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Nickel-Catalyzed Dimerization of [5]Cumulenes (Hexapentaenes)

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Tetraaryl[5]cumulenes react with low-valent nickel complexes at the second double bond to produce novel [4]radialene derivatives that are head-to-head dimers of [5]cumulenes. The head-to-head dimers are also synthesized by a stepwise route. On the other hand, the nickel-catalyzed dimerization of [5]cumulenes with bulky substituents produces other types of extended [4]radialenes and [5]radialenones depending on the bulkiness of the terminal alkyl substituents. Thus, tetrakis-*t*-butyl[5]cumulene and 1,4-bis(2,2,6,6-tetramethylcyclohexylidene)[3]cumulene react at the central double bond to give the corresponding [4]radialene and [5]radialenone, whereas 1,4-bis(2,2,5,5-tetramethylcyclopentylidene)[3]cumulene and its benzo-annelated derivative react at the second double bond in a head-to-tail manner to afford the corresponding extended [4]radialenes. Tetrakis-*t*-butyl[5]radialenone was converted into [5]radialene by using a methylation–dehydration procedure. The extended [4]- and [5]radialenes and [5]radialenones have been fully characterized by spectroscopic analyses, X-ray crystallography, and/or independent chemical synthesis. The properties of these novel exocyclic π-electron systems have been investigated in detail. The aryl-substituted [4]radialenes exhibit facile bond rotation with low energy barriers. The [5]radialene and [5]radialenone form the corresponding cations easily by the addition of an acidic proton. The selectivity of the nickel-catalyzed dimerization of [5]cumulenes is discussed on the basis of theoretical calculations.

Long cumulated sp carbon chains as well as oligomeric acetylenes are among the simplest units for molecular wires.[1–5] Although oligomeric acetylenes have been investigated extensively in recent years,[6,7] long-chain cumulenes have remained mostly unexamined, presumably due to the difficulty of handling cumulenes.[8–11] The aryl-substituted cumulenes were mostly investigated in the 1950's[12–15] and 1960's,[16–20] and the research interests were mainly focused on the electronic spectral behavior of these linear monodisperse π-conjugated systems with relation to color chemistry. Thus, aryl-substituted butatrienes ([3]cumulenes) and hexapentaenes ([5]cumulenes) were investigated extensively.[21–26] However, the chemistry of aryl-substituted [7]- and higher cumulenes was studied only in limited cases.[27] As for the alkyl-substituted allenes and cumulenes, a number of works for the synthetic use of allenes have recently been reported.[28–31] In addition, the syntheses and properties of alkyl-substituted [3]- and higher cumulenes have been reported by several groups,[32–41] but the instability of these compounds in atmospheric oxygen prevents the development of their use.[42–44]

Although cumulenic double bonds have a wide variety of potential reactive sites, which may lead to novel cyclic dimers, trimers, and oligomers, difficulty in controlling the reactivity has prevented the utilization of cumulenes in organic synthesis. One of the most accessible reactions is the formation of radialenes (polymethylenecycloalkanes).[45–47] In our previous studies, we reported the synthesis of [4]- and [6]radialenes using nickel-catalyzed cyclooligomerization of [3]cumulenes.[48,49] Based on our continuing interest in the synthetic use of cumulenes as building blocks for constructing cyclic π-electron systems, we also investigated the reactions of [5]cumulenes with transition-metal complexes and have reported some results in a preliminary form.[50–55] As summarized in Scheme 1, hexapentaene may formally dimerize to yield the symmetrical [2 + 2], [4 + 4], and [6 + 6] dimers. Since the transition-metal-catalyzed dimerization of hexapentaene proceeds via metallacyclic intermediates, head-to-head (H–H) or head-to-tail (H–T) dimers at C_1–C_2, C_2–C_3, or a C_4-symmetric C_3–C_4 dimer are expected to form selectively depending on the regioselectivity of the complexation of hexapentaene with transition metals. The main purpose of this report is to explore the regioselectivity of the transition-metal-catalyzed dimerization of [5]cumulenes.

As has been reported previously, tetra-*t*-butyl[5]cumulene (**1**) dimerizes thermally at 200 °C to afford a C_3–C_4 dimer, tetrakis(di-*t*-butylvinylidene)cyclobutane (**2**),[56–59] whereas the thermal dimerization of tetramethyl[5]cumulene (**3**) at a lower temperature produces a C_1–C_6 dimer, octamethylcyclododeca-1,3,7,9-tetrayne (**4**) (Scheme 2).[60–63] Since the complexation of [5]cumulenes with $[RhCl(PPh_3)_2]$ has recently been shown to take place at the C_2–C_3 double bond to form 1:1 complexes,[64] a new type of dimerization products (C_2–C_3 dimers) can be expected by the reactions of [5]cumulenes with transition-metal complexes, and this strategy could provide a new methodology for preparing novel extended radialenes.

Radialenes and their derivatives have received growing attention from synthetic chemists, spectroscopists, and material scientists.[65–67] Thus, a variety of radialenes with novel electronic properties have been synthesized and their properties have been investigated.[45–47,68–71] Recently, expanded radialenes constructed by the insertion of ethynediyl or buta-1,3-

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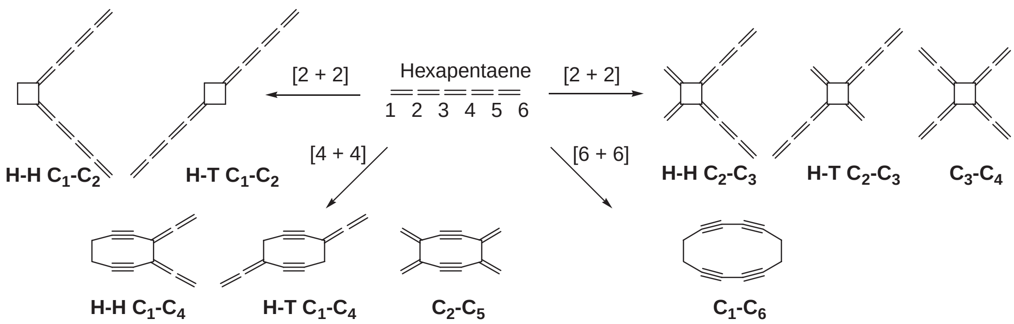
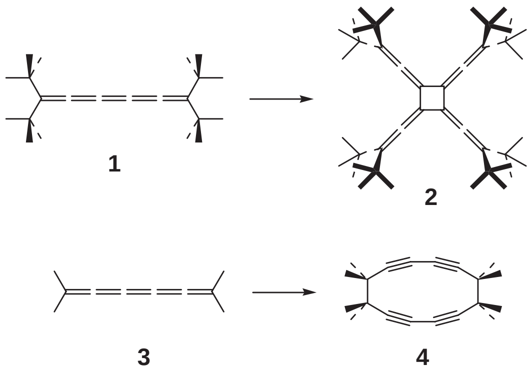
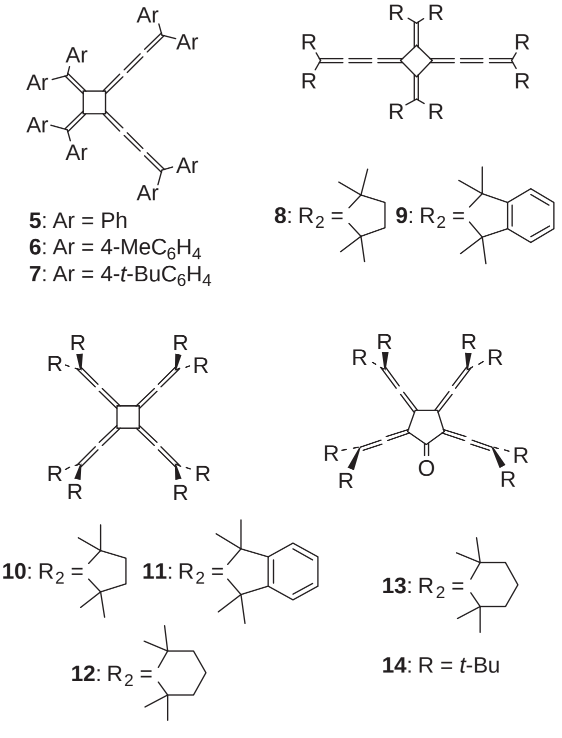


Scheme 1.



Scheme 2.



Scheme 3.

diynediyl moiety into the cyclic radialene framework have been reported.[72,73] These expanded radialenes can be regarded as new carbon allotropes with all carbon networks, new precursors to cyclo[*n*]carbons, and functionalized cross-conjugated π-cavities.[74–76] In contrast, upon insertion of cumulenic sp-carbons into the exocyclic double bond of radialenes, a new series of extended radialenes can be formed. Such π-extended radialenes are expected to constitute novel oligocumulene systems with interesting structures.[50–55]

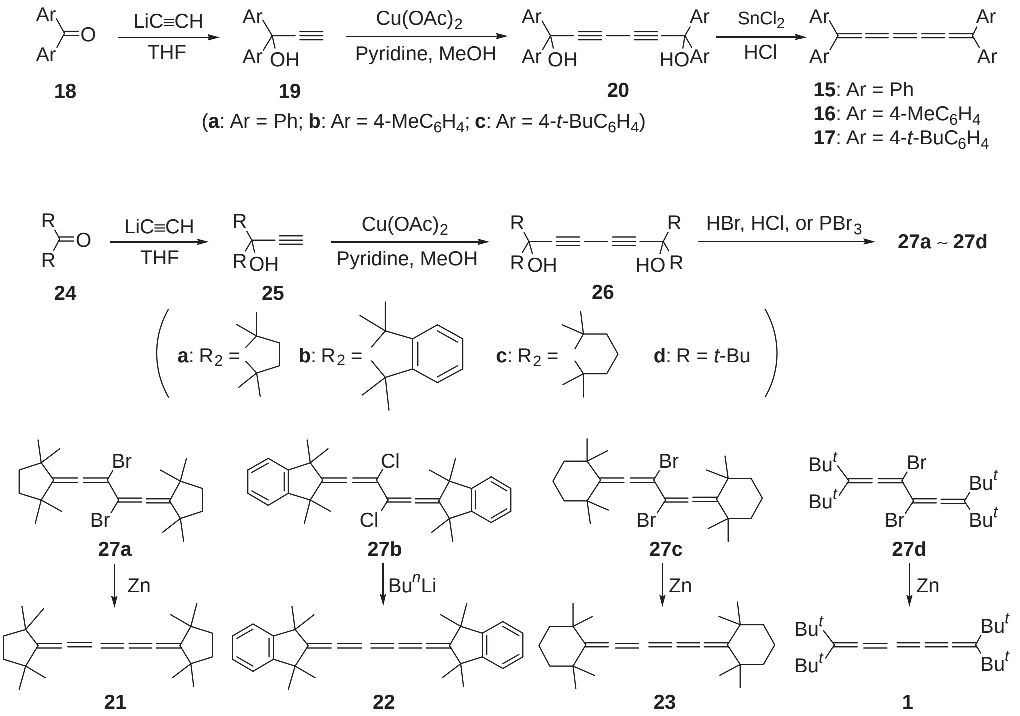
In this paper, we describe the reactions of [5]cumulenes with nickel(0) complexes to produce a variety of extended [4]radialenes and [5]radialenones **2**, **5**–**9**, and **12**–**14**, together with the thermal dimerization of [5]cumulenes to afford extended [4]radialenes **10** and **11**. Furthermore, unique structures and novel electronic properties of radialenes **5**–**12** and radialenones **13** and **14** as well as the characterization of exotic properties of extended [4]radialenes and [5]radialenones are described (Scheme 3).

Results and Discussion

Synthesis of [5]Cumulenes. Tetraphenylhexapentaene (**15**) and tetrakis(4-methylphenyl)hexapentaene (**16**) were prepared according to a literature method (Scheme 4).[8] The final reductive dehydroxylation of **20a** and **b** was carried out using $SnCl_2 \cdot 2H_2O$[77] (1.1 equiv) in dry ether at 0 °C for 1 h to produce **15** and **16** in 87 and 94% yields, respectively. Tetrakis(4-*t*-butylphenyl)hexapentaene (**17**) was prepared starting from 4,4′-di-*t*-butylbenzophenone (**18c**).[78] Thus, the reaction of **18c** with lithium acetylide in THF at room temperature for 4 h led to the acetylenic alcohol **19c** in 95% yield. The oxidative coupling of **19c** with $Cu(OAc)_2 \cdot H_2O$ in methanol–pyridine at 60 °C for 10 h gave **20c** in 85% yield.[79] The reductive dehydroxylation of **20c** with $SnCl_2 \cdot 2H_2O$ in dry THF–ether at 0 °C for 1 h produced **17** in 88% yield. All of the [5]cumulenes **15**–**17** were obtained as stable orange or red crystals.

Although the reductive dehydroxylation of the diols **26a**–**d** with $SnCl_2$ gave no [5]cumulenes, the syntheses of **1** and **21**–**23** were achieved by the dehalogenation of the bis-allenic dihalides **27a**–**d** (Scheme 4). The diol **26a** was converted into the corresponding dibromide **27a** with concd hydrobromic acid in acetic acid (90%), whereas **27b** was prepared by the reaction of **26b** with concd hydrochloric acid in dioxane–acetic acid (78%). The conversions of **26c** and **26d** into **27c** (73%) and **27d** (91%), respectively, were carried out using PBr_3 in benzene at 55 °C.[59] The dehalogenation of the dihalides **27a**, **27b**, **27c**, and **27d** with zinc or butyllithium produced cumulenes **21**, **22**, **23**, and **1** in 95, 96, 90, and 85% yields, respectively. All of the cumulenes were stable yellow compounds that could be stored for a long time at room temperature.

Nickel-Catalyzed Syntheses of Tetraaryl[5]cumulene Dimers. Nickel-catalyzed cyclooligomerization of [3]cumulenes is a simple and efficient method for the synthesis of



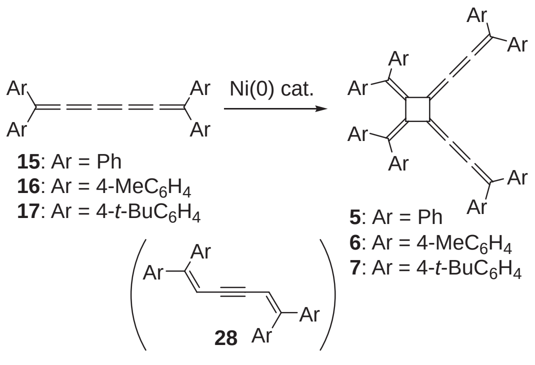
Scheme 4.

Table 1. Nickel-Catalyzed Dimerization of **15**–**17**

Entry	Compd.	Ni(0) complex	mol %	Solv.	Temp/°C	Yields[a)]	
						5–**7**	**28**
1	**15**	$[Ni(PPh_3)_4]$[b)]	50	THF	25	53	0
2	**15**	$[Ni(PPh_3)_4]$[b)]	20	DMF	25	64	0
3	**15**	$[Ni(PPh_3)_4]$[b)]	50	benzene	25	40	10
4	**15**	$[Ni(CO)_2(PPh_3)_2]$	10	benzene	80	61	0
5	**16**	$[Ni(CO)_2(PPh_3)_2]$	25	benzene	80	57	0
6	**17**	$[Ni(CO)_2(PPh_3)_2]$	100	benzene	80	34	0

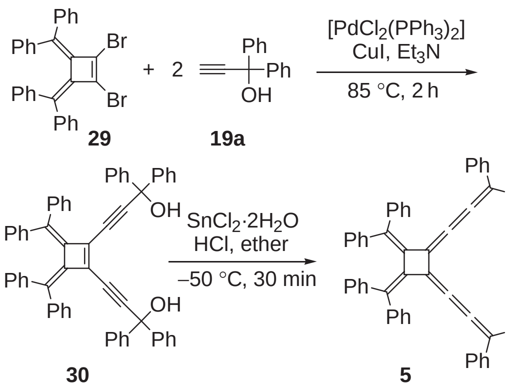
a) Isolated yield. b) Prepared in situ from $[NiBr_2(PPh_3)_2]$, PPh_3, and zinc in a 1:2:4 molar ratio.

[4]- and [6]radialenes.[45–49] However, tetraarylbutatrienes were stable under the oligomerization conditions, and the starting [3]cumulenes were recovered unchanged after the reaction with low-valent nickel complexes, presumably due to the sterically crowded coordination site around the nickel center. Tetraarylhexapentaenes having less crowded ligand positions were expected to react with low-valent nickel complexes to yield oligomers. The reaction of tetraphenylhexapentaene (**15**) with $[Ni(PPh_3)_4]$ proceeded smoothly at ambient temperature to afford the head-to-head (C_2–C_3) dimer **5** as the main product with no formation of a trimer, the [6]radialene derivative[48,49] (Table 1). The reaction of **15** in benzene gave a small amount of the reduction product **28** along with **5**. The reaction of **15** with $[Ni(CO)_2(PPh_3)_2]$ produced solely **5** in 61% yield. Under similar conditions, tetrakis(4-methyphenyl)hexapentaene (**16**) and tetrakis(4-*t*-butylphenyl)hexapentaene (**17**) gave the corresponding dimers **6** and **7** in 57 and 34% yields, respectively (Table 1). The relatively low yield in the dimerization of **17** can be attributed to the existence of bulky substituents, which may have disturbed the C–C bond formation at the C_2-position by a concomitant repulsive interaction. The extended radialenes **5**–**7** have a deep blue color, and the color in solution gradually disappears upon standing at room temperature (Scheme 5).



Scheme 5.

Since the spectroscopic characterization of the extended [4]radialene **5** left some uncertainty, we synthesized **5** by an independent stepwise pathway (Scheme 6). Palladium-catalyzed cross-coupling of 1,2-dibromo-3,4-bis(diphenylmethylidene)-



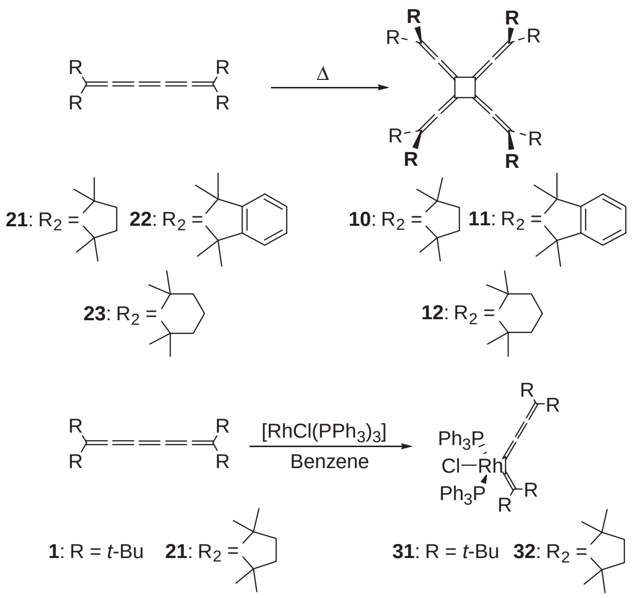
Scheme 6.

cyclobutene (**29**)[80,81] with 1,1-diphenyl-2-propyn-1-ol (**19a**) produced the corresponding enediyne derivative **30** in 73% yield using the Sonogashira reaction. Reductive dehydroxylation of **30** with $SnCl_2 \cdot 2H_2O$ in ether gave **5** in 68% yield. The compound **5** thus obtained exhibited identical spectral data to those of the product from the nickel-catalyzed reaction.

