A New Approach to the Construction of Radialenes by the Nickel-Catalyzed Cyclooligomerization of [3]Cumulenes (Butatrienes)

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Abstract: The zero-valent nickel complexes, which are generated in situ from nickel(II) complexes by reduction with zinc, have been found to catalyze the cyclooligomerization of butatrienes, 2,3-dihalo-1,3-butadienes, 1,4-dichloro-2-butyne, and 1,1-dibromoethylene to give the corresponding [4]- and [6]radialenes. The formation of the [4]- and [6]radialenes depends on the reaction conditions, especially on solvent, and each product of the reactions can be prepared selectively. This method provides access to the synthesis of novel derivatives of radialenes of theoretical and synthetic interest. The spectral and chemical data indicate the highly symmetrical structure of radialenes. The mechanism of this cyclooligomerization is discussed.

Radialenes (polymethylenecycloalkanes) have received considerable attention from both theorists and experimentalists[1-4] because of their particular arrangement of π-electrons and because of advances in the understanding of their potentials as electron donor and acceptor for organic metals[5] and ferromagnetic organic compounds.[6] Of the parent radialenes, [3]-[2] and [4]radialene[3] (**1** and **2**) were reported two decades ago. However, [5]radialene (**3**) was hitherto unknown and [6]radialene (**4**) was synthesized in 1977–1978 by three groups.[4] According to the recently accepted concept, no radialene has unusual resonance destabilization or stabilization despite the potentially destabilizing cyclobutadiene-like and stabilizing benzene-like arrangement of π-electrons. Oxo carbons, which are regarded as oxo derivatives of radialenes, are known to possess unusually large ground-state thermodynamic stability and have been fully investigated.[7] This fact suggests that radialenes receiving the contribution of substituents may have strong stabilization or destabilization based on π-electron conjugation, if a system bears properties like oxo carbons. Thus, radialenes can be expected to show properties as a functionally important π-electron system and as an unique chromophore array. However, the synthetic methodology available to attain radialenes is still very limited, and many compounds containing a radialene framework still remains elusive.[8]


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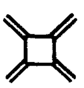
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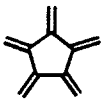
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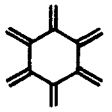
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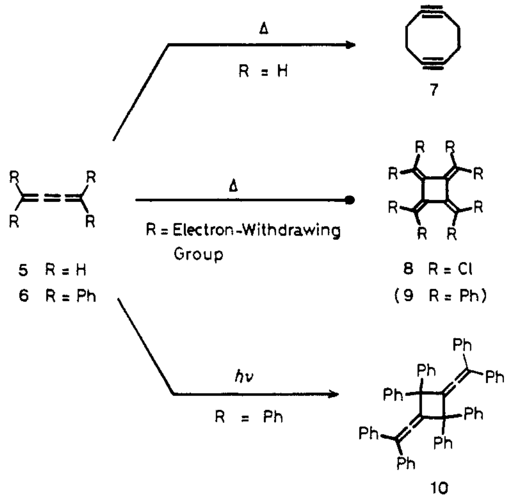
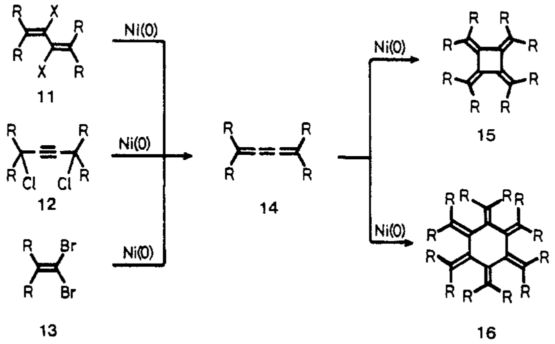
Scheme I



Scheme II



Synthetic Strategy. Among the several strategies, the most efficient for preparing [4]radialene is dimerization of butatrienes. In the case of allenes, dimerization occurs upon heating to produce 1,2- and 1,3-dimethylenecyclobutanes in relatively good yields.[9] However, the parent butatriene (**5**) dimerizes thermally to 1,5-

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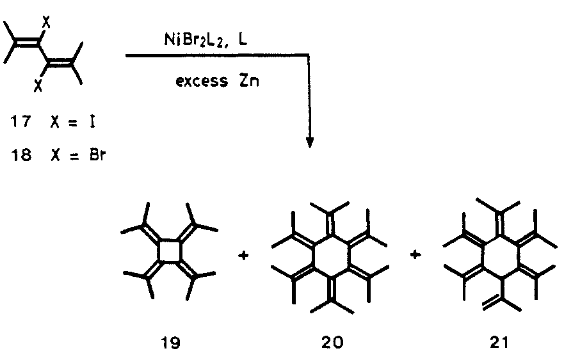
Scheme III



cyclooctadiyne (**7**) as a [4 + 4]cycloadduct (Scheme I).[10] The known thermal [2 + 2] dimerization of butatrienes to [4]radialenes takes place only when electron-withdrawing groups such as Cl are attached to the terminal groups of these compounds.[11] Another example of [2 + 2] cycloaddition of butatriene is the photochemical dimerization of tetraphenylbutatriene (**6**).[12] The dimer of **6** was reported to be octaphenyl[4]radialene (**9**),[12a] but the photodimer was proven to be 1,3-bis(diphenylvinylidene)-2,2,4,4-tetraphenylcyclobutane (**10**) on the basis of X-ray analysis.[12b]

Nickel-catalyzed oligomerization of ethylenes, butatrienes, and acetylenes has been widely investigated.[13] Recently, Ni(CO)$_2$(PPh$_3$)$_2$ has been found to be an effective catalyst for the cyclodimerization of particular butatrienes to [4]radialenes, in which cross-conjugated double bonds are attached as terminal groups.[14] Since nickel(0) complexes convert allene into a mixture of cyclic oligomers containing exo methylene groups,[15,16] nickel-catalyzed cyclooligomerization of simple butatrienes may lead to cyclic polymethylene compounds like [4]- and [6]radialene **15** and **16**.

Table I. Reaction of Dihalogenohexadienes **17** and **18** with Nickel(0) Complex[a]

substr	nickel(0) ligand	time, h	solvent	product yield,[b] % 19	20	21
17[c]	PPh$_3$	3	benzene	48		tr
17[c]	PPh$_3$	3	THF	47	20	
17[c]	PPh$_3$	3	DMF	1	50	
18[d]	PPh$_3$	26	benzene	11		56
18[d]	PPh$_3$	6	THF	21	31	
18[d]	PPh$_3$	3	DMF	5	63	
17[c]	PBu$_3$	3	benzene	48	12	12
18[c]	PBu$_3$	26	benzene	46		31

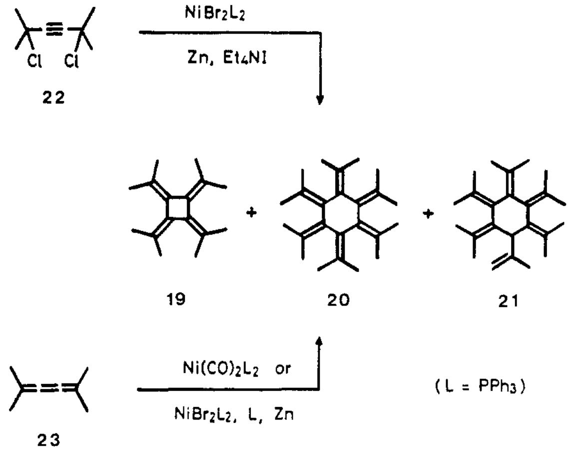
[a] For the experimental procedure, see Experimental Section. [b] Yield based on isolated. [c] A 0.5 equiv of nickel complex was used. [d] A 0.67 equiv of nickel complex was used.

