*), 6.92–7.24, 7.31–7.36, 7.39–7.41, 7.42–7.47, 7.51–7.54, 7.57–7.66 and 7.71–7.82 (m, 25H, C₆H₅); HRMS (APCI, negative) m/z calcd for C₉₅H₄₁ [(M – H)⁻], 1181.3208; found, 1181.3256.

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Supporting Information Available: Optimized geometry (A-G) and CIF files, including lists of positional parameters, thermal displacement parameters, bond lengths, and bond angles for 6, 7, 8, and 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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