Thermal and Nickel-Catalyzed Dimerization of Tetraalkyl[5]cumulenes with Bulky Substituents. Tetraalkylhexapentaenes with bulky substituents showed high stability against light and atmospheric oxygen, presumably due to the protection of the terminal C_{sp^2}-carbon with bulky substituents from approaching molecules. However, the central cumulenic π-system is still reactive towards transition metals to form a dimer. Odd-numbered cumulenes bear two types of double bonds, i.e., double bonds with lateral and perpendicular π-orbitals to substituents. Thermal dimerization of tetra-*t*-butylhexapentaene **1** takes place at the central C_3–C_4 (perpendicular) double bond to form the corresponding dimer **2**,[56–59] and the coordination of **1** to $[Fe_2(CO)_9]$ leads to a very stable 1:1 complex at the central perpendicular bond.[82] However, tetraarylhexapentaenes **15**–**17** dimerize with low-valent nickel complexes to form the C_2–C_3 (lateral) head-to-head dimers **5**–**7**, and the complex formation of **15** with late transition metals reported in literature also occurs at the lateral bonds,[64,83–85] suggesting the favorable reactivity of the C_2–C_3 (lateral) double bond of [5]cumulenes for transition metals. The unique reactivity of **1** can be considered as a result of the steric effect of the bulky substituent, and the reactivities of bulky-substituted [5]cumulenes may be modified by changing the size of terminal substituents.

By considering the bulkiness and synthetic facility, tetra-*t*-butylhexapentaene (**1**) and its counterparts **21**–**23** were chosen as candidates. These four [5]cumulenes have almost similar structures except for the bond angles at the terminal carbon, which affect the steric requirement in the reaction at the C_2–C_3 double bond. The reported X-ray structure of **23** indicates the angle of 122° for the inside of the 6-membered ring at the sp^2 carbon.[86] The corresponding angle can be expected to be larger in **1** and to be smaller in **21** and **22**.

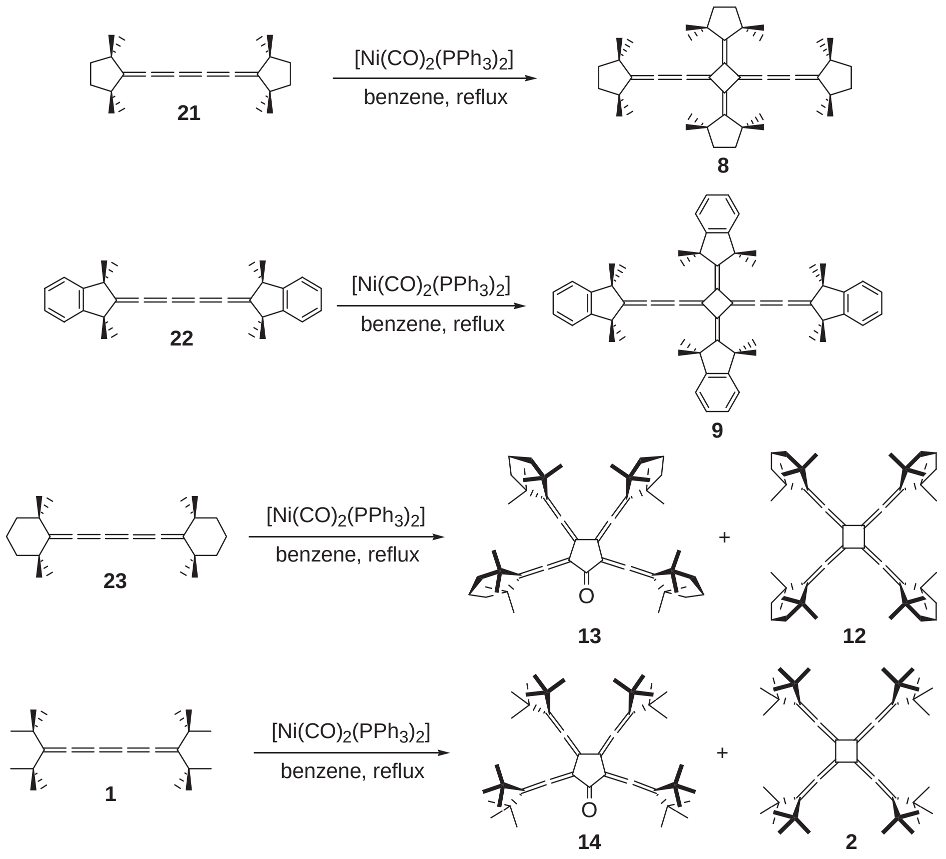
The thermal dimerization of **21**–**23** was attempted according to the reported procedure[56–59] for **1** (Scheme 7). Thus, **23** was heated at 220 °C for 2 min to produce **12** in 91% yield, whereas the heating of **21** at 240 °C for 5 min formed **10** in 69% yield, together with the unchanged **21** (24%). In the case of **22**, the crystals of **22** gradually dimerized without melting at 250–260 °C for 2 h to afford **11** in 21% yield, together with unidentified products. The yield of **11** increased by heating **22** at 270–275 °C for 5 min (51%). The formations of **10**–**12** show that hexapentaenes **21**–**23** reacted only at the central, perpendicular double bond (C_3–C_4) in the thermal dimerization, presumably due to the crisscross structure of the intermediate for the thermal [2 + 2] reaction.



Scheme 7.

In contrast, the reaction of **21** with $[RhCl(PPh_3)_3]$ in benzene at room temperature for 3 h afforded the rhodium complex **32** at the C_2–C_3 double bond in 80% yield (Scheme 7). Surprisingly, the reaction of **1** under similar conditions also produced the corresponding lateral rhodium complex **31**, reflecting the less bulkiness of the $[RhCl(PPh_3)_2]$ group than $[Fe(CO)_4]$ which coordinates at the central C_3–C_4 double bond of **1**.[82] The results imply that the C_2–C_3 lateral double bond of the [5]cumulenes **1** and **21** endows them with better coordination ability.

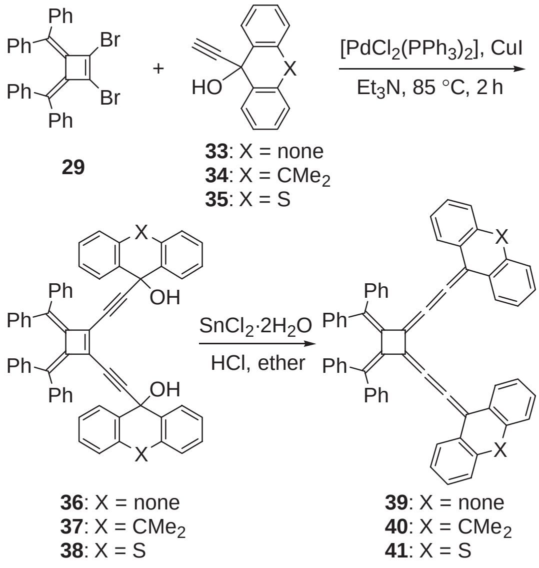
Secondly, dimerization of the [5]cumulenes **1** and **21**–**23** using $[Ni(CO)_2(PPh_3)_2]$ was investigated (Scheme 8). The reaction of **21** with 0.5 equiv of $[Ni(CO)_2(PPh_3)_2]$ in refluxing benzene for 24 h afforded the lateral (C_2–C_3) head-to-tail dimer **8** exclusively in 82% yield. In a similar manner, the reaction of **22** with $[Ni(CO)_2(PPh_3)_2]$ (0.5 equiv) in the presence of PPh_3 (1 equiv) in refluxing benzene for 24 h gave the head-to-tail (C_2–C_3) dimer **9** in 64% yield. Interestingly, the reaction of **23** carrying the even bulkier substituents with 1 equiv of $[Ni(CO)_2(PPh_3)_2]$ in refluxing benzene for 2 days produced the C_3–C_4 [4]radialene **12** (32%) and the corresponding C_3–C_4 [5]radialenone **13** (36%), reflecting the favorable reactivity of the central double bond. In the case of **1** bearing the bulkiest substituents, the reaction of **1** with 1.0 equiv of $[Ni(CO)_2(PPh_3)_2]$ and 3.0 equiv of PPh_3 in refluxing benzene proceeded slowly for 8 days to afford predominantly the [5]radialenone **14** in 74% yield, together with a small amount of the [4]radialene **2** (6%). All [4]radialenes **2**, **8**, **9**, and **12** and [5]radialenones **13** and **14** are stable colorless or yellow crystals at



Scheme 8.

room temperature. The different selectivity observed in the reactions of **21**–**23** and **1** with $[Ni(CO)_2(PPh_3)_2]$ clearly suggests that the bulkiness of the terminal substituents in the [5]cumulenes controls the course of the coordination and the following oligomerization reactions.

Novel Structures and Electronic Properties of Tetraaryl[5]cumulene Dimers. The head-to-head dimers **5**–**7** prepared from tetraarylhexapentaenes **15**–**17** show a deep blue color, presumably due to the unusual bis-butatriene structure. Since the stepwise synthesis of the extended [4]radialene **5** allows us to access novel extended [4]radialenes conjugated with cumulative double bonds, syntheses of the [4]radialenes **39**–**41** with end-cap groups have been planned. The ring systems at the bis-butatriene termini can be expected to provide the [4]radialenes new characteristics of near-IR absorptions, low HOMO–LUMO separations, and redox properties. Thus, a series of [4]radialenes containing terminal fluorene, dimethyldihydroanthracene, and thioxanthene groups have been synthesized by the stepwise route as shown in Scheme 9. The cross-coupling reaction of the dibromide **29** with the acetylenic alcohol **33** under the Sonogashira conditions afforded the corresponding diol **36** in 68% yield. The reductive dehydroxylation of **36** with $SnCl_2$ in dry ether containing gaseous HCl at −50 °C for 30 min produced the extended radialene **39** in 49% yield. In a similar manner, the Sonogashira reaction of **29** with **34** and **35** yielded the diol **37** (62%) and **38** (37%), respectively. The reductive dehydroxylation of **37** and **38** with $SnCl_2 \cdot 2H_2O$ in ether afforded the desired **40** (61%) and **41** (93%), respectively. Although the extended [4]radialenes **39**–**41** possess a crowded molecular structure, they are stable deep-colored crystals at room temperature.



Scheme 9.

The extended [4]radialenes **5**–**7** and **39**–**41** can be expected to possess a twisted C_2-symmetric structure with a puckered conformation to reduce the congestion among the terminal aromatic substituents. The inside aromatic rings (ring A, see Fig. 2) at the C_1-position should be stacked on each other as has been found in aryl-substituted [4]radialenes.[87,88] In the

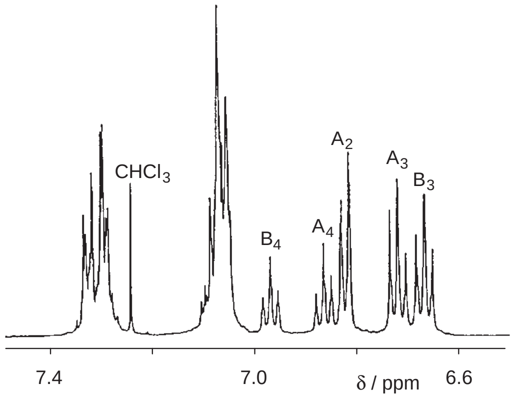


Fig. 1. ^{1}H NMR spectrum of [4]radialene **5**.

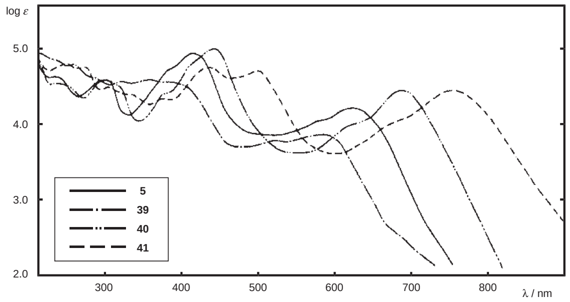
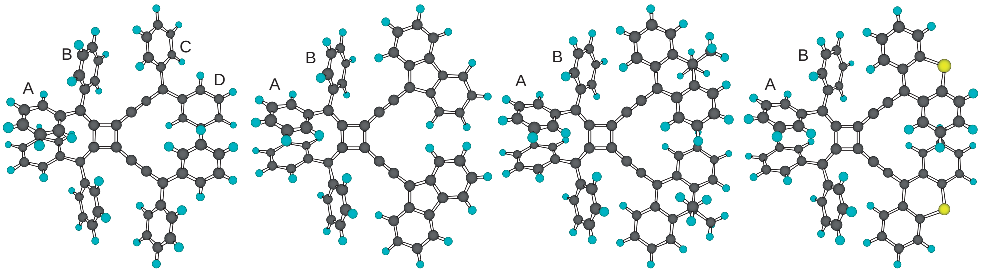


Fig. 3. The electronic spectra of [4]radialenes **5** and **39**–**41** in THF.



5 **39** **40** **41**

Fig. 2. Optimized molecular structures of the extended radialenes **5** and **39**–**41** by density functional calculations (B3LYP/6-31G(d)). Four phenyl rings in **5** and two phenyl rings in **39**, **40**, and **41** are marked as rings A–D and A and B, respectively, as indicated in the structures.

^{1}H NMR spectrum of **5** (Fig. 1), the signals for these stacked phenyl groups were observed separately from the other signals of aromatic protons in a high field at δ 6.88, 6.83, and 6.73 (*p*-, *o*-, and *m*-positions in the ring A). Two triplet signals at δ 6.98 (2H) and 6.68 (4H) were also observed separately to be assigned for *p*- and *m*-positions of the outer phenyl ring at the C_1-position (ring B). The signals of rings C and D protons overlapped in the range of δ 7.34–7.29 (10H) and 7.11–7.06 (14H). In the ^{1}H NMR spectrum of the *p*-tolyl substituted **6**, the aromatic protons gave four sets of AA′XX′-pattern signals at higher fields in the range of δ 7.23–6.52 owing to the electron-donating methyl groups. The corresponding signals for **7**, however, appeared at a lower field in the range of δ 7.46–6.82 ppm. Presumably, repulsive interaction between bulky *t*-butyl groups significantly alter the conformation of the [4]radialene skeleton. This unusual substituent effect was also observed in the electronic spectrum of **7**. The absorption maximum of **5** at the longest wavelength was observed at 623 nm and the corresponding absorption of **6** was shifted to 694 nm. However, the absorption maximum of **7** appeared at 623 nm. This also suggests a conformational change in **7** due to the repulsion between bulky *t*-butyl substituents.

The extended [4]radialenes **39**–**41** are also assumed to have a C_2-symmetric structure, although the increased planarity of the terminal substituents may change the conformation of these molecules. As shown in Fig. 2, the optimized structures of **5** and **39**–**41** calculated by the density functional method (B3LYP/6-31G(d)) suggest that increasing planarity of the terminal substituents causes on increase in the torsional angle of the rings B in these [4]radialenes. In the ^{1}H NMR spectra of **39**–**41**, the signals for the stacked phenyl groups (ring A) appeared at a high field similar to that observed for **5** (δ 6.94–6.86, 6.84–6.87, and 6.76–6.74 for *p*-, *o*-, and *m*-positions, respectively). The spectrum of **39** shows a doublet (2H) at a high field of δ 6.21, which can be assigned to the 1-position of the fluorene ring shielded by the ring B. The spectra of **40** and **41** also show a high-field doublet (2H) at δ 6.29 and 6.26, respectively, assigned to the protons of the 1-position of dihydroanthracene and thioxanthene rings. Furthermore, an additional triplet (2H) appeared at a high field of δ 6.03 for **40** and δ 6.06 for **41**. These high-field shifts of aromatic protons suggest terminal–terminal overlapping between the two aromatic moieties of the end-capped bis-butatriene structure. The ^{1}H NMR signals of some dihydroanthracene and thioxanthene protons in **40** and **41** exhibited broadening at room temperature presumably due to rotation of the butatriene moieties, as described later.

The electronic spectra of **5** and **39**–**41** show very intense broad absorption at the near-IR region (Fig. 3). The longest absorption maxima of **40** and **41** appear at 688 ($\log \varepsilon = 4.44$) and 754 (4.47) nm, respectively. Thus, appreciable bathochromic shifts are observed relative to the absorption of **5**, whereas the longest absorption maximum of **39** is observed at the shorter wavelength of 583 nm ($\log \varepsilon = 3.93$) as compared with those of **40** and **41**. This hypsochromic shift is also unusual because the absorption maxima of the fluorene-substituted butatriene and hexapentaene exhibit a large bathochromic shift (ca. 60 nm) as compared to those of tetraphenyl counterparts.[8,89]

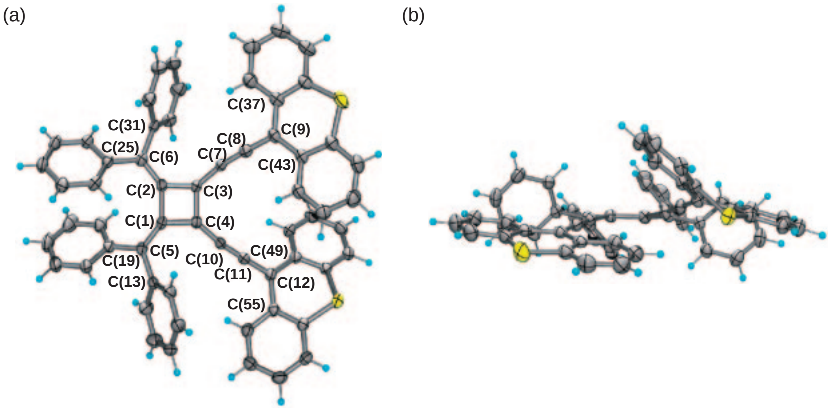


Fig. 4. ORTEP drawing of extended [4]radialene **41**. Selected bond lengths (Å) and angles (°) are as follows: C(1)–C(2) 1.525(3), C(2)–C(3) 1.485(3), C(3)–C(4) 1.459(3), C(4)–C(1) 1.490(3), C(1)–C(5) 1.353(3), C(4)–C(10) 1.357(3), C(10)–C(11) 1.216(3), C(11)–C(12) 1.361(3); C(4)–C(1)–C(2) 88.6(2), C(1)–C(2)–C(3) 88.8(2), C(3)–C(4)–C(1) 91.2(3), C(2)–C(1)–C(5) 140.8(2), C(4)–C(1)–C(5) 130.1(2), C(1)–C(2)–C(6) 140.1(2), C(1)–C(4)–C(10) 138.7(2), C(3)–C(4)–C(10) 129.4(2), C(3)–C(7)–C(8) 169.0(3).