Table II. Reaction of **17**, **18**, and **22** with NiBr$_2$(PPh$_3$)$_2$–Et$_4$NI–Zn[a]

substr	solvent	time, h	product yield,[b] % 19	20	21
17	benzene	5	32	1	8
17	THF	5	61	1	tr
17	DMF	5	50	12	0
18	benzene	27	35	0	9
18	THF	28	72	1	7
18	DMF	26	49	23	0
22	benzene	28	31	2	9
22	THF	26	30	9	18
22	DMF	26	32	15	8

[a] NiBr$_2$(PPh$_3$)$_2$–Et$_4$NI–Zn (0.5:2:5). For the experimental procedure see Experimental Section. [b] Yields based on isolated.

Scheme IV



Nickel(0) complex can be easily prepared by reduction of nickel(II) complex with zinc dust[17] and employed for the coupling of vinyl and aryl halides[18,19] and for reduction of *vic*-dihalides to olefins.[20] Therefore, reduction of 2,3-dihalo-1,3-butadiene (**11**) and 1,4-dichloro-2-butyne (**12**) with nickel(0) complex can be expected to produce butatrienes **14** (Scheme II). Furthermore, the coupling and reduction of **13** with nickel(0) complex can lead to the production of butatrienes **14**. An attractive advantage of this strategy is a single-pot construction of the radialene frameworks via butatrienes. In addition, the combination of nickel(II) complex and zinc enable the reaction to be catalytic by using a stoichiometric amount of zinc.

We reported in preliminary form the nickel-catalyzed oligomerization of 2,5-dimethyl-2,3,4-hexatriene (**14**, R = Me)[21] and postulated the synthetic utility of this type of reaction for construction of the radialene framework. In this paper we detail the successful execution of Scheme I, with a mechanistic feature of cyclooligomerization of butatrienes, and an investigation of the structure and chemistry of radialenes.

Results and Discussion

Nickel-Catalyzed Synthesis of Octamethyl[4]radialene and Dodecamethyl[6]radialene.[21] The starting material 3,4-diiodo- or 3,4-dibromo-2,5-dimethyl-2,4-hexadiene (**17** or **18**), as has been reported previously,[22] can be easily prepared from 2,5-dimethyl-3-hexyne-2,5-diol with hydriodic[22a] or hydrobromic acid.[22b]

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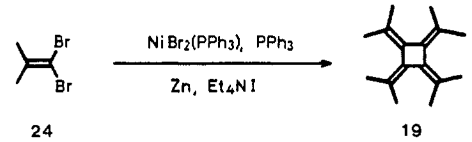
Scheme V

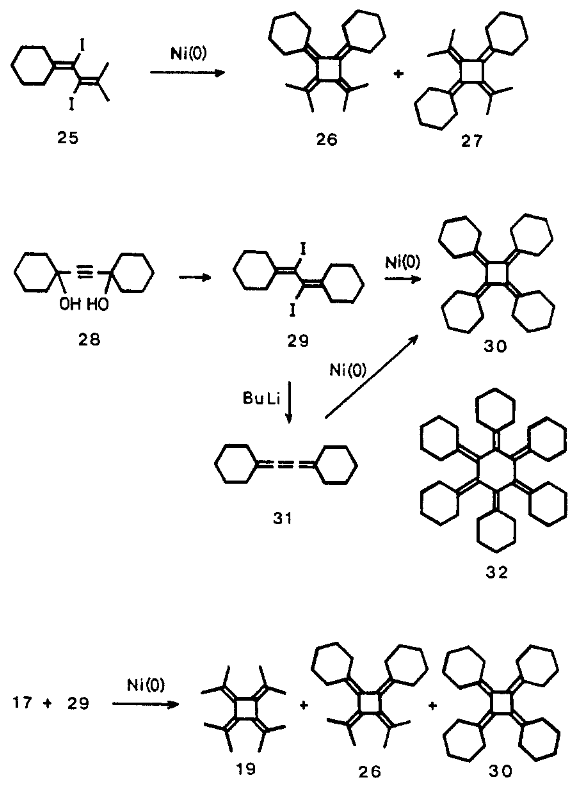


Treatment of **17** or **18** with $Ni(PPh_3)_4$[23] or $Ni(PBu_3)_4$[24] at 50 °C resulted in the formation of the [4]radialene **19**, the [6]radialene **20**, and its isomer **21** (Scheme III). The reaction of **17** or **18** with these nickel(0) complexes is susceptible to solvent and somewhat to halogen, as shown in Table I. Thus, **17** cyclizes predominantly to the [4]radialene **19** in benzene. However, similar treatment of **18** with $Ni(PPh_3)_4$ or $Ni(PBu_3)_4$ gave a mixture of **19** and **21**. In contrast to the results in benzene, the reaction of **17** or **18** in *N*,*N*-dimethylformamide (DMF) gave mainly the [6]radialene **20**, together with small amounts of **19**. The reaction of **17** or **18** in tetrahydrofuran (THF) afforded both **19** and **20**. In the presence of an excess of zinc the reaction is catalytic for **17** or **18**. The reactivity of $Ni(PPh_3)_4$ and $Ni(PBu_3)_4$ in benzene decreased with a larger portion of **17** or **18**, but treatment of **14** with 0.25 equiv of $Ni(PPh_3)_4$ in DMF afforded the same or better selectivity of the products (**19**, trace; **20**, 63%). The formation of **21** was not detected in THF and DMF for either substrate, whereas **21** was a major product in the reaction of **18** with $Ni(PPh_3)_4$ in benzene. In the case of **17**, the reaction at room temperature in benzene resulted in an increase in the yield of **21**. Palladium catalyst may be employed for the cyclooligomerization of butatrienes. However, treatment of **18** with $PdCl_2(PPh_3)_2$ and zinc in 1,2-dimethoxyethane (DME) afforded only small amounts of **19** (5%) and **21** (4%).

Recently, we reported an efficient homocoupling of organic halides using an active nickel complex[25] which is generated in situ by reduction of $NiBr_2(PPh_3)_2$ with zinc in the presence of Et_4NI (no additional PPh_3 is necessary for the preparation of the catalyst). This active nickel complex is also effective for cyclooligomerization of the dihalobutadienes **17** and **18**. Interestingly, all reactions of **17** and **18** with this active nickel complex in benzene, THF, and DMF produce the [4]radialene **19** as a major product, and the yield of **19** increases up to 72% in the case of **18** in THF (Table II). This active nickel complex is available for the reductive cyclooligomerization of 2,5-dimethyl-2,5-dichloro-3-butyne (**22**)[26] to radialenes (Scheme IV), although $Ni(PPh_3)_4$[23] was a less effective catalyst for the reaction of **22** and gave neither 2,5-dimethyl-2,3,4-hexatriene (**23**) nor radialenes. Thus, the reaction of **22** with the active nickel complex in benzene, THF, or DMF produces a mixture of radialenes as shown in Table II. This alternative approach, however, was found to give radialenes in lower yield and also less selectively. This fact may suggest that the reduction of **17** and **18** with this active nickel complex produces the corresponding butatriene **23** more smoothly and effectively than that of **22**, and resultant nickel complex containing **23** as ligand may react with another **23** or its nickel complex more successfully to give radialenes in the former case as compared with the latter.

In addition, the [4]radialene **19** can be prepared from 1,1-dibromo-2-methylpropene (**24**) by using $Ni(PPh_3)_4$ in the presence of Et_4NI (Scheme V). The reaction of **24** with 0.5 equiv of the in situ generated $Ni(PPh_3)_4$ in the presence of Et_4NI in toluene, at −78 °C for 1 h, followed by treatment at 50 °C for 48 h, produced **19** in 17% yield. However, the reaction of **24** with nickel(0) complexes in THF or DMF as solvent gave no radialene derivatives, in accordance with our previous observations.[27]

Scheme VI



The nickel-catalyzed approach to radialenes described in this section has received attention in the field of organometallic chemistry and found application in the literature in the construction of the [4]- and [6]radialene nuclei.[28]

Synthesis of [4]Radialenes Containing Cyclohexane Rings as Terminal Groups. The ready formation of the radialenes **19** and **20** from **17**, **18**, and **22** prompted us to prepare radialenes bearing cyclohexane rings as terminal groups because of a potential usefulness of their derivatives as precursors of organic metals.[5] The starting materials, 1,1,4,4-tetrasubstituted 2,3-diiodo-1,3-butadienes, were prepared by treatment of 1,1,4,4-tetrasubstituted 2-butyne-1,4-diols with HI or Me_3SiI at low temperature.[29]

The reaction of **25** with 0.5 equiv of $Ni(PPh_3)_4$ generated in situ was carried out in benzene at 50 °C for 3 h. The reaction mixture was purified by column chromatography on silica gel to give a mixture of two [4]radialenes, which could be readily separated by fractional recrystallization from ether–methanol. Thus, the head-to-head dimer **26** and the head-to-tail dimer **27** were obtained in 16 and 37% yields, respectively (Scheme VI). Furthermore, treatment of **25** with $Ni(PPh_3)_4$ at room temperature (benzene, 17 h) also resulted in the formation of both **26** (20%) and **27** (24%).

The reaction of the diiodobutadiene **29** with $Ni(PPh_3)_4$ under similar conditions used for **25** (benzene, 50 °C, 21 h) afforded the corresponding [4]radialene **30** (62%). When the reaction of **29** with $Ni(PPh_3)_4$ in benzene at 50 °C was carried out for 3 h, the yield of **30** was reduced to 24% accompanied with a consid-

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[23] $Ni(PPh_3)_4$, which exists in a solid state, dissociates completely to $Ni(PPh_3)_3$ in solution: Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956–2965.

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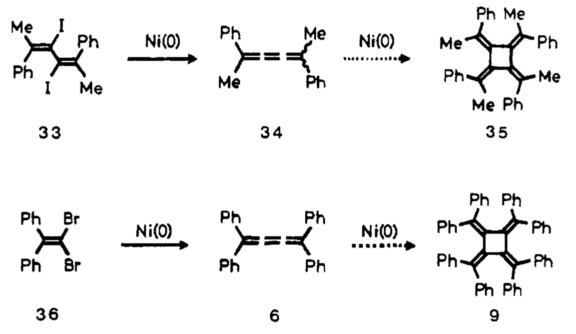
Scheme VII



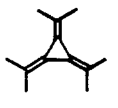
erable amount of bis(pentamethylene)butatriene,[29,30] which can be regarded as the intermediate of the [4]radialene **30**. In order to confirm the structure of the head-to-head dimer **26**, the reaction of a 1:1 mixture of **17** and **29** with $Ni(PPh_3)_4$ was carried out. Besides the homocoupled products (**19**, 6%; **30**, 14%), the expected cross-coupled product **26** could be obtained in 28% yield. The ^1H NMR and IR spectra and the retention time in HPLC were identical with those of the head-to-head dimer **26** obtained from **25**.

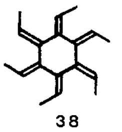
The low-valent active nickel complex generated from $NiBr_2(PPh_3)_2$, Zn, and Et_4NI in benzene can be used for the synthesis of **30** but is less effective catalyst (50 °C, 20 h; yield 44%). Although THF and DMF can be employed as a solvent for the nickel-catalyzed cyclooligomerization of **17**, **18**, **22**, and **23**, treatment of **25** and **29** with $Ni(PPh_3)_4$ generated in situ in THF or DMF gave no radialene derivatives. The reaction of bis(pentamethylene)butatriene (**31**) with $Ni(CO)_2(PPh_3)_2$ in benzene under reflux for 3 days also produces the [4]radialene **30** in 14% yield. In the case of **29** in DMF, a trimer [*m*/*z* 564 (M^+)] was isolated from the reaction mixture together with polymeric material, but the structure was proved to be neither the [6]radialene **32** nor a derivative of **21**.

In contrast to the results described previously, the reaction of 3,4-diiodo-2,5-diphenyl-2,4-hexadiene (**33**)[29a] with $Ni(PPh_3)_4$ in benzene at room temperature gave a mixture of the (*Z*)- and (*E*)-butatrienes **34**[29] and the formation of the corresponding [4]radialene **35** was not observed. In addition, the reaction of 1,1-dibromo-2,2-diphenylethylene (**36**) with $Ni(PPh_3)_4$ in benzene at 50 °C gave tetraphenylbutatriene (**6**) in 60% yield. However, **6** was stable under the reaction conditions and recovered unchanged in the attempted cyclooligomerization using $Ni(PPh_3)_4$. Taking into account the stability of **34** and **6** in the reaction medium, it appears that phenyl-substituted butatrienes do not undergo the cyclodimerization reaction (Scheme VII).[30]

Spectral Data. The ^1H and ^{13}C NMR data show simple and characteristic features reflecting the highly symmetrical structures. The ring sp^2 carbons of radialenes are observed at lower field as compared with the exo methylene sp^2 carbons, and these chemical shifts are due to the terminal alkyl substituents and the ring size of radialenes. This tendency may be recognized by comparison with the chemical shifts of alkyl-substituted butadienes,[31] although the cyclic effect of radialenes may further complicate their chemical shifts as compared with simple acyclic dienes.

The electronic spectra of the [4]radialenes **19**, **27**, and **30** and the [6]radialene **20** are shown in Figure 1 together with hexamethyl[3]radialene (**37**) synthesized by Köbrich.[32] Theoretical treatment of the electronic transitions of radialenes[31] has suggested that the transition energy should increase along with the increase of ring size. In accordance with this calculation, the absorption maximums of methyl-substituted radialenes **19**, **20**, and **37** decrease with increasing ring size (i.e., **37** > **19** > **20**).