The longest absorption maxima of 1,2-bis(9-fluorenylidene)ethene (480 nm) and 1,2-bis(10,10-dimethyl-9,10-dihydroanthracen-9-ylidene)ethene (481 nm) are observed at almost the same wavelength but apparently in a longer region than that of tetraphenylbutatriene (431 nm).[89] In a similar manner, the longest absorption of bis(fluorenylidene)[3]cumulene (543 nm) is observed at much longer region than that of octaphenyl[5]cumulene (489 nm) in benzene.[90]

Fortunately, single crystals of **41** were obtained by recrystallization from a mixture of CS_2–CH_2Cl_2–ether, and the molecular structure of **41** was determined by X-ray analysis. As shown in Fig. 4, **41** has a C_2-symmetric structure with a planar 4-membered ring, although the known substituted [4]radialenes usually adopt a puckered conformation.[87,88,91–93] The puckering angle of the 4-membered ring in **41** is only 1.1°, and the planar structure brings about repulsive interactions among its substituents to cause considerable deformation in the molecular skeleton. Thus, the bond angles of C(2)–C(1)–C(5) and C(1)–C(2)–C(6) (averaged 140.5°) are significantly larger than those of C(4)–C(1)–C(5) and C(3)–C(2)–C(6) (averaged 130.5°). The 4-membered ring is also transformed to a trapezoid, which contains a long C(1)–C(2) bond of 1.525(3) Å, short C(3)–C(4) bond of 1.459(3) Å and two normal C(2)–C(3) and C(1)–C(4) single bonds (averaged 1.488 Å). The buttressed phenyl groups (ring B in Fig. 2) bend away from the exocyclic butatriene units at ring sp^2-carbons (C(3) and C(4)) and at exocyclic sp-carbons (C(7) and C(10)). The averaged angle difference of both sides of the exocyclic double bonds at C(3) and C(4) is 10.2° [$\angle$C(2)–C(3)–C(7) − $\angle$C(4)–C(3)–C(7) = 11.2°; $\angle$C(1)–C(4)–C(10) − $\angle$C(3)–C(4)–C(10) = 9.2°] and the averaged angle for out-of-plane bending at these carbons is 6.8°. Furthermore, significant twisting of the cumulative bonds is also observed, presumably due to a repulsive interaction between two partially overlapped thioxanthene units (ring D in Fig. 2). The torsion angles between the 4-membered ring and the thioxanthene moieties are about 20°. Interestingly, the butatriene units show bond alternation with the shorter C(sp)–C(sp) bond (averaged 1.217 Å) and longer C(sp)–C(sp^2) length (averaged 1.364 Å) as compared with the corresponding bond lengths (1.260 and 1.348 Å) of tetraphenylbutatriene.[94]

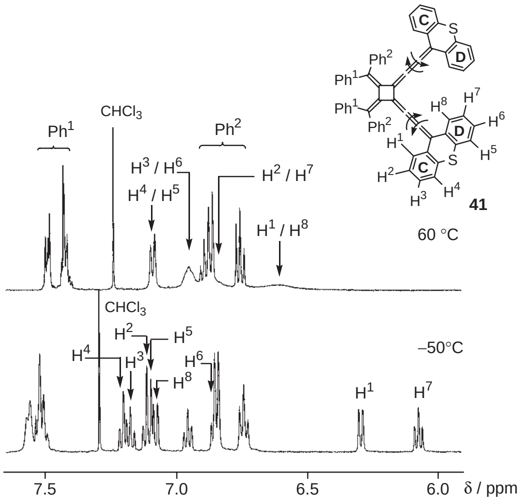


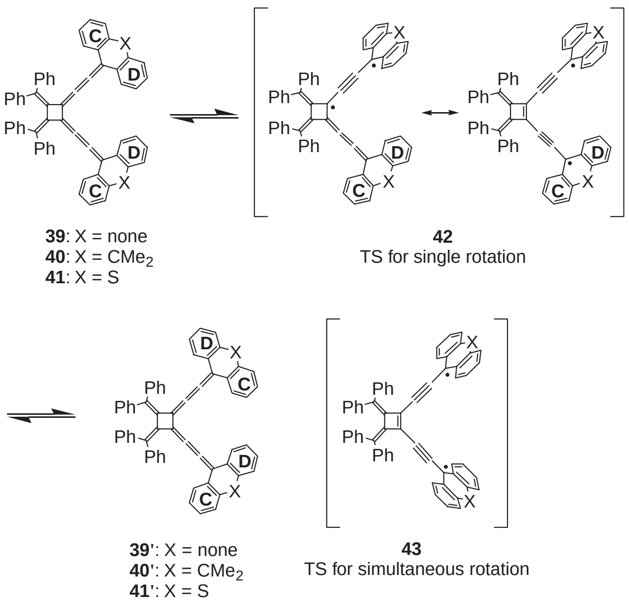
Fig. 5. ^1H NMR of **41** in $CDCl_3$ at 60 and −50 °C.

The ^1H NMR spectra of **39–41** are temperature dependent. As shown in Fig. 5, the signals of the phenyl groups in **41** remain to be sharp throughout the temperature range examined, indicating that the rotation of the phenyl groups is fast on the NMR time scale, and their chemical shifts are similar to those of the octaphenyl analogue **5**. In contrast, the signals of the thioxanthene moieties are very broad at ambient temperature, split into eight separate signals upon lowering the temperature, and coalesce into four signals at high temperatures. This behavior can be reasonably ascribed to the internal rotation about the cumulene bonds. Decoupling and qualitative saturation transfer experiments at low temperatures enabled the signal assignments to be determined as given in Fig. 5. Coalescence of the H^4 and H^5 signals ($\Delta\nu = 52$ Hz) took place at 15 °C, giving a rate constant of $k_c = 116\,s^{-1}$. Quantitative saturation transfer experiments (H^2 was irradiated and H^7 was observed) at -20 ± 1 °C gave the rate constant of $3.6 \pm 0.4\,s^{-1}$.[95,96] A similar temperature dependence of the ^1H NMR spectrum was also observed in **40** at a higher temperature range than that in **41**. The exchange rate was estimated to be $k = 3.5 \pm 0.4\,\mathrm{s^{-1}}$ at 0 °C by the saturation transfer method. The free energies of activation for the cumulenic bond rotation were deduced to be $\Delta G^{\ddagger} = 13.7$ and $14.9\,\mathrm{kcal\,mol^{-1}}$ for **41** (in $CDCl_3$ at −20 °C) and **40** (in $CDCl_3$ at 0 °C), respectively.

In contrast to the ^{1}H NMR spectra of **40** and **41**, the spectrum of **39** at room temperature showed sharp and well-resolved signals, suggesting that the energy barrier for bond rotation in **39** is fairly high as compared to those in **40** and **41**. In fact, the free energy of activation for the rotation was found to be $\Delta G^{\ddagger} = 17.8\,\mathrm{kcal\,mol^{-1}}$ in $C_2D_2Cl_4$ at 27 °C by saturation transfer studies. In any case, the extended [4]radialenes **39–41** exhibit low rotational barriers of the end-cap groups and can be regarded as the first twin-rotor system created on a radialene frame.

In order to discuss the observed energy barriers, the stability of both the ground states and the transition states for rotation should be considered. As shown in Figs. 2 and 4, the inner wings of the thioxanthene and dihydroanthracene rings in **41** and **40** significantly twist and overlap each other with the shortest C···C distance being the sum of the van der Waals radii (3.4 Å). In the case of **39**, however, the fluorene rings do not overlap, even though the twisting is to some extent because of the H···H repulsion. In accordance with these structural features, the H^7 proton signal shows a large upfield shift in **41** (δ 6.06 at −50 °C) and **40** (δ 6.03 at −30 °C) in the ^{1}H NMR spectra ($CDCl_3$) due to the shielding effect of the confronting aromatic ring, while the upfield shift is moderate in **39** (δ 7.10 at 22 °C in $C_2D_2Cl_4$). These molecular deformations cause the destabilization of the ground state, which is larger in **40** and **41** than in **39**. Thus, the molecular deformations in **39–41** at the ground state allow us to estimate the order of the destabilization as **41** $\geq$ **40** $>$ **39**.

A characteristic feature of the overcrowding in **39–41** is the unsymmetrical steric interactions of the end-capped aromatic rings on both terminals of the bis-cumulenic linkage, although the known barriers for the thermal-bond rotation of double bonds have been mainly investigated on the motion of fundamentally symmetrical olefinic and cumulenic bonds.[97] A plausible bond rotation process of **39–41** is depicted in Scheme 10. The butatriene bonds rotate one at a time by way of the transition state **42**, rather than simultaneously by way of **43** because **43** is considered to be far less stable than **42**. This diradicaloid transition state **42** is stabilized by the conjugation of these radicals among both the tricyclic aromatic system and the extended [4]radialene framework. The contribution of the latter conjugation is similar in **39–41**, while the conjugation in the terminal moieties significantly depends on the X part in the tricyclic aromatic group. In **41**, the sulfur atom participates in the conjugation and the transition state for **41** is stabilized more effectively than those for **39** and **40**.



Scheme 10.

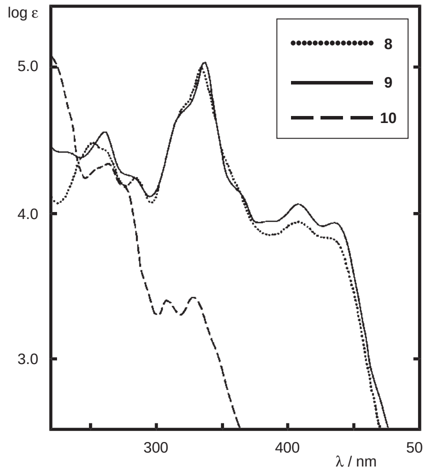


Fig. 6. The electronic spectra of [4]radialenes **8**, **9**, and **10** in THF.

The rotational barriers of the cumulenic double bonds in **39–41** are much lower than the reported barriers for the known butatrienes and bis-butatrienes (20–30 kcal mol^{-1}).[98–101] There has been considerable recent interest in the restricted rotation of single and double bonds because of their potential use in molecular-scale motors, thermochromic devices, molecular switches, and chemosensors.[102–107] Thus, the thermal and photochemical rotation of double bonds has been employed for the bottom-up construction of molecular motors.[108–111] We believe that our bis-butatriene system can contribute to the development of the studies on molecular motors, molecular switches, and chemosensors. To our knowledge, the $\Delta G^{\ddagger}$ value of $13.7\,\mathrm{kcal\,mol^{-1}}$ for **41** is the lowest reported so far for the energy barriers to rotation around an olefinic or cumulenic bond by way of a diradicaloid transition state.

Characteristic Structures of [4]Radialenes Derived from Alkyl-Substituted [5]Cumulenes. The [4]radialenes **2** and **8–12** are very stable toward light and air. Based on the molecular models and MM2 calculations, the polyallenic [4]radialenes **2** and **10–12** have a planer structure with D_{4h} symmetry, whereas the [4]radialenes **8** and **9** are planar D_{2h}-symmetric molecules. The ^{1}H and ^{13}C NMR spectra of **2** and **10–12** reflect their highly symmetric structures. As shown in Fig. 6, the electronic spectra of **8** and **9** exhibit an end absorption up to 450 nm, indicating elongation of π-conjugation, whereas

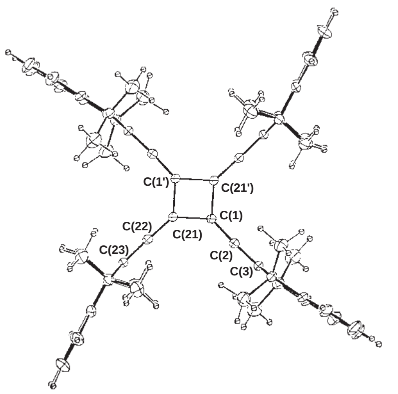


Fig. 7. ORTEP drawing of [4]radialene **11**. Selected bond lengths (Å) and angles (°) as follows: C(1)–C(2) 1.309(4), C(2)–C(3) 1.300(4), C(1)–C(21) 1.499(4), C(1)–C(21′) 1.510(4), C(21)–C(22) 1.304(4), C(22)–C(23) 1.298(4); C(2)–C(1)–C(21) 135.8(3), C(2)–C(1)–C(21′) 133.9(3), C(21)–C(1)–C(21′) 90.2(3), C(1)–C(2)–C(3) 173.9(3), C(1)–C(21)–C(22) 134.8(3), C(22)–C(21)–C(1′) 135.3(3), C(1)–C(21)–C(1′) 89.8(3), C(21)–C(22)–C(23) 177.8(3).

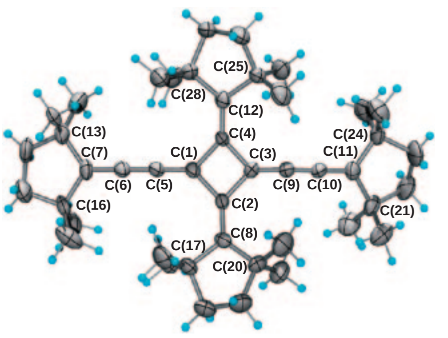


Fig. 8. ORTEP drawing of [4]radialene **8**. Selected bond lengths (Å) and angles (°) as follows: C(1)–C(2) 1.510(6), C(2)–C(3) 1.502(6), C(3)–C(4) 1.492(6), C(4)–C(1) 1.512(6), C(1)–C(5) 1.333(6), C(5)–C(6) 1.263(6), C(6)–C(7) 1.322(6), C(2)–C(8) 1.340(6), C(3)–C(9) 1.333(6), C(9)–C(10) 1.252(6), C(10)–C(11) 1.330(6), C(4)–C(12) 1.333(6); C(4)–C(1)–C(2) 90.2(4), C(1)–C(2)–C(3) 88.5(4), C(2)–C(3)–C(4) 91.3(4), C(3)–C(4)–C(1) 88.8(3), C(13)–C(7)–C(16) 110.2(4), C(17)–C(8)–C(20) 109.9(4), C(21)–C(11)–C(24) 110.4(4), C(25)–C(12)–C(28) 109.0(4).

the spectrum of **10** shows an end absorption only up to 350 nm, corresponding to the existence of an orthogonal allenic π-bond.

To elucidate the exact molecular structure of the [4]radialene with exocyclic allenic bonds, the crystal structure of **11** was determined by X-ray analysis.[51] The crystallographic data revealed that the molecule **11** is located on a crystallographic center of symmetry. The central 4-membered ring of the molecule is perfectly planar. Figure 7 shows the molecular projection of **11** onto the 4-membered ring plane together with the important structural parameters, indicating a very characteristic feature of **11** with a widely spread planar structure in its center. The four benzocyclopentene substituents are approximately perpendicular with the puckered angles of ca. 10° in the cyclopentene rings. Consequently, the molecule has a very beautiful shape like a pinwheel or cogwheel.

The X-ray structures of [4]radialenes previously determined have a puckered 4-membered ring due to the steric repulsion between the neighboring substituents on the exocyclic bonds.[87–89] An extension of the double bonds of [4]radialenes to the allenic bonds in **11** releases the severe steric repulsion between the neighboring substituents. No significant contact shorter than 4 Å was found between the methyl groups in tetramethylindane parts.

The radialene framework of **8** and **9** can be expected to adopt a planar structure with D_{2h} symmetry instead of a puckered structure with C_{2v} symmetry: The Raman spectrum of **9** exhibits very strong cumulenic absorption at 1995 cm^{-1}, while the IR spectrum shows a very weak peak at 1955 cm^{-1}. The molecular structure of **8** was determined by X-ray crystallographic analysis, as shown in Fig. 8. The molecule adopts a slightly puckered conformation with the angle of 11.9° with partial bending of the exocyclic double bonds, presumably due to the packing force in the crystal lattice. The terminal tetramethylcyclopentane rings adopt a half-chair conformation in order to release torsional strain between methyl groups. The bond angles at the inside sp^2-carbon atom of the cyclopentane rings are in the range of 109.0–110.4°. The slight deformation from D_{2h}-symmetry of **8** observed in the crystal can be dissolved in solution because of the lack of serious intramolecular constraints.

Structures and Properties of Extended [5]Radialene and [5]Radialenones. The structures and properties of extended [5]radialenones **13** and **14** have attracted considerable attention because the carbonyl groups in **13** and **14** can be expected to possess high polarities. The structure of **14** was determined by X-ray crystallography (Fig. 9).[52] The central 5-membered ring of **14** clearly shows a highly planar structure: The maximum atomic deviation from the least-squares plane is 0.03 Å. The planar structure extends to the exocyclic allenic bonds with a maximum atomic deviation of 0.24 Å. The bond distances in the carbonyl and allenic moieties of the molecule are normal, while the bond angles C(2)–C(1)–C(10) [129.2(6)°] and C(3)–C(4)–C(40) [129.9(7)°] are significantly larger than the expected value of 126°, although the long distance between the neighboring *t*-butyl substituents causes no short contact. A similar angular deformation was found in tetrakis(1,3-dithiaindanylidene)cyclopentanone due to significant non-bonded repulsion between the substituents of exocyclic bonds.[71] Although the [5]radialenes prefer the half-chair conformation,[112] the planar structure of **14** may be due to the absence of steric strain between the *t*-butyl substituents as the result of the extension of the exocyclic bonds by a cumulenic structure.

Bulky tetramethylcyclohexylidene rings and *t*-butyl groups covering the outside of the [5]radialenones **13** and **14** seem to protect the reactive π-electronic system. An interesting behavior of **13** and **14** is solvatochromism. As shown in Fig. 10, a solution of **14** exhibits a pale yellow color in benzene or THF, but bright yellow in methanol or acetic acid. Similarly, solutions of **13** in benzene and methanol are pale yellow and bright yellow, respectively. The UV–vis spectra of **13** and **14** show strong (215–250 nm, $\log \varepsilon =$ ca. 4.5) and weak (300–430 nm, $\log \varepsilon =$ ca. 3.5) absorptions. Although the strong absorptions

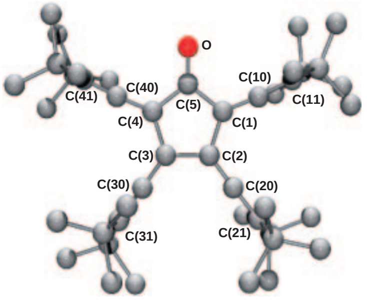


Fig. 9. ORTEP drawing of [5]radialenone **14**. Selected bond lengths (Å) and angles (°) as follows: C(1)–C(2) 1.492, C(2)–C(3) 1.483, C(3)–C(4) 1.490, C(4)–C(5) 1.488, C(5)–C(1) 1.476, C(5)–O 1.206, C(1)–C(10) 1.322, C(10)–C(11) 1.302, C(2)–C(20) 1.318, C(20)–C(21) 1.312, C(3)–C(30) 1.320, C(30)–C(31) 1.310, C(4)–C(40) 1.325, C(40)–C(41) 1.286; C(1)–C(2)–C(3) 107.8, C(2)–C(3)–C(4) 107.8, C(3)–C(4)–C(5) 108.1, C(4)–C(5)–C(1) 107.7, C(5)–C(1)–C(2) 108.4, C(1)–C(2)–C(20) 123.9, C(20)–C(2)–C(3) 128.4, C(2)–C(3)–C(30) 126.4, C(30)–C(3)–C(4) 125.7, C(40)–C(4)–C(5) 122.0, C(4)–C(5)–O 126.2, C(2)–C(1)–C(10) 129.2, C(3)–C(4)–C(40) 129.9, O–C(5)–C(1) 126.0, C(5)–C(1)–C(10) 122.4, C(1)–C(10)–C(11) 175.4, C(2)–C(20)–C(21) 177.7, C(3)–C(30)–C(31) 179.2, C(4)–C(40)–C(41) 175.4. The estimated standard deviations are 0.009–0.011 Å and 0.7–0.8° for bond distances and angles.

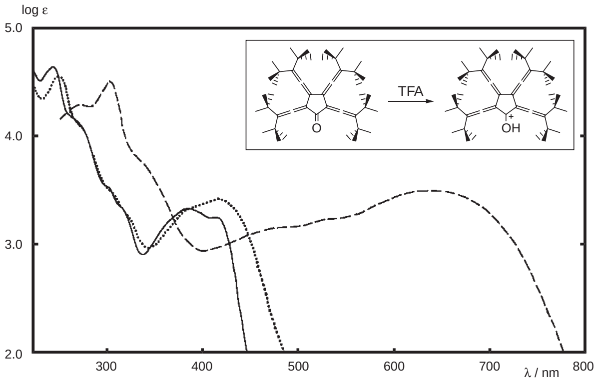
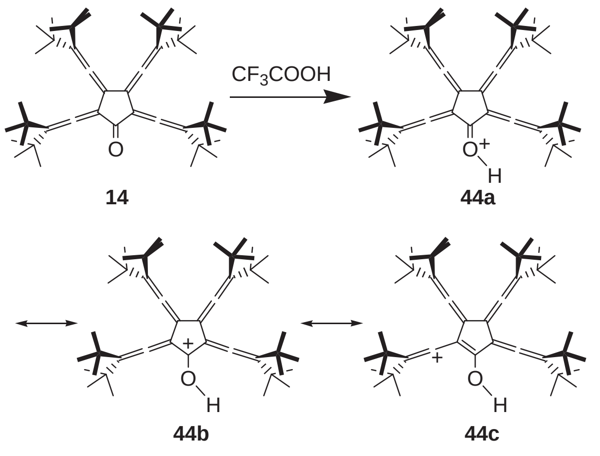
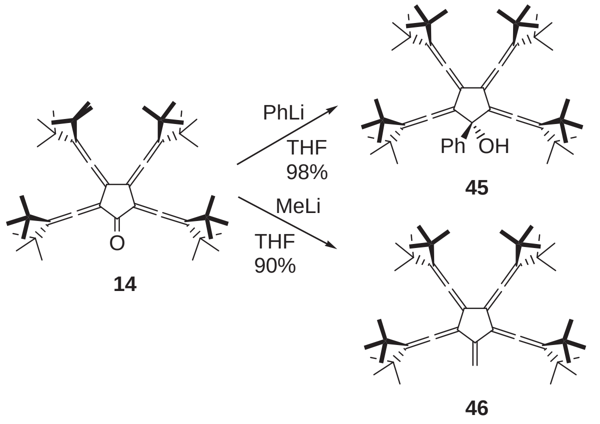


Fig. 10. The electronic spectra of [5]radialenone **14** in THF (solid line), MeOH (dotted line), and TFA (broken line). The bathochromic shift in TFA represents the contribution of the cationic structure of the protonated **14** as shown in Scheme 11.

of **13** and **14** show a small dependence on the solvent, the wavelengths of the weak absorptions vary with the solvent used. Thus, the absorption maxima of **14** appeared at 378 ($\log \varepsilon = 3.36$) and 408 ($\log \varepsilon = 3.27$) nm in THF, and the absorption bands bathochromically shift with an increase in the polarity of the solvent. Although the X-ray analysis of **14** reveals a normal bond length for the carbonyl part, protonation of the C=O group easily exhibits a remarkable solvatochromism. The color of **14** in trifluoroacetic acid (TFA) changes to a deep violet [621 nm ($\log \varepsilon = 3.51$)]. The interesting contribution of the resonance structures **44b** and **44c** for the protonated ketone **44a** is considered to be as shown in Scheme 11.



Scheme 11.



Scheme 12.

In order to confirm the unusual stability of the cationic species **44**, the nucleophilic addition of organolithium reagents was examined (Scheme 12). The reaction of **14** with PhLi in THF gave the corresponding alcohol **45** in 98% yield, whereas a similar reaction of **14** with MeLi directly afforded the [5]-radialene **46** in 90% yield. The facile formation of **46** may be due to either the overcrowded structure of the adduct or the stability of the cationic intermediate.

Solutions of both compounds **45** and **46** in TFA exhibit an intense deep blue color, and the electronic spectra show the absorption maxima at ca. 800 nm ($\log \varepsilon \sim 3.8$) tailing up to 1100 nm (Fig. 11). These spectra suggest the formation of the corresponding carbocations, which have a small HOMO–LUMO gap. The cationic species in solution were found to be stable, and we took the ^{1}H and ^{13}C NMR spectra of the cation derived from **46**. The ^{1}H NMR spectrum of **46** measured in a $CDCl_3$–CF_3COOD (1:1) solution showed that the original signal for the olefinic proton observed at δ 5.02 in $CDCl_3$ disappeared, and that the signals for the protons of the *t*-butyl substituent shifted to a lower field. Disappearance of the olefinic proton signals can be explained by the formation of the carbocation **47**. The equilibrium between carbocation and the original olefin caused H–D exchange at the methyl group in **47** (Scheme 13), and the methyl group in **47**-*d* and **47**-d_2 was observed at δ 2.87 as very weak signals with a complicated coupling pattern due to geminal deuterons. The cationic carbon signal in the ^{13}C NMR appeared at a very low field

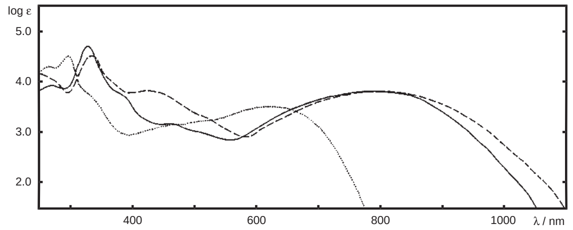
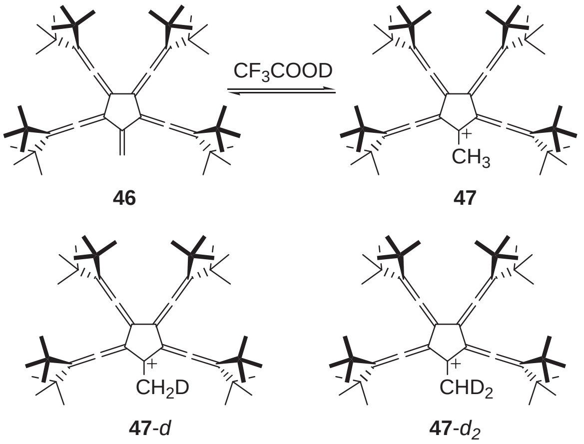


Fig. 11. The electronic spectra of [5]radialenone **14** (dotted line), [5]radialene **46** (solid line), and carbinol **45** (broken line) in TFA.



Scheme 13.

(δ 208.4), shifted from δ 142.7 in the original spectrum of **46**. Considerable low-field shifts were also observed for allenic sp-carbon signals (δ 228 ppm) and for sp^2-, and for even sp^3-carbons. Thus, the NMR spectral characteristics of **47** reflect the highly delocalized nature of the cationic charge.

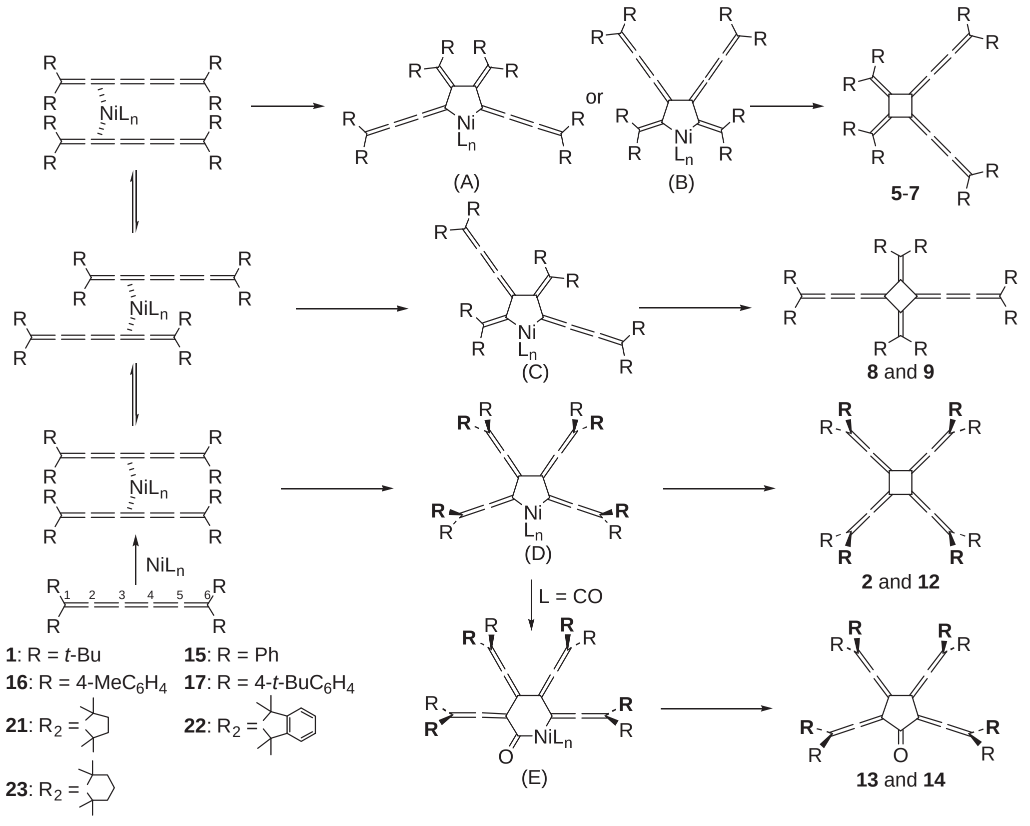
Nickel-Catalyzed Dimerization of [5]Cumulenes. The nickel-catalyzed dimerization of [5]cumulenes reported here is a versatile strategy for the synthesis of novel radialene derivatives conjugated with cumulative double bonds. It is shown that the terminal substituents of [5]cumulenes play a major role in determining the reaction pathway. Since the cyclodimerization of cumulenes proceeds via a nickelacycle intermediate, the regiochemistry of the products may be determined by the formation of the 5-membered nickelacycles from the corresponding bis-π-complexes.[47–49] The preference of the C_2–C_3 double bond in the coordination to transition metals is observed for [5]cumulenes as shown in the formation of rhodium complexes. However, this preference can be deviated by a steric interference of the terminal substituents, and tetra-*t*-butyl[5]cumulene (**1**) forms a C_3–C_4 complex with $Fe(CO)_5$. According to the theoretical investigation of Hoffmann,[113] the regiochemistry of the formation of 5-membered metallacycles from the corresponding bis-olefin complex is governed by the LUMO of the coordinating olefins. The preferable formation of C–C bonds at the carbon atom with a large orbital coefficient in the LUMO should determine the reaction course. When two [5]cumulenes coordinate to nickel(0) at the C_2–C_3 double bond, a large orbital coefficient in the LUMO is expected at the C_2-position (terminal position of the conjugation in the π^*-molecular orbital) and the bis-π-complex should lead to a nickelacycle with the formation of the C–C bond at the C_2 carbon atoms.

A plausible reaction mechanism for the nickel-catalyzed dimerization of [5]cumulenes is depicted in Scheme 14. The reaction of a Ni(0) complex with [5]cumulenes affords a biscumulene complex, which leads to the corresponding 5-membered nickelacycle in the case of [5]cumulenes possessing less-hindered substituents. Tetraaryl[5]cumulenes **5**–**7** can be considered to produce the nickelacycle (A) by the formation of a C–C bond at the C_2-position, and lead to a head-to-head (C_2–C_3) dimer after reductive elimination. In the case of [5]cumulenes with bulky substituents, formation of the similar metallacycle (A) is considered to be difficult because of the concomitant repulsive interaction, which deviates the reaction course. Thus, the cumulenes **1** and **21**–**23** form the metallacycle (C) by changing the bond-forming manner to afford head-to-tail (C_2–C_3) dimers **8** and **9**. The cumulenes with more bulky substituents (**1** and **23**) can not form this metallacycle and lead to the formation of the metallacycle (D) with the shifts of the coordination site. A simple reductive elimination from D affords the symmetric [4]radialenes **2** and **12**, whereas the CO insertion followed by reductive elimination from E results in the formation of the [5]radialenones **13** and **14**.

The nickelacycle intermediates play a critical role in the formation of the dimeric products of [5]cumulenes. Therefore, the theoretical calculations of the intermediates were examined. According to the theoretical calculations (B3LYP/BS-I and BS-II[114]) of the nickelacycle intermediates A–D ($R = H$, $L = PH_3$, and $n = 2$), the most stable isomer is A, which forms from the reaction at the second double bond (C_2–C_3) of [5]cumulene in a head-to-head manner. The other intermediate B, which produces the same dimer after reductive elimination, is less stable than A by 14 kcal mol^{-1}. Thus, a plausible intermediate for the formation of the head-to-head dimer is considered to be A. The preferential formation of A than to B is in good agreement with the general tendency for nickelacycle formation by the oxidative cyclization of two π-corponents. The head-to-tail nickelacycle C formed from the reaction at the same double bond is the second most stable isomer, which has a higher energy than the metallacycle A by 6 kcal mol^{-1}. The nickelacycle D is considerably more unstable than A and not the structure with minimum energy. Therefore, the most preferable intermediate of the nickel-catalyzed dimerization of [5]cumulene is the metallacycle A, which leads to the head-to-head dimer after reductive elimination. Large substituents at the terminal of [5]cumulene would affect the stability of the nickelacycle intermediate due to the steric repulsion among the substituents and the phosphine ligands on the nickel atom. The magnitude of the steric destabilization in the reaction at the second double bond of [5]cumulenes is consistent with those of the bond angles of the geminal substituents at the [5]cumulenes (**1** and **21**–**23**). Thus, the [5]cumulenes with 5-membered ring substituents (**21** and **22**) afforded the head-to-tail dimer via the nickelacycle C, whereas **1** and **23** gave the [4]radialene and the [5]radialenone via the nickelacycle D.

Summary

The nickel-catalyzed reactions of [5]cumulenes provided are an effective method for the syntheses of a variety of [5]cumulene dimers. In the case of tetraaryl[5]cumulenes,



Scheme 14.

head-to-head dimers are selectively formed, reflecting the stability of the metallacyclic intermediate. The tetraaryl[5]cumulene dimers have an extended [4]radialene framework with an intense blue color in solution. Furthermore, this extended [4]radialene system with terminal dimethyldihydroanthracene and thioxanthene units exhibits low rotational barriers for the cumulenic double bonds. The easy rotation of the cumulenic double bonds at ambient temperatures will be useful in developing molecular motors, molecular switches, and chemosensors. The cyclodimerization of [5]cumulenes with bulky alkyl substituents produces head-to-tail [4]radialenes, tetrakis(allenylidene)[4]radialenes, and [5]radialenones. The structures of [4]radialenes and [5]radialenone have been confirmed by X-ray analyses. The preferential formation of [4]radialenes or [5]radialenones depends on the bulky alkyl substituents of [5]cumulenes, the reaction pathway having been proven by MO calculations by considering the stability of the metallacyclic intermediates. The [5]radialenones exhibit solvatochromism. The color of the benzene solution is a pale yellow, whereas the color in methanol is a bright yellow. Additionally, solutions of [5]radialenone in trifluoroacetic acid exhibit an intense blue color, reflecting the formation of stable carbocations. The cationic charge is delocalized on the extended [5]-radialene framework. Finally, we can conclude that the extended [4]radialenes and [5]radialenes have a possible multifunctionality based on the unique arrangements of their cumulated double bonds.

Experimental

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-100, JEOL JNM-PMX 60Si, JNM-FX 90Q, JNM-GSX 400, or JNM-GX 500 instrument. Spectra are reported (in δ) referenced to Me_4Si. Unless otherwise noted, $CDCl_3$ was used as the solvent. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, td = triplet doublet, m = multiplet, and br = broad), coupling constant (Hz), and integration. In the organometallic compounds **31** and **32**, the coupling constants between the carbons and ^{103}Rh (or ^{31}P) are described. IR spectra were taken on a Hitachi EPI-G3 or a Jasco R-800 FT-IR-3 spectrometer. Raman spectra were measured on a Jasco R-800 spectrometer. Electronic spectra were obtained on a Hitachi EPS-3T or a U-3400 instrument and are reported in nanometers ($\log \varepsilon$) (sh = shoulder). Mass spectral analyses (MS) were performed on a JEOL JMS-OISG-2 instrument. Only the intense or structurally diagnostic mass spectral fragment ion peaks are reported. Melting points were determined on a Mettler FP-2 apparatus and are uncorrected.

Preparation of Tetraarylhexapentaenes 15–17. 1,1-Bis(4-*t*-butylphenyl)-2-propyn-1-ol (19c): Gaseous acetylene was introduced into dry THF (200 mL) for 30 min at −78 °C. A solution of *n*-BuLi (1.5 M in hexane, 50 mL, 76 mmol) was added via syringe while passing acetylene through the solution below −50 °C and the mixture was stirred for 1 h at the same temperature. A solution of 18.0 g (61.1 mmol) of 4,4′-di-*t*-butylbenzophenone (**18c**) in 50 mL of dry THF was added dropwise within 10 min. The mixture was allowed to warm to ambient temperature and stirred for 4 h. After cooling to −50 °C, a mixture of 50 mL of saturated aqueous NH_4Cl and 50 mL of water was added and the mixture was allowed to warm to room temperature. The mixture was extracted with 3 × 100 mL of benzene and the extracts were dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by chromatography on alumina with diethyl ether–benzene as the eluent. The resultant solid after removal of the solvent was recrystallized from ether–hexane to give 18.6 g (95%) of the alcohol. **19c**: colorless needles (hexane–ether), mp 176.5–177.5 °C; ^{1}H NMR (60 MHz, CCl_4) δ 7.37 (d, $J = 8$ Hz, 4H), 7.27 (d, $J = 8$ Hz, 4H), 2.67 (s, 1H), 2.28 (s, 1H), 1.33 (s, 18H); Anal. Calcd for $C_{23}H_{28}O$: C, 86.20; H, 8.81%. Found: C, 86.10; H, 8.79%.

1,1-Diphenylpropyn-1-ol (19a): In a similar manner to that described above, **19a** was obtained from benzophenone (**18a**) in 96% yield. **19a**: colorless needles (hexane–ether), mp 46.5–48 °C (lit.[115] 47–48 °C); ^{1}H NMR (60 MHz, CCl_4) δ 7.57–7.03 (m, 10H), 2.77 (s, 1H), 2.63 (s, 1H).

1,1-Bis(4-methylphenyl)propyn-1-ol (19b): In a similar manner to that described above, **19b** was obtained from 4,4′-dimethylbenzophenone (**18b**) in 86% yield. **19b**: colorless needles (hexane–ether), mp 84.5–86.0 °C (lit.[18] 87–88 °C); ^{1}H NMR (60 MHz, CCl_4) δ 7.30 (d, $J = 8$ Hz, 4H), 6.97 (d, $J = 8$ Hz, 4H), 2.61 (s, 1H), 2.47 (s, 1H), 2.28 (s, 6H).

1,1,6,6-Tetrakis(4-*t*-butylphenyl)-2,4-hexadiyne-1,6-diol (20c): To a stirred solution of 4.79 g (24.0 mmol) of $Cu(OAc)_2 \cdot H_2O$ in methanol–pyridine (1:1, 100 mL) was added a solution of 3.85 g (12.0 mmol) of the alcohol **19c** in 100 mL of methanol–pyridine (1:1) at 60 °C and the solution was stirred for 10 h at the same temperature. After cooling to room temperature, the solvent was evaporated in vacuo and a mixture of 100 mL of ether–CS_2 (v/v = 4/1) and 250 mL of 2 M HCl was added to the residue. The aqueous phase was extracted with 2 × 100 mL of ether–CS_2 (v/v = 4/1) and the combined organic phase was washed successively with 2 M HCl, water, and brine, and then dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by recrystallization from ether–hexane to give the diol **20c** (3.26 g, 85%). **20c**: colorless crystals, mp >270 °C; ^{1}H NMR (60 MHz, CCl_4) δ 6.93 (brs, 16H), 1.98 (s, 2H), 0.96 (s, 36H); Anal. Calcd for $C_{46}H_{54}O_2$: C, 86.47; H, 8.52%. Found: C, 86.18; H, 8.66%.

1,1,6,6-Tetraphenyl-2,4-hexadiyne-1,6-diol (20a): In a similar manner to that described above, **20a** was obtained from 1,1-diphenylpropyn-1-ol (**19a**) in 89% yield. **20a**: colorless crystals, mp 147–149 °C (lit.[18] 150–151 °C); ^{1}H NMR (60 MHz, CCl_4) δ 7.58–7.10 (m, 20H), 2.47 (s, 2H).

1,1,6,6-Tetrakis(4-methylphenyl)-2,4-hexadiyne-1,6-diol (20b): In a similar manner to that described above, **20b** was obtained from 1,1-bis(4-methylphenyl)propyn-1-ol (**19b**) in 89% yield. **20b**: colorless crystals, mp 170–171 °C (lit.[18] 205–206 °C); ^{1}H NMR (60 MHz, CCl_4) δ 7.27 (d, $J = 8$ Hz, 8H), 7.00 (d, $J = 8$ Hz, 8H), 2.33 (s, 2H), 2.30 (s, 12H).

1,1,6,6-Tetraphenyl-1,2,3,4,5-hexapentaene (15): A solution of 2.07 g (4.99 mmol) of the diol **20a** in 25 mL of dry ether was cooled to −50 °C and then 1.24 g (5.50 mmol) of $SnCl_2 \cdot 2H_2O$ and 6.0 mL of ether saturated with gaseous HCl was added. The mixture was allowed to warm to 0 °C and stirred for 1 h at 0 °C. The resulting orange solids were filtered off and were washed successively with water, EtOH, and ether to give the cumulene **15** (1.66 g, 87%). **15**: orange prisms, mp >250 °C (lit.[2] 298 °C); ^{1}H NMR (60 MHz, CCl_4) δ 7.59–7.13 (m); IR (KBr) 3046, 1997, 1592, 1490, 1452, 1444, 1279, 1175, 1082, 1028, 921, 770, 755, 694, 632, 622, 608, 523 cm^{-1}; UV $\lambda_{\max}$ (THF) 485 (log ε 4.87), 433 (sh, 4.36), 367 (4.09), 286 (4.51), 271 (4.53), 254 nm (4.70).