37


38

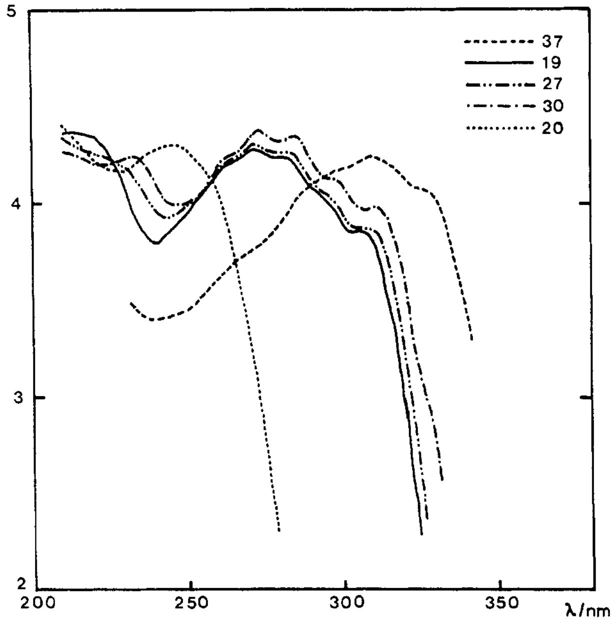


Figure 1. Electronic spectra of the [3]radialene **37**, the [4]radialenes **19**, **27**, and **30**, and the [6]radialene **20** in cyclohexane.

Table III. The C=C Stretching Bands in the Raman Spectra of **19**, **20**, **25**, **26**, and **30** (KBr)[a]

radialene	absorption bands, cm^{-1}
19	1707 (vs, A_1, (p)), 1662 (m, B_2, (dp)), 1650 (s, E, (dp))
30	1695 (vs, A_1, (p)), 1648 (m, B_2, (dp)), 1640 (s, E, (dp))
20	1650 (vs, A_{1g}, (p)), 1637 (s, E_g (dp))
26	1695 (vs), 1654 (m), 1651 (m), 1637 (s)
27	1695 (vs), 1652 (m), 1647 (m), 1638 (s)

[a] Intensities are indicated by a letter following the value: vs, very strong; s, strong; m, medium. A letter in parentheses shows polarization: p, polarized; dp, depolarized.

The X-ray crystal structure determinations on the [4]radialene **19**[28b,32] and the [6]radialenes **20**[28b] and **38**[35] confirm the puckered and chair conformations of radialenes. Although the parent [4]radialene **2** was concluded to bear a planar ring and D_{4h} symmetry on the basis of Raman and IR spectra,[3b] X-ray analysis of **19** indicated the molecular framework with nonplanar D_{2d} symmetry. In order to examine the difference in symmetry between **2** and **19**, we investigated the Raman and IR spectra of **19**, **26**, **27**, and **30**. In the Raman spectra of these [4]radialenes, the C=C stretching bands summarized in Table III are intense and sharp. In the cases of **19** and **30**, which hold D_{2d} symmetry, three bands are observed for the C=C stretching vibrations and explained as Raman-active three fundamental modes (A_1, B_2, and E) on the basis of the simply coupled oscillators model. The highest bands in the spectra of **19** and **30** are readily identified by their polarization and assigned to species A_1 (depolarization measurements were made in CCl_4 solutions). This assignment is supported by the absence of absorption bands (IR-inactive) in the IR spectra of **19** and **30**. The other two bands (species B_2

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(30) (a) For the synthesis of **9**, see: Iyoda, M.; Otani, H.; Oda, M.; Kai, Y.; Baba, Y.; Kasai, N. *J. Am. Chem. Soc.* **1986**, *108*, 5371–5372. (b) Iyoda, M.; Otani, H.; Oda, M.; Kai, Y.; Baba, Y.; Kasai, N. *J. Chem. Soc., Chem. Commun.* **1986**, 1794–1976.

(31) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757–2766.

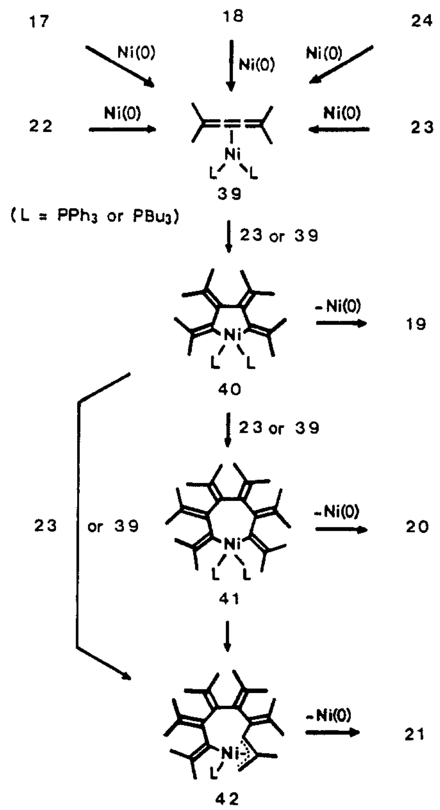
(32) Köbrich, G.; Heinemann, H. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 594–595. Köbrich, G.; Heinemann, H.; Zundorf, W. *Tetrahedron* **1967**, *23*, 565–584.

(33) Heilbronner, E. *Theor. Chim. Acta* **1966**, *4*, 64–68.

(34) Iyoda, M.; Tanaka, S.; Oda, M. Presented in part at the 16th Symposium on Structural Organic Chemistry, Saitama, Japan, September 28–30, 1983; pp 261–264. Although X-ray analysis of **19** gave the indefinite structure due to crystallographic disorder, fairly good conformational information was obtained.

(35) Hopf, H.; Gati, A. *Helv. Chim. Acta* **1965**, *48*, 1289–1296. Marsh, W.; Dunitz, J. D. *Ibid.* **1975**, *58*, 707–712.

Scheme VIII



and E), which are IR-active, are assigned on the basis of intensity and depolarization in the Raman and IR spectra. In the cases of **26** and **27**, which are expected to hold C_2 and C_{2v} symmetry, respectively, four bands are observed for the C=C stretching vibrations corresponding to four Raman-active modes.

Dodecamethyl[6]radialene (**20**) holds a chair conformation with D_{3d} symmetry. For the C=C stretching vibrations, four fundamental modes (A_{1g} and E_g as Raman-active modes, and A_{2u} and E_u as IR-active modes) are expected on the basis of the simply coupled oscillators model. In the Raman spectrum of **20**, the two intense C=C stretching bands are observed as shown in Table III. The band at 1650 cm^{-1} is assigned to species A_{1g} by the depolarization measurement and the other band at 1637 cm^{-1} is assigned to species E_g. The IR spectrum of **20** showed only one absorption at 1639 cm^{-1} as a very weak band.

Finally, the symmetrically substituted [4]radialenes (**19** and **30**) hold D_{2d} symmetry, and the conformation is different from that of the parent [4]radialene (**2**) due to the steric repulsion between the alkyl substituents. The C=C stretching bands in the Raman spectra reflect the symmetrical structure of radialenes.