1,1,6,6-Tetrakis(4-methylphenyl)-1,2,3,4,5-hexapentaene (16): In a similar manner to that described for the preparation of the cumulene **15**, the cumulene **16** was obtained from the diol **20b** in 94% yield. **16**: deep red crystals, mp >250 °C (lit.[18] 318–320 °C); ^{1}H NMR (500 MHz, CD_2Cl_2–CS_2) δ 7.36 (d, $J = 8$ Hz, 8H), 7.15 (d, $J = 8$ Hz, 8H), 2.38 (s, 12H); ^{13}C NMR (125 MHz, CD_2Cl_2–CS_2) δ 147.9, 138.4, 135.4, 129.31, 129.27, 126.3, 123.8, 21.5; IR (KBr) 3016, 2910, 2000, 1600, 1506, 1284, 1175, 1012, 821, 718, 610, 573, 469 cm^{-1}; UV $\lambda_{\max}$ (THF) 502 (log ε 4.89), 497 (4.89), 494 (4.88), 429 (4.19), 372 (4.08), 296 (4.51), 255 nm (4.64).

1,1,6,6-Tetrakis(4-*t*-butylphenyl)-1,2,3,4,5-hexapentaene (17): To a solution of 1.07 g (1.67 mmol) of the diol **20c** in 20 mL of dry THF were added 1.38 g (6.12 mmol) of $SnCl_2 \cdot 2H_2O$ and 10.0 mL of ether saturated with gaseous HCl at 0 °C. The mixture was stirred for 1 h at 0 °C. Then 100 mL of CH_2Cl_2 and 100 mL of water were added. The organic layer was separated and washed successively with water, aqueous $NaHCO_3$, and brine, and then dried over $MgSO_4$. After removal of the solvent, the residue was passed through a short column of alumina with CH_2Cl_2 as the eluent. The collected crystals after removal of the solvent were washed with ether to give the cumulene **17** (893 mg, 88%). **17**: orange crystals, mp >250 °C; ^{1}H NMR (100 MHz) δ 7.55 (d, $J = 9$ Hz, 8H), 7.43 (d, $J = 9$ Hz, 8H), 1.34 (s, 36H); ^{13}C NMR (125 MHz, CD_2Cl_2–CS_2) δ 151.8, 148.6, 135.8, 129.7, 126.9, 126.0, 124.1, 34.9, 31.7; MS (FD) m/z 604 (M^+); IR (KBr) 3050, 2955, 2003, 1602, 1506, 1462, 1364, 1270, 1109, 1013, 834, 614 cm^{-1}; UV $\lambda_{\max}$ (THF) 503 (log ε 4.90), 430 (4.18), 372 (4.09), 297 (4.55), 255 nm (4.66). Anal. Calcd for $C_{46}H_{52}$: C, 91.34; H, 8.66%. Found: C, 91.00; H, 8.65%.

Preparation of Tetraalkylhexapentaenes 1 and 21–23. 1-Ethynyl-2,2,5,5-tetramethylcyclopentanol (25a): Gaseous acetylene was introduced into dry THF (100 mL) for 30 min at −78 °C. A solution of *n*-BuLi (1.5 M, 33 mL, 50 mmol) in hexane was added via syringe while passing acetylene through the solution below −50 °C, and the mixture was stirred for 30 min at the same temperature. The solution of 5.61 g (40.0 mmol) of 2,2,5,5-tetramethylcyclopentanone (**24a**) in 15 mL of dry THF was added dropwise for 10 min and the mixture was allowed to warm to ambient temperature and stirred for 3 h. After addition of water (20 mL) and K_2CO_3 (30 g), the organic layer was separated and the aqueous phase was extracted with 2 × 20 mL of ether. The combined extracts were dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was distilled under reduced pressure to give 30.1 g (96%) of the alcohol. **25a**: colorless liquid, bp 95 °C (31 mmHg); MS m/z 166 (M^+); ^{1}H NMR (90 MHz) δ 2.26 (s, 1H), 1.78 (brs, 1H), 1.72–1.47 (m, 4H), 1.18 (s, 6H), 1.08 (s, 6H); ^{13}C NMR (22.5 MHz) δ 84.7, 84.1, 75.0, 47.0, 37.9, 28.8, 25.0; IR (neat) 3490, 2933, 2858, 2098, 1469, 1387, 1371, 1302, 1256, 1232, 1188, 1150, 1095, 1063, 1017, 975, 865, 647, 630 cm^{-1}; Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91%. Found: C, 79.46; H, 11.06%.

2-Ethynyl-1,1,3,3-tetramethylindan-2-ol (25b): In a similar manner to that described above, **25b** was obtained from 1,1,3,3-tetramethylindan-2-one (**24b**) in 81% yield. **25b**: colorless liquid, bp 83–85 °C (0.1 mmHg); MS m/z 214 (M^+); ^{1}H NMR (100 MHz) δ 7.29–7.07 (m, AA′BB′, 4H), 2.62 (s, 1H), 1.96 (s, 1H), 1.40 (s, 6H), 1.38 (s, 6H); IR (neat) 3509, 3310, 2079 cm^{-1}; Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47%. Found: C, 83.74; H, 8.68%.

1-Ethynyl-2,2,6,6-tetramethylcyclohexanol (25c): In a similar manner to that described above, **25c** was obtained from 2,2,6,6-tetramethylcyclohexanone (**24c**) in 89% yield. **25c**: colorless liquid, bp 120–121 °C (38 mmHg) (lit.[116] bp 129.5 °C at 50 mmHg); MS m/z 180 (M^+); ^{1}H NMR (60 MHz, CCl_4) δ 2.30 (s, 1H), 1.61 (s, 1H), 1.55–1.30 (m, 6H), 1.13 (s, 6H), 1.05 (s, 6H); Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18%. Found: C, 79.94; H, 11.31%.

1,4-Bis(1-hydroxy-2,2,5,5-tetramethylcyclopentyl)butadiyne (26a): To a solution of 24.0 g (120 mmol) of $Cu(OAc)_2 \cdot H_2O$ in a mixture of pyridine (120 mL) and methanol (100 mL) was added a solution of 9.98 g (60.0 mmol) of the alcohol **25a** in 20 mL of pyridine and the solution was stirred for 12 h at 60 °C. After cooling to room temperature, the solvent was evaporated in vacuo and a mixture of 100 mL of ether and 300 mL of 2 M HCl was added to the residue. The aqueous layer was extracted with 2 × 100 mL of ether and the combined extracts were washed successively with 2 M HCl, aqueous 2 M NaOH, water, and brine, and then dried over $MgSO_4$. After removal of the solvent in vacuo, the residual solid was washed with hexane to afford 5.78 g of the product. The washings were concentrated in vacuo and purified by column chromatography on alumina with a mixture of benzene and ether as the eluent to produce an additional 3.18 g of the diol **26a** (total 8.96 g, 90%). **26a**: colorless crystals, mp 178–179 °C; MS m/z 330 (M^+); ^{1}H NMR (90 MHz) δ 1.89 (s, 2H), 1.76–1.47 (m, 8H), 1.18 (s, 12H), 1.08 (s, 12H); ^{13}C NMR (22.5 MHz) δ 84.8, 80.2, 71.4, 47.9, 38.1, 28.8, 25.1; IR (KBr) 3590, 3485, 2945, 2855, 2130, 1470, 1383, 1369, 1317, 1299, 1260, 1225, 1183, 1150, 1092, 1062, 1008, 967, 919, 860 cm^{-1}; Anal. Calcd for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37%. Found: C, 79.83; H, 10.55%.

1,4-Bis(2-hydroxy-1,1,3,3-tetramethyl-2-indanyl)butadiyne (26b): In a similar manner to that described for the preparation of **26a**, the diol **26b** was obtained from the alcohol **25b** in 86% yield. **26b**: colorless crystals (hexane–benzene), mp 205.3–207.2 °C; MS m/z 426 (M^+); ^{1}H NMR (100 MHz) δ 7.30–7.09 (m, AA′BB′, 8H), 2.02 (s, 2H), 1.44 (s, 12H), 1.41 (s, 12H); IR (KBr) 3558, 3449, 2146 cm^{-1}; Anal. Calcd for $C_{30}H_{34}O_2$: C, 84.47; H, 8.03%. Found: C, 84.48; H, 8.06%.

1,4-Bis(1-hydroxy-2,2,6,6-tetramethylcyclohexyl)butadiyne (26c): In a similar manner to that described for the preparation of **26a**, the diol **26c** was obtained from the alcohol **25c** in 89% yield. **26c**: colorless crystals, mp 161–163 °C (lit.[33] mp 173 °C); ^{1}H NMR (60 MHz, CCl_4) δ 1.70 (s, 2H), 1.60–1.30 (m, 12H), 1.17 (s, 12H), 1.08 (s, 12H).

2,3-Dibromo-1,4-bis(2,2,5,5-tetramethylcyclopentylidene)-1,3-butadiene (27a): To a solution of the diol **26a** (2.31 g, 6.99 mmol) in acetic acid (70 mL) was added a solution of 48% HBr and the mixture was stirred for 1 h at ambient temperature. The reaction mixture was diluted with a mixture of water (300 mL) and 2 M NaOH (200 mL), and extracted with ether (500 mL). The organic extracts were washed with 2 M NaOH, water, and brine successively, and then dried over $MgSO_4$. After removal of the solvent under reduced pressure, the collected crude crystals were washed with methanol to afford 2.88 g (90%) of the cumulene **27a**: yellow prisms, mp ca. 250 °C (sublimed); MS m/z 454 (M^+); ^{1}H NMR (60 MHz, CCl_4) δ 1.67 (s, 8H), 1.25 (s, 12H), 1.18 (s, 12H); Anal. Calcd for $C_{22}H_{32}Br_2$: C, 57.91; H, 7.06; Br, 35.02%. Found: C, 57.67; H, 7.07; Br, 35.56%.

2,3-Dichloro-1,4-bis(1,1,3,3-tetramethyl-2-indanylidene)-1,3-butadiene (27b): To a solution of the diol **26b** (853 mg, 2.00 mmol) in a mixture of dioxane (20 mL) and acetic acid (20 mL) was added a solution of 36% HCl (10 mL) and the mixture was stirred for 7 days at ambient temperature. The reaction mixture was poured into water (150 mL) and the crystals formed were collected and washed with water. The crude crystals were dissolved in benzene and the organic solution was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on alumina with a mixture of hexane and benzene as the eluent to give 724 mg (78%) of the product. **27b**: colorless plates (ether–hexane), mp 185–186 °C; MS m/z 462 (M^+); ^{1}H NMR (400 MHz) δ 7.29–7.24 (m, 4H), 7.20–7.17 (m, 4H), 1.52 (s, 12H), 1.51 (s, 12H); ^{13}C NMR (100 MHz) δ 195.6, 148.2*, 136.8*, 127.5*, 122.5, 105.4, 48.3*, 30.81, 30.75 (asterisk shows two types of signals overlapped); Anal. Calcd for $C_{30}H_{32}Cl_2$: C, 77.74; H, 6.96; Cl, 15.30%. Found: C, 77.79; H, 6.97; Cl, 15.42%.

2,3-Dibromo-1,4-bis(2,2,6,6-tetramethylcyclohexylidene)-1,3-butadiene (27c): To a solution of the diol **26c** (3.59 g, 10.0 mmol) in benzene (50 mL) was added PBr_3 (1.5 mL, 15 mmol). The mixture was heated to 55 °C and stirred for 4 h. After cooling to room temperature, the reaction mixture was poured into 200 mL of ice-water (200 mL) and extracted with Et_2O (3 × 100 mL). The combined organic extracts were washed with water and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the collected crystals were washed with methanol to afford **27c** (3.43 g). The combined washings were concentrated in vacuo, and the residue was purified by column chromatography on alumina with hexane as the eluent to give 119 mg of the product. A total of 3.55 g (73%) of the product was obtained. **27c**: colorless crystals (CH_2Cl_2–ethanol), mp 232.5–234.5 °C (lit.[33] 233.5 °C); ^{1}H NMR (60 MHz, CCl_4) δ 1.66–1.40 (m, 12H), 1.23 (s, 12H), 1.16 (s, 12H).

3,4-Dibromo-1,1,6,6-tetra-*t*-butyl-1,2,4,5-hexatetraene (27d): To a stirred solution of the diol **26d** (1.34 g, 4.01 mmol) in benzene (20 mL) was added PBr_3 (1.0 mL, 10 mmol). The mixture was heated to 55 °C and stirred for 6 h. After cooling to room temperature, the mixture was poured into a mixture of water (100 mL) and saturated aqueous Na_2CO_3 (60 mL) and extracted with ether (3 × 60 mL). The combined organic extracts were washed with saturated aqueous Na_2CO_3 and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the residual solids were purified by column chromatography on silica gel with a mixture of benzene and hexane as the eluent. The collected fractions of the product were concentrated in vacuo to give crystals, which were washed with methanol (1.68 g, 91%). **27d**: colorless prisms (CH_2Cl_2–ethanol), mp 229.5–230.5 °C (sublimed, lit.[59] mp 232–233 °C); ^{1}H NMR (60 MHz, CCl_4) δ 1.27 (s).

1,4-Bis(2,2,5,5-tetramethylcyclopentylidene)-1,2,3-butatriene (21): A mixture of the dibromide **27a** (913 mg, 2.00 mmol), zinc powder (654 mg, 10.0 mmol), and THF (20 mL) was irradiated by ultrasonic wave for 30 min under an argon atmosphere and stirred for 30 min. The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as the eluent. The crude crystalline product obtained by evaporation of the fractions was purified by washing with methanol to produce 566 mg (95%) of the cumulene **21**: yellow needles (CH_2Cl_2–hexane), mp 225–226 °C (decomp.); MS m/z 296 (M^+); ^{1}H NMR (90 MHz) δ 1.72 (s, 8H), 1.19 (s, 24H); ^{13}C NMR (22.5 MHz) δ 149.7, 144.7, 132.1, 47.2, 39.6, 29.3; IR (KBr) 2940, 2925, 2870, 2845, 1453, 1449, 1382, 1376, 1360, 1345, 1311, 1304, 1242, 1212, 1111, 1072, 1013, 989, 960, 834, 650, 534 cm^{-1}; Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88%. Found: C, 88.89; H, 10.89%.

1,4-Bis(1,1,3,3-tetramethyl-2-indanylidene)-1,2,3-butatriene (22): To a stirred solution of **27b** (232 mg, 0.501 mmol) in THF (10 mL) was added a solution of *n*-BuLi (1.5 M, 0.40 mL, 0.60 mmol) in hexane via syringe at −70 °C and the mixture was stirred for 1 h. After the addition of 0.5 mL of water, the mixture was allowed to warm to ambient temperature. Then the mixture was diluted with hexane (20 mL), and dried over $MgSO_4$. After evaporation of the solvent under reduced pressure, the residual solid was purified by column chromatography on alumina with a mixture of benzene and hexane (1:1) as the eluent. The crude crystalline product obtained was further purified by washing with hexane to give 189 mg (96%) of the cumulene **22**: pale yellow crystals (pentane), mp ca. 240 °C (decomp.); MS m/z 392 (M^+); ^{1}H NMR (400 MHz) δ 7.28–7.19 (m, AA′BB′, 8H), 1.51 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 148.5, 144.2, 133.2, 127.4, 122.6, 50.3, 30.8; UV–vis λ_{max} (THF) 230 (4.95), 245 (5.22), 324 (4.56), 345 nm (4.57); Anal. Calcd for $C_{30}H_{32}$: C, 91.78; H, 8.22%. Found: C, 91.53; H, 8.24%.

1,4-Bis(2,2,6,6-tetramethylcyclohexylidene)-1,2,3-butatriene (23): In a similar manner to that described for the preparation of **21**, 1,4-bis(2,2,6,6-tetramethylcyclohexylidene)-1,2,3-butatriene (**23**) was obtained (586 mg, 90%) from the reaction of **27c** (969 mg, 2.00 mmol) with zinc powder (654 mg, 10.0 mmol). **23**: yellow prisms, mp 203.5–204.5 °C (decomp., lit.[33] mp 188–189 °C); MS m/z 324 (M^+); ^{1}H NMR (90 MHz) δ 1.60–1.43 (m, 12H), 1.20 (s, 24H); ^{13}C NMR (22.5 MHz) δ 154.3, 138.9, 132.1, 40.6, 37.8, 31.2, 18.9.

1,1,6,6-Tetra-*t*-butyl-1,2,3,4,5-hexapentaene (1): A mixture of the dibromide **27d** (921 mg, 2.00 mmol), zinc powder (2.62 g, 40.1 mmol), and THF (20 mL) was irradiated by ultrasonic waves for 2 h under an argon atmosphere. The reaction mixture was diluted with 20 mL of hexane and filtered. The filtrate was evaporated in vacuo and the residue was purified by column chromatography on alumina with hexane as the eluent. The crystalline product was further purified by washing with methanol to produce 509 mg (85%) of **1**: yellow prisms; mp 184.5–185.5 °C (lit.[57] mp 188–189 °C); ^{1}H NMR (60 MHz, CCl_4) δ 1.28 (s).

Nickel-Catalyzed Dimerization of Tetraaryl[5]cumulenes 15–17. Reaction of 15 with [Ni(PPh$_3$)$_4$]: See Table 1, Entry 1. To a 50 mL round-bottomed two-necked flask containing a magnetic stirring bar was added 186 mg (0.250 mmol) of $[NiBr_2(PPh_3)_2]$, 131 mg (0.500 mmol) of PPh_3, and 65 mg (1.0 mmol) of activated zinc dust. A rubber septum was placed over one neck of the flask and a three-way stopcock adapter attached with an argon-filled balloon in the other. 5 mL of dry THF was added through the septum by a syringe. The flask was evacuated and filled with argon several times (vacuum line). The flask was irradiated with ultrasonic waves for 5 min and the mixture was stirred for 40 min at room temperature. Another 50 mL round-bottomed two-necked flask containing a magnetic stirring bar and a rubber septum was placed, evacuated, and filled with argon. To the flask was added a solution of 190 mg (0.499 mmol) of the cumulene **15** in 25 mL of dry THF and the flask was evacuated and filled with argon. After the red-brown catalyst formed, the solution of the catalyst was added via syringe with stirring and the resulting mixture was stirred for 1 h at room temperature. After the addition of 20 mL of benzene, the mixture was passed through a short column of alumina. The residue after removal of solvent was purified by chromatography on silica gel with a mixture of cyclohexane and benzene as the eluent. The collected crystals after removal of the solvent were washed with Et_2O to give the [4]radialene **5** (101 mg, 53%).