In conclusion, we have shown that the nickel-catalyzed cyclooligomerization of [3]cumulenes (butatrienes) prepared in situ from various precursors provides access to a simple and efficient synthetic method for [4]- and [6]radialenes. This cyclooligomerization takes place only at sp-hybridized carbon atoms of [3]cumulenes, resulting in the formation of products with highly symmetrical structures, in contrast to rather complicating features of nickel-catalyzed oligomerization of allenes,[36,37] which have a central sp-hybridized carbon bonded to two sp^2-hybridized carbons. Although the intermediates **39**–**42** in the nickel-catalyzed reaction of **17**, **18**, and **22**–**24** are not fully characterized in our case, a possible mechanism for the formation of the cyclic dimer and trimers of **23** is anticipated as outlined in Scheme VIII. The first step of this reaction is the formation of the butatriene–nickel complex **39** from various precursors. Stable butatriene–nickel complexes are unknown so far, but the structure is believed to involve a η^2-butatriene complex using the cumulenic sp–sp bond by analogy to the complexes of butatrienes with other transition metals.[14a,38] The complex **39** may be T-shaped,[39] planar about the nickel atom, with the axis of the butatriene chromophore oriented perpendicular to the general plane of the complex. The formation of the bis(butatriene)–π-complex from **39** to **23** (or **39**), followed by π–π coupling, produces the σ-complex **40**.[28a,b] Reductive elimination from **40** produces **19**, in the cases of the reactions of **17** in THF or benzene and the reactions of **17** and **18** in the presence of iodide ion, which may accelerate the reductive elimination. In the case of the reaction of **17** in DMF, further insertion of **23** (or **39**) occurs to give the labile nickelacycloheptane **41** which forms **20** readily via reductive elimination. In the reaction of **18** with Ni(PPh$_3$)$_4$ in benzene, the major product is the trimer **21**, which is probably formed via a π-allyl intermediate **42** that is produced by isomerization of **41** or by direct interaction of **40** with **23** (or **39**). However, no isomerization of **20** to **21** occurred under the reaction conditions.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded on Varian T-60 and XL-100 or JEOL JNM-PMX60Si, JNM-FX90Q, JNM-GSX400, and JNM-GX500 instruments. Spectra are reported (in δ) referenced to Me$_4$Si. Unless otherwise noted, CDCl$_3$ was used as solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant (Hz), and integration. IR spectra were observed on a Hitachi EPI-G3 or Jasco FT-IR-3 spectrometer. Raman spectra were measured on a Jasco R-800 spectrometer. Electronic spectra were obtained on a Hitachi EPS-3T or U-3400 instrument and are reported in nanometers (log ϵ) (sh = shoulder). Mass spectral analyses (MS) were performed on a JEOL JMS-O1SG-2 instrument. Only the more intense or structurally diagnostic mass spectral fragment ion peaks are reported. Melting points were determined on a Mettler FP-2 apparatus and are uncorrected. Column chromatography was carried out with use of EM Reagents silica gel 60, 70–230 mesh ASTM, or neutral alumina activity II–III, 70–230 mesh ASTM. Analytical TLC was performed by using plates (0.25 mm) prepared from EM reagents silica gel GF-254, which were stored in a hot oven and used in a highly activated state for **19**–**21**, **26**, and **27**.

High-pressure liquid chromatography (HPLC) was carried out on a Hitachi 635 apparatus. All solvents were dried by conventional procedures. Reactions involving air-sensitive organometallic reagents were carried out under nitrogen or argon atmosphere.

General Procedure for Table I. Reaction of 17. A 50-mL, round-bottomed, two-necked flask containing a magnetic stirring bar was charged with 1.49 g (2 mmol) of NiBr$_2$(PPh$_3$)$_2$, 1.05 g (4 mmol) of PPh$_3$, and 1.31 g (20 mmol) of activated zinc dust.[40] 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. The flask was evacuated and filled with argon several times (vacuum line). Dry benzene or THF (30 mL) was added via syringe through the septum. The reaction flask was then placed in an oil bath at 50 °C and stirred. After the red-brown catalyst had formed (10–60 min), an argon-purged solution of 1.45 g (4 mmol) of **17**[22a] in the same solvent (2 mL) was added via syringe to the reaction mixture. The resulting mixture was heated at 50 °C for 3 h. Hexane (30 mL) was added, and the mixture was filtered. The filtrate was passed through a short column of Al$_2$O$_3$ (15 g) and eluted with hexane. After removal of the solvent in vacuo, the residue was separated by column chromatography on silica gel (100 g) using hexane as eluent.

When the reaction was carried out in DMF as solvent, the filtered reaction mixture was poured into 2 M hydrochloric acid (100 mL) and extracted with CH$_2$Cl$_2$. The organic phase was washed with water and dried over MgSO$_4$. The solvent was evaporated, and the residue was separated by chromatography on silica gel (100 g).

For the reaction with Ni(PBu$_3$)$_4$, 1.26 g (2.0 mmol) of NiBr$_2$(PBu$_3$)$_2$[41]

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(36) Pasto, D. J.; Huang, N.-Z.; Eigenbrot, C. W. *J. Am. Chem. Soc.* **1985**, *107*, 3160–3172. Pasto, D. J.; Huang, N.-Z. *Organometallics* **1985**, *4*, 1386–1395, and references cited therein.

(37) Otsuka, S.; Mori, K.; Imaizumi, F. *J. Am. Chem. Soc.* **1965**, *87*, 3017–3019. Otsuka, S.; Mori, K.; Suminoe, T.; Imaizumi, F. *Eur. Polym. J.* **1967**, *3*, 73–83. Hoover, F. W.; Lindsey, R. V., Jr. *J. Org. Chem.* **1969**, *34*, 3051–3052. Otsuka, S.; Nakamura, A.; Tani, K.; Ueda, S. *Tetrahedron Lett.* **1969**, 297–300. De-Pasquale, R. J. *J. Organomet. Chem.* **1971**, *32*, 381–393. Otsuka, S.; Tani, K.; Yamagata, T. *J. Chem. Soc., Dalton Trans.* **1973**, 2491–2497.

(38) Stang, P. J.; White, M. R.; Maas, G. *Organometallics* **1983**, *2*, 720–725. White, M. R.; Stang, P. J. *Ibid.* **1983**, *2*, 1654–1658.

(39) Hartley, F. R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 596–606.

(40) Yamamura, S.; Toda, M.; Hirata, Y. *Org. Synth.* **1973**, *53*, 86–90.

and 0.82 g (4.0 mmol) of PBu_3 were used instead of $NiBr_2(PPh_3)_2$ and PPh_3 and the reaction was carried out in a similar manner.

19: colorless crystals (from hexane), mp 155 °C sublimed; ^1H NMR (100 MHz) δ 1.80 (s, 24 H); ^{13}C NMR (22.5 MHz) δ 138.3, 115.6, 23.8; MS, *m/z* 216 (M^+); UV, λ_{max} (cyclohexane) 307 nm (sh, log ϵ 3.86), 283 (sh, 4.23), 272 (4.28), 260 (sh, 4.18); IR (KBr) 1658, 1645, 1440, 1368 cm^{-1}; Raman (KBr) 1707, 1662, 1650 cm^{-1}. Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.71; H, 11.22.