1,2-Bis(3,3-diphenylallenylidene)-3,4-bis(diphenylmethylene)-cyclobutane (5): Deep blue needles (from cyclohexane–ether), mp ca. 210 °C (decomp.); ^{1}H NMR (500 MHz) δ 7.34–7.29 (m, 10H), 7.11–7.06 (m, 14H), 6.98 (t, $J = 8$ Hz, 2H), 6.88 (t, $J = 8$ Hz, 2H), 6.83 (d, $J = 8$ Hz, 4H), 6.73 (t, $J = 8$ Hz, 4H), 6.68 (t, $J = 8$ Hz, 4H); ^{13}C NMR (125 MHz) δ 147.8, 141.1, 140.5, 139.5, 138.7, 138.4, 136.7, 136.5, 131.0, 130.7, 130.2, 129.5, 129.2, 129.0, 128.3, 127.8, 127.7, 127.6, 127.43, 127.36, 127.2, 123.1; MS m/z 760 (M^+); IR (KBr) 3033, 2028, 1970, 1597, 1492, 1447, 1178, 1076, 1031, 770, 693, 627, 525 cm^{-1}; Raman (KBr) 2030, 1970 cm^{-1} (C=C=C); UV λ_{max} (THF) 623 (log ε 4.22), 413 (4.95), 384 (sh, 4.76), 293 (4.58), 230 nm (4.63); Anal. Calcd for $C_{60}H_{40}$: C, 94.70; H, 5.30%. Found: C, 94.36; H, 5.30%. See Table 1, Entry 2. When the reaction was carried out in DMF as the solvent, an aqueous work-up was carried out as follows. The filtered reaction mixture was poured into 200 mL of 2 M HCl and extracted with 3 × 100 mL of a mixture of cyclohexane and benzene (1:1). The organic phase was washed successively with 2 M HCl, aqueous $NaHCO_3$, water, and brine, and then dried over $MgSO_4$. The residue after removal of the solvent was purified by chromatography on silica gel with a mixture of cyclohexane and benzene as the eluent. The [4]radialene **5** (122 mg, 64%) was obtained from 74 mg (0.10 mmol) of $[NiBr_2(PPh_3)_2]$, 52 mg (0.20 mmol) of PPh_3, 26 mg (0.40 mmol) of activated zinc dust in 2 mL of dry DMF, and 190 mg (0.499 mmol) of the cumulene **15** in 25 mL of dry DMF. In this reaction, the reaction mixture was stirred for 10 min at room temperature. See Table 1, Entry 3. When the reaction was carried out in dry benzene similarly to that described above, a mixture of the [4]radialene **5** (76 mg, 40%) and the hydrogenated compound **28** (20 mg, 10%) was obtained from a reaction of the mixture of 186 mg (0.250 mmol) of $[NiBr_2(PPh_3)_2]$, 131 mg (0.500 mmol) of PPh_3, and 65 mg (1.0 mmol) of activated zinc dust, with 190 mg (0.5 mmol) of the cumulene **15** in 25 mL of dry benzene.

1,1,6,6-Tetraphenyl-1,5-hexadien-3-yne (28): Pale yellow needles (from hexane–ether), mp 162–163 °C (lit.[16] 160 °C); ^{1}H NMR (90 MHz) δ 7.43–7.20 (m, 20H), 6.10 (s, 2H); ^{13}C NMR (22.5 MHz) δ 151.9, 141.8, 139.3, 130.0, 128.3, 128.3, 128.2, 128.1, 128.0, 107.7, 93.5; MS m/z 382 (M^+); IR (KBr) 3014, 1952, 1496, 1448, 1442, 1071, 1030, 998, 868, 772, 763, 697, 657, 644, 568, 494, 479 cm^{-1}; UV λ_{max} 365, 361, 251 nm.

Reaction of the Cumulene 15 with [Ni(CO)$_2$(PPh$_3$)$_2$]: To a 50 mL round-bottomed two-necked flask containing a magnetic stirring bar were added 190 mg (0.499 mmol) of the cumulene **15**, 32 mg (50.1 µmol) of $[Ni(CO)_2(PPh_3)_2]$, and 30 mL of dry benzene. The flask was evacuated and filled with argon. The mixture was heated to reflux for 30 min. After cooling to room temperature, the mixture was passed through a short column of alumina with benzene as the eluent. After removal of solvent, the residue was purified by chromatography on silica gel with hexane as the eluent. The collected crystals after removal of the solvent were washed with ether to give the [4]radialene **5** (115 mg, 61%).

Reaction of the Cumulene 16 with [Ni(CO)$_2$(PPh$_3$)$_2$]: In a similar manner to that described for the reaction of the cumulene **15**, the [4]radialene **6** (50 mg, 57%) was obtained from the reaction of 87 mg (0.20 mmol) of the cumulene **16** with 32 mg (50.1 µmol) of $[Ni(CO)_2(PPh_3)_2]$ in dry benzene (30 mL). The collected crystals after chromatography on silica gel were washed with pentane to give the [4]radialene **6**.

1,2-Bis[3,3-bis(4-methylphenyl)allenylidene]-3,4-bis[bis(4-methylphenyl)methylene]cyclobutane (6): Dark blue needles (from hexane–ether), mp ca. 210 °C (decomp.); ^{1}H NMR (500 MHz) δ 7.23 (d, $J = 8.0$ Hz, 4H), 7.06 (d, $J = 8.3$ Hz, 4H), 7.05 (d, $J = 8.3$ Hz, 4H), 6.99 (d, $J = 8.3$ Hz, 4H), 6.88 (d, $J = 8.0$ Hz, 4H), 6.69 (d, $J = 8.0$ Hz, 4H), 6.54 (d, $J = 8.3$ Hz, 4H), 6.52 (d, $J = 8.0$ Hz, 4H), 2.42 (s, 6H), 2.17 (s, 6H), 2.14 (s, 6H), 2.12 (s, 6H); ^{13}C NMR (125 MHz) δ 146.8, 139.1, 138.7, 137.9, 137.7, 137.3, 137.0, 136.8, 136.1, 135.82, 135.78, 135.6, 131.3, 130.8, 129.8, 129.5, 128.81, 128.78, 128.5, 128.4, 127.7, 122.0, 21.5, 21.4, 21.08, 21.06; MS *m/z* 872 (M^+); IR (KBr) 3016, 2912, 2028, 1970, 1606, 1508, 1178, 1109, 1019, 814, 718, 610, 523, 478 cm^{-1}; Raman (KBr) 2029, 1972 cm^{-1} (C=C=C); UV λ_{max} (THF) 694 ($\log\varepsilon$ 4.21), 424 (4.97), 385 (sh, 4.66), 310 (4.62), 238 nm (4.64); Anal. Calcd for $C_{68}H_{56}$: C, 93.54; H, 6.46%. Found: C, 93.25; H, 6.50%.

Reaction of the Cumulene 17 with [Ni(CO)$_2$(PPh$_3$)$_2$]: In a similar manner to that described for the preparation of the [4]radialene **5**, the [4]radialene **7** (61 mg, 34%) was obtained from 181 mg (0.299 mmol) of the cumulene **17**, 192 mg (0.300 mmol) of [Ni(CO)$_2$(PPh$_3$)$_2$] and 90 mL of dry benzene. The collected crystals after chromatography on silica gel with a mixture of hexane and benzene as the eluent were washed with ether to give the [4]radialene **7**.

1,2-Bis[3,3-bis(4-*t*-butylphenyl)allenylidene]-3,4-bis[bis(4-*t*-butylphenyl)methylene]cyclobutane (7): Dark blue microcrystals, mp ca. 220 °C (decomp.); ^{1}H NMR (500 MHz) δ 7.46 (m, 8H), 7.30 (d, $J = 8.7$ Hz, 4H), 7.29 (d, $J = 8.4$ Hz, 4H), 7.16 (d, $J = 8.7$ Hz, 4H), 6.93 (d, $J = 8.4$ Hz, 4H), 6.89 (d, $J = 8.7$ Hz, 4H), 6.82 (d, $J = 8.7$ Hz, 4H), 1.40 (brs, 18H), 1.25 (s, 18H), 1.24 (s, 18H), 1.11 (brs, 18H); ^{13}C NMR (125 MHz) δ 150.9, 150.6, 150.3, 149.3, 148.9, 139.3, 138.2, 137.8, 137.6, 136.1, 135.8, 133.8, 130.3, 130.2, 129.6, 129.2, 129.0, 125.3, 124.9, 124.6, 124.4, 122.0, 34.8, 34.7, 34.43, 34.37, 31.4, 31.4, 31.3, 31.2; MS *m/z* 1208 (M^+); IR (KBr) 3025, 2986, 2958, 2864, 2030, 1606, 1506, 1464, 1396, 1365, 1272, 1200, 1108, 1015, 837, 615, 576 cm^{-1}; Raman (KBr) 2027, 1975 cm^{-1} (C=C=C); UV λ_{max} (THF) 623 ($\log\varepsilon$ 4.19), 515 (sh, 4.09), 416 (4.83), 390 (sh, 4.67), 303 (4.67), 234 nm (4.68); HRMS (FAB$^+$) *m/z* found 1208.8094, calcd for $C_{92}H_{104}$, 1208.8138.

Stepwise Synthesis of Extended [4]Radialene 5. 1,2-Bis(3-hydroxy-3,3-diphenylprop-1-ynyl)-3,4-bis(diphenylmethylene)-cyclobutene (30): To a 50 mL round-bottomed two-necked flask containing a magnetic stirring bar was added a mixture of 540 mg (1.00 mmol) of the dibromide **29**, 521 mg (2.50 mmol) of **19a**, 35 mg (50 µmol) of [PdCl$_2$(PPh$_3$)$_2$], and 10 mg (53 µmol) of CuI. After 20 mL of Et_3N was added, the flask was evacuated and filled with argon. The mixture was heated for 2 h at 85 °C with stirring. Then the mixture was poured into 150 mL of dilute 2 M HCl and extracted with 3×50 mL of ether. The extracts were washed successively with aqueous dilute HCl, water, and brine, and then dried over Na_2SO_4. The residue after removal of the solvent was purified by chromatography on silica gel with benzene as the eluent. The collected crystals from yellow fractions were washed with a mixture of hexane and ether to give the diol **30** (582 mg, 73%). **30**: yellow needles (from hexane–CH_2Cl_2), mp 192–194 °C (decomp.); ^{1}H NMR (400 MHz) δ 7.39–7.34 (m, 8H), 7.29 (d, $J = 7.5$ Hz, 4H), 7.23–7.12 (m, 18H), 6.84 (d, $J = 7.5$ Hz, 4H), 6.79 (t, $J = 7.5$ Hz, 2H), 6.68 (t, $J = 7.5$ Hz, 4H), 2.23 (s, 2H); ^{13}C NMR (100 MHz) δ 144.2, 140.8, 139.9, 139.6, 138.4, 133.4, 131.8, 130.5, 128.1, 127.6, 127.50, 127.48, 127.4, 127.0, 126.0, 107.3, 79.7, 74.7; MS *m/z* 794 (M^+), 776, 671, 612, 182; IR (KBr) 3400, 3035, 3005, 1596, 1490, 1450, 1444, 998, 764, 743, 696, 642 cm^{-1}; Anal. Calcd for $C_{60}H_{42}O_2$: C, 90.65; H, 5.33%. Found: C, 90.42; H, 5.27%.

[4]Radialene 5 from the Diol 30: To a suspension of 40 mg (50 µmol) of the diol **30** and 23 mg (0.10 mmol) of $SnCl_2 \cdot 2H_2O$ in 5 mL of dry ether was added 2 mL of saturated solution of HCl in ether at −50 °C. The suspension was stirred for 30 min at −50 °C and a mixture of 30 mL of CH_2Cl_2 and 20 mL of water was added. Then the organic phase was separated and washed with brine, and then dried over Na_2SO_4. The residue after removal of the solvent was passed through a short column of alumina with benzene as the eluent. The collected crystals were washed with ether to give the [4]radialene **5** (26 mg, 68%).

Thermal Dimerization of Cumulenes with Bulky Substituents 21–23. 1,2,3,4-Tetrakis[(2,2,5,5-tetramethylcyclopentylidene)methylene]cyclobutane (10): To a Pyrex tube with 5 mm diameter was added 59 mg (0.20 mmol) of the cumulene **21** and the tube was sealed under reduced pressure (<0.1 mmHg). The tube was heated for 5 min at 240 °C in an oil bath preheated prior to use. After cooling to room temperature, the mixture in the tube was dissolved in CH_2Cl_2 and the solution was evaporated in vacuo. The residue was purified by chromatography on silica gel to give the [4]radialene **10** (41 mg, 69%), together with the unchanged **21** (14 mg, 24%). **10**: colorless needles (from ether–ethanol), mp ca. 330 °C (decomp.); ^{1}H NMR (90 MHz) δ 1.61 (s, 16H), 1.09 (m, 48H); ^{13}C NMR (22.5 MHz) δ 188.5, 133.4, 112.1, 45.2, 39.8, 30.3; MS *m/z* 592 (M^+); UV λ_{max} (cyclohexane) 328 ($\log\varepsilon$ 3.41), 309 (3.38), 275 (sh, 4.19), 265 (4.34), 257 (sh, 4.29), 218 nm (5.11); Anal. Calcd for $C_{44}H_{64}$: C, 89.12; H, 10.88%. Found: C, 88.94; H, 10.92%.

1,2,3,4-Tetrakis[(1,1,3,3-tetramethyl-2-indanylidene)methylene]cyclobutane (11): The cumulene **22** (78.5 mg, 0.200 mmol) was heated at 270–275 °C for 5 min under an argon atmosphere. After cooling to room temperature, the mixture was purified by column chromatography on alumina with benzene as the eluent to give 40 mg (51%) of the [4]radialene **11**: colorless prisms (ether–hexane), mp 331–333 °C; ^{1}H NMR (400 MHz, CD_2Cl_2–CS_2, 1:4) δ 7.11–7.06 (m, 8H), 6.99 (m, 8H), 1.35 (s, 48H); ^{13}C NMR (100 MHz, CD_2Cl_2–CS_2, 1:4) δ 189.8, 148.5, 134.2, 127.2, 122.4, 112.5, 48.2, 31.6; MS *m/z* 784 (M^+); Raman (KBr) 2030, 1978, 1948, 1900 cm^{-1} (C=C=C); UV λ_{max} (THF) 329 ($\log\varepsilon$ 3.40), 310 (3.39), 279 (sh, 4.27), 271 (4.45), 265 (4.52), 256 nm (sh, 4.43); Anal. Calcd for $C_{60}H_{64}$: C, 91.78; H, 8.22%. Found: C, 91.63; H, 8.26%.

1,2,3,4-Tetrakis[(2,2,6,6-tetramethylcyclohexylidene)methylene]cyclobutane (12): To a Pyrex tube with 10 mm diameter was added 33 mg (0.10 mmol) of the cumulene **23**. The tube was evacuated and filled with gaseous argon. Then the tube was heated for 2 min at 220 °C in an oil bath preheated prior to use. After cooling to room temperature, the mixture in the tube was dissolved in CH_2Cl_2 and the solution was evaporated in vacuo. The residue was purified by chromatography on silica gel with hexane as the eluent. The collected crystals after removal of the solvent were washed with methanol to give the [4]radialene **12** (30 mg, 91%). **12**: colorless needles (from ether–ethanol), mp 315 °C (sublimed); ^{1}H NMR (90 MHz) δ 1.80–1.25 (m, 24H), 1.12 (s, 48H); ^{13}C NMR (22.5 MHz) δ 192.5, 127.6, 109.4, 40.9, 35.5, 31.7, 19.2; MS *m/z* 648 (M^+); IR (KBr) 1957, 1917 cm^{-1}; UV λ_{max} (cyclohexane) 318 ($\log\varepsilon$ 3.42), 300 (3.38), 268 (sh, 4.19), 259 (4.28), 252 (sh, 4.27), 215 nm (5.13); Anal. Calcd for $C_{48}H_{72}$: C, 88.82; H, 11.18%. Found: C, 88.75; H, 11.28%.

Reaction of Tetraalkylhexapentaene with [RhCl(PPh$_3$)$_3$]. Rh-Complex 32 of the Cumulene 21: To a 50 mL round-bottomed two-necked flask with a magnetic stirring bar was added 62 mg (0.21 mmol) of the cumulene **21** and 185 mg (0.200 mmol) of [RhCl(PPh$_3$)$_3$]. The flask was evacuated and filled with argon. Then 25 mL of benzene was added and the mixture was stirred for 3 h at room temperature. The mixture was evaporated in vacuo and the residue was purified by chromatography on silica gel with benzene as the eluent. The collected crystals were recrystallized from a mixture of hexane and CH_2Cl_2 to give the Rh-complex **32** (188 mg, 80%). **32**: yellow prisms (hexane–CH_2Cl_2), mp 183–

185 °C (decomp.); ^{1}H NMR (270 MHz) δ 7.73 (brs, 12H), 7.33–7.22 (m, 18H), 1.66 (m, 4H), 1.51 (s, 6H), 1.44 (t, $J = 7$ Hz, 2H), 1.23 (t, $J = 7$ Hz, 2H), 1.08 (s, 6H), 0.94 (s, 6H), 0.18 (s, 6H); ^{13}C NMR (67.8 MHz) δ 153.4 (d, $J = 1.5$ Hz), 148.3 (d, $J = 2$ Hz), 142.8 (dt, $J = 3.5$ and 2.5 Hz), 138.7 (d, $J = 1.5$ Hz), 135.4 (brt, $J = 5$ Hz), 131.8 (t, $J = 21$ Hz), 129.5, 127.6 (t, $J = 5$ Hz), 113.3 (dt, $J = 18.5$ and 4 Hz), 106.8 (dt, $J = 14.5$ and 4 Hz), 48.5, 46.3, 45.1, 44.6, 40.1, 39.75, 39.69, 39.4, 30.7, 29.9, 29.7, 28.5; MS (FAB) m/z 924 ($M^+ + H - Cl$); IR (KBr) 2018 cm^{-1}; Anal. Calcd for $C_{58}H_{62}ClP_2Rh$: C, 72.61; H, 6.51%. Found: C, 72.44; H, 6.64%.

Rh-Complex 31 of the Cumulene 1: In a similar manner to that described for the preparation of the Rh-complex **32**, the Rh-complex **31** (137 mg, 71%) was obtained from 61 mg (0.20 mmol) of the cumulene **1** and 185 mg (0.200 mmol) of [RhCl(PPh$_3$)$_3$] in 25 mL of benzene. In this reaction, the reaction mixture was stirred for 24 h at room temperature. **31**: yellow prisms (hexane–CH$_2$Cl$_2$), mp 170–173 °C (decomp.); ^{1}H NMR (270 MHz) δ 7.69 (brs, 12H), 7.36–7.23 (m, 18H), 1.64 (s, 9H), 1.09 (s, 9H), 0.99 (s, 9H), 0.68 (s, 9H); ^{13}C NMR (67.8 MHz) δ 159.9 (d, $J = 1.5$ Hz), 144.1 (q, $J = 2$ Hz), 142.7 (dt, $J = 4$ and 3 Hz), 135.1 (brs), 134.0 (d, $J = 1.5$ Hz), 131.8 (t, $J = 21$ Hz), 129.5, 127.6 (t, $J = 1.5$ Hz), 120.5 (dt, $J = 18$ and 3 Hz), 111.4 (dt, $J = 14$ and 4 Hz), 42.2 (d, $J = 1.5$ Hz), 39.7, 38.6, 37.7, 35.2, 32.5, 32.28, 32.26; MS (FAB) m/z 928 ($M^+ + H - Cl$); IR (KBr) 2025 cm^{-1}; Anal. Calcd for $C_{58}H_{66}ClP_2Rh$: C, 72.31; H, 6.90; Cl, 3.68%. Found: C, 71.92; H, 7.00; Cl, 4.07%.

Reaction of the Cumulenes with 1 and 21–23 with [Ni(CO)$_2$(PPh$_3$)$_2$]. 2,3,4,5-Tetrakis(2,2-di-*t*-butylvinylidene)cyclopentanone (14) and 1,2,3,4-Tetrakis(2,2-di-*t*-butylvinylidene)cyclobutane (2): To a 25 mL round-bottomed two-necked flask containing a magnetic stirring bar was added 120 mg (0.399 mmol) of the cumulene **1**, 256 mg (0.400 mmol) of [Ni(CO)$_2$(PPh$_3$)$_2$], 315 mg (1.20 mmol) of PPh$_3$, and 10 mL of dry benzene. The flask was evacuated and filled with argon. The mixture was heated to reflux for 8 days with stirring. After cooling to room temperature, the reaction mixture was passed through a short column of Al$_2$O$_3$ with benzene as the eluent. The residue after removal of the solvent was purified by chromatography on silica gel with a mixture of hexane and benzene as the eluent. The initial fractions after removal of the solvent gave the [4]radialene **2** (7 mg, 6%). **2**: colorless crystals (hexane–ether); ^{1}H NMR (270 MHz) δ 1.20 (s); ^{13}C NMR (67.8 MHz) δ 194.8, 129.9, 108.2, 36.6, 32.4. The following fractions gave the [5]radialenone **14** (93 mg, 74%). **14**: yellow prisms (ether–methanol), mp 220 °C (sublimed); ^{1}H NMR (400 MHz) δ 1.25 (s, 36H), 1.24 (s, 36H); ^{13}C NMR (100 MHz) δ 205.1, 199.2, 192.2, 130.6, 129.0, 107.0, 100.7, 36.7, 36.6, 32.5, 32.2; MS m/z 628 (M$^+$); IR (KBr) 1908, 1691 cm^{-1}; UV λ_{max} (THF) 408 ($\log \varepsilon$ 3.27), 378 (3.36), 315 (sh, 3.36), 300 (sh, 3.75), 270 (sh, 4.15), 244 nm (4.67); Anal. Calcd for $C_{45}H_{72}O$: C, 85.92; H, 11.54%. Found: C, 85.64; H, 11.64%.

2,3,4,5-Tetrakis[(2,2,6,6-tetramethylcyclohexylidene)methylene]cyclopentanone (13): To a 30 mL round-bottomed flask containing a magnetic stirring bar was added 162 mg (0.499 mmol) of the cumulene **23**, 320 mg (0.500 mmol) of [Ni(CO)$_2$(PPh$_3$)$_2$], and 10 mL of dry benzene. The flask was evacuated and filled with gaseous argon. The mixture was heated to reflux for 2 days with stirring. After cooling to room temperature, the mixture was passed through a short column of Al$_2$O$_3$ with benzene as the eluent. The residue after removal of the solvent was purified by chromatography on silica gel with a mixture of hexane and benzene as the eluent. The initial fractions after removal of the solvent gave the [4]radialene **12** (52 mg, 32%) and the following fractions gave the [5]radialenone **13** (61 mg, 36%). **13**: yellow needles (ethanol), mp 226–227 °C; ^{1}H NMR (400 MHz) δ 1.69–1.58 (m, 8H), 1.47–1.34 (m, 16H), 1.19 (s, 12H), 1.17 (s, 12H), 1.14 (s, 12H), 1.12 (s, 12H); ^{13}C NMR (100 MHz) δ 202.4, 196.7, 191.1, 128.1, 126.9, 107.7, 101.4, 41.7, 40.8, 35.9, 35.7, 31.5, 31.4, 30.9, 30.8, 19.3, 19.0; MS m/z 676 (M$^+$); IR (KBr) 1947, 1919, 1691 cm^{-1}; UV λ_{max} (cyclohexane) 408 (sh, $\log \varepsilon$ 3.26), 378 (3.39), 313 (3.47), 298 (3.64), 263 (sh, 4.22), 246 (4.70), 215 nm (4.78); Anal. Calcd for $C_{49}H_{72}O$: C, 86.92; H, 10.72%. Found: C, 86.50; H, 10.73%.

1,3-Bis(2,2,5,5-tetramethylcyclopentylidene)-2,4-bis[2-(2,2,5,5-tetramethylcyclopentylidene)vinylidene]cyclobutane (8): To a 100 mL round-bottomed flask containing a magnetic stirring bar was added 593 mg (2.00 mmol) of the cumulene **21**, 639 mg (1.00 mmol) of [Ni(CO)$_2$(PPh$_3$)$_2$], and 50 mL of dry benzene. The flask was evacuated and filled with gaseous argon. The mixture was heated under reflux for one day with stirring. After cooling to room temperature, the mixture was passed through a short column of Al$_2$O$_3$ with benzene as the eluent. The residue after removal of the solvent was purified by chromatography on silica gel with hexane as the eluent to give the [4]radialene **8** (485 mg, 82%). **8**: yellow needles (hexane–CH$_2$Cl$_2$), mp 281–282 °C (decomp.); ^{1}H NMR (400 MHz) δ 1.68 (s, 8H), 1.65 (s, 8H), 1.45 (s, 24H), 1.23 (s, 24H); ^{13}C NMR (100 MHz) δ 155.9, 155.2, 148.9, 145.2, 136.7, 118.5, 48.0, 46.1, 41.6, 40.6, 30.3, 27.8; MS m/z 592 (M$^+$); Raman (KBr) 2005 (C=C=C), 1637, 1610 cm^{-1} (C=C); UV λ_{max} (cyclohexane) 431 (sh, $\log \varepsilon$ 3.82), 406 (3.93), 334 (4.98), 323 (sh, 4.73), 285 (4.22), 260 (sh, 4.42), 253 nm (4.46); Anal. Calcd for $C_{44}H_{64}$: C, 89.12; H, 10.88%. Found: C, 88.78; H, 10.92%.

1,3-Bis(1,1,3,3-tetramethyl-2-indanylidene)-2,4-bis[2-(1,1,3,3-tetramethyl-2-indanylidene)vinylidene]cyclobutane (9): A solution of 39 mg (0.10 mmol) of the cumulene **22**, 32 mg (50 µmol) of [Ni(CO)$_2$(PPh$_3$)$_2$], 26 mg (0.10 mmol) of PPh$_3$ and 10 mL in dry benzene was heated to reflux for one day under an argon atmosphere. After cooling to room temperature, the mixture was passed through a short column of alumina with benzene as the eluent. The crystals obtained after removal of the solvent were washed with a mixture of hexane and benzene to give the [4]radialene **9** (25 mg, 64%). **9**: yellow needles (benzene–CH$_2$Cl$_2$), mp 365–367 °C (decomp.); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$–CS$_2$, 1:4) δ 7.20–7.08 (m, 16H), 1.78 (s, 24H), 1.58 (s, 24H); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$–CS$_2$, 1:4) δ 156.3, 154.6, 150.0, 149.7, 148.9, 145.9, 137.7, 127.4, 127.1, 122.4, 122.2, 119.0, 50.9, 49.1, 31.8, 29.0; MS m/z 784 (M$^+$); IR (KBr) 1955 cm^{-1}; Raman (KBr) 1995 (cumulene), 1635, 1615, 1590 cm^{-1} (C=C); UV λ_{max} (cyclohexane) 437 ($\log \varepsilon$ 3.89), 408 (4.02), 384 (3.89), 363 (sh, 4.10), 338 (5.03), 318 (sh, 4.66), 285 (sh, 4.23), 282 (4.21), 263 (4.55), 236 nm (4.36); Anal. Calcd for $C_{60}H_{64}$: C, 91.78; H, 8.22%. Found: C, 91.68; H, 8.21%.

Stepwise Synthesis of Extended [4]Radialenes 39–41. 1,2-Bis[2-(9-hydroxyfluoren-9-yl)ethynyl]-3,4-bis(diphenylmethylene)cyclobutene (36): In a similar manner to that described for the preparation of the diol **30**, 536 mg (68%) of the diol **36** was obtained from 540 mg (1.00 mmol) of the dibromide **29** and 516 mg (2.50 mmol) of the alcohol **33**. **36**: yellow needles (hexane–CH$_2$Cl$_2$), mp ca. 205 °C (decomp.); ^{1}H NMR (400 MHz) δ 7.57 (d, $J = 7.5$ Hz, 4H), 7.34 (t, $J = 7.5$ Hz, 4H), 7.29 (d, $J = 7.5$ Hz, 4H), 7.20 (t, $J = 7.5$ Hz, 4H), 7.15 (d, $J = 7.7$ Hz, 4H), 7.05–6.96 (m, 6H), 6.77 (d, $J = 7.5$ Hz, 4H), 6.76 (t, $J = 7.5$ Hz, 2H), 6.65 (t, $J = 7.5$ Hz, 4H), 2.55 (s, 2H); ^{13}C NMR

(100 MHz) δ 146.4, 140.6, 140.3, 139.7, 139.2, 138.2, 133.5, 131.4, 130.6, 129.5, 128.4, 127.6, 127.4, 127.2, 127.0, 124.6, 120.0, 105.1, 75.8, 74.9; MS *m/z* 792 (M^+); IR (KBr) 3520, 3020, 1603, 1488, 1479, 1450, 1443, 1350, 1284, 1178, 1152, 1067, 1019, 1000, 975, 930, 906, 890, 770, 756, 741, 726, 696, 680, 640, 618, 577, 523 cm^{-1}; Anal. Calcd for $C_{60}H_{38}O_2$: C, 91.11; H, 4.84%. Found: C, 90.36; H, 5.46%.

1,2-Bis[2-(9-hydroxy-10,10-dimethyl-9,10-dihydroanthracen-9-yl)ethynyl]-3,4-bis(diphenylmethylene)cyclobutene (37): In a similar manner to that described for the preparation of the diol **30** except the aqueous work-up, 546 mg (62%) of the diol **37** was obtained from 540 mg (1.00 mmol) of the dibromide **29** and 621 mg (2.50 mmol) of the alcohol **34**. To the reaction mixture was added 20 mL of benzene and the mixture was passed through a short column of alumina with benzene as the eluent. The residue after removal of the solvent was purified by chromatography on silica gel with a mixture of ether and benzene as the eluent. **37**: yellow prisms (hexane–CH_2Cl_2), mp >150 °C (decomp.); ^1H NMR (400 MHz) δ 7.78 (dd, $J = 8.0$ and 1.5 Hz, 4H), 7.46 (dd, $J = 8.0$ and 1.0 Hz, 4H), 7.29 (td, $J = 8.0$ and 1.5 Hz, 4H), 7.24 (d, $J = 7.5$ Hz, 4H), 7.19–7.12 (m, 6H), 7.09 (td, $J = 8.0$ and 1.0 Hz, 4H), 6.82 (d, $J = 7.5$ Hz, 4H), 6.78 (t, $J = 7.5$ Hz, 2H), 6.68 (t, $J = 7.5$ Hz, 4H), 2.41 (s, 2H), 1.59 (s, 6H), 1.45 (s, 6H); ^{13}C NMR (100 MHz) δ 142.8, 140.8, 139.8, 138.5, 135.9, 133.2, 131.7, 130.6, 128.5, 127.9, 127.6, 127.4, 127.4, 127.0, 126.6, 125.5, 108.7, 79.1, 67.9, 37.9, 33.1, 32.2; MS *m/z* 874 (M^+); IR (KBr) 3500, 3350, 3040, 3010, 2960, 1598, 1490, 1446, 1042, 962, 910, 758, 720, 698, 647, 570, 524 cm^{-1}; Anal. Calcd for $C_{64}H_{50}O_2$: C, 90.58; H, 5.78%. Found: C, 90.24; H, 5.80%.

1,2-Bis[2-(9-hydroxythioxanthen-9-yl)ethynyl]-3,4-bis(diphenylmethylene)cyclobutene (38): In a similar manner to that described for the preparation of the diol **30** except the manner of aqueous work-up, 315 mg (37%) of the diol **38** was obtained from 540 mg (1.00 mmol) of the dibromide **29** and 596 mg (2.50 mmol) of the alcohol **35**. The work-up was carried out as follows. To the reaction mixture was added 20 mL of benzene and the resulting mixture was passed through a short column of alumina with benzene as the eluent. The residue after removal of the solvent was purified by chromatography on silica gel with a mixture of ether and benzene as the eluent. **38**: yellow needles (from hexane–CH_2Cl_2), mp 181–182 °C (decomp.); ^1H NMR (400 MHz, acetone-d_6) δ 7.76 (d, $J = 7.5$ Hz, 4H), 7.43 (t, $J = 7.5$ Hz, 4H), 7.30 (t, $J = 7.5$ Hz, 4H), 7.27 (t, $J = 7.5$ Hz, 4H), 7.17–7.14 (m, 4H), 7.07–7.03 (m, 6H), 6.84–6.79 (m, 6H), 6.73 (t, $J = 7.5$ Hz, 4H), 2.79 (s, 2H); ^{13}C NMR (100 MHz, acetone-d_6) δ 141.4, 141.0, 140.9, 139.0, 137.8, 134.4, 132.2, 132.0, 131.6, 128.8, 128.4, 128.3, 128.2, 128.0, 127.6, 127.4, 127.3, 106.6, 79.1, 70.6; MS (FD) *m/z* 854 (M^+); IR (KBr) 3513, 3038, 1580, 1562, 1490, 1458, 1442, 1342, 1262, 1170, 1152, 1135, 1060, 1032, 1013, 998, 968, 937, 900, 772, 753, 731, 713, 694, 650, 632, 517, 455 cm^{-1}; Anal. Calcd for $C_{60}H_{38}O_2S_2$: C, 84.28; H, 4.48; S, 7.50%. Found: C, 84.16; H, 4.51; S, 7.42%.

1,2-Bis[2-(9-fluorenylidene)vinylidene]-3,4-bis(diphenylmethylene)cyclobutane (39): To a suspension of 158 mg (0.200 mmol) of the diol **36** and 90 mg (0.40 mmol) of $SnCl_2 \cdot 2H_2O$ in 20 mL of dry ether was added an ethereal solution (8.0 mL) saturated with gaseous HCl at −50 °C. The suspension was stirred for 30 min at −50 °C and a mixture of 30 mL of CH_2Cl_2 and 50 mL of water was added. Then the organic layer was separated and washed with brine, and then dried over Na_2SO_4. The residue after removal of the solvent was passed through a short column of alumina with benzene as the eluent. The crystals obtained after removal of the solvent were washed with ether to give the [4]radialene **39** (74 mg, 49%). **39**: dark blue leaflets (ether–cyclohexane), mp ca. 210 °C (decomp.); ^1H NMR (400 MHz) δ 7.67–7.60 (m, 6H), 7.47–7.40 (m, 10H), 7.32–7.27 (m, 4H), 7.15–7.07 (m, 4H), 6.94 (t, $J = 7.5$ Hz, 2H), 6.85 (d, $J = 7.5$ Hz, 4H), 6.76 (t, $J = 7.5$ Hz, 4H), 6.21 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (100 MHz) δ 141.4, 141.0, 140.9, 139.7, 139.6, 139.3, 139.2, 139.1, 138.5, 135.7, 133.8, 132.0, 131.1, 128.6, 128.5, 128.2, 128.1, 127.5, 127.2, 126.8, 125.0, 124.8, 120.1, 119.9; MS (FAB) *m/z* 757.5 ($M^+ + H$); Raman (KBr) 2022, 1927 cm^{-1} (C=C=C); UV λ_{max} (THF) 583 (log ε 3.93), 532 (sh, 3.81), 379 (sh, 4.55), 355 (4.58), 319 (4.55), 278 (sh, 4.63), 259 (4.80), 227 nm (sh, 4.87); Anal. Calcd for $C_{60}H_{36}$: C, 95.21; H, 4.79%. Found: C, 94.85; H, 4.93%.

1,2-Bis[2-(10,10-dimethyl-9,10-dihydroanthracen-9-ylidene)vinylidene]-3,4-bis(diphenylmethylene)cyclobutane (40): To a solution of 88 mg (0.10 mmol) of the diol **37** in 10 mL of dry ether was added 45 mg (0.20 mmol) of $SnCl_2 \cdot 2H_2O$ and then an ethereal solution (1.0 mL) saturated with gaseous HCl was added at −65 °C. The suspension was stirred for 30 min at −65 °C. Then a mixture of 20 mL of CH_2Cl_2 and 1 mL of Et_3N was added. The mixture was passed through a short column of alumina with benzene as the eluent. The crystals obtained after removal of the solvent were washed with ether to give the [4]radialene **40** (51 mg, 61%). **40**: dark blue needles (hexane–CH_2Cl_2), mp 228–230 °C (decomp.); ^1H NMR (400 MHz, −20 °C) δ 7.59 (t, $J = 7.2$ Hz, 2H), 7.57–7.46 (m, 12H), 7.28 (td, $J = 8.0$ and 1.0 Hz, 2H), 7.14 (td, $J = 8.0$ and 1.0 Hz, 2H), 6.99 (dd, $J = 8.0$ and 1.0 Hz, 2H), 6.97–6.91 (m, 4H), 6.87 (d, $J = 7.7$ Hz, 4H), 6.74 (t, $J = 7.7$ Hz, 4H), 6.29 (dd, $J = 8.0$ and 1.0 Hz, 2H), 6.03 (td, $J = 8.0$ and 1.0 Hz, 2H), 1.66 (s, 12H); ^{13}C NMR (100 MHz, −20 °C) δ 143.7, 143.6, 141.2, 140.7, 139.6, 139.3, 137.1, 133.5, 131.6, 131.5, 131.1, 130.8, 130.0, 129.4, 129.0, 128.2, 128.04, 127.96, 127.57, 127.56, 126.9, 126.5, 125.9, 125.2, 124.1, 116.6, 38.8, 32.5; MS *m/z* 840 (M^+); IR (KBr) 2015, 1945 cm^{-1}; Raman (KBr) 2030, 1955 cm^{-1} (C=C=C); UV λ_{max} (THF) 688 (log ε 4.44), 630 (sh, 4.01), 442 (5.01), 380 (sh, 4.41), 319 (sh, 4.50), 300 (4.59), 239 nm (4.54); Anal. Calcd for $C_{66}H_{48}$: C, 94.25; H, 5.75%. Found: C, 93.77; H, 5.95%.

1,2-Bis(diphenylmethylene)-3,4-bis[2-(9-thioxanthenylidene)vinylidene]cyclobutane (41): To a solution of 86 mg (0.10 mmol) of the diol **38** in 10 mL of dry ether was added a 45 mg (0.20 mmol) of $SnCl_2 \cdot 2H_2O$ and then an ethereal solution (1.0 mL) saturated with gaseous HCl was added at −65 °C. The suspension was stirred for 30 min at −65 °C and a mixture of 20 mL of CH_2Cl_2 and 1 mL of Et_3N was added. Then the mixture was passed through a short column of alumina with benzene as the eluent. The crystals obtained after removal of the solvent were washed with ether to give the [4]radialene **41** (76 mg, 93%). **41**: dark green leaflets (CS_2–CH_2Cl_2–ether), mp ca. 250 °C (decomp.); ^1H NMR (400 MHz, −60 °C) δ 7.57–7.51 (m, 10H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.19 (t, $J = 8.0$ Hz, 2H), 7.12 (t, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.97 (t, $J = 7.5$ Hz, 2H), 6.86 (t, $J = 8.0$ Hz, 2H), 6.84 (d, $J = 7.5$ Hz, 4H), 6.74 (t, $J = 7.5$ Hz, 4H), 6.26 (d, $J = 8.0$ Hz, 2H), 6.06 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, 30 °C) δ 141.4, 140.9, 139.8, 137.8, 136.8, 132.0, 131.8, 131.3, 131.1, 131.0, 130.3, 130.2, 129.2, 128.2, 127.7, 127.5, 127.3, 126.7, 124.8, 115.4; MS *m/z* 820 (M^+); IR (KBr) 2020, 1948 cm^{-1}; Raman (KBr) 2025, 1950 cm^{-1} (C=C=C); UV λ_{max} (THF) 754 (log ε 4.47), 684 (sh, 4.05), 498 (4.72), 434 (4.76), 374 (4.34), 325 (sh, 4.41), 303 (4.49), 273 (4.77), 247 nm (4.80); Anal. Calcd for $C_{60}H_{36}S_2$: C, 87.77; H, 4.42; S, 7.81%. Found: C, 87.20; H, 4.50; S, 8.06%.

Reactions of [5]Radialenone 14 with Organometallic Reagents. 2,3,4,5-Tetrakis(3,3-di-*t*-butylallenylidene)-1-phenylcyclopentan-1-ol (45): To a 50 mL round-bottomed two-necked flask containing a magnetic stirring bar was added a solution of 189 mg (0.300 mmol) of [5]radialenone **14** in 5 mL of dry THF. The flask was evacuated and filled with argon. A solution of 0.20 mL (0.36 mmol) of PhLi [1.5 M in ether–cyclohexane (3:7)] was added via syringe with stirring at −60 °C and the mixture was stirred for 30 min at the same temperature. Then the mixture was allowed to warm to room temperature and further stirred for 30 min at room temperature. After cooling to 0 °C, 1 mL of saturated aqueous NH_4Cl was added and then anhydrous K_2CO_3 was added. The viscous aqueous phase was extracted with 2 × 10 mL of ether and the combined organic extracts were evaporated in vacuo. The residue was purified by chromatography on silica gel with a mixture of hexane and benzene as the eluent to give the alcohol **45** (208 mg, 98%). **45**: colorless needles (pentane), mp 197–198 °C; ^{1}H NMR (270 MHz) δ 7.56 (d, $J = 7$ Hz, 2H), 7.20 (t, $J = 7$ Hz, 2H), 7.10 (t, $J = 7$ Hz, 1H), 2.13 (s, 1H), 1.24 (s, 18H), 1.23 (s, 18H), 1.22 (s, 18H), 0.92 (s, 18H); ^{13}C NMR (67.8 MHz) δ 199.6, 198.1, 147.0, 129.9, 127.6, 127.1, 126.0, 125.6, 113.3, 104.0, 81.1, 36.8, 36.63, 36.60, 35.9, 32.7, 32.4, 32.3, 32.2; MS m/z 706.5 (M^+); IR (KBr) 3565, 2950, 2895, 2858, 1912, 1908, 1603, 1483, 1450, 1392, 1363, 1214, 1132, 1052, 1040, 1032, 1020, 980, 950, 927, 905, 872, 822, 792, 736, 702, 691, 673, 597, 578, 523, 505 cm^{-1}; UV λ_{max} (cyclohexane) 313 (sh, log ε 3.35), 294 (sh, 3.58), 266 (sh, 3.98), 206 nm (4.93); Anal. Calcd for $C_{51}H_{78}O$: C, 86.62; H, 11.12%. Found: C, 86.47; H, 11.22%.