20: colorless crystals (from ether–methanol), mp 210 °C sublimed; ^1H NMR (400 MHz) δ 1.63 (s, 36 H); ^{13}C NMR (100 MHz) δ 136.8, 122.6, 21.2; MS, *m/z* 324 (M^+); UV, λ_{max} (cyclohexane) 248 nm (log ϵ 4.32), 240 (sh, 4.31); IR (KBr) 1638, 1455, 1445, 1380, 1370 cm^{-1}; Raman (KBr) 1637, 1650 cm^{-1}. Anal. Calcd for $C_{24}H_{36}$: C, 88.82; H, 11.18. Found: C, 88.81; H, 11.30.

21: colorless crystals (from ether–methanol), mp 155 °C sublimed; ^1H NMR (500 MHz) δ 4.66 (m, 1 H), 4.47 (s, 1 H), 1.79 (s, 6 H), 1.66 (s, 6 H), 1.65 (br s, 3 H), 1.63 (s, 6 H), 1.61 (s, 6 H), 1.56 (s, 6 H); ^{13}C NMR (125 MHz) δ 147.4, 136.8, 135.0, 134.8, 125.9, 124.4, 122.8, 110.0, 50.3, 22.9, 21.9, 21.4, 21.2, 20.1; MS, *m/z* 324 (M^+), 309, 281; UV, λ_{max} (cyclohexane) 247.5 nm (log ϵ 4.21); IR (KBr) 3062, 1650, 1645, 1630, 1450, 1370 cm^{-1}; Raman (KBr) 1650, 1635, 1632 cm^{-1}. Anal. Calcd for $C_{24}H_{36}$: C, 88.81; H, 11.30. Found: C, 88.68; H, 11.29.

Reaction of 18. A flask was charged with 1.49 g (2 mmol) of $NiBr_2(PPh_3)_2$, 1.05 g (4 mmol) of PPh_3, and 1.31 g (20 mmol) of activated zinc, evacuated, and filled with argon. Dry benzene, THF, or DMF (30 mL) was added, and the resultant mixture was stirred at 50 °C. After the red-brown catalyst had formed, a solution of 804 mg (3 mmol) of **18**[22b] in the same solvent (2 mL) was added to the suspension containing $Ni(PPh_3)_4$. The mixture was warmed at 50 °C, until the reaction was completed, and worked up in a similar manner as above.

General Procedure for Table II. In a 50-mL round-bottomed, two-necked flask containing a magnetic stirring bar and filled with argon and stoppered with a rubber septum were placed 1.49 g (2.0 mmol) of $NiBr_2(PPh_3)_2$, 2.06 g (8 mmol) of Et_4NI, and 1.31 g (20 mmol) of activated zinc in 25 mL of benzene, THF, or DMF. The solution was heated at 50 °C and stirred until the dark red-brown catalyst has formed. A solution of 4 mmol of the halides **17**, **18**, or **22** in the same solvent (5 mL) was added, and the resulting mixture was stirred at 50 °C for 5–28 h. The reaction mixture was worked up, and the products were separated by column chromatography on silica gel (100 g) to give **19**–**21** in yields shown in Table II.

Reaction of 2,5-Dimethyl-2,3,4-hexatriene (23) with $Ni(PPh_3)_4$. Reaction in Benzene. A solution of 10 mmol of **23** in benzene (15 mL), which was prepared from 3.62 g (10 mmol) of **17** with BuLi (10 mmol) in ether at −50 °C,[26,42] was added to a suspension of $Ni(PPh_3)_4$, which was generated in situ from 0.74 g (1 mmol) of $NiBr_2(PPh_3)_2$, 0.53 g (2 mmol) of PPh_3, and 0.66 g (10 mmol) of activated zinc in benzene (15 mL) at 50 °C. The mixture was stirred at 50 °C for 3 h and then filtered. The filtrate was passed through a short column of Al_2O_3 (30 g) with benzene as eluent. After removal of the solvent in vacuo, the residue was separated by column chromatography on silica gel (100 g) using hexane as eluent to give **19** (76 mg, 7%) and **21** (206 mg, 19%).

Reaction in DMF. A solution of 10 mmol of **23** in DMF (15 mL), prepared from 3.62 g (10 mmol) of **17** with BuLi,[42] was added to a suspension of $Ni(PPh_3)_4$, which was generated from 0.74 g (1 mmol) of $NiBr_2(PPh_3)_2$, 0.53 g (2 mmol) of PPh_3, and 0.66 g (10 mmol) of activated zinc. The mixture was stirred at 50 °C for 3 h and then filtered. The filtrate was poured into 2 M hydrochloric acid (100 mL) and extracted with CH_2Cl_2. The organic phase was washed with water and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was passed through a short column of Al_2O_3 (20 g) and chromatographed on silica gel (100 g) to give **19** (25 mg, 2%), **20** (150 mg, 14%), and **21** (130 mg, 12%).

Reaction of 23 with $Ni(CO)_2(PPh_3)_2$. To a solution of 10 mmol of **23** in benzene (150 mL), prepared from 3.62 g (10 mmol) of **17** with BuLi,[42] were added 0.64 g (1 mmol) of $Ni(CO)_2(PPh_3)_2$ and 0.52 g (2 mmol) of PPh_3, and the solution was heated to reflux for 24 h. After removal of most of the solvent, the reaction mixture was passed through a short column of Al_2O_3 (30 g) with benzene as eluent. The product was then chromatographed on silica gel (250 g) and eluted with hexane to give **19** (70 mg, 6.5%), **20** (22 mg, 2%), and **21** (325 mg, 30%).

Reaction of 1,1-Dibromo-2-methylpropene (24) with $Ni(PPh_3)_4$ in the Presence of Et_4NI. A flask was charged with 2.26 g (3 mmol) of $NiBr_2(PPh_3)_2$, 1.57 g (6 mmol) of PPh_3, 3.09 g (12 mmol) of Et_4NI, and 1.96 g (30 mmol) of activated zinc, evacuated, and filled with argon. Dry toluene (30 mL) was added and the resultant mixture stirred at 50 °C for 1 h. The suspension of the nickel catalyst was cooled to −78 °C, and a solution of 1.31 g (6 mmol) of **24** in toluene (5 mL) was added. The reaction mixture was allowed to warm at room temperature and then heated at 50 °C. After being stirred at 50 °C for 48 h, the mixture was filtered and the filtrate was evaporated in vacuo. The residue was passed through a short column on Al_2O_3 (15 g) and eluted with hexane. The products were chromatographed on silica gel (100 g) to give **19** (56 mg, 17%).

2,3-Diiodo-4-methyl-1-pentamethylene-1,3-pentadiene (25). To concentrated hydriodic acid (60 mL) was added 19.1 g (105 mmol) of 1,4-dihydroxy-4-methyl-1-pentamethylene-2-pentyne[27] at 0 °C. The mixture was stirred at 0 °C for 4 h and then at room temperature for 16 h. The reaction mixture was subjected to aqueous workup, and the resulting brown solid was chromatographed on silica gel to give **25** (27.0 g, 64%): colorless crystals (from methanol), mp 52.5–53.0 °C; ^1H NMR (100 MHz) δ 2.5–2.2 (m, 4 H), 1.94 (s, 3 H), 1.73 (s, 3 H), 1.7–1.4 (m, 6 H); ^{13}C NMR (22.5 MHz) δ 146.5, 139.7, 100.0, 98.7, 39.9, 31.5, 29.8, 27.2, 26.5, 26.1, 20.4; MS, *m/z* 402 (M^+), 275, 148. Anal. Calcd for $C_{11}H_{16}I_2$: C, 32.86; H, 4.01; I, 63.13. Found: C, 32.86; H, 4.01; I, 63.13.

Reaction of 25 with $Ni(PPh_3)_4$. To a suspension of $Ni(PPh_3)_4$ prepared from 0.74 g (1 mmol) of $NiBr_2(PPh_3)_2$, 0.53 g (2 mmol) of PPh_3, and 0.66 g (10 mmol) of activated zinc in benzene (15 mL) was added 804 mg (2 mmol) of **25** in one portion. The mixture was heated at 50 °C for 3 h and then filtered. The filtrate was passed through a short alumina column (15 g, benzene–hexane) and chromatographed on silica gel (10 g) with hexane as eluent to give 156 mg (53%) of a mixture of **26** and **27** in a ratio of 3:7, as determined by HPLC. Pure **26** was obtained by recrystallizations of the mixture from ether–methanol and then from ether. Pure **27** was also obtained by recrystallization of the mother liquor from methanol.

The reaction of **25** with $Ni(PPh_3)_4$ in benzene at room temperature for 17 h gave **26** and **27** in 20 and 24% yields, respectively.

26: colorless crystals (from ether), mp 172.5–173.5 °C; ^1H NMR (90 MHz) δ 2.36–2.08 (br s, 8 H), 1.78 (s, 12 H), 1.65–1.44 (br s, 12 H); ^{13}C NMR (22.5 MHz) δ 138.3, 134.4, 123.0, 114.6, 33.12, 33.07, 28.0, 27.9, 26.5, 23.84, 23.78; MS, *m/z* 296 (M^+); UV, λ_{max} (cyclohexane) 309 nm (log ϵ 3.91), 296 (sh, 4.06), 283 (4.29), 272.5 (4.33), 261 (sh, 4.21), 231 (sh, 4.21); IR (KBr) 1658, 1654, 1640 cm^{-1}; Raman (KBr) 1695, 1654, 1651, 1637 cm^{-1}. Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 88.94; H, 10.87.

27: colorless crystals (from methanol), mp 153.5–157.5 °C; ^1H NMR (90 MHz) δ 2.36–2.04 (br s, 8 H), 1.77 (s, 12 H), 1.68–1.40 (br s, 12 H); ^{13}C NMR (22.5 MHz) δ 137.2, 134.8, 123.2, 114.6, 33.1, 28.1, 26.5, 23.8; MS, *m/z* 296 (M^+); UV, λ_{max} (cyclohexane) 309 nm (log ϵ 3.89), 296 (sh, 4.05), 283 (4.29), 272 (4.33), 262 (sh, 4.22), 250 (sh, 4.00), 227.5 (sh, 4.22); IR (KBr) 1658, 1654, 1640 cm^{-1}; Raman (KBr) 1695, 1654, 1651, 1637 cm^{-1}. Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 88.73; H, 10.91.

2,3-Diiodo-1,4-bis(pentamethylene)-1,3-butadiene (29). To a solution of 2.22 g (10 mmol) of **28**[29] in CH_2Cl_2 (100 mL) was added a solution of 7.1 mL (50 mmol) of $(CH_3)_3SiI$ in CH_2Cl_2 (20 mL) at −30 °C over a period of 30 min. The mixture was stirred at −30 °C for 1 h. The reaction mixture was subjected to aqueous workup, and the resulting brown solid was chromatographed on silica gel to give **29** (2.44 g, 55%): colorless crystals (from ether–methanol), mp 95–97 °C; ^1H NMR (90 MHz) δ 2.33–2.25 (m, 8 H), 1.53 (m, 12 H); ^{13}C NMR (22.5 MHz) δ 146.5, 97.6, 40.1, 31.8, 27.4, 26.7, 26.3; MS, *m/z* 442 (M^+), 315, 188; IR (KBr) 2920, 2850, 1593, 1449 cm^{-1}. Anal. Calcd for $C_{14}H_{20}I_2$: C, 38.03; H, 4.56; I, 57.41. Found: C, 38.01; H, 4.51; I, 57.42.

Reaction of 29 with $Ni(PPh_3)_4$. To a suspension of $Ni(PPh_3)_4$ prepared from 1.49 g (2 mmol) of $NiBr_2(PPh_3)_2$, 1.05 g (4 mmol) of PPh_3, and 1.31 g (20 mmol) of activated zinc in benzene (30 mL) was added 1.33 g (3 mmol) of **29** in one portion. The mixture was stirred under argon at 50 °C for 21 h and then filtered. The solution was filtered through a short alumina column (benzene–hexane) and then chromatographed on silica gel (hexane) to give **30** (349 mg, 62%): colorless plates (from ether–methanol), mp 159–160 °C; ^1H NMR (100 MHz) δ 2.18 (br s, 16 H), 1.54 (br s, 24 H); ^{13}C NMR (22.5 MHz) δ 134.2, 122.1, 33.1, 28.0, 26.5; MS, *m/z* 376 (M^+); UV, λ_{max} (cyclohexane) 311 nm (log ϵ 3.99), 297.5 (sh, 4.14), 284.5 (4.37), 273 (4.39), 262.5 (sh, 4.26), 233.5 (4.26); IR (KBr) 1648, 1640 cm^{-1}; Raman (KBr) 1695, 1648, 1640 cm^{-1}. Anal. Calcd for $C_{28}H_{40}$: C, 89.29; H, 10.71. Found: C, 89.05; H, 10.75.

1,4-Bis(pentamethylene)-1,2,3-butatriene (31). To a solution of 531 mg (1.2 mmol) of **29** in ether (15 mL) was added 0.8 mL (1.2 mmol) of a 1.5 M solution of BuLi in hexane at −70 °C. The mixture was stirred at −70 °C for 2 h and then at −50 °C for 10 min. Pentane (15 mL) was added, and the temperature was raised to −20 °C. Water was

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[41] Jensen, K. A.; Nielsen, P. H.; Pedersen, C. T. *Acta Chem. Scand.* **1963**, *17*, 1115–1125.