2,3,4,5-Tetrakis(3,3-di-*t*-butylallenylidene)-1-methylenecyclopentane ([5]Radialene, 46): To a 50 mL round-bottomed two-necked flask containing a magnetic stirring bar was added a solution of 189 mg (0.300 mmol) of the [5]radialenone **14** in 5 mL of dry THF. The flask was evacuated and filled with argon. A solution of 0.22 mL (0.33 mmol) of MeLi (1.5 M in ether) was added via syringe at −60 °C and the mixture was stirred for 20 min at this temperature. Then the mixture was allowed to warm to room temperature and further stirred for 30 min at room temperature. After cooling to 0 °C, 1 mL of saturated aqueous NH_4Cl was added. Then anhydrous K_2CO_3 was added and the viscous aqueous phase was extracted with 2 × 10 mL of ether. The combined organic phase was evaporated in vacuo and the residue was purified by chromatography on silica gel with a mixture of hexane and benzene as the eluent to give the [5]radialene **46** (170 mg, 90%): pale yellow needles (pentane), mp 228–229.5 °C (decomp.); ^{1}H NMR (270 MHz) δ 5.02 (s, 2H), 1.24 (s, 36H), 1.23 (s, 36H); ^{13}C NMR (67.8 MHz) δ 199.3 (s), 199.1 (s), 142.7 (s), 129.2 (s), 127.9 (s), 107.0 (s), 104.3 (s), 100.2 (t), 37.1 (s), 36.5 (s), 32.6 (q), 32.4 (q); MS m/z 626.5 (M^+); IR (KBr) 3068, 2950, 2895, 2855, 1957, 1929, 1912, 1717, 1618, 1604, 1482, 1470, 1448, 1392, 1363, 1235, 1214, 1110, 1039, 1026, 979, 961, 926, 896, 855, 833, 824, 718, 698, 646, 576, 503, 482 cm^{-1}; UV λ_{max} (cyclohexane) 360 (sh, log ε 2.91), 340 (sh, 3.32), 331 (3.37), 229 (sh, 4.77), 222 (4.85), 217 nm (sh, 4.83); Anal. Calcd for $C_{46}H_{74}$: C, 88.11; H, 11.89%. Found: C, 87.95; H, 11.96%.

X-ray Crystallography of the Extended [4]Radialene 8. A yellow crystal with the dimensions 0.20 × 0.30 × 0.40 mm^3 obtained by recrystallization from CH_2Cl_2–ethyl acetate was used for the diffraction measurement. All measurements were performed on a Rigaku AFC5R diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation at 23 °C. Among a total of 9759 reflections measured, 9548 were unique and the observed 2361 reflections that had $I > 3.00\sigma(I)$, were used for the refinement. The crystal structure was solved by a direct method and refined by the full-matrix least-squares method. All of the non-hydrogen atoms were refined anisotropically. Crystal data for **8**: $C_{44}H_{64}$, MW 592.99, monoclinic, space group $P2_1/n$ (No. 14), $a = 25.381(3)$ Å, $b = 6.387(3)$ Å, $c = 26.478(2)$ Å, $\beta = 118.190(8)°$, $V = 3783(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.041$ g cm^{-3}, $F(000) = 1312$, μ(Mo Kα) = 0.54 cm^{-1}, $R = 0.053$, $R_w = 0.052$, GOF = 1.61. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-280611 for compound **8**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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References

1 J. M. Tour, *Chem. Rev.*, **96**, 537 (1996).
2 P. F. H. Schwab, M. D. Levin, and J. Michl, *Chem. Rev.*, **99**, 1863 (1999).
3 R. E. Martin and F. Diederich, *Angew. Chem., Int. Ed.*, **38**, 1350 (1999).
4 J. M. Tour, *Acc. Chem. Res.*, **33**, 791 (2000).
5 D. K. James and J. M. Tour, *Chem. Mater.*, **16**, 4423 (2004).
6 "Modern Acetylene Chemistry," ed by P. J. Stang and F. Diederich, Wiley-VCH, Weinheim (1995).
7 M. B. Nielsen and F. Diederich, *Chem. Rec.*, **2**, 189 (2002).
8 H. Fischer, "The Chemistry of Alkenes," ed by S. Patai, Wiley-Interscience, New York (1964), p. 1025.
9 H. Hopf, "The Chemistry of Ketenes, Allenes, and Related Compounds," ed by S. Patai, Wiley-Interscience, New York (1980), p. 779.
10 H. Hopf, "Classics in Hydrocarbon Chemistry," Wiley-VCH, Weinheim (2000), p. 171.
11 L. Brandsma, "Synthesis of Acetylenes, Allenes, and Cumulenes," Elsevier, Amsterdam (2004).
12 P. Cadiot and A. Willemart, *Bull. Soc. Chim. Fr.*, **1951**, 100.
13 R. Kuhn and H. Krauch, *Chem. Ber.*, **88**, 309 (1955).
14 R. Kuhn and H. Fischer, *Chem. Ber.*, **92**, 1849 (1959).
15 D. Y. Curtin and W. H. Richardson, *J. Am. Chem. Soc.*, **81**, 4719 (1959).
16 R. Kuhn and H. Fischer, *Chem. Ber.*, **94**, 3060 (1961).
17 W. M. Jones and C. D. Broaddus, *J. Org. Chem.*, **26**, 2316 (1961).
18 W. Ried, W. Schlegelmilch, and S. Piesch, *Chem. Ber.*, **96**, 1221 (1963).
19 R. Kuhn, H. Fischer, and H. Fischer, *Chem. Ber.*, **97**, 1760

(1964).

20 H. Fischer and H. Fischer, *Chem. Ber.*, **100**, 755 (1967).

21 I. M. Blake, L. H. Rees, T. D. W. Claridge, and H. L. Anderson, *Angew. Chem., Int. Ed.*, **39**, 1818 (2000).

22 G. Dyker, S. Borowski, G. Henkel, A. Kellner, I. Dix, and P. G. Jones, *Tetrahedron Lett.*, **41**, 8259 (2000).

23 M. Ogasawara, H. Ikeda, K. Ohtsuka, and T. Hayashi, *Chem. Lett.*, **2000**, 776.

24 K. Mizuno, H. Maeda, H. Sugita, S. Nishioka, T. Hirai, and A. Sugimoto, *Org. Lett.*, **3**, 581 (2001).

25 W. Skibar, H. Kopacka, K. Wurst, C. Salzmann, K.-H. Ongania, F. F. de Biani, P. Zanello, and B. Bildstein, *Organometallics*, **23**, 1024 (2004).

26 T. Kawase, Y. Minami, N. Nishigaki, S. Okano, H. Kurata, and M. Oda, *Angew. Chem., Int. Ed.*, **44**, 316 (2004).

27 R. Kuhn and H. Zahn, *Chem. Ber.*, **84**, 566 (1951).

28 "Modern Allene Chemistry," ed by N. Krause and A. S. K. Hashmi, Wiley-VCH, Weinheim (2004), Vols. 1 and 2.

29 H. F. Schuster and G. M. Coppola, "Allenes in Organic Synthesis," Wiley-Interscience, New York (1984).

30 A. S. K. Hashmi, *Angew. Chem., Int. Ed.*, **39**, 3590 (2000).

31 T. L. Gilchrist, *J. Chem. Soc., Perkin Trans. 1*, **2001**, 2491.

32 W. M. Schubert, T. H. Liddicoet, and W. A. Lanka, *J. Am. Chem. Soc.*, **76**, 1929 (1954).

33 F. Bohlmann and K. Kieslich, *Chem. Ber.*, **87**, 1363 (1954).

34 L. Skattebøl, *Tetrahedron Lett.*, **6**, 2175 (1965).

35 F. T. Bond and D. E. Bradway, *J. Am. Chem. Soc.*, **87**, 4799 (1965).

36 G. Maier, *Tetrahedron Lett.*, **6**, 3603 (1965).

37 W. R. Moore and T. M. Ozretich, *Tetrahedron Lett.*, **8**, 3205 (1967).

38 L. K. Bee, J. Beeby, J. W. Everett, and P. J. Garratt, *J. Org. Chem.*, **40**, 2212 (1975).

39 T. Yoshida, R. M. Williams, and E. Negishi, *J. Am. Chem. Soc.*, **96**, 3690 (1974).

40 H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, **1976**, 841.

41 M. Tigchelaar, H. Kleijn, C. J. Elsevier, J. Meijor, and P. Vermeer, *Tetrahedron Lett.*, **22**, 2237 (1981).

42 W. L. Krestinsky, *Chem. Ber.*, **59**, 1930 (1926).

43 L. Skattebøl, *Tetrahedron*, **21**, 1357 (1965).

44 M. Iyoda, K. Nishioka, M. Nose, S. Tanaka, and M. Oda, *Chem. Lett.*, **1984**, 131.

45 L. Hagelee, R. West, J. Calabrese, and J. Norman, *J. Am. Chem. Soc.*, **101**, 4888 (1979).

46 B. Hagenbruch, K. Hesse, S. Hünig, and G. Klug, *Liebigs Ann. Chem.*, **1981**, 256.

47 G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **27**, 185 (1988).

48 M. Iyoda, S. Tanaka, H. Otani, M. Nose, and M. Oda, *J. Chem. Soc., Chem. Commun.*, **1983**, 1058.

49 M. Iyoda, S. Tanaka, H. Otani, M. Nose, and M. Oda, *J. Am. Chem. Soc.*, **110**, 8494 (1988).

50 M. Iyoda, Y. Kuwatani, and M. Oda, *J. Am. Chem. Soc.*, **111**, 3761 (1989).

51 M. Iyoda, M. Oda, Y. Kai, N. Kanehisa, and N. Kasai, *Chem. Lett.*, **1990**, 2149.

52 M. Iyoda, Y. Kuwatani, M. Oda, Y. Kai, N. Kanehisa, and N. Kasai, *Angew. Chem., Int. Ed. Engl.*, **29**, 1062 (1990).

53 Y. Kuwatani, G. Yamamoto, and M. Iyoda, *Org. Lett.*, **5**, 3371 (2003).

54 M. Iyoda, Y. Kuwatani, M. Oda, K. Tatsumi, and A. Nakamura, *Angew. Chem., Int. Ed. Engl.*, **30**, 1670 (1991).

55 M. Iyoda, Y. Kuwatani, and M. Oda, *J. Chem. Soc., Chem. Commun.*, **1992**, 399.

56 H. D. Hartzler, *J. Am. Chem. Soc.*, **88**, 3155 (1966).

57 H. D. Hartzler, *J. Am. Chem. Soc.*, **93**, 4527 (1971).

58 T. Inoue, T. Kaneda, and S. Misumi, *Tetrahedron Lett.*, **15**, 2969 (1974).

59 T. Negi, T. Kaneda, H. Mizuno, T. Toyoda, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **47**, 2398 (1974).

60 L. T. Scott and G. J. DeCicco, *Tetrahedron Lett.*, **17**, 2663 (1976).

61 G. Santiago, K. N. Houk, G. J. DeCicco, and L. T. Scott, *J. Am. Chem. Soc.*, **100**, 692 (1978).

62 M. Kaftory, I. Agmon, M. Ladika, and P. J. Stang, *J. Am. Chem. Soc.*, **109**, 782 (1987).

63 P. J. Stang, *Acc. Chem. Res.*, **15**, 348 (1982).

64 H. Werner, R. Wiedemann, N. Mahr, P. Steinert, and J. Wolf, *Chem.—Eur. J.*, **2**, 561 (1996).

65 H. Hopf, *Angew. Chem., Int. Ed. Engl.*, **31**, 931 (1992).

66 Y. Zhao, K. Campbell, and R. R. Tykwinski, *J. Org. Chem.*, **67**, 336 (2002).

67 T. Höpfner, P. G. Jones, B. Ahrens, I. Dix, L. Ernst, and H. Hopf, *Eur. J. Org. Chem.*, **2003**, 2596.

68 S. K. Koster and R. West, *J. Org. Chem.*, **40**, 2300 (1975).

69 T. Sugimoto, H. Awaji, Y. Misaki, Z. Yoshida, Y. Kai, H. Nakagawa, and N. Kasai, *J. Am. Chem. Soc.*, **107**, 5797 (1985).

70 T. Sugimoto, Y. Misaki, T. Kajita, Z. Yoshida, Y. Kai, and N. Kasai, *J. Am. Chem. Soc.*, **109**, 4106 (1987).

71 T. Sugimoto, Y. Misaki, Y. Arai, Y. Yamamoto, Z. Yoshida, Y. Kai, and N. Kasai, *J. Am. Chem. Soc.*, **110**, 628 (1988).

72 M. B. Nielsen, M. Schreiber, Y. G. Baek, P. Seiler, S. Lecomte, C. Boudon, R. R. Tykwinski, J.-P. Gisselbrecht, V. Gramlich, P. J. Skinner, C. Bosshard, P. Günter, M. Goss, and F. Diederich, *Chem.—Eur. J.*, **7**, 3263 (2001).

73 Y. Tobe, R. Umeda, N. Iwasa, and M. Sonoda, *Chem.—Eur. J.*, **9**, 5549 (2003).

74 U. H. F. Bunz, *Top. Curr. Chem.*, **201**, 131 (1999).

75 U. H. F. Bunz, Y. Rubin, and Y. Tobe, *Chem. Soc. Rev.*, **28**, 107 (1999).

76 F. Diederich, *Chem. Commun.*, **2001**, 219.

77 H. Stephen, *J. Chem. Soc., Trans.*, **127**, 1874 (1925).

78 N. P. Buu-Hoi, R. Royer, N. D. Xuong, and K. V. Thang, *Bull. Soc. Chim. Fr.*, **1955**, 1204.

79 P. Siemsen, R. C. Livingston, and F. Diederich, *Angew. Chem., Int. Ed.*, **39**, 2632 (2000).

80 F. Toda, H. Ishihara, and K. Akagi, *Tetrahedron Lett.*, **10**, 2531 (1969).

81 F. Toda, K. Kumada, N. Ishiguro, and K. Akagi, *Bull. Chem. Soc. Jpn.*, **43**, 3535 (1970).

82 R. B. King and C. A. Harmon, *J. Organomet. Chem.*, **88**, 93 (1975).

83 L. Song, A. M. Arif, and P. J. Stang, *J. Organomet. Chem.*, **395**, 219 (1990).

84 I. Kovacik, M. Laubender, and H. Werner, *Organometallics*, **16**, 5607 (1997).

85 B. Bildstein, M. Schweiger, H. Angleitner, H. Kopacka, K. Wurst, K.-H. Ongania, M. Fontani, and P. Zanello, *Organometallics*, **18**, 4286 (1999).

86 H. Irngartinger and W. Götzmann, *Angew. Chem., Int. Ed. Engl.*, **25**, 340 (1986).

87 M. Iyoda, H. Otani, M. Oda, Y. Kai, Y. Baba, and N. Kasai, *J. Am. Chem. Soc.*, **108**, 5371 (1986).

88 H. Hart, L. Ward, K. Tanaka, and F. Toda, *Tetrahedron Lett.*, **23**, 2125 (1982).

89 H. Fischer and W. D. Hell, *Angew. Chem., Int. Ed. Engl.*, **6**, 954 (1967).

90 R. Kuhn and K. Wallenfels, *Ber. Dtsch. Chem. Ges.*, **71**, 783 (1938).

91 F. D. van Remoortere and F. P. Boer, *J. Am. Chem. Soc.*, **92**, 3355 (1970).

92 F. W. Nader and C.-D. Waker, *Angew. Chem., Int. Ed. Engl.*, **24**, 852 (1985).

93 T. Matsuo, A. Sekiguchi, M. Ichinohe, K. Ebata, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **71**, 1705 (1988).

94 Z. Berkovitch-Yellin and L. Leiserowitz, *Acta Crystallogr., Sect. B*, **33**, 3657 (1997).

95 J. Sandström, "Dynamic NMR Spectroscopy," Academic Press, London (1982), Chap. 4.

96 G. Yamamoto, *Bull. Chem. Soc. Jpn.*, **65**, 1967 (1992).

97 P. U. Biedermann, J. J. Stezowski, and I. Agranat, *Eur. J. Org. Chem.*, **2001**, 15.

98 R. Kuhn and K. L. Scholler, *Chem. Ber.*, **87**, 598 (1954).

99 K. Bertsch, G. Karich, and J. C. Jochims, *Chem. Ber.*, **110**, 3304 (1977).

100 A. Auffrant, B. Jaun, P. D. Jarowski, K. N. Houk, and F. Diederich, *Chem.—Eur. J.*, **10**, 2906 (2004).

101 The rotational barrier (28.9 kcal mol^{-1}) of *p*-nitrophenyl substituted tetraethynylethene dianion was calculated and discussed on the basis of the formation of the bis-butatriene structure: A. Hilger, J.-P. Gisselbrecht, R. R. Tykwinski, C. Boudon, M. Schreiber, R. E. Martin, H. P. Lüthi, M. Gross, and F. Diederich, *J. Am. Chem. Soc.*, **119**, 2069 (1997).

102 E. M. Geertsema, N. Koumura, M. K. J. ter Wiel, A. Meetsma, and B. L. Feringa, *Chem. Commun.*, **2002**, 2962.

103 J. Raker and J. E. Glass, *J. Org. Chem.*, **67**, 6113 (2002).

104 Z. Dominguez, H. Dang, M. J. Strouse, and M. A. Garcia-Garibay, *J. Am. Chem. Soc.*, **124**, 7719 (2002).

105 A. Levy, P. U. Biedermann, and I. Agranat, *Org. Lett.*, **2**, 1811 (2000).

106 C.-T. Chen and Y.-C. Chou, *J. Am. Chem. Soc.*, **122**, 7662 (2000).

107 N. Koumura, E. M. Geertsema, A. Meetsma, and B. L. Feringa, *J. Am. Chem. Soc.*, **122**, 12005 (2000).

108 R. P. Feynman, "Miniaturization," ed by H. D. Gilbert, Reinhold, New York (1961).

109 K. E. Drexler, "Nanosystems: Molecular Machinery, Manufacturing, and Computation," Wiley, New York (1992).

110 T. R. Kelly, H. De Silva, and R. A. Silva, *Nature*, **401**, 150 (1999).

111 N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada, and B. L. Feringa, *Nature*, **401**, 152 (1999).

112 M. Iyoda, H. Otani, M. Oda, Y. Kai, Y. Baba, and N. Kasai, *J. Chem. Soc., Chem. Commun.*, **1986**, 1794.

113 A. Stockis and R. Hoffmann, *J. Am. Chem. Soc.*, **102**, 2952 (1980).

114 M. Sumimoto, N. Iwane, T. Takahama, and S. Sakaki, *J. Am. Chem. Soc.*, **126**, 10457 (2004).

115 M. Midland, *J. Org. Chem.*, **40**, 2250 (1975).

116 H. Sobotka and J. D. Chanly, *J. Am. Chem. Soc.*, **71**, 4136 (1949).