[42] 2,5-Dimethyl-2,3,4-hexatriene (**23**) is very labile for atmospheric oxygen. Therefore, this compound was used for the reaction with the nickel(0) complex, immediately after the preparation.

added and allowed to warm at room temperature. $MgSO_4$ (1 g) was added to remove water and filtered off. Removal of the solvent, followed by filtration through a silica gel column (pentane), gave **31** (173 mg, 77%), which was sublimed at 80 °C (3 Torr). **31**: colorless crystals, mp 81.5–82.0 °C; ^1H NMR (90 MHz, CCl_4) δ 2.20 (br s, 8 H), 1.59 (br s, 12 H); ^{13}C NMR (22.5 MHz, CCl_4) δ 152.0, 114.8, 34.6, 27.5, 26.1; MS, *m/z* 188 (M^+); UV, λ_{max} (cyclohexane) 272 nm (log ϵ 3.84), 265 (3.83); IR (CCl_4) 2933, 2853, 1450, 1346, 1225 cm^{-1}. Attempted elemental analysis of **31** was unsuccessful because of its instability to atmospheric oxygen. The butatriene **31** can be stored in CCl_4 or hexane solution under argon.

Reaction of 31 with $Ni(CO)_2(PPh_3)_2$. To a solution of 942 mg (5 mmol) of **31** in benzene (150 mL) were added 640 mg (1 mmol) of $Ni(CO)_2(PPh_3)_2$ and 512 mg (2 mmol) of PPh_3. The mixture was heated to reflux under nitrogen for 3 days. The reaction mixture was filtered through a short silica gel column (benzene) and chromatographed on silica gel (hexane) to give the [4]radialene **30** (134 mg, 14%).

Codimerization of 17 and 29 with $Ni(PPh_3)_4$. To a suspension of $Ni(PPh_3)_4$ prepared from $NiBr_2(PPh_3)_2$, PPh_3, and zinc [1.49 g (2 mmol), 1.05 g (4 mmol), and 1.31 g (30 mmol), respectively] were added 725 mg (2 mmol) of **17** and 884 mg (2 mmol) of **29**. The resulting mixture was stirred under argon at room temperature for 50 h and then filtered. The filtrate was passed through a short alumina column and then chromatographed on silica gel to give **19** (6%), **26** (28%), and **30** (14%). Pure sample of these compounds were obtained by further separation using preparative TLC.

Reaction of 33 with $Ni(PPh_3)_4$. To a suspension of $Ni(PPh_3)_4$ prepared from $NiBr_2(PPh_3)_2$, PPh_3, and zinc in benzene (7 mL), [373 mg (0.5 mmol), 263 mg (1 mmol), and 328 mg (5 mmol), respectively] was added 550 mg (1.1 mmol) of **33** in one portion. The mixture was stirred at room temperature for 24 h and worked up in a similar manner used for **29** to give a mixture of (*E*)- and (*Z*)-**34**[30] (19 mg, 27%).

Reaction of 36 with $Ni(PPh_3)_4$. To a suspension of $Ni(PPh_3)_4$ prepared from $NiBr_2(PPh_3)_2$, PPh_3, and zinc in benzene (30 mL) at 50 °C [1.51 g (2 mmol), 1.06 g (4 mmol), and 1.31 g (20 mmol), respectively] was added 680 mg (2 mmol) of **36** in one portion. The mixture was stirred at 50 °C for 21 h and worked up to give **6** (207 mg, 60%).

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Static Structure of a Regular Intermediate Controls the Course of the Thermal 1,3-Sigmatropic Rearrangement of 6-Methylenebicyclo[3.1.0]hex-2-enyl Derivatives[1]

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Abstract: The rearrangements of derivatives of the title structure bearing oxygen substituents at C_4 occur at measurable rates in the temperature range 50–100 °C in benzene solution. The products are 2-methylenebicyclo[3.1.0]hex-3-enes substituted at C-6. The stereochemistry of these processes shows the intervention in each case of a true intermediate. Either stereoisomer of the 4-methoxy reactant gives the same 97:3 mixture of 6-*endo*- and 6-*exo*-methoxy products. Similar results are observed starting with the 4-*endo*-methoxy-4-*exo*-methyl reactant, which gives largely the 6-*endo*-methoxy product. In the case of the rearrangement of optically active ethylene ketal of bicyclo[3.1.0]hex-3-en-2-one, the rearranged cyclopropanone ketal is devoid of optical activity (>99% racemized), and the starting material is recovered 12% racemized. These data suggest the intermediacy of a symmetrical achiral biradical intermediate, which lives long enough to lose mechanistic memory of its origin and which cyclizes to rearrangement product about 6.5 times as fast as it cyclizes back to starting material.

Structural or stereochemical symmetrization experiments traditionally have provided one of the most decisive means of mechanistic investigation. The power of this method comes from the conviction that a statically or dynamically symmetrical intermediate in a symmetrical environment would necessarily give equal quantities of two or more symmetry-related products.[2] A similar criterion pertains to quasi-symmetrical intermediates, which give identical product distributions from two or more different precursors. These criteria are especially strong in their exclusionary form,[3] in which the observation of a biased product distribution is taken as compelling evidence *against* a symmetrical (or quasi-symmetrical) intermediate.

Although a number of effectively symmetrical intermediates have been brought to light, especially in the field of carbocation chemistry,[3a,b,4] the literature of thermal rearrangements is notably lacking in such examples. In part, this may be ascribed to the difference in lifetime of the intermediates: If the stereochemical test of carbocation symmetry depends upon an intermolecular capture in solution, the carbocation presumably must live at least as long as the time (of the order of nanoseconds) needed for diffusive encounters with the capturing nucleophile. In contrast, a biradical in a thermal unimolecular reorganization may have

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(1) Preliminary communication: Pikulin, S.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 8274.

(2) (a) True symmetry is not achieved in most such studies, since "symmetrization", when detected by isotopic position labeling, for example, is perturbed by kinetic or equilibrium secondary isotope effects. Even when the experimental design proposes racemization via an achiral species as the criterion, the "electro-weak advantage" associated with parity nonconservation prevents strict equality of the amounts of enantiomeric products.[2b] Although the isotope effects cannot be ignored, the parity effect will be indetectably small in most mechanistic studies. (b) Mason, S. F. *Nouv. J. Chim.* **1986**, *10*, 739, and references cited therein. (c) Although in the absence of dynamical effects, a symmetrical intermediate is required to give equal amounts of two or more isotopomers or enantiomers, the converse is not necessarily true; that is, "reaction symmetry" does not imply structural symmetry of an intermediate.[2d,e] (d) Burwell, R. L.; Pearson, R. G. *J. Phys. Chem.* **1966**, *70*, 300. (e) Salem, L.; Durup, J.; Bergeron, G.; Cazes, D.; Chapuisat, X.; Kagan, H. *J. Am. Chem. Soc.* **1970**, *92*, 4472.

(3) (a) For an early example, see the refutation of tricyclene as an intermediate in the carbonium ion chemistry of the camphene/isobornyl solvolysis system: Meerwein, H.; van Emster, K. *Ber. Dtsch. Chem. Ges.* **1920**, *53*, 1815. (b) Review: Berson, J. A. In *Molecular Rearrangements*, de Mayo, P., Ed.; Interscience: New York, 1963; Vol. I, Chapter 3, pp 115, 149. (c) Review: Berson, J. A. *Angew. Chem. Int. Ed. Engl.* **1968**, *10*, 779.

(4) (a) Bartlett, P. D. *Nonclassical Ions*; Benjamin: New York, 1965. (b) Brown, H. C. (with comments by Schleyer, P. v. R.) *The Nonclassical Ion Problem*; Plenum: New York, 1977.